Reactivity of E_n Ligand Complexes

Synthesis, Redox Chemistry and Subsequent Reactions

Dissertation

zur Erlangung des

DOKTORGRADES DER NATURWISSENSCHAFTEN

(Dr. rer. nat.)

der Naturwissenschaftlichen Fakultät für Chemie und Pharmazie

der Universität Regensburg



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Regensburg 2020

Diese Arbeit wurde angeleitet von Prof. Dr. Manfred Scheer.

Das Promotionsgesuch wurde eingereicht am: 04.03.2020

Datum des wissenschaftlichen Kolloquiums: 05.06.2020

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Affidavit

I hereby confirm that this thesis “Reactivity of E_n Ligand Complexes - Synthesis, Redox Chemistry and Subsequent Reactions” is the result of my own work. I did not receive any help or support from third parties or commercial consultants. All sources and/or concepts applied directly or indirectly are listed and specified in the thesis stating the relevant literature.

Eidesstattliche Erklärung

Ich erkläre hiermit an Eides statt, dass ich die vorliegende Arbeit mit dem Titel „Reactivity of E_n Ligand Complexes - Synthesis, Redox Chemistry and Subsequent Reactions ” ohne unzulässige Hilfe Dritter und ohne Benutzung anderer als der angegebenen Hilfsmittel angefertigt habe; die aus anderen Quellen direkt oder indirekt übernommenen Daten und Konzepte sind unter Angabe des Literaturzitats gekennzeichnet.

_____

Martin Piesch

The practical work leading to this thesis has been conducted between **July 2016** and **February 2020** at the Department of Inorganic Chemistry at the University of Regensburg under the supervision of Prof. Dr. Manfred Scheer.

List of Publications:

- F. Dielmann, A. Timoshkin, M. Piesch, G. Balázs, M. Scheer, "The Cobalt *cyclo*-P_4 Sandwich Complex and Its Role in the Formation of Polyphosphorus Compounds", *Angew. Chem.* **2017**, *129*, 1693-1698, *Angew. Chem. Int. Ed.* **2017**, *56*, 1671-1675.
- C. School, R. Köppe, M. Piesch, M. T. Gamer, S. N. Konchenko, M. Scheer, P. W. Roesky, "Open Chain Polyarsenides of the Lanthanides", *Chem. Eur. J.* **2018**, *24*, 7890-7895.
- M. Elsayed Moussa, M. Piesch, M. Fleischmann, A. Schreiner, M. Seidl, M. Scheer, "Highly soluble Cu(I)-acetonitrile salts as building blocks for novel phosphorus-rich organometallic-inorganic compounds", *Dalton Trans.* **2018**, *47*, 16031-16035.
- M. Piesch, M. Seidl, M. Stubenhofer, M. Scheer, „Ring Expansions of Nonpolar Polyphosphorus Rings", *Chem. Eur. J.* **2019**, *25*, 6311-6316.
- M. Piesch, S. Reichl, M. Seidl, G. Balázs, M. Scheer, "Ring Contraction by NHC-assisted Pnictogen-Atom Abstraction", *Angew. Chem.* **2019**, *131*, 16716-16721; *Angew. Chem. Int. Ed.* **2019**, *58*, 16563-16568.
- M. Piesch, F. Dielmann, S. Reichl, M. Scheer, "A general pathway to heterobimetallic triple-decker complexes", *Chem. Eur. J.* **2020**, *26*, 1518-1524.
- M. Piesch, C. Graßl, M. Scheer, "Element-Element Bond Formation upon Oxidation and Reduction", *Angew. Chem. Int. Ed.* 10.1002/anie.201916622

dedicated to Lisa and my parents

“Alle Ding’ sind Gift and nichts ohn‘ Gift; allein die Dosis macht, das ein Ding‘ kein Gift ist“

Paracelsus

Preface

Some of the presented results have been published during the preparation of this thesis (vide supra). The relevant content is reprinted with the permission of WILEY-VCH publishing. The corresponding citation and license number are given at the beginning of the respective chapters.

Each chapter includes a list of authors. At the beginning of each chapter the individual contribution of each author is described. Additionally, if some of the presented results have already been discussed in other thesis, it is stated at the beginning of the respective chapters.

To ensure uniform design of this work, all chapters are divided into “Introduction”, “Results and Discussion”, “Conclusion”, “Supporting Information” and “References”. Furthermore, all chapters have the same text settings, numeration of compounds, figures, schemes and tables begins anew. The depicted molecular structures may differ in their style. A general “Introduction” and the “Research Objectives” are given at the beginning of this thesis. In addition, a comprehensive “Summary” of this work is presented at the end of this thesis

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1. Introduction

1.1 Phosphorus and its heavy Analog Arsenic

Phosphorus can be described as an element of life next to carbon. It is omnipresent in daily life and an average human contains approx. 700 g of phosphorus in its organism, starting from building blocks in DNA (nucleotides) over ATP as an energy source in biological systems, part of bones and teeth. 1-1.2 g phosphorus has to be taken up every day by daily diet. On the other hand, phosphorus compounds are widely used as fertilizer in agriculture or agents for fire prevention.[1] In public opinion phosphorus has a bad reputation e.g. due to its use as firebombs in world war II. It was discovered in 1669 by the alchemist Hennig Brand, who tried to create the “philosophers stone” when he evaporated urine and heated the residue under exclusion of air. By that way the luminescent material was found which was named phosphorus (greek for light bearer). The element can be present in different crystalline modifications like white, violet, fibrous, black phosphorus and the amorphous red one. The white phosphorus consists of P_4 tetrahedra and is the most reactive allotrope, which is self-igniting under air.[2] It melts at 44.25 °C and boils at 280.5 °C. At temperatures over 200 °C a transition into the amorphous red phosphorus takes place. Red phosphorus can be tempered at ca. 600 °C to yield another crystalline modification, the violet, also called *Hittorf's* phosphorus.[3] This allotrope consist of pentagonal tubes based on P_2, P_3, P_8 and P_9 units cross linked by P-P bonds (Figure 1). A similar modification can be obtained when gaseous phosphorus is cooled down very slowly.

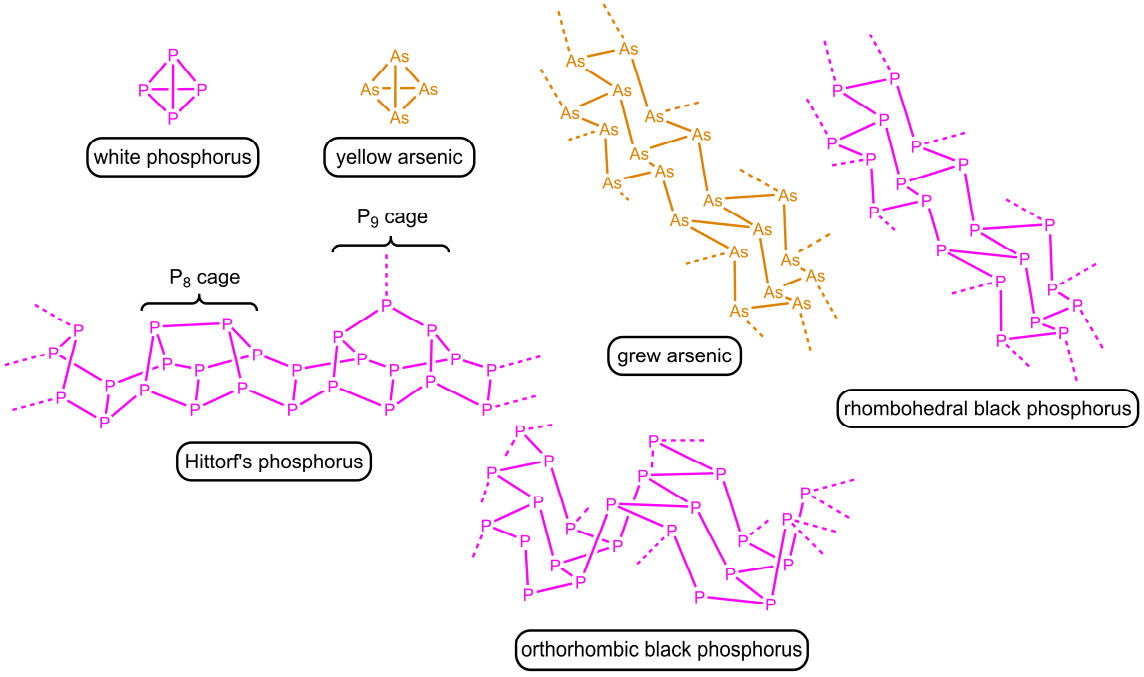
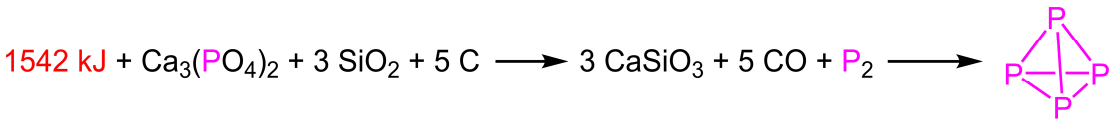


Figure 1. Selected allotropic modifications of phosphorus and arsenic.

By this way fibrous phosphorus is obtained. This allotrope shows similar tubes like violet phosphorus, but only linked to double strands.[4] Violet phosphorus can be transformed under pressure to black phosphorus which shows a layer structure based on six membered rings, while single layers are in zigzag conformation.[5] This orthorhombic black modification can be transformed to rhombohedral and cubic, metallic black phosphorus depending on the applied pressure. The structural motif of the rhombohedral black phosphorus is the same as for grey arsenic, what is the stable modification at ambient conditions.[1] Yellow arsenic, the analog modification of white phosphorus (As_4 tetrahedron) can be obtained from grey arsenic upon heating as an As_4 vapor. This vapor can be transported via a gas stream and quenched in a solvent of choice,[6] which then can be used for subsequent chemistry,[7] what was reported by *Bettendorf* for the first time.[8]

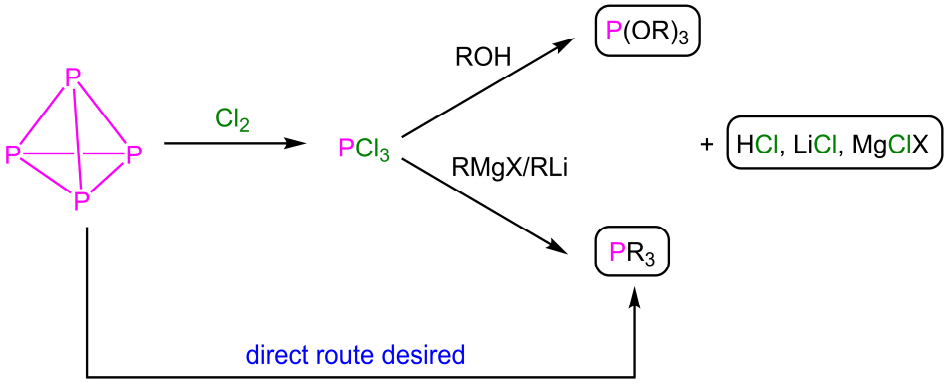
1.2 E_4 activation - E_n Ligand Complexes

Due to the high oxophilicity of phosphorus it cannot be found in its elemental form in nature, but in many different minerals (e.g. apatite) as salts of phosphoric acid. In industry different kind of apatites are used to produce white phosphorus (in industry called yellow phosphorus) on large scale in an extremely energy consuming process in an electric arc furnace. $Ca_3(PO_4)_2$ is transferred in the presence of quartzite and coke to P_4 and stochiometric amounts of $CaSiO_3$ (Scheme 1).[1]



Scheme 1. Industrial synthesis of P_4.

For the synthesis of organophosphorus compounds white phosphorus is oxidized with chlorine gas (formation of PCl_3) and subsequently reacted with alcohols (formation of $P(OR)_3$) or with organolithium/Grignard reagents (formation of PR_3, Scheme 2). These processes share one problem: A stochiometric amount of waste (HCl, LiCl, MgClX) is produced.[9] Therefore, a direct route would be desired avoiding the use of chlorine gas. A suitable way is the activation and transformation of P_4 and subsequently also of As_4 in the coordination sphere of transition metal fragments.



Scheme 2. Synthesis of organophosphorus compounds in industry.

The activation of white phosphorus and yellow arsenic has become a large field of research. In 1971 *Ginsberg and Lindsell* reported the first polyphosphorus (P_n) ligand complex $[Rh(PPh_3)Cl(\eta^2\text{-}P_4)]$ (**I**)[10]. Interestingly, the first polyarsenic (As_n) ligand complex $[Co(CO)_3(\eta^3\text{-}As_3)]$ (**II**) was already reported in 1969 by *Dahl* starting from $AsMe_5$ as an arsenic source (Figure 2).[11] Starting from that, a plethora of polypnictogen (E_n) ligand complexes have been synthesized with up to 24 P atoms[12] and 18 As atoms, respectively.[13] The most convenient synthetic route displays the thermolysis of P_4/As_4 with suitable carbonyl complexes of the type $[(Cp^RM(CO)_n)_2]$ (e.g. M = Cr,[14,15] Mo,[16–18] W,[19] Fe,[20–22] Ru,[21] Co[23], Ni[24–26]) or photolysis of $[Cp^RM(CO)_4]$ (e.g. M = V,[27] Nb,[28,29] Ta[28]) yielding a large variety of compounds. Another approach is the reaction of transition metal complexes bearing labile ligands (e.g. ethene, toluene, acetonitrile, …) with P_4 and As_4 under mild conditions.[30,31]

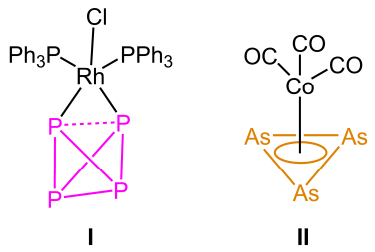
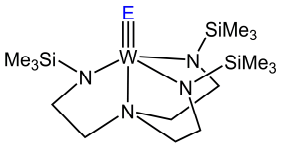


Figure 2. First reported P_n and As_n ligand complexes.

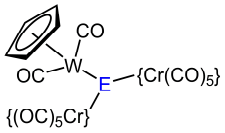
One principle of ordering polypnictogen ligand complexes is to sort by the number E atoms incorporated. The cyclic derivatives have a special aromatic character and in this introduction only complexes with cyclic E_n ligands including Cp ligands are considered for n = 3-6. For n = 1, the E_1 ligand can either be terminal like in $[(N_3N)W{\equiv}E]$ (E = P (**IIIa**),[32] As (**IIIb**)[33]) or bridging two to four metal fragments like in $[\{CpW(CO)_2\}\{Cr(CO)_5\}_2(\mu_3\text{-}E)]$[34] (E = P (**IVa**), As(**IVb**)) as an example. For n = 2, the E_2 units can be part of tetrahedral complexes based on group six metals $[(CpM(CO)_2)_2(\mu,\eta^2{:}\eta^2\text{-}E_2)]$ (M = Cr (**V**), Mo (**VI**), W (**VII**); E = P,[16,35,36] As[37]) or two E_2 ligands can also be incorporated in triple-decker complexes like in $[(Cp'''Co)_2(\mu,\eta^2{:}\eta^2\text{-}E_2)_2]$ (E = P (**VIIIa**),[23] As (**VIIIb**)[38]). *Cyclo*-E_3 ligands can arise as end-deck in the Ni complexes $[Cp^RNi(\eta^3\text{-}E_3)]$ (E = P (**IXa**)[26], As(**IXb**)[24]), in group six complexes of the

type $[Cp^RM(CO)_2(\eta^3\text{-}E_3)]$ (M = Cr (E = P (**Xa**)[35,39], As (**Xb**)[40,41]), Mo (E = P (**XIa**)[42], As (**XIb**)[43]), W (E = P (**XIIa**)[44], As (**XIIb**)[45])) or as middle decks like in $[(Cp'''Ni)_2(\mu,\eta^3\text{:}\eta^3\text{-}P_3)]$[46] (**XIII**). *Cyclo*-E_4 ligands can be incorporated in group five metal complexes of the type $[Cp^RM(CO)_2(\eta^4\text{-}E_4)]$ (M = V (E = P (**XIV**)),[27] Nb (E = P (**XVa**)[29], As(**XVb**)[47]), Ta (E = P (**XVI**))[28,48]) or as end deck in the sandwich complex $[Cp'''Co(\eta^4\text{-}P_4)]$ (**XVII**) which was reported in 2017.[30] *Cyclo*-P_4 ligands have also been reported stabilized by $\{Cr(CO)_5\}$ or $\{Cp''Fe(CO)_2\}$ fragments like $[Cp^RCo(\mu_4,\eta^4\text{:}\eta^1\text{:}\eta^1\text{:}\eta^1\text{-}P_4)\{Cr(CO)_5\}_3]$ (**XVIII**),[49] $[Cp^RM(\mu_5,\eta^4\text{:}\eta^1\text{:}\eta^1\text{:}\eta^1\text{:}\eta^1\text{-}P_4)\{Cr(CO)_5\}_4]$ (M = Co (**XIXa**),[50] Rh (**XIXb**)[51]) and $[(Cp''Fe)\}(\mu,\eta^4\text{:}\eta^1\text{-}P_4)\{Cp''Fe(CO)_2\}]$ (**XX**).[52] The *cyclo*-E_5 ligand is present in the ferrocene analog complexes pentaphospha- and pentaarsaferrocene $[Cp^RFe(\eta^5\text{-}E_5)]$ (E = P (**XXIa**),[20,21] As (**XXIb**)[22]), the ruthenium analog compound $[Cp^RRu(\eta^5\text{-}E_5)]$ (E = P(**XXIIa**),[21] As(**XXIIb**)[53]) or as middle deck in triple-decker complexes of group six or seven elements $[(Cp^RM)_2(\mu,\eta^5\text{:}\eta^5\text{-}E_5)]$ (M = Cr (E = P (**XXIIIa**)[15,54], As (**XXIIIb**)[40,55]), M = Mo (E = As(**XXIV**)[56]), M = Mn (E = P(**XXV**)[57])). The benzene analogous *cyclo*-E_6 ligand can only be stabilized as middle-deck in triple-decker complexes of the type $[(Cp^RM)_2(\mu,\eta^6\text{:}\eta^6\text{-}E_6)]$ (M = Ti (E = P (**XXVI**)[58]), V (E = P (**XXVII**)[19]), Nb (E = P (**XXVIII**)[29,59]), Mo (E = P (**XXIXa**),[17,18,60] As (**XXIXb**)[61]), W (E = P (**XXX**)[19]) while it has to be noted, that the Ti complex shows a P_6 middle deck in zigzag conformation and not planar as in all other cases. Examples of E_n ligand complexes are depicted in Figure 3. While all mentioned triple-decker complexes are homometallic, there are also heterobimetallic compounds known. They can be prepared by thermolysis or photolysis of suitable carbonyl complexes with preformed E_n ligand complexes, with complexes containing labile ligands or with cationic transition metal moieties.

n = 1

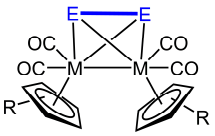


E = P (**IIIa**), As (**IIIb**)

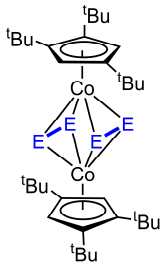


E = P (**IVa**), As (**IVb**)

n = 2



M = Cr , E = P (**Va**), As (**Vb**)
M = Mo , E = P (**VIa**), As (**VIb**)
M = W , E = P (**VIIa**), As (**VIIb**)

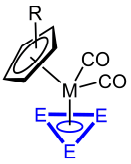


E = P (**VIIIa**), As (**VIIIb**)

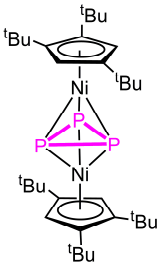
n = 3



E = P (**IXa**), As (**IXb**)

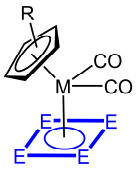


M = Cr , E = P (**Xa**), As (**Xb**)
M = Mo , E = P (**XIa**), As (**XIb**)
M = W , E = P (**XIIa**), As (**XIIb**)

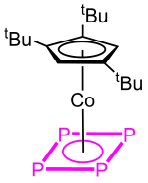


XIII

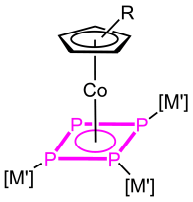
n = 4



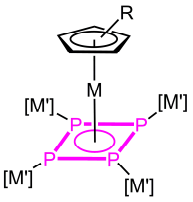
M = V , E = P (**XIV**)
M = Nb , E = P (**XVa**), As (**XVb**)
M = Ta , E = P (**XVI**)



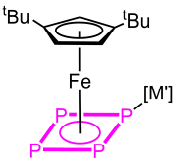
XVII



M' = $\{Cr(CO)_5\}$ (**XVIII**)

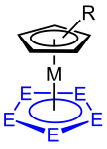


M = Co, M' = $\{Cr(CO)_5\}$ (**XIXa**)
M = Rh, M' = $\{Cr(CO)_5\}$ (**XIXb**)

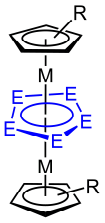


M' = $\{Cp''Fe(CO)_2\}$ (**XX**)

n = 5

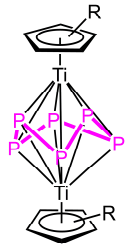


M = Fe , E = P (**XXIa**), As (**XXIb**)
M = Ru , E = P (**XXIIa**), As (**XXIIb**)

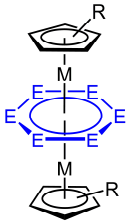


M = Cr , E = P (**XXIIIa**), As (**XXIIIb**)
M = Mo , E = As (**XXIV**)
M = Mn, E = P (**XXV**)

n = 6



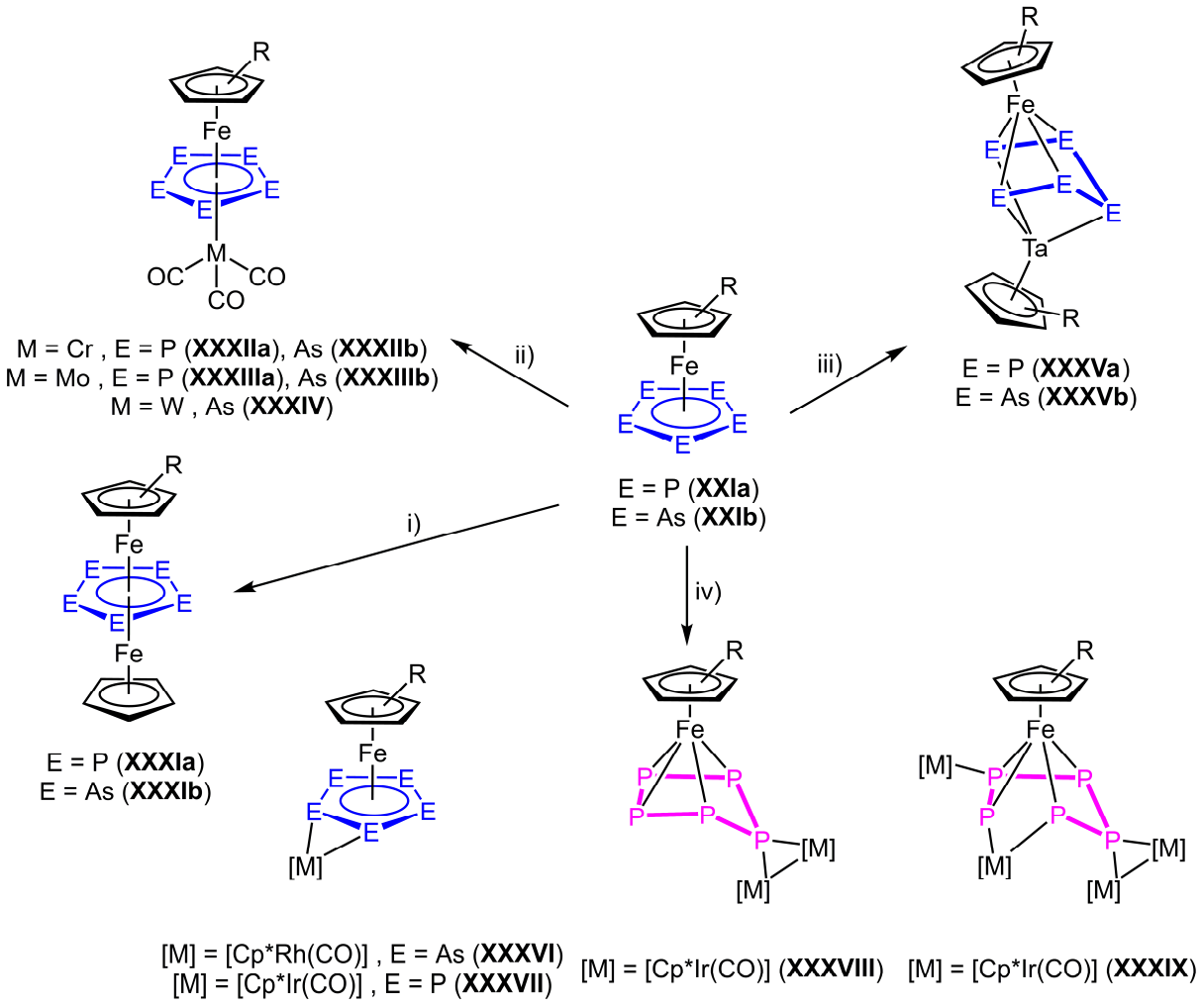
XXVI



M = V , E = P (**XXVII**)
M = Nb , E = P (**XXVIII**)
M = Mo, E = P (**XXIXa**), As (**XXIXb**)
M = W, E = P (**XXX**)

Figure 3. Selected E_n ligand complexes.

This chemistry was investigated for [Cp^{R}Fe(η^5-E$_5$)] (E = P (**XXIa**), As (**XXIb**)). The reaction of **XXIa**,**b** with {CpFe$^+$} fragments yields the cationic triple-decker complexes [(Cp^{R}Fe)(CpFe)(μ,η^5:η^5-E$_5$)][PF$_6$] (E = P (**XXXIa**),[62] As (**XXXIb**)[63]) which represent no heterobimetallic complexes but still consist of two different Cp^{R}Fe fragments. Reacting **XXIa**,**b** with [M(CO)$_3$(MeCN)$_3$] (M = Cr, Mo, W) gives [(Cp*Fe)(M(CO)$_3$)(μ,η^5:η^5-E$_5$)] (M = Cr (E = P (**XXXIIa**), As (**XXXIIb**)), Mo (E = P (**XXXIIIa**), As (**XXXIIIb**)), W (E = As (**XXXIV**))].[64] The cothermolysis of **XXIa**,**b** with [Cp''Ta(CO)$_4$] yields selectively the heterobimetallic [(Cp*Fe)(Cp''Ta)(μ,η^4:η^3-E$_5$)] (E = P (**XXXVa**)[65], As (**XXXVb**)[66]). **XXIa**,**b** can be reacted with the rhodium and iridium carbonyls [(Cp*M(CO))$_2$] (M = Rh, Ir) and [Cp*Ir(CO)$_2$] to yield for E = As the rhodium complex [(Cp*Fe)(Cp*Rh(CO))(μ,η^5:η^2-As$_5$)] (**XXXVI**)[67] and for E = P a set of iridium complexes with one, two and four {Cp*Ir(CO)} fragments in [(Cp*Fe)(Cp*Ir(CO))(μ,η^5:η^2-P$_5$)] (**XXXVII**)[67], [(Cp*Fe)(Cp*Ir(CO))$_2$(μ,η^4:η^1:η^1-P$_5$)] (**XXXVIII**)[65] and [(Cp*Fe)(Cp*Ir(CO))$_4$(μ,η^4:η^2:η^1:η^1:η^1-P$_5$)] (**XXXIX**).[65] All mentioned heterometallic complexes are depicted in Scheme 3.



Scheme 3. Selected heterometallic E$_n$ ligand complexes. Reaction of **XXIa**,**b** with i) [CpFe]$^+$ units, ii) [M(CO)$_3$(MeCN)$_3$] (M = Cr, Mo, W), iii) [Cp''Ta(CO)$_4$] and iv) [(Cp*M(CO))$_2$] (M = Rh, Ir) and [Cp*Ir(CO)$_2$].

1.3 Reactivity of E_n Ligand Complexes

The frontier molecular orbitals of [Cp*Fe(η^5-E_5)] (E = P (**XXIa**), As (**XXIb**)) reveal that both HOMO and LUMO are mainly located at the *cyclo*-E_5 ligand suggesting a possible reactivity towards electrophiles and nucleophiles.[68] The frontier molecular orbitals have been recalculated on the B3LYP/def2-TZVP level of theory and are depicted in Figure 4.

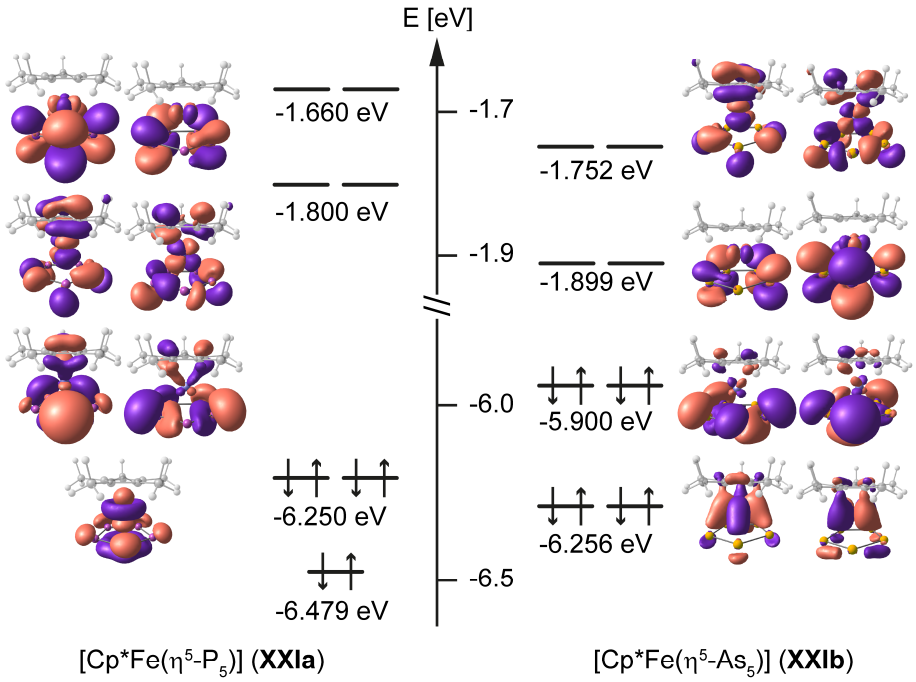
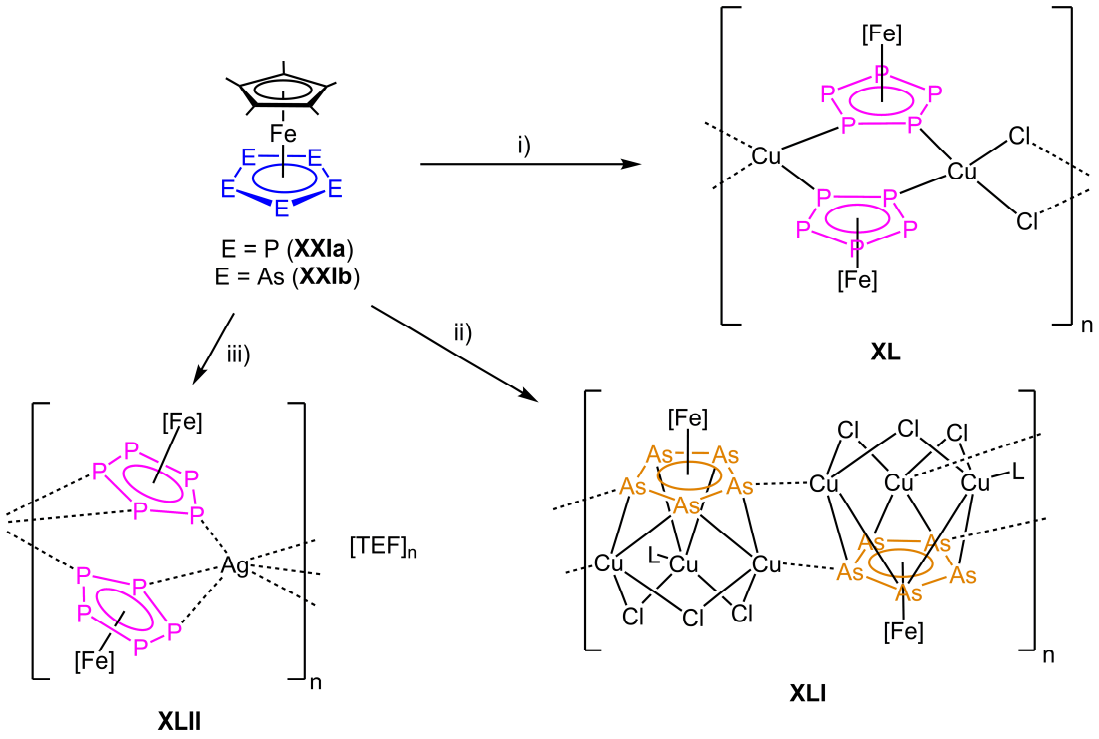


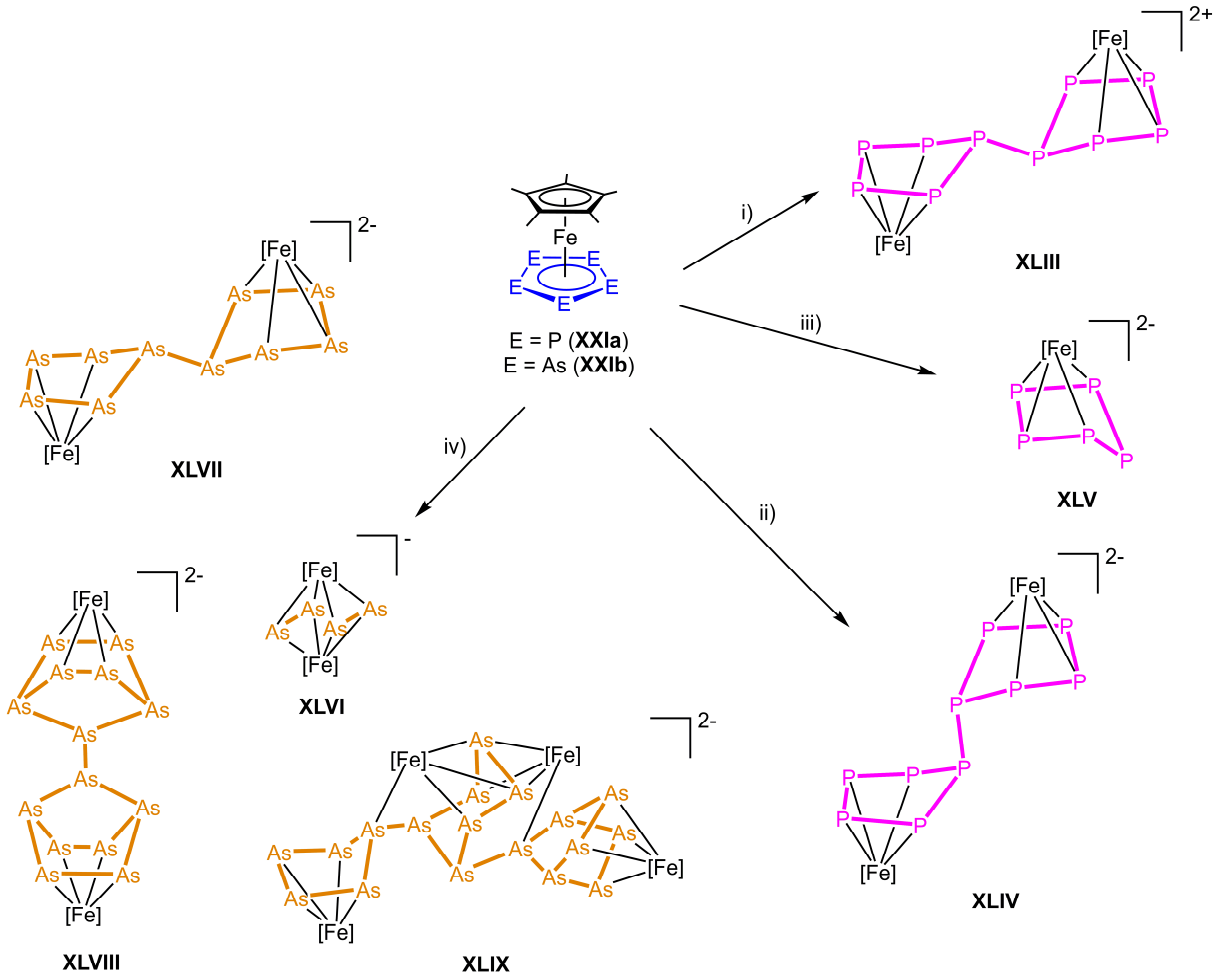
Figure 4. Frontier molecular orbitals of **XXIa** (left) and **XXIb** (right) (B3LYP/def2-TZVP level of theory).

The chemistry of [Cp*Fe(η^5-P_5)] **XXIa** has been widely investigated. It has been used for supramolecular coordination chemistry involving coinage metal salts, in which molecular, oligomeric, polymeric (1D - 3D) or supramolecular aggregates (fullerene analog) are accessible depending on the reaction conditions. The reaction of **XXIa** with CuX (X = Cl, Br, I) yields 1D and 2D polymers[69] (e.q. [Cp*Fe(μ_3,η^5:η^1:η^1-P_5)CuCl]$_n$ (**XL**) or fullerene-like supramolecular aggregates.[70] For the arsenic compound [Cp*Fe(η^5-As_5)] **XXIb** this kind of chemistry was also investigated, but to far less extend (e.g. [Cp*Fe(μ_4,η^5:η^2:η^2:η^1-As_5)(CuCl)$_3$(MeCN)]$_n$ (**XLI**) from the reaction with CuCl).[68] The Cu atoms in **XL** are coordinated by two P atoms of two molecules **XXIa** in a η^1 mode, while in **XLI** the Cu atoms are coordinated by one edge of the As_5 ligand in η^2 mode and additionally by one As atom of a neighbored molecule **XLI** in η^1 mode (for two of three Cu atoms). The third copper atom is saturated by an acetonitrile molecule. When instead coinage metals salts containing weakly coordinating anions like [TEF]$^-$ (= {Al(OC(CF_3)$_4$}$^-$) are used, cationic soluble polymers like [Cp*Fe(μ_3,η^5:η^2:η^1-P_5)Ag]$_n$[TEF]$_n$ (**XLII**) are formed (Scheme 4).[71]



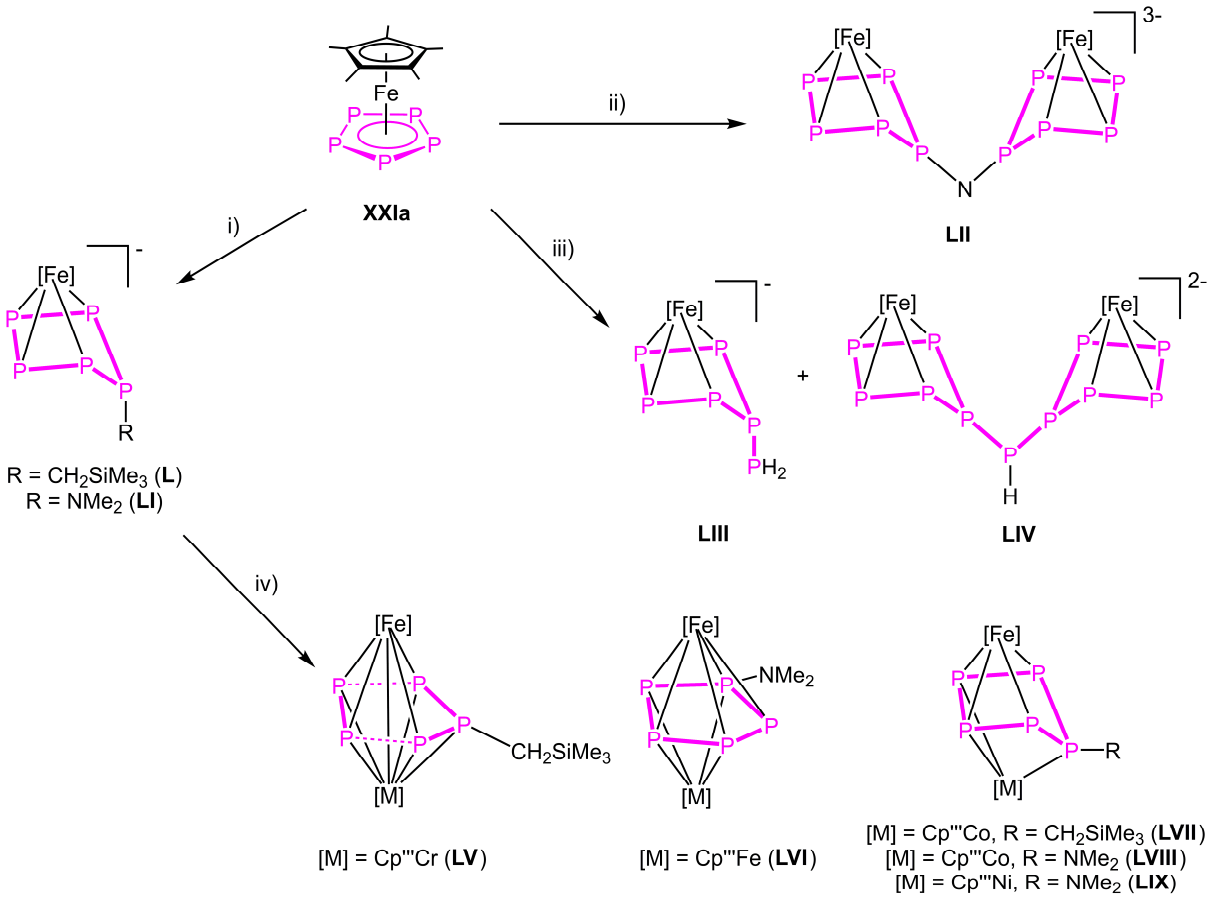
Scheme 4. Selected reactions of **XXIa**,**b** with CuCl and Ag[TEF], [Fe] = Cp*Fe, L = MeCN.

The redox chemistry of the phosphorus complex **XXIa** was studied by *Geiger and Winter* by spectroelectrochemical methods indicating a set of possible redox processes.[72] The preparative oxidation of **XXIa** to $[(Cp^*Fe)_2(\mu,\eta^4{:}\eta^4\text{-}P_{10})]^{2+}$ (**XLIII**) was achieved by our group using thiathrenium hexafluoroantimonate.[73] The abstraction of one electron leads formally to the radical species $[Cp^*FeP_5]^{+\cdot}$ which dimerizes to **XLIII**. On the other hand, the reduction with KH transfers one electron and a related radical species $[Cp^*FeP_5]^{-\cdot}$ is formed which dimerizes to $[(Cp^*Fe)_2(\mu,\eta^4{:}\eta^4\text{-}P_{10})]^{2-}$ (**XLIV**). When instead an excess of elemental potassium is used, the dianion $[Cp^*Fe(\eta^4\text{-}P_5)]^{2-}$ (**XLV**) can be isolated. While these redox reactions are quite selective, the reduction of the analog arsenic compound **XXIb** does not proceed selectively and several fragmentation products are obtained, namely $[(Cp^*Fe)_2(\mu,\eta^2{:}\eta^2\text{-}As_2)_2]^{-}$ (**XLVI**), $[(Cp^*Fe)_2(\mu,\eta^4{:}\eta^4\text{-}As_{10})]^{2-}$ (**XLVII**), $[(Cp^*Fe)_2\ (\mu,\eta^2{:}\eta^2{:}\eta^2{:}\eta^2\text{-}As_{14})]^{2-}$ (**XLVIII**) and $[(Cp^*Fe)_4\ (\mu_4,\eta^4{:}\eta^3{:}\eta^3{:}\eta^2{:}\eta^2{:}\eta^1{:}\eta^1\text{-}As_{18})]^{2-}$ (**XLIX**).[13] The attempts to oxidize **XXIb** were not successful so far. All mentioned redox reactions are depicted in Scheme 5.



Scheme 5. Reactivity of **XXIa**,**b** towards i) thianthrenium hexafluoroantimonate, ii) KH, iii) K(exc) and iv) KH, [Fe] = Cp*Fe.

The reactivity of **XXIa** towards main group nucleophiles was investigated in our group. The *cyclo*-P_5 ligand can be functionalized with carbon-, nitrogen- and phosphorus based nucleophiles like $LiCH_2SiMe_3$, $LiNMe_2$, $NaNH_2$ or $LiPH_2$.[74] In these reactions, anionic complexes of the type $[Cp^*Fe(\eta^4\text{-}P_5R)]^-$ are first formed. For R = CH_2SiMe_3 and NMe_2 these complexes display the final products (**L** and **LI**). In the case of $NaNH_2$ and $LiPH_2$ subsequent reactions take place and the complexes $[(Cp^*Fe)_2(\mu,\eta^4\text{:}\eta^4\text{-}(P_5)_2N)]^{3-}$ (**LII**), $[Cp^*Fe(\eta^4\text{-}P_5PH_2)]^-$ (**LIII**) and $[(Cp^*Fe)_2(\mu,\eta^4\text{:}\eta^4\text{-}(P_5)_2PH)]^{2-}$ (**LIV**). The anionic complexes **L** and **LI** can be quenched with $[(Cp'''MX)_2]$ (M = Cr (X = Cl), Co (X = Cl), Ni (X = Br)) yielding the substituted triple-decker complexes $[(Cp^*Fe)(Cp'''Cr)(\mu,\eta^5\text{:}\eta^4\text{-}P_5CH_2SiMe_3)]$ (**LV**), $[(Cp^*Fe)(Cp'''Fe)(\mu,\eta^5\text{:}\eta^4\text{-}P_5NMe_2)]$ (**LVI**) and $[(Cp^*Fe)(Cp'''M)(\mu,\eta^5\text{:}\eta^4\text{-}P_5R)]$ (M = Co (R = CH_2SiMe_3 (**LVII**), NMe_2 (**LVIII**)), Ni (R = NMe_2 (**LIX**)).[75] All mentioned reactions are depicted in Scheme 6.



Scheme 6. Reactivity of **XXIa** towards i) $LiCH_2SiMe_3$ or $LiNMe_2$, ii) $NaNH_2$, iii) $LiPH_2$ and electrophilic quenching with iv) $[(Cp'''MX)_2]$ (M = Cr (X = Cl), Co (X = Cl), Ni (X = Br)), [Fe] = Cp*Fe.

1.4 References

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2. Research Objectives

The redox chemistry and reactivity of [Cp*Fe(η^5-P_5)] and [Cp'''Ni(η^3-P_3)] towards main group nucleophiles was investigated in our group. In these reactions products with functionalized *cyclo*-P_3 and *cyclo*-P_5 ligands were obtained and sometimes a further fragmentation and/or aggregation of the phosphorus ligands was observed. The long existing gap in the series of sandwich complexes with *cyclo*-P_n (n = 3 (Ni), 5 (Fe, Cr), 6 (Mo)) ligands was closed with the synthesis of [Cp'''Co(η^4-P_4)] by *Fabian Dielmann* and reported in 2017, although no reactivity studies have been performed. Accordingly, the first research objectives of this work were:

- Investigation of the redox chemistry of [Cp'''Co(η^4-P_4)]
- Investigation of the reactivity of [Cp'''Co(η^4-P_4)] towards main group nucleophiles

The oxidation chemistry of [$(Cp^RMo)_2(\mu,\eta^6{:}\eta^6\text{-}P_6)$] and [$(CpMo(CO)_2)_2(\mu,\eta^2{:}\eta^2\text{-}E_2)$] (E = P - Bi) was also investigated. The oxidation of the first one leads only to a distortion of the P_6 ligand while in the second case an E-E bond formation takes place. An interesting complex for the investigation of the redox chemistry is [$(Cp'''Co)_2(\mu,\eta^2{:}\eta^2\text{-}E_2)$] (E = P, As) which carries two independent E_2 units coordinated each by two {Cp'''Co} fragments. The question is, how this complex will respond the addition or withdrawal of electrons. Therefore, the second research objective of this work was:

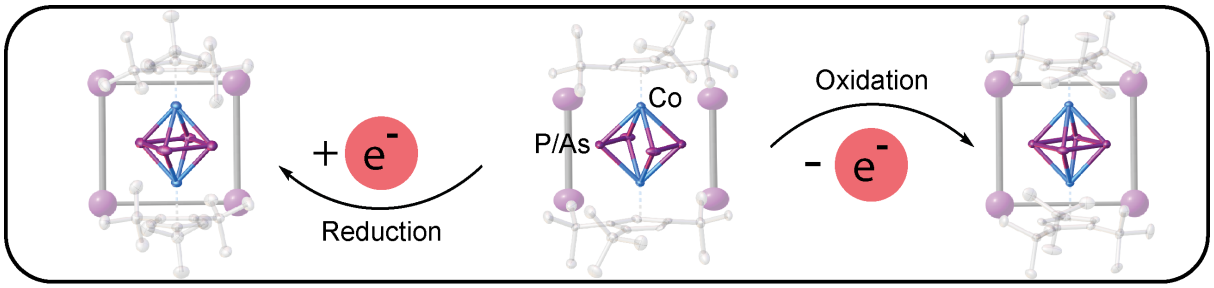
- Investigation of the redox chemistry of [$(Cp'''Co)_2(\mu,\eta^2{:}\eta^2\text{-}E_2)$] (E = P, As)
- Electrophilic quenching of the obtained anionic products

The investigation of the redox chemistry should also be extended to heterobimetallic triple-decker complexes. *Fabian Dielmann* reported in his Ph. D. thesis the synthesis of two new representatives of this category: [(Cp*Fe)(Cp'''Co)($\mu,\eta^5{:}\eta^4$-P_5)] and [(Cp'''Co)(Cp'''Ni)($\mu,\eta^3{:}\eta^3$-P_3)]. Since only the synthesis has been reported and their properties were not studied, the third scope of this work has been:

- Reproduction of the synthesis of both triple-decker complexes and the investigation of their dynamic behavior in solution and blocking of the processes by coordination of {$W(CO)_5$} fragments
- Synthesis of the arsenic analogous complex [(Cp*Fe)(Cp'''Co)($\mu,\eta^5{:}\eta^4$-As_5)] and its chemistry
- Investigation of the redox chemistry of [(Cp*Fe)(Cp'''Co)($\mu,\eta^5{:}\eta^4$-E_5)] (E = P, As) and study the reactivity of them towards main group nucleophiles.

3. Element-Element Bond Formation upon Oxidation and Reduction

Martin Piesch, Christian Graßl and Manfred Scheer



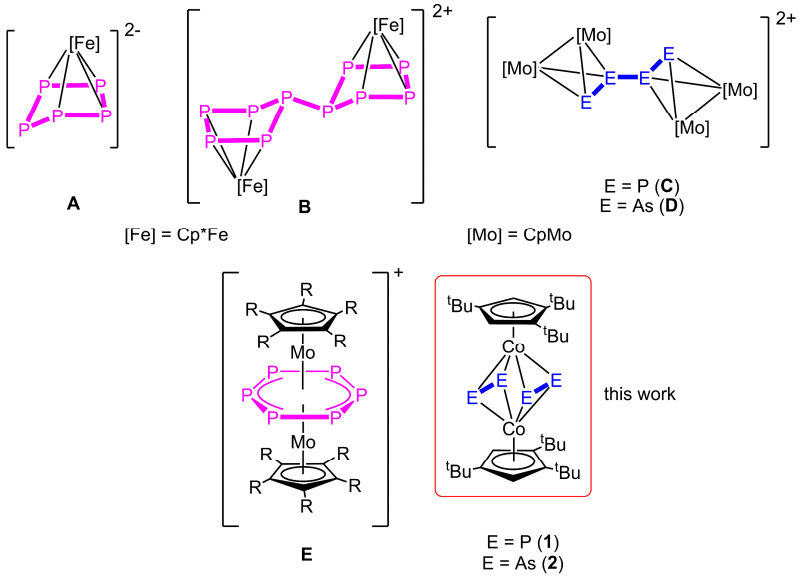
- Synthesis and characterization of all compounds was performed by Martin Piesch except **6** (Christian Graßl)
- DFT calculations were performed by Martin Piesch
- X-ray measurements and calculations were done by Martin Piesch (**3a**, **3b**, **4a**, **4b**, **5**, **7**, **8**, **9**, **10**) and Christian Graßl (**6**) and finally checked by Michael Seidl
- Manuscript was written by Martin Piesch
- Figures were made by Martin Piesch
- The cyclic voltammograms were recorded by Martin Weber and Felix Riedelberger
- This chapter is already published as: M. Piesch, Ch. Graßl, M. Scheer, *Angew. Chem. Int. Ed.* 10.1002/anie.201916622

3.1 Introduction

Abstract: *The redox chemistry of [(Cp'''Co)$_2$(μ,η^2:η^2-E$_2$)$_2$] (E = P (**1**), As (**2**); Cp''' = 1,2,4-tritertbutyl-cyclopentadienyl) was investigated. Both compounds can be oxidized and reduced, each of them twice. That way, the monocations [(Cp'''Co)$_2$(μ,η^4:η^4-E$_4$)][X] (E = P, X = BF$_4$ (**3a**), [FAl] (**3b**), E = As, X = BF$_4$ (**4a**), [FAl] (**4b**)), the dications [(Cp'''Co)$_2$(μ,η^4:η^4-E$_4$)][TEF]$_2$ (E = P (**5**), As (**6**)) and the monoanions [K(18-c-6)(dme)$_2$][(Cp'''Co)$_2$(μ,η^4:η^4-E$_4$)] (E = P (**7**), As (**8**)) were isolated. A further reduction of **7** leads to the dianionic complex [K(18-c-6)(dme)$_2$][K(18-c-6)][(Cp'''Co)$_2$(μ,η^3:η^3-P$_4$)] (**9**), in which the cyclo-P$_4$ ligand rearranges to a chain-like P$_4$ ligand in **9**. Further reduction of **8** can be achieved with an excess of potassium under the formation of [K(dme)$_4$][(Cp'''Co)$_2$(μ,η^3:η^3-As$_3$)] (**10**) and the elimination of an As$_1$ unit. **10** represents the first example of an allylic As$_3$ ligand incorporated in a triple-decker complex. All compounds were comprehensively characterized and their electronic structures were elucidated by DFT calculations.*

Oxidation and reduction reactions have been widely used for element-element bond formation or cleavage reactions. For example, the elemental modifications of sulfur (S_8), phosphorus (P_4 or red phosphorus) or grey arsenic can be easily degraded in reduction processes by bond cleavages to the corresponding S_6^{2-}, P^{3-} or As^{3-} units, respectively.[1] On the other hand, oxidation reactions lead, in general, to bond formation reactions. In the case of S_8, one new S-S bond is formed by the oxidation to S_8^{2+}, while for the oxidation of white phosphorus an additional aggregation takes place to form a P_9^+ moiety.[2] An analogous reactivity can be observed for cyclic phosphines or arsines such as ^{t}Bu$_4$E$_4$ (E = P, As).[3] Both compounds can be reduced and degraded to E_2 fragments by using elemental potassium.[4] While this behavior is particularly true for saturated main group compounds containing lone pairs, the situation is different for unsaturated species. In this case, the reduction leads in general to the population of π* orbitals and formation of radical anions which can lead to bond formation.[5–8] For example, phosphinines,[5] diboryl compounds[6] and (TPB)Cu$^+$ (TPB = tris[2-(diisopropylphosphino)-phenyl]borane)[7] form new formal one electron bonds (P···P, B···B and Cu···B) upon reduction. Polypnictogen ligands in the coordination sphere of transition metals reveal also an interesting redox chemistry. The redox chemistry of pentaphosphaferrocene [Cp*Fe(η^5-P$_5$)] (Cp* = pentamethyl-cyclopentadienyl) was studied spectroelectrochemically by *Winter* and *Geiger,*[9] and experimentally by our group resulting in one oxidized and two reduced products.[10] Depending on the reducing agent, one or two electrons can be transferred to [Cp*Fe(η^5-P$_5$)]. When potassium hydride was used, a single-electron transfer occurred leading to a proposed intermediate [Cp*FeP$_5$]$^-$ dimerizing to the dinuclear complex [(Cp*Fe)$_2$(μ,η^4:η^4-P$_{10}$)]$^{2-}$. When elemental potassium was used in excess, the reaction led to the dianionic species [Cp*Fe(η^4-P$_5$)]$^{2-}$ (**A,** scheme 1). On the other hand, when using

thianthrenium hexafluoroantimonate as a strong oxidant, the dinuclear compound $[(Cp^*Fe)_2(\mu,\eta^4{:}\eta^4\text{-}P_{10})]^{2+}$ (**B**) was isolated. In these reactions, the polyphosphorus ligand in $[Cp^*Fe(\eta^5\text{-}P_5)]$ responds to the addition or withdrawal of one electron either by folding the P_5 ring or/and by forming a new external P-P bond.[10] The redox chemistry of the analogous arsenic compound $[Cp^*Fe(\eta^5\text{-}As_5)]$ leads, via reduction, to a mixture of anionic species containing As_4, As_{10}, As_{14} and As_{18} ligands, while all attemps at an oxidation have failed so far.[11] A similar behavior including the formation of external E-E bonds upon oxidation was reported for the complexes $[\{CpMo(CO)_2\}_2(\mu,\eta^2{:}\eta^2\text{-}E_2)]$ (E = P – Bi), which result for E = P, As in the formation of complexes **C** and **D** (Scheme 1).[12]



Scheme 1. Selective examples of reduced and oxidized polypnictogen ligand complexes.

Not only sandwich complexes with an E_n ligand as a lower-deck show an instructive redox chemistry but also homometallic triple-decker complexes with the corresponding E_n ligand as a middle deck. $[(Cp^RMo)_2(\mu,\eta^6{:}\eta^6\text{-}P_6)]$, as an example, can be easily oxidized to $[(Cp^RMo)_2(\mu,\eta^6{:}\eta^6\text{-}P_6)]^+$ (**E**) retaining its initial triple-decker geometry in the solid state, whereas the *cyclo*-P_6 ligand in **E** tends to slightly distort in a bis-allylic manner.[13] Therefore, in contrast to the usual polypnictogen complexes, oxidations have the opposite effect of elongating P-P bonds, but strengthening Mo-Mo bonds.

Intrigued by the diversity of the structural changes upon oxidation and/or reduction of the polypnictogen (E_n) ligand complexes, we were interested in using E_n ligand complexes that combine the features of triple-decker complexes and separated E_n units, and we were keen to explore, if the redox behavior follows the traditional path (oxidation: forming a bond; reduction: cleaving a bond) or whether new avenues to novel and structurally unprecedented products are opened. Therefore, we decided to investigate the redox chemistry of the cobalt complexes $[(Cp'''Co)_2(\mu,\eta^2{:}\eta^2\text{-}E_2)_2]$ (E = P (**1**), As (**2**); Cp''' = 1,2,4-tritertbutyl-cyclopentadienyl), which are

easily accessible by the reaction of the toluene complex [(Cp'''Co)$_2$(μ,η^4:η^4-C$_7$H$_8$)] with white phosphorus or yellow arsenic in gram scale.[14,15]

3.2 Results and Discussion

To obtain a first insight into their redox properties, the frontier molecular orbitals of **1** and **2** were computed (Figure 1). The HOMO shows bonding character within the E_2 units and antibonding character between them. Therefore, the abstraction of electrons by oxidation should induce a cyclization, whereas the E-E distance of the former E_2 unit will be elongated. The situation for the LUMO, which is a linear combination of π* orbitals of the E_2 units, is vice versa. It shows bonding character between the two separated E_2 units and antibonding character within the E_2 unit. Again, the population of this orbital by adding electrons by reduction should induce a cyclization to form an E_4 ligand while the bond within every E_2 unit will be elongated.

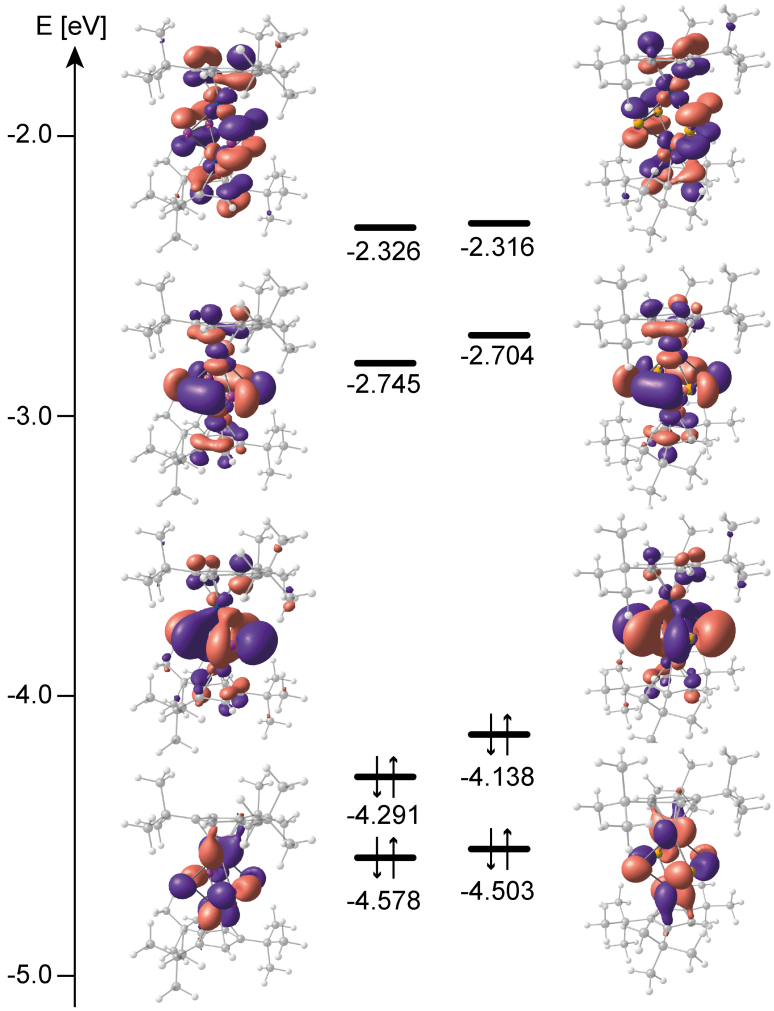


Figure 1. Frontier molecular orbitals of **1** (left) and **2** (right). BP86/def2-TZVP level of theory.

To obtain an overview of how redox processes proceed, cyclic voltammetry measurements were performed in different solvents. We found that the nature of the redox processes is strongly dependent on the solvent used. In the case of **1,** there are two reversible oxidation processes in CH_2Cl_2 at -367 and 351 mV and a, most likely, irreversible reduction around -2350 mV (against $[Cp_2Fe]/[Cp_2Fe]^+$). When the solvent is changed to thf, only one reversible oxidation at -336 mV and one reversible reduction at -2304 mV are found (Figure 2). The cyclic voltammogram of **2** in dme shows two reversible oxidations at -463 and 8 mV and two reversible reductions at -2144 and -2644 mV against $[Cp_2Fe]/[Cp_2Fe]^+$ (cf. Figure 3).

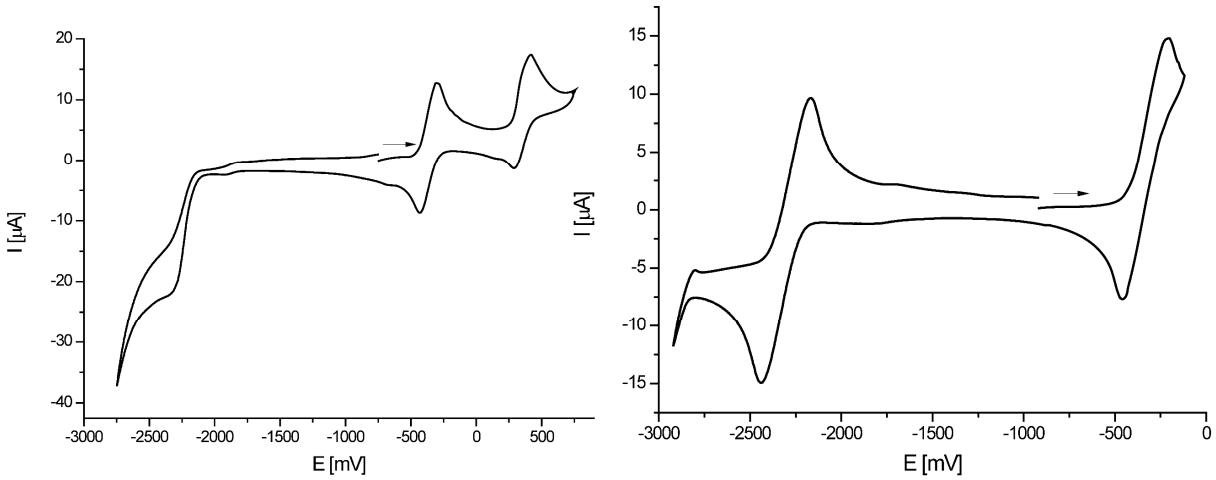


Figure 2. Cyclic voltammogram of **1** in CH_2Cl_2 (left) and in thf (right) against $[Cp_2Fe]/[Cp_2Fe]^+$ (electrolyte $^nBu_4NPF_6$, scan rate: 100 mV/s. temperature: r.t.).

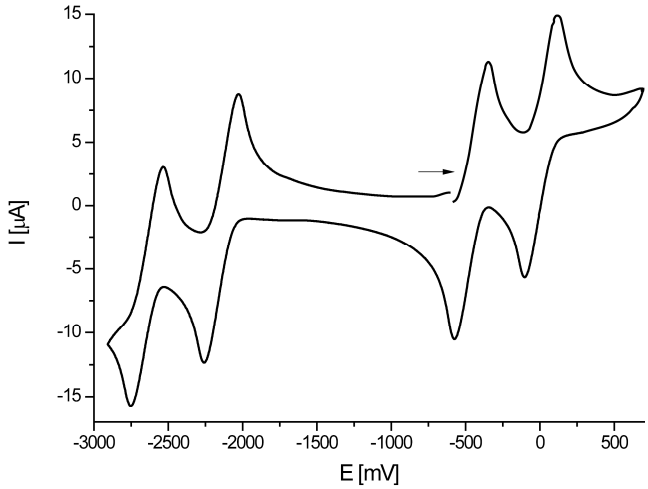
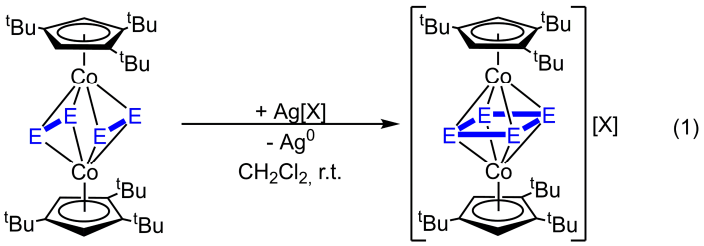


Figure 3. Cyclic voltammogram of **2** in dme against $[Cp_2Fe]/[Cp_2Fe]^+$ (electrolyte $N^nBu_4PF_6$, scan rate: 100 mV/s. temperature: r.t.).

For the chemical oxidation, we chose Ag^+ as a suitable oxidant, due to the rather low oxidation potentials of **1** and **2**.[16]

Both compounds can be oxidized using one equivalent of an Ag(I) salt containing a weakly coordinating anion [X] (X = BF_4 or [FAl] ([FAl{$OC_6F_{10}(C_6F_5)$}$_3$])) leading to the isostructural compounds $[(Cp'''Co)_2(\mu,\eta^4{:}\eta^4\text{-}E_4)][X]$ (E = P, X = BF_4 (**3a**) (66 %), [FAl] (**3b**) (56 %), E = As, X

= BF_4 (**4a**) (65 %), [FAl] (**4b**) (42 %)) (Eq. 1), in which two new E-E bonds were formed to obtain a new triple decker sandwich complex with a cyclobutadiene-like formal E_4^{3-} middle deck.



E = P (**1**)
E = As (**2**)

E = P, X = BF_4 (**3a**, 66 %), [FAl] (**3b**, 56 %)
E = As, X = BF_4 (**4a**, 65 %), [FAl] (**4b**, 42 %)

Crystals suitable for single crystal X-ray structure analysis are obtained from concentrated solutions in CH_2Cl_2, layered with pentane (**3b**, **4a**, **4b**) or hexane (**3a**) at -30 °C. Since the compounds **3a**/**3b** and **4a**/**4b** are isostructural and differ solely in the used anion, only the structures of **3a** and **4a** in the solid state are depicted in Figure 4. The structures reveal triple-decker complexes with *cyclo*-E_4 ligands coordinating in η^4:η^4 fashion to two {Cp'''Co} fragments. The geometry of the *cyclo*-E_4 ligand is slightly distorted and differs a little in all compounds. For **3a** and **4a**, there are rectangular *cyclo*-E_4 ligands with two shorter E-E bonds (P1-P2 2.1860(9), P2-P3 2.1837(8), As1-As2/As3-As4 2.3882(2) Å) and two longer E-E bonds (P1-P4 2.3022(8), P2-P3 2.2960(8), As1-As4/As2-As3 2.5198(2) Å), which might be viewed as *cyclo*-butadiene-like units. In **3b**, the E_4 ligand has a trapezoid shape with three shorter P-P bonds (P1-P2 2.2205(6), P2-P3 2.2358(6), P3-P4 2.2069(7) Å) and one longer one (P1-P4 2.3139(6) Å). In **4b**, the As_4 ligand is disordered over three positions with site occupancies of 5, 25 and 70 %, preventing the accurate description of the As_4 unit.

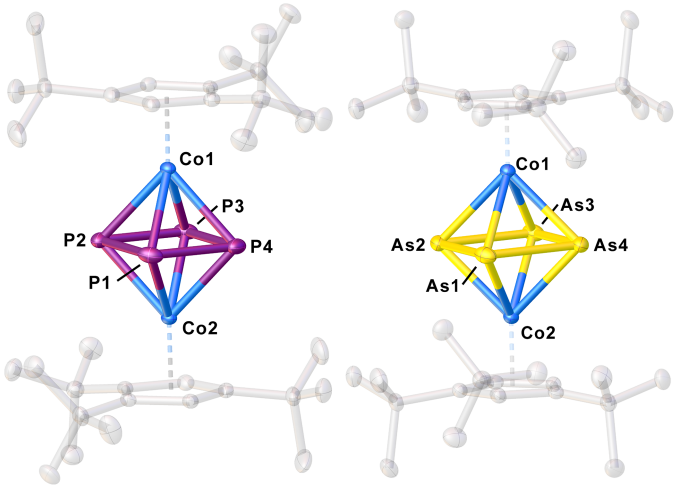


Figure 4. Structure of the cations in **3a** (left) and **4a** (right) in the solid state. Thermal ellipsoids are shown at 50 % probability level. Hydrogen atoms, anions and solvent molecules are omitted for clarity.

The DFT optimization of the geometries of **3a** and **3b** (BP86/def2-TZVP level of theory; **3a**^{c}, **3b**^{c}) reveals a rectangular E_4 ligand (similar to that observed in the crystal structure) for **3a** and

a trapezoid-shaped ligand for **3b,** which is more widened than in **3b** (2.51332 Å (optimized geometry of **3b^c**) and 2.3139(6) Å (experimental structure of **3b**)). The geometry optimizations were both started from the atomic coordinates obtained from the X-ray structure. However, starting from a symmetric *cyclo*-P_4, this geometry is retained in the optimized structure of **3a^c**, the same as for the finally trapezoid-shaped ligand in **3b^c**. The energy difference between the two isomers is only 3 kJ/mol, with the trapezoid isomer being favored. Both geometries represent minima on the energy hypersurface (cf. SI). The structural differences between **3a** and **3b** can be attributed to packing effects, since the size of the counter ion differs significantly. DFT calculations show a similar behavior for the arsenic compounds **4a** and **4b**. The formation of one P-P bond and of a trapezoid-shaped ligand are reminiscent of the coordination of **1** to $\{W(CO)_5\}$ fragments leading to ($[(Cp'''Co)_2(\mu,\eta^4{:}\eta^4{:}\eta^1{:}\eta^1\text{-}P_4)\{W(CO)_5\}_2]$).[17] However, in this complex, the P1-P2 and P3-P4 distances are significantly shorter (2.070(8) and 2.093(9) Å), the P2-P3 distance is quite the same (2.276(8) Å) and the P1-P4 distance is longer (2.962(8) Å) than the corresponding distances in **3b**. An analogous As compound is unknown. The compounds **3a**/**3b** and **4a**/**4b** are paramagnetic. The ^{1}H NMR spectra in solution at room temperature reveal strongly shifted broad signals for the Cp''' ligands. The EPR spectra (solid and in frozen solution at 77K) show an isotropic resonance with the g_{iso} values indicating one unpaired electron each (77 K, solid: **3a**: g_{iso} = 2.037, **3b**: g_{iso} = 2.024, **4a**: g_{iso} = 2.121, **4b**: g_{iso} = 2.094, cf. SI). The Evans NMR reveals an effective magnetic moment of 1.23 μ_B for **3b** and 2.01 μ_B for **4b** corresponding to about one unpaired electron each.

The pnictogen ligands in the starting material **1** and **2** can be described as separated E_2^{2-} units (if Co^{III} moieties are assumed). By oxidation, one electron is removed and, formally, a *cyclo*-E_4^{3-} ligand is formed. The SOMO (**3a**: α-188, **4a**: α-224, cf. SI) reveals that the unpaired electron is located mainly on the E_4^{3-} ligand (electron density within the short E-E bonds and between them with a minor contribution of the Co atoms, cf. SI). The spin density is homogenously distributed over all E und Co atoms, and the absence of a hyperfine coupling to Co in the EPR spectra also underlines the presence of a formal *cyclo*-E_4^{3-} ligand. Likewise, the decrease of the formal charges (Mulliken charges, cf. SI) of the E_4 ligand as compared to the starting complexes emphasizes this description. It has to be noted that, this description of **3a** and **4a** is only a formalism, while the electron density in the SOMOs is also distributed over both Co atoms and Cp''' ligands and the covalent character of the bonding between the E_4 ligand and metal has to be considered.

By reacting **1** and **2** with Ag[TEF] ([TEF] = $[Al\{OC(CF_3)_3\}_4]$), the dications $[(Cp'''Co)_2(\mu,\eta^4{:}\eta^4\text{-}E_4)][TEF]_2$ (E = P (**5**), As (**6**)) are obtained in crystalline yields of 68 and 69 %, respectively (Eq. 2), which now represent *cyclo*-E_4^{2-} middle decks with four equivalent bonds.

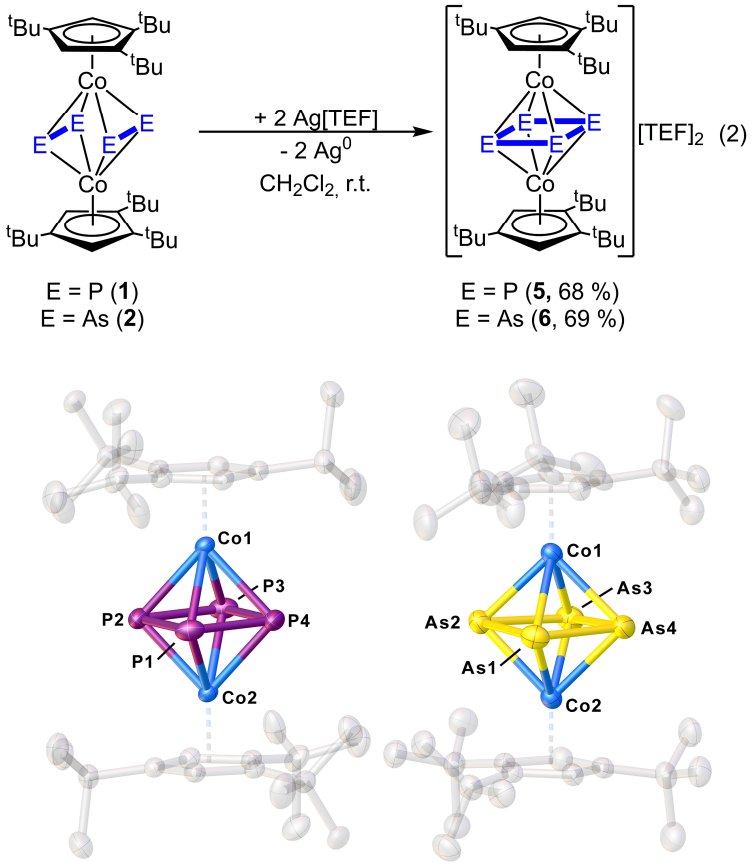


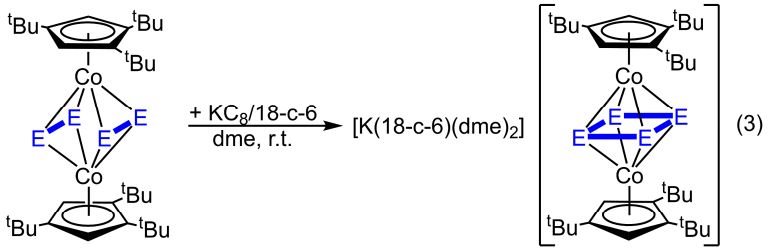
Figure 5. Structure of the dications in **5** (left) and **6** (right) in the solid state. Thermal ellipsoids are shown at 50 % probability level. Hydrogen atoms, anions and solvent molecules are omitted for clarity.

The structures of **5** and **6** in the solid state (Figure 5) show triple-decker complexes with a *cyclo*-E_4 ligand as a middle deck. In **5**, the P_4 unit is planar with very similar P-P distances (2.236(2) and 2.239(2) Å), representing single bonds, which is confirmed by the Wiberg bond indices (WBI) of 0.92.[18] The P-P bond lengths in **5** are longer than in the complexes with a *cyclo*-P_4 ligand as an end-deck as in [Cp'''Co(η^4-P_4)] (2.1557(18)-2.1699(14) Å).[19] In contrast to **5**, the *cyclo*-As_4 ligand in **6** is slightly folded (fold angle 3 °). The As-As bond lengths are between 2.4355(9) and 2.4759(9) Å and lie in the range of single bonds, confirmed by WBIs between 0.80 and 0.93 (the DFT optimized geometry reveals a trapezoid-shaped As_4 ligand with a fold angle of 6.4 °).[18] The As-As distances are also longer than in complexes with a *cyclo*-As_4 ligand as an end-deck such as [Cp*Nb$(CO)_2$(η^4-As_4)] (2.345(4)-2.409(4) Å).[20] The structural motif of the dication is reminiscent of the Cp^{tBu} (C_5Me_4*t*Bu)-substituted compound [$(Cp^{tBu}Co)_2$(μ,η^4:η^4-As_4)][$Co_3Cl_8(thf)_2$], obtained, however, by starting from $As_7(SiMe_3)_3$ as an As source.[21] This complex shows As-As distances of 2.4552(10) and 2.4680(11) Å). In the ^{1}H NMR spectrum of **5**, two broad singlets centered at δ = 1.82 and 1.71 ppm for the *t*Bu groups of the Cp''' ligand can be detected, but no signals for the H atoms bonding the Cp ring, indicating a dynamic process in solution. The $^{31}P\{^1H\}$ NMR spectrum at room temperature shows one broad singlet at δ = 494.0 ppm ($\omega_{1/2}$ = 4000 Hz). Upon cooling to -80 °C, the signals in the ^{1}H NMR spectra broaden further and still no resonance for the Cp bond H atoms can be

found. The signal in the $^{31}P\{^1H\}$ NMR spectra broadens too and eventually disappears completely. Warming an NMR sample of **5** in o-difluorobenzene containing a C_6D_6 capillary to 80 °C, the signals in the ^1H NMR spectra remain unchanged. In the $^{31}P\{^1H\}$ NMR spectrum, a singlet can be observed whose intensity decreases at 80 °C. In the ^1H NMR spectrum of **6**, three singlets centered at δ = 6.50, 1.66 and 1.50 ppm can be detected, with the signal for the Cp bond H atoms (6.50 ppm) being low field shifted by ca. 2 ppm in comparison to the starting material. Both **5** and **6** are EPR-silent.

The abstraction of another electron of the E_4^{3-} ligand in **3** and **4** leads to a further change in the geometry and the ligand can now be described as a *cyclo*-E_4^{2-} unit. Identical P-P bonds in the completely planar middle deck in **5** indicate the presence of an aromatic P_4^{2-} ligand. The HOMO of **5** shows the electron density to be homogenously distributed between all P atoms (indicating four equivalent bonds) and on both Co atoms (shape of a d orbital, cf. SI). In the case of **6**, the As_4^{2-} ligand is not completely planar and the As-As distances differ slightly from each other. The optimized geometry shows a trapezoid-shaped ligand with one side being more open than the structure in the solid state suggests. Therefore, the HOMO shows electron density within the three shorter As-As bonds and located at the Co atoms (d orbitals). Since the formal charges (Mulliken charges, cf. SI) of the E_4 ligand in **5** and **6** decrease further compared to the monocations and related to **1** and **2**, the formal description of the ligand as E_4^{2-} seems appropriate. All mentioned oxidations of **1** and **2** are fully reversible. The addition of the stoichiometric amounts of KC_8 yields selectively back the starting materials **1** and **2**.

In the related cyclic voltammograms, both compounds **1** and **2** show reversible reduction processes at rather negative redox potentials. Potassium graphite was chosen as a suitable reduction agent. By using a small excess over 1 eq. of KC_8, the monoanions $[K(18\text{-c-}6)(dme)_2][(Cp'''Co)_2(\mu,\eta^4{:}\eta^4\text{-}E_4)]$ (E = P (**7**), As (**8**)) can be obtained in crystalline yields of 56 and 40 %, respectively, which now represent *cyclo*-butadiene-like E_4^{5-} middle decks (Eq. 3). Due to their anionic character, **7** and **8** are extremely sensitive towards air and moisture.



E = P (**1**)
E = As (**2**)

E = P (**7**, 56 %)
E = As (**8**, 40 %)

(3)

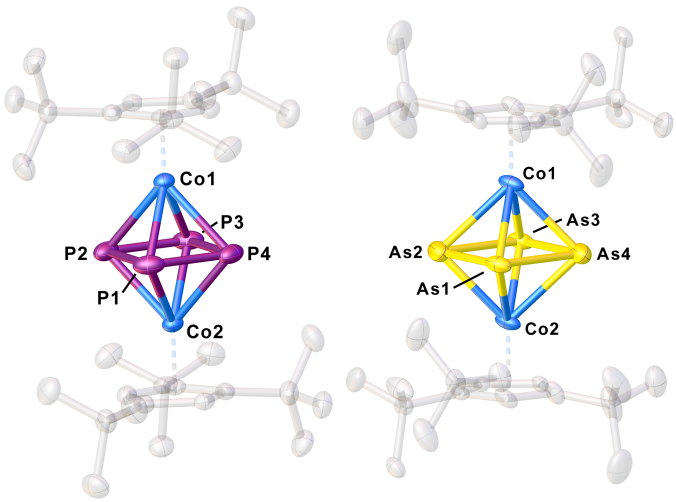


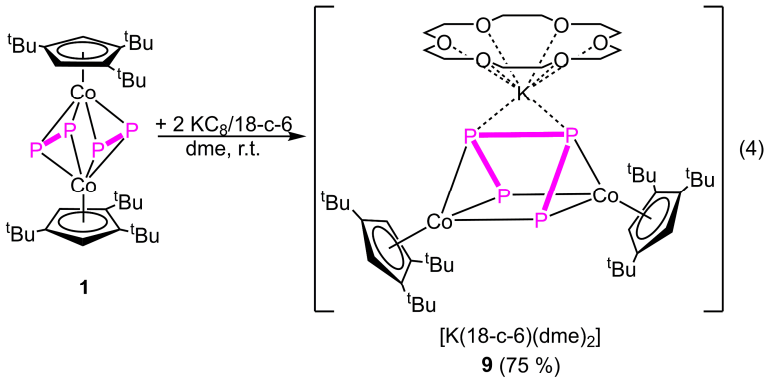
Figure 6. Structure of the anions in **7** (left) and **8** (right) in the solid state. Thermal ellipsoids are shown at 50 % probability level. Hydrogen atoms, cations and solvent molecules are omitted for clarity.

The structures in the solid state (Figure 6) reveal a rectangular *cyclo*-E_4 middle deck for both compounds. Two shorter E-E bonds (P1-P2/P3-P4 2.1288(9), As1-As2/As3-As4 2.3074(16) Å) and two longer E-E bonds (P1-P4/P2-P3 2.3606(8), As1-As4/As2-As3 2.5852(15) Å) are present. All bonds are in the range of shortened and elongated single bonds, respectively, also confirmed by the WBIs for the short (**7**: 1.18, **8**: 1.15) and long bonds (**7**: 0.68, **8**: 0.63).[18,22] Compounds **7** and **8** are both paramagnetic as indicated by the paramagnetic shift of the signals of the Cp''' ligand in the ^{1}H NMR spectra in solution and by the absence of signals in the ^{31}P{^{1}H} NMR spectrum (for **7**). Both compounds are EPR-active and show resonances in solution (frozen solution) and in the solid state (room temperature and at 77 K). The spectra of both compounds show a rhombically structured signal at 77 K in the solid state (**7**: g_x = 2.0840, g_y = 2.0638, g_z = 1.9897, **8**: g_x = 2.2765, g_y = 2.0724, g_z = 2.0752). The effective magnetic moment was determined by the Evans method to be 1.93 μ_B (**7**) and 2.35 μ_B (**8**), respectively, corresponding to about one unpaired electron each.

The DFT calculations reveal that the SOMO (**7**: α-189, **8**:α-225) is mainly located between E1-E4 and E2-E3 in a binding fashion with some participation of a d orbital of the Co atoms and an antibonding π orbital of the Cp''' ligands. The spin density is spread over the E_4 ligand and the Co atoms while mainly being located on Co, explaining the rhombic signals in the EPR spectra of **7** and **8**. The summed Mulliken charges (cf. SI) also indicate that the additional electron was transferred to the E_4 ligand and the formal description as E_4^{5-} moieties seems to be appropriate, although the spin density distribution, indicates a partly charge delocalization also on Co atoms and Cp''' ligands.

According to the cyclic voltammograms, **1** shows only one reversible reduction while **2** reveals two of them. Based on this observation, we attempted to access the doubly reduced product of **1**. Indeed, the reduction of **1** leads to the dianionic compound [K(18-c-6)(dme)$_2$][K(18-c-6)][(Cp'''Co)$_2$(μ,η^3:η^3-P_4)] (**9**) obtained in crystalline yields of 75 %

(Eq. 4). Probably, during the reaction, first the monoanion **7** is formed followed by a further reduction to the dianion **9**. The second reduction step occurs by the cleavage of a P-P bond in **7** followed by the rearrangement of the P_4 unit. Compound **9** is extremely sensitive towards air and moisture.



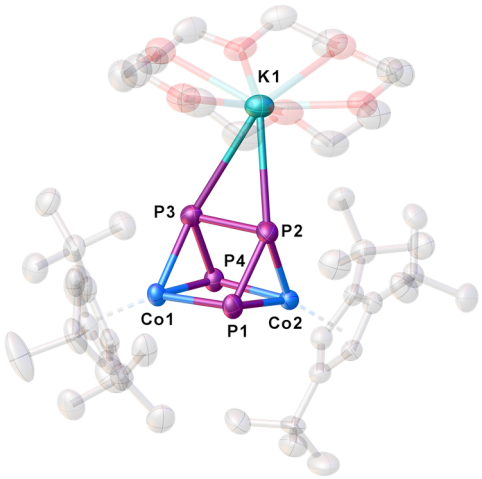


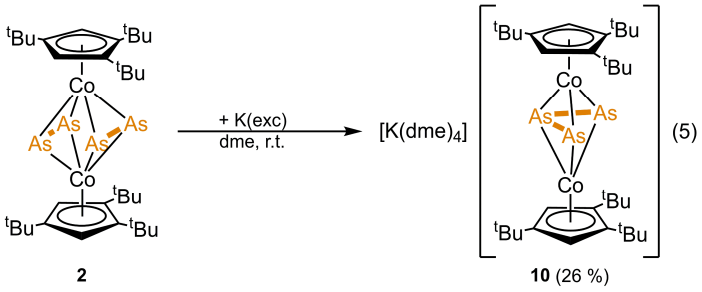
Figure 7. Structure of the dianion in **9** with one coordinating counterion in the solid state. Thermal ellipsoids are shown at 50 % probability level. Hydrogen atoms, the second cation and solvent molecules are omitted for clarity.

The structure of **9** in the solid state (Figure 7) reveals a prismatic structural motif consisting of two {Cp'''Co} fragments and four P atoms. There are two shorter P-P bonds (P1-P2 2.1582(11), P3-P4 2.1615(11) Å) and one longer one (P2-P3 2.2646(10) Å).The P1···P4 distance is with 2.8396(12) Å too long for a P-P bond, but below the sum of the van der Waals radii (Σ_{vdW} = 3.80 Å).[23] Therefore, an interaction between the two nuclei can be expected. This is indeed confirmed by the WBI of 0.24. The P_4 ligand can be best described as being butadiene-like. The Co_2P_4 prismatic structural motif is reminiscent of the samarium complex $[(Cp'''Co)_2(Cp^*_2Sm)(\mu_3,\eta^3{:}\eta^2\text{-}P_4)]$.[24] The $Co_2P_4^{2-}$ scaffold is also isoelectronic to the Ni_2P_4 unit in the complex $[(Cp^{iPr}Ni)_2(\mu,\eta^3{:}\eta^3\text{-}P_4)]$.[25]

In the $^{31}P\{^1H\}$ NMR spectrum of **9** in thf two doublets centered at δ = 20.6 and -7.5 ppm with a $^1J_{PP}$ coupling constant of 263 Hz can be assigned due to the two inequivalent P atoms in **9**. The fact that the cyclic P_4 ligand in **7** rearranges upon addition of another electron is not obvious. The first step of the reaction would be formally a reduction to $[(Cp'''Co)_2(\mu,\eta^4{:}\eta^4\text{-}P_4)]^{2-}$

(**I-9a**). But, in comparison to the anion of **9, I-9a** is 41.46 kJ/mol higher in energy. The coordination of a $[K(18\text{-c-}6)]^+$ unit to the edge of the P_4 ligand in **9** contributes with 193.73 kJ/mol to the stabilization of the product. Interestingly, when the potassium counterions are fully separated from the P_n ligand complex by using 2,2,2-cryptand instead of 18-c-6, no formation of **9** can be observed. Thus, by reacting **1** with an excess of potassium graphite in the presence of the 2,2,2-cryptand yields only the monoanion **7**.

Both reductions of **1** and the reduction of **2** are fully reversible. The addition of stoichiometric amounts of $AgBF_4$ to **7**, **8** and **9**, respectively, yields selectively the related starting materials. While the Co_2As_4 prism is known as a structural motif of the samarium compound ($[(Cp'''Co)_2(Cp^*_2Sm)(\mu_3,\eta^3{:}\eta^3{:}\eta^2\text{-}As_4)]$),[26] it cannot be obtained by the reduction of **2** with two equivalents of potassium graphite. Probably, an additional coordination to a Lewis acid such as Cp^*_2Sm is needed to obtain a stable compound. From the stoichiometric reaction, only the monoanion **8** can be isolated. Using an excess of potassium (four fold or higher), one arsenic atom is abstracted and $[K(dme)_4][(Cp'''Co)_2(\mu,\eta^3{:}\eta^3\text{-}As_3)]$ (**10**) can be isolated in crystalline yields of 26 % (Eq. 5).



In this reaction, the formation of a black precipitate is observed. Compound **10** is extremely sensitive towards air and moisture.

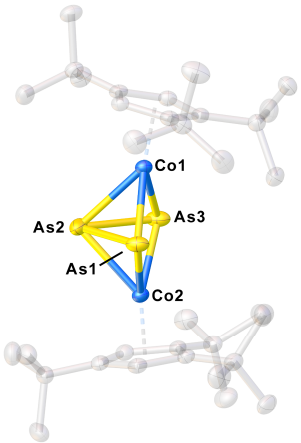


Figure 8. Structure of the monoanion in **10** in the solid state. Thermal ellipsoids are shown at 50 % probability level. Hydrogen atoms, cations and solvent molecules are omitted for clarity.

The structure in the solid state (Figure 8) reveals a bent triple-decker complex with an allylic As_3 ligand. The As1-As2 (2.4216(4) Å) and As2-As3 (2.4055(4) Å) bonds are in the range of single bonds, which is also confirmed by WBIs of 0.99.[18] The distance As1-As3 is 3.0224(5) Å, being too long to be considered as a bond. Since the distance is still below the sum of the van der Waals radii (Σ_{vdW} = 3.76 Å), an interaction between the two atoms can be expected, which is confirmed by a WBI of 0.20.[23] Alternatively, **10** can be described as a nido cluster with a Co_2As_3 core according to the Wade and Mingos rules. There are barely any triple-decker sandwich complexes known including Cp ligands and a P_3 ligand as a middle deck, and none with an As_3 ligand. The Ni compounds $[(Cp'''Ni)_2((\mu,\eta^3:\eta^3\text{-}P_3)]^-$, $[(Cp'''Ni)_2((\mu,\eta^3:\eta^3\text{-}P_3)]$ and the heterobimetallic $[(Cp'''Co)(Cp'''Ni)((\mu,\eta^3:\eta^3\text{-}P_3)]]$ have been reported.[27] While the nickel complexes formally possess one or two electrons more than **10**, the latter is isoelectronic to **10**. Therefore, **10** represents the first example of a triple-decker complex with an allylic As_3 ligand.

3.3 Conclusion

It could be shown that the cobalt complexes $[(Cp'''Co)_2(\mu,\eta^2:\eta^2\text{-}E_2)_2]$ (E = P (**1**), As (**2**)) exhibit a unique redox chemistry far from the usual behavior of a triple decker complex or of polypnictogen rings and cages. Instead, they display a distinctive platform where E-E bond formations can be performed using both oxidation and reduction reactions, with these processes being completely reversible. Via reduction and oxidation, the two separate E_2^{2-} units in **1** and **2**, respectively, can be transformed into cyclobutadiene-like E_4^{3-} moieties (**3a**, **3b**, **4a**, **4b**) and E_4^{5-} moieties (**7**, **8**), respectively, or finally into *cyclo*-E_4^{2-} ligands in **5** and **6**. Further reduction of the monoanions **7** und **8** leads either to the cleavage of a P-P bond followed by the rearrangement into a Co_2P_4 scaffold or, in the case of an $(As_2)_2$ unit, to the abstraction of one arsenic atom to yield a bent triple decker complex with an allylic As_3 ligand as a middle deck (**10**), which represents the first example of a triple-decker complex with such a ligand. All redox processes (except for the formation of **10**) are fully reversible and can be selectively reversed when stoichiometric amounts of KC_8 or $AgBF_4$, respectively, are added. Even the formation of two P-P bonds as well as the cleavage of one P-P bond in the formation of **9** can be reverted stepwise upon addition of one or two equivalents of $AgBF_4$. Moreover, these results show also clearly the similarities and the different behavior of the $(As_2)_2$ entity in **2** and the $(P_2)_2$ moiety in **1** within these redox processes.

3.4 Supporting Information

3.4.1 Synthetic procedures and experimental details

Synthetic Procedures: All manipulations were performed under an atmosphere of dry argon using standard glove-box and Schlenk techniques. All solvents were degassed and purified by standard procedures. The compounds $[(Cp'''Co)_2(\mu,\eta^2{:}\eta^2\text{-}P_2)_2]$[14] (**1**), $[(Cp'''Co)_2(\mu,\eta^2{:}\eta^2\text{-}As_2)_2]$[15] (**2**), Ag[TEF][28], Ag[FAl][29], KC_8[30] were prepared according to literature procedures. $Ag[BF_4]$, 18-c-6, K and KH were purchased commercially.

The NMR spectra were recorded with a Bruker Avance 400 spectrometer (^{1}H: 400.13 MHz, ^{31}P: 161.976 MHz). The chemical shifts are given in ppm referenced to external $SiMe_4$ (^{1}H) and H_3PO_4 (^{31}P). Elemental analyses were determined with an Elementar Vario EL III apparatus. The X-Band EPR measurements were carried out with a MiniScope MS400 device with a frequency of 9.44 GHz and a rectangular resonator TE102 of the company Magnettech GmbH. The ESI-MS spectra were acquired on a ThermoQuest Finnigan MAT TSQ 7000 mass spectrometer.

3.4.1.1 Synthesis of $[(Cp'''Co)_2(\mu,\eta^4{:}\eta^4\text{-}P_4)][X]$ (X = BF_4 (3a), [FAl] (3b))

AgX (X = BF_4: 27.5 mg, 0.14 mmol, 1 eq, X = [FAl]: 204 mg, 0.14 mmol, 1 eq) was dissolved in CH_2Cl_2. The silver salt was added to a stirred solution of $[(Cp'''Co)_2(\mu,\eta^2{:}\eta^2\text{-}P_2)_2]$ (**1**) (100 mg, 0.14 mmol, 1 eq) in CH_2Cl_2. The color changed from dark purple to green to brown and a black precipitate (Ag^0) is obtained. After stirring for 1h it was filtrated over diatomaceous earth and the solvent removed *in vacuo*. The residue was dissolved in CH_2Cl_2, layered with hexane and stored at -30 °C. After a few days **3a** and **3b** can be obtained as green blocks. The supernatant was decanted off, the resulting crystals were washed with hexane three times and dried *in vacuo*. Yield: **3a**: 73 mg (66 %), **3b**: 164 mg (56 %).

3a: **^{1}H NMR** (CD_2Cl_2, 25 °C): δ [ppm] = 2.87 (s, 9H, $C_5H_2{}^tBu_3$), 2.70 (s, 18H, $C_5H_2{}^tBu_3$), -29.97 (br, $\omega_{1/2}$ = 696 Hz, 2H, $C_5H_2{}^tBu_3$).

^{31}P{^{1}H} NMR (CD_2Cl_2, 25 °C): no signal detectable between -600 and +600 ppm (paramagnetic).

^{19}F{^{1}H} NMR (CD_2Cl_2, 25 °C): δ [ppm] = -152.4 (s, BF_4).

X-band EPR (77 K, frozen solution) g_{iso} = 2.037, (77 K, solid) g_{iso} = 2.037.

ESI-MS (CH_2Cl_2): *m/z* = 677.2 (100 %, $[M\text{-}P]^+$),

EA $C_{34}H_{58}Co_2P_4BF_4$ x 0.3 CH_2Cl_2: calc [%]: C 50.19; H 7.20; found [%]: C 50.57; H 7.16.

3b: **^{1}H NMR** (CD_2Cl_2, 25 °C): δ [ppm] = 2.88 (s, 9H, $C_5H_2{}^tBu_3$), 2.71 (s, 18H, $C_5H_2{}^tBu_3$), -24.76 (br, $\omega_{1/2}$ = 124 Hz, 2H, $C_5H_2{}^tBu_3$).

^{31}P{^{1}H} NMR (CD_2Cl_2, 25 °C): no signal detectable between -600 and +600 ppm (paramagnetic).

^{19}F{^{1}H} NMR (CD_2Cl_2, 25 °C): δ [ppm] = -112.6 (d, J_{F-F} = 285 Hz, 6F), -117.1 (d, J_{F-F} = 279 Hz, 6F), -121.8 (d, J_{F-F} = 279 Hz, 3F), -127.9 (s, 6F), -130.6 (d, J_{F-F} = 274 Hz, 6F), -137.2 (d, J_{F-F} = 276 Hz, 6F), -141.2 (d, J_{F-F} = 274 Hz, 3F), -154.3 (t, J_{F-F} = 22 Hz, 6F), -165.0 (t, J_{F-F} = 18 Hz, 6F), -172.0 (s, AlF, 1F) .

Evans-NMR (CD_2Cl_2, 25 °C): μ_{eff} = 1.23 μ_B corresponding to 0.59 unpaired electrons.

X-band EPR (77 K, frozen solution) g_{iso} = 2.029, (77 K, solid) g_{iso} = 2.024.

ESI-MS (CH_2Cl_2): *m/z* = 677.3 (100 %, $[M-P]^+$).

EA $C_{70}H_{58}O_3AlF_{46}Co_2P_4$: calc [%]: C 40.21; H 2.80; found [%]: C 40.73; H 2.95.

3.4.1.2 Synthesis of [(Cp'''Co)$_2$(μ,η^4:η^4-As$_4$)][X] (X = BF$_4$ (4a), [FAl] (4b))

AgX (X = BF_4: 22 mg, 0.11 mmol, 1 eq, X = [FAl]: 168 mg, 0.11 mmol, 1 eq) and [(Cp'''Co)$_2$(μ,η^2:η^2-As$_2$)$_2$] (**2**) (100 mg, 0.11 mmol, 1 eq) were weighed in together and dissolved in CH_2Cl_2. No color change was observed. After stirring for 1h it was filtrated over diatomaceous earth, where a dark residue remains (Ag^0) and the solvent was removed *in vacuo*. The residue was dissolved in ortho-difluoro benzene (**4a**) and CH_2Cl_2 (**4b**), layered with hexane (**4a**) and pentane (**4b**) and stored at -30 °C. After a few days **4a** and **4b** can be obtained as green blocks. The supernatant was decanted off, the resulting crystals washed with hexane three times and dried *in vacuo*.

Yield: **4a**: 72 mg (65 %), **4b**: 174 mg (68 %).

4a: **^{1}H NMR** (CD_2Cl_2, 25 °C): δ [ppm] = 2.78 (s, 9H, $C_5H_2{}^tBu_3$), 2.57 (s, 18H, $C_5H_2{}^tBu_3$), -23.93 (br, 2H, $C_5H_2{}^tBu_3$).

^{19}F{^{1}H} NMR (CD_2Cl_2, 25 °C): δ [ppm] = -150.4 (s, BF_4).

X-band EPR (77 K, frozen solution) g_{iso} = 2.118, (77 K, solid) g_{iso} = 2.121, (293 K, solid) g_{iso} = 1.993.

ESI-MS (CH_2Cl_2): *m/z* = 809.1 (95 %, $[M-As]^+$), 825.1 (20 %, $[M-As+O]^+$), 915.9 (100 %, $[M+2O]^+$), 931.9 (80 %, $[M+3O]^+$).

EA $C_{34}H_{58}Co_2As_4BF_4$: calc [%]: C 42.05; H 6.02; found [%]: C 42.12; H 5.85.

4b: **^{1}H NMR** (CD_2Cl_2, 25 °C): δ [ppm] = 2.86 (s, 9H, $C_5H_2{}^tBu_3$), 2.65 (s, 18H, $C_5H_2{}^tBu_3$), -24.70 (br, 2H, $C_5H_2{}^tBu_3$),

^{19}F{^{1}H} NMR (CD_2Cl_2, 25 °C): δ [ppm] = -112.5 (d, J_{F-F} = 279 Hz, 6F), -117.1 (d, J_{F-F} = 280 Hz, 6F), -121.7 (d, J_{F-F} = 275 Hz, 3F), -127.8 (s, 6F), -130.6 (d, J_{F-F} = 279 Hz, 6F), -137.0 (d, J_{F-F} = 279 Hz, 6F), -140.9 (d, J_{F-F} = 279 Hz, 3F), -154.1 (t, J_{F-F} = 21 Hz, 6F), -164.8 (t, J_{F-F} = 20 Hz, 6F), -172.0 (s, AlF, 1F).

Evans-NMR (CD_2Cl_2, 25 °C): μ_{eff} = 2.01 μ_B corresponding to 1.25 unpaired electrons.

X-band EPR (77 K, frozen solution) g_{iso} = 2.118, (293 K, liquid) g_{iso} = 2.078, (77 K, solid) g_{iso} = 2.094.

ESI-MS (CH_2Cl_2): *m/z* = 809.1 (100 %, $[M-As]^+$), 825.1 (5 %, $[M-As+O]^+$), 931.9 (15%, $[M+3O]^+$).

EA $C_{70}H_{58}O_3AlF_{46}Co_2As_4$: calc [%]: C 37.11; H 2.58; found [%]: C 37.39; H 2.80.

3.4.1.3 Synthesis of $[(Cp'''Co)_2(\mu,\eta^4{:}\eta^4\text{-}P_4)][TEF]_2$ (5)

Ag[TEF] (324 mg, 0.28 mmol, 2.1 eq) and $[(Cp'''Co)_2(\mu,\eta^2{:}\eta^2\text{-}P_2)_2]$ (**1**) (100 mg, 0.14 mmol, 1 eq) were weighed separately and dissolved in CH_2Cl_2. The silver salt was added to **1** while the color changed from dark purple to brown and a dark precipitate (Ag^0) was obtained. After stirring for 1h it was filtrated over diatomaceous earth and the solvent removed *in vacuo*. The residue was dissolved in CH_2Cl_2, layered with hexane and stored at -30 °C. After a few days **5** can be obtained as brown blocks. The supernatant was decanted off, the resulting crystals washed with hexane three times and dried *in vacuo*.

Yield: 278 mg (75 %)

^{1}H NMR (CD_2Cl_2, 25 °C): δ [ppm] = 1.82 (s, 18H, $C_5H_2{}^tBu_3$), 1.71 (s, 9H, $C_5H_2{}^tBu_3$).

^{31}P{^{1}H} NMR (CD_2Cl_2, 25 °C): δ [ppm] = 494.2 (br, $\omega_{1/2}$ = 4432 Hz, P_4).

^{31}P NMR (CD_2Cl_2, 25 °C): δ [ppm] = 494.0 (br, $\omega_{1/2}$ = 4198 Hz, P_4).

^{19}F{^{1}H} NMR (CD_2Cl_2, 25 °C): δ [ppm] = -75.6 (s, [TEF]).

ESI-MS (CH_2Cl_2): *m/z* = 708.1 (50 %, $[M]^+$), 374.1 (100 %, $[(Cp'''Co)P_2+F+H]^+$).

EA $C_{66}H_{58}O_8Al_2F_{72}Co_2P_4$: calc [%]: C 29.99; H 2.21; found [%]: C 29.89; H 2.28.

3.4.1.4 Synthesis of $[(Cp'''Co)_2(\mu,\eta^4:\eta^4\text{-}As_4)][TEF]_2$ (6)

Ag[TEF] (281.6 mg, 0.23 mmol, 2 eq) and $[(Cp'''Co)_2(\mu,\eta^2:\eta^2\text{-}As_2)_2]$ (**2**) (100 mg, 0.11 mmol, 1 eq) were weighed separately and dissolved in CH_2Cl_2. The silver salt was added to **2** while the color changed from dark green to olive green and a dark precipitate (Ag^0) was obtained. After stirring for 1h the it was filtrated over diatomaceous earth and the solvent removed *in vacuo*. The residue was dissolved in CH_2Cl_2, layered with hexane and stored at -30 °C. After a few days **6** can be obtained as green blocks. The supernatant was decanted off, the resulting crystals washed with hexane three times and dried *in vacuo*.

Yield: 254 mg (80 %)

^{1}H NMR (CD_2Cl_2, 25 °C): δ [ppm] = 6.50 (s, 4H, $C_5H_2{}^t\text{Bu}_3$), 1.66 (s, 18H, $C_5H_2{}^tBu_3$), 1.50 (s, 9H, $C_5H_2{}^tBu_3$).

^{19}F{^{1}H} NMR (CD_2Cl_2, 25 °C): δ [ppm] = -75.5 (s, [TEF]).

ESI-MS (CH_2Cl_2): *m/z* = 442.1 (100 %, $[M]^{2+}$).

EA $C_{66}H_{58}O_8Al_2F_{72}Co_2As_4$: calc [%]: C 28.12; H 2.07; found [%]: C 28.56; H 2.40.

3.4.1.5 Synthesis of $[K(18\text{-}c\text{-}6(dme)_2][(Cp'''Co)_2(\mu,\eta^4:\eta^4\text{-}P_4)]$ (7)

$[(Cp'''Co)_2(\mu,\eta^2:\eta^2\text{-}P_2)_2]$ (**1**) (100 mg, 0.14 mmol, 1 eq), 18-c-6 (45 mg, 0.14 mmol, 1 eq) and KC_8 (22 mg, 0.16 mmol, 1.1 eq) were weighed in together and dissolved in dimethoxyethane. The color changed from dark purple to green. After stirring for 1 h it was filtrated over diatomaceous earth and the solvent removed *in vacuo*. The green residue was dissolved in dimethoxyethane, layered with hexane and stored at -30 °C. After a few days **7** can be obtained as green plates. The supernatant was decanted off, the resulting crystals washed with hexane three times and dried *in vacuo*.

Yield: 93 mg (56 %)

^{1}H NMR (thf-d_8, 25 °C): δ [ppm] = 3.70 (s, 24H, 18-c-6), 3.18 (br, $\omega_{1/2}$ = 92 Hz, 18H, $C_5H_2{}^tBu_3$), 2.21 (br, $\omega_{1/2}$ = 89 Hz, 36H, $C_5H_2{}^tBu_3$).

^{31}P{^{1}H} NMR (CD_2Cl_2, 25 °C): no Signal detectable between -600 and +600 ppm (paramagnetic).

Evans-NMR (thf-d_8, 25 °C): μ_{eff} = 1.93 μ_B corresponding to 1.17 unpaired electrons.

X-band EPR (77 K, liquid) g_{iso} = 2.0297, (77 K, solid), g_x = 2.0840, g_y = 2.0638, g_z = 1.9897, g_{iso} = 2.0458

ESI-MS (dme): *m/z* = 677.1 (100 %, $[M-P]^-$).

EA $C_{46}H_{82}O_6KCo_2P_4$: calc [%]: C 54.59; H 8.17; found [%]: C 54.34; H 7.89.

3.4.1.6 Synthesis of $[K(18\text{-c-}6(dme)_2][(Cp'''Co)_2(\mu,\eta^4:\eta^4\text{-}As_4)]$ (8)

$[(Cp'''Co)_2(\mu,\eta^2:\eta^2\text{-}As_2)_2]$ (**2**) (100 mg, 0.11 mmol, 1 eq), 18-c-6 (29mg, 0.11 mmol, 1 eq) and KC_8 (16 mg, 0.12 mmol, 1.1 eq) were weighed in together and dissolved in dimethoxyethane. The color changed from dark green to brown. After stirring for 1 h it was filtrated over diatomaceous earth and the solvent removed *in vacuo*. The brown residue was dissolved in dimethoxyethane, layered with hexane and stored at -30 °C. After a few days **8** can be obtained as brown blocks. The supernatant was decanted off, the resulting crystals washed with hexane three times and dried *in vacuo*.

Yield: 110 mg (71 %)

^{1}H NMR (thf-d_8, 25 °C): δ [ppm] = 3.69 (s, 24H, 18-c-6), 3.22 (br, $\omega_{1/2}$ = 122 Hz, 18H, $C_5H_2{}^tBu_3$), 2.65 (br, $\omega_{1/2}$ = 110 Hz, 36H, $C_5H_2{}^tBu_3$).

Evans-NMR (thf-d_8, 25 °C): μ_{eff} = 2.35 μ_B corresponding to 1.55 unpaired electrons.

X-band EPR (77 K, liquid) g_{iso} = 2.1181, (77 K, solid) g_x = 2.2765, g_y = 2.0724, g_z = 2.0752, g_{iso} = 2.1414, (293 K, solid) g_{iso} = 2.0883.

ESI-MS (dme): *m/z* = 809.9 (100 %, $[M-As]^-$).

EA $C_{54}H_{102}O_{10}KCo_2As_4$: calc [%]: C 47.41; H 7.52; found [%]: C 47.84; H 7.06.

3.4.1.7 Synthesis of $[K(18\text{-c-}6(dme)_2][K(18\text{-c-}6)][(Cp'''Co)_2(\mu,\eta^3:\eta^3\text{-}P_4)]$ (9)

$[(Cp'''Co)_2(\mu,\eta^2:\eta^2\text{-}P_2)_2]$ (**1**) (100 mg, 0.14 mmol, 1 eq), 18-c-6 (90 mg, 0.28 mmol, 2 eq) and KC_8 (44 mg, 0.32 mmol, 2.2 eq) were weighed in together and dissolved in dimethoxyethane. The color changed from dark purple to brown. After stirring for 1 h it was filtrated over diatomaceous earth and the solvent removed *in vacuo*. The brown residue was dissolved in dimethoxyethane, layered with hexane and stored at -30 °C. After a few days **9** can be obtained as brown blocks. The supernatant was decanted off, the resulting crystals washed with hexane three times and dried *in vacuo*.

Yield: 150 mg (75 %)

^{1}H NMR (thf-d_8, 25 °C): *δ* [ppm] = 4.13 (s, 4H, $C_5H_2{}^tBu_3$), 3.65 (s, 24H, 18-c-6), 3.43 (s, dme, 8H), 3.27 (s, dme, 12H), 1.40 (s, 18H, $C_5H_2{}^tBu_3$), 1.33 (s, 9H, $C_5H_2{}^tBu_3$).

^{31}P{^{1}H} NMR (thf-d_8, 25 °C): *δ* [ppm] = 20.6 (d, $^{1}J_{P\text{-}P}$ = 263 Hz, 2P, P_4), -7.5 (d, $^{1}J_{P\text{-}P}$ = 263 Hz, 2P, P_4).

^{31}P NMR (thf-d_8, 25 °C): *δ* [ppm] = 20.5 (d, $^{1}J_{P\text{-}P}$ = 263 Hz, 2P, P_4), -7.5 (d, $^{1}J_{P\text{-}P}$ = 263 Hz, 2P, P_4).

ESI-MS (dme): *m/z* = 677.2 (45 %, $[M\text{-}P]^-$), 646.2 (45 %, $[M\text{-}2P]^-$), 354.0 (100 %, $[Cp'''CoP_2]^-$).

EA $C_{66}H_{126}O_{16}K_2Co_2P_4$: calc [%]: C 52.99; H 8.49; found [%]: C 52.52; H 8.04.

3.4.1.8 Synthesis of [K(dme)$_4$][(Cp'''Co)$_2$(μ,η^3:η^3-As$_3$)] (10)

[(Cp'''Co)$_2$(μ,η^2:η^2-As$_2$)$_2$] (**1**) (100 mg, 0.11 mmol, 1 eq) and K (20 mg, 0.50 mmol, 4.5 eq) were weighed in together and dimethoxyethane was added. The color changed from dark green to brown within 3 days. It was filtrated over diatomaceous earth and the solvent removed *in vacuo*. The brown residue was dissolved in dimethoxyethane and layered with hexane at room temperature. After a few days **10** can be obtained as brown blocks. The supernatant was decanted off, the resulting crystals washed with hexane three times and dried *in vacuo*.

Yield: 35 mg (26 %)

^{1}H NMR (thf-d_8, 25 °C): *δ* [ppm] = 4.46 (s, 4H, $C_5H_2{}^tBu_3$), 1.30 (s, 18H, $C_5H_2{}^tBu_3$), 0.92 (s, 9H, $C_5H_2{}^tBu_3$).

ESI-MS (dme): *m/z* = 809.1 (15 %, $[M]^-$), 516.9 (100 %, $[Cp'''CoAs_3]^-$).

EA $C_{42}H_{78}O_4KCo_2As_3$: calc [%]: C 49.02; H 7.65; found [%]: C 48.72; H 7.35.

3.4.2 EPR studies

3.4.2.1 [(Cp'''Co)$_2$(μ,η^4:η^4-P$_4$)][X] (X = BF$_4$ (3a), [FAl] (3b))

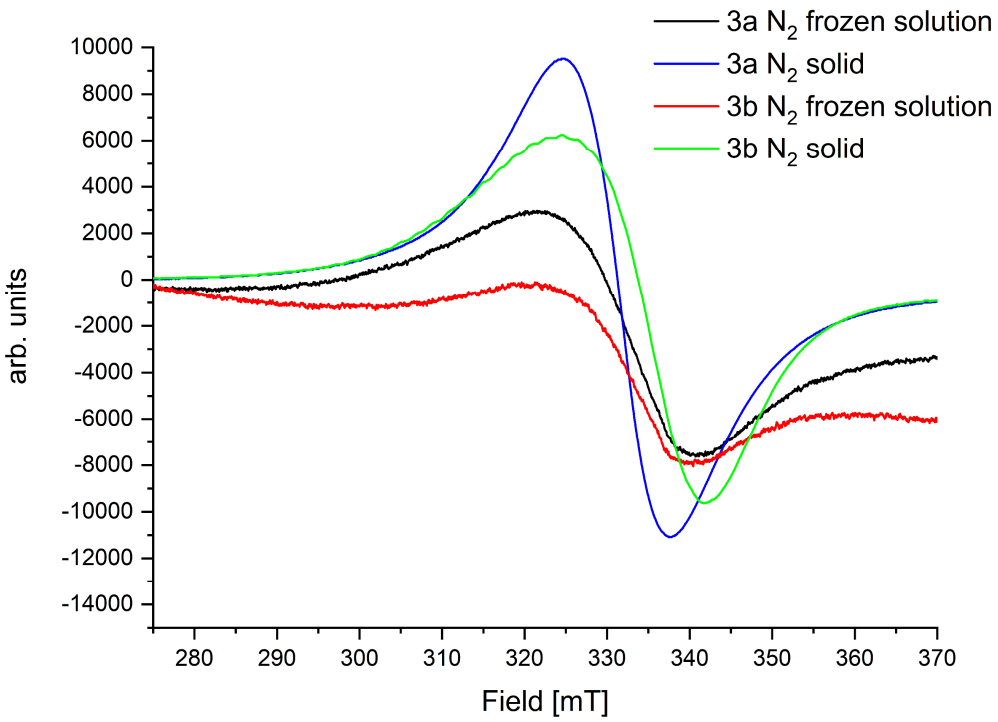


Figure S1: X-Band EPR spectra of **3a** and **3b** solid and in frozen solution at 77K.

3.4.2.2 [(Cp'''Co)$_2$(μ,η^4:η^4-As$_4$)][X] (X = BF$_4$ (4a), [FAl] (4b))

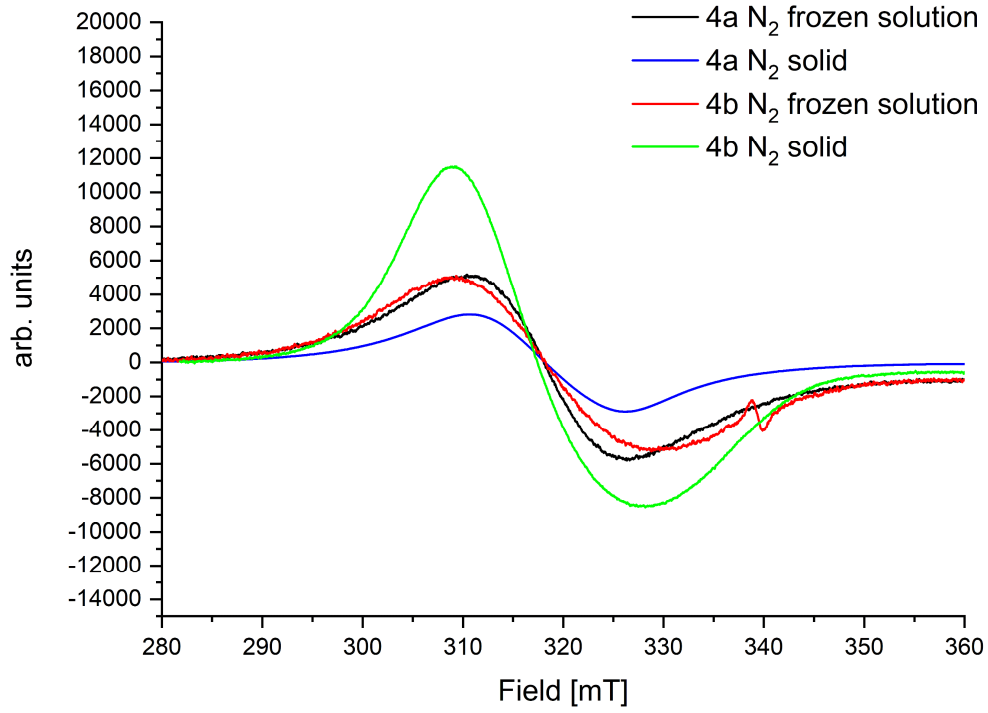


Figure S2: X-Band EPR spectra of **4a** and **4b** solid and in frozen solution at 77K.

3.4.2.3 [K(18-c-6(dme)$_2$][(Cp'''Co)$_2$(μ,η^4:η^4-P$_4$)] (7)

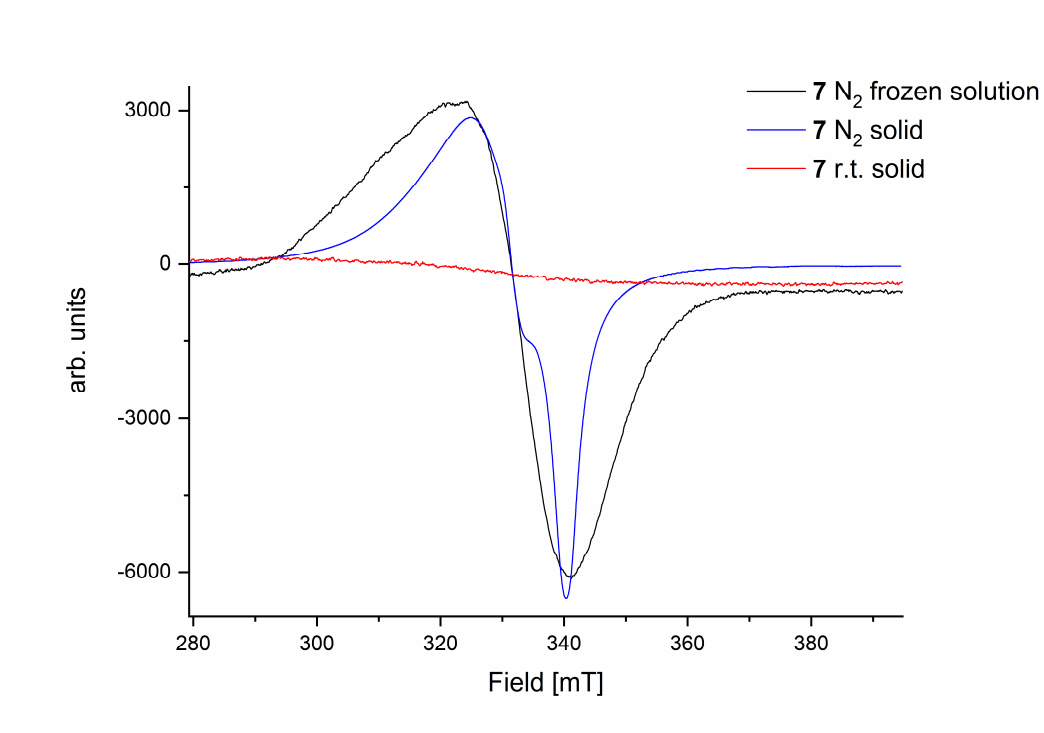


Figure S3: X-Band EPR spectrum of **7** solid and in frozen solution at 77K and r.t.

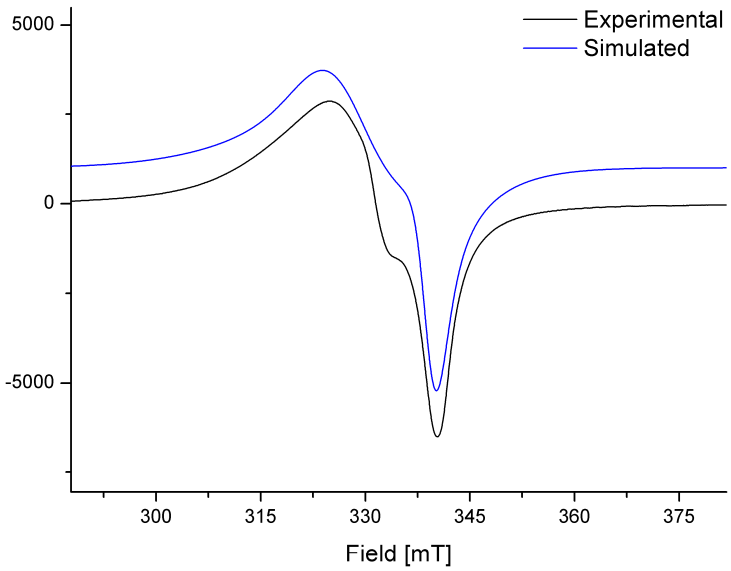


Figure S4: X-Band EPR spectrum of **7 (**solid at 77K) and simulated spectrum.

The EPR spectrum has been simulated with the EasySpin program.[31]
g_x = 2.0840, g_y = 2.0638, g_z = 1.9897, g_{iso} = 2.0458
Sys.S = 1/2;
Sys.g = [2.0638 2.0840 1.9897];
Sys.lw = [1.52];

Sys.HStrain = [300 1105 70];
Exp.mwFreq = 9.440920;
Exp.Range = [274.4295 394.4625];
Exp.nPoints = 4096;
Exp.Temperature = 77;
Exp.ModAmp = 0.2;

3.4.2.4 [K(18-c-6(dme)$_2$][(Cp'''Co)$_2$(μ,η^4:η^4-As$_4$)] (8)

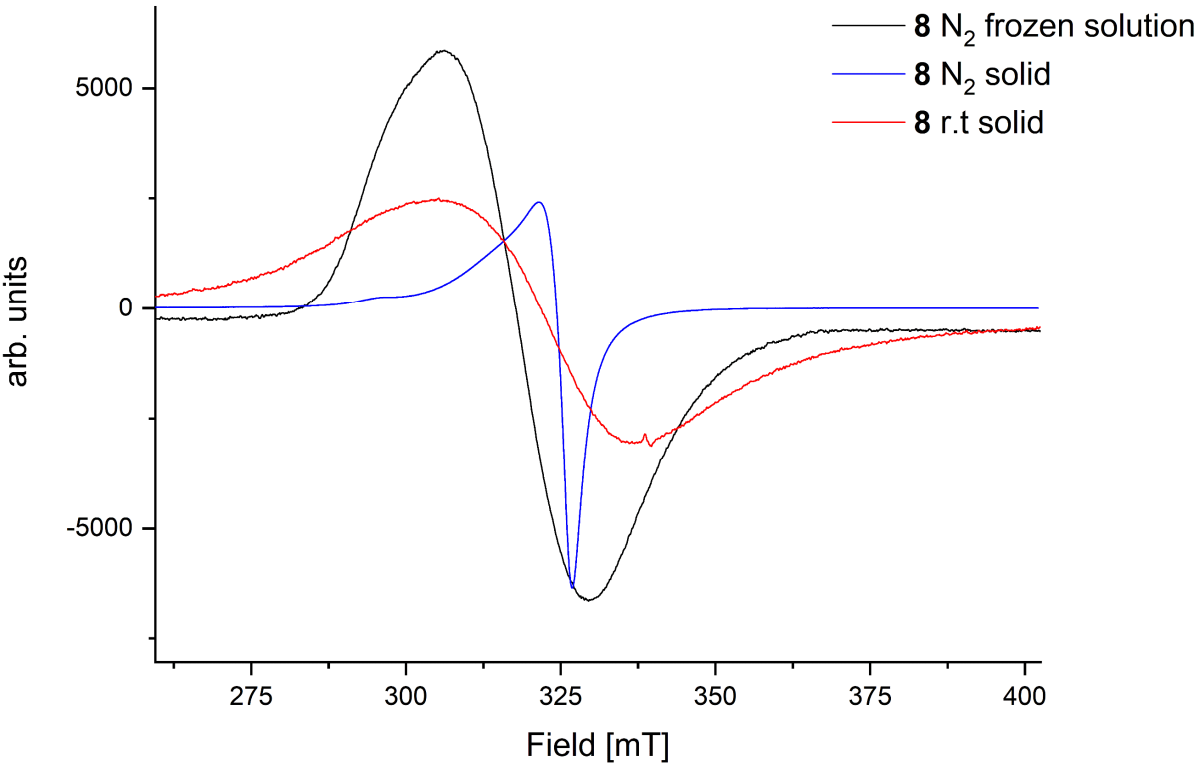


Figure S5: X-Band EPR spectrum of **8** solid and in frozen solution at 77K and r.t.

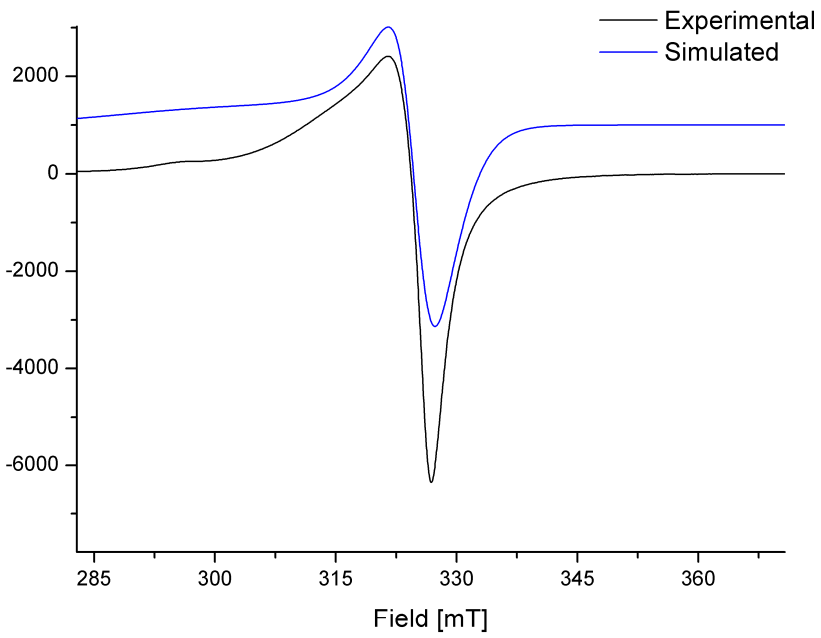


Figure S6: X-Band EPR spectrum of **8** (solid at 77K) and simulated spectrum.

The EPR spectrum has been simulated with the EasySpin program.[31]
g_x = 2.2765, g_y = 2.0724, g_z = 2.0752, g_{iso} = 2.1414
Sys.S = 1/2;
Sys.g = [2.27651 2.07237 2.07521];
Sys.lw = [3.79479];
Sys.HStrain = [954.3 237.4 6.9];

Exp.mwFreq = 9.440920;
Exp.Range = [251.36753 402.1245];
Exp.nPoints = 4096;
Exp.Temperature = 77;
Exp.ModAmp = 0.05;

3.4.3 NMR studies

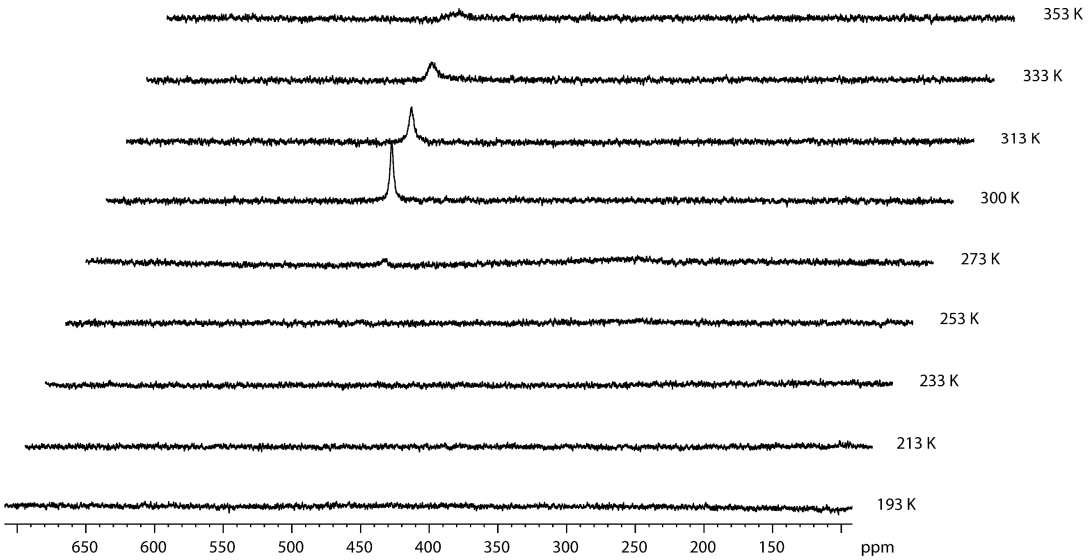


Figure S7: Various temperature $^{31}P\{^{1}H\}$ NMR study of **5**. Solvent CD_2Cl_2 (193 K - 273 K) and difluorobenzene with C_6D_6 capillary (300 K – 353 K). Unstable lock at 353 K.

3.4.4 Details on single crystal X-ray structure analysis

The X-ray diffraction experiments were performed on either an Gemini Ultra diffractometer (Oxford diffraction) with an AtlasS2 detector with Cu-K*α* radiation (λ = 1.54178 Å) (**5**) and Mo radiation (λ = 0.71073 Å) (**3a**, **3b**, **4a**) or a GV 50 diffractometer (Rigaku, formerly Agilent Technologies) with TitanS2 detector from applying Cu-K*α* radiation (λ = 1.54178 Å) (**4b**, **7**, **8**, **9**, **10**) or SuperNova (Agilent Technologies) with an Atlas detector applying Cu-K*α* radiation (λ = 1.54178 Å) (**6**). All measurements were performed at 123 K. An analytical absorption correction[32] (**3a**, **3b**, **4a**, **4b**, **5**, **7**, **8**, **9**), a numerical absorption correction based on gaussian integration over a multifaceted crystal model using *CrysAlis Pro* (**10**) or a multi-scan absorption correction using *CrysAlisPro* (**6**) using spherical harmonicsas implemented in SACLE3 ABSPACK was applied.[33] All structures were solved by direct methods with ShelXT[34] and Olex2[35] and refined by full-matrix least-squares method against F^2 in anisotropic approximation using ShelXL[34]. Hydrogen atoms were refined in calculated positions using riding on pivot atom model.

CCDC-1973590 (**3a**), CCDC-1973591 (**3b**), CCDC-1973592 (**4a**), CCDC-1973593 (**4b**), CCDC-1973594 (**5**), CCDC-1973595 (**6**), CCDC-1973596 (**7**), CCDC-1973597 (**8**), CCDC-1973598 (**9**) and CCDC-1973599 (**10**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: + 44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

3.4.4.1 $[(Cp'''Co)_2(\mu,\eta^4{:}\eta^4\text{-}P_4)][BF_4]$ (3a)

Compound **3a** crystallizes from a concentrated solution in CH_2Cl_2 layered with hexane at -30 °C in the triclinic space group $P\bar{1}$ as dark green blocks. The asymmetric unit contains one complete and two half units of the cation (located on symmetry center), two BF_4 anions and four CH_2Cl_2 molecules. One BF_4 anion is disordered over two positions (occupancy 0.22 and 0.78), three CH_2Cl_2 are disordered over two positions (occupancy of 0.07 and 0.93, 0.14 and 0.86, 0.28 and 0.72), one CH_2Cl_2 is disordered over three positions (occupancy 0.26, 0.29 and 0.45). The restraints DFIX, SADI and SIMU were applied to describe the disorder of the CH_2Cl_2 molecules and the restraints DANG, SADI, SIMU and RIGU were applied to describe the disorder of the BF_4 anion. The structure in solid state is shown in Figure S8 and S9. The given bond lengths and angles are taken from to the non-disordered cation.

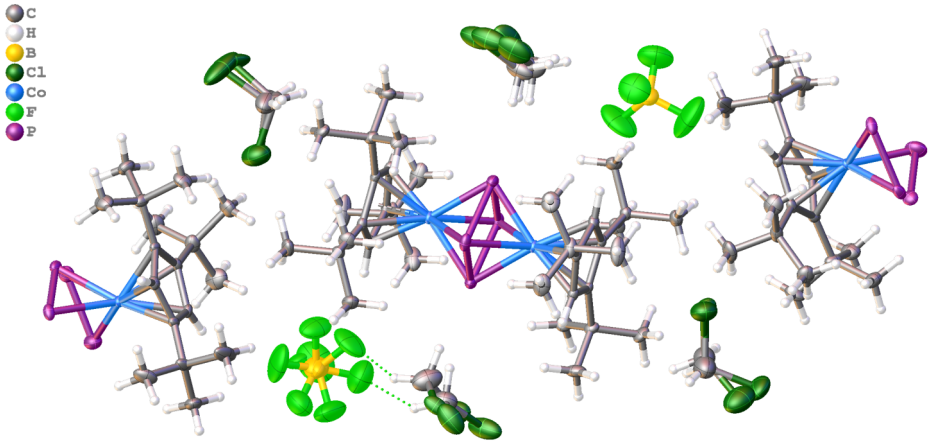


Figure S8: Molecular structure of **3a** in solid state. Thermal ellipsoids are drawn with 50 % probability level.

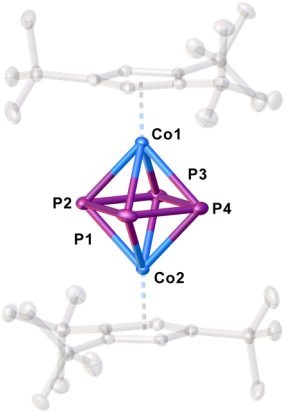


Figure S9: Molecular structure of **3a** in solid state. Thermal ellipsoids are drawn with 50 % probability level. Anions and solvent molecules are omitted for clarity. Only the complete cation within the asymmetric unit is depicted here. Selected bond lengths [Å] and angles [°]: P1-P2 2.1860(9), P2-P3 2.3022(8), P3-P4 2.1837(8), P4-P1 2.2960(8), Co1-Co2 3.3629(6), P1-P2-P3 89-39(3), P2-P3-P4 90.44(3), P3-P4-P1 89.61(3), P4-P1-P2 90.55(3).

3.4.4.2 $[(Cp'''Co)_2(\mu,\eta^4{:}\eta^4\text{-}P_4)][FAl]$ (3b)

Compound **3b** crystallizes from a concentrated solution in CH_2Cl_2 layered with hexane at -30 °C in the triclinic space group $P\bar{1}$ as dark green blocks. The asymmetric unit contains one set of cation and anion. Solvent molecules could not be determined in distinct positions due to heavy disorder. A solvent mask was calculated and 267.0 electrons were found in a volume of 990.0 $Å^3$ in one void. This is consistent with the presence of two CH_2Cl_2 and one hexane per formula unit which account for 268.0 electrons. The structure in solid state is shown in Figure S10 and S11.

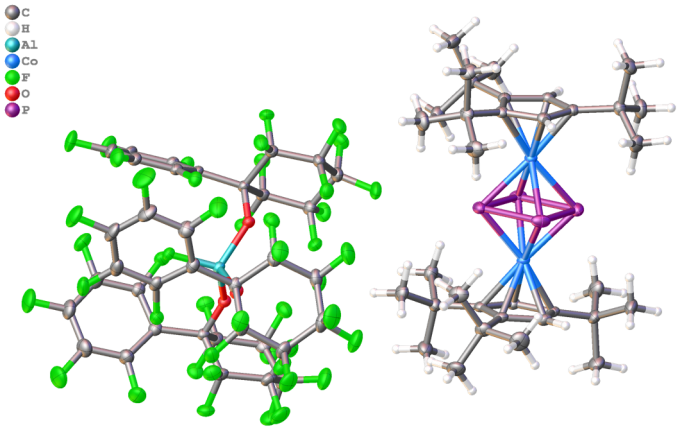


Figure S10 Molecular structure of **3b** in solid state. Thermal ellipsoids are drawn with 50 % probability level.

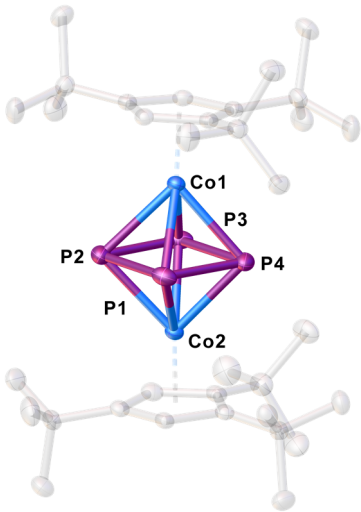


Figure S11: Molecular structure of **3b** in solid state. Thermal ellipsoids are drawn with 50 % probability level. Anion is omitted for clarity. Selected bond lengths [Å] and angles [°]: P1-P2 2.2358(6), P2-P3 2.2069(7), P3-P4 2.3139(6), P4-P1 2.2205(6), Co1-Co2 3.3762(6), P1-P2-P3 90.57(2)), P2-P3-P4 89.75(2), P3-P4-P1 88.24(2)(3), P4-P1-P2 91.44(2).

3.4.4.3 $[(Cp'''Co)_2(\mu,\eta^4{:}\eta^4\text{-}As_4)][BF_4]$ (4a)

Compound **4a** crystallizes from a concentrated solution in ortho-difluoro benzene layered with hexane at -30 °C in the triclinic space group $P\bar{1}$ as dark green blocks. The asymmetric unit contains two half units of the cation (located on symmetry center), one BF_4 anion and three molecules of o-difluorobenzene. The BF_4 anion is disordered over two positions (occupancy 0.20 and 0.80) and one o-difluorobenzene molecule is disordered over two positions (occupancy 0.47 and 0.53). The restraints DELU and SIMU were applied to describe the disorder of the BF_4 anion. The restraints SADI and SIMU were applied to describe the disorder of the o-difluorobenzene molecule. The structure in solid state is shown in Figure S12 and S13.

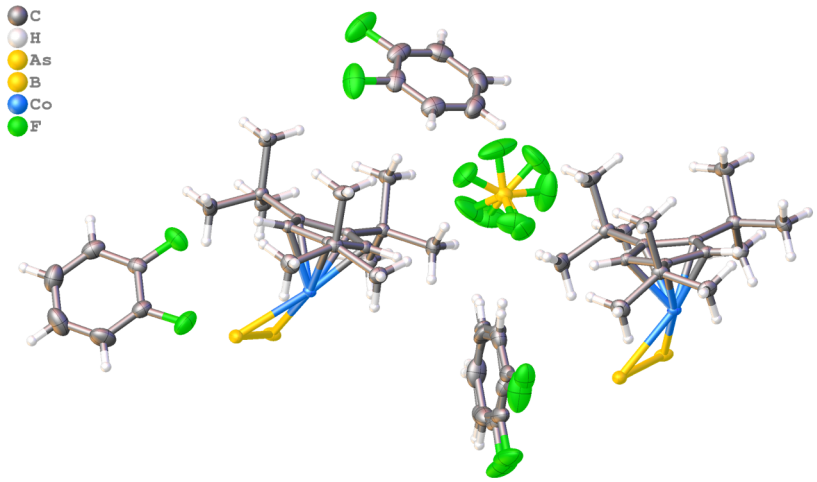


Figure S12: Molecular structure of **4a** in solid state. Thermal ellipsoids are drawn with 50 % probability level.

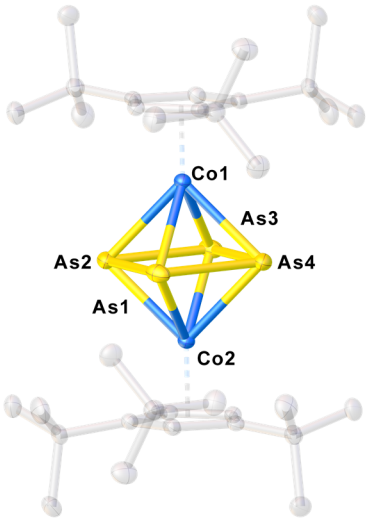


Figure S13: Molecular structure of **4a** in solid state. Thermal ellipsoids are drawn with 50 % probability level. Anion and solvent molecules are omitted for clarity. Selected bond lengths [Å] and angles [°]: As1-As2 2.3882(3), As1-As2' 2.5198(2), As1'-As2' 2.3882(3), As1'-As2 2.5198(2), Co1-Co1' 3.4335(5), As1-As2-As1' 90.180(6), As2-As1'-As2' 89.820(6), As1'-As2'-As1 90.180(6), As2'-As1-As2 89.820(6).

3.4.4.4 [(Cp'''Co)$_2$(μ,η^4:η^4-As$_4$)][FAl] (4b)

Compound **4b** crystallizes from a concentrated solution in CH_2Cl_2 layered with pentane at -30 °C in the triclinic monoclinic space group $P2_1/c$ as dark green blocks. The asymmetric unit contains one cation, one anion and a CH_2Cl_2 with an occupancy of 0.75. The As_4 middle deck of the cation is disordered over three positions (occupancy of 0.05, 0.25 and 0.70) and the CH_2Cl_2 is disordered over three positions (occupancy of 0.15, 0.20 and 0.40). The bond lengths and angles were taken from the part with the highest occupancy (Figure S8). The structure in solid state is shown in Figure S14 and S15.

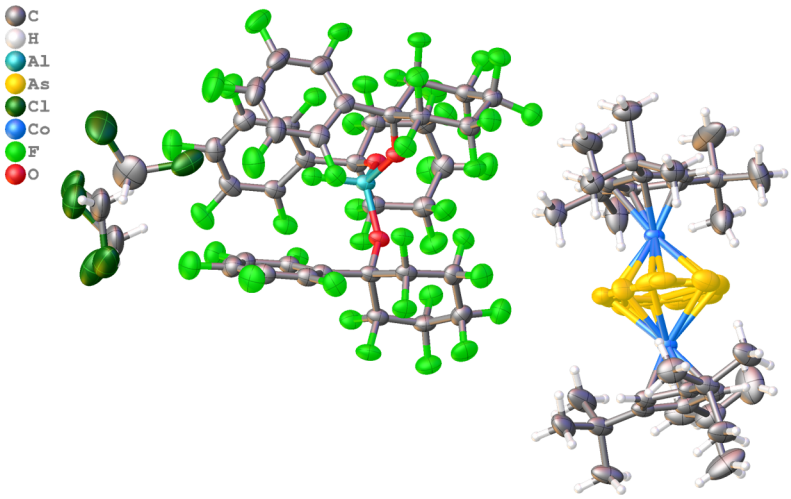


Figure S14: Molecular structure of **4b** in solid state. Thermal ellipsoids are drawn with 50 % probability level.

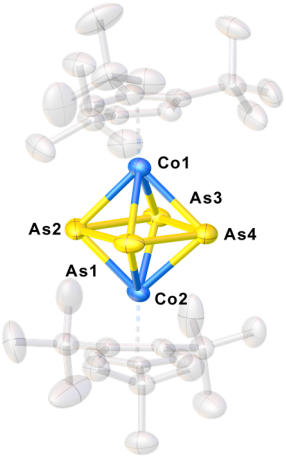


Figure S15: Molecular structure of **4b** in solid state. Thermal ellipsoids are drawn with 50 % probability level. Anion and solvent molecules are omitted for clarity, only part 1 (occupancy 0.7) is depicted. Selected bond lengths [Å] and angles [°]: As1-As2 2.429(6), As2-As3 2.561(3), As3-As4 2.4254(17), As4-As1 2.429(3), Co1-Co2 3.3902(9), As1-As2-As3 88.32(14), As2-As3-As4 88.56(10), As3-As4-As1 91.52(12), As4-As1-As2 91.58(15).

3.4.4.5 $[(Cp'''Co)_2(\mu,\eta^4{:}\eta^4\text{-}P_4)][TEF]_2$ (5)

Compound **5** crystallizes from a concentrated solution in CH_2Cl_2 layered with hexane at -30 °C in the monoclinic space group $P2_1/n$ as dark brown blocks. The asymmetric unit contains half a cation (located on symmetry center), one [TEF] anion and one CH_2Cl_2 molecule. The P ligand is disordered over two positions (occupancy of 0.40 and 0.60), two ^{t}Bu groups of the Cp''' ligand are disordered over two positions (occupancy of 0.40 and 0.60, 0.48 and 0.52) all four $OC(CF_3)_3$ groups of the anion are disordered over two positions and the CH_2Cl_2 molecule is disordered over two positions (occupancy of 0.41 and 0.59). The restraints SADI and SIMU were applied to describe the disorder of the CH_2Cl_2 molecule. The restraints SADI and SIMU were applied to describe the disorder of the cation. The restraints SADI, SIMU and ISOR were applied to describe the disorder of the [TEF] anion. The bond lengths and angles were taken from the part with the highest occupancy. The structure in solid state is shown in Figure S16 and S17.

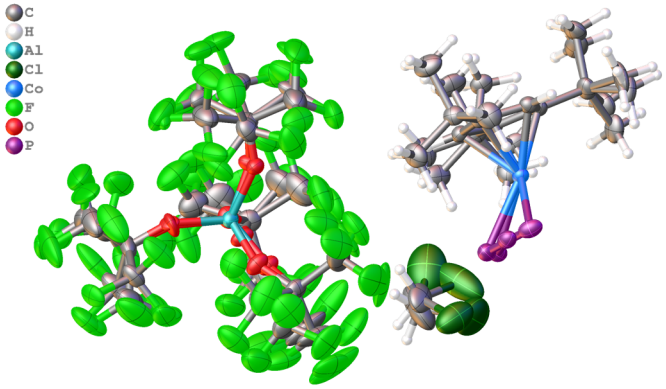


Figure S16: Molecular structure of **5** in solid state. Thermal ellipsoids are drawn with 50 % probability level.

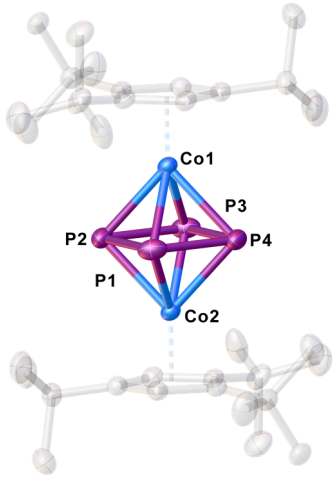


Figure S17: Molecular structure of **5** in solid state. Thermal ellipsoids are drawn with 50 % probability level. Anion and solvent molecules are omitted for clarity. Selected bond lengths [Å] and angles [°]: P1-P2 2.239(2), P2-P1' 2.236(2), P1'-P2' 2.239(2), P2'-P1 2.236(2), Co1-Co1' 3.3814(10), P1-P2-P1' 89.98(7), P2-P1'-P2' 90.02(7), P1'-P2'-P1 89.98(7), P2'-P1-P2 90.02(7).

3.4.4.6 $[(Cp'''Co)_2(\mu,\eta^4{:}\eta^4\text{-}As_4)][TEF]_2$ (6)

Compound **6** crystallizes from a concentrated solution in CH_2Cl_2 layered with hexane at -30 °C in the monoclinic space group $P2_1/c$ as green blocks. The asymmetric unit contains one cation, two [TEF] anions and one half CH_2Cl_2. The CH_2Cl_2 is disordered over two positions (occupancy of 0.25 and 0.25) and one CF_3 group of the [TEF] anion is disordered over two positions (occupancy of 0.36 and 0.74). The restraints SADI and DFIX were applied to describe the disorder of the CH_2Cl_2 molecule. The restraints SADI and SIMU were applied to describe the [TEF] anions. The structure in solid state is shown in Figure S18 and S19.

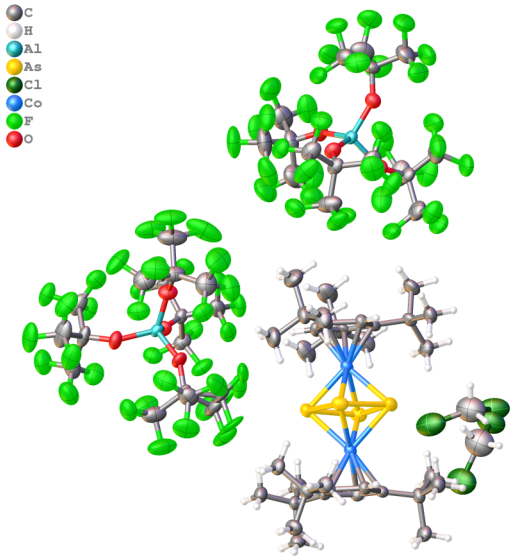


Figure S18: Molecular structure of **6** in solid state. Thermal ellipsoids are drawn with 50 % probability level.

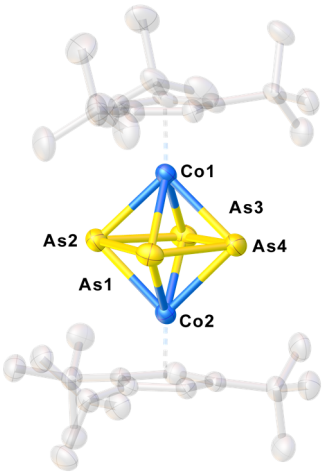


Figure S19: Molecular structure of **6** in solid state. Thermal ellipsoids are drawn with 50 % probability level. Anions and solvent molecules are omitted for clarity. Selected bond lengths [Å] and angles [°]: As1-As2 2.4476(9). As2-As3 2.4759(9), As3-As4 2.4520(9), As4-As1 2.4355(9), Co1-Co2 3.4105(12), As1-As2-As3 89.49(3), As2-As3-As4 89.46(3), As3-As4-As 90.33(3), As4-As1-As2 90.51(3).

3.4.4.7 $[K(18\text{-}c\text{-}6)(dme)_2][(Cp'''Co)_2(\mu,\eta^4{:}\eta^4\text{-}P_4)]$ (7)

Compound **7** crystallizes from a concentrated solution in dimethoxyethane layered with hexane at -30 °C in the triclinic space group $P\bar{1}$ as green plates. The asymmetric unit contains one half cation and half an anion. The crown ether is disordered over two positions (occupancy of 0.36 and 0.64). The structure in solid state is shown in Figure S20 and S21.

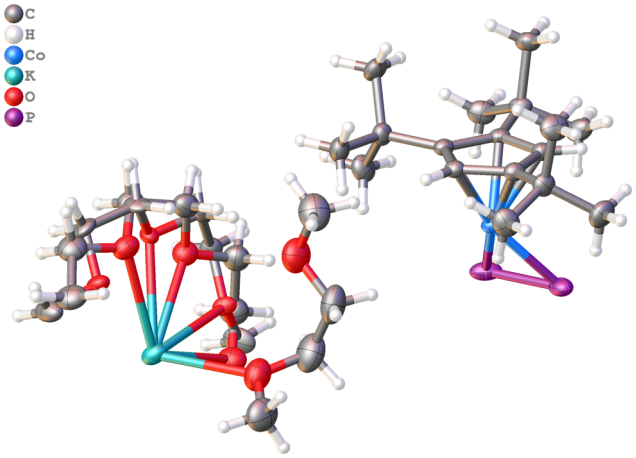


Figure S20: Molecular structure of **7** in solid state. Thermal ellipsoids are drawn with 50 % probability level.

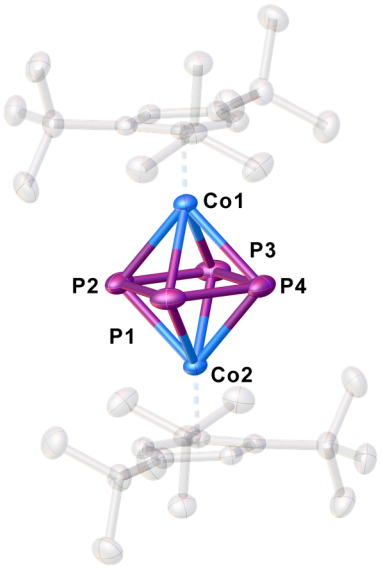


Figure S21: Molecular structure of **7** in solid state. Thermal ellipsoids are drawn with 50 % probability level. Cation is omitted for clarity. Selected bond lengths [Å] and angles [°]: P1-P2 2.1288(9), P2-P1' 2.3606(8), P1'-P2' 2.1288(9), P2'-P1 2.3606(8), Co1-Co1' 3.4136(7), P1-P2-P1' 89.96(3), P2-P1'-P2' 90.04(3), P1'-P2'-P1 89.96(3), P2'-P1-P2 90.04(3).

3.4.4.8 $[K(18\text{-}c\text{-}6)(dme)_2][(Cp'''Co)_2(\mu,\eta^4{:}\eta^4\text{-}As_4)]$ (8)

Compound **8** crystallizes from a concentrated solution in dimethoxyethane layered with hexane at -30 °C in the triclinic space group $P\bar{1}$ as brown blocks. The asymmetric unit contains one half cation and half an anion. The As_4 middle deck is disordered over two positions (occupancy of 0.20 and 0.80) and the crown ether is disordered over two positions (occupancy of 0.37 and 0.63). The restraint SADI was applied to describe the disorder of the As ligand. The two parts of the As_4 unit differ strong from each other. The major part (0.8) has a rectangular shape and while the second part (0.2) possesses a trapezoid shape. Therefore, only the bond lengths and angles are given for the first part (Figure S16). The structure in solid state is shown in Figure S22 and S23.

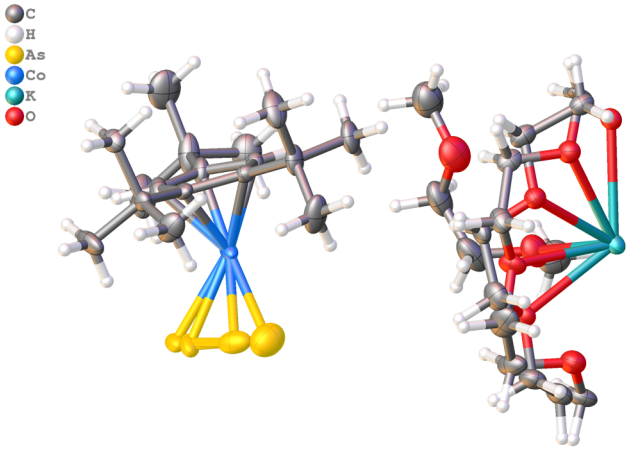


Figure S22: Molecular structure of **8** in solid state. Thermal ellipsoids are drawn with 50 % probability level.

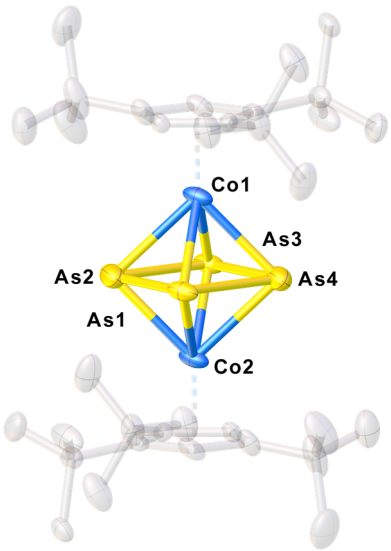


Figure S23: Molecular structure of **8** in solid state. Thermal ellipsoids are drawn with 50 % probability level. Cation is omitted for clarity. Selected bond lengths [Å] and angles [°]: As1-As2 2.3074(16), As2-As1' 2.5852(15), As1'-As2' 2.3074(16), As2'-As1 2.5852(15), Co1-Co1' 3.4864(14), As1-As2-As1' 88.19(5), As2-As1'-As2' 92.81(5), As1'-As2'-As1 88.19(5), As2'-As1-As2 92.81(5).

3.4.4.9 [K(18-c-6)(dme)$_2$][K(18-c-6)][(Cp'''Co)$_2$(μ,η^3:η^3-P$_4$)] (9)

Compound **9** crystallizes from a concentrated solution in dimethoxyethane layered with hexane at -30 °C in the monoclinic space group $P2_1/n$ as brown blocks. The asymmetric unit contains one dianion, two potassium cations chelated by two crown ethers and three dimethoxyethane molecules in total. One crown ether is disordered over two positions (occupancy of 0.38 and 0.72) and one dimethoxyethane molecule is disordered over two positions (occupancy of 0.40 and 0.60). The restraints SADI and SIMU were applied to describe the disorder. The structure in solid state is shown in Figure S24 and S25.

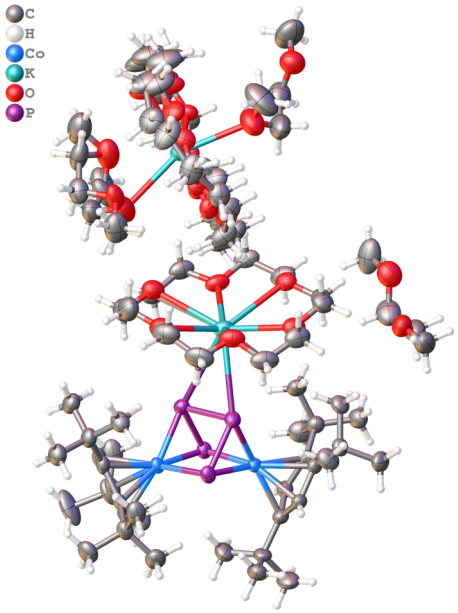


Figure S24: Molecular structure of **9** in solid state. Thermal ellipsoids are drawn with 50 % probability level.

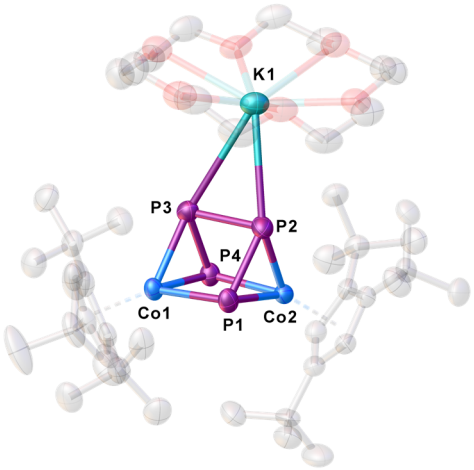


Figure S25: Molecular structure of **9** in solid state. Thermal ellipsoids are drawn with 50 % probability level. Cation is omitted for clarity. Selected bond lengths [Å] and angles [°]: P1-P2 2.1581(11), P2-P3 2.2646(10), P3-P4 2.1614(11), P1-P4 2.8396(12), Co1-Co2 3.4882(6), P1-P2-P3 83.78(4), P2-P3-P4 84.14(4), P1-Co1-P4 77.99(3), Co1-P4-Co2 100.96(3), P1-Co2-P4 78.38(3), Co1-P1-Co2 102.15(3), P1-P2-Co2 61.24(3), P1-Co2-P2 57.12(3), P2-P1-Co2 61.64(3), Co1-P1-P2 99.23(4), P2-P3-Co1 94.98(3), P1-Co1-P3 82.01(3), Co1-P3-P4 61.88(3), P3-P4-Co1 61.42(3), P3-Co1-P4 56.70(3), P3-P2-Co2 94.93(4), P2-Co2-P4 82.44(3), Co2-P4-P3 98.48(3).

3.4.4.10 $[K(dme)_4][(Cp'''Co)_2(\mu,\eta^3:\eta^3\text{-}As_3)]$ (10)

Compound **10** crystallizes from a concentrated solution in dimethoxyethane layered with hexane at room temperature in the triclinic space group $P\bar{1}$ as brown blocks. The asymmetric unit contains one anion and one potassium complexed by four dimethoxyethane molecules. The structure in solid state is shown in Figure S26 and S27.

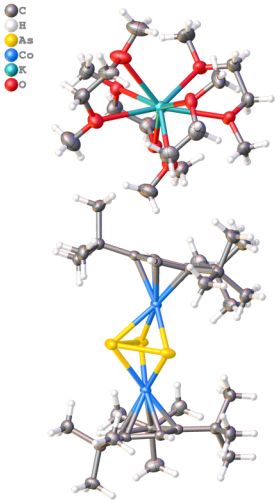


Figure S26: Molecular structure of **10** in solid state. Thermal ellipsoids are drawn with 50 % probability level.

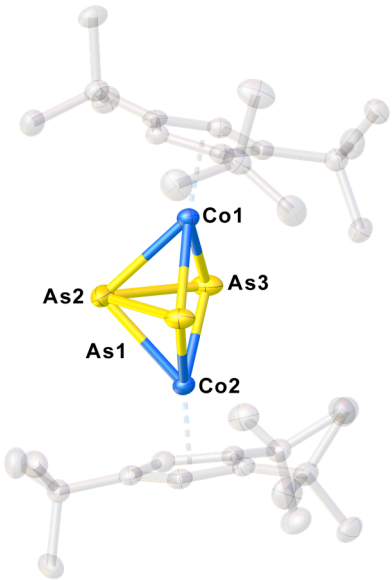


Figure S27: Molecular structure of **10** in solid state. Thermal ellipsoids are drawn with 50 % probability level. Cation is omitted for clarity. Selected bond lengths [Å] and angles [°]: As1-As2 2.4216(4), As2-As3 2.4055(4), As1-As3 3.0224(5), Co1-Co2 3.5089(5), As1-As2-As3 77.527(12)

3.4.4.11 Crystallographic information

Table S1: Crystallographic data for all compounds

	3a	3b	4a	4b	5	6
Formula	1973590	1973591	1973592	1973593	1973594	1973595
$D_{calc.}$/ g cm^{-3}	$C_{72}H_{124}B_2Cl_8Co_4F_8P_8$	$C_{77}H_{74}AlCl_4Co_2F_{46}O_3P_4$	$C_{52}H_{70}As_4BCo_2F_{10}$	$C_{70.75}H_{59.5}AlAs_4Cl_{1.5}Co_2F_{46}O_3$	$C_{34}H_{31}AlCl_2CoF_{36}O_4P_2$	$C_{66.5}H_{59}Al_2As_4ClCo_2F_{72}O_8$
μ/mm^{-1}	1.410	1.679	1.619	1.808	1.832	1.943
Formula Weight	1.147	0.694	3.122	6.627	5.968	6.336
Colour	1930.40	2331.88	1313.43	2329.38	1406.34	2861.08
Shape	clear dark green	clear dark green	clear dark green	green	clear dark brown	brown
Size/mm^3	block	block	plate	block	block	plate
T/K	0.43×0.40×0.18	0.38×0.21×0.08	0.45×0.25×0.13	0.15×0.12×0.11	0.36×0.23×0.21	0.27×0.17×0.02
Crystal System	123	123	123(1)	122.99(11)	123.15	123.0(2)
Space Group	triclinic	triclinic	triclinic	monoclinic	monoclinic	monoclinic
a/Å	*P*-1	*P*-1	*P*-1	$P2_1/c$	$P2_1/n$	$P2_1/c$
b/Å	10.0364(2)	14.2453(3)	9.99870(10)	23.4066(7)	14.50660(10)	16.2595(2)
c/Å	20.0826(5)	17.2300(3)	12.6065(2)	19.8495(6)	13.58360(10)	26.4319(4)
α/°	22.7052(6)	19.7170(6)	21.7726(3)	20.2867(6)	26.1495(2)	23.4564(3)
β/°	94.451(2)	100.723(2)	81.2550(10)	90	90	90
γ/°	91.257(2)	96.353(2)	84.4430(10)	114.792(4)	98.2550(10)	103.971(2)
V/Å^3	94.428(2)	101.113(2)	85.8030(10)	90	90	90
Z	4547.17(19)	4611.61(19)	2694.98(6)	8556.7(5)	5099.42(7)	9782.6(2)
Z'	2	2	2	4	4	4
Wavelength/Å	1	1	1	1	1	1
Radiation type	0.71073	0.71073	0.71073	1.54184	1.54184	1.54178
θ_{min}/°	MoK_α	MoK_α	MoK_α	CuK_α	CuK_α	CuK_α
θ_{max}/°	3.337	3.284	3.336	3.047	3.299	3.262
Measured Refl.	30.034	30.034	32.374	75.644	72.877	73.873
Independent Refl.	106013	80878	78809	55940	22649	39471
Reflections with I > 2(I)	26546	26864	17950	17063	9875	19235
R_{int}	19787	20905	15610	14689	9327	12713
Parameters	0.0316	0.0312	0.0263	0.0474	0.0178	0.0601
Restraints	1175	1153	761	1306	1277	1496
Largest Peak	557	0	332	192	982	91
Deepest Hole	1.101	1.432	0.561	1.347	0.840	1.058
GooF	-0.625	-0.403	-0.260	-0.918	-0.528	-1.332
wR_2 (all data)	1.040	1.041	1.049	1.037	1.030	0.993
wR_2	0.1211	0.0932	0.0538	0.1874	0.1566	0.1879
R_1 (all data)	0.1099	0.0873	0.0515	0.1764	0.1538	0.1760
R_1	0.0634	0.0525	0.0312	0.0695	0.0576	0.0914
	0.0441	0.0375	0.0235	0.0617	0.0553	0.0663

	7	8	9	10
Formula	1973596	1973597	1973598	1973599
$D_{calc.}$/ g cm^{-3}	$C_{54}H_{102}Co_2KO_{10}P_4$	$C_{54}H_{102}As_4Co_2KO_{10}$	$C_{70}H_{136}Co_2K_2O_{18}P_4$	$C_{50}H_{98}As_3Co_2KO_8$
μ/mm^{-1}	1.270	1.449	1.245	1.347
Formula Weight	6.140	7.485	5.151	7.182
Colour	1192.19	1367.99	1585.72	1209.00
Shape	clear light green	brown	clear dark brown	clear dark brown
Size/mm^3	plate	block	block	block
T/K	0.41×0.36×0.10	0.27×0.23×0.13	0.41×0.25×0.15	0.27×0.24×0.18
Crystal System	122.99(16)	122.99(13)	123.01(15)	122.99(10)
Space Group	triclinic	triclinic	monoclinic	triclinic
a/Å	P-1	P-1	$P2_1/n$	P-1
b/Å	11.3685(4)	11.2938(7)	15.2061(4)	13.2319(2)
c/Å	12.5908(5)	12.6909(7)	20.4275(7)	14.1119(2)
α/°	12.8137(5)	12.8681(6)	27.5269(9)	16.9382(3)
β/°	114.715(4)	114.916(5)	90	93.2780(10)
γ/°	92.097(3)	92.121(5)	98.231(3)	106.789(2)
V/Å^3	107.720(3)	107.415(5)	90	98.1480(10)
Z	1558.36(12)	1567.42(17)	8462.4(5)	2981.33(9)
Z'	1	1	4	2
Wavelength/Å	0.5	0.5	1	1
Radiation type	1.54184	1.54184	1.54184	1.54184
θ_{min}/°	CuK_α	CuK_α	CuK_α	CuK_α
θ_{max}/°	3.868	3.857	2.704	2.740
Measured Refl.	67.072	67.051	67.077	67.078
Independent Refl.	16261	16305	45051	32115
Reflections with I > 2(I)	5548	5553	15066	10596
R_{int}	5297	5231	12825	9946
Parameters	0.0472	0.0434	0.0536	0.0292
Restraints	414	432	1089	603
Largest Peak	0	1	166	0
Deepest Hole	0.699	0.862	0.767	1.008
GooF	-0.335	-1.909	-0.395	-0.503
wR_2 (all data)	1.042	1.071	1.049	1.024
wR_2	0.1104	0.1805	0.1539	0.0843
R_1 (all data)	0.1086	0.1778	0.1451	0.0826
R_1	0.0425	0.0611	0.0607	0.0344
	0.0406	0.0590	0.0524	0.0319

3.4.5 Computational details

Gaussian 09 program[36] was used throughout. Density functional theory (DFT) in form of Becke's three-parameter hybrid functioncal B3LYP[37] with def2-SVP or def2-TZVP all electron basis set[38] or BP86[39] (Becke's exchange and Perdew 86 correlation functional) with def2-SVP or def2-TZVP all electron basis set was employed. Solvents effects has been accounted for by using continuous polarizable continuum model (CPM).[40] The dielectric constant of dichloromethane (ε = 8.93) has been used in the calculations of the cations (**3a**, **3b**, **4a**, **4b**, **5**, **6**) and the dielectric constant of thf (ε = 7.4257) has been used in the calculations of the anions (**7**, **8**, **9**, **10**). The Natural Bond Orbital (NBO) analysis has been performed with the NBO6 program.[41] The dispersion correction GD3BJ was applied.[42] The figures for the supporting information concerning the DFT calculations were created with Chemcraft.[43]

The results from the calculations using B3LYP/def2-SVP without the correction GD3BJ are in good agreement with the data obtained from single crystal X-ray structure analysis for the cations **3a**, **3b**, **4a**, **4b**, **5**, **6** and anion **10**, but not for the neutral compounds **1** and **2** and the anions **7**, **8**, **9**. (cf. Table S3).

The results from the calculations using BP86/def2-SVP without the correction GD3BJ are in good agreement with the data obtained from single crystal X-ray structure analysis for the neutral compounds **1**, **2**, cations **5**, **6**, anions **7**, **8**, **9**, **10**, but not for the cations **3a**, **3b**, **4a**, **4b**. (cf. Table S4).

The results from the calculations using BP86/def2-TZVP including the correction GD3BJ are in good agreement with the data obtained from single crystal X-ray structure analysis except for **3b**, **4b** (cf. Table S5). The data from the crystal structures reveal for **3a**, **4a** a rectangular E_4 ligand, while for **3b** a trapezoid shape is revealed. For **4b** no clear result can be given due to a threefold disorder of the middle deck. The DFT calculations for **3a** and **4a** display the real situation quite good, while for **3b** and **4b** the trapezoid shape is more widened than in the crystal structure. For **3a**, **3b** the nature of the stationary points has been checked by frequency analysis which show no imaginary frequencies and display minima on the energy hyper surface. Therefore, the differences between **3a** and **3b** and **4a** and **4b** are probably due to packing effects.

Table S2: Total energies for all optimized geometries (BP86/def2-TZVP level of theory) including solvent effects and dispersion correction GD3BJ.

	total energy [Ha]
1 $[(Cp'''Co)_2(\mu,\eta^2:\eta^2\text{-}P_2)_2]$	-5463.1272277
2 $[(Cp'''Co)_2(\mu,\eta^2:\eta^2\text{-}As_2)_2]$	-13042.1875737
3a $[(Cp'''Co)_2(\mu,\eta^4:\eta^4\text{-}P_4)]^+$	-5462.9657223
3b $[(Cp'''Co)_2(\mu,\eta^4:\eta^4\text{-}P_4)]^+$	-5462.9669736
4a $[(Cp'''Co)_2(\mu,\eta^4:\eta^4\text{-}As_4)]^+$	-13042.0297028
4b $[(Cp'''Co)_2(\mu,\eta^4:\eta^4\text{-}As_4)]^+$	-13042.0305076
5 $[(Cp'''Co)_2(\mu,\eta^4:\eta^4\text{-}P_4)]^{2+}$	-5462.7648132
6 $[(Cp'''Co)_2(\mu,\eta^4:\eta^4\text{-}As_4)]^{2+}$	-13041.8392395
7 $[(Cp'''Co)_2(\mu,\eta^4:\eta^4\text{-}P_4)]^-$	-5463.2278009
8 $[(Cp'''Co)_2(\mu,\eta^4:\eta^4\text{-}As_4)]^-$	-13042.2816847
9 $[(Cp'''Co)_2(\mu,\eta^3:\eta^3\text{-}P_4)]^{2-}$	-5463.2967325
10 $[(Cp'''Co)_2(\mu,\eta^3:\eta^3\text{-}As_3)]^-$	-10806.0801740
I-9a $[(Cp'''Co)_2(\mu,\eta^4:\eta^4\text{-}P_4)]^{2-}$	-5463.28094029
$[K(18\text{-}c\text{-}6)]^+$	-1523.36443541
I-9b $[K(18\text{-}c\text{-}6)]$ $[(Cp'''Co)_2(\mu,\eta^3:\eta^3\text{-}P_4)]$	-6986.71916472

Table S3: Summarized bond distances and Wiberg Bond Indices (black: from structure in solid state, blue: from DFT calculations, red: related WBIs, BP86/def2-SVP level of theory, including solvent effects, no dispersion correction GD3BJ).

	1	2	3a	3b	4a	4b	5	6	7	8	9	10
Co1-Co2	3.1639(8)	3.2508(8)	3.3629(6)	3.3762(6)	3.4335(5)	3.3902(9)	3.3814(10)	3.4105(12)	3.4136(7)	3.4864(14)	3.4882(6)	3.5089(5)
	3.17899	3.28775	3.31725	3.30896	3.44241	3.41930	3.37828	3.45304	3.37919	3.47170	3.54673	3.54755
	0.08	0.08	0.12	0.12	0.10	0.11	0.10	0.10	0.13	0.12	0.14	0.22
E1-E2	2.052(3)	2.2795(5)	2.1860(9)	2.2205(6)	2.3882(2)	2.429(6)	2.236(2)	2.4355(9)	2.1288(9)	2.3074(16)	2.1582(11)	2.4216(4)
	2.10397	2.31441	2.20849	2.20276	2.41061	2.40763	2.29132	2.45431	2.15783	2.37125	2.21134	2.46809
	1.29	1.26	1.04	1.04	1.03	1.03	0.93	0.96	1.13	1.11	1.06	0.96
E2-E3	2.664(2)	2.8209(4)	2.2960(8)	2.2358(6)	2.5198(2)	2.429(6)	2.239(2)	2.4520(9)	2.3606(8)	2.5852(15)	2.2646(10)	2.4055(4)
	2.71663	2.86746	2.29168	2.28268	2.58850	2.50535	2.29318	2.49597	2.48518	2.66664	2.31339	2.46083
	0.36	0.38	0.89	0.90	0.75	0.85	0.92	0.90	0.62	0.62	0.91	0.97
E3-E4	2.052(3)	2.2795(5)	2.1837(8)	2.2069(7)	2.3882(2)	2.4254(17)	2.236(2)	2.4759(9)	2.1288(9)	2.3074(16)	2.1615(11)	3.0224(5)
	2.10397	2.31441	2.21511	2.252793	2.41061	2.42765	2.29132	2.54399	2.15783	2.37125	2.21422	3.02001
	1.29	1.26	1.03	1.01	1.03	1.00	0.93	0.85	1.13	1.11	1.06	0.22
E1-E4	2.664(2)	2.8209(4)	2.3022(8)	2.3139(6)	2.5198(2)	2.561(3)	2.239(2)	2.4476(9)	2.3606(8)	2.5852(15)	2.8396(12)	
	2.71663	2.86746	2.54523	2.55332	2.58850	2.68266	2.29318	2.49581	2.48518	2.66664	2.84817	
	0.36	0.38	0.60	0.59	0.75	0.64	0.92	0.90	0.62	0.62	0.22	

Table S4: Summarized bond distances and Wiberg Bond Indices (black: from structure in solid state, blue: from DFT calculations, red: related WBIs, B3LYP/def2-SVP level of theory, including solvent effects, no dispersion correction GD3BJ).

	1	2	3a	3b	4a	4b	5	6	7	8	9	10
Co1-Co2	3.1639(8)	3.2508(8)	3.3629(6)	3.3762(6)	3.4335(5)	3.3902(9)	3.3814(10)	3.4105(12)	3.4136(7)	3.4864(14)	3.4882(6)	3.5089(5)
	3.15077	3.29552	3.49056	3.48690	3.57164	3.57203	3.45701	3.52607	3.40722	3.55453	3.49401	3.54124
	0.06	0.06	0.10	0.10	0.09	0.09	0.08	0.08	0.09	0.08	0.08	0.1340
E1-E2	2.052(3)	2.2795(5)	2.1860(9)	2.2205(6)	2.3882(2)	2.429(6)	2.236(2)	2.4355(9)	2.1288(9)	2.3074(16)	2.1582(11)	2.4216(4)
	2.06233	2.28570	2.20512	2.19801	2.41269	2.40975	2.26720	2.45177	2.12024	2.34511	2.19040	2.45501
	1.41	1.33	1.05	1.06	1.04	1.05	0.97	0.98	1.24	1.21	1.10	0.98
E2-E3	2.664(2)	2.8209(4)	2.2960(8)	2.2358(6)	2.5198(2)	2.429(6)	2.239(2)	2.4520(9)	2.3606(8)	2.5852(15)	2.2646(10)	2.4055(4)
	2.81810	2.90266	2.31176	2.28934	2.51952	2.50067	2.26947	2.47823	2.55627	2.71006	2.28543	2.45302
	0.28	0.35	0.91	0.94	0.90	0.92	0.97	0.95	0.57	0.62	0.95	0.98
E3-E4	2.052(3)	2.2795(5)	2.1837(8)	2.2069(7)	2.3882(2)	2.4254(17)	2.236(2)	2.4759(9)	2.1288(9)	2.3074(16)	2.1615(11)	3.0224(5)
	2.06233	2.28570	2.20506	2.21599	2.41269	2.42514	2.26720	2.50266	2.12024	2.34511	2.18992	3.05157
	1.41	1.33	1.05	1.04	1.04	1.03	0.97	0.92	1.24	1.21	1.10	0.19
E1-E4	2.664(2)	2.8209(4)	2.3022(8)	2.3139(6)	2.5198(2)	2.561(3)	2.239(2)	2.4476(9)	2.3606(8)	2.5852(15)	2.8396(12)	
	2.81810	2.90266	2.31225	2.33264	2.51952	2.52974	2.26947	2.47732	2.55627	2.71006	2.97910	
	0.28	0.35	0.91	0.89	0.90	0.89	0.97	0.95	0.57	0.62	0.14	

Table S5: Summarized bond distances and Wiberg Bond Indices (black: from structure in solid state, blue: from DFT calculations, red: related WBIs, BP86/def2-TZVP level of theory, including solvent effects and dispersion correction GD3BJ).

	1	2	3a	3b	4a	4b	5	6	7	8	9	10
Co1-Co2	3.1639(8)	3.2508(8)	3.3629(6)	3.3762(6)	3.4335(5)	3.3902(9)	3.3814(10)	3.4105(12)	3.4136(7)	3.4864(14)	3.4882(6)	3.5089(5)
	3.16431	3.2260	3.30199	3.26452	3.36322	3.33403	3.32414	3.37722	3.33241	3.38668	3.47834	3.47049
	0.03	0.03	0.04	0.05	0.04	0.04	0.04	0.04	0.05	0.05	0.06	0.09
E1-E2	2.052(3)	2.2795(5)	2.1860(9)	2.2205(6)	2.3882(2)	2.429(6)	2.236(2)	2.4355(9)	2.1288(9)	2.3074(16)	2.1582(11)	2.4216(4)
	2.08555	2.30690	2.18312	2.17849	2.40173	2.39475	2.26214	2.44891	2.14259	2.36550	2.18602	2.44809
	1.34	1.32	1.07	1.07	1.04	1.05	0.92	0.93	1.18	1.15	1.12	0.99
E2-E3	2.664(2)	2.8209(4)	2.2960(8)	2.2358(6)	2.5198(2)	2.429(6)	2.239(2)	2.4520(9)	2.3606(8)	2.5852(15)	2.2646(10)	2.4055(4)
	2.64316	2.85987	2.36471	2.25590	2.59094	2.49204	2.27302	2.49020	2.42464	2.66240	2.27440	2.44877
	0.40	0.38	0.75	0.91	0.71	0.85	0.92	0.87	0.68	0.63	0.95	0.99
E3-E4	2.052(3)	2.2795(5)	2.1837(8)	2.2069(7)	2.3882(2)	2.4254(17)	2.236(2)	2.4759(9)	2.1288(9)	2.3074(16)	2.1615(11)	3.0224(5)
	2.08555	2.30690	2.18319	2.20406	2.40173	2.42036	2.26214	2.53942	2.14259	2.36550	2.18984	3.05967
	1.34	1.32	1.07	1.02	1.04	1.00	0.92	0.80	1.18	1.15	1.11	0.20
E1-E4	2.664(2)	2.8209(4)	2.3022(8)	2.3139(6)	2.5198(2)	2.561(3)	2.239(2)	2.4476(9)	2.3606(8)	2.5852(15)	2.8396(12)	
	2.64316	2.85987	2.37037	2.51332	2.59094	2.71241	2.27302	2.49018	2.42464	2.66240	2.81695	
	0.40	0.38	0.74	0.57	0.71	0.57	0.92	0.87	0.68	0.63	0.24	

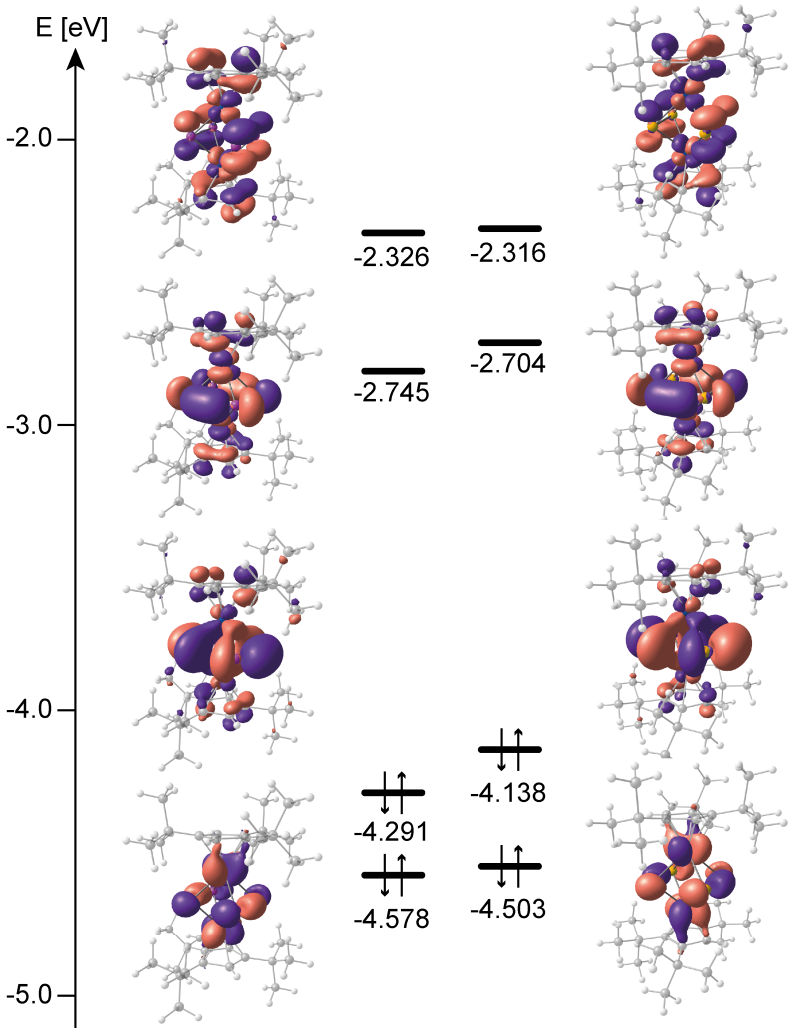


Figure S28: Frontier orbitals of **1** (left) and **2** (right) at the BP86/def2-TZVP level of theory.

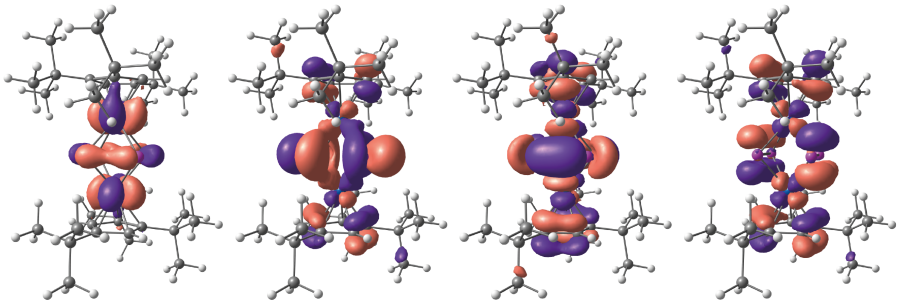


Figure S29: Frontier orbitals of **3a** (a-spin orbitals) at the BP86/def2-TZVP level of theory.

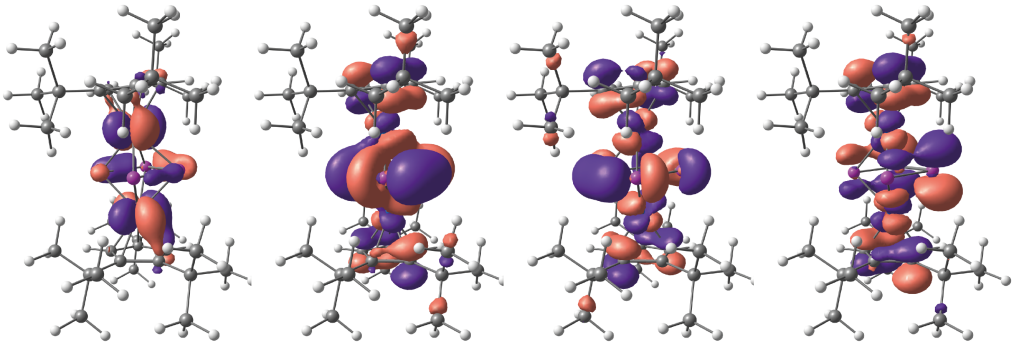


Figure S30: Frontier orbitals of **3b** (a-spin orbitals) at the BP86/def2-TZVP level of theory.

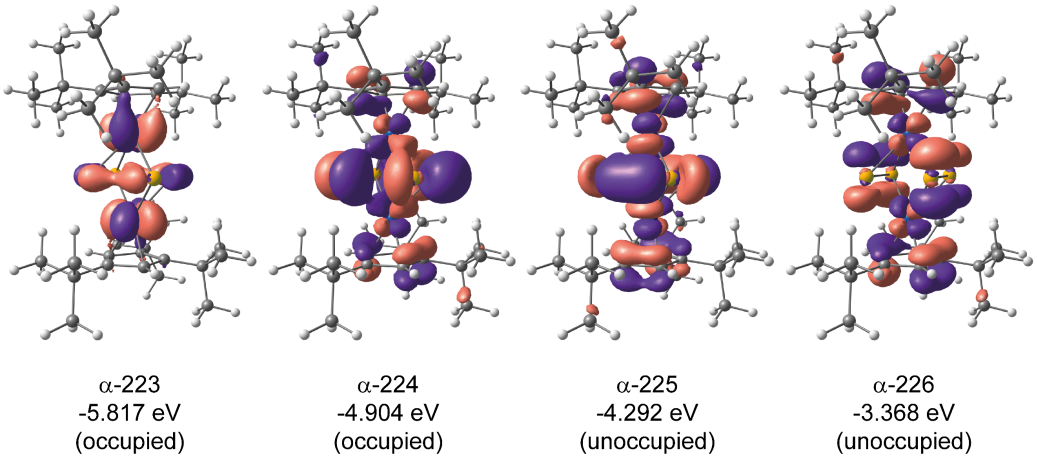


Figure S31: Frontier orbitals of **4a** (a-spin orbitals) at the BP86/def2-TZVP level of theory.

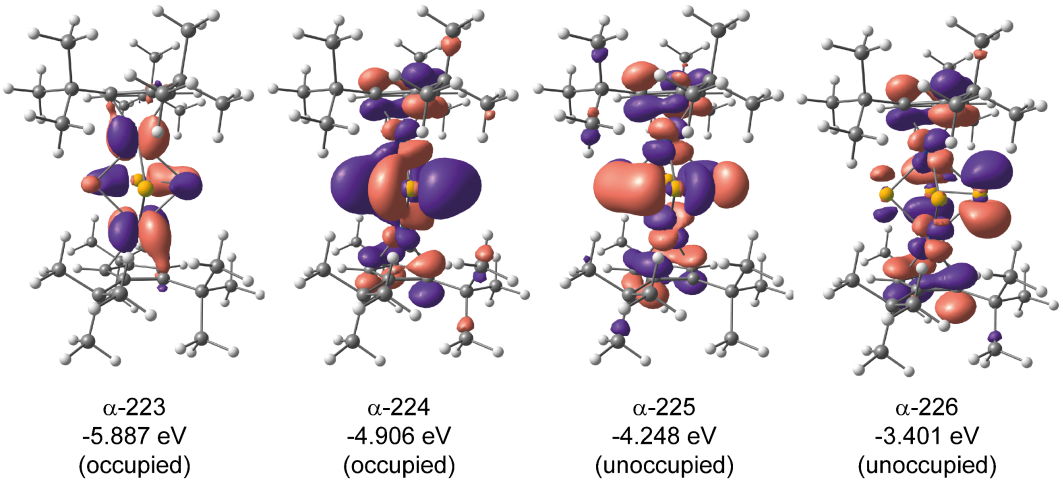


Figure S32: Frontier orbitals of **4b** (a-spin orbitals) at the BP86/def2-TZVP level of theory.

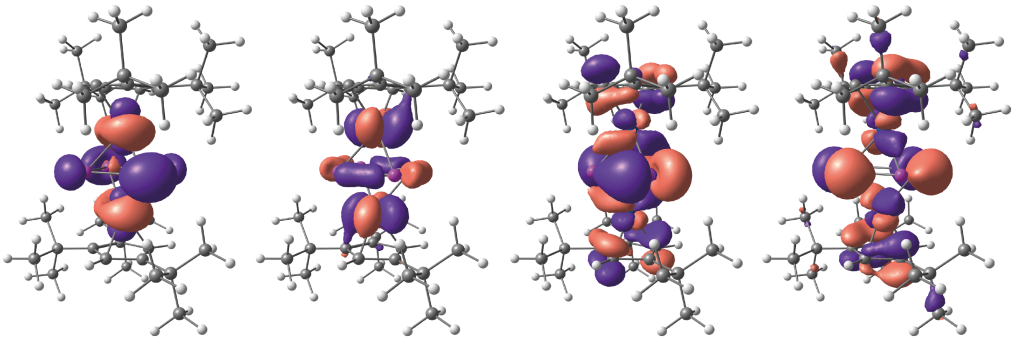


Figure S33: Frontier orbitals of **5** at the BP86/def2-TZVP level of theory.

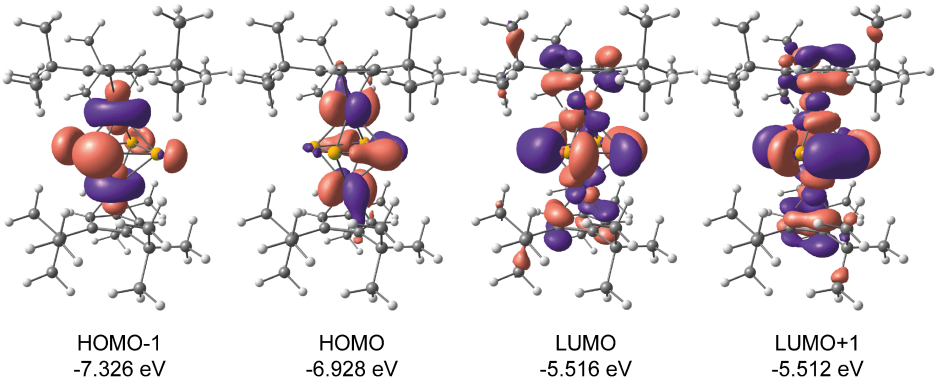


Figure S34: Frontier orbitals of **6** at the BP86/def2-TZVP level of theory.

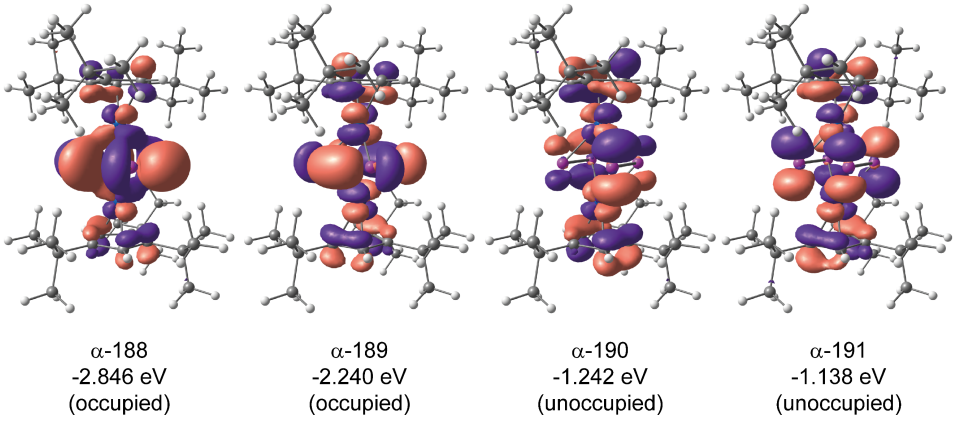


Figure S35: Frontier orbitals of **7** (a-spin orbitals) at the BP86/def2-TZVP level of theory.

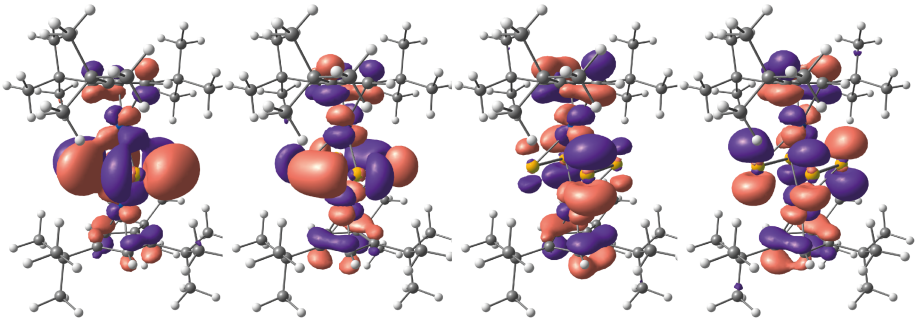


Figure S36: Frontier orbitals of **8** (a-spin orbitals) at the BP86/def2-TZVP level of theory.

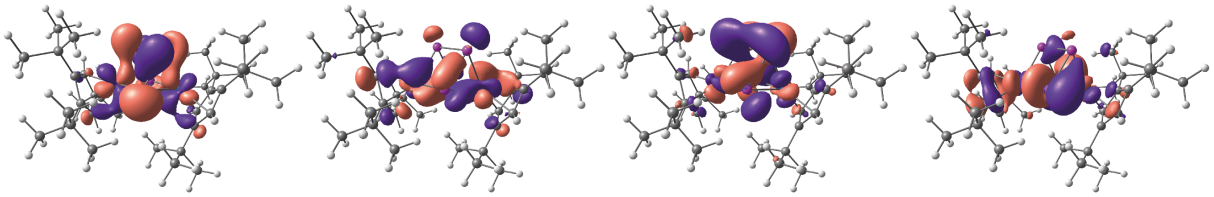


Figure S37: Frontier orbitals of **9** at the BP86/def2-TZVP level of theory.

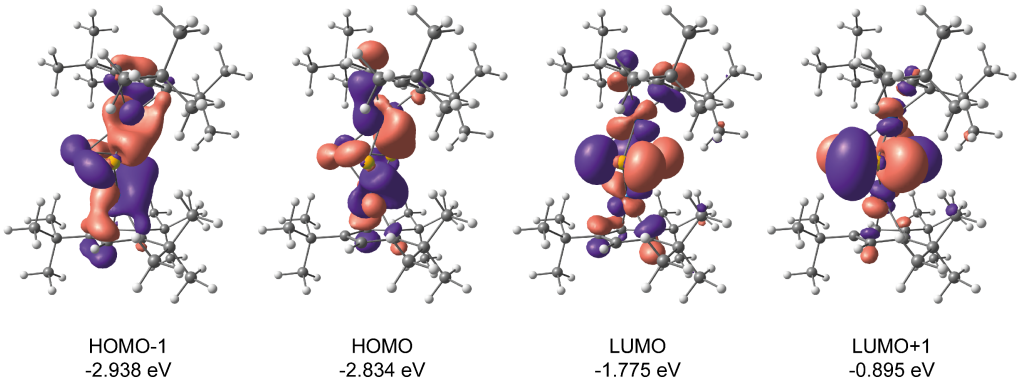


Figure S38: Frontier orbitals of **10** at the BP86/def2-TZVP level of theory.

Table S6: Summarized Mulliken charges for all compounds.

		2x [Cp'''Co]	E_4
1	$[(Cp'''Co)_2(P_2)_2]$	+1.05	-1.05
2	$[(Cp'''Co)_2(As_2)_2]$	+0.46	-0.46
3a	$[(Cp'''Co)_2P_4]^+$	+1.83	-0.83
3b	$[(Cp'''Co)_2P_4]^+$	+1.83	-0.83
4a	$[(Cp'''Co)_2As_4]^+$	+1.16	-0.16
4b	$[(Cp'''Co)_2As_4]^+$	+1.16	-0.16
5	$[(Cp'''Co)_2P_4]^{2+}$	+2.50	-0.50
6	$[(Cp'''Co)_2As_4]^{2+}$	+1.69	+0.31
7	$[(Cp'''Co)_2P_4]^-$	+0.66	-1.66
8	$[(Cp'''Co)_2As_4]^-$	+0.18	-1.18
9	$[(Cp'''Co)_2P_4]^{2-}$	-0.25	-1.75
10	$[(Cp'''Co)_2As_3]^-$	-0.02	-0.98

When the E_2 in **1** and **2** are considered to be formally E_2^{2-} a trend of a decrease of the charge of the formally E_4^{4-} (two times E_2^{2-}) ligand to E_4^{3-} (**3a**, **3b**, **4a**, **4b**) and to E_4^{2-} (**5**, **6**) can be observed by oxidation processes. On the other hand, reduction leads to and stronger increase of the anion charge at the E_4 ligand compared to the Cp'''Co fragments and the ligands can formally be described as E_4^{5-} (**7**, **8**). The summarized Mulliken charges of **9** reveal that the second reduction step occurs mainly on the Cp'''Co fragment (change from positive to negative charge, while negative charge at P_4 ligand increases only slightly compared to **7**). Therefore, a description as a P_4^{6-} is not appropriate. For **10** the Mulliken charges reveal that the anion charge is localized at the As_3 ligand, which could be described as As_3^{5-}.

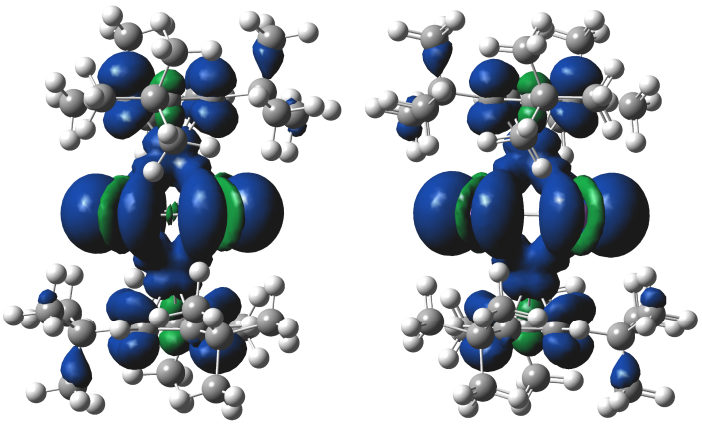


Figure S39: Spin density of **3a** (left) and **4a** (right) at the BP86/def2-TZVP level of theory.

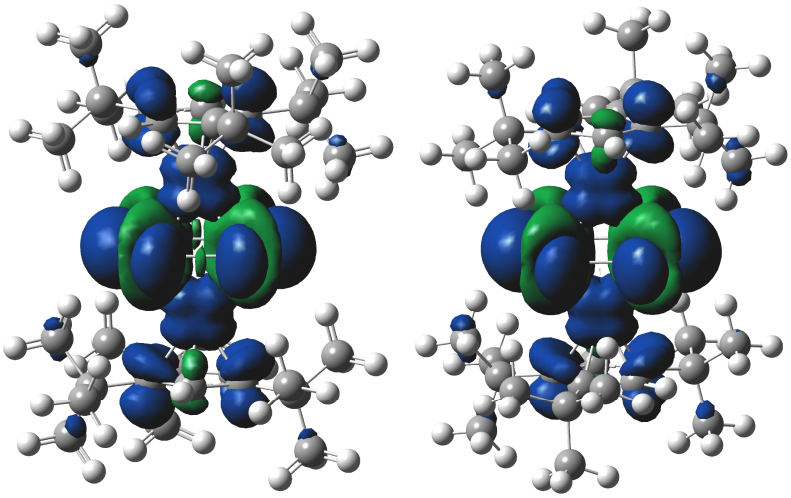
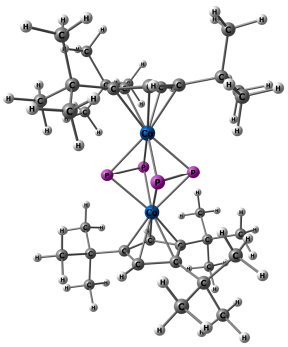


Figure S40: Spin density of **7** (left) and **8** (right) at the BP86/def2-TZVP level of theory.

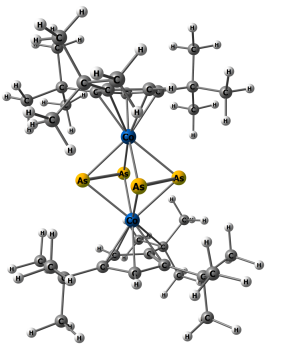
Table S7: Spin densities (with hydrogen atoms summed into heavy atoms) from the optimized geometry of **3a**, **4a**, **7** and **8** (BP86/def2-TZVP level of theory).

3a			4a			7			8		
1	Co	0,24305	1	As	0,043432	1	Co	0,348469	1	As	0,037781
2	Co	0,243644	2	As	0,140361	2	P	0,040746	2	Co	0,358041
3	P	0,122909	3	Co	0,235877	3	P	0,028819	3	As	0,026166
4	P	0,117787	4	C	0,038634	4	C	0,036345	4	C	-0,008693
5	P	0,039392	6	C	0,022927	5	C	-0,009708	6	C	0,033604
6	P	0,039945	7	C	-0,0032	7	C	0,001278	7	C	0,00159
7	C	0,040765	8	C	-0,008335	8	C	0,024015	8	C	0,031274
9	C	0,021481	9	C	0,02863	10	C	0,030521	9	C	0,018868
10	C	-0,004678	11	C	-0,000231	11	C	-0,003534	11	C	-0,000226
11	C	-0,003922	12	C	-0,002266	12	C	0,000569	12	C	0,000853
12	C	0,02144	13	C	0,000482	13	C	-0,004129	16	C	0,000285
13	C	0,04089	17	C	-0,000031	14	C	0,000509	20	C	-0,000091
15	C	-0,003783	21	C	-0,000748	18	C	0,000115	24	C	-0,002716
16	C	-0,002866	25	C	-0,00004	22	C	0,000475	25	C	-0,003051
17	C	0,040033	26	C	0,001827	26	C	0,000786	26	C	-0,001143
19	C	0,039857	30	C	-0,000105	30	C	-0,000764	30	C	0,001949
21	C	-0,002896	34	C	-0,000111	34	C	0,000917	34	C	0,001052
22	C	-0,002918	38	C	0,000229	38	C	0,001869	38	C	0,000748
23	C	0,000075	42	C	-0,000559	42	C	0,001637	42	C	0,001729
24	C	0,000107	46	C	0,003227	46	C	0,001064	46	C	0,00198
25	C	0,002993	50	As	0,043432	50	Co	0,348469	50	As	0,037781
29	C	0,000157	51	As	0,140361	51	P	0,040746	51	Co	0,358041
33	C	0,000086	52	Co	0,235877	52	P	0,028819	52	As	0,026166
37	C	0,000771	53	C	0,038634	53	C	0,036345	53	C	-0,008693
38	C	-0,000428	55	C	0,022927	54	C	-0,009708	55	C	0,033604
42	C	-0,000761	56	C	-0,0032	56	C	0,001278	56	C	0,00159
46	C	0,000416	57	C	-0,008335	57	C	0,024015	57	C	0,031274
50	C	0,003224	58	C	0,02863	59	C	0,030521	58	C	0,018868
54	C	-0,000633	60	C	-0,000231	60	C	-0,003534	60	C	-0,000226
58	C	0,001853	61	C	-0,002266	61	C	0,000569	61	C	0,000853
62	C	0,000447	62	C	0,000482	62	C	-0,004129	65	C	0,000285
63	C	-0,000469	66	C	-0,000031	63	C	0,000509	69	C	-0,000091
67	C	0,00193	70	C	-0,000748	67	C	0,000115	73	C	-0,002716
71	C	-0,000049	74	C	-0,00004	71	C	0,000475	74	C	-0,003051
75	C	-0,000079	75	C	0,001827	75	C	0,000786	75	C	-0,001143
79	C	-0,000078	79	C	-0,000105	79	C	-0,000764	79	C	0,001949
83	C	0,00048	83	C	-0,000111	83	C	0,000917	83	C	0,001052
87	C	-0,000018	87	C	0,000229	87	C	0,001869	87	C	0,000748
91	C	-0,000117	91	C	-0,000559	91	C	0,001637	91	C	0,001729
95	C	-0,000035	95	C	0,003227	95	C	0,001064	95	C	0,00198

Table S8: Optimized geometry of **1** (left) and **2** (right). XYZ coordinates in angstroms. BP86/def2-TZVP level of theory.

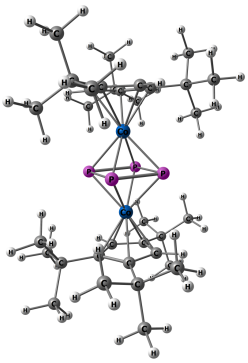


Co	-0.621875000	-1.176957000	0.855140000	Co	0.621875000	1.176957000	-0.855140000
P	0.505552000	-1.112342000	-1.148004000	P	-0.505552000	1.112342000	1.148004000
P	1.547031000	-0.432470000	0.526091000	P	-1.547031000	0.432470000	-0.526091000
C	-0.335290000	-3.132161000	1.585498000	C	0.335290000	3.132161000	-1.585498000
C	-1.515563000	-3.062877000	0.722168000	C	1.515563000	3.062877000	-0.722168000
C	-2.411637000	-2.112995000	1.337600000	C	2.411637000	2.112995000	-1.337600000
H	-3.378284000	-1.831297000	0.934148000	H	3.378284000	1.831297000	-0.934148000
C	-1.847279000	-1.582648000	2.530156000	C	1.847279000	1.582648000	-2.530156000
C	-0.561127000	-2.189298000	2.652956000	C	0.561127000	2.189298000	-2.652956000
H	0.146826000	-1.971817000	3.443359000	H	-0.146826000	1.971817000	-3.443359000
C	0.878568000	-4.072358000	1.625607000	C	-0.878568000	4.072358000	-1.625607000
C	1.813354000	-3.987337000	0.404022000	C	-1.813354000	3.987337000	-0.404022000
H	2.584675000	-4.769266000	0.484429000	H	-2.584675000	4.769266000	-0.484429000
H	1.298494000	-4.113793000	-0.550290000	H	-1.298494000	4.113793000	0.550290000
H	2.318135000	-3.011798000	0.377427000	H	-2.318135000	3.011798000	-0.377427000
C	1.759397000	-3.741390000	2.850032000	C	-1.759397000	3.741390000	-2.850032000
H	1.218830000	-3.878005000	3.798038000	H	-1.218830000	3.878005000	-3.798038000
H	2.627436000	-4.416932000	2.858672000	H	-2.627436000	4.416932000	-2.858672000
H	2.138739000	-2.710126000	2.801863000	H	-2.138739000	2.710126000	-2.801863000
C	0.362419000	-5.515804000	1.820234000	C	-0.362419000	5.515804000	-1.820234000
H	-0.203048000	-5.876822000	0.952955000	H	0.203048000	5.876822000	-0.952955000
H	1.212437000	-6.198120000	1.975860000	H	-1.212437000	6.198120000	-1.975860000
H	-0.294556000	-5.577126000	2.701011000	H	0.294556000	5.577126000	-2.701011000
C	-2.025821000	-3.869727000	-0.479114000	C	2.025821000	3.869727000	0.479114000
C	-0.954079000	-4.500153000	-1.377599000	C	0.954079000	4.500153000	1.377599000
H	-1.451016000	-5.009122000	-2.217523000	H	1.451016000	5.009122000	2.217523000
H	-0.292887000	-3.727974000	-1.795709000	H	0.292887000	3.727974000	1.795709000
H	-0.345296000	-5.248524000	-0.859119000	H	0.345296000	5.248524000	0.859119000
C	-2.934481000	-4.987621000	0.089679000	C	2.934481000	4.987621000	-0.089679000
H	-3.364651000	-5.579220000	-0.733292000	H	3.364651000	5.579220000	0.733292000
H	-2.373977000	-5.667453000	0.746200000	H	2.373977000	5.667453000	-0.746200000
H	-3.761225000	-4.558756000	0.674864000	H	3.761225000	4.558756000	-0.674864000
C	-2.878488000	-2.971433000	-1.402504000	C	2.878488000	2.971433000	1.402504000
H	-3.241257000	-3.567748000	-2.252961000	H	3.241257000	3.567748000	2.252961000
H	-3.759405000	-2.553662000	-0.898351000	H	3.759405000	2.553662000	0.898351000
H	-2.279292000	-2.136367000	-1.791420000	H	2.279292000	2.136367000	1.791420000
C	-2.546849000	-0.713414000	3.555309000	C	2.546849000	0.713414000	-3.555309000
C	-1.536743000	0.052993000	4.423953000	C	1.536743000	-0.052993000	-4.423953000
H	-2.070517000	0.668552000	5.163551000	H	2.070517000	-0.668552000	-5.163551000
H	-0.877575000	-0.633462000	4.975381000	H	0.877575000	0.633462000	-4.975381000
H	-0.911135000	0.715168000	3.808763000	H	0.911135000	-0.715168000	-3.808763000
C	-3.356550000	-1.674994000	4.459300000	C	3.356550000	1.674994000	-4.459300000
H	-3.882379000	-1.107342000	5.242744000	H	3.882379000	1.107342000	-5.242744000
H	-4.104665000	-2.229801000	3.873893000	H	4.104665000	2.229801000	-3.873893000
H	-2.694227000	-2.405922000	4.946582000	H	2.694227000	2.405922000	-4.946582000
C	-3.512917000	0.276306000	2.882933000	C	3.512917000	-0.276306000	-2.882933000
H	-4.046050000	0.858634000	3.649729000	H	4.046050000	-0.858634000	-3.649729000
H	-2.974891000	0.976808000	2.227939000	H	2.974891000	-0.976808000	-2.227939000
H	-4.266251000	-0.246140000	2.275449000	H	4.266251000	0.246140000	-2.275449000

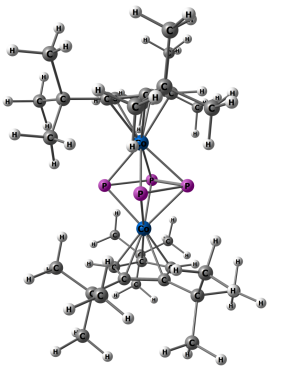


As	1.619009000	-0.369156000	0.795032000	As	-1.619009000	0.369156000	-0.795032000
As	-0.049965000	1.062148000	1.493360000	As	0.049965000	-1.062148000	-1.493360000
Co	0.681485000	1.210684000	-0.816153000	Co	-0.681485000	-1.210684000	0.816153000
C	1.903719000	1.604581000	-2.473461000	C	-1.903719000	-1.604581000	2.473461000
C	2.491877000	2.115909000	-1.278504000	C	-2.491877000	-2.115909000	1.278504000
C	1.633431000	3.086117000	-0.655939000	C	-1.633431000	-3.086117000	0.655939000
C	0.425687000	3.161497000	-1.485402000	C	-0.425687000	-3.161497000	1.485402000
C	0.637092000	2.250610000	-2.587431000	C	-0.637092000	-2.250610000	2.587431000
C	2.601267000	0.733050000	-3.497924000	C	-2.601267000	-0.733050000	3.497924000
C	3.606215000	1.648818000	-4.239064000	C	-3.606215000	-1.648818000	4.239064000
C	3.373302000	-0.414115000	-2.823926000	C	-3.373302000	0.414115000	2.823926000
C	1.604102000	0.160488000	-4.516411000	C	-1.604102000	-0.160488000	4.516411000
C	2.199337000	3.925439000	0.498424000	C	-2.199337000	-3.925439000	-0.498424000
C	3.188750000	3.085248000	1.337505000	C	-3.188750000	-3.085248000	-1.337505000
C	2.993483000	5.087424000	-0.149294000	C	-2.993483000	-5.087424000	0.149294000
C	1.176620000	4.509121000	1.482066000	C	-1.176620000	-4.509121000	-1.482066000
C	-0.803792000	4.079735000	-1.454721000	C	0.803792000	4.079735000	1.454721000
C	-1.667821000	3.951939000	-0.184573000	C	1.667821000	3.951939000	0.184573000
C	-0.340753000	5.541835000	-1.646529000	C	0.340753000	5.541835000	1.646529000
C	-1.739281000	3.745595000	-2.637140000	C	1.739281000	3.745595000	2.637140000
H	3.461018000	1.817071000	-0.894242000	H	-3.461018000	-1.817071000	0.894242000
H	-0.084427000	2.050813000	-3.370847000	H	0.084427000	-2.050813000	3.370847000
H	3.088456000	2.493479000	-4.717369000	H	-3.088456000	-2.493479000	4.717369000
H	4.135484000	1.080300000	-5.019390000	H	-4.135484000	-1.080300000	5.019390000
H	4.354199000	2.057789000	-3.543734000	H	-4.354199000	-2.057789000	3.543734000
H	4.096919000	-0.038585000	-2.086247000	H	-4.096919000	0.038585000	2.086247000
H	3.929323000	-0.990576000	-3.578754000	H	-3.929323000	0.990576000	3.578754000
H	2.683657000	-1.092807000	-2.301928000	H	-2.683657000	1.092807000	2.301928000
H	0.844197000	-0.463018000	-4.022270000	H	-0.844197000	0.463018000	4.022270000
H	2.133700000	-0.465330000	-5.250114000	H	-2.133700000	0.465330000	5.250114000
H	1.089196000	0.960687000	-5.068603000	H	-1.089196000	-0.960687000	5.068603000
H	2.707483000	2.180174000	1.735589000	H	-2.707483000	-2.180174000	-1.735589000
H	3.544400000	3.688187000	2.185922000	H	-3.544400000	-3.688187000	-2.185922000
H	4.073749000	2.782566000	0.761935000	H	-4.073749000	-2.782566000	-0.761935000
H	3.479933000	5.690959000	0.632992000	H	-3.479933000	-5.690959000	-0.632992000
H	2.340742000	5.747972000	-0.735705000	H	-2.340742000	-5.747972000	0.735705000
H	3.773826000	4.699532000	-0.820261000	H	-3.773826000	-4.699532000	0.820261000
H	0.579477000	3.713103000	1.949810000	H	-0.579477000	-3.713103000	-1.949810000
H	0.498496000	5.228310000	1.010929000	H	-0.498496000	-5.228310000	-1.010929000
H	1.714092000	5.041602000	2.281147000	H	-1.714092000	-5.041602000	-2.281147000
H	-2.118595000	2.950522000	-0.139434000	H	2.118595000	-2.950522000	0.139434000
H	-2.480573000	4.694267000	-0.220730000	H	2.480573000	-4.694267000	0.220730000
H	-1.107938000	4.104657000	0.739830000	H	1.107938000	-4.104657000	-0.739830000
H	0.233280000	5.912870000	-0.789177000	H	-0.233280000	-5.912870000	0.789177000
H	-1.216713000	6.196706000	-1.771785000	H	1.216713000	-6.196706000	1.771785000
H	0.288964000	5.636415000	-2.543915000	H	-0.288964000	-5.636415000	2.543915000
H	-1.252075000	3.908896000	-3.609495000	H	1.252075000	-3.908896000	3.609495000
H	-2.622416000	4.399505000	-2.590173000	H	2.622416000	-4.399505000	2.590173000
H	-2.091559000	2.704528000	-2.585579000	H	2.091559000	-2.704528000	2.585579000

Table S9: Optimized geometry of **3a** (left) and **3b** (right). XYZ coordinates in angstroms. BP86/def2-TZVP level of theory.



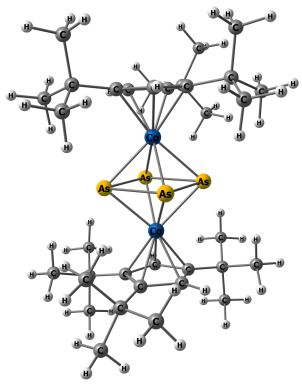
Co	1.623356000	0.297110000	0.034795000	H	3.150617000	-3.460338000	2.414647000
Co	-1.623835000	-0.297840000	-0.035208000	C	-5.375643000	1.163161000	2.022156000
P	-0.299903000	1.496051000	0.511110000	H	-5.582686000	0.129778000	2.335134000
P	0.300824000	-1.501666000	-0.505538000	H	-5.963020000	1.369562000	1.117826000
P	-0.033191000	0.379094000	-1.562512000	H	-5.715251000	1.842048000	2.818381000
P	0.033375000	-0.387697000	1.563131000	C	-2.379406000	-3.865984000	-1.395445000
C	3.180899000	0.986209000	1.190668000	H	-1.383181000	-3.460229000	-1.625568000
H	3.068007000	1.305021000	2.219739000	H	-3.059552000	-3.607725000	-2.219652000
C	3.470919000	-0.356206000	-0.698021000	H	-2.299200000	-4.961803000	-1.359002000
C	-3.436705000	0.372876000	-0.775924000	C	3.113158000	-1.061373000	-3.098124000
C	3.437849000	-0.371126000	0.775336000	H	3.350883000	-0.069834000	-3.503277000
C	-3.470212000	0.357874000	0.697507000	H	3.022953000	-1.132672000	-2.965322000
C	-3.181924000	-0.984831000	-1.191343000	H	3.409259000	-1.801152000	-3.854954000
H	-3.069449000	-1.303792000	-2.220416000	C	-2.898109000	-3.342266000	-0.047373000
C	3.038641000	1.838902000	0.057257000	C	-5.197891000	1.928005000	-1.613732000
C	-3.041500000	-1.837885000	-0.057906000	H	-5.351447000	2.445391000	-0.660476000
C	3.209926000	1.000286000	-1.087762000	C	-5.886236000	1.071213000	-1.652805000
H	3.132797000	1.342712000	-2.113434000	H	-5.468242000	2.623284000	-2.421887000
C	-3.211913000	-0.999209000	1.087083000	C	-3.113620000	1.061778000	3.098215000
C	-3.135431000	-1.341943000	2.112703000	H	-2.023145000	1.131280000	2.966725000
C	-3.857890000	1.370605000	1.779118000	H	-3.353561000	0.070539000	3.502806000
C	3.859320000	-1.368524000	-1.779723000	H	-3.409292000	1.801839000	3.854939000
C	3.738869000	-1.460895000	1.808191000	C	-3.632113000	0.886306000	-3.236795000
C	-3.735127000	1.463396000	-1.808581000	H	-4.360196000	0.081375000	-3.411924000
C	5.376475000	-1.158688000	-2.024311000	H	-3.853930000	-1.153773000	-4.214034000
C	-5.376507000	1.364218000	-1.120591000	H	-2.820589000	0.102564000	-3.506706000
H	5.965107000	-1.364218000	-1.120591000	H	-3.841512000	1.689972000	-3.956766000
H	5.581579000	-0.124948000	-2.337391000	C	1.965716000	3.815625000	-1.086614000
H	5.716368000	-1.836975000	-2.820929000	H	0.930790000	3.485476000	-0.914202000
C	3.594818000	-2.848119000	-1.469956000	H	2.288289000	3.438588000	-2.067042000

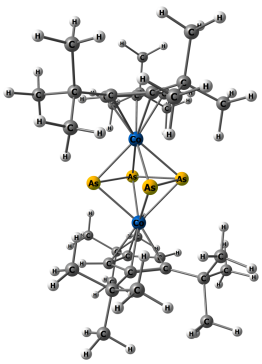


Co	-1.621901000	0.299170000	-0.002466000	H	-3.312384000	4.882276000	-0.168844000
Co	1.642242000	0.296902000	-0.052234000	H	-3.777216000	3.627434000	-1.335111000
P	-0.013420000	0.423202000	-1.707481000	C	-5.046326000	3.089588000	1.037462000
P	0.012127000	2.013608000	-0.107780000	H	-5.658929000	2.807674000	0.168852000
P	0.039333000	0.564274000	1.518412000	H	-5.257257000	4.140433000	1.285150000
P	0.004746000	-1.227262000	-0.246821000	H	-5.346546000	2.464082000	1.890592000
C	-3.336677000	-0.563405000	-0.837963000	C	-2.721195000	3.310107000	1.973997000
C	-3.208064000	-0.885533000	0.589165000	H	-2.984724000	2.693406000	2.844693000
C	-3.225322000	0.379748000	1.292921000	H	-2.921417000	4.359358000	2.233897000
H	-3.138797000	0.485728000	2.368451000	H	-1.641372000	3.204749000	1.792160000
C	-3.350247000	1.462112000	0.382085000	C	3.389220000	-2.223165000	-1.323535000
C	-3.379480000	0.873119000	-0.902217000	C	2.690768000	-2.084205000	-2.694753000
H	-3.422897000	1.435910000	-1.845289000	H	1.616901000	-1.878221000	-2.572378000
C	3.267048000	-0.918851000	-0.528866000	H	2.792627000	-3.030461000	-3.244102000
C	3.245127000	-0.573000000	0.904635000	H	3.126513000	-1.295753000	-3.321099000
C	3.334808000	0.865528000	0.976714000	C	2.812252000	-3.489072000	-0.674207000
H	3.318391000	1.439117000	1.895836000	H	3.293301000	-3.747904000	0.274003000
C	3.402189000	1.430074000	-0.329846000	H	2.971172000	-4.333212000	-1.360804000
C	3.350338000	0.329476000	-1.236580000	H	1.729277000	-3.394528000	-0.511022000
H	3.353125000	0.425316000	-2.316675000	C	4.907691000	-2.423703000	-1.567034000
C	-3.535886000	-1.422919000	-2.091244000	H	5.334160000	-1.567370000	-2.109041000
C	-3.711772000	-0.517641000	-0.329132000	H	5.065669000	-3.329844000	-2.170437000
H	-4.590352000	0.137486000	-3.242626000	H	5.455644000	-2.537697000	-0.621941000
H	-3.853930000	-1.153773000	-4.214034000	C	3.275955000	-1.420051000	2.179603000
H	-2.820589000	0.102564000	-3.506706000	C	2.049958000	-2.336542000	2.361904000
C	-4.850701000	-2.220161000	-1.923877000	H	1.155594000	-1.726465000	2.563807000
H	-4.795093000	-2.966977000	-1.123702000	H	2.208424000	-2.989586000	3.232689000
H	-5.078454000	-2.748546000	-2.861302000	H	1.842142000	-2.967927000	1.496119000
H	-5.686932000	-1.542015000	-1.699491000	C	4.588478000	-2.240037000	2.177801000

H	2.523671000	-3.034217000	-1.307146000	H	1.968812000	4.914137000	-1.131640000	C	-2.357985000	-2.362011000	-2.415387000	H	4.621178000	-2.980918000	1.371683000
H	4.154280000	-3.216029000	-0.604206000	C	3.635177000	-0.883633000	3.236288000	H	-1.487004000	-1.774453000	-2.741300000	H	4.686375000	-2.774995000	3.133555000
H	3.907138000	-3.446593000	-2.337986000	H	2.624799000	-0.504619000	3.449669000	H	-2.641294000	-3.025397000	-3.245918000	H	5.457542000	-1.575733000	2.064635000
C	-3.590748000	2.849928000	1.470144000	H	4.361655000	-0.077147000	3.410892000	H	-2.050126000	-2.984527000	-1.572880000	C	3.317108000	-0.507398000	3.424539000
H	-4.148348000	3.218953000	0.603676000	H	3.846554000	-1.686628000	3.956425000	C	-3.250917000	-2.175514000	1.409764000	H	4.214819000	0.126717000	3.442959000
H	-2.519103000	3.034595000	1.309022000	C	-2.767047000	2.662487000	-1.757632000	C	-4.737825000	-2.363751000	1.811541000	H	3.334687000	-1.139244000	4.323624000
H	-3.903527000	3.448559000	2.337906000	H	-1.777373000	2.360117000	-2.131230000	H	-5.103221000	-1.496160000	2.379340000	H	2.425827000	0.134565000	3.486378000
C	2.893345000	3.343062000	0.046551000	H	-2.636983000	3.074737000	-0.755393000	H	-4.837458000	-3.258790000	2.443027000	C	3.618346000	2.881967000	-0.687398000
C	5.202578000	-1.922291000	1.612858000	H	-3.142228000	3.462257000	-2.413040000	H	-5.379827000	-2.489814000	0.929573000	C	2.890820000	3.253893000	-1.990713000
H	5.889089000	-1.064030000	1.651995000	C	-1.973051000	-3.816475000	1.087244000	C	-2.745237000	-3.448027000	0.718135000	H	3.204302000	2.618685000	-2.831055000
H	5.356933000	-2.439032000	0.659372000	H	-2.297098000	-3.439653000	2.067277000	H	-3.322578000	-3.715731000	-0.172043000	H	3.117902000	4.296500000	-2.255608000
H	5.474656000	-2.617264000	2.420708000	H	-0.937313000	-3.487589000	0.917140000	H	-2.828228000	-4.285798000	1.425385000	H	1.800755000	3.160754000	-1.876257000
C	2.376179000	3.866479000	1.395302000	H	-1.977595000	-4.915006000	1.131642000	H	-1.685809000	-3.352631000	0.439604000	C	3.161189000	3.811022000	0.448272000
H	3.058006000	3.609339000	2.218462000	C	4.319793000	3.898075000	-0.204739000	C	-2.414756000	-2.026100000	2.700137000	H	2.087430000	3.691773000	0.656485000
H	1.380894000	3.459391000	1.627108000	H	4.710081000	3.562112000	-1.176467000	H	-1.357643000	-1.835562000	2.462422000	H	3.337289000	4.857775000	0.162373000
H	2.294431000	4.962179000	1.358696000	H	5.014900000	3.567627000	0.580686000	H	-2.470596000	-2.962947000	3.271575000	H	3.717761000	3.620250000	1.376824000
C	2.773665000	-2.662332000	1.758101000	H	4.292342000	4.997701000	-0.203822000	H	-2.770574000	-1.222059000	3.356324000	C	5.146244000	3.044752000	-0.892919000
H	2.645267000	-3.076257000	0.756345000	C	-4.325679000	-3.895508000	0.201362000	C	-3.536171000	2.920720000	0.728974000	H	5.695543000	2.783620000	0.023199000
H	1.782943000	-2.362290000	2.130783000	H	-5.019013000	-3.563980000	-0.585175000	C	-3.157765000	3.830843000	-0.449981000	H	5.374034000	4.090030000	-1.149041000
H	3.150617000	-3.460338000	2.414647000	H	-4.717141000	-3.559206000	1.172504000	H	-2.101303000	3.705539000	-0.729963000	H	5.505887000	2.400856000	-1.708574000
H	3.150617000	-3.460338000	2.414647000	H	-4.299696000	-4.995173000	0.200272000										

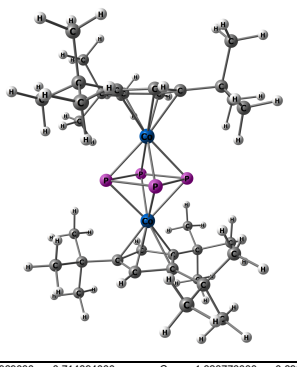
Table S10: Optimized geometry of **4a** (left) and **4b** (right). XYZ coordinates in angstroms. BP86/def2-TZVP level of theory.

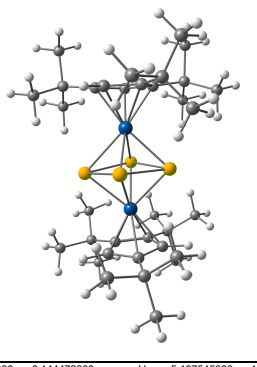




As	0.196259000	-0.831844000	-1.544446000	As	-0.196259000	0.831844000	1.544446000	As	0.006347000	2.083485000	-0.092724000	C	-4.937634000	-2.242653000	-1.901517000
As	-1.613937000	0.421588000	-0.585075000	As	1.613937000	-0.421588000	0.585075000	As	0.036909000	0.494428000	1.698585000	H	-4.910230000	-2.989657000	-1.100004000
Co	-0.634288000	-1.403644000	0.674741000	Co	0.634288000	1.403644000	-0.674741000	As	-0.014794000	0.305436000	-1.838676000	H	-5.185362000	-2.763686000	-2.838117000
C	-0.790997000	-2.499062000	2.408607000	C	0.790997000	2.499062000	-2.408607000	Co	-1.659931000	0.226029000	0.016740000	H	-5.747276000	-1.532715000	-1.677915000
H	-0.372518000	-2.194399000	3.360609000	H	0.372518000	2.194399000	-3.360609000	As	0.000827000	-1.459437000	-0.182444000	C	-5.114574000	2.990604000	1.031762000
C	-2.244267000	-2.737281000	0.595809000	C	2.244267000	2.737281000	-0.595809000	Co	1.673777000	0.223695000	-0.029201000	H	-5.714607000	2.691918000	0.159965000
C	-0.106169000	-3.283431000	1.435708000	C	0.106169000	3.283431000	-1.435708000	C	-3.404815000	0.802922000	-0.908584000	H	-5.351297000	4.037096000	1.274874000
C	-2.104315000	-2.134111000	1.932948000	C	2.104315000	2.134111000	-1.932948000	H	-3.449861000	1.360949000	-1.836441000	H	-5.406207000	2.360669000	1.884585000
C	-1.002529000	-3.406763000	0.329724000	C	1.002529000	3.406763000	-0.329724000	C	3.417550000	1.366662000	-0.336396000	C	-3.731581000	-0.595875000	-3.314550000
H	-0.775008000	-3.940462000	-0.586383000	H	0.775008000	3.940462000	0.586383000	C	3.364969000	0.820012000	0.977932000	H	-4.594575000	0.081399000	-3.243724000
C	1.210939000	-4.008204000	1.594219000	C	-1.210939000	4.008204000	-1.594219000	H	3.358560000	1.406716000	1.889012000	H	-3.879002000	-1.234801000	-4.196619000
C	-3.407450000	-2.943367000	-0.380738000	C	3.407450000	2.943367000	0.380738000	C	3.365388000	0.252516000	-1.227130000	H	-2.824143000	0.002108000	-3.486563000
C	-3.636554000	-0.084069000	2.286444000	C	3.636554000	0.084069000	-2.286444000	H	3.367822000	0.333345000	-2.308385000	C	-3.347852000	-2.233905000	1.439734000
H	-4.033083000	-0.175155000	1.273931000	H	4.033083000	0.175155000	-1.273931000	C	-3.264228000	0.318555000	1.306952000	C	-2.896766000	-3.533848000	0.762160000
H	-2.838733000	0.673633000	2.268378000	H	2.838733000	-0.673633000	-2.268378000	H	-3.194473000	0.429604000	2.383389000	H	-3.481179000	-3.785521000	-0.127999000
H	-4.438970000	0.290679000	2.938811000	H	4.438970000	-0.290679000	-2.938811000	C	-3.381106000	1.397769000	0.391141000	H	-3.018456000	-4.360400000	1.477165000
C	2.007387000	-4.036767000	0.278552000	C	-2.007387000	4.036767000	-0.278552000	C	-3.254349000	-0.950805000	0.609717000	H	-1.832659000	-3.490556000	0.487794000
H	2.328724000	-3.026452000	-0.013970000	H	-2.328724000	3.026452000	0.013970000	C	-3.371729000	-0.634379000	-0.818953000	C	-2.452296000	-2.482254000	-2.379782000
H	1.418457000	-4.459533000	-0.547299000	H	-1.418457000	4.459533000	0.547299000	C	3.290387000	-0.621601000	0.926772000	H	-1.557798000	-1.933874000	-2.710916000
H	2.906456000	-4.657081000	0.403549000	H	-2.906456000	4.657081000	-0.403549000	C	3.306148000	-0.986792000	-0.501364000	H	-2.758684000	-3.146492000	-3.201449000
C	2.062098000	-3.388969000	2.712976000	C	-2.062098000	3.388969000	-2.712976000	C	3.373174000	-1.449815000	2.213339000	H	-2.169977000	-3.104646000	-1.528024000
H	1.549503000	-3.438999000	3.684305000	H	-1.549503000	3.438999000	-3.684305000	C	3.465590000	-2.297711000	-1.280686000	C	2.937201000	-3.574553000	-0.612622000
H	2.298064000	-2.335581000	2.501575000	H	-2.298064000	2.335581000	-2.501575000	C	3.658827000	2.809316000	-0.717301000	H	3.435121000	-3.807031000	0.333900000
H	3.010780000	-3.936821000	2.804951000	H	-3.010780000	3.936821000	-2.804951000	C	-3.598846000	2.853902000	0.733781000	H	3.116772000	-4.420980000	-1.291304000
C	-3.092167000	-1.409540000	2.852675000	C	3.092167000	1.409540000	-2.852675000	C	3.235691000	3.764350000	0.409342000	H	1.852940000	-3.517252000	-0.438429000
C	-2.888561000	-3.026996000	-1.833963000	C	2.888561000	3.026996000	1.833963000	H	2.164426000	3.664305000	0.640384000	C	4.988373000	-2.452877000	-1.530899000
C	-2.185246000	-3.853851000	-1.992762000	H	2.185246000	3.853851000	1.992762000	H	3.421545000	4.803950000	0.104227000	H	5.383246000	-1.591590000	-2.088536000
H	-2.396656000	-2.090055000	-2.136262000	H	2.396656000	2.090055000	2.136262000	H	3.805117000	3.578956000	1.331225000	H	5.173027000	-3.362856000	-2.120874000
H	-3.741783000	-3.191796000	-2.506818000	H	3.741783000	3.191796000	2.506818000	C	2.936314000	3.182427000	-2.022954000	H	5.545307000	-2.533430000	-0.587753000
C	-2.414848000	-1.060706000	4.195793000	C	2.414848000	1.060706000	-4.195793000	H	3.219850000	2.518192000	-2.851497000	C	3.397908000	-0.518009000	3.444424000
H	-1.548286000	-0.397419000	4.058850000	H	1.548286000	0.397419000	-4.058850000	H	3.201048000	4.209959000	-2.311747000	H	4.275151000	0.144216000	3.443997000
H	-2.089258000	-1.958753000	4.739411000	H	2.089258000	1.958753000	-4.739411000	H	1.843703000	3.133614000	-1.904264000	H	3.443863000	-1.134331000	4.353334000
H	-3.139742000	-0.529937000	4.829147000	H	3.139742000	0.529937000	-4.829147000	C	-3.592997000	-1.495985000	-2.067973000	H	2.487742000	0.097629000	3.504687000
C	-4.513568000	-1.879987000	-0.379314000	C	4.513568000	1.879987000	0.379314000	C	5.188981000	2.933870000	-0.936250000	C	4.718808000	-2.214359000	2.200479000
H	-4.118345000	-0.892865000	-0.659741000	H	4.118345000	0.892865000	0.659741000	H	5.738751000	2.665704000	-0.022442000	H	4.761170000	-2.975966000	1.414172000
H	-5.029448000	-1.794198000	0.582212000	H	5.029448000	1.794198000	-0.582212000	H	5.441205000	3.970996000	-1.202723000	H	4.862129000	-2.718256000	3.167424000
H	-5.266839000	-2.158795000	-1.130293000	H	5.266839000	2.158795000	1.130293000	H	5.525558000	2.274277000	-1.749249000	H	5.556785000	-1.519098000	2.046713000
C	0.841120000	-5.462455000	1.986924000	C	-0.841120000	5.462455000	-1.986924000	C	2.758414000	-2.201199000	-2.650856000	C	2.195587000	-2.418882000	2.435132000
H	0.248481000	-5.946469000	1.197174000	H	-0.248481000	5.946469000	-1.197174000	H	1.676777000	-2.041456000	-2.527328000	H	1.281096000	-1.851416000	2.667207000
H	0.257905000	-5.481350000	2.918955000	H	-0.257905000	5.481350000	-2.918955000	H	2.900008000	-3.146176000	-3.193906000	H	2.411988000	-3.062481000	3.300560000
H	1.759237000	-6.048767000	2.140164000	H	-1.759237000	6.048767000	-2.140164000	H	3.156252000	-1.398590000	-3.284311000	H	1.989627000	-3.062090000	1.577434000
C	-4.248516000	-2.386541000	3.174405000	C	4.248516000	2.386541000	-3.174405000	C	-2.804200000	3.265040000	1.984543000	C	-4.842799000	-2.358082000	1.838026000
H	-3.854484000	-3.327684000	3.584946000	H	3.854484000	3.327684000	-3.584946000	H	-3.057551000	2.640363000	2.852663000	H	-5.172793000	-1.475757000	2.404752000
H	-4.854815000	-2.627045000	2.293819000	H	4.854815000	2.627045000	-2.293819000	H	-3.033314000	4.308638000	2.243648000	H	-4.982931000	-3.248045000	2.469010000
H	-4.910569000	-1.933981000	3.926953000	H	4.910569000	1.933981000	-3.926953000	H	-1.720329000	3.186683000	1.812762000	H	-5.486608000	-2.456061000	0.953769000
C	-4.024610000	-4.317466000	-0.009765000	C	4.024610000	4.317466000	0.009765000	C	-3.237140000	3.771418000	-0.444288000	C	-2.511976000	-2.114914000	2.733093000
H	-4.424954000	-4.317388000	1.012730000	H	4.424954000	4.317388000	-1.012730000	H	-2.177186000	3.671148000	-0.721585000	H	-1.440840000	-2.020112000	2.500461000
H	-3.272485000	-5.116112000	-0.081206000	H	3.272485000	5.116112000	0.081206000	H	-3.416963000	4.819623000	-0.166046000	H	-2.647494000	-3.028357000	3.328937000
H	-4.846242000	-4.551049000	-0.703187000	H	4.846242000	4.551049000	0.703187000	H	-3.847300000	3.551452000	-1.331882000	H	-2.804368000	-1.266671000	3.364029000

Table S11: Optimized geometry of **5** (left) and **6** (right). XYZ coordinates in angstroms. BP86/def2-TZVP level of theory.

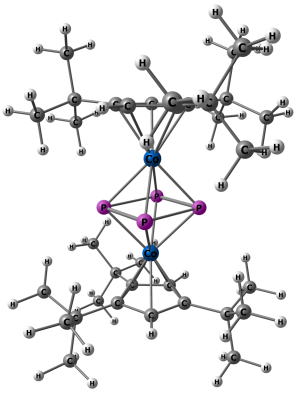


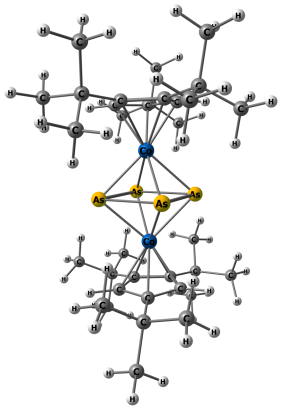


Co	1.328776000	0.696969000	-0.714894000	Co	-1.328776000	-0.696969000	0.714894000	Co	-1.674446000	0.218648000	-0.144472000	H	-5.197545000	1.102059000	2.644135000
P	-0.021513000	-1.133888000	-1.139011000	P	0.021513000	1.133888000	1.139011000	Co	1.674367000	-0.218485000	-0.143747000	H	-5.188474000	-0.138308000	3.925731000
P	-0.975376000	0.912933000	-0.879568000	P	0.975376000	-0.912933000	0.879568000	As	-0.244970000	-1.200462000	-1.475988000	C	-2.608832000	0.585485000	3.420666000
C	2.619432000	2.286603000	-0.601791000	C	-2.619432000	-2.286603000	0.601791000	As	-0.113350000	-1.263853000	1.009908000	H	-1.543222000	0.377575000	3.236562000
H	2.558407000	3.060639000	0.155053000	H	-2.558407000	-3.060639000	-0.155053000	As	0.112952000	1.265463000	1.008214000	H	-2.807287000	0.369039000	4.478825000
C	3.359835000	1.058267000	-0.452770000	C	-3.359835000	-1.058267000	0.452770000	As	0.245218000	1.198885000	-1.477575000	H	-2.785610000	1.657470000	3.271574000
C	1.949478000	2.335996000	-1.860593000	C	-1.949478000	-2.335996000	1.860593000	C	-3.155113000	1.374812000	0.676692000	C	-3.241606000	-1.759950000	2.995347000

C	2.239618000	1.091293000	-2.499470000	C	-2.239618000	-1.091293000	2.499470000	H	-3.000729000	2.194465000	1.370040000	H	-2.198149000	-2.050766000	2.807156000
H	1.838753000	0.788883000	-3.459898000	H	-1.838753000	-0.788883000	3.459898000	C	-3.210140000	1.514243000	-0.740939000	H	-3.904857000	-2.490224000	2.522545000
C	3.109101000	0.280384000	-1.680310000	C	-3.109101000	-0.280384000	1.680310000	C	-3.391617000	0.192823000	-1.255072000	H	-3.405856000	-1.825350000	4.079899000
C	1.185122000	3.502769000	-2.428931000	C	-1.185122000	-3.502769000	2.428931000	H	-3.435183000	-0.053246000	-2.309490000	C	3.845359000	2.224637000	-0.479419000
C	4.285514000	0.903099000	0.750037000	C	-4.285514000	-0.903099000	-0.750037000	C	-3.495752000	-0.766050000	-0.184636000	C	3.929849000	2.455939000	-2.002973000
C	3.652879000	-1.047311000	-2.204453000	C	-3.652879000	1.047311000	2.204453000	C	-3.342041000	-0.000381000	1.067899000	H	4.710317000	1.842232000	-2.473564000
C	2.280291000	4.474452000	-2.952453000	C	-2.280291000	-4.474452000	2.952453000	C	3.391031000	-0.192690000	-1.255293000	H	4.180542000	3.510094000	-2.182604000
H	2.922286000	4.828172000	-2.133548000	H	-2.922286000	-4.828172000	2.133548000	H	3.434057000	0.053607000	-2.309675000	H	2.969372000	2.257172000	-2.502841000
H	1.792121000	5.344766000	-3.413655000	H	-1.792121000	-5.344766000	3.413655000	C	3.495736000	0.766000000	-0.184721000	C	2.834520000	3.255561000	0.059538000
H	2.912056000	3.987457000	-3.708307000	H	-2.912056000	-3.987457000	3.708307000	C	3.342400000	0.000170000	1.067773000	H	2.577436000	3.113656000	1.110617000
C	0.284872000	3.071939000	-3.597022000	C	-0.284872000	-3.071939000	3.597022000	C	3.155337000	-1.374973000	0.676389000	H	1.905965000	3.221150000	-0.531443000
H	0.866729000	2.631712000	-4.418907000	H	-0.866729000	-2.631712000	4.418907000	H	3.001280000	-2.194819000	1.369572000	H	3.252286000	4.265774000	-0.054410000
H	-0.242050000	3.949677000	-3.994990000	H	0.242050000	-3.949677000	3.994990000	C	3.209862000	-1.514191000	-0.741272000	C	5.258523000	2.485116000	0.101210000
H	-0.473664000	2.342382000	-3.276620000	H	0.473664000	-2.342382000	3.276620000	C	-3.208533000	2.805416000	-1.516815000	H	5.278654000	2.443451000	1.195647000
C	0.351996000	4.218071000	-1.351921000	C	-0.351996000	-4.218071000	1.351921000	C	-2.220717000	3.829159000	-0.931945000	H	5.592483000	3.486435000	-0.205220000
H	-0.476032000	3.582757000	-1.002786000	H	0.476032000	-3.582757000	1.002786000	H	-1.178904000	3.504819000	-1.076542000	H	5.977472000	1.748839000	-0.284957000
H	-0.086687000	5.131645000	-1.775717000	H	0.086687000	-5.131645000	1.775717000	H	-2.381556000	3.998635000	0.141318000	C	3.512344000	0.316972000	2.551890000
H	0.956076000	4.508745000	-0.481814000	H	-0.956076000	-4.508745000	0.481814000	H	-2.343401000	4.791942000	-1.446550000	C	3.241669000	1.759561000	2.995097000
C	3.694518000	1.596951000	1.997353000	C	-3.694518000	-1.596951000	-1.997353000	C	-2.909604000	2.570874000	-3.004843000	H	2.198098000	2.049872000	2.806693000
H	3.512805000	2.669213000	1.856994000	H	-3.512805000	-2.669213000	-1.856994000	H	-1.918600000	2.116787000	-3.153097000	H	3.904675000	2.490118000	2.522385000
H	4.409315000	1.496346000	2.824843000	H	-4.409315000	-1.496346000	-2.824843000	H	-2.920775000	3.532258000	-3.536111000	H	3.405688000	1.825103000	4.079676000
H	2.753776000	1.120934000	2.313604000	H	-2.753776000	-1.120934000	-2.313604000	H	-3.664452000	1.921122000	-3.474007000	C	4.994950000	-0.043420000	2.858901000
C	3.325317000	-2.270908000	-1.324695000	C	-3.325317000	2.270908000	1.324695000	C	-4.655376000	3.354970000	-1.364018000	H	5.689840000	0.568470000	2.269683000
H	3.577632000	-2.141987000	-0.270708000	H	-3.577632000	2.141987000	0.270708000	H	-4.887909000	3.572311000	-0.311985000	H	5.198849000	-1.101625000	2.643693000
H	3.879253000	-3.142126000	-1.701556000	H	-3.879253000	3.142126000	1.701556000	H	-5.394243000	2.635331000	-1.743668000	H	5.189689000	0.138910000	3.925126000
H	2.253177000	-2.512157000	-1.400220000	H	-2.253177000	2.512157000	1.400220000	H	-4.746653000	4.285802000	-1.941568000	C	2.610165000	-0.586161000	3.420617000
C	5.582532000	1.660543000	0.340915000	C	-5.582532000	-1.660543000	-0.340915000	C	-3.845550000	-2.224622000	-0.479415000	H	1.544480000	-0.378404000	3.236876000
H	6.061412000	1.201224000	-0.533275000	H	-6.061412000	-1.201224000	0.533275000	C	-5.258738000	-2.484941000	0.101207000	H	2.808992000	-0.369890000	4.478732000
H	6.289945000	1.627041000	1.181839000	H	-6.289945000	-1.627041000	-1.181839000	H	-5.278918000	-2.443356000	1.195646000	H	2.787086000	-1.658070000	3.271199000
H	5.371859000	2.713312000	0.106198000	H	-5.371859000	-2.713312000	-0.106198000	H	-5.592844000	-3.486189000	-0.205305000	C	3.208203000	-2.805353000	-1.517169000
C	4.646260000	-0.525902000	1.173751000	C	-4.646260000	0.525902000	-1.173751000	H	-5.977560000	-1.748520000	-0.284917000	C	2.908830000	-2.570878000	-3.005121000
H	3.755692000	-1.086494000	1.491647000	H	-3.755692000	1.086494000	-1.491647000	C	-2.834742000	-3.255561000	0.059599000	H	1.917652000	-2.117085000	-3.153087000
H	5.321519000	-0.467079000	2.038436000	H	-5.321519000	0.467079000	-2.038436000	H	-2.577904000	-3.113744000	1.110736000	H	2.920146000	-3.532245000	-3.536417000
H	5.165872000	-1.091043000	0.394391000	H	-5.165872000	1.091043000	-0.394391000	H	-1.906100000	-3.220948000	-0.531195000	H	3.660360000	-1.920887000	-3.474469000
C	5.185071000	-0.884687000	-2.376015000	C	-5.185071000	0.884687000	2.376015000	H	-3.252373000	-4.265812000	-0.054563000	C	2.220743000	-3.829336000	-0.932068000
H	5.415544000	-0.010366000	-3.001035000	H	-5.415544000	0.010366000	3.001035000	C	-3.929999000	-2.455959000	-2.002954000	H	1.178830000	-3.505277000	-1.076555000
H	5.581452000	-1.778766000	-2.876966000	H	-5.581452000	1.778766000	2.876966000	H	-2.969557000	-2.257083000	-2.502836000	H	2.381694000	-3.998673000	0.141193000
H	5.707947000	-0.774089000	-1.420030000	H	-5.707947000	0.774089000	1.420030000	H	-4.710552000	-1.842381000	-2.473577000	H	2.343633000	-4.792105000	-1.446629000
C	3.065655000	-1.347711000	-3.599808000	C	-3.065655000	1.347711000	3.599808000	H	-4.180579000	-3.510153000	-2.182570000	C	4.655188000	-3.354629000	-1.364774000
H	1.970186000	-1.448457000	-3.569456000	H	-1.970186000	1.448457000	3.569456000	C	-3.511545000	-0.317232000	2.552093000	H	4.888060000	-3.572048000	-0.312831000
H	3.473272000	-2.304677000	-3.952808000	H	-3.473272000	2.304677000	3.952808000	C	-4.993949000	0.043817000	2.859441000	H	5.393827000	-2.634820000	-1.744554000
H	3.334343000	-0.578317000	-4.336685000	H	-3.334343000	0.578317000	4.336685000	H	-5.689192000	-0.567911000	2.270460000	H	4.746481000	-4.285384000	-1.942448000

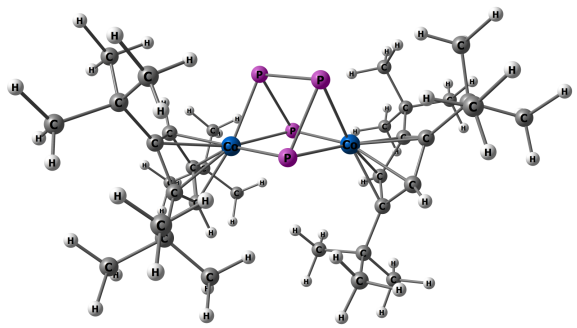
Table S12: Optimized geometry of **7** (left) and **8** (right). XYZ coordinates in angstroms. BP86/def2-TZVP level of theory.



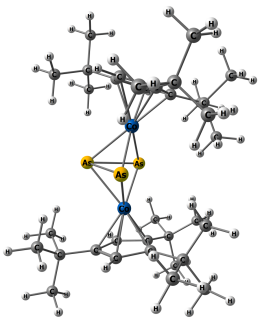


Co	-0.045337000	-1.531347000	-0.655103000	Co	0.045337000	1.531347000	0.655103000	As	1.280361000	-0.518600000	1.132660000	As	-1.280361000	0.518600000	-1.132660000
P	1.126116000	-0.480599000	1.062261000	P	-1.126116000	0.480599000	-1.062261000	Co	-0.051659000	-1.558577000	0.659979000	Co	0.051659000	1.558577000	0.659979000
P	-1.014362000	-0.489879000	1.156877000	P	1.014362000	0.489879000	-1.156877000	As	-1.079097000	-0.545610000	1.299482000	As	1.079097000	0.545610000	-1.299482000
C	-1.286196000	-3.053300000	-1.391464000	C	1.286196000	3.053300000	1.391464000	C	-0.351937000	-2.641095000	-2.398727000	C	0.351937000	2.641095000	2.398727000
C	-0.348273000	-2.620698000	-2.401550000	C	0.348273000	2.620698000	2.401550000	H	-0.621120000	-2.182390000	-3.343611000	H	0.621120000	2.182390000	3.343611000
H	-0.622013000	-2.162638000	-3.345175000	H	0.622013000	2.162638000	3.345175000	C	-1.294225000	-3.077403000	-1.392852000	C	1.294225000	3.077403000	1.392852000
C	-0.481467000	-3.563978000	-0.278710000	C	0.481467000	3.563978000	0.278710000	C	-0.492712000	-3.590421000	-0.279438000	C	0.492712000	3.590421000	0.279438000
C	0.896741000	-3.420039000	-0.672741000	C	-0.896741000	3.420039000	0.672741000	C	0.989046000	-2.871504000	-1.966743000	C	-0.989046000	2.871504000	1.966743000
H	1.747099000	-3.696420000	-0.058729000	H	-1.747099000	3.696420000	0.058729000	C	0.887308000	-3.442440000	-0.667594000	C	-0.887308000	3.442440000	0.667594000
C	0.992967000	-2.844300000	-1.970557000	C	-0.992967000	2.844300000	1.970557000	H	1.734861000	-3.726872000	-0.053170000	H	-1.734861000	3.726872000	0.053170000
C	2.264363000	-2.663155000	-2.776685000	C	-2.264363000	2.663155000	2.776685000	C	-0.804174000	-4.383517000	0.998106000	C	0.804174000	4.383517000	-0.998106000
C	-0.794719000	-4.321151000	1.018955000	C	0.794719000	4.321151000	-1.018955000	C	-0.753667000	-5.887428000	0.634153000	C	0.753667000	5.887428000	-0.634153000
C	-2.797534000	-3.042206000	-1.666086000	C	2.797534000	3.042206000	1.666086000	H	-1.524136000	-6.147779000	-0.105281000	H	1.524136000	6.147779000	0.105281000
C	-3.071057000	-2.460518000	-3.069744000	C	3.071057000	2.460518000	3.069744000	H	-0.916623000	-6.504733000	1.532923000	H	0.916623000	6.504733000	-1.532923000
H	-2.711602000	-1.423028000	-3.140387000	H	2.711602000	1.423028000	3.140387000	H	0.226363000	-6.148549000	0.207582000	H	-0.226363000	6.148549000	-0.207582000
H	-4.156369000	-2.456138000	-3.253162000	H	4.156369000	2.456138000	3.253162000	C	-3.076118000	-2.474375000	-3.072334000	C	3.076118000	2.474375000	3.072334000
H	-2.595290000	-3.055806000	-3.863060000	H	2.595290000	3.055806000	3.863060000	H	-2.731354000	-1.430091000	-3.114494000	H	2.731354000	1.430091000	3.114494000
C	-2.125515000	-3.968133000	1.699610000	C	2.125515000	3.968133000	-1.699610000	H	-4.160162000	-2.481133000	-3.262766000	H	4.160162000	2.481133000	3.262766000
H	-2.165326000	-2.893454000	1.931792000	H	2.165326000	2.893454000	-1.931792000	H	-2.587131000	-3.041978000	-3.877681000	H	2.587131000	3.041978000	3.877681000
H	-2.204599000	-4.529104000	2.644163000	H	2.204599000	4.529104000	-2.644163000	C	-2.150007000	-4.082977000	1.673864000	C	2.150007000	4.082977000	-1.673864000
H	-2.996543000	-4.231400000	1.089273000	H	2.996543000	4.231400000	-1.089273000	H	-2.220117000	-3.017485000	1.938996000	H	2.220117000	3.017485000	-1.938996000
C	-3.608891000	-2.167156000	-0.690163000	C	3.608891000	2.167156000	0.690163000	H	-2.224045000	-4.673280000	2.600682000	H	2.224045000	4.673280000	-2.600682000
H	-3.458493000	-2.439595000	0.356135000	H	3.458493000	2.439595000	-0.356135000	H	-3.008513000	-4.349639000	1.047318000	H	3.008513000	4.349639000	-1.047318000
H	-4.683265000	-2.254874000	-0.922299000	H	4.683265000	2.254874000	0.922299000	C	-2.803207000	-3.089157000	-1.682613000	C	2.803207000	3.089157000	1.682613000
H	-3.310235000	-1.114596000	-0.802523000	H	3.310235000	1.114596000	0.802523000	C	2.260371000	-2.739791000	-2.783036000	C	-2.260371000	2.739791000	2.783036000
C	-0.780220000	-5.834873000	0.696878000	C	0.780220000	5.834873000	-0.696878000	C	0.280997000	-4.110258000	2.065176000	C	-0.280997000	4.110258000	-2.065176000
H	-1.565568000	-6.099512000	-0.025347000	H	1.565568000	6.099512000	0.025347000	H	1.270885000	-4.471960000	1.755773000	H	-1.270885000	4.471960000	-1.755773000
H	-0.943842000	-6.423811000	1.614329000	H	0.943842000	6.423811000	-1.614329000	H	0.016963000	-4.633710000	2.997184000	H	-0.016963000	4.633710000	-2.997184000
H	0.188600000	-6.128661000	0.265704000	H	-0.188600000	6.128661000	-0.265704000	H	0.356194000	-3.031936000	2.275664000	H	-0.356194000	3.031936000	-2.275664000
C	0.307838000	-4.038407000	2.065553000	C	-0.307838000	4.038407000	-2.065553000	C	-3.301843000	-4.550970000	-1.734945000	C	3.301843000	4.550970000	1.734945000
H	1.285348000	-4.434544000	1.758657000	H	-1.285348000	4.434544000	-1.758657000	H	-2.713292000	-5.133236000	-2.460596000	H	2.713292000	5.133236000	2.460596000
H	0.041847000	-4.522599000	3.017959000	H	-0.041847000	4.522599000	-3.017959000	H	-4.358678000	-4.580287000	-2.045919000	H	4.358678000	4.580287000	2.045919000
H	0.410108000	-2.955528000	2.236108000	H	-0.410108000	2.955528000	-2.236108000	H	-3.225574000	-5.052392000	-0.762142000	H	3.225574000	5.052392000	0.762142000
C	2.052165000	-1.658849000	-3.921019000	C	-2.052165000	1.658849000	3.921019000	C	-3.653529000	-2.268899000	-0.692453000	C	3.653529000	2.268899000	0.692453000
H	1.270615000	-2.000805000	-4.616134000	H	-1.270615000	2.000805000	4.616134000	H	-3.519375000	-2.574100000	0.347036000	H	3.519375000	2.574100000	-0.347036000
H	2.984220000	-1.538450000	-4.495230000	H	-2.984220000	1.538450000	4.495230000	H	-4.720362000	-2.375637000	-0.949749000	H	4.720362000	2.375637000	0.949749000
H	1.757869000	-0.676511000	-3.520871000	H	-1.757869000	0.676511000	3.520871000	H	-3.382043000	-1.205229000	-0.760913000	H	3.382043000	1.205229000	0.760913000
C	-3.333576000	-4.490831000	-1.669666000	C	3.333576000	4.490831000	1.669666000	C	2.064192000	-1.779754000	-3.967224000	C	-2.064192000	1.779754000	3.967224000
H	-2.771250000	-5.108401000	-2.386949000	H	2.771250000	5.108401000	2.386949000	H	1.273423000	-2.135865000	-4.644718000	H	-1.273423000	2.135865000	4.644718000
H	-4.395246000	-4.501081000	-1.964751000	H	4.395246000	4.501081000	1.964751000	H	2.996233000	-1.701934000	-4.548859000	H	-2.996233000	1.701934000	4.548859000
H	-3.255824000	-4.966688000	-0.684397000	H	3.255824000	4.966688000	0.684397000	H	1.789481000	-0.774197000	-3.613580000	H	-1.789481000	0.774197000	3.613580000
C	2.639782000	-4.038949000	-3.376374000	C	-2.639782000	4.038949000	3.376374000	C	3.427559000	-2.247307000	-1.910225000	C	-3.427559000	2.247307000	1.910225000
C	2.824023000	-4.775306000	-2.579491000	C	-2.824023000	4.775306000	2.579491000	H	3.208690000	-1.247750000	-1.505577000	H	-3.208690000	1.247750000	1.505577000
H	3.551857000	-3.957774000	-3.990005000	H	-3.551857000	3.957774000	3.990005000	H	4.353823000	-2.198058000	-2.504524000	H	-4.353823000	2.198058000	2.504524000
H	1.827309000	-4.421452000	-4.013123000	H	-1.827309000	4.421452000	4.013123000	H	3.603953000	-2.924739000	-1.061780000	H	-3.603953000	2.924739000	1.061780000
C	3.413703000	-2.174035000	-1.878393000	C	-3.413703000	2.174035000	1.878393000	C	2.602859000	-4.145337000	-3.333593000	C	-2.602859000	4.145337000	3.333593000
H	3.158961000	-1.201708000	-1.431190000	H	-3.158961000	1.201708000	1.431190000	H	2.774210000	-4.855869000	-2.510967000	H	-2.774210000	4.855869000	2.510967000
H	4.338404000	-2.066187000	-2.467333000	H	-4.338404000	2.066187000	2.467333000	H	3.513491000	-4.106240000	-3.953390000	H	-3.513491000	4.106240000	3.953390000
H	3.612403000	-2.884337000	-1.062436000	H	-3.612403000	2.884337000	1.062436000	H	1.779203000	-4.532464000	-3.952854000	H	-1.779203000	4.532464000	3.952854000

Table S13: Optimized geometry of **9** (left) and **10** (right). XYZ coordinates in angstroms. BP86/def2-TZVP level of theory.

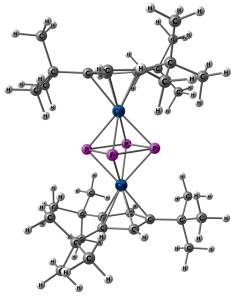


Co	1.697046000	0.214761000	-0.374324000	H	1.925082000	4.610013000	1.714438000
Co	-1.741385000	-0.192737000	-0.042681000	H	2.205809000	3.024146000	2.476518000
P	0.171880000	-1.366342000	0.020546000	C	4.367881000	3.749085000	0.858794000
P	-0.919125000	-1.236683000	-1.873731000	H	4.703183000	3.274242000	1.794121000
P	0.610598000	0.378780000	-2.346081000	H	4.325938000	4.839907000	1.019358000
P	-0.243267000	1.353175000	-0.585351000	H	5.122288000	3.542218000	0.084017000
C	3.340439000	-0.597136000	0.665757000	C	2.549127000	3.889776000	-0.870454000
C	3.701435000	-0.371113000	-0.734290000	H	3.276462000	3.718730000	-1.678413000
C	3.556329000	1.047744000	-0.953720000	H	2.464163000	4.978546000	-0.718008000
H	3.695182000	1.540523000	-1.909633000	H	1.570848000	3.501241000	-1.193226000
C	3.117021000	1.701303000	0.230504000	C	-4.634202000	-1.682594000	-0.862202000
C	3.000245000	0.688903000	1.228735000	C	-4.031945000	-3.103459000	-0.773764000
H	2.715870000	0.861403000	2.261513000	H	-2.973617000	-3.090860000	-1.076067000
C	-3.813441000	-0.712392000	0.000764000	H	-4.582235000	-3.779011000	-1.448231000
C	-3.649708000	0.740204000	0.007058000	H	-4.102928000	-3.518875000	0.241129000
C	-2.863941000	1.041679000	1.184710000	C	-4.686728000	-1.341886000	-2.360171000
H	-2.525613000	2.034792000	1.461767000	H	-5.216797000	-0.404533000	-2.563492000
C	-2.542115000	-0.145026000	1.903944000	H	-5.219794000	-2.143386000	-2.897865000
C	-3.145208000	-1.215192000	1.172623000	H	-3.665500000	-1.267753000	-2.762792000
H	-3.067534000	-2.263000000	1.441515000	C	-6.076179000	-1.746976000	-0.303600000
C	3.498998000	-1.797821000	1.609196000	H	-6.064599000	-2.058972000	0.752109000
C	2.548371000	-1.647550000	2.817839000	H	-6.680944000	-2.474212000	-0.872145000
H	2.799713000	-0.776576000	3.439541000	H	-6.574601000	-0.769249000	-0.360329000
H	2.617584000	-2.542946000	3.456483000	C	-4.173215000	1.862941000	-0.900236000
H	1.510741000	-1.543320000	2.472416000	C	-3.791012000	3.235435000	-0.303099000
C	4.949049000	-1.799160000	2.148623000	H	-4.214750000	3.377470000	0.703340000
H	5.681894000	-1.909701000	1.337375000	H	-4.179137000	4.035547000	-0.953733000
H	5.095762000	-2.628639000	2.861584000	H	-2.697266000	3.344479000	-0.242624000
H	5.162777000	-0.853322000	2.670060000	C	-5.713927000	1.834912000	-0.991435000
C	3.181637000	-3.168039000	0.991430000	H	-6.084381000	0.927147000	-1.482635000
H	2.160930000	-3.161632000	0.579740000	H	-6.080908000	2.701118000	-1.567574000
H	3.238848000	-3.943247000	1.773449000	H	-6.161057000	1.878039000	0.014428000
H	3.884872000	-3.449097000	0.199733000	C	-3.543895000	1.836369000	-2.309809000
C	4.203849000	-1.297398000	-1.851963000	H	-2.452319000	1.934665000	-2.216120000
C	5.532359000	-1.982085000	-1.463263000	H	-3.934870000	2.672212000	-2.916439000
H	6.291054000	-1.228179000	-1.198944000	H	-3.739236000	0.901374000	-2.841896000
H	5.919292000	-2.575013000	-2.309140000	C	-1.815594000	-0.229040000	3.232696000
H	5.420565000	-2.657518000	-0.606633000	C	-0.593662000	0.705225000	3.230303000
C	3.152996000	-2.346398000	-2.273106000	H	0.103372000	0.416369000	2.430271000
H	2.849069000	-2.996288000	-1.448504000	H	-0.072170000	0.664175000	4.201591000
H	3.551827000	-2.977039000	-3.087283000	H	-0.893921000	1.748438000	3.048375000
H	2.248744000	-1.826232000	-2.621941000	C	-2.781731000	0.195439000	4.362646000
C	4.494134000	-0.469051000	-3.122566000	H	-3.115804000	1.234704000	4.218558000
H	3.579639000	0.029914000	-3.475801000	H	-2.292967000	0.124031000	5.349585000
H	4.851415000	-1.139666000	-3.920498000	H	-3.674914000	-0.448975000	4.373861000
H	5.267376000	0.294739000	-2.947236000	C	-1.342046000	-1.668589000	3.486631000
C	2.986224000	3.199791000	0.432986000	H	-2.195405000	-2.356649000	3.594667000
C	1.956644000	3.523585000	1.527907000	H	-0.744238000	-1.721166000	4.410952000
H	0.959295000	3.188249000	1.206365000	H	-0.726565000	-2.010852000	2.639905000

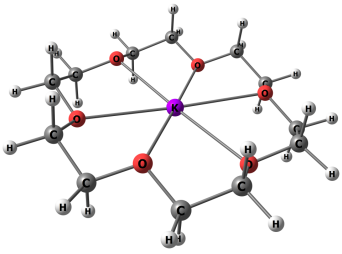


As	0.030293000	-0.143947000	-1.531031000	H	3.704208000	-4.679814000	0.099602000
As	-0.000968000	-2.065628000	-0.013590000	C	5.380436000	-2.767241000	1.192531000
As	-0.030868000	-0.164080000	1.527958000	H	5.669483000	-2.082889000	2.004490000
Co	1.734811000	-0.282317000	0.026754000	H	5.969996000	-2.506001000	0.300519000
Co	-1.735204000	-0.280847000	-0.030531000	H	5.645545000	-3.793584000	1.494537000
C	3.143886000	1.083202000	0.582062000	C	3.078831000	-3.029953000	2.168491000
C	3.317802000	0.704688000	-0.834955000	H	3.306243000	-4.065558000	2.467079000
C	3.589123000	-0.710496000	-0.848606000	H	1.996596000	-2.939887000	1.991913000
H	3.742042000	-1.304653000	-1.742769000	H	3.340578000	-2.371662000	3.010209000
C	3.572323000	-1.231986000	0.480406000	C	-3.460404000	1.511719000	2.137961000
C	3.334364000	-0.130067000	1.346445000	H	-4.932151000	1.976102000	2.255920000
H	3.231838000	0.205104000	2.423068000	H	-5.221358000	2.639345000	1.430732000
C	-3.311777000	0.708074000	0.838728000	H	-5.086737000	2.517809000	3.203377000
C	-3.143460000	1.087625000	-0.578777000	C	-5.606800000	1.106710000	2.242232000
C	-3.340708000	-0.124205000	-1.343752000	H	-6.164698000	0.613159000	3.360016000
H	-3.243907000	-0.197990000	-2.421014000	H	-3.881551000	-0.214814000	3.450417000
C	-3.576978000	-1.226545000	-0.477503000	H	-3.239960000	1.215582000	4.278717000
C	-3.586331000	-0.706540000	0.851971000	H	-2.149506000	0.192141000	3.299927000
H	-3.736124000	-1.301389000	1.746166000	C	-2.522357000	2.720302000	2.260005000
C	2.946770000	2.435152000	1.287116000	H	-1.478580000	2.398806000	2.128313000
C	1.600510000	3.114983000	0.964564000	H	-2.624700000	3.166498000	3.261696000
H	1.412788000	3.206918000	-0.107415000	H	-2.742160000	3.504922000	1.527617000
H	1.572563000	4.121812000	1.413446000	C	-2.945491000	2.440233000	-1.282094000
H	0.775853000	2.519847000	1.381599000	H	-4.110344000	3.396070000	-0.943309000
C	4.114991000	3.388801000	0.954022000	H	-5.079491000	2.912068000	-1.138901000
H	5.082225000	2.903233000	1.155245000	H	-4.047168000	4.303572000	-1.564760000
H	4.050089000	4.296798000	1.574587000	C	-4.095007000	3.711464000	0.106685000
H	4.106014000	3.703493000	-0.096254000	H	-5.392763000	-2.755911000	-1.182306000
C	2.957374000	2.233294000	2.817351000	H	-5.977919000	-2.492001000	-0.288196000
H	2.145772000	1.559154000	3.129691000	C	-5.662548000	-3.781540000	-1.482576000
H	2.801477000	3.204826000	3.311127000	H	-5.682586000	-2.071144000	-1.993640000
H	3.914209000	1.821211000	3.171275000	C	-5.510766000	-3.640847000	0.226351000
C	3.472337000	1.509451000	-2.132732000	H	-2.443611000	-3.557593000	0.480986000
C	2.538666000	2.721380000	-2.255380000	H	-3.715858000	-4.673858000	-0.095871000
H	1.493531000	2.403598000	-2.125763000	C	-4.097099000	-3.450481000	1.137680000
H	2.644397000	3.168097000	-3.256494000	H	-3.096198000	-3.027634000	-2.167076000
C	2.760199000	3.504601000	-1.521996000	H	-3.354564000	-2.365757000	-3.006996000
C	3.176210000	0.613134000	-3.356310000	H	-3.332837000	-4.060850000	-2.466787000
H	3.890649000	-0.216963000	-3.446230000	H	-2.012871000	-2.947288000	-1.992912000
H	3.254863000	1.216174000	-4.274320000				
H	2.159614000	0.195269000	-3.298192000				
C	4.945810000	1.969308000	-2.246560000				
H	5.235133000	2.630216000	-1.419472000				
H	5.104315000	2.512228000	-3.192676000				
H	5.617734000	1.097818000	-2.232834000				
C	3.865429000	-2.659706000	0.898984000				
C	3.501408000	-3.646514000	-0.223153000				
H	4.090511000	-3.456889000	-1.132869000				
H	2.435099000	-3.561896000	-0.480812000				

Table S14: Optimized geometry of **I-9a** (left) and [K(18-c-6)]$^+$ (right). XYZ coordinates in angstroms. BP86/def2-TZVP level of theory.



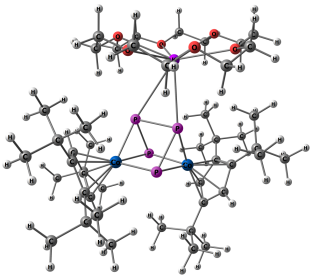
Co	-0.063406000	-1.566761000	-0.681762000	Co	0.063406000	1.566761000	0.681762000
P	1.171239000	-0.460263000	0.975015000	P	-1.171239000	0.460263000	-0.975015000
P	-1.064948000	-0.452443000	1.083871000	P	1.064948000	0.452443000	-1.083871000
C	-1.297731000	-3.107145000	-1.423974000	C	1.297731000	3.107145000	1.423974000
C	-0.360018000	-2.673228000	-2.435215000	C	0.360018000	2.673228000	2.435215000
H	-0.632549000	-2.216401000	-3.380214000	H	0.632549000	2.216401000	3.380214000
C	-0.491770000	-3.613201000	-0.310220000	C	0.491770000	3.613201000	0.310220000
C	0.886933000	-3.481987000	-0.710074000	C	-0.886933000	3.481987000	0.710074000
H	1.737209000	-3.766888000	-0.098505000	H	-1.737209000	3.766888000	0.098505000
C	0.981168000	-2.902929000	-2.006329000	C	-0.981168000	2.902929000	2.006329000
C	2.250974000	-2.722975000	-2.816796000	C	-2.250974000	2.722975000	2.816796000
C	-0.804182000	-4.345827000	1.001792000	C	0.804182000	4.345827000	-1.001792000
C	-2.808200000	-3.124535000	-1.706882000	C	2.808200000	3.124535000	1.706882000
C	-3.083849000	-2.571237000	-3.121687000	C	3.083849000	2.571237000	3.121687000
H	-2.747727000	-1.526925000	-3.201574000	H	2.747727000	1.526925000	3.201574000
H	-4.167557000	-2.596790000	-3.318222000	H	4.167557000	2.596790000	3.318222000
H	-2.581471000	-3.164150000	-3.900606000	H	2.581471000	3.164150000	3.900606000
C	-2.137395000	-3.976012000	1.668498000	C	2.137395000	3.976012000	-1.668498000
C	-2.182612000	-2.890108000	1.842235000	C	2.182612000	2.890108000	-1.842235000
H	-2.212736000	-4.490739000	2.640593000	H	2.212736000	4.490739000	-2.640593000
H	-3.006031000	-4.277211000	1.071044000	H	3.006031000	4.277211000	-1.071044000
C	-3.635288000	-2.241391000	-0.753262000	C	3.635288000	2.241391000	0.753262000
H	-3.518793000	-2.522507000	0.295264000	H	3.518793000	2.522507000	-0.295264000
H	-4.705450000	-2.307766000	-1.016575000	H	4.705450000	2.307766000	1.016575000
H	-3.308168000	-1.194050000	-0.843862000	H	3.308168000	1.194050000	0.843862000
C	-0.783320000	-5.870343000	0.735532000	C	0.783320000	5.870343000	-0.735532000
H	-1.568485000	-6.162195000	0.022429000	H	1.568485000	6.162195000	-0.022429000
H	-0.942040000	-6.433116000	1.671683000	H	0.942040000	6.433116000	-1.671683000
H	0.186410000	-6.172382000	0.310957000	H	-0.186410000	6.172382000	-0.310957000
C	0.292372000	-4.017673000	2.041404000	C	-0.292372000	4.017673000	-2.041404000
H	1.272455000	-4.420178000	1.748608000	H	-1.272455000	4.420178000	-1.748608000
H	0.029040000	-4.464529000	3.013914000	H	-0.029040000	4.464529000	-3.013914000
H	0.386553000	-2.925675000	2.156403000	H	-0.386553000	2.925675000	-2.156403000
C	2.059052000	-1.659411000	-3.909966000	C	-2.059052000	1.659411000	3.909966000
H	1.256072000	-1.943474000	-4.607215000	H	-1.256072000	1.943474000	4.607215000



K	2.890314000	8.774167000	16.488374000	C	3.367565000	9.049245000	12.862636000
O	1.491209000	8.412762000	18.932765000	H	2.923388000	8.054396000	12.669769000
O	0.300653000	9.885898000	16.790252000	H	3.936465000	9.353211000	11.964100000
O	1.446929000	9.590792000	14.187786000	C	5.291031000	8.039328000	13.816431000
O	4.234805000	8.987553000	13.999394000	H	5.907111000	8.317523000	12.940974000
O	5.408752000	7.513243000	16.151122000	H	4.869408000	7.032464000	13.635476000
O	4.279870000	7.809077000	18.761439000	C	6.162991000	8.026062000	15.048279000
C	0.419978000	9.343020000	19.121428000	H	7.045715000	7.386846000	14.858964000
H	0.824396000	10.355043000	19.313061000	H	6.520172000	9.048247000	15.276196000
H	-0.194371000	9.046813000	19.992096000	C	6.185593000	7.459207000	17.351857000
C	-0.448510000	9.352815000	17.887241000	H	6.541420000	8.472034000	17.620432000
H	-0.788654000	8.326710000	17.651079000	H	7.069856000	6.811169000	17.205861000
C	-1.341669000	9.976555000	18.079147000	C	5.336979000	6.891531000	18.463088000
C	-0.469859000	9.924865000	15.584758000	H	4.916280000	5.913382000	18.161900000
H	-1.363831000	10.561261000	15.722796000	H	5.969710000	6.733933000	19.356596000
H	-0.809250000	8.905813000	15.319003000	C	3.437511000	7.331403000	19.815110000
C	0.377130000	10.497376000	14.474730000	H	4.026892000	7.187342000	20.739996000
H	-0.252904000	10.640966000	13.576986000	H	2.993740000	6.357779000	19.533304000
H	0.783324000	11.483073000	14.771446000	C	2.349561000	8.344270000	20.075664000
C	2.280632000	10.062905000	13.124649000	H	1.773900000	8.034291000	20.967786000
H	2.724742000	11.039683000	13.395117000	H	2.792331000	9.337817000	20.279211000
H	1.684396000	10.198829000	12.203000000				

H	2.987040000	-1.539651000	-4.493005000	H	-2.987040000	1.539651000	4.493005000
H	1.797371000	-0.693175000	-3.452397000	H	-1.797371000	0.693175000	3.452397000
C	-3.330392000	-4.578097000	-1.690520000	C	3.330392000	4.578097000	1.690520000
H	-2.766638000	-5.197133000	-2.406362000	H	2.766638000	5.197133000	2.406362000
H	-4.396420000	-4.607990000	-1.973368000	H	4.396420000	4.607990000	1.973368000
H	-3.233145000	-5.041004000	-0.700509000	H	3.233145000	5.041004000	0.700509000
C	2.599092000	-4.072504000	-3.488726000	C	-2.599092000	4.072504000	3.488726000
H	2.752581000	-4.856585000	-2.731314000	H	-2.752581000	4.856585000	2.731314000
H	3.521043000	-3.987869000	-4.089712000	H	-3.521043000	3.987869000	4.089712000
H	1.782316000	-4.396556000	-4.153119000	H	-1.782316000	4.396556000	4.153119000
C	3.412818000	-2.298660000	-1.900619000	C	-3.412818000	2.298660000	1.900619000
H	3.159910000	-1.361554000	-1.378862000	H	-3.159910000	1.361554000	1.378862000
H	4.333428000	-2.148875000	-2.489101000	H	-4.333428000	2.148875000	2.489101000
H	3.619029000	-3.067266000	-1.140329000	H	-3.619029000	3.067266000	1.140329000

Table S15: Optimized geometry of **I-9b** (left) and $[K(18\text{-c-}6)]^+$ (right). XYZ coordinates in angstroms. BP86/def2-TZVP level of theory.



Co	-2.381617000	-0.549916000	0.279376000	H	6.842089000	-0.817341000	-1.369665000	H	-6.930489000	-0.702130000	-1.007097000	H	2.820021000	3.060574000	-3.614876000
Co	-0.218840000	2.149150000	-0.073152000	C	6.047244000	0.268049000	0.326265000	H	-2.814563000	3.361032000	-2.009863000	H	1.262350000	3.889468000	-3.424341000
K	2.957712000	-1.763855000	-0.062027000	H	7.040696000	0.595072000	0.690414000	C	-4.215559000	-0.602316000	-3.186163000	C	3.517484000	2.638144000	-1.151262000
P	-1.484795000	0.751338000	-1.301794000	H	5.323152000	1.079598000	0.524562000	H	-3.194443000	-0.193635000	-3.135043000	H	4.010277000	2.921004000	-0.214422000
P	0.620361000	0.269103000	-0.957209000	C	5.522692000	-0.715243000	2.408831000	H	-4.757118000	-0.087346000	-3.996769000	H	4.290453000	2.622823000	-1.936957000
P	-0.235635000	-1.121228000	0.647631000	H	4.787143000	0.085252000	2.610605000	H	-4.157600000	-1.662938000	-3.452188000	H	3.110058000	1.623433000	-1.048290000
P	-0.987383000	0.760268000	1.471829000	H	6.497370000	-0.405117000	2.832948000	C	-3.180190000	-3.377056000	-1.233685000	C	2.986792000	5.039949000	-1.665476000
O	3.078495000	-2.041689000	-3.076626000	C	5.085239000	-1.999770000	3.067141000	C	-4.382325000	-3.947194000	-2.017954000	H	2.217120000	5.742903000	-2.018701000
O	4.831699000	-0.338195000	-1.638555000	H	5.786395000	-2.819189000	2.815442000	H	-5.191929000	-4.229247000	-1.326714000	H	3.828385000	5.060578000	-2.378918000
O	5.639792000	-0.925254000	0.999272000	H	5.097965000	-1.861378000	4.165531000	H	-4.077278000	-4.849291000	-2.574195000	H	3.352363000	5.401376000	-0.693645000
O	3.770810000	-2.329114000	2.622497000	C	3.274387000	-3.512195000	3.252292000	H	-4.795550000	-3.236305000	-2.741414000	C	2.051819000	3.288107000	1.994699000
O	2.163407000	-4.297002000	1.285226000	H	3.142121000	-3.338809000	4.337457000	C	-2.025687000	-3.000543000	-2.185422000	C	1.335446000	3.428758000	3.355825000
O	1.486702000	-3.724459000	-1.428560000	H	3.997923000	-4.339974000	3.119760000	H	-2.252879000	-2.117457000	-2.789601000	H	0.911625000	4.435355000	3.491396000
C	-4.251116000	-0.925614000	-0.607789000	C	1.947973000	-3.883091000	2.638719000	H	-1.797349000	-3.843937000	-2.861718000	H	2.058198000	3.248852000	4.167612000
C	-3.585813000	-2.200383000	-0.337012000	H	1.499914000	-4.709176000	3.224923000	H	-1.133790000	-2.756993000	-1.590168000	H	0.525530000	2.689672000	3.448917000
C	-3.380306000	-2.242338000	1.087353000	H	1.251036000	-3.022282000	2.657342000	C	-2.659250000	-4.542689000	-0.367010000	C	3.195450000	4.325543000	1.990654000
H	-2.869330000	-3.039266000	1.615859000	C	0.928545000	-4.690538000	0.673132000	H	-1.786976000	-4.235811000	0.224156000	H	3.810066000	4.271407000	1.083922000
C	-3.884578000	-1.068154000	1.710110000	H	0.194702000	-3.869519000	0.786497000	H	-2.353436000	-5.374859000	-1.021072000	H	3.859731000	4.169030000	2.857051000
C	-4.431094000	-0.263372000	0.665049000	H	0.536422000	-5.605319000	1.159603000	H	-3.432932000	-4.916571000	0.321025000	H	2.785740000	5.345791000	2.053759000
H	-4.919257000	0.695396000	0.804611000	C	1.155387000	-4.956175000	-0.793947000	C	-3.964720000	-0.826737000	3.207204000	C	2.612976000	1.849740000	1.975929000
C	1.202033000	3.651327000	-0.596325000	H	1.965426000	-5.697319000	-0.944782000	C	-4.080400000	0.672555000	3.527605000	H	1.785657000	1.134227000	2.089741000
C	1.058265000	3.552955000	0.856170000	H	0.223712000	-5.368739000	-1.225215000	H	-3.170705000	1.196996000	3.198196000	H	3.323573000	1.714375000	2.810171000
C	-0.336080000	3.823093000	1.131339000	C	1.487814000	-3.805238000	-2.851589000	H	-4.203293000	0.820021000	4.613139000	H	3.123190000	1.609143000	1.039331000
H	-0.788007000	3.785380000	2.116891000	H	0.507276000	-4.169078000	-3.211525000	H	-4.948518000	1.124922000	3.024374000	C	-2.507864000	4.501604000	-0.183355000
C	-1.054475000	4.085950000	-0.071100000	H	2.270633000	-4.509505000	-3.196735000	C	-5.219976000	-1.553478000	3.744221000	C	-3.384698000	3.604858000	0.707552000
C	-0.092171000	3.990682000	-1.122690000	C	1.736652000	-2.423107000	-3.401675000	H	-6.129950000	-1.172016000	3.255002000	H	-3.271361000	2.550810000	0.416788000
H	-0.317116000	4.120410000	-2.175815000	H	1.594900000	-2.428789000	-4.500058000	H	-5.324664000	-1.404724000	4.832347000	H	-4.445634000	3.896075000	0.627227000
C	3.360574000	-0.700550000	-3.487711000	H	1.027094000	-1.701054000	-2.950983000	H	-5.157565000	-2.634877000	3.547179000	H	-3.089541000	3.688781000	1.764400000
H	2.633070000	-0.010214000	-3.018678000	C	-4.944094000	-0.354996000	-1.854226000	C	-2.715223000	-1.384871000	3.911498000	C	-2.648693000	5.970900000	0.275985000
H	3.281532000	-0.609226000	-4.589019000	C	-5.076997000	1.177118000	-1.723358000	H	-2.609383000	-2.467433000	3.745480000	H	-2.331438000	6.082782000	1.324251000
C	4.766472000	-0.355491000	-3.064735000	H	-5.726457000	1.466891000	-0.885740000	H	-2.779005000	-1.214717000	4.998980000	H	-3.694867000	6.311531000	0.194957000
H	5.486163000	-1.094929000	-3.467583000	H	-5.517663000	1.590584000	-2.644403000	H	-1.815164000	-0.881804000	3.524381000	H	-2.022313000	6.634318000	-0.340821000
H	5.031892000	0.641077000	-3.467503000	H	-4.089165000	1.632738000	-1.573049000	C	2.402497000	3.612588000	-1.550322000	C	-2.982946000	4.383275000	-1.639957000
C	6.127714000	0.001916000	-1.157298000	C	-6.372927000	-0.944340000	-1.925041000	C	1.942533000	3.164624000	-2.956545000	H	-2.438820000	5.081211000	-2.295397000
H	6.496778000	0.918199000	-1.657368000	H	-6.358084000	-2.037390000	-2.031037000	H	1.430497000	2.192187000	-2.894419000	H	-4.057208000	4.616363000	-1.714552000
				H	-6.921896000	-0.522049000	-2.783887000								

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4. Synthesis and Redox Chemistry of $[(Cp'''Co)_3E_4]$ (E = P, As) Cluster Complexes

Martin Piesch, Michael Seidl and Manfred Scheer

- Synthesis and characterization of all compounds was performed by Martin Piesch
- DFT calculations were performed by Martin Piesch
- X-ray measurements and calculations were done by Martin Piesch and finally checked by Michael Seidl
- Manuscript was written by Martin Piesch
- Figures were made by Martin Piesch
- The cyclic voltammograms were recorded by Martin Weber and Felix Riedelberger

4.1 Introduction

Abstract: *The synthesis of the cluster complexes [(Cp'''Co)$_3$(μ_3,η^2:η^2-E$_3$)(μ_3-E)] (E = P (**3**), As (**4**)) starting from the anionic triple-decker complexes [K(18cr6)(dme)$_2$][(Cp'''Co)$_2$(μ,η^4:η^4-E$_4$)] (E = P (**1**), As (**2**)) by quenching with [(Cp'''CoCl)$_2$] is reported. Both show a distinct redox chemistry, which was studied by cyclic voltammetry. Afterwards the monoanions [K(L)(sol)$_n$][(Cp'''Co)$_3$(μ_3,η^2:η^2-E$_3$)(μ_3-E)] (E = P, L = 18cr6, sol = dme, n = 2 (**5**), E = As, L = 2,2,2-crypt, n = 0 (**6**)), monocations [(Cp'''Co)$_3$(μ_3,η^2:η^2-E$_3$)(μ_3-E)][FAl] (E = P (**7**), As (**8**)) and dications [(Cp'''Co)$_3$(μ_3,η^3:η^3-E$_4$)][TEF]$_2$ (E = P (**9**), As (**10**)) could be synthesized and isolated in moderate to good yields. All compounds were characterized by single crystal X-ray structure analysis, NMR and EPR spectroscopy, mass spectrometry and elemental analysis.*

Since the discovery of ferrocene in 1951 and its structural characterization this complex and its derivatives play an important role in chemistry in general and in redox chemistry in special. It is used as a reference system ([(Cp_2Fe]/[$Cp_2Fe)^+$])[1] in electrochemical investigation such as cyclic voltammetry. Moreover, ferrocene containing fragments are widely used as molecular switches in redox switchable catalysis (RSC).[2] The reversibility of the redox processes of the ferrocene moiety is mandatory in these systems. For some systems more redox states are needed and more than one ferrocene unit have to be incorporated e.g. in macrocycles.[3] On the other hand many ligands are also known to be redox active supporting a reversible redox chemistry over several stages. $[Ru(bpy)_3]^{2+}$ as an example is well known in photocatalytic reactions comprising a multi stage redox system.[4] Also polypnictogen ligands are known to be redox active. Pentaphospha- and pentaarsaferrocene [Cp*Fe(η^5-E$_5$)] (E = P, As) as ferrocene analogs containing a heteroatomic ring show a distinct redox chemistry.[5] However, most of the observed redox processes are irreversible indicated by dimerization or fragmentation processes. In contrast, in general triple-decker complexes bearing E_n ligands as middle decks show reversible redox processes. E.g. [(Cp^RMo)$_2$(μ,η^6:η^6-P$_6$)] (**A,** Figure 1) can be singly oxidized reversibly, while the geometry of the complex is only slightly distorted leading to [(Cp^RMo)$_2$(μ,η^6:η^6-P$_6$)]$^+$ while the P_6 ligand shows a bis-allylic distortion. Recently we reported about the distinct redox chemistry of the cobalt complexes [(Cp'''Co)$_2$(μ,η^2:η^2-E$_2$)$_2$] (E = P (**B**), As (**C**)).[6] For E = P four (one and two electron oxidation and reduction) and for E = As three (one and two electron oxidation and one electron reduction) fully reversible redox processes can be conducted by using this system. Especially the obtained anionic complexes are extremely sensitive towards air and moisture. The high redox flexibility of this type of complexes is enabled by the presence of two metals in the molecule. In order to increase the redox flexibility, the incorporation of a third metal fragment could be an option. Additionally, the higher steric protection by the adjacent ligands would increase the stability of the products

towards air and moisture. Moreover, it could be shown, that the electrophilic quenching of anionic complexes like $[(Cp^*Fe)(\mu,\eta^4{:}\eta^4\text{-}P_{10})]^{2-}$ with $[(Cp'''CoCl)_2]$ yields the neutral triple-decker complex $[(Cp^*Fe)(Cp'''Co)(\mu,\eta^5{:}\eta^4\text{-}P_5)]$ (**D**, Figure 1).[7]

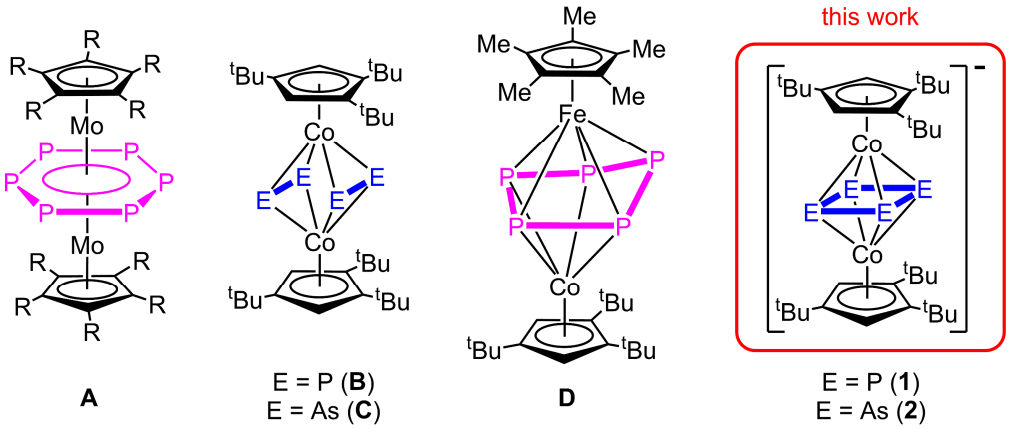
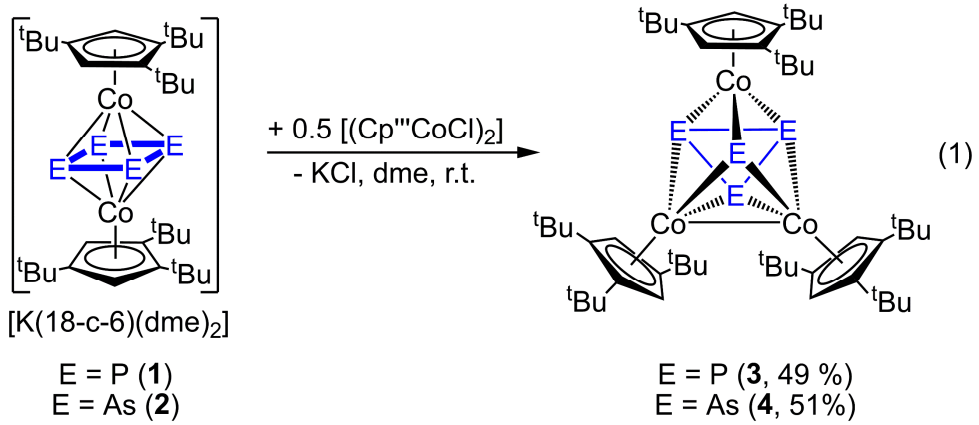


Figure 1: selected homo- and heterobimetallic triple decker complexes.

This attempt of introducing a third metal into a complex should now be transferred to the reduced species of **B** and **C** $([K(18cr6)(dme)_2][(Cp'''Co)_2(\mu,\eta^4{:}\eta^4\text{-}E_4)]$ (E = P (**1**), As (**2**)).

4.2 Results and Discussion

Complexes **1** and **2** can be generated *in situ* starting from **B** or **C** with KC_8 without the use of 18-c-6. **1** and **2** can be reacted with $[(Cp'''CoCl)_2]$ at room temperature to give $[(Cp'''Co)_3(\mu_3,\eta^2{:}\eta^2{:}\eta^2\text{-}E_3)(\mu_3\text{-}E)]$ (E = P (**3**), As (**4**)) in crystalline yields of 49 % (**3**) and 51 % (**4**) after column chromatographic workup, a synthesis which can be conducted in gram scale (cf. Eq. 1).



Crystals suitable for single crystal X-ray structure analysis can be obtained from concentrated solutions in CH_2Cl_2 layered with CH_3CN at -30 °C. The structures of the compounds in the solid state are depicted in Figure 2.

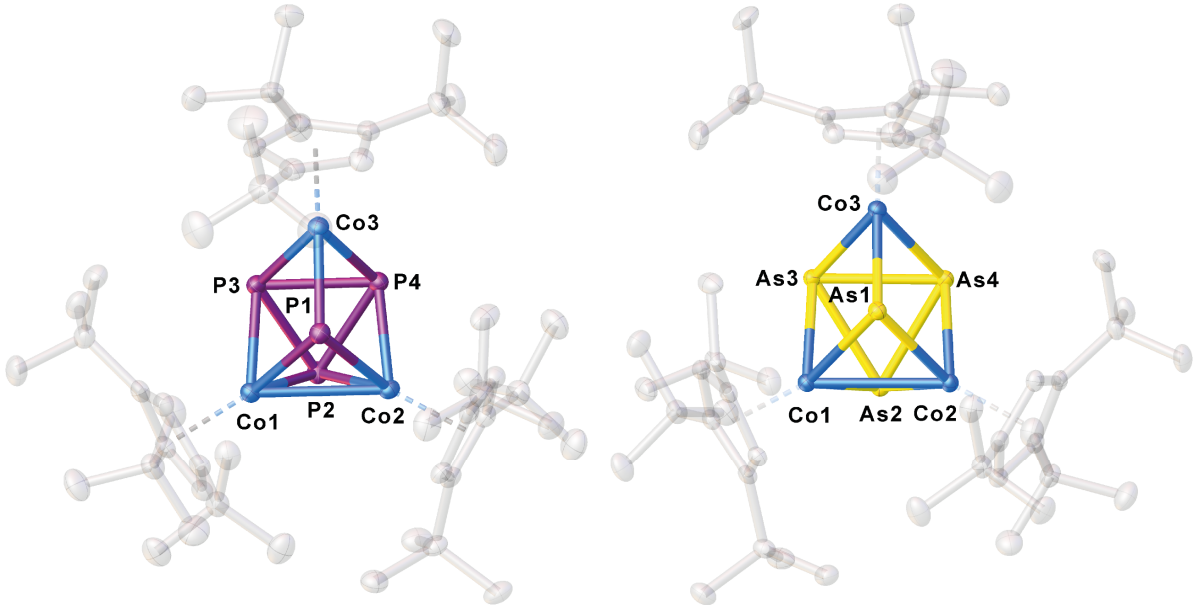


Figure 2: Molecular structures of **3** (left) and **4** (right) in solid state. Thermal ellipsoids are drawn with 50 % probability level. Hydrogen atoms are omitted for clarity.

Both compounds are isostructural and crystallize in the orthorhombic space group *Pbca* with similar cell parameters. The structures in the solid state reveal each a trinuclear cluster consisting of three {Cp'''Co} fragments connected by a *cyclo*-E_3 ligand in η^2:η^2:η^2 mode and a capping E_1 ligand in μ_3 mode. Alternatively, the structure of **3** and **4** can be considered as a strongly distorted E_4 tetrahedron in which three {Cp'''Co} fragments are capping three faces. **3** and **4** show one shorter Co-Co distance (Co1-Co2 **3**: 2.7276(4), **4**: 2.8191(3) Å) and two longer ones (Co1-Co3: **3**: 3.5721(7), **4**: 3.6879(6), Co2-Co3: **3**: 3.5527(6), **4**: 3.7061(7) Å). The Co1-Co2 distance is in the range of an elongated single bond (ca. 2.5 Å).[8,9] This is also in line with the calculated Wiberg Bond Indices (WBIs) of 0.34 (**3**) and 0.33 (**4**). The bond distances within the *cyclo*-E_3 ligands are in the range of elongated single bonds (P-P bonds 2.2965(6)-2.3798(6) Å in **3**, As-As bonds 2.5407(2)-2.5974(2) Å in **4**), which is also consistent with the WBIs (P-P bonds 0.60-0.68, As-As bonds 0.58-0.63).[8] The E_1 ligand is located asymmetrically over the *cyclo*-E_3 ligand with two shorter E-E distances (P1-P3 2.6343(7) Å, P1-P4 2.6564(7) Å, As1-As3 2.8688(7) Å, As1-As4 2.8511(7) Å) and one longer one (P1-P2 3.1648(6) Å, As1-As2 3.4065(6) Å). The Wiberg Bond Indices for these pairs reveal a weak interaction between P1···P3 (0.33), P1···P4 (0.36), As1···As3 (0.36) and As1···As4 (0.33) and almost no interaction for P1···P2 (0.09) and As1···As2 (0.09). In each ^{1}H-NMR spectra of **3** and **4** three singlets at δ = 4.86, 1.52 and 1.33 ppm (**3**) and δ = 4.56, 1.54 and 1.38 ppm (**4**) can be observed with an integral ratio of 6:54:27 corresponding to three equivalent Cp''' ligands in solution. This suggests a dynamic behavior in solution while the formal Co1-Co2 bond is cleaved and all Cp''' ligands become equivalent on the NMR time scale. VT-NMR investigations reveal that this process is still present at -80 °C. In the ^{31}P{^{1}H} NMR spectrum

of **3** two singlets with an integral ratio of 1:3 at δ = 648.0 and 358.5 ppm can be detected. Although these NMR data and an even number of electrons suggest diamagnetic complexes, **3** and **4** are EPR active both in solution and solid state and show an isotropic resonance with g_{iso} values of 2.064 (**3**) and 2.004 (**4**), respectively (at 77 K). All attempts to detect a signal corresponding to the zero field splitting failed. This indicates, that in solution the Co1-Co2 bond of **3** and **4** is broken leading to cobalt centered diradicals. An alternative explanation is the hypothetical triplet ground state which is only disfavored by 22.46 kJ·mol^{-1} (**3**) and 17.04 kJ·mol^{-1} (**4**) at the BP86/def2-SVP level of theory. In the Evans NMR no shift of the solvent signal can be detected. The redox properties of **3** and **4** were investigated by cyclic voltammetry (Figure 3).

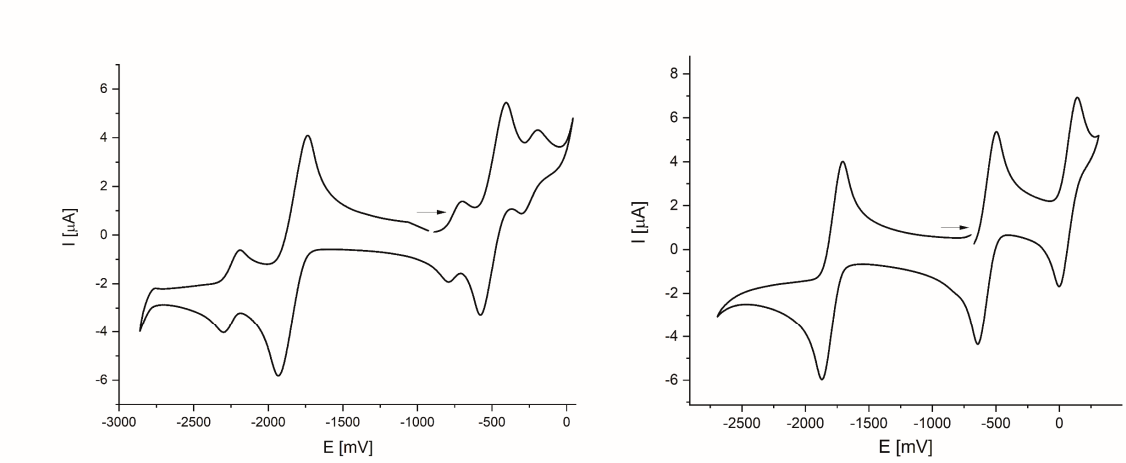
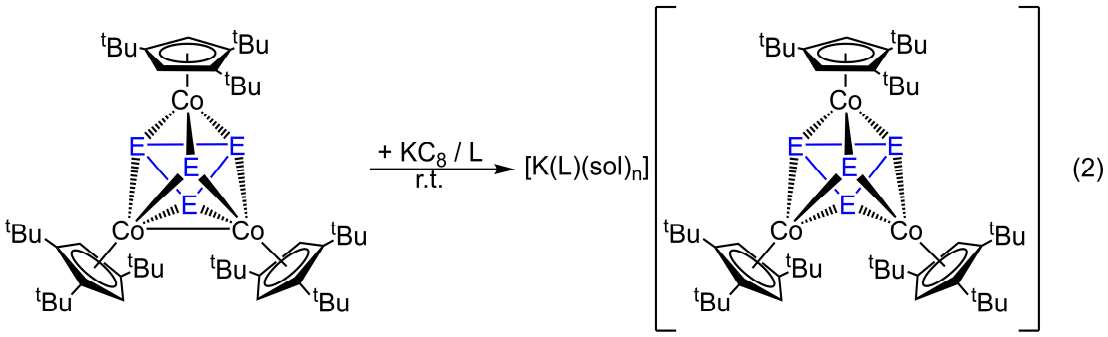


Figure 3. Cyclic voltammogram of **3** (left) and **4** (right) in thf against $[Cp_2Fe]/[Cp_2Fe]^+$ (electrolyte $[^nBu_4N][PF_6]$, rate of feed: 100 mV/s. temperature: r.t.).

For **3** three electrochemically reversible oxidation processes at -744, -492 and -248 mV and two electrochemically reversible reduction processes at -2245 and -1834 mV against $[Cp_2Fe]/[Cp_2Fe]^+$ can be observed. For **4** two electrochemically reversible oxidation processes at -569 and 69 mV and one electrochemically reversible reduction process at -1790 mV against $[Cp_2Fe]/[Cp_2Fe]^+$ can be detected. Due to the very low values for the reduction potential, potassium graphite was chosen as a suitable reducing agent. Reacting **3** and **4** with potassium graphite in the precence of 18-c-6 or 2,2,2-cryptand, respectivley, yield the anionic complexes $[K(L)(sol)_n][(Cp'''Co)_3(\mu_3,\eta^2:\eta^2\text{-}E_3)(\mu_3\text{-}E)]$ (E = P, L = 18cr6, sol = dme, n = 2 (**5**), E = As, L = 18-c-6, sol = thf, n = 2 (**6a**), E = As, L = 2,2,2-crypt, n=0 (**6b**)) in crystalline yields of 49 % (**5**), 67 % (**6a**) and 30 % (**6b**) (Eq. 2), respectively. Crystals suitable for single crystal X-ray structure analysis can be obtained from a concentrated solution in dme (**5**) or thf (**6a**, **6b**) layered with hexane at -30 °C after a few days. The structures in the solid state are depicted in Figure 4.



E = P (**3**)
E = As (**4**)

E = P, L = 18-c-6, sol = dme, n = 2 (**5**, 49 %)
E = As, L = 18-c-6, sol = thf, n = 2 (**6a**, 67 %)
E = As, L = 2,2,2-crypt, n = 0 (**6b**, 61 %)

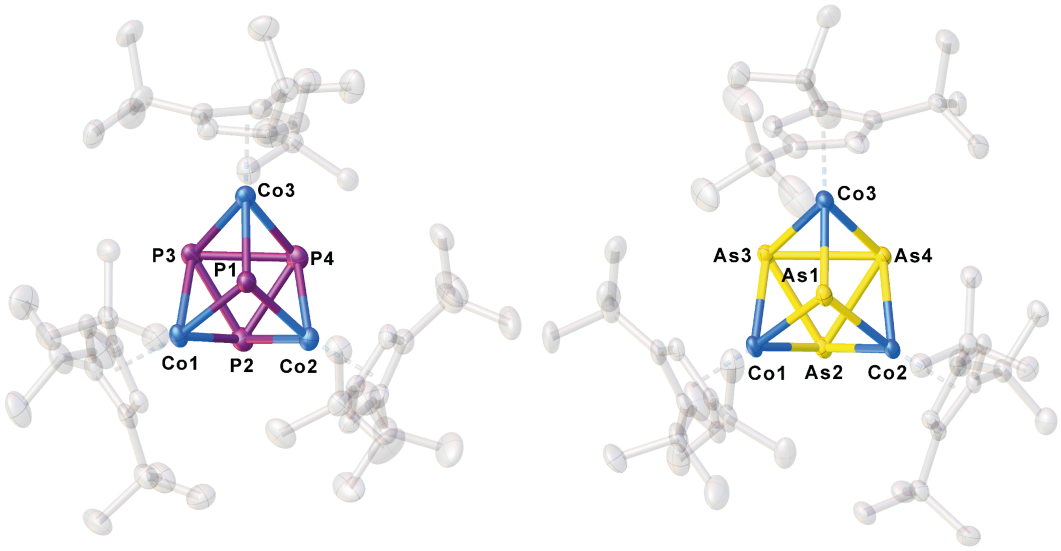
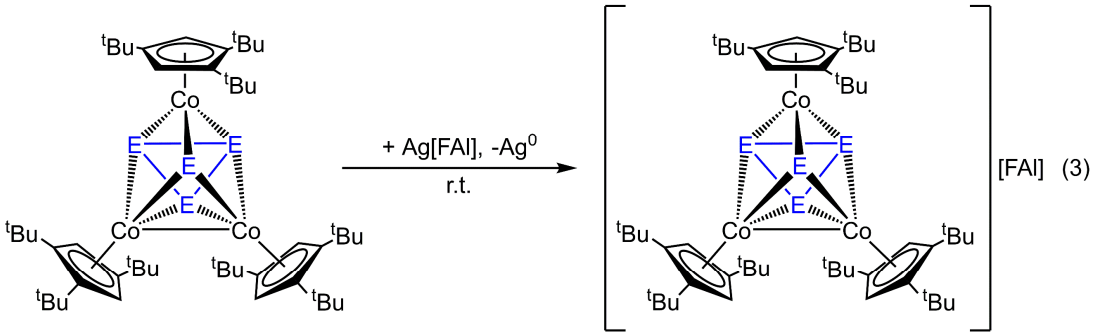


Figure 4: Molecular structure of the anions in **5** (left) and **6b** (right) in solid state. Thermal ellipsoids are drawn with 50 % probability level. Hydrogen atoms, cations and solvent molecules are omitted for clarity.

Due to the sever disorder in the solid state structure of **6a** only the metric parameters of **6b** will be discussed. Both **5** and **6b** respond to the reduction with a subtly change in the geometry. The Co1-Co2 (**5**: 2.9907(6) Å, **6b**: 3.1459(5) Å) distance is elongated by 0.22 Å in **5** and 0.33 Å in **6b** (WBIs of 0.27 (**5**) and 0.23 (**6**)) in comparison with **3** and **4**. All other Co-Co and E-E distances differ only slightly from the corresponding distances in **3** and **4**, respectively. The elongation of the Co1-Co2 distance agrees with the population of the LUMO of **3** and **4**, which both reveal antibonding character between Co1 and Co2 (cf. SI). Also, the HOMO of **5** and **6** show antibonding character between these Co atoms (cf. SI). Compound **5** and **6** are paramagnetic. In the ^{1}H NMR spectra in thf-d_8 broad and strongly shifted signals can be detected. In the ^{31}P{^{1}H} NMR spectrum of **5** in thf-d_8 no signals are observed. The EPR spectra (solution and solid) shown isotropic resonances with g_{iso} values indicating one unpaired electron (77 K, solid: **5**: g_{iso} = 2.081, **6b**: g_{iso} = 2.121, cf. SI). The effective magnetic moment in solution was determined by the Evans method to be 2.04 μ_B (**5**) and 2.03 μ_B (**6**) which corresponds each to about one unpaired electron. The reduction of **3** and **4** can be easily

reversed by addition of one equivalent of $AgBF_4$. According to the low redox potentials for the oxidation processes, Ag^+ with the weakly coordinating anion [FAl] (= ([FAl{$OC_6F_{10}(C_6F_5)$}$_3$]) was chosen as a suitable oxidation agent. The reaction of **3** and **4** with one equivalent Ag[FAl] leads under release of Ag^0 to the mono cations [(Cp'''Co)$_3$(μ_3,η^2:η^2:η^2-E_3)(μ_3-E)][FAl] (E = P (**7**), As (**8**)), which could be isolated in a crystalline yields of 48 % (**7**) and 52 % (**8**) (Eq. 3).



Crystals suitable for single crystal X-ray structure analysis were obtained from concentrated solutions in CH_2Cl_2 layered with toluene at -30 °C after a few days. The structures in solid state are depicted in Figure 5.

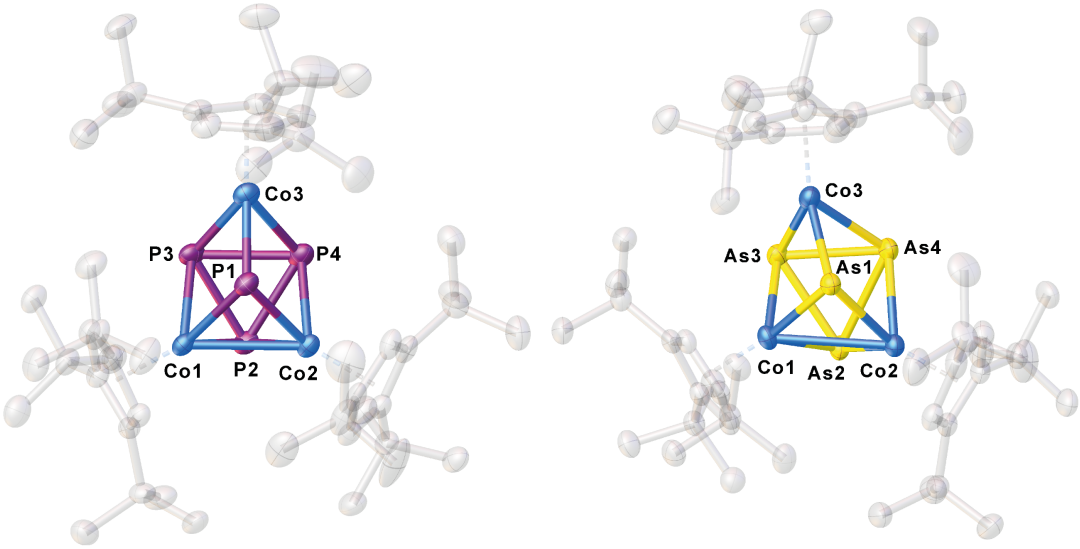
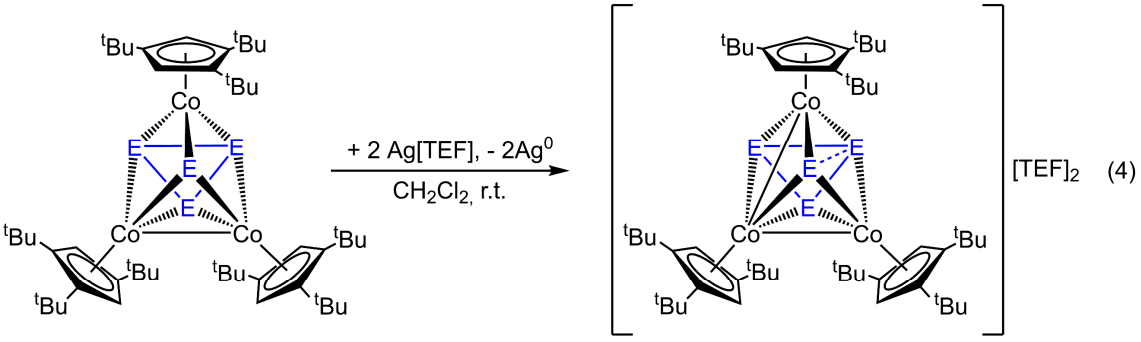


Figure 5: Molecular structure of the cations in **7** (left) and **8** (right) in solid state. Thermal ellipsoids are drawn with 50 % probability level. Hydrogen atoms, anions and solvent molecules are omitted for clarity.

Due to the oxidation the degree of structural changes is different for the phosphorus and arsenic compound. The structure in solid state reveals for **7** only very small geometrical changes compared to **3** (cf. SI). However, in the case of **8** the geometry is significantly distorted. The Co1-Co2 distance (**7**: 2.7152(8) Å, **8**: 2.8632(4) Å) differ only slightly from the corresponding distance in **3** and **4**, respectively. The Co1-Co3 distance (**7**: 3.5324(9), **8**: 3.2732(5) Å) in **7** is only 0.02 Å shorter than in **3** while the distance in **8** is shortened by 0.41 Å compared to **4**. In **8** the As1 atom is shifted towards As4 (As1-As4, **4**: 2.8511(7) Å, **8**:

2.7016(4) Å), while the As1-As3 distance (As1-As3, **4**: 2.8688(7) Å, **8**: 3.3011(7) Å) is elongated significantly. The As1-As4 distances lies in the range of an elongated single bond, what is indicated by a WBI of 0.52. This distance is comparable with the elongated As-As single bond in [(Cp*Co)(Cp*Co(CO))(μ,η^4:η^2-As$_4$)].[10] Compound **7** and **8** are paramagnetic. The ^{1}H NMR spectra in CD_2Cl_2 show broad and strongly shifted signals. The ^{31}P{^{1}H} NMR spectrum of **7** is silent. While the X-band EPR spectra of **7** show an isotropic signal only in solution at room temperature (g_{iso} = 2.003), the spectra of **8** show an isotropic signal at room temperature in solution and in the solid state (g_{iso} = 2.142 and 2.003) as well as a rhombic signal at 77 K in solid state (g_x = 2.2253, g_y = 2.1555, g_z = 2.0140, g_{iso} = 2.1316). The effective magnetic moment in solution was determined by Evans method to be 1.40 μ_B (**7**) and 1.47 μ_B (**8**) which corresponds each to roughly one unpaired electron. Using Ag[TEF] ([TEF] = [Al{OC(CF$_3$)$_3$}$_4$]) the compound **3** and **4** can be oxidized to the dications [(Cp'''Co)$_3$(μ$_3$,η^2:η^2-E$_3$)(μ$_3$-E)][TEF]$_2$ (E = P (**9**), As (**10**)) in crystalline yields of 63 % (**9**) and 80 % (**10**) (Eq. 4).



(4)

E = P (**3**)
E = As (**4**)

E = P (**9**, 63 %)
E = As (**10**, 80 %)

Crystals suitable for single crystal X-ray structure analysis were obtained after a few days from concentrated solutions in o-difluoro benzene layered with hexane at -30 °C. The structures in solid state are depicted in Figure 6. The solid state structure reveals further changes in the cluster geometry which was observed for **8** and is now present for both **9** and **10**. The structures in the solid state reveal two shorter Co-Co distances (Co1-Co2 **9**: 2.8044(3) Å, **10**: 2.8904(6) Å, Co1-Co3 **9**: 2.7825(4) Å, **10**: 2.8724(5) Å). In both dications two strong metal-metal interactions are present indicated by WBIs 0.24 (**9**), 0.23 and 0.21 (**10**). The E1 atom is shifted further into the direction of E4, while a strong interaction between P1-P4 (2.5625(6) Å, WBI of 0.55) and As1-As4 (2.7614(4) Å, WBI of 0.56) is present.

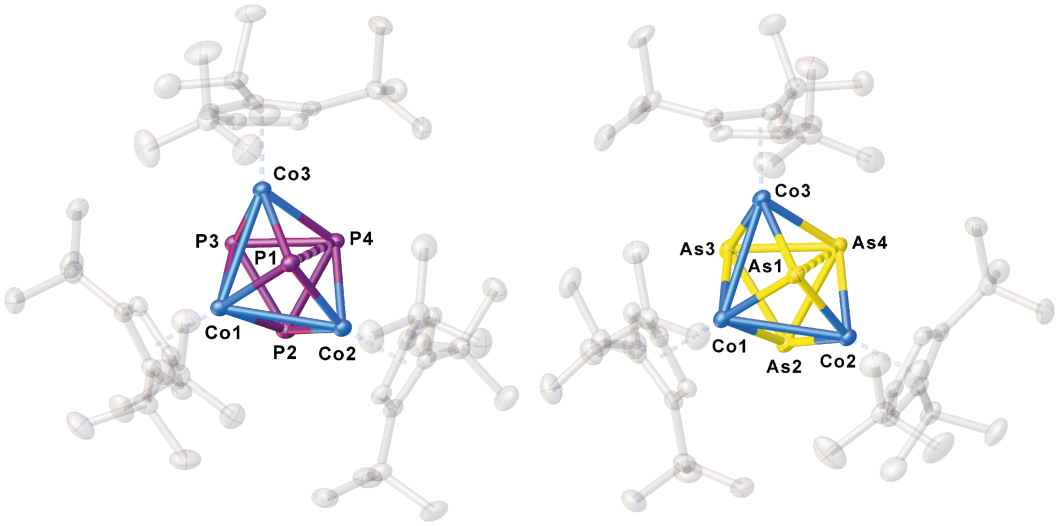


Figure 6: Molecular structure of the dications in **9** (left) and **10** (right) in solid state. Thermal ellipsoids are drawn with 50 % probability level. Hydrogen atoms, anions and solvent molecules are omitted for clarity.

Both P1-P4 and As1-As4 are now in the range of elongated single bonds but slightly longer than literature known widened single bonds like in $[(NacNacCu)_2(\mu,\eta^2{:}\eta^2\text{-}E_4)]$ (P-P 2.4122(8)-2.4285(8), As-As 2.6562(4)-2.6617(4) Å).[8,11] The bond lengths within the E_3 units are comparable with those in **7** and **8**. Compound **9** and **10** are both diamagnetic. In each ^{1}H-NMR spectrum in CD_2Cl_2 of **9** and **10** three singlets at δ = 5.41, 1.47 and 1.38 ppm (**9**) and δ = 5.07, 1.45 and 1.43 ppm (**10**) with an integral ratio of 6:54:27 can be observed corresponding to three equivalent Cp''' ligands in solution. In the $^{31}P\{^1H\}$ NMR spectrum of **9** in CD_2Cl_2 two broad singlets with an integral ratio of 1:3 at δ = 1104.3 and 489.7 ppm can be detected. All oxidation processes can be completely reversed by addition of stochiometric amounts of KC_8.

4.3 Conclusion

It could be shown that the cage complexes $[(Cp'''Co)_3(\mu_3,\eta^2{:}\eta^2{:}\eta^2\text{-}E_3)(\mu_3\text{-}E)]$ (E = P (**3**), As (**4**)) obtained by the electrophilic quenching of the anionic compounds **1** and **2** with $[(Cp'''CoCl)_2]$ show a distinct fully reversible redox chemistry. By reaction with KC_8 and Ag^+, respectively, the monoanions **5**, **6a**, **6b**, monocations **7**, **8** and dications **9** and **10** were obtained and fully characterized. All redox processes are fully reversible and can be completely reversed by addition of stochiometric amounts of suitable oxidant and reductant, respectively. The redox processes lead only to slight changes in the geometry and no fragmentation of the Co_3E_4 core was observed. The initial Co-Co bond in **3** and **4** is cleaved by addition of electrons (**5**, **6a**, **6b**). Both oxidation steps have no influence on this Co-Co bond. The withdrawal of electrons leads to a distortion and the third {Cp'''Co} fragment is shifted into the direction of one other {Cp'''Co} fragment. After the second oxidation step another Co-Co bond is formed.

4.4 Supporting Information

4.4.1 Synthetic procedures and experimental details

Synthetic Procedures: All manipulations were performed under an atmosphere of dry argon using standard glove-box and Schlenk techniques. All solvents were degassed and purified by standard procedures. The compounds $[K(18\text{-c-}6)(dme)_2][(Cp'''Co)_2(\mu,\eta^4{:}\eta^4\text{-}E_4)]$ (E = P (**1**), As (**2**))[6], $[(Cp'''CoCl)_2]$[12], $[KC_8]$[13], Ag[TEF][14], Ag[FAl][15] were prepared according to literature procedures. 18-c-6, 2,2,2-cryptand were purchased commercially.

The NMR spectra were recorded with a Bruker Avance 400 spectrometer (^{1}H: 400.13 MHz, ^{31}P: 161.976 MHz). The chemical shifts are given in ppm referenced to external $SiMe_4$ (^{1}H) and H_3PO_4 (^{31}P). Elemental analyses were determined with an Elementar Vario EL III apparatus.The X-Band EPR measurements were carried out with a MiniScope MS400 device with a frequency of 9.44 GHz and a rectangular resonator TE102 of the company Magnettech GmbH. The LIFDI-MS spectra were recorded with a Finnigan MAT 95 mass spectrometer. The ESI-MS spectra were acquired on a ThermoQuest Finnigan MAT TSQ 7000 mass spectrometer.

4.4.1.1 Synthesis of $[(Cp'''Co)_3(\mu_3,\eta^2{:}\eta^2\text{-}P_3)(\mu_3\text{-}P)]$ (3)

A solution of $[(Cp'''CoCl)_2]$ (275 mg, 0.4194 mmol, 1 eq) in thf was added to stirred solution of **1** (1.0 g, 0.8388 mmol, 2 eq) in thf at room temperature, while the color changed from green to dark red within a few minutes. The solvent was removed *in vacuo*. The residue was dissolved in a small amount of CH_2Cl_2, silica was added and the solvent removed *in vacuo*. The preabsorbed compound was purified by column chromatography (SiO_2, hexane, 20x3.5 cm). Using hexane as an eluent **3** can be obtained as a dark red fraction. After removing the solvent *in vacuo,* the residue was dissolved in CH_2Cl_2 and layered with acetonitrile. After storage at -30 °C for a few days, **3** can be obtained as dark red blocks. The supernatant was decanted off and the crystalline compound dried *in vacuo*.

Yield: 410 mg (49 %).

^{1}H NMR (toluene-d_8, 25 °C): *δ* [ppm] = 4.86 (s, 6H, $C_5H_2{}^t\text{Bu}_3$), 1.52 (s, 54H, $C_5H_2{}^tBu_3$), 1.33 (s, 27H, $C_5H_2{}^tBu_3$).

^{31}P{^{1}H} NMR (toluene-d_8, 25 °C): *δ* [ppm] = 648.0 (s, 1P, *P*), 358.5 (s, 3P, P_3).

^{31}P NMR (toluene-d_8, 25 °C): *δ* [ppm] = 648.0 (s, 1P, *P*), 358.5 (s, 3P, P_3).

LIFDI-MS (toluene): *m/z* = 1000.4 (100 %, $[M]^+$).

EA $C_{51}H_{87}Co_3P_4$: calc [%]: C 61.25; H 8.76; found [%]: C 61.04; H 8.30.

X-band EPR (77 K, solid) g_{iso} = 2.059, (293 K, solid) g_{iso} = 2.061, (293 K, liquid) g_{iso} = 2.064.

4.4.1.2 Synthesis of [(Cp'''Co)$_3$(μ_3,η^2:η^2-As$_3$)(μ_3-As)] (4)

A solution of [(Cp'''CoCl)$_2$] (566 mg, 0.8633 mmol, 1 eq) in thf was added to stirred solution of **2** (2.362 g, 1.7266 mmol, 2 eq) in thf at room temperature, while the color changed from brown to brown-green within a few minutes. The solvent was removed *in vacuo*. The residue was dissolved in a small amount of CH_2Cl_2, silica was added and the solvent removed *in vacuo*. The preabsorbed compound was purified by column chromatography (SiO_2, hexane, 20x3.5 cm). Using hexane as an eluent **4** can be obtained as a brown fraction. After removing the solvent *in vacuo,* the residue was dissolved in CH_2Cl_2 and layered with acetonitrile. After storage at -30 °C for a few days, **4** can be obtained as dark brown blocks. The supernatant was decanted off and the crystalline compound dried *in vacuo*.

Yield: 1.050 g (51 %).

^{1}H NMR (C_6D_6, 25 °C): δ [ppm] = 4.56 (s, 6H, $C_5H_2{}^t$Bu$_3$), 1.54 (s, 54H, $C_5H_2{}^tBu_3$), 1.38 (s, 27H, $C_5H_2{}^tBu_3$).

LIFDI-MS (toluene): *m/z* = 1176.2 (100 %, $[M]^+$), 10.26.4 (100 %, $[M- 2As]^+$).

EA $C_{51}H_{87}Co_3As_4$: calc [%]: C 52.06; H 7.45; found [%]: C 51.81; H 7.49.

X-band EPR (77 K, liquid) g_{iso} = 2.006, (293 K, liquid) g_{iso} = 2.004.

4.4.1.3 Synthesis of [K(18-c-6)(dme)$_2$][(Cp'''Co)$_3$(μ_3,η^2:η^2-P$_3$)(μ_3-P)] (5)

A suspension of KC_8 (20.3 mg, 0.15 mmol, 1.5 eq) in dme was added to stirred solution of **3** (100 mg, 0.10 mmol, 1 eq) and 18-c-6 (26.4 mg, 0.10 mmol, 1 eq) in dme. The color changed from brown to red-brown. After stirring for 1 hour, the solution was filtered over diatomaceous earth. The solvent was removed in vacuo, the residue dissolved in dme and layered with hexane. After storage at -30 °C for a few days, **5** could be obtained in form of dark brown plates. The supernatant was decanted off, washed with hexane a few times and dried *in vacuo*.

Yield: 72 mg (49 %).

^{1}H NMR (thf-d_8, 25 °C): δ [ppm] =10.57 (br), 3.34 (s, 18-c-6), 2.37 (br), 2.06 (br), -4.64 (br).

$^{31}P\{^{1}H\}$ NMR (thf-d_8, 25 °C): no signal detectable between -600 and +800 ppm (paramagnetic).

ESI-MS (dme): no fragment can be assigned properly.

EA $C_{71}H_{131}O_{10}KCo_3P_4$: calc [%]: C 57.44; H 8.89; found [%]: C 57.65; H 8.60.

X-band EPR (77 K, liquid) g_{iso} = 2.075, (77 K, solid) g_{iso} = 2.081, (293 K, liquid) g_{iso} = 2.080, (293 K, solid) g_{iso} = 2.085.

Evans-NMR (thf-d_8, 25 °C): μ_{eff} = 2.04 μ_B corresponding to 1.27 unpaired electrons.

4.4.1.4 Synthesis of [K(18-c-6)(thf$_2$)][(Cp'''Co)$_3$(μ_3,η^2:η^2-As$_3$)(μ_3-As)] (6a)

A suspension of KC_8 (13.5 mg, 0.10 mmol, 1.2 eq) in thf was added to stirred solution of **4** (100 mg, 0.085 mmol, 1 eq) and 18-c-6 (22.5 mg, 0.085 mmol, 1 eq) in thf. The color changed from brown to green. After stirring for 1 hour, the solution was filtered over diatomaceous earth. The solvent was removed in vacuo, the residue dissolved in thf and layered with hexane. After storage at -30 °C for a few days, **6a** could be obtained in form of dark green blocks. The supernatant was decanted off, washed with hexane a few times and dried *in vacuo*.

Yield: 92 mg (67 %).

^{1}H NMR (thf-d_8, 25 °C): δ [ppm] = 3.63 (s, thf), 2.44 (br, $C_5H_2{}^tBu_3$), 1.78 (s, thf).

ESI-MS (dme): no fragment can be assigned properly.

4.4.1.5 Synthesis of [K(2,2,2-crypt)][(Cp'''Co)$_3$(μ_3,η^2:η^2-As$_3$)(μ_3-As)] (6b)

A suspension of KC_8 (13.5 mg, 0.10 mmol, 1.2 eq) in dme was added to stirred solution of **4** (100 mg, 0.085 mmol, 1 eq) and 2,2,2-cryptand (32 mg, 0.085 mmol, 1 eq) in dme. The color changed from brown to green. After stirring for 1 hour, the solution was filtered over diatomaceous earth. The solvent was removed in vacuo, the residue dissolved in thf and layered with hexane. After storage at -30 °C for a few days, **6b** could be obtained in form of dark green blocks. The supernatant was decanted off, washed with hexane a few times and dried *in vacuo*.

Yield: 82 mg (61 %).

^{1}H NMR (thf-d_8, 25 °C): δ [ppm] = 3.64 (s, crypt), 2.60 (br, crypt), 2.52 (br, $C_5H_2{}^tBu_3$). Signals of 2,2,2-cryptand are overlapping with solvent signal and very broad signal of Cp''' at 2.52 ppm.

ESI-MS (dme): no fragment can be assigned properly.

EA $C_{71}H_{127}O_8KCo_3As_4$: calc [%]: C 52.50; H 7.88; found [%]: C 52.00; H 7.65.

X-band EPR (77 K, liquid) g_{iso} = 2.110, (77 K, solid) g_{iso} = 2.121, (293 K, liquid) g_{iso} = 2.125, (293 K, solid) g_{iso} = 2.120.

Evans-NMR (thf-d_8, 25 °C): μ_{eff} = 2.03 μ_B corresponding to 1.27 unpaired electrons.

4.4.1.5 Synthesis of [(Cp'''Co)$_3$(μ_3,η^2:η^2-P_3)(μ_3-P)][FAl] (7)

A solution of Ag[FAl] (148.9 mg, 0.10 mmol, 1 eq) in CH_2Cl_2 was added to a stirred solution of **3** (100 mg, 0.10 mmol, 1 eq) in CH_2Cl_2. The color changed from dark red to brown, while a black solid precipitated (Ag^0). After stirring for 1 hour, it was filtered over diatomaceous earth. The solvent was removed *in vacuo*. The residue was dissolved in CH_2Cl_2 and layered with toluene. After storage at -30 °C for a few days, **7** could be obtained as dark brown needles. The supernatant was decanted off, washed with hexane and dried *in vacuo*.

Yield: 111 mg (48 %).

^{1}H NMR (CD_2Cl_2, 25 °C): δ [ppm] = 3.31 (br, 27H, $C_5H_2{}^tBu_3$), 2,44 (br, 54H, $C_5H_2{}^tBu_3$), -7.39 (br, 6H, $C_5H_2{}^tBu_3$).

^{31}P{^{1}H} NMR (CD_2Cl_2, 25 °C): no signal detectable between -600 and +800 ppm (paramagnetic).

^{19}F{^{1}H} NMR (CD_2Cl_2, 25 °C): δ [ppm] = -112.6 (d, J_{F-F} = 285 Hz, 6F), -117.1 (d, J_{F-F} = 279 Hz, 6F), -121.8 (d, J_{F-F} = 279 Hz, 3F), -127.9 (s, 6F), -130.6 (d, J_{F-F} = 274 Hz, 6F), -137.2 (d, J_{F-F} = 276 Hz, 6F), -141.2 (d, J_{F-F} = 274 Hz, 3F), -154.3 (t, J_{F-F} = 22 Hz, 6F), -165.0 (t, J_{F-F} = 18 Hz, 6F), 172.0 (s, AlF, 1F).

ESI-MS (CH_2Cl_2): *m/z* = 1001.4 (100 %, $[M+H]^+$), 1019.4 (80 %, $[M+F]^+$).

EA $C_{87}H_{87}F_{46}O_3AlCo_3P_4$ x (CH_2Cl_2 + C_7H_8): calc [%]: C 44.58; H 3.82; found [%]: C 44.61; H 3.82.

X-band EPR (293 K, liquid) g_{iso} = 2.003.

Evans-NMR (CD_2Cl_2, 25 °C): μ_{eff} = 1.40 μ_B corresponding to 0.72 unpaired electrons.

4.4.1.6 Synthesis of $[(Cp'''Co)_3(\mu_3,\eta^2{:}\eta^2{:}\eta^2\text{-}As_3)(\mu_3\text{-}As)][FAl]$ (8)

A solution of Ag[FAl] (126.6 mg, 0.085 mmol, 1 eq) in CH_2Cl_2 was added to a stirred solution of **4** (100 mg, 0.085 mmol, 1 eq) in CH_2Cl_2. The color changed from brown to red-brown, while a black solid precipitated (Ag^0). After stirring for 1 hour, it was filtered over diatomaceous earth. The solvent was removed *in vacuo*. The residue was dissolved in CH_2Cl_2 and layered with toluene. After storage at -30 °C for a few days, **8** could be obtained as dark brown needles. The supernatant was decanted off, washed with hexane and dried *in vacuo*.

Yield: 113 mg (52 %).

^{1}H NMR (CD_2Cl_2, 25 °C): δ [ppm] = 2.67 (br, 81H, $C_5H_2{}^tBu_3$), -11.36 (br, 6H, $C_5H_2{}^tBu_3$).

^{19}F{^{1}H} NMR (CD_2Cl_2, 25 °C): δ [ppm] = -112.6 (d, $J_{F\text{-}F}$ = 285 Hz, 6F), -117.1 (d, $J_{F\text{-}F}$ = 279 Hz, 6F), -121.8 (d, $J_{F\text{-}F}$ = 279 Hz, 3F), -127.9 (s, 6F), -130.6 (d, $J_{F\text{-}F}$ = 274 Hz, 6F), -137.2 (d, $J_{F\text{-}F}$ = 276 Hz, 6F), -141.2 (d, $J_{F\text{-}F}$ = 274 Hz, 3F), -154.3 (t, $J_{F\text{-}F}$ = 22 Hz, 6F), -165.0 (t, $J_{F\text{-}F}$ = 18 Hz, 6F), 172.0 (s, AlF, 1F).

ESI-MS (CH_2Cl_2): *m/z* = 1.176.2 (100 %, $[M]^+$).

EA $C_{94}H_{95}F_{46}O_3AlCo_3As_4$: calc [%]: C 42.60; H 3.61; found [%]: C 42.05; H 3.48.

X-band EPR (77 K, solid) g_x = 2.2253, g_y = 2.1555, g_z = 2.0140, g_{iso} = 2.1316, (293 K, liquid) g_{iso} = 2.003, (293 K, solid) g_{iso} = 2.142.

Evans-NMR (CD_2Cl_2, 25 °C): μ_{eff} = 1.47 μ_B corresponding to 0.78 unpaired electrons.

4.4.1.7 Synthesis of $[(Cp'''Co)_3(\mu_3,\eta^2{:}\eta^2{:}\eta^2\text{-}P_3)(\mu_3\text{-}P)][TEF]_2$ (9)

A solution of Ag[TEF] (248.4 mg, 0.20 mmol, 2 eq) in difluoro-benzene was added to a stirred solution of **3** (100 mg, 0.10 mmol, 1 eq) in difluoro-benzene. The color changed from dark red to brown, while a black solid precipitated (Ag^0). After stirring for 1 hour, it was filtered over diatomaceous earth. The solvent was removed *in vacuo*. The residue was dissolved in difluoro-benzene and layered with toluene. After storage at -30 °C for a few days, **9** could be obtained as dark brown blocks. The supernatant was decanted off, washed with hexane and dried *in vacuo*.

Yield: 185 mg (63 %).

^{1}H NMR ($C_6H_4F_2$ + C_6D_6-capillary, 25 °C): δ [ppm] = 5.41 (s, 6H, $C_5H_2{}^tBu_3$), 1.47 (s, 54H, $C_5H_2{}^tBu_3$), 1.38 (s, 27H, $C_5H_2{}^tBu_3$).

^{31}P{^{1}H} NMR ($C_6H_4F_2$ + C_6D_6-capillary, 25 °C): δ [ppm] = 1104.3 (br, 1P, *P*), 489.7 (br, 3P, P_3)

$^{19}F\{^{1}H\}$ NMR ($C_6H_4F_2$ + C_6D_6-capillary, 25 °C): *δ* [ppm] = -75.5 (s, [TEF]).

ESI-MS ($C_6H_4F_2$): *m/z* = 1017.4 (100 %, $[M+OH]^+$), 1000.4 (40 %, $[M]^+$), 677.2 (60 %, $[(Cp'''Co)_2P_3]^+$).

EA $C_{83}H_{87}F_{72}O_8Al_2Co_3P_4$: calc [%]: C 33.96; H 2.99; found [%]: C 33.81; H 2.90.

4.4.1.8 Synthesis of $[(Cp'''Co)_3(\mu_3,\eta^2{:}\eta^2{-}As_3)(\mu_3{-}As)][TEF]_2$ (10)

A solution of Ag[TEF] (98.6 mg, 0.085 mmol, 2 eq) in difluoro-benzene was added to a stirred solution of **4** (50 mg, 0.0425 mmol, 1 eq) in difluoro-benzene. The color changed from brown to red-brown, while a black solid precipitated (Ag^0). After stirring for 1 hour, it was filtered over diatomaceous earth. The solvent was removed *in vacuo*. The residue was dissolved in difluoro-benzene and layered with hexane. After storage at -30 °C for a few days, **10** could be obtained as dark brown rods. The supernatant was decanted off, washed with hexane and dried *in vacuo*.

Yield: 105 mg (80 %).

^{1}H NMR ($C_6H_4F_2$ + C_6D_6-capillary, 25 °C): *δ* [ppm] = 5.07 (s, 6H, $C_5H_2{}^tBu_3$), 1.45 (s, 54H, $C_5H_2{}^tBu_3$), 1.43 (s, 27H, $C_5H_2{}^tBu_3$).

$^{19}F\{^{1}H\}$ NMR ($C_6H_4F_2$ + C_6D_6-capillary, 25 °C): *δ* [ppm] = -75.5 (s, [TEF]).

ESI-MS ($C_6H_4F_2$): *m/z* = 1176.2 (100 %, $[M]^+$), 588.1 (10 %, $[M]^{2+}$).

EA $C_{83}H_{87}F_{72}O_8Al_2Co_3As_4$: calc [%]: C 32.04; H 2.82; found [%]: C 32.48; H 2.80.

4.4.2 EPR studies

4.4.2.1 $[(Cp'''Co)_3(\mu_3,\eta^2{:}\eta^2\text{-}P_3)(\mu_3\text{-}P)]$ (3)

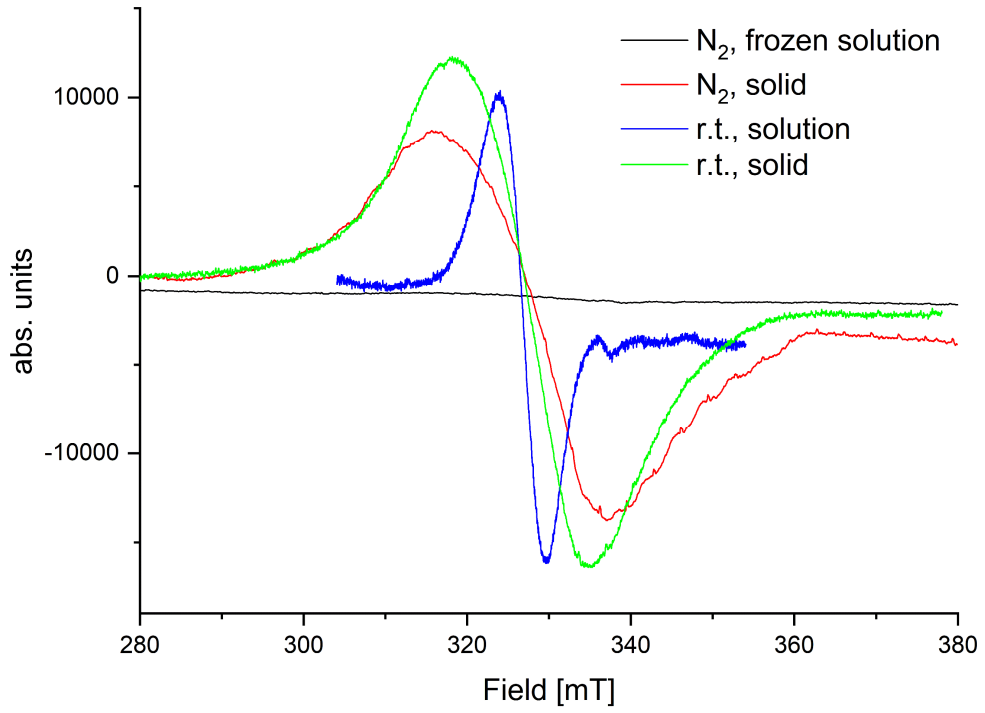


Figure S1: EPR spectra of **3** in solid state (r.t. (green), liquid nitrogen (red) and in CH_2Cl_2 solution (r.t. (blue), liquid nitrogen (black)).

4.4.2.2 $[(Cp'''Co)_3(\mu_3,\eta^2{:}\eta^2\text{-}As_3)(\mu_3\text{-}As)]$ (4)

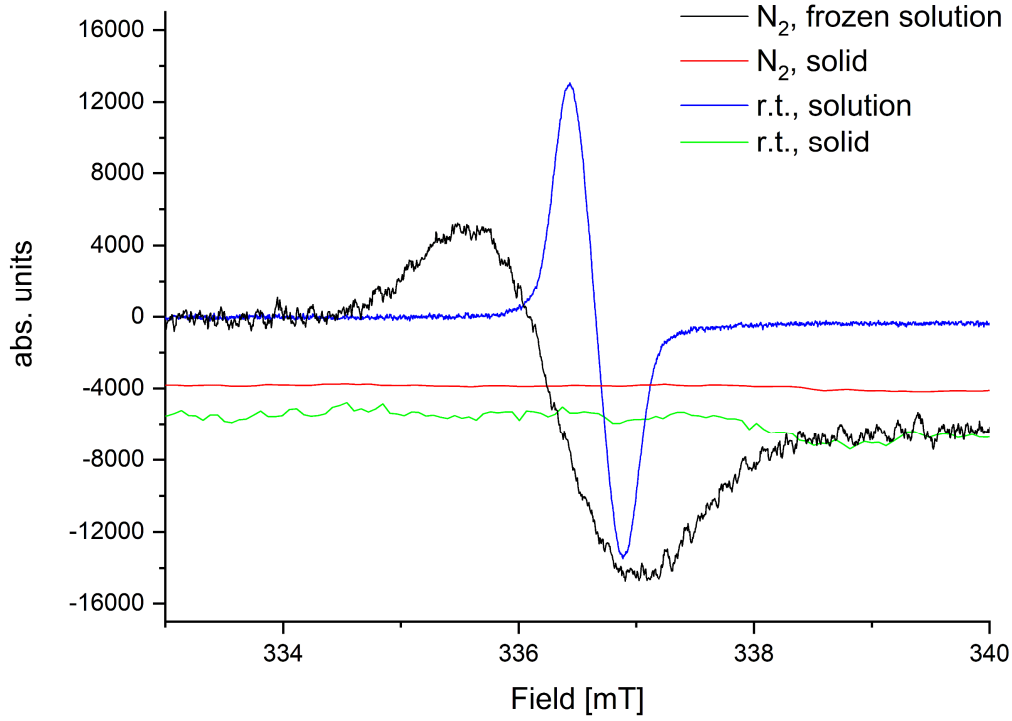


Figure S2: EPR spectra of **4** in solid state (r.t. (green), liquid nitrogen (red) and in CH_2Cl_2 solution (r.t. (blue), liquid nitrogen (black)).

4.4.2.3 [K(18-c-6)(dme)$_2$][(Cp'''Co)$_3$(μ_3,η^2:η^2-P$_3$)(μ_3-P)] (5)

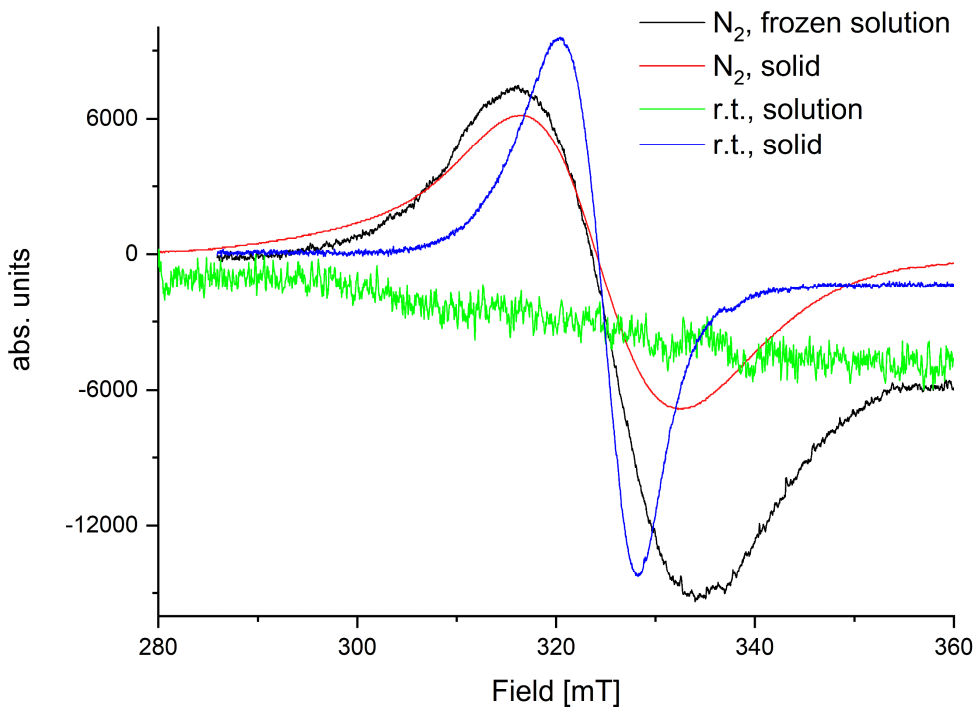


Figure S3: EPR spectra of **5** in solid state (r.t. (green), liquid nitrogen (red) and in dme solution (r.t. (blue), liquid nitrogen (black)).

4.4.2.4 [K(2,2,2-crypt)][(Cp'''Co)$_3$(μ_3,η^2:η^2-As$_3$)(μ_3-As)] (6b)

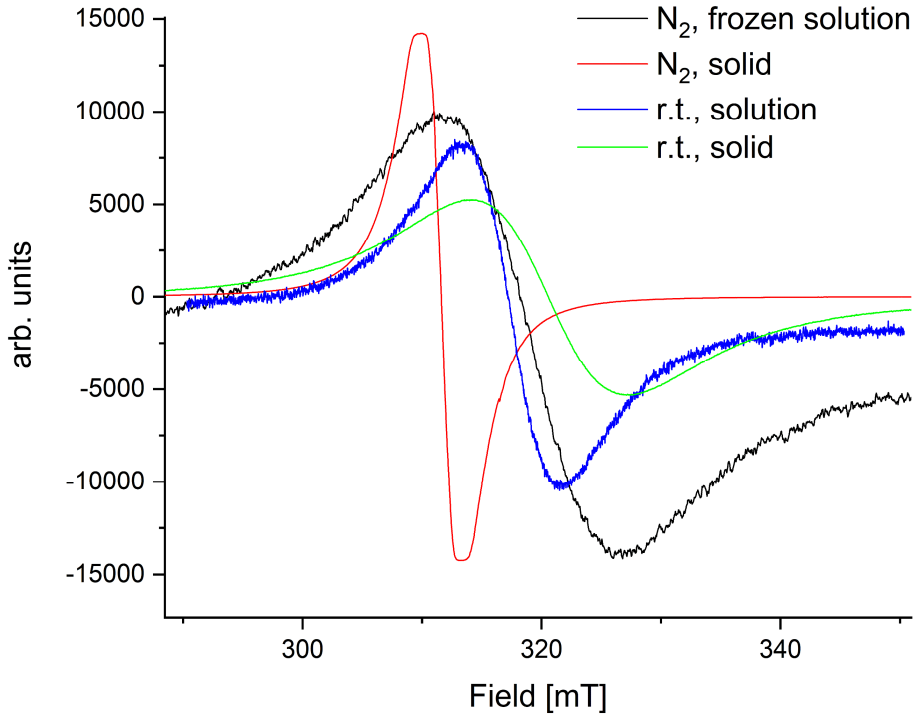


Figure S4: EPR spectra of **6b** in solid state (r.t. (green), liquid nitrogen (red) and in dme solution (r.t. (blue), liquid nitrogen (black)).

4.4.2.5 $[(Cp'''Co)_3(\mu_3,\eta^2{:}\eta^2\text{-}P_3)(\mu_3\text{-}P)][FAl]$ (7)

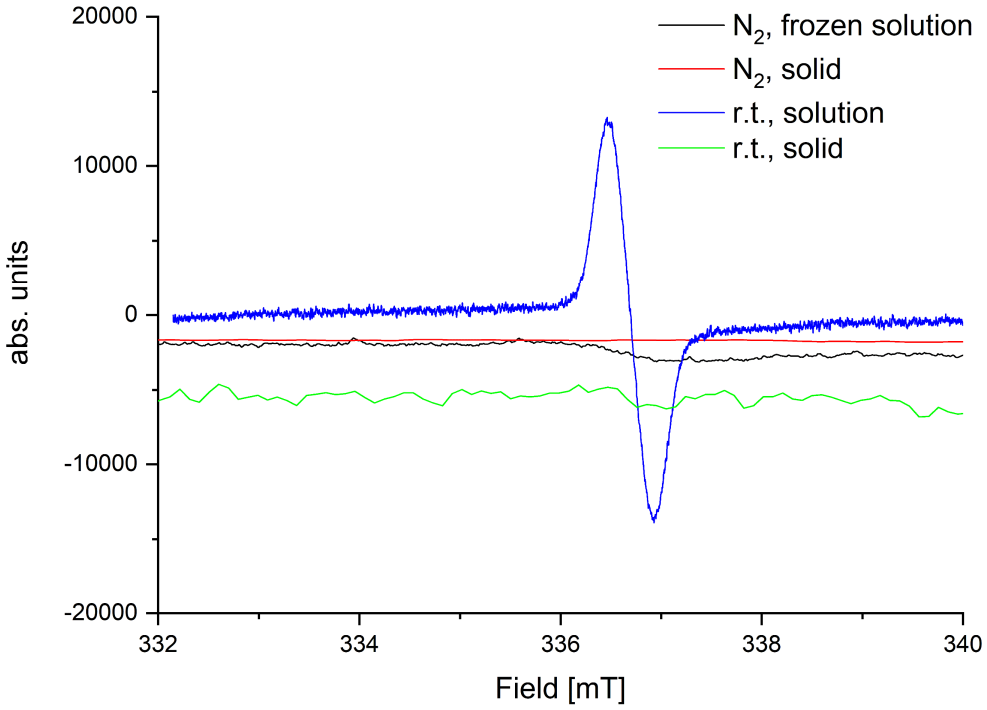


Figure S5: EPR spectra of **7** in solid state (r.t. (green), liquid nitrogen (red) and in CH_2Cl_2 solution (r.t. (blue), liquid nitrogen (black)).

4.4.2.6 $[(Cp'''Co)_3(\mu_3,\eta^2{:}\eta^2\text{-}As_3)(\mu_3\text{-}As)][FAl]$ (8)

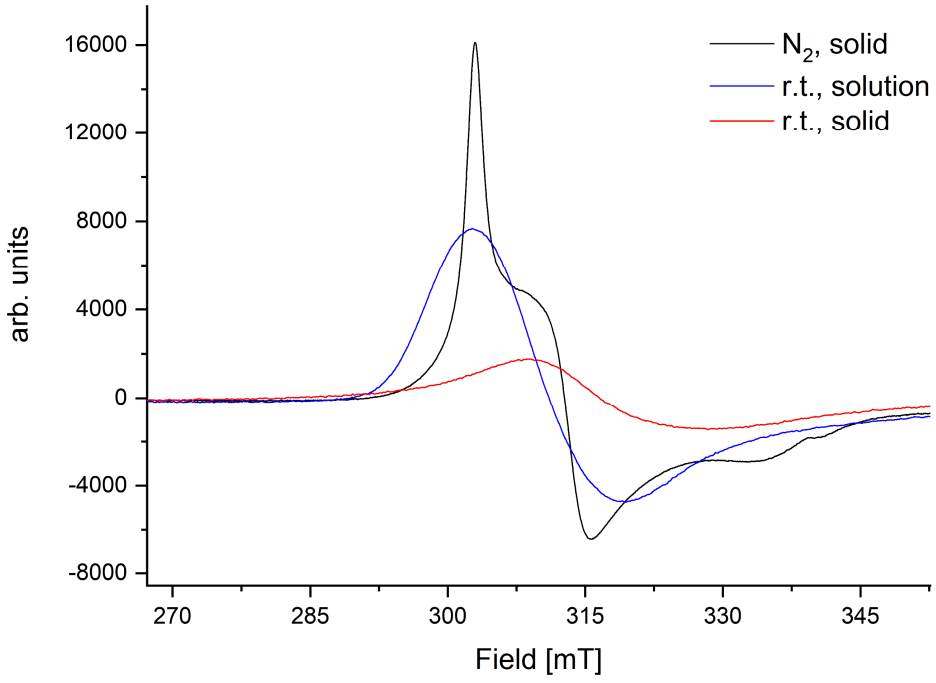


Figure S6: EPR spectra of **8** in solid state (r.t. (green), liquid nitrogen (red) and in CH_2Cl_2 solution (r.t. (blue), liquid nitrogen (black)).

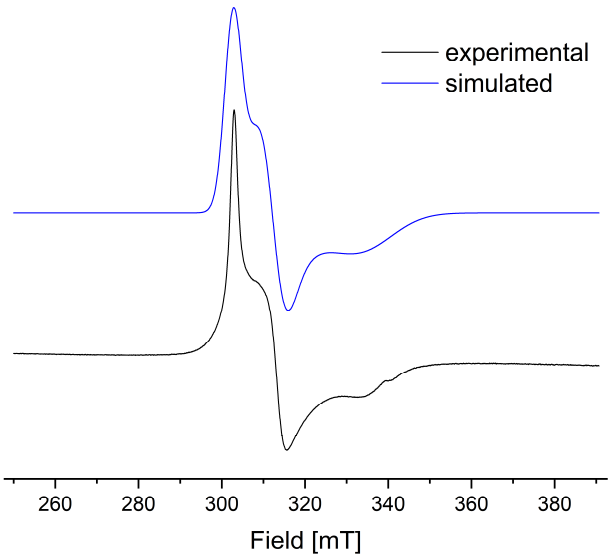


Figure S7: EPR spectrum of **8** in solid state in liquid nitrogen (experimental (black) and simulated (blue).

The EPR spectrum has been simulated with the EasySpin program.[16]

g_x = 2.2253, g_y = 2.1555, g_z = 2.0140, g_{iso} = 2.1316
Sys.S = 1/2;
Sys.g = [2.2253 2.1555 2.014];
Sys.lw = [4.5];
Sys.HStrain = [30 145 485];

Exp.mwFreq = 9.440920;
Exp.Range = [249.9825 390.6755];
Exp.nPoints = 4096;
Exp.Temperature = 77;
Exp.ModAmp = 0.2;

4.4.3 Details on single crystal X-ray structure analysis

The X-ray diffraction experiments were performed on either an Gemini Ultra diffractometer (Oxford diffraction) with an AtlasS2 detector Mo radiation (λ = 0.71073 Å) (**4**, **5**, **6a**, **6b**, **7**, **9**, **10**), a GV 50 diffractometer (Rigaku, formerly Agilent Technologies) with TitanS2 detector from applying applying Cu-K*α* radiation (λ = 1.54178 Å) (**3**) or Cu-K*β* radiation (λ = 1.39222 Å) (**8**). All measurements were performed at 123 K. An analytical numeric absorption correction[17] using a multifaceted crystal model based on expressions derived by R.C. Clark & J.S. Reid using spherical harmonicsas implemented in SACLE3 ABSPACK was applied (**4**, **5**, **6a**, **7**, **8**, **9**, **10**).[18] A numerical absorption correction based on gaussian integration over a multifaceted crystal model using *CrysAlisPro* using spherical harmonicsas implemented in SACLE3 ABSPACK was applied (**3**, **6b**). All structures were solved by direct methods with ShelXT[19] and Olex2[20] and refined by full-matrix least-squares method against F^2 in anisotropic approximation using ShelXL[21]. Hydrogen atoms were refined in calculated positions using riding on pivot atom model.

4.4.3.1 $[(Cp'''Co)_3(\mu_3,\eta^2{:}\eta^2\text{-}P_3)(\mu_3\text{-}P)]$ (3)

Compound **3** crystallizes from a concentrated solution in CH_2Cl_2 layered with CH_3CN at -30 °C in the orthorhombic spacegroup *Pbca* as dark red blocks. The asymmetric unit contains one molecule of **3**. The structure in solid state is depicted in Figure 8.

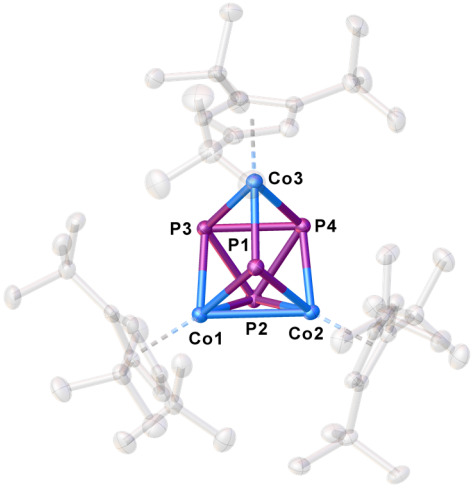


Figure S8: Molecular structure of **3** in solid state. Hydrogen atoms are omitted for clarity Thermal ellipsoids are drawn with 50 % probability level. Selected bond lengths [Å] and angles [°]: Co1-Co2 2.7276(4), Co1-Co3 3.5721(7), Co2-Co3 3.5527(6), P1-P2 3.1648(6), P1-P3 2.6343(7), P1-P4 2.6564(7), P2-P3 2.2965(6), P2-P4 2.3230(6), P3-P4 2.3798(6).

4.4.3.2 $[(Cp'''Co)_3(\mu_3,\eta^2{:}\eta^2\text{-}As_3)(\mu_3\text{-}As)]$ (4)

Compound **4** crystallizes from a concentrated solution in CH_2Cl_2 layered with CH_3CN at -30 °C in the orthorhombic spacegroup *Pbca* as dark brown blocks. The asymmetric unit contains one molecule of **4**. The structure in solid state is depicted in Figure 9.

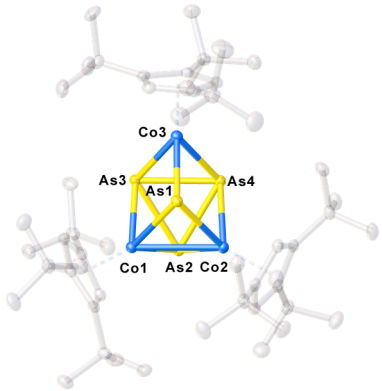


Figure S9: Molecular structure of **4** in solid state. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn with 50 % probability level. Selected bond lengths [Å] and angles [°]: Co1-Co2 2.8191(3), Co1-Co3 3.6879(6), Co2-Co3 3.7061(7), As1-As2 3.4065(6), As1-As3 2.8688(7), As1-As4 2.8511(7), As2-As3 2.5777(2), As2-As4 2.5407(2), As3-As4 2.5974(2).

4.4.3.3 $[K(18\text{-c-}6)(dme)_2][(Cp'''Co)_3(\mu_3,\eta^2{:}\eta^2\text{-}P_3)(\mu_3\text{-}P)]$ (5)

Compound **5** crystallizes from a concentrated solution in dme layered with hexane at -30 °C in the monoclinic spacegroup *C2/c* as dark brown plates. The asymmetric unit contains one molecule of **5**, one potassium ion chelated by one molecule 18-c-6 and two dme molecules and 0.7 separated molecules dme. All dme molecules and 18-c-6 are disordered over two or three positions. The structure in solid state is depicted in Figure S10 and S11.

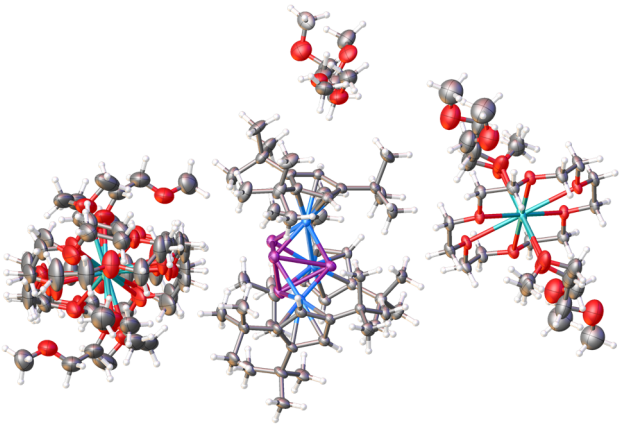


Figure S10: Molecular structure of **5** in solid state. Thermal ellipsoids are drawn with 50 % probability level.

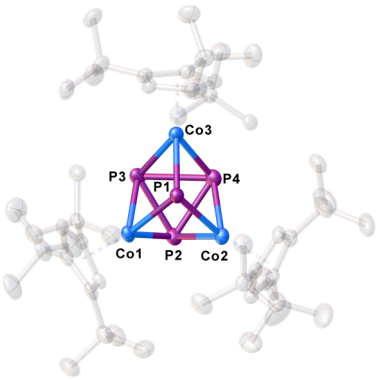


Figure S11: Molecular structure of **5** in solid state. Thermal ellipsoids are drawn with 50 % probability level. Cation, hydrogen atoms and solvent molecules are omitted for clarity. Selected bond lengths [Å] and angles [°]: Co1-Co2 2.9907(6), Co1-Co3 3.5217(5), Co2-Co3 3.5525(8), P1-P2 3.0380(13), P1-P3 2.6746(11), P1-P4 2.6577(12), P2-P3 2.2808(12), P2-P4 2.2781(12), P3-P4 2.3998(12).

4.4.3.4 [K(18-c-6)(thf)$_2$] [(Cp'''Co)$_3$(μ_3,η^2:η^2-As$_3$)(μ_3-As)] (6a)

Compound **6a** crystallizes from a concentrated solution in thf layered with hexane at -30 °C in the cubic spacegroup *Pa*$\bar{3}$ as dark green blocks. The asymmetric unit contains a third of the anion of **6a**, potassium ions chelated by one molecule 18-c-6 and two molecules thf (split over two positions) and three uncoordinated thf molecules. The anion of **6a** and all thf molecules are disordered over several positions. The structure in solid state is depicted in Figure S12. Since the central Co_3As_4 motif is disordered no further bond lengths are given here.

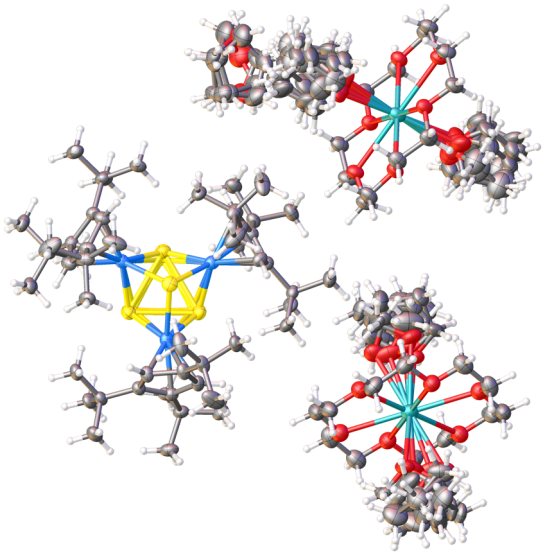


Figure S12: Molecular structure of **6a** in solid state. Thermal ellipsoids are drawn with 50 % probability level.

4.4.3.5 [K(2,2,2-crypt)] [(Cp'''Co)$_3$(μ_3,η^2:η^2-As$_3$)(μ_3-As)] (6b)

Compound **6** crystallizes from a concentrated solution in thf layered with hexane at -30 °C in the triclinic spacegroup $P\bar{1}$ as dark green blocks. The asymmetric unit contains two molecules of **5**, two potassium ions chelated by each one molecule 2,2,2-cryptand and 6.25 molecules thf. A solvent mask was calculated and 500.0 electrons were found in a volume of 2934.0 Å^3 in two voids per unit cell. This is consistent with the presence of 4.75 thf and 1.75 thf per formula unit which account for 520.0 electrons. One molecule **6b** and one 2,2,2-cryptand are disordered over two positions. The structure in solid state is depicted in Figure S13 and S14.

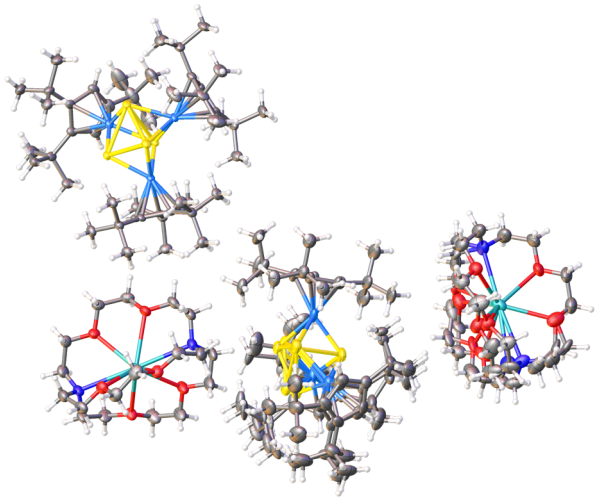


Figure S13: Molecular structure of **6b** in solid state. Thermal ellipsoids are drawn with 50 % probability level.

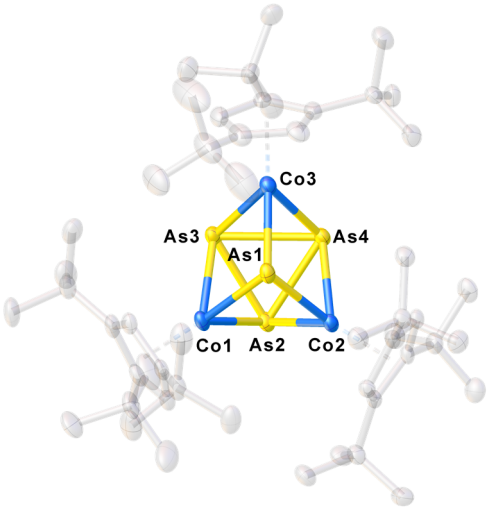


Figure S14: Molecular structure of **6b** in solid state. Thermal ellipsoids are drawn with 50 % probability level. Cations, hydrogen atoms and one molecule of **6b** are omitted for clarity. Depicted is only the non-disordered molecule of **6b**. Selected bond lengths [Å] and angles [°]: Co1-Co2 3.1459(5), Co1-Co3 3.6910(6), Co2-Co3 3.7070(6), As1-As2 3.2429 (8), As1-As3 2.8979(4), As1-As4 2.8523(4), As2-As3 2.5324(4), As2-As4 2.5660(4), As3-As4 2.6508(4).

4.4.3.6 $[(Cp'''Co)_3(\mu_3,\eta^2{:}\eta^2\text{-}P_3)(\mu_3\text{-}P)][FAl]$ (7)

Compound **7** crystallizes from a concentrated solution in CH_2Cl_2 layered with toluene at -30 °C in the orthorhombic spacegroup $P2_12_12_1$ as dark brown needles. The asymmetric unit contains one molecule of **7**, one [FAl] anion, 1.5 molecules toluene and one molecule CH_2Cl_2. A refinement as a two-component inversion twin was applied. The structure in solid state is depicted in Figure S15 and S16.

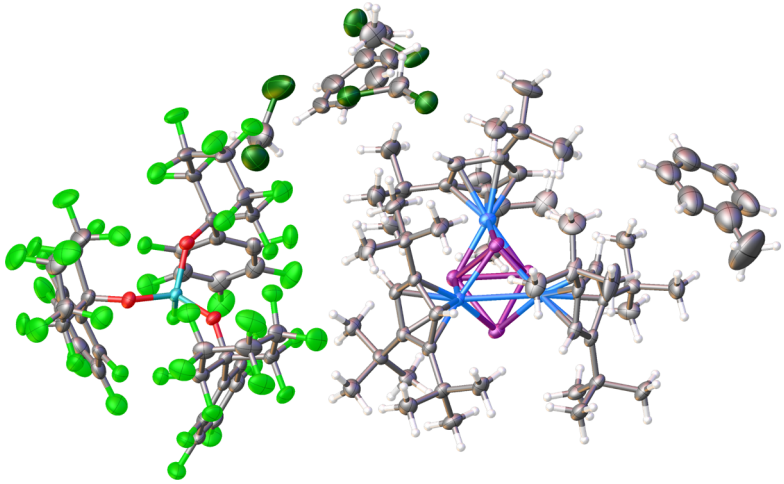


Figure S15: Molecular structure of **7** in solid state. Thermal ellipsoids are drawn with 50 % probability level.

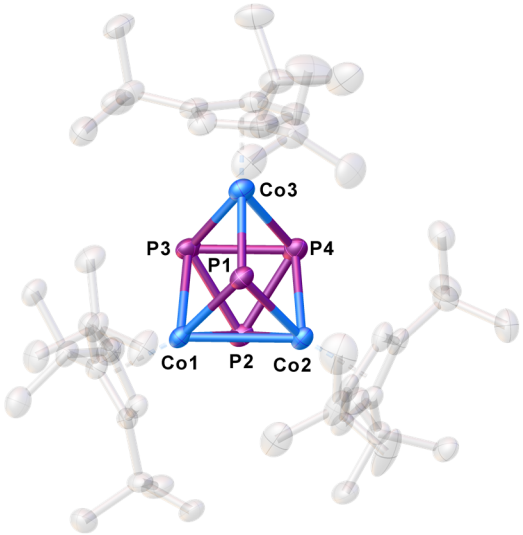


Figure S16: Molecular structure of **7** in solid state. Thermal ellipsoids are drawn with 50 % probability level. Anion, hydrogen atoms and solvent molecules are omitted for clarity. Selected bond lengths [Å] and angles [°]: Co1-Co2 2.7152(8), Co1-Co3 3.5324(9), Co2-Co3 3.5501(9), P1-P2 3.0869(17), P1-P3 2.6223(17), P1-P4 2.6214(17), P2-P3 2.3156(17), P2-P4 2.3083(18), P3-P4 2.3693(18).

4.4.3.7 $[(Cp'''Co)_3(\mu_3,\eta^2{:}\eta^2{-}As_3)(\mu_3{-}As)][FAl]$ (8)

Compound **8** crystallizes from a concentrated solution in CH_2Cl_2 layered with toluene at -30 °C in the monoclinic spacegroup $P2_1/n$ as dark brown needles. The asymmetric unit contains one molecule of **8**, one [FAl] anion, one molecules toluene and 1.5 molecule CH_2Cl_2. A solvent mask was calculated and 386.0 electrons were found in a volume of 2766.2 Å^3 in one void. This is consistent with the presence of one toluene and 1.3 CH_2Cl_2 per unit cell which account for 386.0 electrons. One CH_2Cl_2 and two ^{t}Bu substituent of two Cp''' are disordered over two positions. The structure in solid state is depicted in Figure S17 and S18.

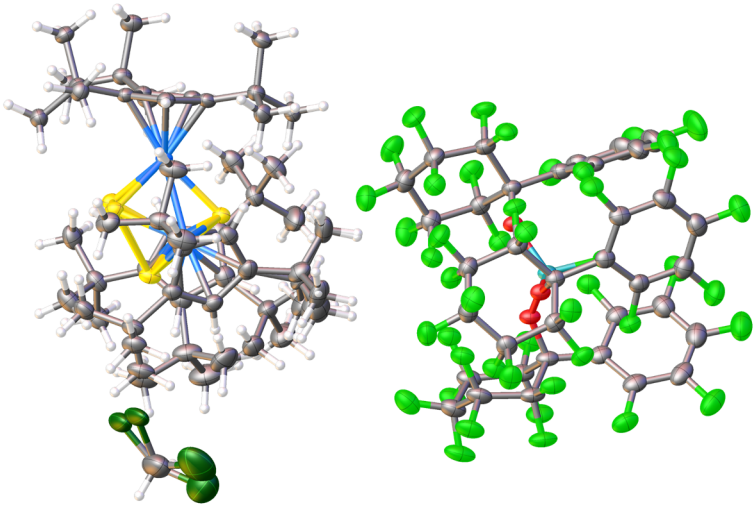


Figure S17: Molecular structure of **8** in solid state. Thermal ellipsoids are drawn with 50 % probability level.

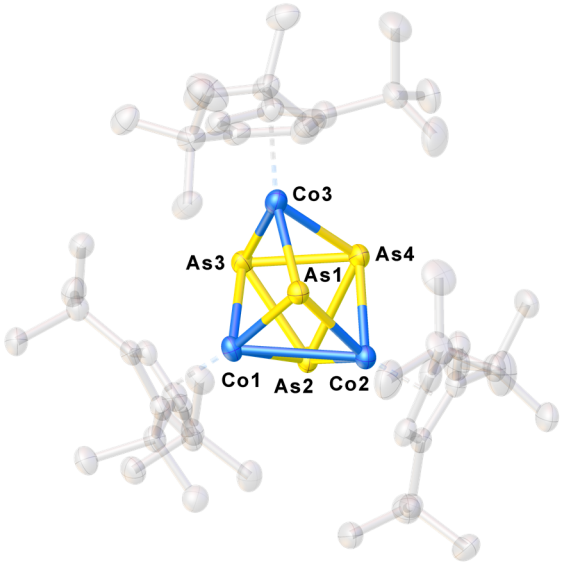


Figure S18: Molecular structure of **8** in solid state. Thermal ellipsoids are drawn with 50 % probability level. Anion, hydrogen atoms and solvent molecules are omitted for clarity. Depicted is the part with the highest occupancy. Selected bond lengths [Å] and angles [°]: Co1-Co2 2.8632(4), Co1-Co3 3.2732(5), Co2-Co3 3.8114(6), As1-As2 3.4639(8), As1-As3 3.3011(7), As1-As4 2.7016(4), As2-As3 2.4924(4), As2-As4 2.6168(4), As3-As4 2.5990(4).

4.4.3.8 $[(Cp'''Co)_3(\mu_3,\eta^2{:}\eta^2\text{-}P_3)(\mu_3\text{-}P)][TEF]_2$ (9)

Compound **9** crystallizes from a concentrated solution in ortho-difluoro benzene layered with toluene at -30 °C in the monoclinic spacegroup $P2_1/c$ as dark brown blocks. The asymmetric unit contains one molecule of **9**, two [TEF] anions, two molecules ortho-difluoro benzene. Both [TEF] anions and one ortho-difluoro benzene are disordered over two or three positions. The structure in solid state is depicted in Figure S19 and S20.

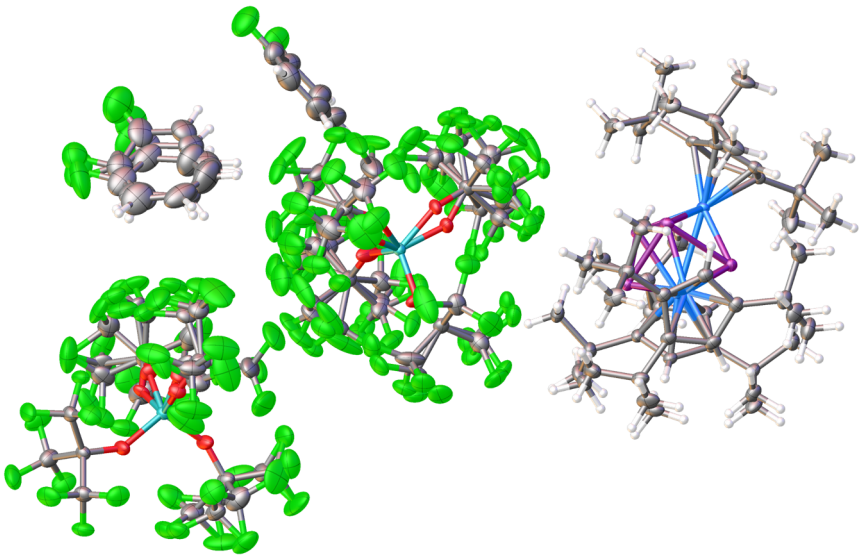


Figure S19: Molecular structure of **9** in solid state. Thermal ellipsoids are drawn with 50 % probability level.

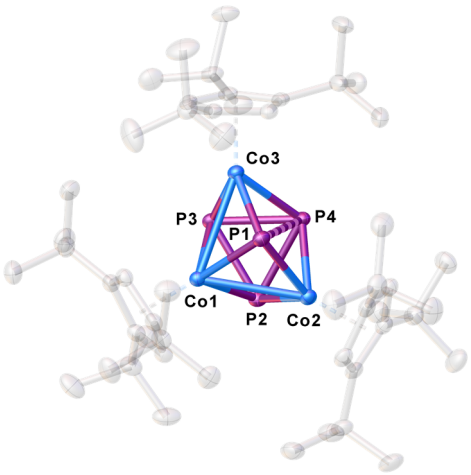


Figure S20: Molecular structure of **9** in solid state. Thermal ellipsoids are drawn with 50 % probability level. Anions, hydrogen atoms and solvent molecules are omitted for clarity. Selected bond lengths [Å] and angles [°]: Co1-Co2 2.8044(3), Co1-Co3 2.7825(4), Co2-Co3 3.5832(6), P1-P2 3.3006(8), P1-P3 3.3058(7), P1-P4 2.5629(7), P2-P3 2.2509(7), P2-P4 2.3549(7), P3-P4 2.3529(7).

4.4.3.9 $[(Cp'''Co)_3(\mu_3,\eta^2{:}\eta^2{:}\eta^2\text{-}As_3)(\mu_3\text{-}As)][TEF]_2$ (10)

Compound **10** crystallizes from a concentrated solution in ortho-difluoro benzene layered with hexane at -30 °C in the monoclinic spacegroup $P2_1/c$ as dark brown rods. The asymmetric unit contains one molecule of **10**, two [TEF] anions, two molecules ortho-difluoro benzene. Both [TEF] anions and one ortho-difluoro benzene are disordered over two positions. The structure in solid state is depicted in Figure S21 and S22.

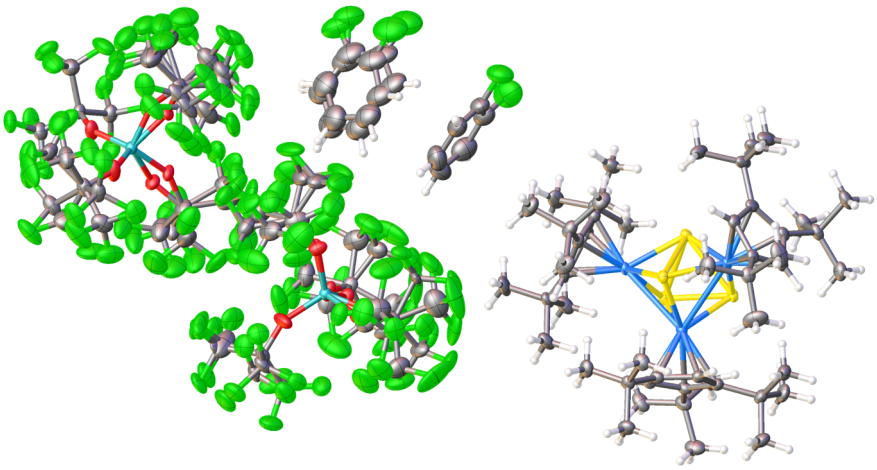


Figure S21: Molecular structure of **10** in solid state. Thermal ellipsoids are drawn with 50 % probability level.

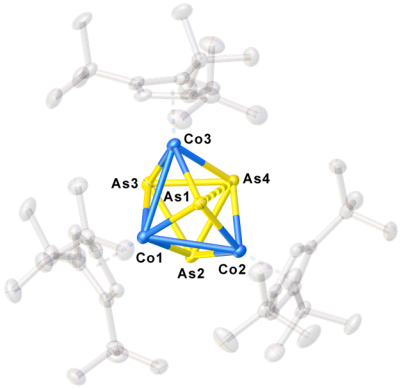


Figure S22: Molecular structure of **10** in solid state. Thermal ellipsoids are drawn with 50 % probability level. Anions, hydrogen atoms and solvent molecules are omitted for clarity. Selected bond lengths [Å] and angles [°]: Co1-Co2 2.8904(6), Co1-Co3 2.8724(6), Co2-Co3 3.7182(7), As1-As2 3.5278(8), As1-As3 3.5357(6), As1-As4 2.7612(4), As2-As3 2.5002(4), As2-As4 2.5828(5), As3-As4 2.5745(4).

4.4.3.10 Crystallographic information

Table S1: Crystallographic data for all compounds

	3	4	5	6a	6b	7	8	9	10
Formula	$C_{51}H_{87}Co_3P_4$	$C_{51}H_{87}As_4Co_3$	$C_{143.26}H_{264.82}Co_6K_2O_{20.6}P_8$	$C_{83}H_{151}As_4Co_3KO_{11}$	$As_8C_{183}Co_6H_{336}K_2N_4O_{23.25}$	$C_{97.33}H_{99.68}AlCl_{2.04}Co_3F_{46}O_3P_4$	$C_{95.5}H_{98}AlAs_4Cl_3Co_3F_{46}O_3$	$C_{95}H_{95}Al_2Co_3F_{76}O_8P_4$	$C_{95}H_{95}Al_2As_4Co_3F_{76}O_8$
$D_{calc.}$/ g cm^{-3}	1.271	1.489	1.184	1.370	1.391	1.563	1.558	1.748	1.837
μ/mm^{-1}	8.744	3.472	0.760	2.123	1.993	0.688	4.249	0.647	1.679
Formula Weight	1000.87	1176.67	2996.62	1840.60	3995.68	2591.37	2791.76	3163.33	3339.13
Colour	clear dark red	dark green	clear dark black	dark green	clear dark brown	clear dark black	black	clear dark brown	clear dark brown
Shape	plate	plate	plate	block	plate	needle	plate	block	block
Size/mm^3	0.22×0.13×0.10	0.56×0.35×0.07	0.62×0.38×0.19	0.32×0.31×0.18	0.74×0.16×0.05	0.60×0.22×0.13	0.53×0.18×0.05	0.97×0.51×0.33	0.66×0.40×0.26
T/K	122.97(18)	123(1)	123(1)	123(1)	123(1)	123(1)	122.96(19)	123	123(1)
Crystal System	orthorhombic	orthorhombic	monoclinic	cubic	triclinic	orthorhombic	monoclinic	monoclinic	monoclinic
Space Group	*Pbca*	*Pbca*	*C*2/*c*	*Pa*-3	*P*-1	$P2_12_12_1$	$P2_1/n$	$P2_1/c$	$P2_1/c$
Flack Parameter						0.303(12)			
Hooft Parameter						0.293(4)			
a/Å	19.4559(3)	19.5349(2)	48.6818(7)	26.1345(2)	13.7243(2)	18.4370(3)	19.9550(2)	15.1151(2)	15.1331(2)
b/Å	19.5911(2)	19.5646(3)	18.7066(2)	26.1345(2)	23.0765(5)	19.6028(3)	18.6643(2)	29.3614(4)	29.4398(4)
c/Å	27.4497(4)	27.4612(3)	18.5485(3)	26.1345(2)	31.2024(6)	30.4654(6)	31.9870(4)	27.2982(4)	27.3516(3)
α/°	90	90	90	90	97.709(2)	90	90	90	90
β/°	90	90	95.7100(10)	90	96.634(2)	90	92.6370(10)	97.1190(10)	97.7030(10)
γ/°	90	90	90	90	100.190(2)	90	90	90	90
V/Å^3	10462.8(2)	10495.5(2)	16807.8(4)	17850.2(4)	9539.5(3)	11010.7(3)	11900.8(2)	12021.6(3)	12075.6(3)
Z	8	8	4	8	2	4	4	4	4
Z'	1	1	0.5	0.333333	1	1	1	1	1
Wavelength/Å	1.54184	0.71073	0.71073	0.71073	0.71073	0.71073	1.39222	0.71073	0.71073
Radiation type	Cu K_α	Mo K_α	Mo K_α	Mo K_α	Mo K_α	Mo K_α	Cu K_β	Mo K_α	Mo K_α
θ_{min}/°	3.220	3.300	3.422	3.307	3.266	3.308	3.220	3.337	3.349
θ_{max}/°	67.072	30.033	26.732	32.495	27.103	26.732	72.468	28.700	29.575
Measured Refl.	54693	47222	67541	41237	84897	73402	169249	193736	121227
Independent Refl.	9322	15283	17782	9676	41905	23208	31962	30981	33166
Reflections with I > 2(I)	8872	13085	14595	7469	31174	20507	26254	26265	28272
R_{int}	0.0450	0.0235	0.0287	0.0307	0.0338	0.0443	0.0674	0.0332	0.0375
Parameters	550	550	1218	575	1948	1534	1437	2773	2548
Restraints	0	0	724	636	375	153	38	1423	1452
Largest Peak	0.315	0.695	1.677	1.276	0.930	1.367	1.305	1.443	0.841
Deepest Hole	-0.285	-0.308	-0.776	-1.472	-0.597	-0.574	-0.945	-0.570	-0.784
GooF	1.035	1.045	1.052	1.020	1.030	1.020	1.056	1.042	1.170
wR_2 (all data)	0.0654	0.0644	0.1618	0.0983	0.1011	0.1324	0.1189	0.1149	0.1224
wR_2	0.0644	0.0613	0.1509	0.0899	0.0938	0.1240	0.1123	0.1089	0.1181
R_1 (all data)	0.0283	0.0333	0.0696	0.0632	0.0632	0.0547	0.0532	0.0531	0.0636
R_1	0.0264	0.0249	0.0557	0.0427	0.0430	0.0466	0.0430	0.0435	0.0531

4.4.4 Computational Details

Gaussian 09 program package was used throughout.[22] Density functional theory (DFT) in form of BP86[23] (Becke's exchange and Perdew 86 correlation functional) with def2-SVP all electron basis set[24] was employed. For solvents effects has been accounted by using continuous polarizable continuum model (CPM).[25] The dielectric constant of dichloromethane (ε = 8.93) has been used in the calculations of the cations (**7**, **8**, **9**, **10**) and the dielectric constant of thf (ε = 7.4257) has been used in the calculations of the anions (**5**, **6**). The Natural Bond Orbital (NBO) analysis has been performed with the NBO6 program.[26] The figures for the supporting information concerning the DFT calculations were created with Chemcraft.[27]

Table S2: Total energies for all optimized geometries (BP86/def2-SVP level of theory).

	total energy [Ha]
$[(Cp'''Co)_3(\mu_3,\eta^2{:}\eta^2{:}\eta^2\text{-}P_3)(\mu_3\text{-}P)]$ (**3**) singlet	-7508.2179195
$[(Cp'''Co)_3(\mu_3,\eta^2{:}\eta^2{:}\eta^2\text{-}P_3)(\mu_3\text{-}P)]$ (**3**) triplet	-7508.2093639
$[(Cp'''Co)_3(\mu_3,\eta^2{:}\eta^2{:}\eta^2\text{-}As_3)(\mu_3\text{-}As)]$ (**4**) singlet	-15086.6341208
$[(Cp'''Co)_3(\mu_3,\eta^2{:}\eta^2{:}\eta^2\text{-}As_3)(\mu_3\text{-}As)]$ (**4**) triplet	-15086.6276294
$[(Cp'''Co)_3(\mu_3,\eta^2{:}\eta^2{:}\eta^2\text{-}P_3)(\mu_3\text{-}P)]^-$ (**5**) dublet	-7508.3292535
$[(Cp'''Co)_3(\mu_3,\eta^2{:}\eta^2{:}\eta^2\text{-}As_3)(\mu_3\text{-}As)]^-$ (**6**) dublet	-15086.7451359
$[(Cp'''Co)_3(\mu_3,\eta^2{:}\eta^2{:}\eta^2\text{-}P_3)(\mu_3\text{-}P)]^+$ (**7**) dublet	-7508.06533448
$[(Cp'''Co)_3(\mu_3,\eta^2{:}\eta^2{:}\eta^2\text{-}As_3)(\mu_3\text{-}As)]^+$ (**8**) dublet	-15086.4847500
$[(Cp'''Co)_3(\mu_3,\eta^2{:}\eta^2{:}\eta^2\text{-}P_3)(\mu_3\text{-}P)]^{2+}$ (**9**) singlet	-7507.87805237
$[(Cp'''Co)_3(\mu_3,\eta^2{:}\eta^2{:}\eta^2\text{-}As_3)(\mu_3\text{-}As)]^{2+}$ (**10**) singlet	-15086.3000135

Table S3: Summarized bond distances and Wiberg bond indices (black: from structure in solid state, blue: from DFT calculations, red: related WBIs, BP86/def2-SVP level of theory).

	3	**4**	**5**	**6**	**7**	**8**	**9**	**10**
Co1-Co2	2.7276(4)	2.8191(3)	2.9906(6)	3.14606(7)	2.7153(7)	2.8632(4)	2.8042(3)	2.8905(6)
	2.70812	2.82061	2.97350	3.17996	2.73009	2.83882	2.76670	2.90094
	0.34	0.33	0.27	0.23	0.32	0.28	0.24	0.23
Co1-Co3	3.5721(7)	3.6879(6)	3.5214(5)	3.69113(8)	3.5337(8)	3.2732(5)	2.7825(3)	2.8722(6)
	3.57285	3.75189	3.56947	3.71911	3.64144	3.42824	2.80022	2.86676
	0.16	0.16	0.17	0.15	0.15	0.13	0.22	0.21
Co2-Co3	3.5527(6)	3.7061(7)	3.5524(8)	3.70707(9)	3.5499(7)	3.8114(6)	3.5836(6)	3.7182(7)
	3.59540	3.72135	3.56124	3.72199	3.61619	3.82244	3.62242	3.78448
	0.17	0.15	0.16	0.15	0.15	0.14	0.14	0.13
E1-E2	3.1648(6)	3.4065(6)	3.0375(13)	3.24297(7)	3.0878(13)	3.4639(8)	3.3002(8)	3.5279(8)
	3.21277	3.42967	3.12513	3.28621	3.09773	3.48253	3.35547	3.55814
	0.09	0.09	0.11	0.12	0.11	0.09	0.07	0.07
E1-E3	2.6343(7)	2.8685(7)	2.6744(11)	2.89764(8)	2.6219(13)	3.3011(7)	3.3054(7)	3.5359(6)
	2.71023	2.87050	2.71811	2.91243	2.58191	3.23854	3.34826	3.57158
	0.33	0.36	0.32	0.31	0.45	0.16	0.07	0.08
E1-E4	2.6564(7)	2.8511(7)	2.6572(12)	2.81586(6)	2.6209(14)	2.7016(4)	2.5625(6)	2.7614(4)
	2.68434	2.90597	2.72677	2.91268	2.61048	2.76644	2.56469	2.74474
	0.36	0.33	0.332	0.32	0.41	0.52	0.55	0.56
E2-E3	2.2965(6)	2.5777(2)	2.2807(12)	2.53244(6)	2.3157(13)	2.4924(4)	2.2507(6)	2.5005(4)
	2.34906	2.63144	2.34232	2.58264	2.41905	2.54664	2.28627	2.53288
	0.68	0.58	0.72	0.67	0.60	0.69	0.77	0.70
E2-E4	2.3230(6)	2.5407(2)	2.2777(12)	2.56599(5)	2.3075(14)	2.6168(4)	2.3549(6)	2.5829(5)
	2.38915	2.58705	2.33396	2.59492	2.37676	2.67050	2.42403	2.64371
	0.62	0.63	0.73	0.65	0.66	0.56	0.62	0.62

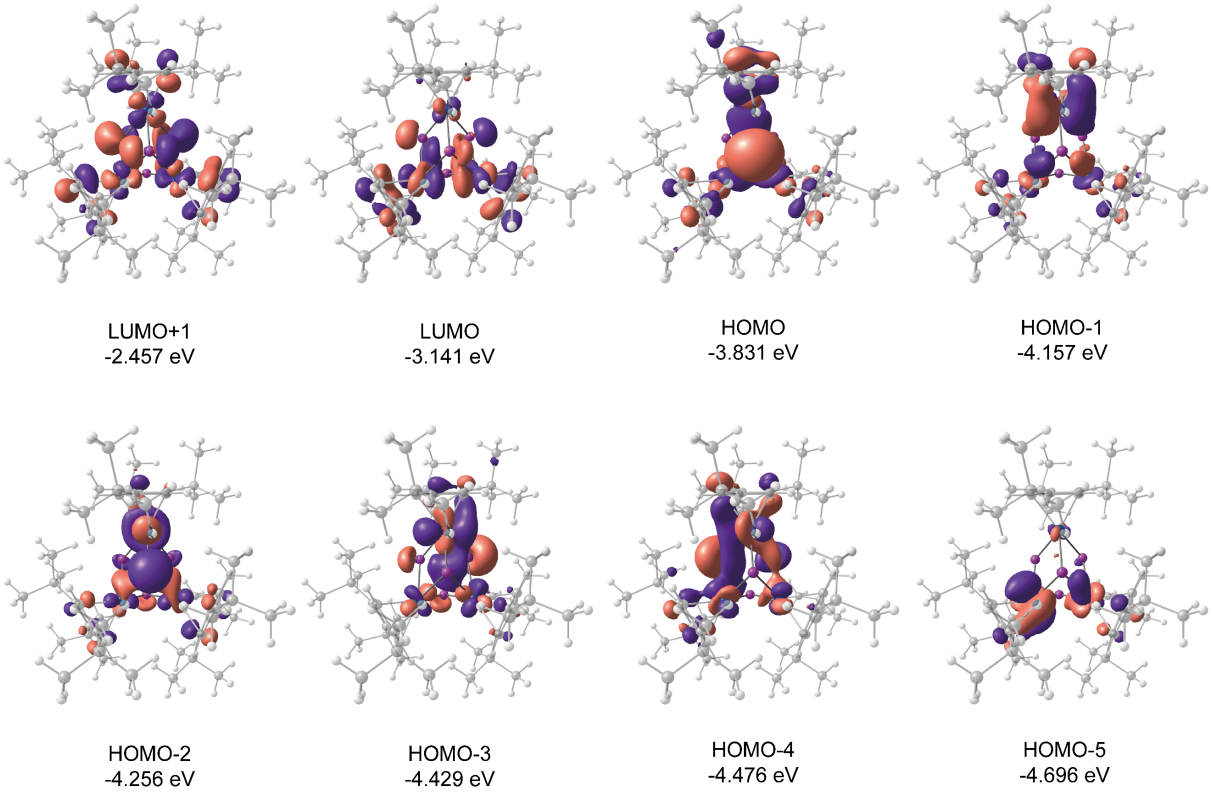


Figure S23: Frontier orbitals of **3** singlet (BP86/def2-SVP level of theory).

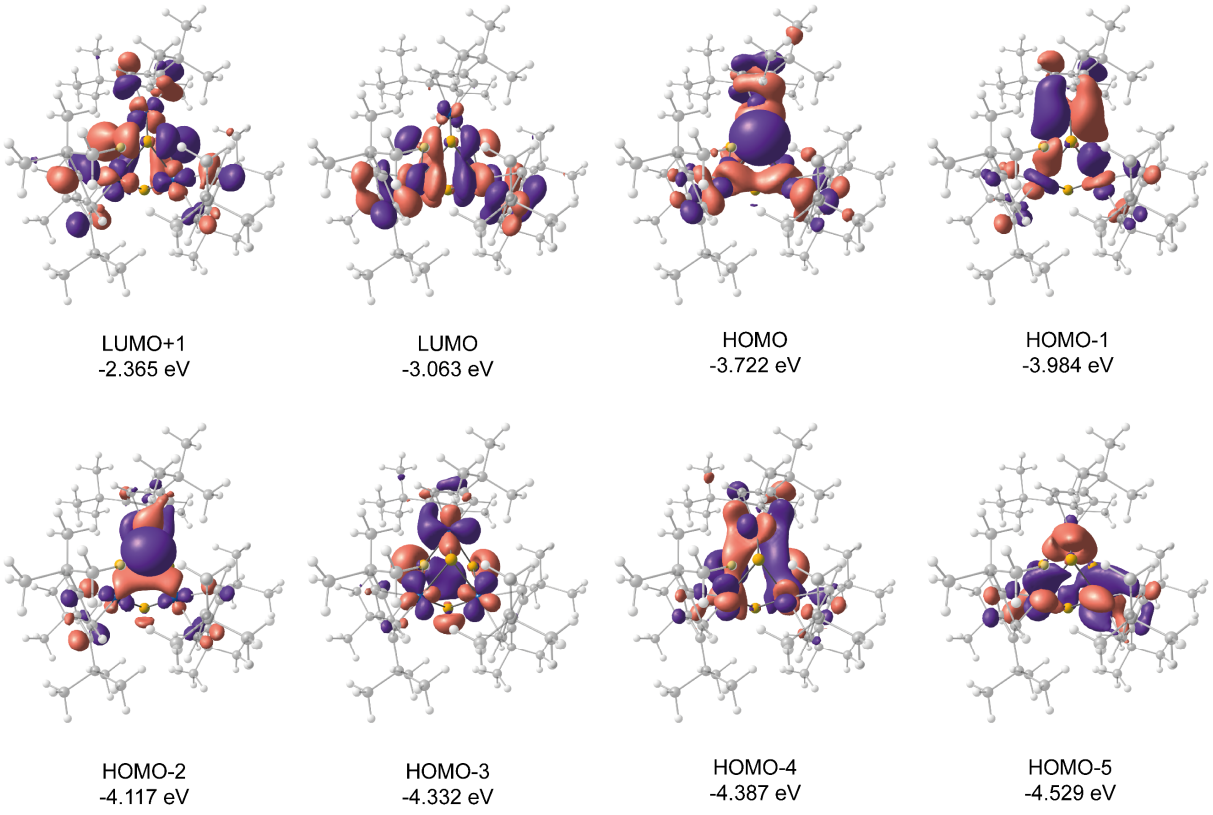


Figure S24: Frontier orbitals of **4** singlet (BP86/def2-SVP level of theory).

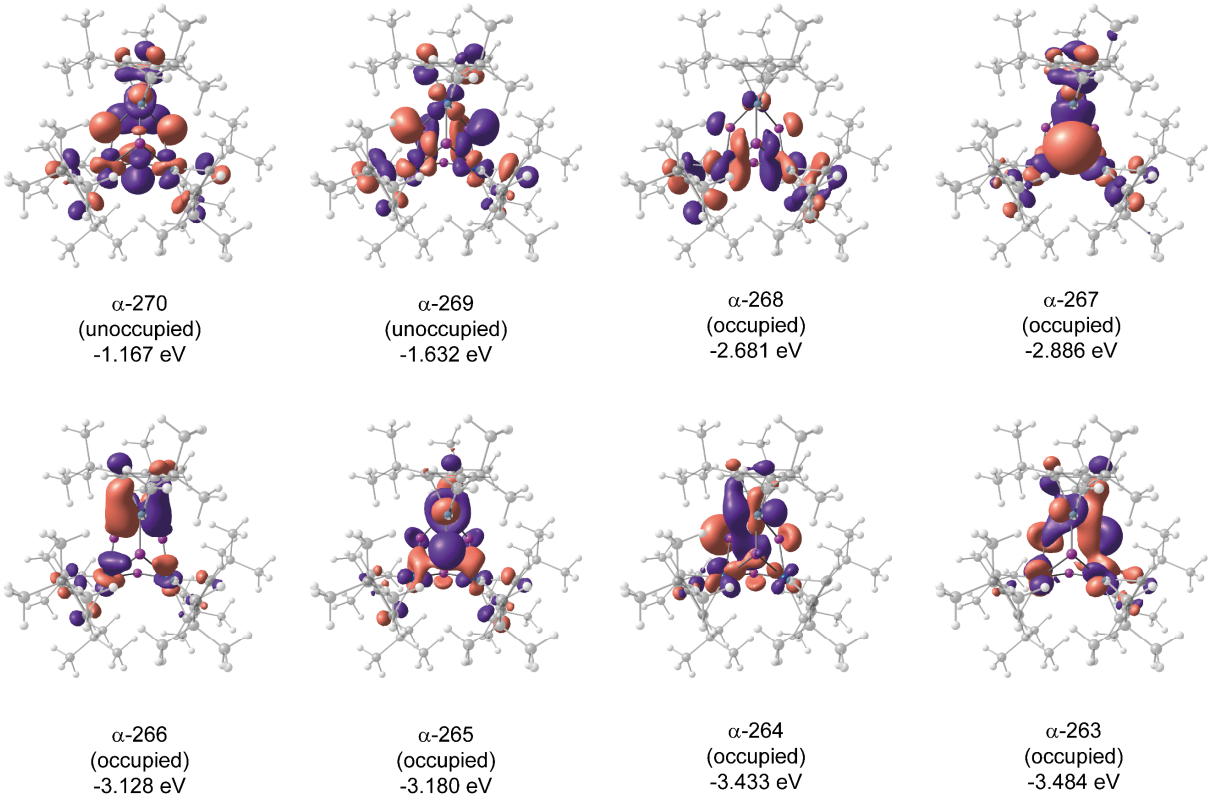


Figure S25: Frontier orbitals of **5** dublet (α orbitals, BP86/def2-SVP level of theory).

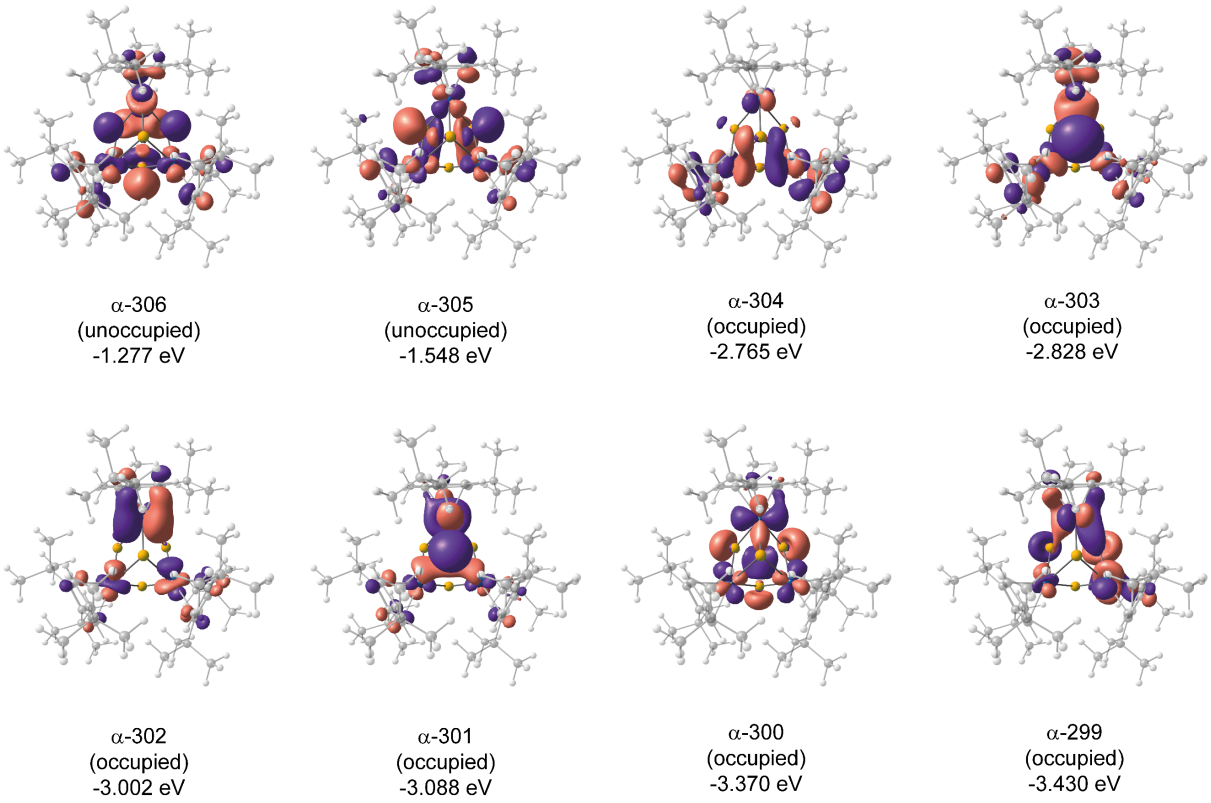


Figure S26: Frontier orbitals of **6** dublet (α orbitals, BP86/def2-SVP level of theory).

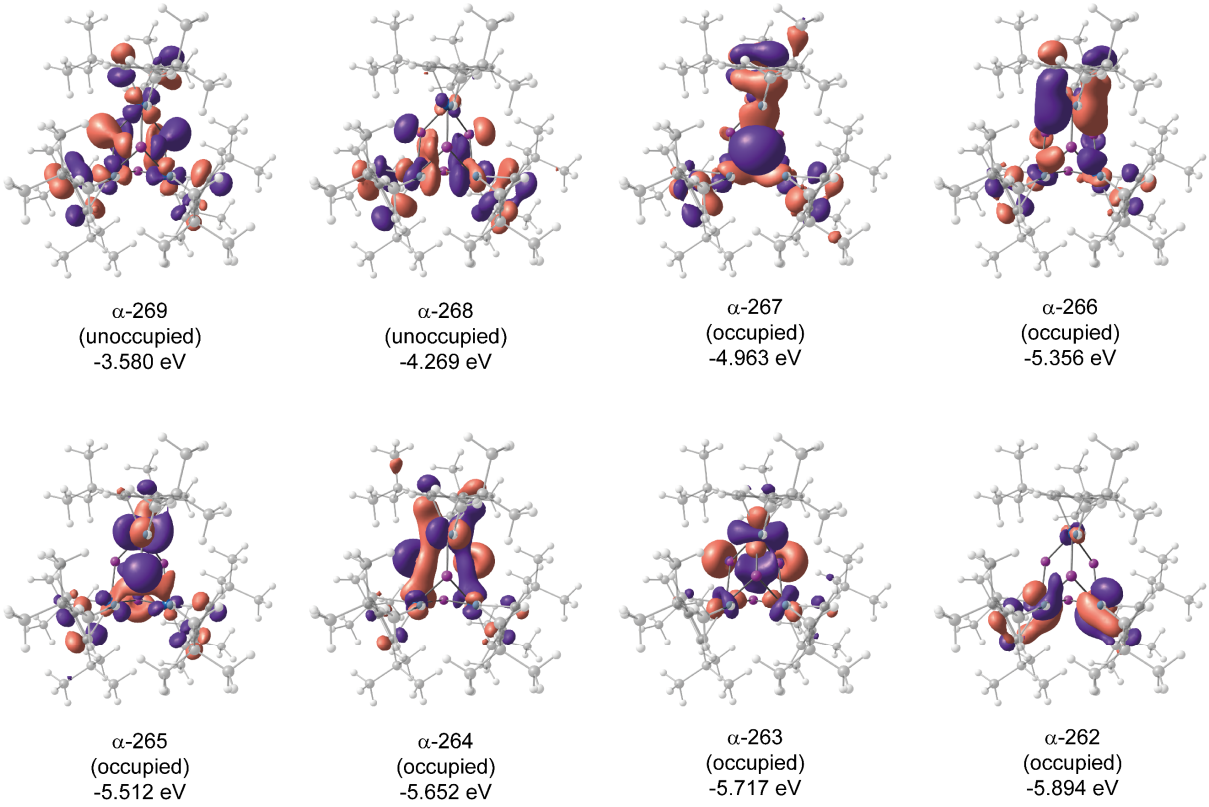


Figure S27: Frontier orbitals of **7** dublet (α orbitals, BP86/def2-SVP level of theory).

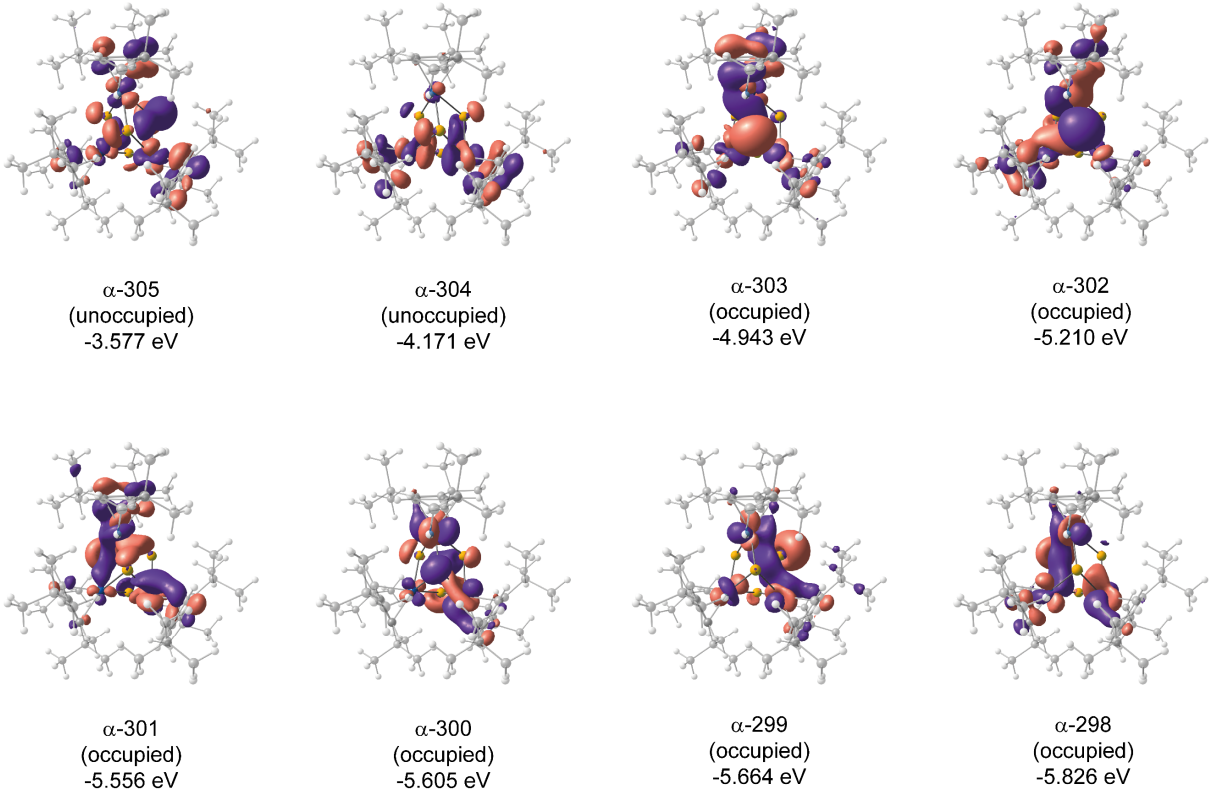


Figure S28: Frontier orbitals of **8** dublet (BP86/def2-SVP level of theory).

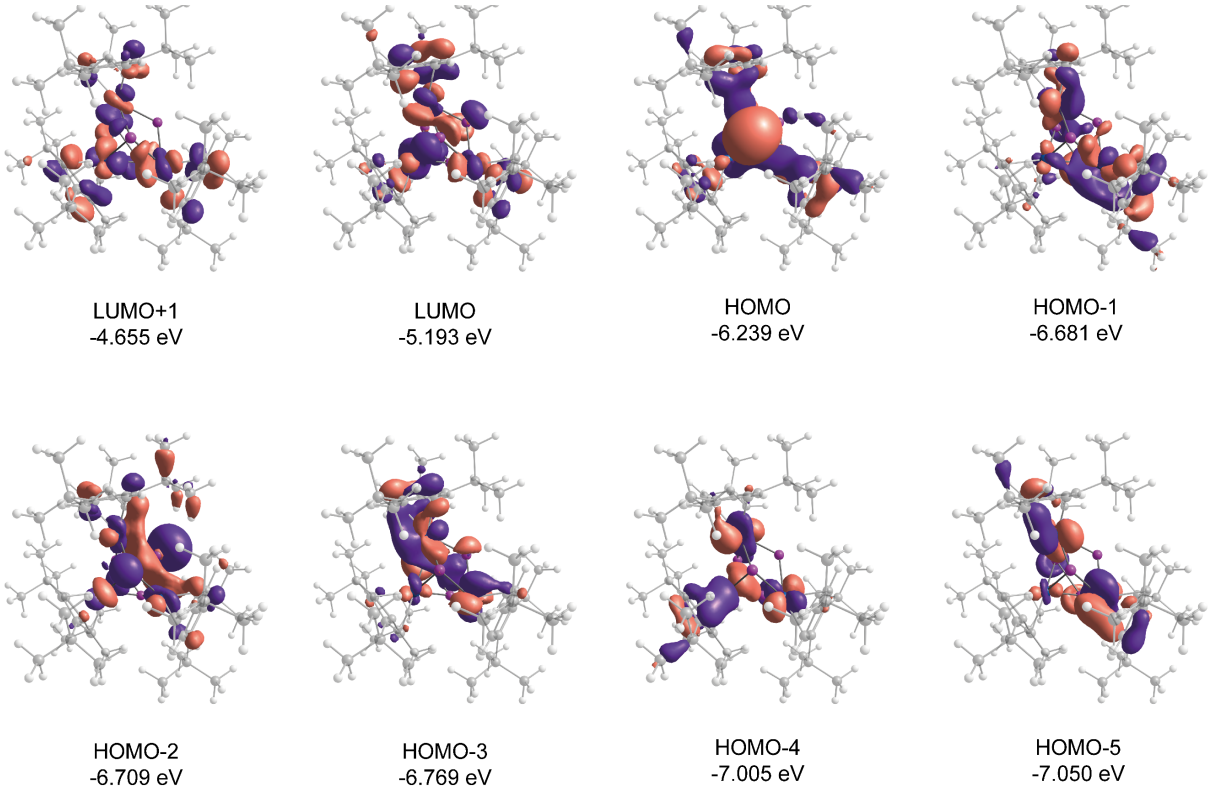


Figure S29: Frontier orbitals of **9** singlet (BP86/def2-SVP level of theory).

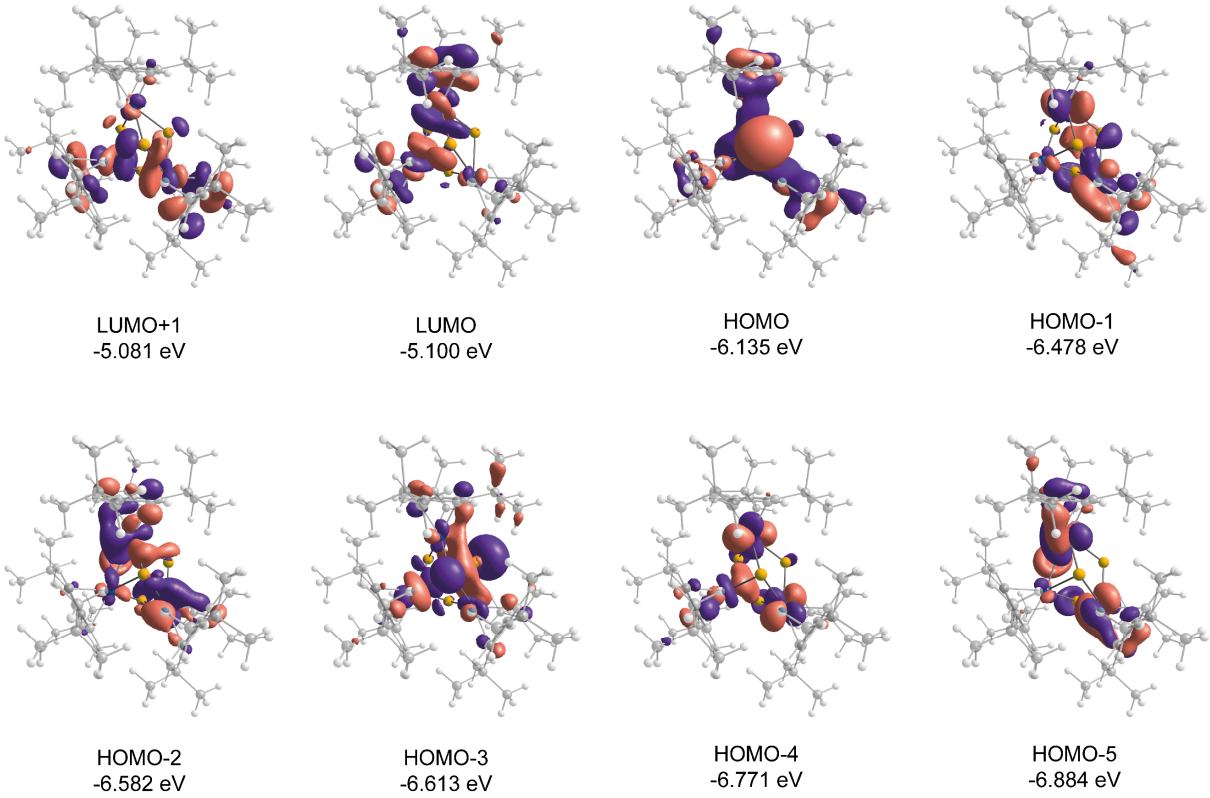
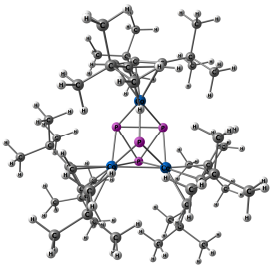


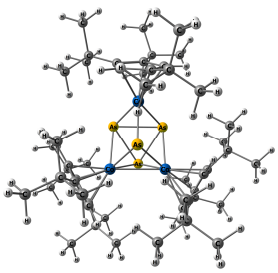
Figure S30: Frontier orbitals of **10** singlet (BP86/def2-SVP level of theory).

Table S4: Optimized geometry of **3** (singlet, left) and **3** (triplet, right). XYZ coordinates in angstroms. BP86/def2-TZVP level of theory.



C	-1.340793000	3.449408000	-0.303899000	C	-4.300057000	-2.477279000	-0.638658000	C	-1.353172000	3.605095000	-0.242811000	C	-4.226339000	-2.529445000	-0.658590000
C	-2.591124000	2.833572000	-0.771278000	C	-4.434495000	-2.138797000	-2.138084000	C	-2.579476000	2.972791000	-0.735987000	C	-4.348402000	-2.179709000	-2.156630000
C	-3.123222000	2.112025000	0.359325000	H	-3.817839000	-1.255465000	-2.403643000	C	-3.122901000	2.219176000	0.376125000	H	-3.701988000	-1.316896000	-2.418857000
H	-4.069492000	1.564023000	0.349269000	H	-5.492999000	-1.904435000	-2.377006000	H	-4.060631000	1.656839000	0.340434000	H	-5.398415000	-1.904509000	-2.388850000
C	-2.308129000	2.298021000	1.526155000	H	-4.132695000	-2.976029000	-2.794154000	C	-2.317457000	2.387107000	1.551224000	H	-4.081751000	-3.023807000	-2.818862000
C	-1.195195000	3.079679000	1.090456000	C	-4.987428000	-1.331825000	0.145379000	C	-1.210115000	3.198589000	1.140519000	C	-4.828341000	-1.334549000	0.123330000
H	-0.383286000	3.425145000	1.737799000	H	-5.114926000	-1.571118000	1.219771000	H	-0.405266000	3.534120000	1.802275000	H	-4.981205000	-1.563531000	1.196681000
C	-1.676633000	-3.357266000	-0.708781000	H	-6.001208000	-1.152008000	-0.268082000	C	-1.635166000	-3.520439000	-0.741272000	H	-5.822173000	-1.073482000	-0.295609000
C	-2.846074000	-2.671601000	-0.145750000	H	-4.407394000	-0.393401000	0.069057000	C	-2.786854000	-2.810432000	-0.163859000	H	-4.168482000	-0.447481000	0.050967000
C	-2.530094000	-2.403459000	1.244280000	C	-5.095385000	-3.775969000	-0.318735000	C	-2.468783000	-2.578817000	1.231093000	C	-5.097814000	-3.778288000	-0.342631000
H	-3.213336000	-1.915766000	1.947139000	H	-4.697575000	-4.657439000	-0.855503000	H	-3.141882000	-2.096884000	1.947745000	H	-4.751712000	-4.677573000	-0.887679000
C	-1.245629000	-2.922346000	1.592314000	H	-6.161518000	-3.652433000	-0.607140000	C	-1.176814000	-3.103799000	1.554936000	H	-6.155537000	-3.591545000	-0.627975000
C	-0.712970000	-3.454135000	0.374606000	H	-5.060047000	-3.999628000	0.767683000	C	-0.667867000	-3.646611000	0.328275000	H	-5.073050000	-4.012412000	0.741869000
H	0.266406000	-3.934892000	0.287473000	C	-0.664662000	-3.132249000	2.990377000	H	0.302685000	-4.141958000	0.228689000	C	-0.574161000	-3.296399000	2.945501000
C	4.105061000	-0.854695000	-0.181739000	C	0.878512000	-3.159159000	2.954567000	C	4.071780000	-0.814116000	-0.239641000	C	0.966746000	-3.361263000	2.880598000
C	4.153363000	0.465496000	-0.822821000	H	1.262170000	-3.997275000	2.337193000	C	4.069926000	0.537179000	-0.830580000	H	1.317631000	-4.213412000	2.263068000
C	3.812613000	1.423298000	0.212062000	H	1.284159000	-3.292850000	3.979349000	C	3.759067000	1.449417000	0.254034000	H	1.388616000	-3.496866000	3.898668000
H	3.763552000	2.506816000	0.062766000	H	1.282096000	-2.212916000	2.538886000	H	3.686538000	2.536200000	0.151821000	H	1.387311000	-2.429404000	2.450067000
C	3.614623000	0.770648000	1.475412000	C	-1.135025000	-2.037052000	3.967255000	C	3.593988000	0.738988000	1.487056000	C	-0.993882000	-2.161878000	3.901427000
C	3.771384000	-0.625877000	1.214570000	H	-0.808795000	-1.037111000	3.616827000	C	3.772829000	-0.648870000	1.165986000	H	-0.650488000	-1.180011000	3.515208000
H	3.686111000	-1.413823000	1.970220000	H	-0.706456000	-2.210311000	4.976659000	H	3.709995000	-1.466907000	1.891455000	H	-0.548549000	-2.316007000	4.906691000
C	-0.416954000	4.564016000	-0.861286000	H	-2.239310000	-2.026824000	4.074747000	C	-0.426068000	4.728012000	-0.775661000	H	-2.094618000	-2.113598000	4.030057000
C	0.972859000	4.515641000	-0.172648000	C	-1.181959000	-4.510873000	3.488962000	C	0.959009000	4.669192000	-0.078335000	C	-1.115042000	-4.647220000	3.492364000
H	0.919841000	4.754485000	0.907678000	H	-2.290722000	-4.530624000	3.535496000	H	0.899153000	4.867084000	1.010020000	H	-2.222510000	-4.636146000	3.563763000
H	1.642243000	5.267839000	-0.638664000	H	-0.790791000	-4.724998000	4.506771000	H	1.624824000	5.443729000	-0.512093000	H	-0.706345000	-4.848312000	4.505965000
H	1.449906000	3.519464000	-0.279079000	H	-0.855636000	-5.331125000	2.816262000	H	1.440966000	3.679806000	-0.222673000	H	-0.826978000	-5.491239000	2.831766000
C	-1.059553000	5.927177000	-0.471546000	C	4.555746000	-2.274626000	-0.608078000	C	-1.074387000	6.086845000	-0.380915000	C	4.534468000	-2.206717000	-0.736431000
H	-2.051340000	6.075469000	-0.939477000	C	3.818899000	-3.352193000	0.230455000	H	-2.063740000	6.232128000	-0.855581000	C	3.829418000	-3.330242000	0.068540000
H	-0.400964000	6.761807000	-0.794876000	H	4.062685000	-3.298881000	1.309830000	H	-0.418382000	6.928088000	-0.692402000	H	4.089756000	-3.316583000	1.145346000
H	-1.191897000	6.003279000	0.627553000	H	4.115066000	-4.363267000	-0.118623000	H	-1.216966000	6.153368000	0.717600000	H	4.139342000	-4.320241000	-0.325571000
C	-0.163140000	4.531538000	-2.383123000	H	2.719108000	-3.256858000	0.122537000	C	-0.150429000	4.710632000	-2.293787000	H	2.726518000	-3.252793000	-0.020064000
H	0.268008000	3.556456000	-2.691267000	C	4.310474000	-2.643384000	-2.087202000	H	0.285354000	3.737881000	-2.603227000	C	4.270002000	-2.513504000	-2.226111000
H	0.564285000	5.325955000	-2.652207000	H	3.234881000	-2.559777000	-2.347373000	H	0.580450000	5.507849000	-2.545087000	H	3.191522000	-2.417559000	-2.468257000
H	-1.078813000	4.718700000	-2.973546000	H	4.621715000	-3.695298000	-2.259828000	H	-1.056324000	4.901453000	-2.897958000	H	4.576564000	-3.557841000	-2.445435000
C	-3.416552000	2.985785000	-2.079034000	H	4.889435000	-2.015900000	-2.789012000	C	-3.375634000	3.112601000	-2.061953000	H	4.844233000	-1.859570000	-2.907754000
C	-2.700862000	2.485410000	-3.357144000	C	6.074039000	-2.393036000	-0.292892000	C	-2.615218000	2.613637000	-3.314908000	C	6.060128000	-2.313801000	-0.453527000
H	-1.702995000	2.932720000	-3.499905000	H	6.673297000	-1.665237000	-0.874247000	H	-1.626684000	3.086217000	-3.439495000	H	6.638217000	-1.551448000	-1.011694000
H	-3.315764000	2.727189000	-4.250398000	H	6.441767000	-3.413229000	-0.536398000	H	-3.213373000	2.825859000	-4.226988000	H	6.437585000	-3.315811000	-0.751205000
H	-2.561021000	1.385832000	-3.326310000	H	6.270369000	-2.204238000	0.782844000	H	-2.448742000	1.518291000	-3.262993000	H	6.274580000	-2.172895000	0.626116000
C	-3.829212000	4.472430000	-2.256062000	C	4.557792000	0.940935000	-2.242718000	C	-3.805036000	4.591991000	-2.254040000	C	4.443686000	1.079583000	-2.234905000
H	-4.330827000	4.860629000	-1.344941000	C	3.608801000	0.431075000	-3.356852000	H	-4.345611000	4.970767000	-1.361339000	C	3.506179000	0.586979000	-3.365865000
H	-4.540574000	4.568151000	-3.103737000	H	3.493335000	-0.665741000	-3.355016000	H	-4.485849000	4.679019000	-3.127555000	H	3.454762000	-0.512003000	-3.437948000
H	-2.965608000	5.127858000	-2.476364000	H	3.994205000	0.734250000	-4.354329000	H	-2.944198000	5.261806000	-2.440097000	H	3.859655000	0.976982000	-4.344598000
C	-4.735703000	2.178185000	-1.976407000	H	2.597211000	0.872197000	-3.235152000	C	-4.683424000	2.283041000	-1.991502000	H	2.473951000	0.960677000	-3.203861000
H	-4.547568000	1.096694000	-1.823175000	C	6.022304000	0.525990000	-2.547407000	H	-4.478769000	1.204084000	-1.839217000	C	5.917685000	0.718507000	-2.562156000
H	-5.303745000	2.284295000	-2.923662000	H	6.711054000	0.887014000	-1.754865000	H	-5.232902000	2.384115000	-2.950287000	H	6.601260000	1.066218000	-1.759314000
H	-5.389411000	2.539766000	-1.156035000	H	6.351270000	0.969045000	-3.511674000	H	-5.359859000	2.630009000	-1.183376000	H	6.227706000	1.209638000	-3.509145000
C	-2.708218000	2.063101000	2.982575000	H	6.148033000	-0.570442000	-2.629598000	C	-2.696607000	2.050160000	2.992655000	H	6.071138000	-0.369924000	-2.690244000
C	-1.461344000	1.932361000	3.883238000	C	4.519561000	2.489773000	-2.319346000	C	-1.442230000	1.921895000	3.882322000	C	4.359261000	2.628172000	-2.247993000
H	-0.786630000	1.134112000	3.510751000	H	3.502908000	2.886858000	-2.122179000	H	-0.753225000	1.146954000	3.486648000	H	3.334925000	2.986937000	-2.020728000
H	-1.757188000	1.691079000	4.925704000	H	4.807920000	2.814277000	-3.340937000	H	-1.727094000	1.639656000	4.917542000	H	4.623288000	3.000097000	-3.259702000
H	-0.878853000	2.876300000	3.916642000	H	5.227564000	2.962393000	-1.607527000	H	-0.879757000	2.876348000	3.943893000	H	5.066549000	3.092752000	-1.528437000
H	-3.599625000	0.816316000	-1.138277000	C	3.495404000	1.441678000	2.943485000	C	-3.510757000	0.743691000	-1.963038000	C	3.465071000	1.341209000	2.885058000
H	-4.529194000	0.897994000	2.538090000	C	2.644810000	2.726500000	2.759678000	H	-4.459021000	0.819210000	2.492169000	C	2.666822000	2.661588000	2.852009000
H	-3.900969000	0.687787000	4.199099000	H	3.091095000	3.471808000	2.069644000	H	-3.774458000	0.505733000	4.115087000	H	3.156741000	3.424444000	2.212783000
H	-3.060468000	-0.094259000	2.818413000	H	2.563775000	3.204880000	3.758661000	H	-2.924564000	-0.098374000	2.646643000	H	2.584527000	3.088514000	3.873669000
C	-3.523195000	3.310640000	3.426916000	H	1.623322000	2.491322000	2.398362000	C	-3.570522000	3.222209000	3.519558000	H	1.643449000	2.491000000	2.460479000
H	-2.921394000	4.238014000	3.330962000	C	2.865952000	0.484385000	3.878103000	H	-3.015677000	4.182748000	3.482658000	C	2.776103000	0.357395000	3.854330000
H	-3.834975000	3.211371000	4.489076000	H	1.848920000	0.173834000	3.560061000	H	-3.874819000	3.040213000	4.572891000	H	1.760833000	0.094769000	3.491030000
H	-4.437424000	3.433746000	2.809656000	H	2.786334000	0.983523000	4.866886000	H	-4.490867000	3.339335000	2.910585000	H	2.681299000	0.811003000	4.863216000
C	-1.406474000	-4.086437000	-2.057612000	H	3.479498000	-0.429632000	4.018116000	C	-1.389094000	-4.215102000	-2.109307000	H	3.353637000	-0.583159000	3.968086000
C	-0.025555000	-4.793502000	-2.014325000	C	4.932768000	1.811941000	3.302527000	C	-0.034576000	-4.970914000	-2.087147000	C	4.906061000	1.629444000	3.391411000
H	0.800115000	-4.067640000	-1.865922000	H	5.574687000	0.909100000	3.371877000	H	0.816537000	-4.279512000	-1.920702000	H	5.510558000	0.699445000	3.429981000
H	0.152243000	-5.303263000	-2.983920000	H	4.912660000	2.296943000	4.302538000	H	0.125073000	-5.462800000	-3.069101000	H	4.880946000	2.065975000	4.413078000
H	0.028330000	-5.564726000	-1.218451000	H	5.414306000	2.513582000	2.589844000	H	-0.007224000	-5.762402000	-1.309950000	H	5.429324000	2.344951000	2.723622000
C	-1.372740000	-3.161970000	-3.300175000	Co	-1.166878000	1.284034000	-0.012992000	C	-1.316274000	-3.242911000	-3.313754000	Co	-1.185054000	1.397165000	0.047683000
H	-2.273062000	-2.532391000	-3.400630000	Co	-1.053855000	-1.421400000	0.019736000	H	-2.200318000	-2.589136000	-3.400270000	Co	-1.007107000	-1.579935000	0.050575000
H	-1.281289000	-3.778839000	-4.219977000	Co	2.204076000	0.099868000	0.013844000	H	-1.224961000	-3.822957000	-4.257354000	Co	2.165002000	0.115619000	0.061692000
H	-0.494730000	-2.485625000	-3.202054000	P	0.279414000	0.024253000	1.157837000	H	-0.425070000	-2.587120000	-3.234936000	P	0.176450000	-0.005722000	1.031681000
C	-2.461816000	-5.205571000	-2.262218000	P	-1.100222000	-0.102471000	-1.740700000	C	-2.482612000	-5.288337000	-2.354268000	P	-1.112987000	-0.105359000	-1.670062000
H	-2.530133000	-5.861934000	-1.369595000	P	0.778823000	1.210063000	-1.227421000	H	-2.555772000	-5.987157000	-1.494723000	P	0.722334000	1.287085000	-1.178974000
H	-2.174064000	-5.838347000	-3.128598000	P	0.914582000	-1.231435000	-1.127635000	H	-2.232271000	-5.884165000	-3.257857000	P	0.889652000	-1.263243000	-1.136577000
H	-3.471070000	-4.803589000	-2.471121000					H	-3.482974000	-4.845773000	-2.519285000						

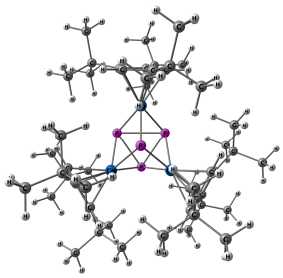
Table S5: Optimized geometry of **4** (singlet, left) and **4** (triplet, right). XYZ coordinates in angstroms. BP86/def2-TZVP level of theory.

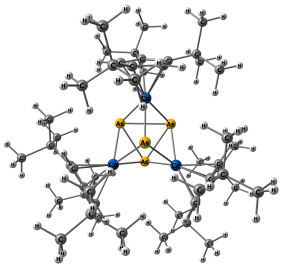


As	1.293862000	-0.115609000	-1.750851000	H	0.914619000	-5.360972000	2.912003000	As	1.363260000	-0.123371000	-1.604216000	H	0.769982000	-5.551206000	2.953899000
As	-0.276085000	0.039221000	1.294459000	H	0.859097000	-4.763783000	4.606107000	As	-0.147786000	0.009344000	1.191328000	H	0.675888000	-4.898335000	4.626026000
As	-0.805719000	1.314751000	-1.262335000	H	2.350343000	-4.555712000	3.624162000	As	-0.740374000	1.388175000	-1.201881000	H	2.194723000	-4.738690000	3.677733000
As	-0.960819000	-1.325296000	-0.136385000	C	5.173514000	-3.812204000	-0.140092000	As	-0.938492000	-1.340582000	-0.126660000	C	5.108661000	-3.939142000	-0.166148000
Co	1.244478000	1.339393000	0.049118000	H	5.124244000	-4.009091000	0.950901000	Co	1.264858000	1.504984000	0.103389000	H	5.068937000	-4.123471000	0.927369000
Co	1.123734000	-1.478236000	0.096031000	H	6.242485000	-3.684660000	-0.416056000	Co	1.062377000	-1.691224000	0.125112000	H	6.171884000	-3.781813000	-0.448676000
Co	-2.271043000	0.119164000	0.074140000	H	4.792809000	-4.711053000	-0.660571000	Co	-2.249428000	0.151210000	0.098570000	H	4.753494000	-4.857085000	-0.673897000
C	3.188699000	2.145169000	0.428768000	C	3.657390000	3.292756000	3.491127000	C	3.188927000	2.287899000	0.424928000	C	3.758823000	3.186849000	3.559770000
H	4.132302000	1.592704000	0.397929000	H	4.564105000	3.395597000	2.859356000	H	4.114650000	1.707876000	0.362000000	H	4.664345000	3.268277000	2.923430000
C	2.388102000	2.318282000	1.607728000	H	3.983694000	3.183761000	4.547978000	C	2.406530000	2.447503000	1.619104000	H	4.086600000	2.972294000	4.599868000
C	1.746075000	3.422551000	-0.591865000	H	3.076066000	4.234200000	3.406261000	C	1.648988000	3.649728000	-0.623244000	H	3.252806000	4.174698000	3.555309000
C	0.768290000	-3.498403000	0.481707000	C	2.715891000	2.692107000	-3.292078000	C	0.679032000	-3.745462000	0.447953000	C	2.622623000	2.806014000	-3.257264000
H	-0.205327000	-3.991274000	0.394554000	H	2.550473000	1.596923000	-3.345316000	H	-0.296042000	-4.234432000	0.358313000	H	2.436774000	1.712379000	-3.253996000
C	-4.234493000	0.448060000	-0.735312000	H	3.324524000	2.983740000	-4.174704000	C	-4.160003000	0.533032000	-0.744252000	H	3.209516000	3.045806000	-4.169861000
C	2.909579000	-2.724746000	-0.026916000	H	1.730419000	3.176351000	-3.383994000	C	2.809155000	-2.643771000	-0.058948000	H	1.643771000	3.305338000	-3.343018000
C	1.288400000	-2.947250000	1.697480000	C	-3.536310000	1.522595000	2.895238000	C	1.192028000	-3.183399000	1.663702000	C	-3.471266000	1.497968000	2.916578000

C	2.577684000	-2.435380000	1.354669000	C	0.130871000	-4.919609000	-1.879007000	C	2.490158000	-2.678880000	1.331858000	C	0.027142000	-5.092726000	-1.953060000
H	3.254702000	-1.939442000	2.057913000	H	0.074058000	-5.664482000	-1.058789000	H	3.166121000	-2.187725000	2.040090000	H	-0.030369000	-5.865845000	-1.159429000
C	-4.159774000	-0.856894000	-0.063630000	H	-0.023195000	-5.463965000	-2.833776000	C	-4.135831000	-0.796303000	-0.098990000	H	-0.135065000	-5.601489000	-2.925972000
C	-3.879930000	1.433617000	0.269109000	H	-0.710345000	-4.204731000	-1.768793000	C	-3.826586000	1.491260000	0.292957000	H	-0.808151000	-4.376393000	-1.811174000
H	-3.853043000	2.514226000	0.094306000	C	3.670344000	0.798225000	3.195293000	H	-3.773007000	2.574464000	0.145093000	C	3.559118000	0.721681000	3.073334000
C	-3.799157000	-0.590555000	1.319889000	H	3.102374000	-0.100242000	2.890964000	C	-3.800768000	-0.568961000	1.290711000	H	2.922100000	-0.088645000	2.667071000
H	-3.696074000	-1.359446000	2.092895000	H	3.993750000	0.665098000	4.249107000	H	-3.712911000	-1.355357000	2.047811000	H	3.844454000	0.458642000	4.113848000
C	1.271984000	3.109036000	1.195963000	H	4.586697000	0.855719000	2.572605000	C	1.307341000	3.285636000	1.244485000	H	4.491565000	0.757590000	2.473356000
H	0.470416000	3.448395000	1.859498000	C	4.523748000	-2.231132000	-2.010226000	H	0.519587000	3.620585000	1.926668000	C	4.406937000	-2.416244000	-2.059011000
C	2.645726000	2.889187000	-0.684841000	H	4.233837000	-3.085191000	-2.649742000	C	2.637853000	3.072083000	-0.663410000	H	4.144629000	-3.287727000	-2.686531000
C	0.712295000	-3.163739000	3.097917000	H	5.584188000	-1.997657000	-2.241041000	C	0.589309000	3.348625000	3.058841000	H	5.462254000	-2.157936000	-2.287183000
C	1.483169000	-3.311315000	-3.192870000	H	3.907503000	-1.356436000	-2.306210000	C	1.372689000	-3.434897000	-3.207248000	H	3.771350000	-1.561525000	-2.371688000
H	0.608859000	-2.628966000	-3.181642000	C	-2.648465000	2.780426000	2.790537000	H	0.500029000	-2.751489000	-3.158702000	C	-2.563074000	2.742408000	2.828534000
H	1.394575000	-3.954476000	-4.094721000	H	-1.622814000	2.506688000	2.469783000	H	1.275069000	-4.038099000	-4.135554000	H	-1.549872000	2.460545000	2.475719000
H	2.389307000	-2.691926000	-3.305814000	H	-2.584730000	3.295447000	3.772622000	H	2.276959000	-2.810734000	-3.302111000	H	-2.468908000	3.225960000	3.823911000
C	1.405830000	3.508357000	-0.191660000	H	-3.052605000	3.508653000	2.057824000	C	1.430487000	3.713741000	-0.134387000	H	-2.970341000	3.499585000	2.127700000
C	2.805915000	2.065680000	3.057102000	C	-4.646305000	2.431374000	-2.277178000	C	2.809790000	2.068837000	3.044064000	C	-4.484464000	2.556060000	-2.253207000
C	0.511522000	4.675329000	-0.693319000	H	-5.321199000	2.932879000	-1.553305000	C	0.520111000	4.871545000	-0.621262000	H	-5.170923000	3.060412000	-1.542314000
C	-0.830620000	-3.204837000	3.073654000	H	-4.973068000	2.726780000	-3.296099000	C	-0.953678000	-3.363790000	3.002117000	H	-4.769669000	2.878957000	-3.276072000
H	-1.250725000	-2.256779000	2.679180000	H	-3.618980000	2.824868000	-2.132858000	H	-1.348408000	-2.422726000	2.566111000	H	-3.453656000	2.921549000	-2.067533000
H	-1.226798000	-3.361191000	4.098975000	C	-6.172156000	0.473157000	-2.373888000	H	-1.375378000	-3.479469000	4.022753000	C	-6.060249000	0.642347000	-2.420156000
H	-1.210732000	-4.035339000	2.443945000	H	-6.308102000	-0.624787000	-2.393105000	H	-1.334497000	-4.208082000	2.391446000	H	-6.224139000	-0.450160000	-2.483534000
C	-3.653152000	0.814061000	1.545120000	H	-6.540186000	0.870690000	-3.343988000	C	-3.624112000	0.831756000	1.550088000	H	-6.398845000	1.084808000	-3.381214000
C	-4.625415000	-2.290009000	-0.433578000	H	-6.821986000	0.878847000	-1.570301000	C	-4.628859000	-2.207336000	-0.513950000	H	-6.714537000	1.036951000	-1.614674000
C	4.369467000	-2.530829000	-0.504730000	C	-6.124474000	-2.403893000	-0.032829000	C	4.258006000	-2.694410000	-0.548857000	C	-6.139032000	-2.287745000	-0.148629000
C	1.183313000	-2.074674000	4.082117000	H	-6.263203000	-2.186533000	1.046374000	C	1.052984000	-2.226911000	4.010265000	H	-6.294768000	-2.098039000	0.933592000
H	2.288575000	-2.056170000	4.177536000	H	-6.501698000	-3.430758000	-0.229126000	H	2.156062000	-2.212875000	4.127720000	H	-6.540546000	-3.296778000	-0.384474000
H	0.767756000	-2.264524000	5.094051000	H	-6.756475000	-1.692885000	-0.600785000	H	0.613888000	-2.368809000	5.020069000	H	-6.737936000	-1.542094000	-0.707755000
H	0.845960000	-1.071089000	3.751907000	C	2.572813000	-5.309717000	-2.075735000	H	0.735545000	-1.233068000	3.631303000	C	2.469538000	-5.482420000	-2.171035000
C	0.278044000	4.762577000	-2.216472000	H	3.582162000	-4.903816000	-2.275800000	C	0.238531000	4.927506000	-2.137390000	H	3.485279000	-5.070642000	-2.320713000
H	1.205853000	4.973747000	-2.779381000	H	2.307425000	-5.968198000	-2.929884000	H	1.146084000	5.126118000	-2.736611000	H	2.224102000	-6.092768000	-3.066299000
H	-0.425597000	5.594236000	-2.430852000	H	2.630000000	-5.940781000	-1.164378000	H	-0.474793000	5.751808000	-2.348517000	H	2.503347000	-6.161765000	-1.293674000
H	-0.173487000	3.829607000	-2.612605000	C	3.954843000	4.542691000	-2.079747000	H	-0.220921000	3.982476000	-2.495012000	C	3.895792000	4.699695000	-2.140362000
C	-0.887836000	4.625033000	-0.025870000	H	3.122657000	5.252038000	-2.250324000	C	-0.862152000	4.812207000	0.081083000	H	3.055047000	5.403807000	-2.289468000
H	-1.404629000	3.661948000	-0.218826000	H	4.665301000	4.656540000	-2.926056000	H	-1.365438000	3.838243000	-0.092859000	H	4.569035000	4.797727000	-3.018646000
H	-1.521896000	5.439261000	-0.433551000	H	4.479330000	4.847748000	-1.150183000	H	-1.516893000	5.614497000	-0.317838000	H	4.458168000	5.026649000	-1.240751000
H	-0.840613000	4.769421000	1.070996000	C	-2.957012000	0.579910000	3.971595000	H	-0.791527000	4.966990000	1.175641000	C	-2.889277000	0.516943000	3.956124000
C	3.465805000	3.070789000	-1.991992000	H	-3.604999000	-0.306535000	4.132064000	C	3.417379000	3.229494000	-1.997267000	H	-3.548430000	-0.362746000	4.107369000
C	1.503204000	-4.195491000	-1.921973000	H	-2.874241000	1.109583000	4.944091000	C	1.401471000	-4.373632000	-1.974946000	H	-2.777405000	1.019226000	4.939896000
C	1.574729000	1.962408000	3.982977000	H	-1.946259000	0.222340000	3.684285000	C	1.579555000	1.993941000	3.972831000	H	-1.891448000	0.149578000	3.638421000
H	1.009986000	2.916845000	4.022845000	C	4.736763000	2.184327000	-1.955117000	H	1.065887000	2.973946000	4.056300000	C	4.694155000	2.350136000	-1.978880000
H	1.888363000	1.722455000	5.005929000	H	5.427956000	2.468470000	-1.135452000	H	1.484261000	1.692795000	4.986995000	H	5.399976000	2.647948000	-1.176589000
H	0.876669000	1.172814000	3.634415000	H	5.290797000	2.298567000	-2.909760000	H	0.840289000	1.254069000	3.600061000	H	5.226993000	2.457414000	-2.946406000
C	-4.692817000	0.886053000	-2.150103000	H	4.483072000	1.110405000	-1.844182000	C	-4.574247000	1.010342000	-2.159116000	H	4.450360000	1.275437000	-1.851847000
C	-3.798593000	0.335517000	-3.289333000	C	-3.840626000	-3.346594000	0.388581000	C	-3.674093000	0.455297000	-3.291930000	C	-3.890001000	-3.301251000	0.301252000
H	-2.778011000	0.767735000	-3.223762000	H	-2.747767000	-3.256377000	0.217690000	H	-2.645501000	0.864105000	-3.207549000	H	-2.792124000	-3.239278000	0.151507000
H	-4.222571000	0.617374000	-4.277393000	H	-4.155146000	-4.366265000	0.082892000	H	-4.079548000	0.759601000	-4.280855000	H	-4.227591000	-4.305092000	-0.030606000
H	-3.695486000	-0.762191000	-3.265229000	H	-4.021679000	-3.265291000	1.478389000	H	-3.594856000	-0.644494000	-3.281551000	H	-4.090071000	-3.236902000	1.388864000
C	5.033525000	-1.356145000	0.256446000	C	-4.468187000	-2.697913000	-1.914266000	C	4.867593000	-1.470991000	0.182507000	C	-4.449703000	-2.587198000	-1.999697000
H	4.442002000	-0.427507000	0.149960000	H	-5.081858000	-2.084755000	-2.599216000	H	4.237129000	-0.570680000	0.039048000	H	-5.031445000	-1.943527000	-2.684500000
H	6.049860000	-1.174465000	-0.150005000	H	-4.797188000	-3.751189000	-2.040538000	H	5.879725000	-1.260283000	-0.220931000	H	-4.804551000	-3.628007000	-2.154512000
H	5.151503000	-1.566060000	1.337943000	H	-3.409747000	-2.635034000	-2.242026000	H	4.983216000	-1.639393000	1.271428000	H	-3.382708000	-2.548166000	-2.302077000
C	1.189264000	5.992216000	-0.210656000	C	-4.970200000	1.947788000	3.317248000	C	1.197557000	6.201560000	-0.178590000	C	-4.892376000	1.932320000	3.372941000
H	1.302179000	5.999738000	0.893062000	H	-5.416518000	2.646197000	2.579039000	H	1.345972000	6.223800000	0.920781000	H	-5.338300000	2.658294000	2.661827000
H	0.566100000	6.866639000	-0.496988000	H	-4.954442000	2.455800000	4.305860000	H	0.559256000	7.067984000	-0.456118000	H	-4.851842000	2.411718000	4.374689000
H	2.195242000	6.131521000	-0.651234000	H	-5.640208000	1.066316000	3.394986000	H	2.188429000	6.341708000	-0.652414000	H	-5.575293000	1.059727000	3.437172000
C	1.241208000	-4.542306000	3.586423000					C	1.087220000	-4.714337000	3.610152000				

Table S6: Optimized geometry of **5** (dublet, left) and **6** (dublet, right). XYZ coordinates in angstroms. BP86/def2-TZVP level of theory.

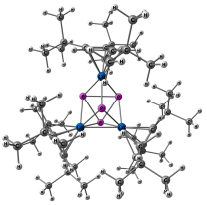


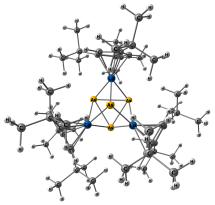


Co	-0.927173000	1.605539000	0.035465000	H	4.641874000	-3.023285000	-3.345889000	As	-0.184516000	-0.032661000	1.284155000	C	3.511020000	-0.505100000	3.154165000
Co	2.156201000	-0.192624000	0.012740000	H	3.340679000	-3.030178000	-2.115993000	As	-1.032167000	1.274187000	-1.177011000	H	4.433455000	-0.430947000	2.542088000
Co	-1.210212000	-1.354373000	0.012578000	C	-3.485065000	-0.601910000	3.071660000	As	-0.675511000	-1.421620000	-1.228210000	H	3.786279000	-0.264271000	4.203686000
P	0.202033000	-0.014207000	1.160250000	H	-2.825218000	0.195750000	2.680722000	As	1.285919000	0.205980000	-1.645017000	H	2.797994000	0.260673000	2.791947000
P	0.942785000	1.225331000	-1.142568000	H	-3.748584000	-0.363726000	4.124702000	Co	0.912225000	1.735685000	0.104418000	C	4.228955000	2.645727000	-2.068325000
P	-1.065166000	0.151482000	-1.691628000	H	-4.424936000	-0.590461000	2.481849000	Co	1.321307000	-1.417686000	0.071571000	H	3.628836000	1.769809000	-2.394050000
P	0.691077000	-1.302491000	-1.192710000	C	5.956201000	-0.787041000	-2.574790000	Co	-2.218533000	-0.276924000	0.073034000	H	5.294341000	2.442987000	-2.309113000
C	-2.400561000	-2.290421000	1.533616000	H	6.130347000	0.303660000	-2.648521000	C	2.621898000	3.056889000	-0.047207000	H	3.921070000	3.519569000	-2.672079000
C	-2.400666000	2.623567000	1.236149000	H	6.255895000	-1.236498000	-3.546582000	C	1.432787000	3.736228000	-0.678240000	C	-4.570911000	-1.185214000	-2.187243000
H	-3.102712000	2.153436000	1.932638000	H	6.636221000	-1.185475000	-1.791900000	C	2.330938000	2.755863000	1.341809000	C	-3.692124000	-0.568451000	-3.305051000
C	-1.333876000	-3.150476000	1.111509000	C	0.751900000	-4.720736000	-0.133504000	H	3.035930000	2.287644000	2.037219000	H	-3.655052000	0.533141000	-3.259752000
H	-0.540070000	-3.523758000	1.766922000	H	1.270958000	-3.750114000	-0.274059000	C	0.467782000	3.766480000	0.490909000	H	-4.081882000	-0.860509000	-4.305289000
C	-1.099498000	3.099857000	1.587752000	H	1.381046000	-5.520439000	-0.578215000	H	-0.526558000	4.219846000	0.424285000	H	-2.647872000	-0.935853000	-3.220377000
C	3.559288000	-0.910328000	1.466747000	H	0.688594000	-4.923094000	0.954022000	C	0.838142000	4.742012000	3.631181000	C	0.709263000	-4.900426000	-2.219649000
C	-3.207153000	-2.085669000	0.367770000	C	-4.815019000	-2.101936000	-1.966114000	H	1.943222000	4.836117000	3.683990000	H	0.191295000	-3.991045000	-2.588851000
H	-4.120572000	-1.482638000	0.345704000	H	-5.478800000	-2.421287000	-1.136276000	H	0.430270000	4.908636000	4.652455000	H	0.073590000	-5.778401000	-2.463575000
C	-0.553414000	3.658425000	0.383679000	H	-5.393479000	-2.192222000	-2.909483000	H	0.460005000	5.553168000	2.974016000	H	1.655072000	-5.020326000	-2.779674000
H	0.430471000	4.133723000	0.317725000	H	-4.572622000	-1.029542000	-1.824576000	C	1.509881000	-3.188794000	1.206261000	C	1.648652000	-1.987628000	3.983908000
C	4.099656000	-0.637574000	-0.833952000	C	-1.218022000	4.309977000	-2.049174000	H	0.737375000	-3.597410000	1.866583000	H	0.841260000	-1.320389000	3.613973000
C	-1.505117000	3.586137000	-0.702877000	C	-0.919482000	4.661816000	3.515533000	C	-3.817112000	0.296514000	1.317058000	H	1.914881000	-1.684536000	5.019115000
C	3.774295000	0.478915000	1.201774000	H	-0.533312000	5.466734000	2.855243000	H	-3.781656000	1.057801000	2.103806000	H	1.241846000	-3.019356000	4.034614000
H	3.726243000	1.271209000	1.956664000	H	-0.515393000	4.832750000	4.537558000	C	1.015938000	3.199403000	1.690415000	C	0.925604000	-4.830453000	-0.692937000
C	4.102488000	0.687045000	-0.198541000	H	-2.024304000	4.762976000	3.562461000	C	2.527647000	-2.266860000	1.620453000	C	-0.485755000	-4.896231000	-0.052861000
C	-2.682553000	2.890931000	-0.160310000	C	-4.204633000	2.333982000	-2.196717000	C	-1.119720000	3.264434000	3.058158000	H	-0.449650000	-5.017366000	1.047580000
C	-2.711944000	-2.866487000	-0.749847000	H	-3.924078000	3.189710000	-2.838917000	H	-1.536005000	3.350777000	4.048727000	H	-1.038640000	-5.789044000	-0.459996000
C	3.414557000	-1.572396000	2.837188000	H	-5.246475000	2.055426000	-2.463246000	H	-1.457829000	2.302841000	2.619561000	H	-1.071154000	-3.980674000	-0.277548000
C	3.728002000	-1.576657000	0.206388000	H	-3.538253000	1.482412000	-2.447023000	H	-1.557687000	4.086105000	2.454287000	C	-2.386991000	-2.988301000	2.732478000
H	3.637216000	-2.658845000	0.064241000	C	6.131708000	2.158461000	-0.332482000	C	3.325012000	-2.031162000	0.453111000	H	-2.721906000	-3.731423000	1.979618000
C	-2.775523000	-1.966408000	2.980445000	H	6.326408000	1.970747000	0.744131000	H	4.201524000	-1.375874000	0.424892000	H	-2.284170000	-3.518530000	3.703973000
C	-1.509755000	-3.549924000	-0.271349000	H	6.533689000	3.164223000	-0.585300000	C	1.148544000	4.487903000	-1.917761000	H	-1.388616000	-2.616731000	2.423042000
C	-4.119193000	2.665313000	-0.691890000	H	6.703176000	1.406926000	-0.912904000	C	2.874816000	-2.853454000	-0.656258000	C	3.715116000	-2.942121000	-1.961101000
C	2.469526000	-2.790861000	2.765131000	C	-1.137701000	3.369686000	-3.278209000	C	0.422690000	3.343830000	3.093768000	C	-0.068406000	-0.866116000	-2.444186000
H	1.446325000	-2.480854000	2.718453000	H	-0.282686000	2.667111000	-3.169035000	C	0.966106000	2.263164000	4.050482000	H	-6.709241000	-1.314134000	-1.561188000
H	2.369249000	-3.268447000	3.763728000	H	-0.974514000	3.970602000	-4.199954000	H	2.069144000	2.326246000	4.155398000	H	-6.389730000	-1.285378000	-3.422552000
H	2.851699000	-3.561181000	2.063737000	H	-2.049039000	2.764834000	-3.422769000	H	0.710780000	1.249868000	3.674968000	H	-6.274834000	0.221064000	-2.467912000
C	-0.509402000	3.258595000	2.989563000	C	-0.639777000	-4.711790000	-0.819450000	H	0.527443000	2.386370000	5.063924000	C	-4.429365000	-2.723626000	-2.331402000
C	4.608754000	2.086201000	-0.636936000	C	-4.777969000	1.481773000	0.060090000	C	-3.556913000	-1.096509000	1.517140000	H	-3.382717000	-3.055180000	-2.173649000
C	2.867486000	-0.567308000	3.873064000	H	-4.138509000	0.579593000	0.001697000	C	1.153366000	3.587692000	-3.178049000	H	-4.724009000	-3.026849000	-3.358540000
H	3.563221000	0.285042000	4.021905000	H	-5.766322000	1.250179000	-0.389526000	H	2.097087000	3.032197000	-3.309445000	H	-5.081445000	-3.272857000	-1.620731000
H	2.729181000	-1.059924000	4.859476000	H	-4.952720000	1.708187000	1.130830000	H	0.993569000	4.210317000	-4.085786000	C	4.326887000	-4.363090000	-2.096162000
H	1.890655000	-0.162452000	3.535734000	C	3.545735000	-0.592303000	-3.366875000	H	0.332416000	2.843117000	-3.123881000	H	4.891891000	-4.641724000	-1.181610000
C	-1.526514000	-1.960632000	3.887529000	H	3.509866000	-0.961224000	-3.213586000	C	-4.182379000	0.556940000	-0.066514000	H	5.031496000	-4.395741000	-2.955415000
H	-1.058111000	-2.965752000	3.940737000	H	3.896180000	-0.940986000	-4.363455000	C	-3.731115000	-1.710565000	0.228972000	H	3.558401000	-5.140699000	-2.269496000
H	-1.798759000	-1.665950000	4.923568000	H	3.502208000	0.509550000	-3.384796000	H	-3.615881000	-2.782787000	0.036001000	C	2.940124000	-2.580575000	-3.252033000
H	-0.766607000	-1.250225000	3.499240000	C	-2.787917000	-2.489032000	-3.330111000	C	-4.158514000	-0.739115000	-0.760125000	H	2.051700000	-3.213795000	-3.412379000
C	4.477838000	-1.135323000	-2.254005000	H	-2.494962000	-1.424082000	-3.222071000	C	4.736784000	1.671904000	0.151291000	H	3.604125000	-2.695352000	-4.136528000
C	-3.535479000	-2.973797000	-2.064014000	H	-3.449164000	-2.584342000	-4.218997000	H	4.875717000	1.837620000	1.238127000	H	2.593857000	-1.526734000	-3.212867000
C	1.032042000	3.166268000	2.952829000	H	-1.866791000	-3.061724000	-3.533802000	H	5.742204000	1.483339000	-0.280546000	C	-6.271552000	1.948895000	-0.066567000
H	1.353329000	2.195749000	2.520021000	C	-4.021864000	-4.433415000	-2.268477000	H	4.114864000	0.763955000	0.020960000	H	-6.831567000	1.200966000	-0.662167000
H	1.451094000	3.256073000	3.977989000	H	-3.186264000	-5.132440000	-2.462597000	C	-0.258134000	5.140529000	-1.870140000	H	-6.723149000	2.947096000	-0.258159000
H	1.476834000	3.978463000	2.341163000	H	-4.709715000	-4.488883000	-3.139981000	H	-1.053452000	4.376909000	-1.743907000	H	-6.421542000	1.704779000	1.005778000
C	4.822415000	-2.049950000	3.288240000	H	-4.572115000	-4.800432000	-1.376289000	H	-0.450536000	5.671734000	-2.826220000	C	3.931390000	-2.954318000	3.552261000
H	5.239623000	-2.795659000	2.578983000	C	-1.337239000	-6.049914000	-0.440139000	H	-0.348532000	5.882941000	-1.050458000	H	3.521499000	-3.984778000	3.495587000
H	4.777848000	-2.521197000	4.294857000	H	-1.475619000	-6.123604000	0.658876000	C	4.077362000	2.885579000	-0.551592000	H	4.221685000	-2.758370000	4.608098000
H	5.534065000	-1.198840000	3.339617000	H	-0.718199000	-6.914739000	-0.765397000	C	-4.586570000	2.401029000	-1.890607000	H	4.851000000	-2.921197000	2.930875000
C	3.914645000	3.196855000	0.195039000	H	-2.334667000	-6.148873000	-0.910920000	H	-3.514982000	2.411279000	-2.180285000	C	-3.385706000	-1.817856000	2.855163000
H	2.812004000	3.139400000	0.088714000	C	-2.276261000	5.416461000	-2.298570000	H	-4.983190000	3.432035000	-2.012264000	C	1.692653000	-6.103841000	-0.231804000
H	4.248675000	4.195001000	-0.159325000	H	-3.284047000	5.002095000	-2.491486000	H	-5.134109000	1.757734000	-2.604031000	H	2.710227000	-6.154003000	-0.666723000
H	4.158537000	3.137458000	1.274302000	H	-1.993560000	6.023160000	-3.186295000	C	1.711658000	-3.597322000	-0.170759000	H	1.143822000	-7.021084000	-0.538948000
C	4.371150000	2.454599000	-2.117999000	H	-2.350476000	6.101587000	-1.427503000	C	2.886792000	-1.911385000	3.064826000	H	1.798226000	-6.121946000	0.872956000
H	4.935256000	1.809388000	-2.816753000	C	-3.747420000	-3.074130000	3.472985000	C	2.162610000	5.649610000	-2.092109000	C	4.914348000	-1.960803000	-1.893989000
H	4.708007000	3.498364000	-2.296648000	H	-4.669865000	-3.101893000	2.855395000	H	2.165833000	6.312293000	-1.200773000	H	4.578210000	-0.911480000	-1.772381000
H	3.292411000	2.391956000	-2.371720000	H	-4.045803000	-2.895977000	4.529727000	H	1.891858000	6.267597000	-2.975856000	H	5.493465000	-2.021337000	-2.839424000

C	-1.057883000	2.182486000	3.947743000	H	-3.272038000	-4.076114000	3.415859000	H	3.197093000	5.287503000	-2.246909000	H	5.607367000	-2.203492000	-1.062339000
H	-2.158931000	2.259875000	4.064195000	C	0.154853000	5.029553000	-1.980220000	C	-4.757395000	1.954204000	-0.422614000	C	-2.891708000	-0.844840000	3.946914000
H	-0.607086000	2.293882000	4.957123000	H	0.186626000	5.796231000	-1.178471000	C	4.886142000	4.152046000	-0.150697000	H	-1.924498000	-0.387674000	3.649938000
H	-0.819009000	1.170408000	3.560169000	H	0.349197000	5.544746000	-2.944676000	H	4.495564000	5.066258000	-0.639948000	H	-2.747990000	-1.381263000	4.909416000
C	-4.969285000	3.931038000	-0.386428000	H	0.979782000	4.307416000	-1.812136000	H	5.954308000	4.040158000	-0.439535000	H	-3.621278000	-0.027720000	4.127164000
H	-4.970965000	4.146793000	0.702605000	C	-0.370840000	-4.684462000	-2.339240000	H	4.843539000	4.312816000	0.946800000	C	-4.772876000	-2.380376000	3.272377000
H	-6.023562000	3.778018000	-0.705742000	H	-1.289301000	-4.826007000	-2.938750000	C	-4.083516000	3.052059000	0.442018000	H	-5.520984000	-1.565063000	3.367368000
H	-4.583546000	4.829383000	-0.906285000	H	0.323451000	-5.509077000	-2.608752000	H	-4.303153000	2.937444000	1.522192000	H	-4.710020000	-2.904612000	4.251445000
C	4.372573000	-2.681350000	-2.324022000	H	0.104086000	-3.723937000	-2.631289000	H	-4.457242000	4.052722000	0.138028000	H	-5.154811000	-3.102941000	2.520685000
H	5.062137000	-3.180477000	-1.611777000					H	-2.981773000	3.036728000	0.315768000				

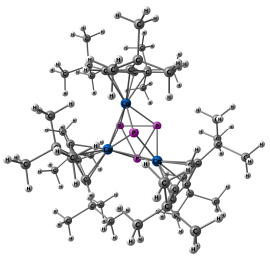
Table S7: Optimized geometry of **7** (dublet, left) and **8** (dublet, right). XYZ coordinates in angstroms. BP86/def2-TZVP level of theory.

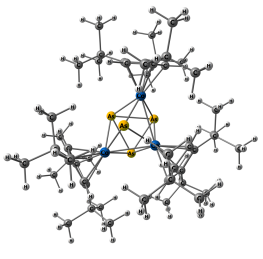




Co	1.064205000	-1.432761000	0.053175000	C	-4.389599000	2.477533000	-2.403167000	As	-1.280047000	0.370435000	-1.740671000	H	4.672916000	2.426023000	1.438416000
Co	1.190325000	1.294186000	0.017616000	H	-5.117637000	2.976038000	-1.731102000	As	0.148098000	-0.294541000	1.365170000	C	4.287322000	-1.826572000	-2.130684000
Co	-2.229394000	0.120146000	0.080479000	H	-4.629191000	2.787716000	-3.440820000	As	1.181262000	0.950925000	-1.440097000	C	4.878509000	1.723283000	-1.955757000
P	-0.261722000	0.027433000	1.058026000	H	-3.374866000	2.860536000	-2.170861000	Co	-0.601859000	1.586325000	0.119997000	H	5.334645000	0.981849000	-2.636468000
P	1.123157000	-0.103226000	-1.709817000	C	5.063644000	-3.820752000	-0.284647000	As	0.452243000	-1.551699000	-1.080279000	H	5.418249000	2.680069000	-2.111189000
P	-0.926294000	-1.232083000	-1.095633000	H	6.132293000	-3.711080000	-0.565705000	Co	2.152420000	-0.454942000	0.120759000	H	3.824205000	1.879808000	-2.266170000
P	-0.779602000	1.227326000	-1.201769000	H	4.659005000	-4.700327000	-0.819016000	Co	-1.620692000	-1.062294000	0.044652000	C	-1.672430000	-4.456848000	-0.630540000
C	2.615301000	2.824135000	-0.763619000	H	5.017140000	-4.032355000	0.803558000	C	0.119446000	3.072079000	3.167627000	C	3.548356000	-1.111528000	-3.289039000
C	2.306147000	2.319614000	1.540154000	C	-4.549638000	-2.273727000	-0.637958000	C	1.321648000	4.703170000	-1.750441000	H	2.453071000	-1.279473000	-3.218914000
C	0.658259000	-3.138776000	3.004131000	C	-5.928684000	0.537164000	-2.632262000	H	1.919808000	3.771468000	-1.681267000	H	3.885359000	-1.530700000	-4.260429000
C	3.129901000	2.111859000	0.376641000	H	-6.071858000	-0.557064000	-2.710562000	H	1.588681000	5.356715000	-0.895394000	H	3.724524000	-0.022897000	-3.315151000
H	4.068842000	1.551382000	0.381059000	H	-6.224881000	0.980442000	-3.605901000	H	1.636015000	5.223367000	-2.677910000	C	-3.974114000	0.153377000	3.052437000
C	1.234164000	-2.937762000	1.604986000	H	-6.626516000	0.919510000	-1.858474000	C	-3.436406000	3.510833000	-0.535927000	H	-3.139669000	0.843969000	2.829392000
C	-4.112491000	0.469616000	-0.868353000	C	2.747949000	2.448488000	-3.340637000	C	4.978362000	1.318097000	-0.470961000	H	-4.334208000	0.369593000	4.079127000
C	1.370952000	-3.149986000	-3.289322000	H	2.622512000	1.347090000	-3.306378000	C	3.391135000	-1.468707000	1.579856000	H	-4.807771000	0.371351000	2.355092000
H	1.286181000	-3.762754000	-4.211274000	H	3.367925000	2.689141000	-4.229412000	C	3.848346000	-0.139220000	1.330353000	C	0.262288000	3.437545000	0.554717000
H	2.278518000	-2.528891000	-3.376247000	H	1.748504000	2.888923000	-3.494320000	H	3.940245000	0.638855000	2.096193000	H	1.334683000	3.650182000	0.506866000
H	0.495205000	-2.469270000	-3.263044000	C	-3.844717000	-3.344038000	0.235952000	C	1.624385000	2.739172000	3.215680000	C	-2.161799000	-2.727411000	1.200661000
C	-0.011168000	-4.768390000	-2.015286000	H	-2.741147000	-3.258266000	0.162656000	H	1.994334000	2.804680000	4.259356000	H	-1.515529000	-3.240617000	1.919351000
H	-0.830849000	-4.034987000	-1.869704000	H	-4.133901000	-4.355497000	-0.114833000	H	2.223790000	3.446645000	2.607438000	C	-3.886168000	4.914364000	-0.032105000
H	-0.079944000	-5.542273000	-1.223787000	H	-4.123635000	-3.281866000	1.306022000	H	1.821336000	1.712784000	2.846009000	H	-4.943824000	5.092665000	-0.319167000
H	-0.189586000	-5.271214000	-2.987517000	C	2.838515000	-2.692209000	-0.140767000	C	3.430099000	-2.131870000	0.305809000	H	-3.273602000	5.729762000	-0.461506000
C	2.518919000	-2.415196000	1.248117000	C	-3.839163000	-0.609410000	1.190575000	H	3.139751000	-3.175389000	0.146892000	H	-3.816254000	4.982085000	1.073039000
H	3.203279000	-1.923946000	1.947592000	H	-3.777069000	-1.389829000	1.956183000	C	4.210771000	0.036261000	-0.065245000	C	-2.286923000	-3.099294000	-0.195520000
C	1.379821000	-4.081541000	-2.051880000	C	1.097519000	-2.019206000	3.966951000	C	-3.706675000	-1.316038000	0.297614000	C	6.473660000	1.091186000	-0.103088000
C	-0.882380000	-3.214302000	2.968147000	H	2.200229000	-1.968881000	4.072308000	H	-4.469693000	-0.537810000	0.203142000	H	6.588325000	0.862713000	0.976504000
H	-1.318912000	-2.285463000	2.546671000	H	0.676404000	-2.197136000	4.977689000	C	-3.072595000	-1.681666000	1.535278000	H	7.062028000	2.006791000	-0.323682000
H	-1.280926000	-3.348311000	3.994682000	H	0.738154000	-1.030805000	3.614954000	C	-0.653934000	2.130028000	4.110890000	H	6.917358000	0.253410000	-0.675782000
H	-1.241808000	-4.070308000	2.361639000	C	4.773776000	2.159145000	-1.935543000	H	-0.564650000	1.073185000	3.784731000	C	3.883657000	-3.321780000	-2.218666000
C	4.294770000	-2.510612000	-0.627201000	H	5.417031000	2.532082000	-1.112433000	H	-1.731349000	2.387624000	4.161464000	H	4.431415000	-3.950451000	-1.487522000
C	1.199677000	3.099950000	1.088234000	H	5.350390000	2.260391000	-2.877293000	H	-0.247692000	2.203591000	5.140683000	H	4.124817000	-3.703741000	-3.231720000
H	0.384684000	3.457790000	1.725010000	H	4.591396000	1.077541000	-1.776611000	C	-1.789110000	2.865319000	1.340470000	H	2.794619000	-3.464725000	-2.061844000
C	1.660669000	-3.361866000	-0.702897000	C	-3.499490000	0.379026000	-3.385992000	H	-2.600377000	2.553427000	2.005947000	H	-3.159657000	-2.058587000	-3.392427000
C	2.422103000	-5.215609000	-2.248423000	H	-2.487340000	0.819719000	-3.265943000	C	-0.444384000	3.657431000	-3.149308000	H	-2.721715000	-1.042520000	-3.469386000
H	2.125572000	-5.841492000	-3.115804000	H	-3.867887000	0.659192000	-4.395272000	H	-0.182584000	4.317154000	-4.002883000	H	-3.778774000	-2.220148000	-4.299426000
H	2.474100000	-5.873759000	-1.356561000	H	-3.395377000	-0.718322000	-3.354818000	H	-1.489190000	3.332461000	-3.282445000	H	-2.330488000	-2.783891000	-3.416575000
H	3.437673000	-4.829288000	-2.453480000	C	3.592348000	0.843686000	3.162740000	H	0.202085000	2.758692000	-3.217097000	C	-4.894626000	-3.488090000	-2.220336000
C	-3.693674000	0.796402000	1.447275000	H	3.070817000	-0.077249000	2.841943000	C	-4.386377000	2.467499000	0.101535000	H	-4.266035000	-4.388929000	-2.353639000
C	2.686582000	2.079034000	2.997726000	H	3.878813000	0.721826000	4.227478000	H	-4.026466000	1.437985000	-0.090087000	H	-5.578658000	-3.429442000	-3.092410000
C	-3.833432000	1.440655000	0.174555000	H	4.529614000	0.936384000	2.577246000	H	-5.400838000	2.571612000	-0.333082000	H	-5.513975000	-3.629007000	-1.310466000
H	-3.776542000	2.522090000	0.017175000	C	-2.968042000	0.527626000	3.859588000	H	-4.489758000	2.598799000	1.196029000	C	-4.710193000	-2.241065000	3.281330000
C	0.215585000	4.523500000	-2.414058000	H	-3.561615000	-0.399346000	3.995908000	C	-0.083556000	4.539787000	3.643876000	H	-5.556954000	-2.068502000	2.585416000
H	1.141704000	4.697475000	-2.990924000	H	-2.914524000	1.034003000	4.845307000	H	0.293294000	4.657607000	4.681837000	H	-5.067740000	-2.043689000	4.314084000
H	-0.497376000	5.325961000	-2.693906000	H	-1.938531000	0.238317000	3.562943000	H	-1.156600000	4.821817000	3.632418000	H	-4.422632000	-3.310539000	3.214968000
C	-0.224665000	3.555489000	-2.731274000	C	1.431494000	1.940211000	3.884450000	H	0.466301000	5.252593000	2.995193000	C	-0.351656000	-4.743359000	0.131931000
C	3.454189000	2.962221000	-2.062655000	H	0.829405000	2.871443000	3.899200000	C	-1.989469000	3.290587000	-0.032980000	H	0.062771000	-5.712737000	-0.211290000
C	0.695381000	-3.455996000	0.386110000	H	1.721769000	1.717568000	4.931657000	C	-0.425444000	3.020918000	1.741189000	H	-0.492719000	-4.822015000	1.227155000
H	-0.286114000	-3.931946000	0.297113000	H	0.776644000	1.119599000	3.525003000	C	3.961752000	-1.265388000	-0.721336000	H	0.419776000	-3.968462000	-0.061033000
C	-4.462174000	0.931589000	-2.304846000	C	-5.057615000	1.803727000	3.241286000	C	-4.050989000	-2.185011000	-2.133477000	C	4.516282000	-2.799804000	3.325928000
C	3.865052000	4.449288000	-2.246340000	H	-5.540671000	2.493347000	2.518639000	C	-0.669637000	3.671447000	-0.539345000	H	4.823368000	-3.559676000	2.577819000
H	3.006704000	5.101776000	-2.491935000	H	-5.059976000	2.291889000	4.238734000	C	-0.200865000	4.415768000	-1.821205000	H	4.422854000	-3.304547000	4.310780000
H	4.590909000	4.530908000	-3.081944000	H	-5.677880000	0.885984000	3.306218000	C	-3.638788000	3.425870000	-2.061871000	H	5.327155000	-2.045984000	3.400880000
H	4.352989000	4.847392000	-1.332546000	C	1.221394000	-4.496463000	3.515003000	H	-3.289239000	2.451560000	-2.463000000	C	5.822939000	-1.768255000	-2.354456000
C	1.358144000	3.451718000	-0.309908000	H	0.918698000	-5.333138000	2.852178000	H	-3.123246000	4.233656000	-2.612137000	H	6.204114000	-0.731844000	-2.419356000
C	4.990145000	-1.368596000	0.154677000	H	0.834218000	-4.706980000	4.534060000	H	-4.719859000	3.515151000	-2.293911000	H	6.083192000	-2.278469000	-3.305429000
H	6.010562000	-1.213141000	-0.249812000	H	2.329715000	-4.480058000	3.564269000	C	-3.293755000	-2.189804000	-0.778695000	H	6.364975000	-2.281099000	-1.532964000
H	5.103151000	-1.596056000	1.232886000	C	1.098917000	-5.916714000	-0.490425000	C	2.784086000	-1.104890000	4.020088000	C	2.072979000	-3.222920000	2.856760000
H	4.433229000	-0.417931000	0.057091000	H	2.100485000	6.050931000	-0.939987000	H	3.565369000	-0.328010000	4.148445000	H	1.097804000	-2.783352000	2.561214000
C	-4.111871000	-0.852153000	-0.209303000	H	1.205780000	6.000259000	0.610556000	H	2.659736000	-1.612797000	4.998875000	H	1.945681000	-3.708870000	3.846239000
C	-3.599659000	1.469634000	2.813037000	H	0.453503000	6.751620000	-0.835680000	H	1.827015000	-0.600277000	3.774853000	H	2.329478000	-4.017990000	2.127238000
C	4.446712000	-2.190986000	-2.128595000	C	-6.078434000	-2.371193000	-0.360575000	C	-3.506950000	-1.309495000	2.951342000	C	-2.378173000	-1.571593000	3.971446000
H	3.855784000	-1.295404000	-2.411473000	H	-6.302993000	-2.173737000	0.707786000	C	-0.900117000	5.803100000	-1.867721000	H	-2.117329000	-2.647877000	4.032104000
H	4.136889000	-3.028221000	-2.780269000	H	-6.442090000	-3.391313000	-0.605924000	H	-0.768793000	6.352379000	-0.912407000	H	-2.697537000	-1.252122000	4.984653000
H	5.511645000	-1.980175000	-2.356312000	H	-6.656022000	-1.646800000	-0.967121000	H	-1.983691000	5.728530000	-2.075836000	H	-1.457293000	-1.012779000	3.704979000
C	-0.954709000	4.528793000	-0.217792000	C	-2.779685000	2.774647000	2.759788000	H	-0.449816000	6.415441000	-2.676605000	C	-2.694539000	-5.545909000	-0.182228000
H	-1.603740000	5.291969000	-0.692450000	H	-1.742414000	2.566067000	2.407341000	C	-1.375160000	-4.638472000	-2.133615000	H	-3.669187000	-5.441524000	-0.695853000
H	-0.917403000	4.762693000	0.863840000	H	-2.733788000	3.254196000	3.739237000	H	-2.289852000	-4.628808000	-2.753752000	H	-2.877751000	-5.498243000	0.910690000
H	-1.450504000	3.543139000	-0.339666000	H	-3.226379000	3.509391000	2.039515000	H	-0.891936000	-5.625078000	-2.287867000	H	-2.289422000	-6.552383000	-0.418111000
C	-4.273848000	-2.659954000	-2.106586000	C	3.482915000	3.340668000	3.443608000	H	-0.677559000	-3.863690000	-2.513478000	C	-5.052239000	-1.002618000	-2.183847000
H	-4.830436000	-2.036796000	-2.829573000	H	4.400194000	3.472714000	2.833633000	C	3.164964000	-2.134933000	2.936199000	H	-5.842527000	-1.082679000	-1.410201000
H	-4.593902000	-3.709663000	-2.269896000	H	3.787271000	3.238695000	4.506552000	C	4.469696000	2.528488000	0.354321000	H	-5.556744000	-0.995370000	-3.171472000
H	-3.191915000	-2.597739000	-2.345422000	H	2.869498000	4.259820000	3.346836000	H	3.377466000	2.670621000	0.221104000	H	-4.543823000	-0.023885000	-2.066263000
C	0.443872000	4.559459000	-0.888607000					H	4.981196000	3.451898000	0.014794000				

Table S8: Optimized geometry of **9** (singlet, left) and **10** (singlet, right). XYZ coordinates in angstroms. BP86/def2-TZVP level of theory.





Co	1.761783000	-0.777205000	0.042951000	H	0.408762000	2.069697000	5.017899000	As	-0.073353000	-0.505798000	1.423816000	H	2.155834000	-2.168639000	5.049448000
Co	-1.856528000	-0.613491000	-0.011196000	H	-0.004042000	0.956048000	3.676754000	As	-1.207200000	0.676673000	-1.734748000	H	1.452622000	-0.989661000	3.902547000
Co	0.073745000	1.414793000	0.025551000	C	-2.148607000	5.516317000	-0.211465000	As	1.319327000	0.499403000	-1.707667000	C	6.466217000	-0.676016000	0.021147000
P	-0.061444000	-0.472072000	1.280729000	H	-2.093351000	5.528782000	0.896041000	As	-0.098594000	-1.632069000	-1.079081000	C	-5.705218000	-2.017624000	-2.264058000
P	1.190460000	0.411268000	-1.704506000	H	-3.099608000	6.002847000	-0.511913000	Co	-1.946565000	-0.592781000	0.046688000	H	-5.364913000	-3.066672000	-2.350370000
P	-0.071157000	-1.551008000	-1.045949000	H	-1.313088000	6.125256000	-0.603585000	Co	1.831993000	-0.795941000	0.106254000	H	-6.317558000	-1.791945000	-3.160986000
P	-1.092107000	0.535975000	-1.741256000	C	5.070713000	0.044497000	-0.682675000	Co	0.084800000	1.476800000	0.123186000	H	-6.362154000	-1.936902000	-1.373762000
C	-3.948751000	-0.298184000	0.191517000	C	3.744858000	-3.426971000	3.270710000	C	3.557170000	-0.899732000	1.336597000	C	-3.600848000	-1.184042000	-3.419954000
H	-4.484991000	0.647255000	0.068692000	H	3.870812000	-4.246215000	2.533604000	H	3.856487000	-0.164646000	2.090860000	H	-2.898841000	-0.329279000	-3.512504000
C	-2.846766000	-2.048659000	1.150645000	H	3.622708000	-3.882900000	4.275138000	C	-2.975723000	-1.998612000	1.219259000	H	-4.219192000	-1.196235000	-4.340851000
H	-2.367425000	-2.698362000	1.889533000	H	4.673349000	-2.820471000	3.277571000	H	-2.530711000	-2.659458000	1.969799000	H	-3.006522000	-2.111360000	-3.401652000
C	1.365372000	3.006965000	0.431550000	C	-4.447680000	-1.076717000	-2.237610000	C	-3.564954000	-0.732505000	1.507548000	C	-4.211302000	-4.572076000	-0.109346000
H	2.457381000	2.936679000	0.422408000	C	5.108042000	1.362362000	0.132055000	C	0.537032000	2.803244000	1.767326000	H	-4.367520000	-4.467962000	0.983450000
C	0.552055000	2.814149000	1.602778000	H	4.163195000	1.931578000	0.044707000	C	3.997056000	-0.859869000	-0.046395000	H	-4.109840000	-5.652876000	-0.340249000

C	3.259764000	-2.054577000	-0.782817000	H	5.920954000	2.006408000	-0.257919000	C	0.630452000	3.525281000	-0.505610000	H	-5.116739000	-4.196230000	-0.622582000
C	-3.461896000	-0.796845000	1.451434000	H	5.318758000	1.198191000	1.206871000	C	1.386944000	3.023392000	0.628533000	C	3.184179000	-1.823414000	-3.305243000
C	3.355586000	-2.779351000	-2.153033000	C	6.398234000	-0.711953000	-0.367326000	H	2.477383000	2.935690000	0.651668000	H	2.086396000	-1.658723000	-3.342857000
C	2.519520000	-4.086302000	-2.129947000	H	6.483083000	-0.933284000	0.716145000	C	2.781212000	-2.070095000	1.605232000	H	3.464713000	-2.347113000	-4.242192000
H	2.884418000	-4.808842000	-1.372239000	H	7.258714000	-0.072314000	-0.653753000	C	3.378191000	-2.024545000	-0.705704000	H	3.680926000	-0.838654000	-3.311199000
H	2.599380000	-4.578443000	-3.119880000	H	6.481518000	-1.665792000	-0.919638000	C	2.607186000	-2.698014000	0.327379000	C	-4.521805000	-1.009265000	-2.188219000
H	1.442345000	-3.891182000	-1.949277000	C	-1.526184000	-4.439454000	0.098646000	H	2.042944000	-3.621837000	0.166766000	C	2.369607000	2.140014000	3.403351000
C	2.529827000	-2.673691000	0.313177000	H	-0.591477000	-3.895396000	-0.153462000	C	-0.788804000	3.004709000	1.276678000	H	2.662553000	2.166194000	4.472157000
H	1.942143000	-3.592697000	0.220513000	H	-1.381467000	-5.494980000	-0.206128000	H	-1.697997000	2.905575000	1.877456000	H	3.142147000	2.697545000	2.836770000
C	1.020357000	2.805535000	3.053779000	H	-1.649170000	-4.434096000	1.198387000	C	-3.146989000	-2.348205000	-0.177512000	H	2.383887000	1.083306000	3.075818000
C	2.770178000	-1.993463000	1.553079000	C	-2.328361000	4.086234000	-2.293401000	C	-0.775186000	3.511810000	-0.086128000	C	3.712047000	-3.595173000	3.268472000
C	-0.790358000	2.979759000	1.147010000	H	-1.596289000	4.730378000	-2.811966000	C	-3.920517000	-0.219921000	2.897698000	H	3.857516000	-4.372978000	2.491073000
H	-1.679620000	2.894588000	1.778688000	H	-3.332880000	4.499245000	-2.515405000	C	2.696557000	-3.985160000	-2.189520000	H	3.565933000	-4.105465000	4.243208000
C	-3.024632000	-2.394464000	-0.245985000	H	-2.282731000	3.070072000	-2.736634000	H	2.985086000	-4.752380000	-1.443268000	H	4.639335000	-2.990017000	3.330723000
C	0.568626000	3.456170000	-0.694929000	C	4.832985000	-3.206746000	-2.383881000	H	2.836948000	-4.434348000	-3.193189000	C	5.045278000	-3.163478000	-2.207209000
C	-2.743782000	-3.856923000	-0.665357000	H	5.499634000	-2.348268000	-2.584992000	H	1.613044000	-3.770863000	-2.077682000	H	5.749951000	-2.317551000	-2.309996000
C	-0.822730000	3.433005000	-0.234281000	H	4.880115000	-3.876489000	-3.266738000	C	-4.015465000	-0.221202000	0.239716000	H	5.156977000	-3.798770000	-3.109683000
C	2.777193000	3.844076000	-1.893761000	H	5.232424000	-3.764893000	-1.512673000	H	-4.520822000	0.740351000	0.108958000	H	5.349446000	-3.766473000	-1.327380000
H	3.233238000	4.383530000	-1.039536000	C	-4.004409000	-4.653411000	-0.202211000	C	0.888689000	3.647730000	-3.113894000	C	5.119555000	1.394332000	0.393029000
H	3.233991000	4.246159000	-2.819839000	H	-4.155071000	-4.571594000	0.893296000	H	1.162509000	2.584772000	-3.276281000	H	4.202603000	1.975732000	0.178149000
H	3.060970000	2.774385000	-1.831985000	H	-3.864565000	-5.725833000	-0.450834000	H	1.399740000	4.236103000	-3.903175000	H	5.984558000	2.026653000	0.109863000
C	3.554027000	-0.850927000	1.199993000	H	-4.926798000	-4.303042000	-0.703081000	H	-0.195752000	3.743923000	-3.274467000	H	5.186520000	1.235341000	1.486677000
H	3.894478000	-0.087643000	1.907019000	C	-2.817528000	-0.836372000	3.901516000	C	2.470482000	-2.703873000	2.958576000	C	-2.684298000	-4.125063000	-2.069703000
C	1.242184000	4.029885000	-1.967801000	H	-2.849609000	-1.942727000	3.967252000	C	5.171730000	0.075408000	-0.418418000	H	-3.556304000	-3.872533000	-2.699410000
C	-3.358396000	3.329014000	-0.162313000	H	-3.079741000	-0.440822000	4.903462000	C	-3.326822000	3.456082000	-0.139024000	H	-2.501666000	-5.211602000	-2.193365000
H	-3.314482000	2.244750000	-0.374195000	H	-1.774646000	-0.534681000	3.667525300	H	-3.360799000	2.430030000	-0.553056000	H	-1.793486000	-3.594888000	-2.465059000
H	-4.286466000	3.733995000	-0.611152000	C	1.240185000	-3.449263000	2.970646000	H	-4.223338000	3.996349000	-0.501910000	C	2.878617000	3.866378000	-1.647218000
H	-3.443740000	3.466218000	0.932066000	H	1.326596000	-4.305417000	2.271911000	H	-3.412597000	3.391073000	0.961264000	H	3.351699000	4.318371000	-0.752845000
C	-3.801857000	-0.289610000	2.846489000	H	0.326930000	-2.875543000	2.710981000	C	-3.838150000	-1.198115000	-0.810279000	H	3.375113000	4.300181000	-2.537793000
C	2.495601000	-2.551753000	2.945476000	H	1.100515000	-3.867192000	3.988042000	C	3.563858000	-2.702133000	-2.090027000	H	3.099265000	2.778608000	-1.650968000
C	-2.133548000	4.056092000	-0.763933000	C	-5.586574000	-2.133329000	-2.336520000	C	0.967623000	2.752470000	3.230904000	C	-2.062170000	5.606100000	0.075401000
C	3.926348000	-0.874168000	-0.200707000	H	-6.202081000	-1.917896000	-3.233774000	C	1.358480000	4.146919000	-1.726123000	H	-2.077333000	5.516985000	1.180659000
C	0.785514000	3.391056000	-3.302474000	H	-6.251987000	-2.094829000	-1.449690000	C	-2.980155000	-0.803819000	3.972801000	H	-2.973416000	6.157725000	-0.235845000
H	1.165502000	2.352996000	-3.397679000	H	-5.202751000	-3.165601000	-2.438339000	H	-3.055643000	-1.908260000	4.035583000	H	-1.181114000	6.213166000	-0.207044000
H	1.211091000	3.971429000	-4.146593000	C	2.372609000	-1.443296000	4.008765000	H	-3.247706000	-0.399798000	4.969946000	C	-5.369021000	-0.735678000	3.156322000
H	-0.307997000	3.363203000	-3.431188000	H	3.283143000	-0.813030000	4.062548000	H	-1.921107000	-0.543493000	3.770763000	H	-6.082284000	-0.323357000	2.413980000
C	1.023338000	4.305643000	3.477987000	H	2.229536000	-1.899258000	5.009285000	C	-5.136193000	0.409632000	-2.294623000	H	-5.699107000	-0.416127000	4.166796000
H	1.709734000	4.904031000	2.844587000	H	1.501275000	-0.788186000	3.809330000	H	-5.938124000	0.584484000	-1.549283000	H	-5.420279000	-1.842532000	3.109574000
H	1.364520000	4.390098000	4.530578000	C	-5.226900000	-0.851670000	3.138604000	H	-5.588893000	0.531404000	-3.298972000	C	-1.732123000	-4.447394000	0.207596000
H	0.009976000	4.750263000	3.407512000	H	-5.540935000	-0.545939000	4.158373000	H	-4.370868000	1.205467000	-2.182661000	H	-0.771156000	-3.940350000	-0.023154000
C	2.448883000	2.250035000	3.194877000	H	-5.243016000	-1.959481000	3.089490000	C	1.013726000	4.244693000	3.679432000	H	-1.618152000	-5.508662000	-0.090330000
H	3.182208000	2.829258000	2.598520000	H	-5.972498000	-0.460811000	2.416542000	H	1.735947000	4.827292000	3.071639000	H	-1.874378000	-4.433999000	1.305005000
H	2.494772000	1.191219000	2.879522000	C	0.985018000	5.564127000	-1.991304000	H	1.331441000	4.302390000	4.741133000	C	-3.924819000	1.317267000	2.975118000
H	2.770949000	2.301905000	4.254211000	H	-0.068147000	5.819064000	-2.210098000	H	0.018579000	4.726161000	3.590596000	H	-4.616389000	1.768864000	2.236238000
C	-3.514129000	-1.185813000	-3.467450000	H	1.607564000	6.020426000	-2.788061000	C	5.290622000	0.459805000	-1.906989000	H	-2.908338000	1.719579000	2.802974000
H	-2.816511000	-0.323618000	-3.507887000	H	1.267386000	6.036493000	-1.028274000	H	5.497307000	-0.406474000	-2.560786000	H	-4.254149000	1.645569000	3.981421000
H	-4.125161000	-1.160987000	-4.392857000	C	5.031742000	0.421578000	-2.177476000	H	6.136086000	1.165928000	-2.032419000	C	1.186408000	5.690877000	-1.630098000
H	-2.914006000	-2.109609000	-3.485249000	H	5.842598000	1.145695000	-2.394424000	H	4.378629000	0.969287000	-2.280553000	H	0.145054000	6.016313000	-1.811901000
C	2.848735000	-1.953625000	-3.359975000	H	4.070621000	0.901940000	-2.453760000	C	-2.194342000	4.385679000	-2.134190000	H	1.824340000	6.175131000	-2.397748000
H	1.745581000	-1.830956000	-3.315018000	H	5.189034000	-0.445541000	-2.844010000	H	-1.431526000	5.061266000	-2.560067000	H	1.501418000	6.071575000	-0.636902000
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C	-5.122398000	0.316397000	-2.316124000	H	-4.570559000	1.676461000	2.191438000	C	2.320250000	-1.656900000	4.079643000	H	1.330539000	-4.428568000	2.166878000
H	-4.392220000	1.141668000	-2.192845000	C	-2.500692000	-4.119193000	-2.165362000	H	3.228933000	-1.031003000	4.188019000				
H	-5.928805000	0.442172000	-1.565515000	H	-3.384655000	-3.897337000	-2.789854000								
H	-5.584404000	0.435333000	-3.316427000	H	-2.269130000	-5.194243000	-2.306231000								
C	0.054654000	2.025834000	3.968125000	H	-1.635652000	-3.540983000	-2.549002000								
H	-0.971076000	2.445623000	3.949486000												

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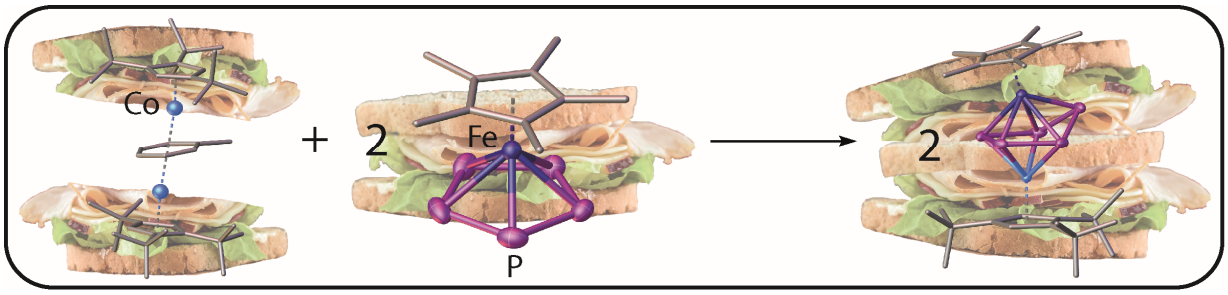
5. A General Pathway to Heterobimetallic Triple-Decker Complexes

Martin Piesch, Fabian Dielmann, Stephan Reichl and Manfred Scheer



- Synthesis and characterization of **1**, **3**, **5** were performed by Fabian Dielmann and was already part of his Ph. D. thesis

- Synthesis and characterization of **2a**, **2b**, **4**, publishable crystal structures of **1** and **3** and further VT NMR investigations of **3** were performed by Martin Piesch

- DFT calculations were performed by Martin Piesch

- X-ray measurements and calculations were done by Martin Piesch (**1**, **2a**, **2b**, **3**, **4**) and Fabian Dielmann (**5**) and finally checked by Michael Seidl

- Manuscript was written by Martin Piesch

- Figures were made by Martin Piesch

- This chapter is already published as:
  M. Piesch, F. Dielmann, S. Reichl, M. Scheer, *Chem. Eur. J.* **2020**, *26*, 1518-1524.

5.1 Introduction

Abstract: *A systematic study on the reactivity of the triple-decker complex [(Cp'''Co)$_2$(μ,η^4:η^4-C$_7$H$_8$)] (**A**) towards sandwich complexes containing cyclo-P$_3$, cyclo-P$_4$ and cyclo-P$_5$ ligands under mild conditions is presented. That way, the heterobimetallic triple-decker sandwich complexes [(Cp*Fe)(Cp'''Co)(μ,η^5:η^4-P$_5$)] (**1**) and [(Cp'''Co)(Cp'''Ni)(μ,η^3:η^3-P$_3$)] (**3**) were synthesized and fully characterized. In solution, these complexes exhibit a unique fluxional behavior, which was investigated by variable temperature NMR spectroscopy. The dynamic processes can be blocked by coordination to {W(CO)$_5$} fragments, leading to the complexes [(Cp*Fe)(Cp'''Co)(μ$_3$,η^5:η^4:η^1-P$_5$){W(CO)$_5$}] (**2a**), [(Cp*Fe)(Cp'''Co)(μ$_4$,η^5:η^4:η^1:η^1-P$_5$){(W(CO)$_5$)$_2$}] (**2b**) and [(Cp'''Co)(Cp'''Ni)(μ$_3$,η^3:η^2:η^1-P$_3$){W(CO)$_5$}] (**4**), respectively. The thermolysis of **3** leads to the tetrahedrane complex [(Cp'''Ni)$_2$(μ,η^2:η^2-P)$_2$] (**5**). All compounds were fully characterized using single crystal X-ray structure analysis, NMR spectroscopy, mass spectrometry and elemental analysis.*

The transformation of the P_4 tetrahedron of white phosphorus in the coordination sphere of transition metal complexes yielding functionalized phosphorus compounds is a widely investigated field of research. Most reactions proceed by thermolysis of carbonyl complexes such as [(Cp^{R}M(CO)$_n$)$_2$] (e.g. M = Cr,[1] Mo,[2,3] W,[4] Fe,[5,6] Co,[7] Ni[8]) or photolysis of [Cp^{R}M(CO)$_4$] (e.g. M = V,[9] Nb,[10,11] Ta[11]) with P_4 under harsh reaction conditions, yielding the thermodynamically most stable products. In contrast, organometallic compounds bearing labile ligands can be used to perform reactions with white phosphorus under much milder conditions, even at very low temperatures. Here, in general, kinetic products or metastable compounds can be obtained. As an example, the [nacnacM(L)] complexes (M = Cu, L = MeCN,[12] M = Fe, L = toluene,[13] M = Co, L = toluene,[14]) have been used in the reaction with P_4 yielding a plethora of kinetic products. Another type of complex used in the activation of P_4 is the reactive cobalt toluene triple-decker complex [(Cp'''Co)$_2$(μ,η^4:η^4-C$_7$H$_8$)] (**A**) (Cp''' = η^5-C$_5$H$_2$^{t}Bu$_3$), which dissociates in solution into a {Cp'''Co(C$_7$H$_8$)} and {Cp'''Co} fragment.[15] Its reactivity towards white phosphorus strongly depends on the reaction conditions. Thus, at r.t., the cleavage of the P_4 tetrahedron into two P_2 units to form [(Cp'''Co)$_2$(μ,η^2:η^2-P$_2$)$_2$] (**D**) or, at low temperatures, the metal-controlled aggregation of P_4 molecules occur to form large neutral polyphosphorus cages with e.g. a P_{12}, P_{16} and P_{24} ligand, respectively.[16] All reactions of the mentioned carbonyl or nacnac complexes with P_4 lead to either sandwich complexes with a P_n ligand as an end deck (e.g. [Cp*Fe(η^5-P$_5$)][5]) or a middle deck in homometallic triple-decker complexes (e.g. [(Cp*Mo)$_2$(μ,η^6:η^6-P$_6$)][3]). But no heterobimetallic compounds can be obtained that way. Moreover, there are only very few examples known that are accessible from reactions of [Cp*M(η^5-P$_5$)] (M = Fe, Ru) with cationic fragments[17] or carbonyl compounds.[18] Most of them are based on rare or expensive metals such as tantalum, rhodium or iridium and are

synthesized in only moderate yields, partially under harsh conditions (Figure 1). On the other hand, substituted derivatives of heterobimetallic triple-decker complexes can be obtained from the electrophilic quenching of pentaphosphaferrocene ([Cp*Fe(η^4-P_5R)]$^-$) functionalized by main group nucleophiles such as [(Cp*Fe)(Cp'''Co)(μ,η^4:η^3-P_5NMe_2)][19] (Figure 1).

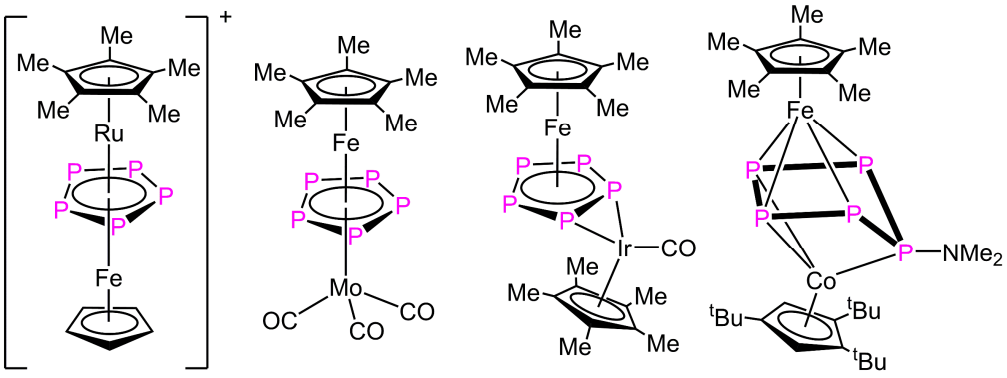
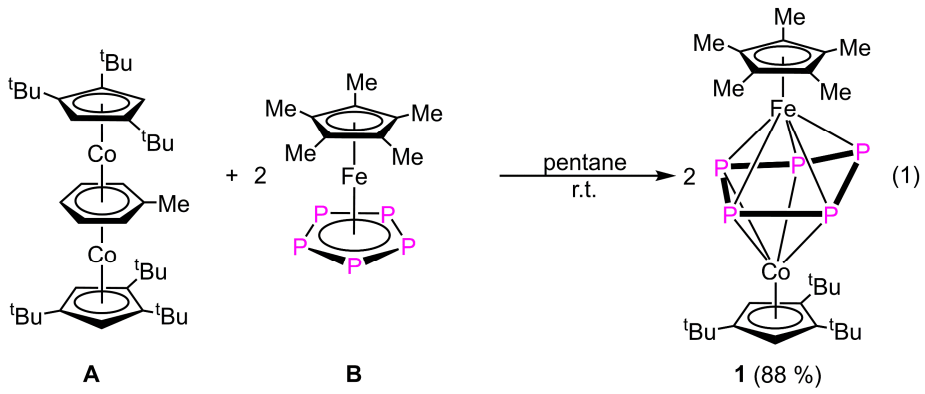


Figure 1. Selected examples of heterobimetallic triple-decker complexes.

The question arises as to how heterobimetallic triple-decker complexes can be synthesized easier and in high yields under mild conditions including cheap and abundant metals. Therefore we investigated the reaction of [(Cp'''Co)$_2$(μ,η^4:η^4-C_7H_8)] (**A**) with compounds containing *cyclo*-P_n ligands as end-decks such as [Cp*Fe(η^5-P_5)] (**B**), [Cp'''Co(η^4-P_4)] (**C**) and [Cp'''Ni(η^3-P_3)] (**E**) at room temperature. Herein, we report the synthesis and properties of two new mixed metal triple-decker sandwich complexes comprising *cyclo*-P_n (n = 3 and 5) middle decks, respectively, as well as their reaction behavior towards white phosphorus and their thermal stability.

5.2 Results and Discussion

The reaction of $[(Cp'''Co)_2(\mu,\eta^4{:}\eta^4\text{-}C_7H_8)]$ (**A**) with pentaphosphaferrocene ($[Cp^*Fe(\eta^5\text{-}P_5)]$ (**B**)) in pentane at room temperature leads to the quantitative formation of $[(Cp^*Fe)(Cp'''Co)(\mu,\eta^5{:}\eta^4\text{-}P_5)]$ (**1**), which is obtained as a red air-sensitive solid in crystalline yields of 88 % (Eq. 1).



In contrast to the thermolysis of **B** with cobalt carbonyl compounds,[20] the formation of **1** proceeds without the fragmentation of the cyclo-P_5 ligand (the thermolysis leads to the formation of P_4, P_2 and P_1 ligand-containing complexes). Alternatively, **1** can be also obtained by the reaction of $[K_2(dme)_3][(Cp^*Fe)_2(\mu,\eta^4{:}\eta^4\text{-}P_{10})]$ with $[(Cp'''CoCl)_2]$ in lower yield (cf. SI).

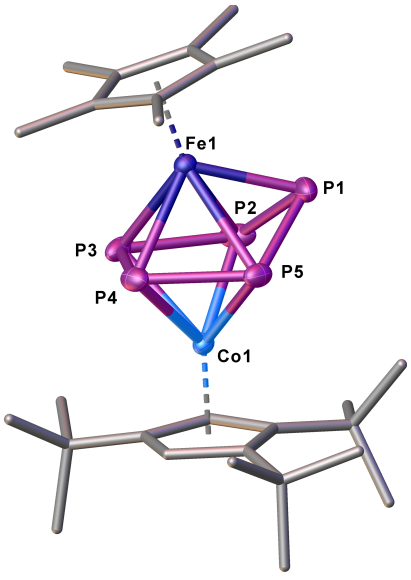


Figure 2. Structure of one independent molecule of **1** in the solid state. Thermal ellipsoids are shown at 50 % probability level. Hydrogen atoms are omitted for clarity, with one independent molecule of **1** being depicted.

The crystal structure of **1** reveals a dinuclear complex bearing a *cyclo*-P_5 ligand in an envelope conformation, coordinating in η^4 fashion to the {Cp'''Co} fragment and η^5 fashion to the {Cp*Fe}

fragment (Figure 2). Both {Cp^RM} fragments are twisted approximately 16 ° to each other and P1 is bent out of the plane by approx. 34.7 °. Three of the P-P bond lengths in **1** are almost identical to those in **B** (P1-P2 2.1459(10) Å, P1-P5 2.1498(10) Å, P3-P4 2.1283(10) Å), in **B** average 2.120(2) Å), while two are elongated (P2-P3 2.2441(11) Å, P4-P5 2.2407(10) Å), which is confirmed by the WBIs of P1-P2, P3-P4 and P1-P5 (0.99, 0.95, 0.99) and P2-P3 and P4-P5 (0.79, 0.80). Compound **1** shows a dynamic behavior in solution, which was studied by variable temperature NMR spectroscopy. At room temperature, the ^{1}H NMR spectrum reveals four sharp singlets corresponding to one Cp* and one freely rotating Cp''' ligand, while the $^{31}P\{^1H\}$ NMR spectrum shows one very broad signal at δ = -160 ppm ($\omega_{1/2}$ = 16000 Hz). Upon cooling to -80 °C, the signals in the ^{1}H NMR spectra remain unchanged, while the broad signal observed in the $^{31}P\{^1H\}$ NMR spectrum at room temperature splits into three sharp multiplets centered at δ = 288.7, -207.3 and -250.3 ppm, respectively, with an integral ratio of 1:2:2 displaying an AMM'XX' spin system. The corresponding coupling constants were obtained from the simulation of the $^{31}P\{^1H\}$ NMR spectrum at 213 K (cf. SI). The magnitude of the $^1J_{PP}$ coupling correlates nicely with the P-P bond lengths observed in the solid state structure, indicating that this structure is presumably present in solution at 213 K. On the other hand, when warming the sample to 90 °C, the signals in the ^{1}H NMR spectra do not change, while the broad signal in the $^{31}P\{^1H\}$ NMR spectrum sharpens to a singlet at δ = -115.3 ppm ($\omega_{1/2}$ = 500 Hz). At this temperature, the dynamic process (Figure 3) speeds up and all five P atoms become equivalent in the NMR. The free activation enthalpy $\Delta G_T^{\ddagger}$ of this process at the coalescence temperature (T_c = 293 K) amounts to 48.2 kJ·mol^{-1} (cf. SI).[21] All these findings indicate that the dynamic process proceeds at the *cyclo*-P_5 ligand. Compound **1** is thermally stable. Refluxing **1** in toluene for one day leads to only minor decomposition. As a decomposition product, [Cp*Fe(η^5-P_5)] has been identified by $^{31}P\{^1H\}$ NMR spectroscopy.

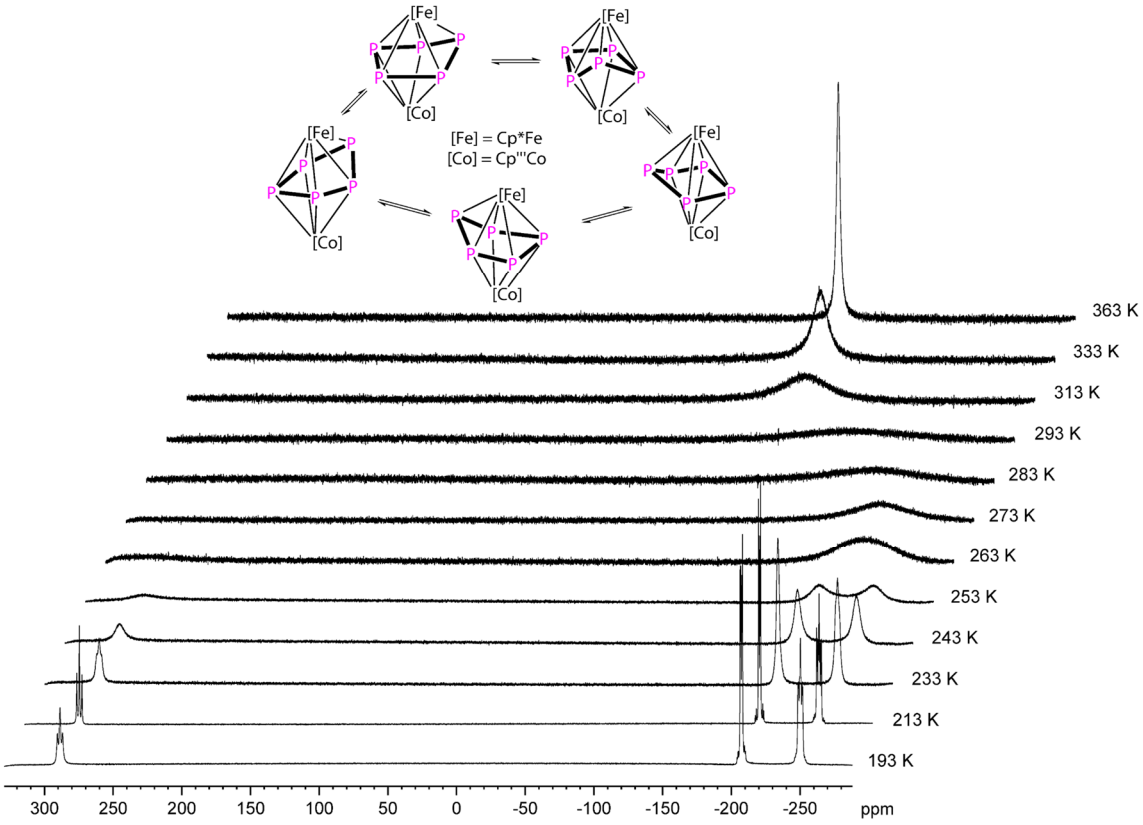
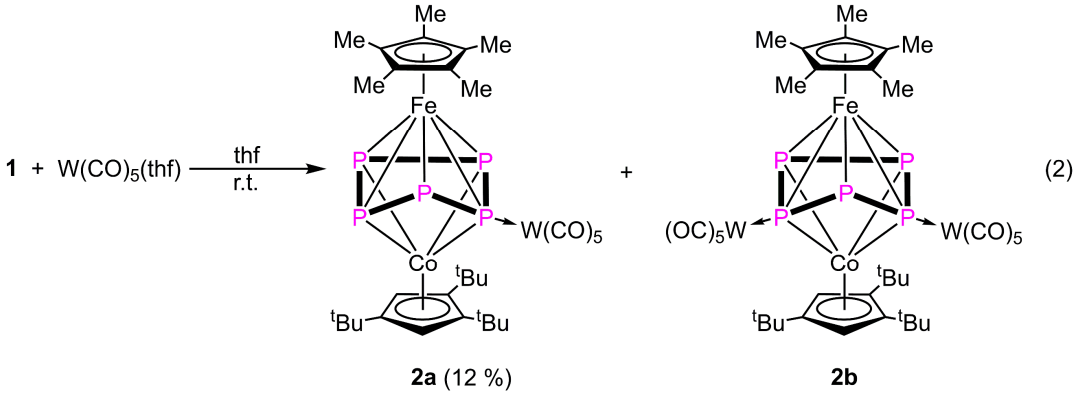


Figure 3. VT $^{31}P\{^{1}H\}$ NMR spectra of **1** in toluene-d_8 at different temperatures between 193 and 363 K and the proposed dynamic process.

In order to block the dynamic process in solution at room temperature, **1** was reacted with an excess of [W(CO)$_5$(thf)] (2.2 eq) and the mono and dicoordinated compounds [(Cp*Fe)(Cp'''Co)(μ$_3$,η^5:η^4:η^1-P$_5$){W(CO)$_5$}] (**2a**) and [(Cp*Fe)(Cp'''Co)(μ$_4$,η^5:η^4:η^1:η^1-P$_5$){W(CO)$_5$}$_2$] (**2b**) are formed (Eq. 2). The stoichiometric reaction (1:1) leads to a selective formation of **2a** (according to $^{31}P\{^{1}H\}$ NMR). According to the $^{31}P\{^{1}H\}$ NMR spectrum of the reaction mixture, **2a** and **2b** are formed in an approx. 1:1 ratio. After workup of the reaction mixture by thin layer chromatography, only **2a** can be isolated as a pure product, in addition to some minor amounts of **2b**. It is assumed that one {W(CO)$_5$} fragment is removed during the chromatography. Single crystals of **2a** suitable for X-ray diffraction could be obtained from a concentrated solution in pentane stored at -30 °C.



For compound **2b**, few crystals could be obtained by evaporating the solvent from a toluene solution of the crude reaction mixture. The structure of **2a** in the solid state reveals a *cyclo*-P_5 ligand in an envelope conformation, while a {$W(CO)_5$} fragment is coordinated to the P2 atom (Figure 4). For **2b**, an additional coordination of a {$W(CO)_5$} fragment at P5 is observed (Figure 4). The $^{31}P\{^1H\}$ NMR spectrum of the reaction mixture at room temperature reveals three sharp multiplets for **2b** and four broad signals for **2a**. These four broad signals indicate a dynamic process for **2a** in solution. VT $^{31}P\{^1H\}$ NMR spectroscopic investigations of **2a** reveal that the broad signals sharpen into five multiplets displaying an AMNXY spin system upon cooling down to 193 K (cf. SI).

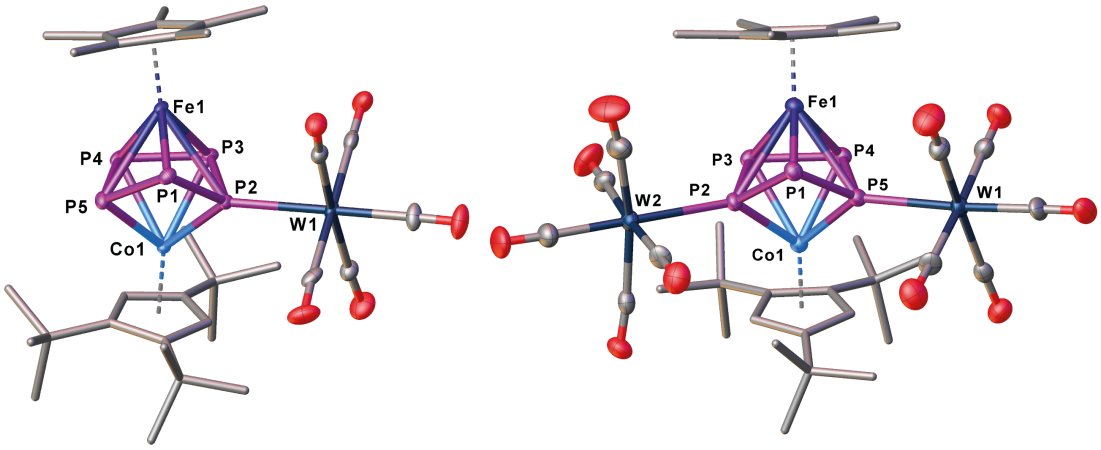
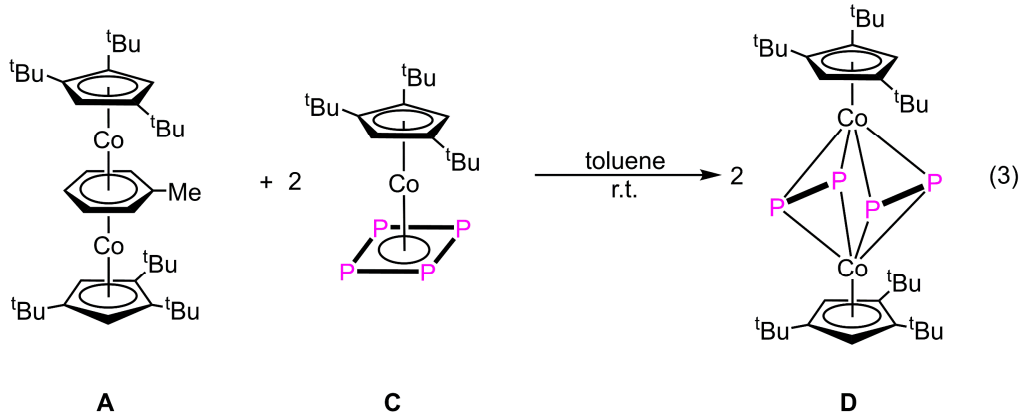


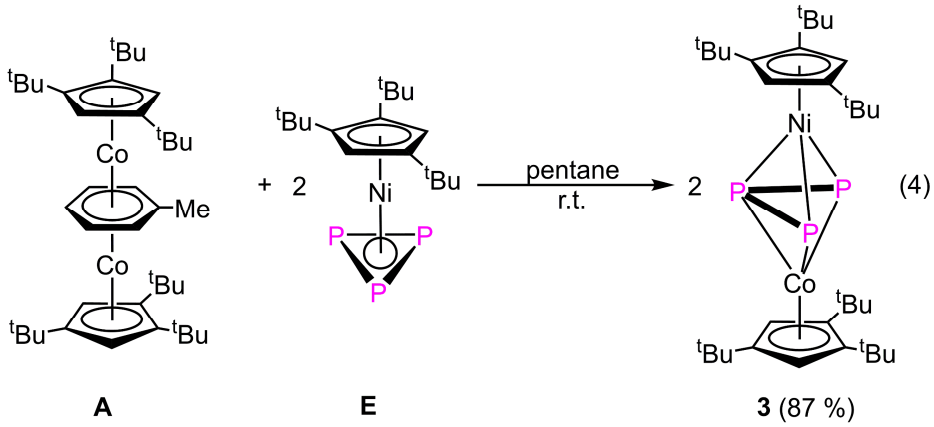
Figure 4. Molecular structure of **2a** (left) and **2b** (right) in the solid state. Thermal ellipsoids are shown at 50 % probability level. Hydrogen atoms are omitted for clarity

The reaction of [(Cp'''Co)$_2$(μ,η^4:η^4-C_7H_8)] (**A**) with [Cp'''Co(η^4-P_4)] (**C**) in toluene at room temperature leads to the quantitative formation of [(Cp'''Co)$_2$(μ,η^2:η^2-P_2)$_2$] (**D**) (Eq. 3).[7] The *cyclo*-P_4 ligand in **C** is selectively fragmented into two separated P_2 units upon coordination to another Cp'''Co fragment in **D**. Compound **D** was already reported.[7]



A **C** **D**

Stirring a pentane solution of **A** with [Cp'''Ni(η^3-P_3)] (**E**) at room temperature for few minutes results in the quantitative formation of the dinuclear complex [(Cp'''Co)(Cp'''Ni)(μ,η^3:η^3-P_3)] (**3**) (Eq. 4).



A **E** **3** (87 %)

Compound **3** is an orange-brown air-sensitive solid. The crystal structure analysis of **3** (Figure 5) reveals a dinuclear complex bearing an allylic P_3 ligand. Since both metal fragments contain the Cp''' ligand, the attribution of the atom types of the metal was made based on their anisotropic displacement parameters. Due to the similarity of the bond lengths, a mixed-site occupation cannot be excluded. The P_3 ligand coordinates to the metals with two short M-P bonds to P1/P3 (between 2.1826(5) and 2.1931(5) Å) and one elongated M-P bond to P2 (2.3457(4) and 2.3538(5) Å). The Cp''' ligands are tilted by 18° to each other. Compared to the P-P bond lengths in **E**[8] (average: 2.098(2) Å), the P1-P2 (2.1895(6) Å) and P2-P3 (2.1945(6) Å) bond lengths in **3** are elongated upon coordination to another metal fragment and lie in the range of P-P single bonds.[22] The Wiberg Bond Indices for P1-P2 and P2-P3 with values of 0.96 and 0.96 underline this description. The P1-P3 distance of 2.7619(6) Å is considerably longer than a P-P single bond, but lies below the sum of the van der Waals radii of phosphorus (Σ_{vdW} = 3.80 Å).[23] The Wiberg Bond Index of 0.22 indicates a weak interaction between the two phosphorus atoms P1 and P3.

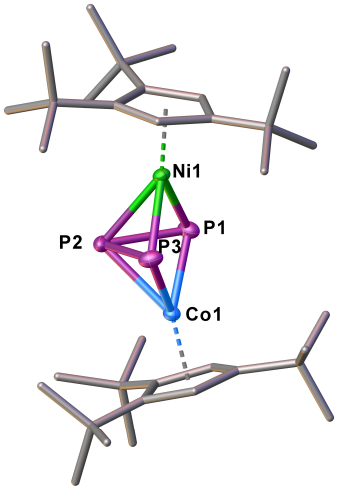
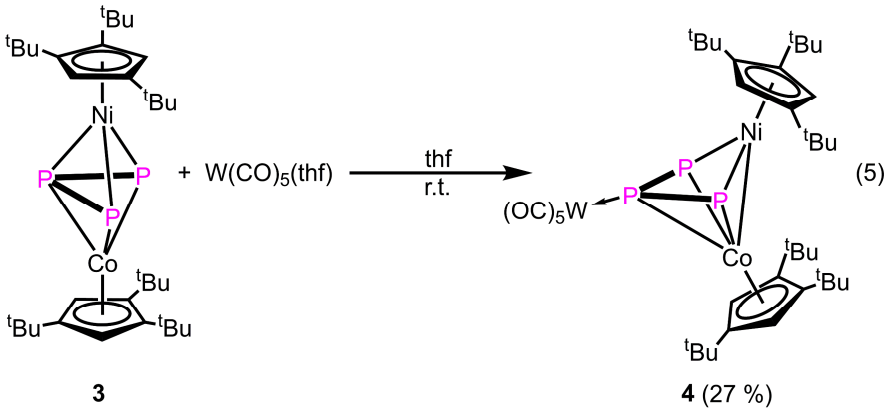


Figure 5. Structure of **3** in the solid state. Thermal ellipsoids are shown at 50 % probability level. Hydrogen atoms are omitted for clarity.

In the ^{1}H and $^{31}P\{^{1}H\}$ NMR spectra of **3**, a dynamic process can be observed that is dependent on the temperature and the solvent used (CD_2Cl_2 or toluene-d_8) (Figure 6). The $^{31}P\{^{1}H\}$ NMR in CD_2Cl_2 spectrum shows three broad signals centered at δ = 377.3, 249.7 and 133.1 ppm with an integral ratio of 0.19:1:0.12. Upon cooling, the relative intensity of the broad signals centered at δ = 366.8 and 126.2 ppm increases in comparison to the singlet at δ = 237.8 ppm, while they sharpen and split into a doublet and a triplet with a $^{1}J_{PP}$ of 357 Hz. This clearly confirms the presence of a fixed allylic P_3 ligand (**3b**) at low temperature (Figure 6). The singlet at δ = 237.8 ppm can be assigned to the compound **3a** bearing a *cyclo*-P_3 ligand. The ratio of **3a** and **3b** is dependent on the temperature, but also on the polarity of the solvent used (cf. Figure 6). At low temperatures, compound **3b** is predominant (63 % in toluene and 83 % in dichloromethane at 183 K according to the $^{31}P\{^{1}H\}$ NMR spectra, Figure 6). The situation can also be monitored in the VT ^{1}H NMR spectra (cf. SI). Warming up a solution of **3** in toluene-d_8 to 363 K, in the $^{31}P\{^{1}H\}$ NMR spectrum, the signals for **3b** disappear completely while the singlet assigned to **3a** broadens. Above 323 K, decomposition is observed and two new sharp singlets at δ = 285.8 and -43.7 ppm arise, which can be assigned to a new Ni complex (**5**, vide infra) and **D**.[7] All these spectroscopic data clearly show that, in solution, there is an equilibrium between **3a** and **3b**. The phosphorus atoms in **3** contain a lone pair of electrons, possibly available for coordination (cf. Figure S23), which raises the question as to whether the equilibrium between **3a** and **3b** can be shifted by coordination to a $\{W(CO)_5\}$ fragment. Reacting **3** with an excess of $[W(CO)_5(thf)]$ (2.2 eq) yields $[(Cp'''Co)(Cp'''Ni)(\mu_3,\eta^3{:}\eta^2{:}\eta^1\text{-}P_3)\{W(CO)_5\}]$ (**4**) as a major product (coordination of $\{W(CO)_5\}$ at the central P atom (P2)) beside small amounts of **I4-B**/**I4-C** (coordination of $\{W(CO)_5\}$ at the outer P atom (P1 or P3). According to the $^{31}P\{^{1}H\}$ NMR spectrum of the reaction mixture **4** and **I4-B**/**I4-C** are present in a ratio of 1:0.04:0.1.



3 **4** (27 %)

Despite many attempts, only **4** could be isolated and fully characterized. Single crystals of **4** suitable for X-ray structure analysis can be obtained from a concentrated solution in CH_2Cl_2 layered with MeCN at room temperature. In **4**, the $\{W(CO)_5\}$ fragment is coordinated to the central P atom of the three-membered chain (Figure 7). Upon the coordination of **3** to $\{W(CO)_5\}$,

the Cp''' metal fragments are further tilted towards each other (from 18 ° to 52 °) and the Co-Ni distance (2.6182(7) Å) is significantly shortened compared to **3** (3.3941(5) Å), indicating the presence of an metal-metal bond (WBI of 0.43, cf. Figure S24). The P_3 ligand is coordinated in η^3 fashion to Co and in η^2 fashion to Ni. The assignment of the Co and Ni positions in the structure of **4** is based on the anisotropic displacement parameters and is also supported by DFT calculations at the B3LYP/def2-SVP level, showing that this isomer is energetically more favored (by 45.31 kJ·mol^{-1}) compared to the isomer with exchanged Co and Ni positions.

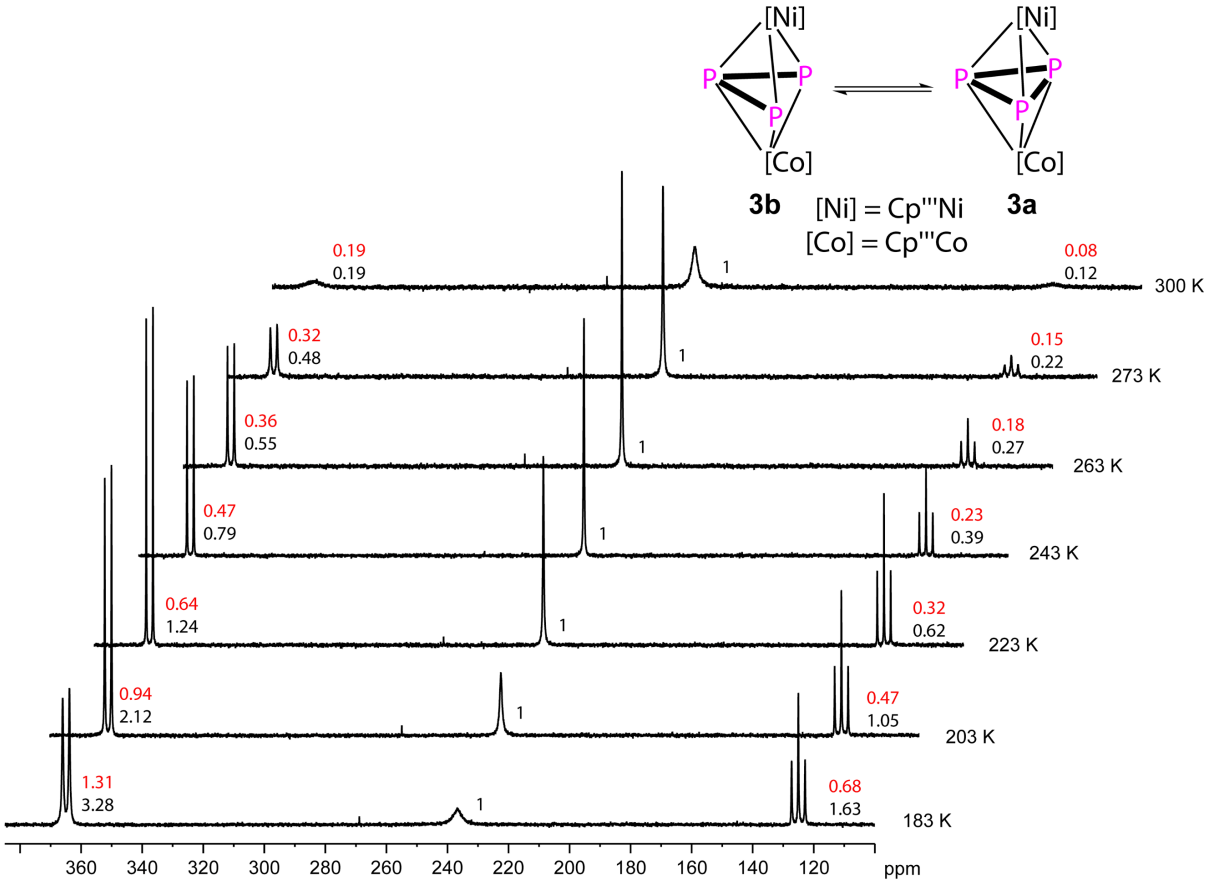


Figure 6. VT $^{31}P\{^1H\}$ NMR spectra of **3** in CD_2Cl_2 at different temperatures between 183 and 300 K and the proposed temperature-dependent equilibrium. Integral ratio given for measurement in CD_2Cl_2 (black) and toluene-d_8 (red).

The P1-P2 and P2-P3 bonds (2.1214(11) and 2.1234(12) Å) are shortened, while the P1-P3 distance is lengthened (3.0011(12) Å) compared to **3**. This is also in line with the WBIs (P1-P2 (1.09), P2-P3 (1.08) and P1-P3 (0.12)) indicating the presence of an allylic P_3 ligand. The $^{31}P\{^1H\}$ NMR spectrum of **4** in C_6D_6 at room temperature reveals a doublet at δ = 354.3 ppm ($^1J_{PP}$ = 408 Hz) and a triplet at δ = 114.6 ppm ($^1J_{PP}$ = 408 Hz), the latter with tungsten satellites ($^1J_{PW}$ = 203 Hz). According to DFT calculations (Figure 8), the coordination on the central phosphorus atom in **3** to a {W(CO)$_5$} fragment (**I4-A**) is energetically disfavored (by 15.01 kJ·mol^{-1}), but the final rearrangement of **I4-A** to **4** is with -34.36 kJ·mol^{-1} exothermic. In contrast, the coordination of the outer phosphorus atoms in **3** to the {W(CO)$_5$} fragment (**I4-**

B/**I4-C**) is exothermic with -15.39 and -17.96 kJ·mol^{-1}, respectively, showing that **I4-B**/**I4-C** represents the kinetic products, while **4** is the thermodynamic product of the reaction.

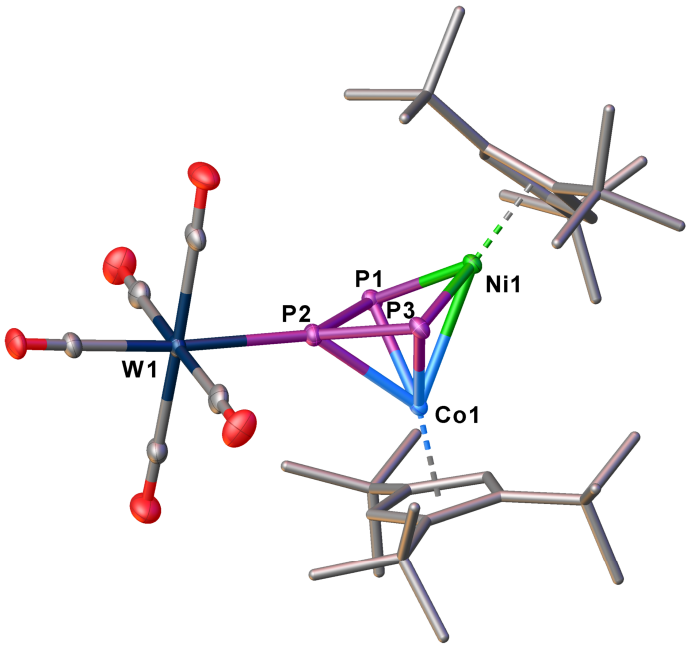
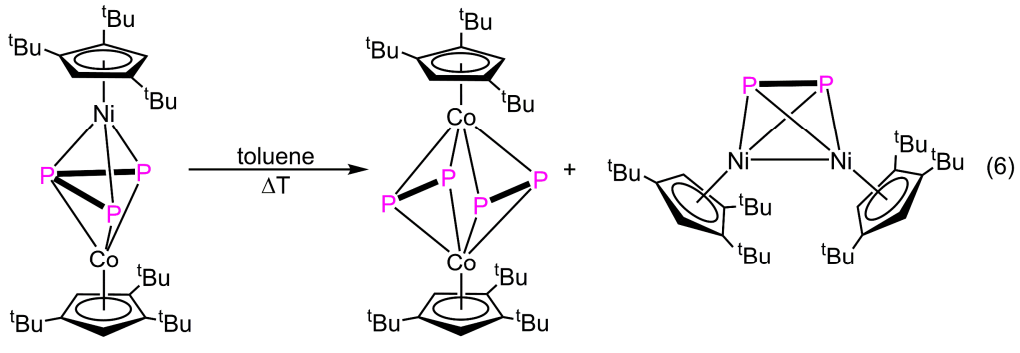


Figure 7. Structure of **4** in the solid state. Thermal ellipsoids are shown at 50 % probability level. Hydrogen atoms are omitted for clarity. Detailed bond lengths and angles are given in the SI.

The VT NMR spectra of compound **3** reveal a decomposition starting at 50 °C (Figure S11).The thermolysis in boiling toluene for one day leads to the formation of [(Cp'''Co)$_2$(μ,η^2:η^2-P$_2$)$_2$] (**D**) and [(Cp'''Ni)$_2$(μ,η^2:η^2-P$_2$)] (**5**) (Eq. 6). This result shows a ready fragmentation into [Cp'''Co(P$_2$)] and [Cp'''Ni≡P], which dimerize to **D** and **5**, respectively. The latter fragment was already proposed to dimerize as a {Cr(CO)$_5$} coordinated species in the formation of [(Cp^{iPr}Ni)$_2$(μ,η^2:η^2:η^1:η^1-P$_2$){Cr(CO)$_5$}$_2$].[24]



Crystals suitable for X-ray single crystal structure analysis can be obtained by storing a concentrated solution of **5** in hexane at -30 °C. The structure of **5** in the solid state (Figure 9) reveals a tetrahedral moiety consisting of two Ni and two P atoms. The P-P bond length (2.0805(8) Å) lies in the range of an elongated P-P double bond with a WBI of 1.35.[22,25] The

Ni-Ni distance in **5** is 2.5848(5) Å, representing a single bond (WBI of 0.52). Similar P-P and Ni-Ni distances of 2.053(5) and 2.571(1) Å, respectively, have been reported for the related complex $[(Cp^{iPr}Ni)_2(\mu,\eta^2{:}\eta^2\text{-}P_2)]$ (Cp^{iPr} = C_5HiPr_4).[26] The $^{31}P\{^1H\}$ NMR spectrum of **5** contains a sharp singlet at δ = 282.7 ppm.

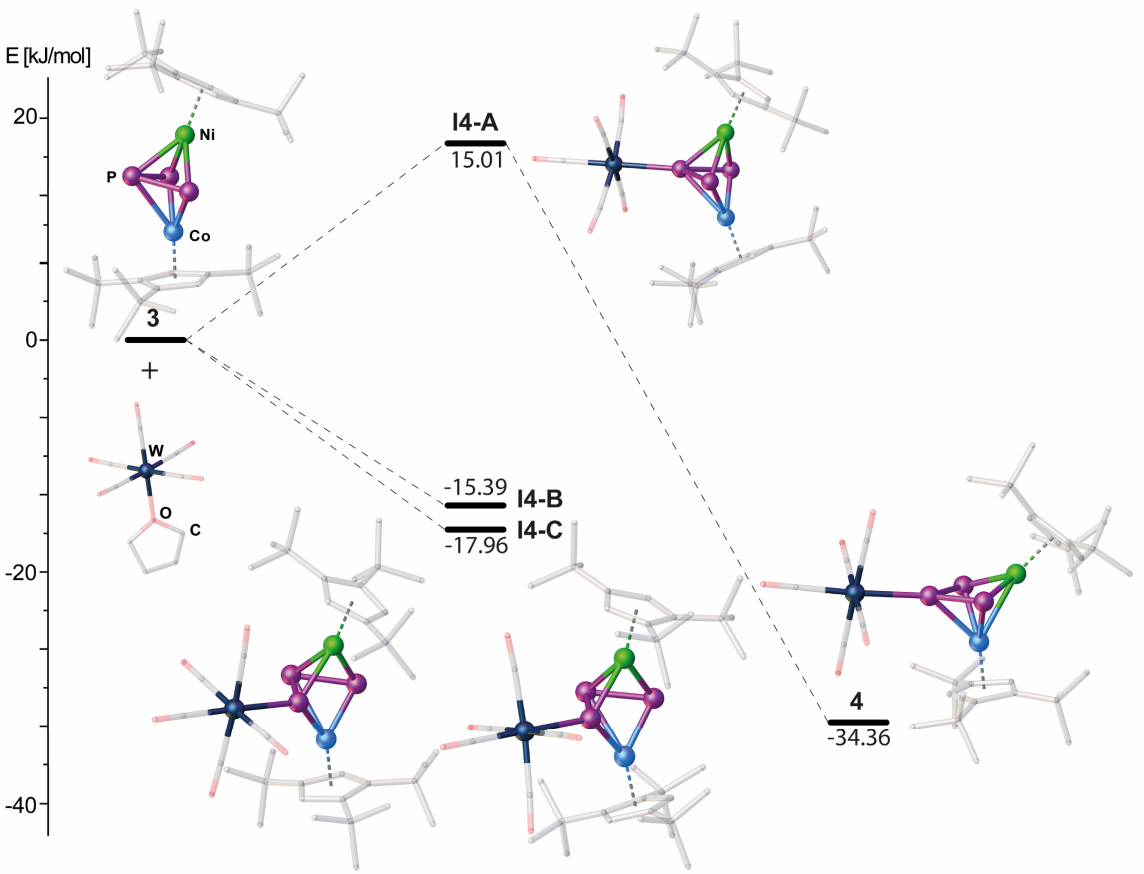


Figure 8. Energetic profile of the reaction of **3** with $[W(CO)_5(thf)]$. B3LYP/def2-SVP level of theory.

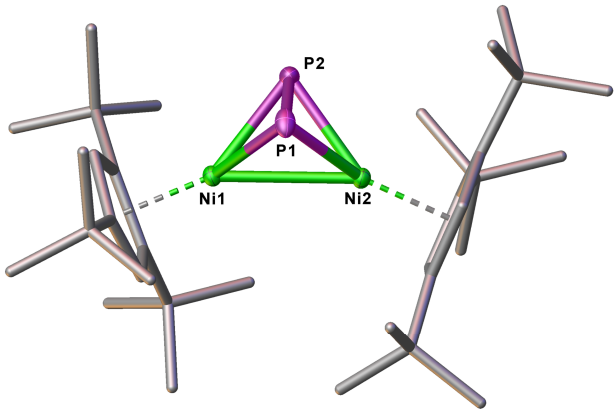


Figure 9. Structure of **5** in the solid state. Thermal ellipsoids are shown at 50 % probability level. Hydrogen atoms are omitted for clarity. Detailed bond lengths and angles are given in the SI.

Due to the dynamic behavior of **1** and **3** in solution, we assumed that the Cp'''Co fragment is labile and could be removed in the presence of a suitable reaction partner. Hence, a solution

of **1** in hexane was stirred with an excess of P_4 at room temperature. After column chromatographic workup, [Cp*Fe(η^5-P_5)] (**B**) could be isolated as a byproduct and separated from the additionally formed [(Cp'''Co)$_n$P$_m$] complexes [(Cp'''Co)$_2$(μ,η^4:η^2:η^1-P_8)] (isomer one, 29 %, isomer two, 6 %), [Cp'''Co(η^4-P_4)] (**C**, 14 %) and [(Cp'''Co)$_3$(μ_3,η^4:η^2:η^2:η^1-P_{12})] (11 %) (based on cobalt). All these Co complexes can also be obtained from the reaction of white phosphorus with **A** at room temperature as previously reported.[16] In an analogous manner, complex **3** was reacted with P_4. According to the $^{31}P\{^1H\}$ NMR spectrum, [Cp'''Ni(η^3-P_3)] (**E**) is quantitatively formed, next to the cobalt complexes [Cp'''Co(η^4-P_4)] (**C**, 40 %) and [(Cp'''Co)$_2$(μ,η^2:η^2-P_2)$_2$] (**D**, 42 %), beside traces (< 1 %) of other P-rich compounds.

5.3 Conclusion

A novel synthetic route to two new previously unknown heterobimetallic triple-decker complexes was developed. Both can be obtained in gram scale under mild reaction conditions. [(Cp'''Co)$_2$(μ,η^4:η^4-C_7H_8)] (**A**) serves as a source of unsaturated {Cp'''Co} fragments, reacting with [Cp*Fe(η^5-P_5)] (**B**) and [Cp'''Ni(η^3-P_3)] (**E**) to yield [(Cp*Fe)(Cp'''Co)(μ,η^5:η^4-P_5)] (**1**) and [(Cp'''Co)(Cp'''Ni)(μ,η^3:η^3-P_3)] (**3**), respectively. Both compounds exhibit unique fluxionalities in solution, which can be blocked by coordination to {W(CO)$_5$} fragments resulting in [(Cp*Fe)(Cp'''Co)(μ_3,η^5:η^4:η^1-P_5){W(CO)$_5$}] (**2a**)) or ([(Cp*Fe)(Cp'''Co)(μ_4,η^5:η^4:η^1:η^1-P_5){W(CO)$_5$}$_2$] (**2b**) and [(Cp'''Co)(Cp'''Ni)(μ_3,η^3:η^2:η^1-P_3){W(CO)$_5$}] (**4**), respectively. Additionally, **3** is thermally unstable and fragmentizes upon warming into [(Cp'''Co)$_2$(μ,η^2:η^2-P_2)$_2$] (**D**) and [(Cp'''Ni)$_2$(μ,η^2:η^2-P_2)] (**5**). The {Cp'''Co} fragment in **1** and **3** is still labile and can be released offering another reaction partner as for instance P_4.

5.4 Supporting Information

5.4.1. Synthetic procedures and experimental details

Synthetic Procedures: All manipulations were performed under an atmosphere of dry argon using standard glove-box and Schlenk techniques. All solvents were degassed and purified by standard procedures. The compounds [(Cp'''Co)$_2$(μ,η^4:η^4-C$_7$H$_8$)] (**A**)[15], [Cp*Fe(η^5-P$_5$)] (**B**)[5], [Cp'''Co(η^4-P$_4$)] (**C**)[16], [Cp'''Ni(η^3-P$_3$)] (**E**)[8], [K$_2$(dme)$_3$][(Cp*Fe)$_2$(μ,η^4:η^4-P$_{10}$)][27] and [(Cp'''CoCl)$_2$][28] were prepared according to literature procedures.

The NMR spectra were recorded with a Bruker Avance 400 spectrometer (^{1}H: 400.13 MHz, ^{31}P: 161.976 MHz). The chemical shifts are given in ppm referenced to external SiMe$_4$ (^{1}H) and H$_3$PO$_4$ (^{31}P). Elemental analyses were determined with an Elementar Vario EL III apparatus. All mass spectra were recorded with a Finnigan MAT 95 mass spectrometer (LIFDI-MS and EI-MS).

5.4.1.1 Synthesis of [(Cp*Fe)(Cp'''Co)(μ,η^5:η^4-P$_5$)] (1)

A solution of **A** (2.93 g, 4.336 mmol, 1 eq) in 100 mL hexane was added dropwise to a stirred solution of **B** (3.00 g, 8.672 mmol, 2 eq) in 200 mL hexane at room temperature. Thereby, the reaction mixture turned violet. After stirring the mixture for 2 hours, the solvent was removed under reduces pressure. The residue was dissolved in 20 mL CH_2Cl_2, mixed with silica and dried *in vacuo*. The preabsorbed crude mixture was purified by column chromatography (SiO_2, hexane, 15 x 4 cm). Compound **1** can be eluted using toluene as a strong dark red/violet fraction. After removing the solvent *in vacuo*, the residue was dissolved in CH_2Cl_2, layered with acetonitrile and storage at -30 °C. After a few days, **1** can be obtained as dark violet blocks. The supernatant was decanted off and dried *in vacuo*.

Yield: 4.88 g (88 %).

^{1}H NMR (toluene-d$_8$, 293 K): δ [ppm] = 3.68 (s, 2H, C$_5$*H*$_2$^{t}Bu$_3$), 1.39 (s, 18H, C$_5$H$_2$^{t}*Bu*$_3$), 1.31 (s, 9H, C$_5$H$_2$^{t}*Bu*$_3$), 1.30 (s, 15H, C$_5$*Me*$_5$).

^{1}H NMR (toluene-d$_8$, 213 K): δ [ppm] = 3.77 (s, 2H, C$_5$*H*$_2$^{t}Bu$_3$), 1.45 (s, 18H, C$_5$H$_2$^{t}*Bu*$_3$), 1.34 (s, 9H, C$_5$H$_2$^{t}*Bu*$_3$), 1.27 (s, 15H, C$_5$*Me*$_5$).

^{31}P{^{1}H} NMR (toluene-d$_8$, 363 K): δ [ppm] = -115.3 (s, $\omega_{1/2}$ = 500 Hz).

^{31}P{^{1}H} NMR (toluene-d$_8$, 293 K): δ [ppm] = -164.7 (s, $\omega_{1/2}$ = 16000 Hz).

$^{31}P\{^{1}H\}$ NMR (toluene-d_8, 213 K): δ [ppm] = 289.3 (t, 1P; P_A), −205.8 (m, 2P; $P_M/P_{M'}$), −249.1 (m, 2P; $P_X/P_{X'}$). Corresponding coupling constants are taken from the simulation (Figure S1) and given in table S1.

LIFDI-MS (toluene): *m/z* = 638.2 (100 %, $[M]^+$).

EA: $C_{27}H_{44}CoFeP_5$: calc [%]: C: 50.81; H: 6.95; found [%]: C: 50.97; H: 6.90.

alternative procedure:

A solution of $[(Cp'''CoCl)_2]$ (73 mg, 0.10 mmol, 1 eq) in dme was added to a stirred solution of $[K_2(dme)_3][(Cp^*Fe)_2(\mu,\eta^4{:}\eta^4\text{-}P_{10})]$ (112 mg, 0.10 mmol eq) in dme at room temperature and stirred overnight. A color change from dark brown to violet was observed. The solvent was removed *in vacuo*, the residue extracted with hexane and filtered over diatomaceous earth. After removing the solvent *in vacuo*, the residue was dissolved in CH_2Cl_2, layered with acetonitrile and storage at -30 °C. After a few days, **1** can be obtained as dark violet blocks. The supernatant was decanted off and dried *in vacuo*.

Yield: 58 mg (41 %).

5.4.1.2 Reaction of $[(Cp^*Fe)(Cp'''Co)(\mu,\eta^5{:}\eta^4\text{-}P_5)]$ (1) with $[W(CO)_5(thf)]$

A solution of $W(CO)_6$ (246 mg, 0.70 mmol, 2.2 eq) in 50 mL thf was radiated for 3 hours, while the color changed to yellow. The $W(CO)_5(thf)$ solution was added to a stirred solution of **1** (200 mg, 0.3133, 1 eq) in 20 mL thf. After stirring for 1 h (solution turned from red/violet to brown) the solvent was removed *in vacuo*. The residue was dissolved in 10 mL hexane and purified by a short column chromatography (SiO_2, hexane, 12x3 cm) to remove remaining $[W(CO)_6]/[W(CO)_5(thf)]$. Using hexane/toluene (1:1) a dark brown fraction can be eluted. Removing the solvent *in vacuo* yields as dark brown powder (220 mg). The $^{31}P\{^{1}H\}$ NMR spectrum and mass spectrum both reveal a mixture of $[(Cp^*Fe)(Cp'''Co)(\mu_3,\eta^5{:}\eta^4{:}\eta^1\text{-}P_5)\{W(CO)_5\}]$ (**2a**) and $[(Cp^*Fe)(Cp'''Co)(\mu_4,\eta^5{:}\eta^4{:}\eta^1{:}\eta^1\text{-}P_5)\{W(CO)_5\}_2]$ (**2b**). By slow evaporation of solution in toluene very few crystals of **2b** could be obtained. The crude product was further purified by preparative thin layer chromatography (SiO_2,1mm 20x20 cm, hexane). The first strong dark brown and second very weak brown fraction were scratched of the plate, extracted with Et_2O and filtered over diatomaceous earth. The solvent was removed *in vacuo*. A concentrated solution of the first fraction in pentane was stored at -30°C. After a few days, **2a** can be obtained as black blocks. The supernatant (only **2a** according to $^{31}P\{^{1}H\}$ NMR) was decanted off and the crystals dried *in vacuo*. NMR spectra of fraction two reveals **2b**.

Crude reaction mixture:

^{31}P{^{1}H} NMR (C_6D_6, 293 K): δ [ppm] = 235.9 (t, 1P, P_A, **2b**), 190.1(br, **2a**), -110.7 (br, **2a**), -157.8 (m, 2P, $P_{M/M'}$, **2b**),-176.2 (t(br), **2a**), -182.3 (m, 2P, $P_{X/X'}$, **2b**), -209.8 (br, **2a**).

The spectrum is depicted in Figure S3.

LIFDI-MS (toluene): *m/z* = 1286.00 (100 %, [**2b**]$^+$), 962.06 (95 %, [**2a**]$^+$).

Compound **2a**: Yield: 46 mg (12 %).

^{1}H NMR (toluene-d_8, 293 K): δ [ppm] = 3.98 (br, 2H, , $C_5H_2{}^tBu_3$), 1.50 (br, 18H, $C_5H_2{}^tBu_3$), 1.31 (s, 9H, $C_5H_2{}^tBu_3$), 1.28 (s, 15H, C_5Me_5).

^{31}P{^{1}H} NMR (toluene-d_8, 293 K): δ [ppm] = 187.7 (br, 1P, P_A), -109.3 (br, 1P, P_M), -175.5 (t, 1P, P_N), -208.4 (br, 2P, P_X/P_Y).

^{1}H NMR (toluene-d_8, 193 K): δ [ppm] = 4.38 (s, 1H, $C_5H_2{}^tBu_3$), 3.66 (s, 1H, $C_5H_2{}^tBu_3$), 2.08 (s, 9H, $C_5H_2{}^tBu_3$), 1.31 (s, 9H, $C_5H_2{}^tBu_3$), 1.18 (s, 15H, C_5Me_5), 1.08 (s, 9H, $C_5H_2{}^tBu_3$).

^{31}P{^{1}H} NMR (toluene-d_8, 193 K): δ [ppm] = 249.9 (m, 1P; P_A), −-112.2 (m, 1P; P_M), −192.6 (m, 1P; P_N), −234.6 (m, 1P; P_X), −242.0 (m, 1P; P_Y). Corresponding coupling constants are taken from the simulation (Figure S6) and given in table S3.

LIFDI-MS (toluene): *m/z* = 961.97 (100 %, [M]$^+$).

EA $C_{32}H_{44}O_5FeCoP_5W$: calc [%]: C: 39.95; H: 4.61; found [%]: C: 40.27; H: 4.64.

ATR-IR (Ge crystal): $\bar{\upsilon}$ = 2065 (s, CO), 1990 (w, CO), 1972 (w, CO), 1943 (s, CO), 1905 (vs, CO), 1862 (w, CO) cm^{-1}.

Compound **2b**: Yield: only few crystals.

^{1}H NMR (C_6D_6, 293 K): δ [ppm] = 4.26 (s, 2H, , $C_5H_2{}^tBu_3$), 1.37 (s, 9H, $C_5H_2{}^tBu_3$), 1.30 (s, 18H, $C_5H_2{}^tBu_3$), 1.23 (s, 15H, C_5Me_5).

^{31}P{^{1}H} NMR (C_6D_6, 293 K): δ [ppm] = 236.0 (t, 1P; P_A), −157.7 (m, 2P; P_M/$P_{M'}$), −181.9 (m, 2P; P_X/$P_{X'}$). Corresponding coupling constants are taken from the simulation (Figure S6) and given in table S3.

LIFDI-MS (toluene): *m/z* = 1286.00 (100 %, [M]$^+$).

5.4.1.3 Synthesis of [(Cp'''Co)(Cp'''Ni)(μ,η³:η³-P₃] (3)

A solution of **A** (1.76 g, 2.60 mmol, 2 eq) in 100 mL pentane was added dropwise to a stirred solution of **E** (2.00 g, 5.20 mmol, 1 eq) in 200 mL hexane at room temperature. Thereby, the reaction mixture turned brown. After stirring the mixture for 2 hours, the solvent was removed under reduces pressure. The residue was dissolved in 20 mL CH_2Cl_2, mixed with silica and dried *in vacuo*. The preabsorbed crude mixture was purified by column chromatography (SiO_2, hexane, 15 x 4.5 cm). Using hexane, a weak brown fraction was eluted. Compound **3** can be eluted using hexane/toluene 1:1 as a dark brown fraction. After removing the solvent *in vacuo*, the residue was dissolved in CH_2Cl_2, layered with MeCN and storage at -30 °C. After a few days, **3** can be obtained as dark brown rods. The supernatant was decanted off and dried in vacuo.

Yield: 3.06 g (87 %).

^{1}H NMR (C_6D_6, 293 K): δ [ppm] = 4.96 (s, 2H, $C_5H_2{}^tBu_3$), 4.85 (s, 2H, $C_5H_2{}^tBu_3$), 1.42 (s, 18H, $C_5H_2{}^tBu_3$), 1.37 (s, 18H, $C_5H_2{}^tBu_3$), 1.12 (s, 18H, $C_5H_2{}^tBu_3$).

^{31}P{^{1}H} NMR (C_6D_6, 293 K): δ [ppm] = 376.5 (s, $\omega_{1/2}$ = 20 Hz, 2P, *chain*-P_3), 248.6 (br, $\omega_{1/2}$ = 148 Hz, 10P, *cyclo*-P_3), 132.3 (s, $\omega_{1/2}$ = 11 Hz, 1P, *chain*-P_3).

^{1}H NMR (toluene-d_8, 223 K): δ [ppm] = 5.24 (s, 2H, $C_5H_2{}^tBu_3$), 5.21 (s, 2H, $C_5H_2{}^tBu_3$), 4.99 (s, 2H, $C_5H_2{}^tBu_3$), 4.66 (s, 2H, $C_5H_2{}^tBu_3$), 1.40 (s, 18H, $C_5H_2{}^tBu_3$), 1.36 (s, 18H, $C_5H_2{}^tBu_3$), 1.33 (s, 18H, $C_5H_2{}^tBu_3$), 1.31 (s, 9H, $C_5H_2{}^tBu_3$), 1.29 (s, 18H, $C_5H_2{}^tBu_3$), 1.27 (s, 9H, $C_5H_2{}^tBu_3$), 0.98 (s, 9H, $C_5H_2{}^tBu_3$), 0.94 (s, 9H, $C_5H_2{}^tBu_3$).

^{31}P{^{1}H} NMR (toluene-d_8, 223 K): δ [ppm] = 373.2 (d,$^1J_{PP}$ = 359 Hz ,2P, *chain*-P_3), 239.4 (s, 3P, *cyclo*-P_3), 130.6 (t, $^1J_{PP}$ = 359 Hz, 1P, *chain*-P_3).

LIFDI-MS (toluene): *m/z* = 676.2 (100 %, $[M]^+$).

EA: $C_{34}H_{58}CoNiP_3$: calc [%]: C: 60.29; H: 8.63; found [%]: C: 60.17; H: 8.63.

5.4.1.4 Synthesis of [(Cp'''Co)(Cp'''Ni)(μ₃,η³:η²:η¹-P₅){W(CO)₅}] (4)

A solution of $W(CO)_6$ (229 mg, 0.65 mmol, 2.2 eq) in 50 mL thf was radiated for 3 hours, while the color changed to yellow. The $W(CO)_5$(thf) solution was added to a stirred solution of **3** (200 mg, 0.295, 1 eq) in 10 mL thf. After stirring for 1 h the solvent of the resulting brown solution was removed *in vacuo*. The residue was dissolved in CH_2Cl_2, SiO_2 added and the solvent removed *in vacuo*. The preabsorbed product was purified by column chromatography (SiO_2, hexane, 15 x 2.5 cm). Using hexane as an eluent a red to brown fraction (**4**) can be

obtained. The solvent was removed *in vacuo*. The residue was dissolved in CH_2Cl_2 and layered with acetonitrile at room temperature. After a few days **4** can be obtained in form of dark brown blocks. The supernatant was decanted off and the remaining crystals were dried *in vacuo*.

Yield: 81 mg (27 %).

^{1}H NMR (C_6D_6, 293 K): δ [ppm] = 4.99 (s, 2H, $C_5H_2{}^t$Bu$_3$), 4.91 (s, 2H, $C_5H_2{}^t$Bu$_3$), 1.45 (s, 18H, $C_5H_2{}^tBu_3$), 1.31 (s, 18H, $C_5H_2{}^tBu_3$), 1.30 (s, 9H, $C_5H_2{}^tBu_3$), 1.22 (s, 9H, $C_5H_2{}^tBu_3$).

^{31}P{^{1}H} NMR (C_6D_6, 293 K): δ [ppm] = 354.3 (d, $^1J_{PP}$ = 408 Hz, 2P, P_A), 114.6 (t, $^1J_{PP}$ = 408 Hz, $^1J_{PW}$ = 203 Hz, 1P, P_X).

^{31}P NMR (C_6D_6, 293 K): δ [ppm] = 354.3 (d, $^1J_{PP}$ = 408 Hz, 2P, P_A), 114.6 (t, $^1J_{PP}$ = 408 Hz, $^1J_{PW}$ = 203 Hz, 1P, P_X).

LIFDI-MS (toluene/CH_2Cl_2): *m/z* = 1000.2 (100 %, $[M]^+$).

EA $C_{39}H_{58}O_5CoNiP_3W$: calc [%]: C: 46.78; H: 5.84; found [%]: C: 46.71; H: 5.64.

ATR-IR (Ge crystal): $\bar{\nu}$ = 2064 (s, CO), 1986 (m, CO), 1977 (m, CO), 1929 (vs, CO), 1916 (s, CO), 1892 (w, CO) cm^{-1}.

5.4.1.5 Synthesis of [(Cp'''Ni)$_2$(μ,η^2:η^2-P$_2$)] (5)

A solution of **3** (70 mg, 0.104 mmol) in 20 mL toluene was stirred heated under reflux for one day. The solvent was removed under reduced pressure and the resulting brown solid was purified by a short column chromatography (SiO_2, hexane, 12 x 2 cm) using hexane/toluene 6:1 as an eluent. At first a red fraction of **5** was eluted, followed by a violet fraction of **D**. The solvent of the red fraction was removed *in vacuo*, the residue was dissolved in a small amount hexane and stored at -30 °C. After a few days **5** can be obtained as red blocks. The supernatant was decanted off and dried *in vacuo*.

Yield: 17 mg (51 %).

^{1}H NMR (C_6D_6, 293 K): δ [ppm] = 5.34 (s, 2H, $C_5H_2{}^t$Bu$_3$), 1.38 (s, 18H, $C_5H_2{}^tBu_3$), 1.34 (s, 9H, $C_5H_2{}^tBu_3$).

^{31}P{^{1}H} NMR (C_6D_6, 293 K): δ [ppm] = 282.7 (s, Ni_2P_2).

LIFDI-MS (toluene): *m/z* = 644.5 (100 %, $[M]^+$).

EI-MS (70 eV, toluene): *m/z* = 644.2 (100 %, $[M]^+$).

5.4.2 NMR studies

5.4.2.1 [(Cp*Fe)(Cp'''Co)(μ,η^5:η^4-P$_5$)] (1)

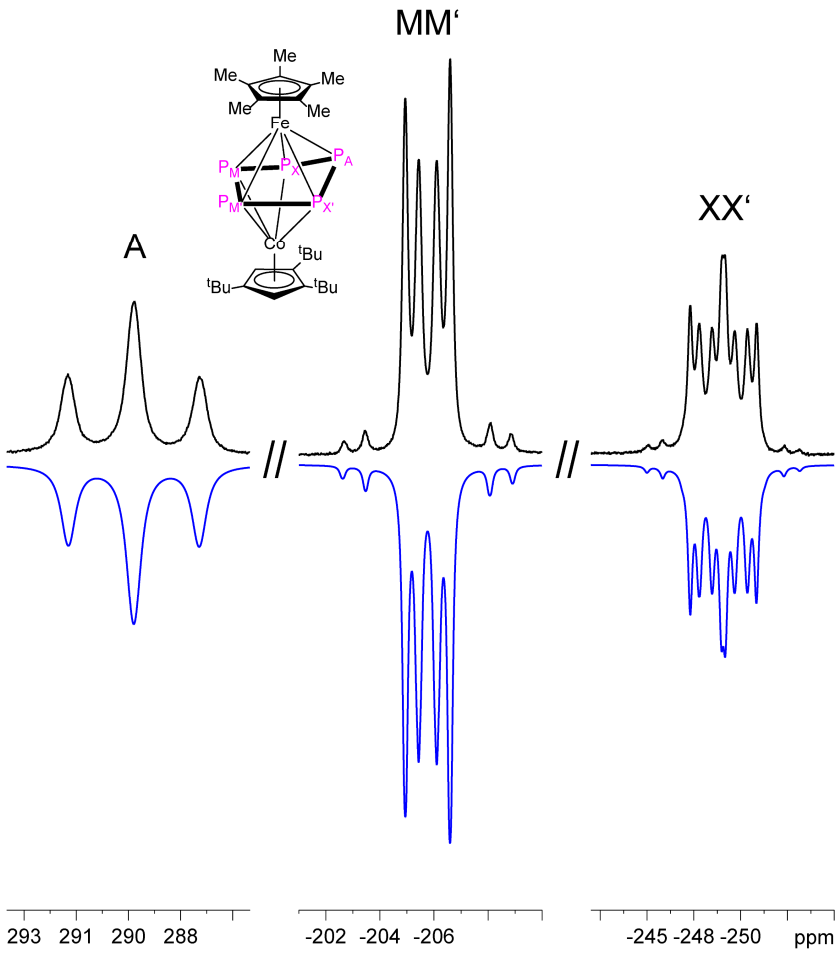


Figure S1: $^{31}P\{^1H\}$ NMR spectrum of **1** in toluene-d$_8$ at 213 K (measured top (black) and simulated bottom (blue)).

Table S1: Coupling constants obtained from the simulation in Figure **S1**.

	J [Hz]		δ [ppm]
$^1J_{P_AP_X} = {}^1J_{P_AP_{X'}}$	304.86	P_A	289.4
$^1J_{P_MP_X} = {}^1J_{P_{M'}P_{X'}}$	286.90	$P_{M/M'}$	-205.8
$^1J_{P_MP_{M'}}$	-386.68	$P_{X/X'}$	-249.1
$^1J_{P_XP_{X'}}$	76.73		
$^2J_{P_AP_M} = {}^2J_{P_AP_{M'}}$	13.27		
$^2J_{P_MP_{X'}} = {}^2J_{P_{M'}P_X}$	-18.19		
R-factor [%]	0.45		

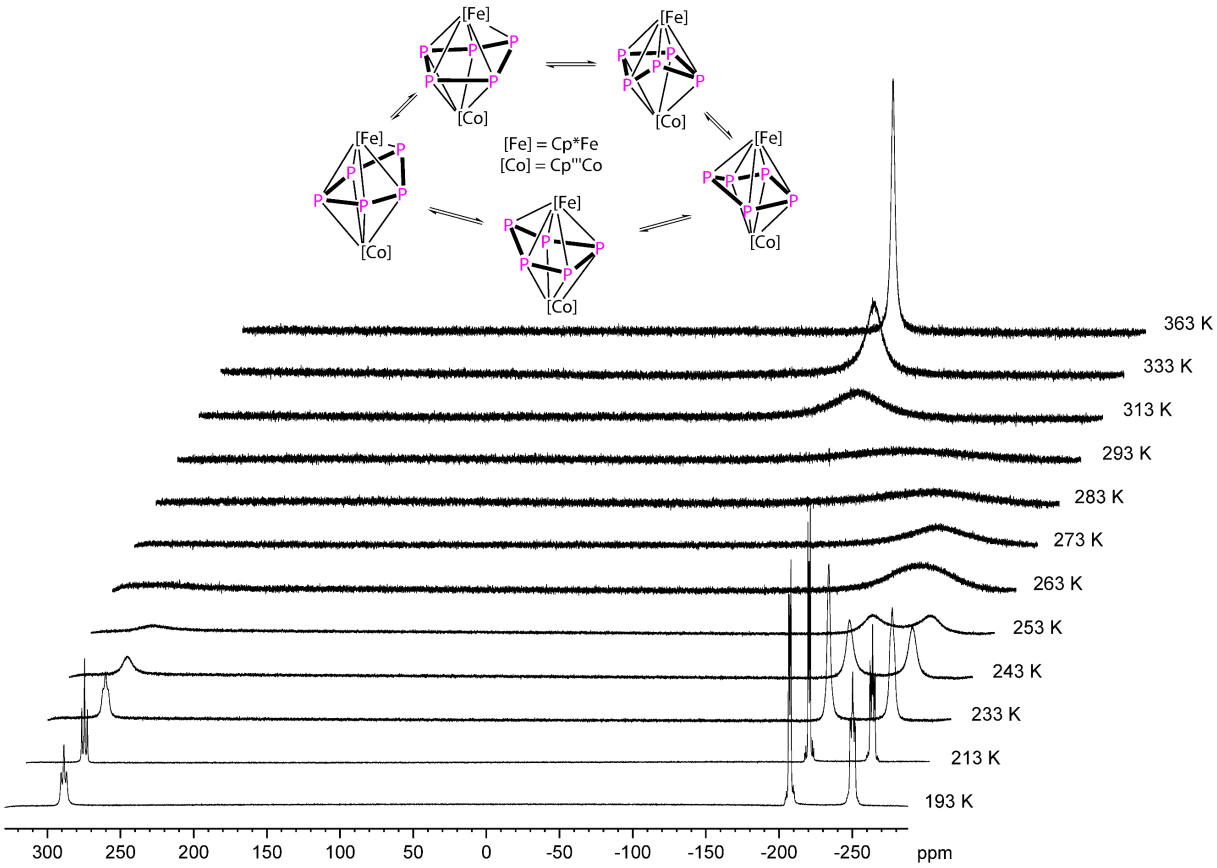


Figure S2:$^{31}P\{^{1}H\}$ NMR spectra of **1** in toluene-d_8 at different temperatures between 193 and 363 K and the proposed dynamic process.

Determination of activation barrier of the dynamic process illustrated in Figure S2.

The free activation enthalpy $\Delta G^{\ddagger}_{T_c}$ of this process can be calculated using the coalescence temperature T_c and the rate constant k_c at this temperature.[21] The rate constant k_c can be determined from the distance $\Delta\nu$ of the signals at δ = -205.8 and -249.1 ppm and their coupling constant J. Thereby, the distance of the two signals is calculated at a temperature, which is as far as possible below the coalescence temperature.

$$k_c = 2.22\sqrt{\Delta\nu^2 + 6J^2}$$

Moreover, the free activation enthalpy $\Delta G^{\ddagger}_{T_c}$ can be determined with the aid of the Eyring equation.

$$k = \chi\frac{k_B T}{h}e^{-\frac{\Delta G^{\ddagger}_{T_c}}{RT}}$$

$$\Delta G^{\ddagger}_{T_c} = -RT_c\ln\left(\frac{hk_c}{\chi k_B T_c}\right)$$

k_B = 1.3805 · 10^{-23} J K^{-1} (Boltzmann constant)

R = 8.3145 J K^{-1} mol^{-1} (universal gas constant)

h = 6.6261 · 10^{-34} J s

χ = transmission coefficient, generally equal to 1

The distance $\Delta\nu$ of the signals was calculated to be 6959.9 Hz with a coupling constant J of 286.6 Hz, which enables the calculation of the rate constant k_c to be 15529.5 s^{-1}. By entering this value into the Eyring equation the free activation enthalpy $\Delta G^{\ddagger}_{T_c}$ is 48.2 kJ mol^{-1}.

5.4.2.2 Reaction of [(Cp*Fe)(Cp'''Co)(μ,η^5:η^4-P$_5$)] (1) with [W(CO)$_5$(thf)]

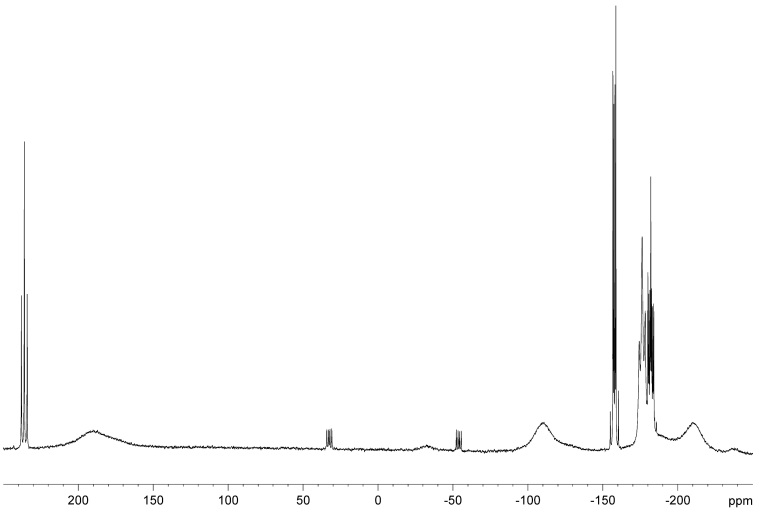


Figure S3: $^{31}P\{^1H\}$ NMR spectrum of the crude reaction mixture of the reaction of **1** with [W(CO)$_5$(thf)].

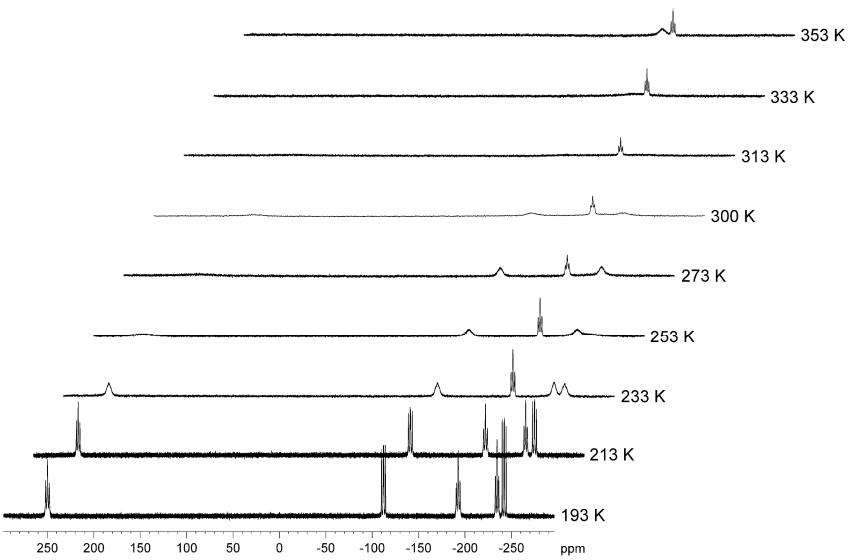


Figure S4:^{1}H NMR spectra of **2a** in toluene-d$_8$ at different temperatures between 193 and 353 K.

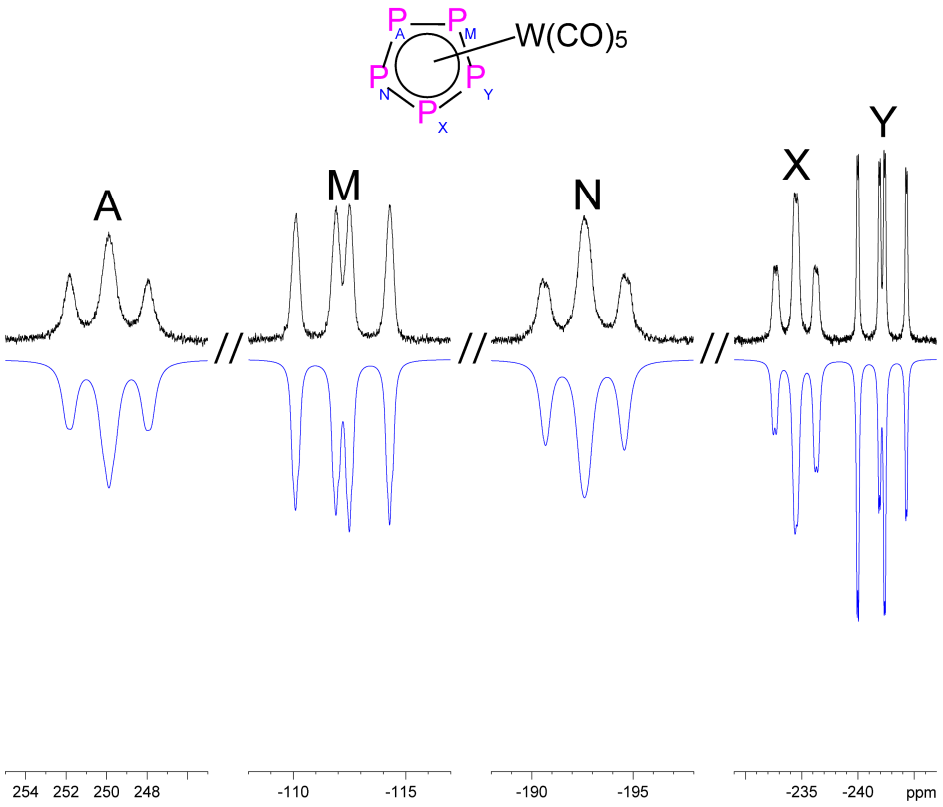


Figure S5: $^{31}P\{^{1}H\}$ NMR spectrum of **2a** in toluene-d_8 at 193 K (measured top (black) and simulated bottom (blue)).

Table S2: Coupling constants obtained from the simulation in Figure **S5**.

	J [Hz]		δ [ppm]
$^{1}J_{P_AP_M}$	290.22		
$^{1}J_{P_AP_N}$	342.91		
$^{2}J_{P_AP_X}$	50.52	P_A	249.9
$^{2}J_{P_AP_Y}$	2.46	P_M	-112.2
$^{2}J_{P_MP_N}$	20.98	P_N	-192.6
$^{2}J_{P_MP_X}$	20.51	P_X	-234.6
$^{2}J_{P_MP_Y}$	393.49	P_Y	-242.0
$^{1}J_{P_NP_X}$	293.79		
$^{2}J_{P_NP_Y}$	14.93		
$^{1}J_{P_XP_Y}$	312.23		
R-factor [%]	2.56		

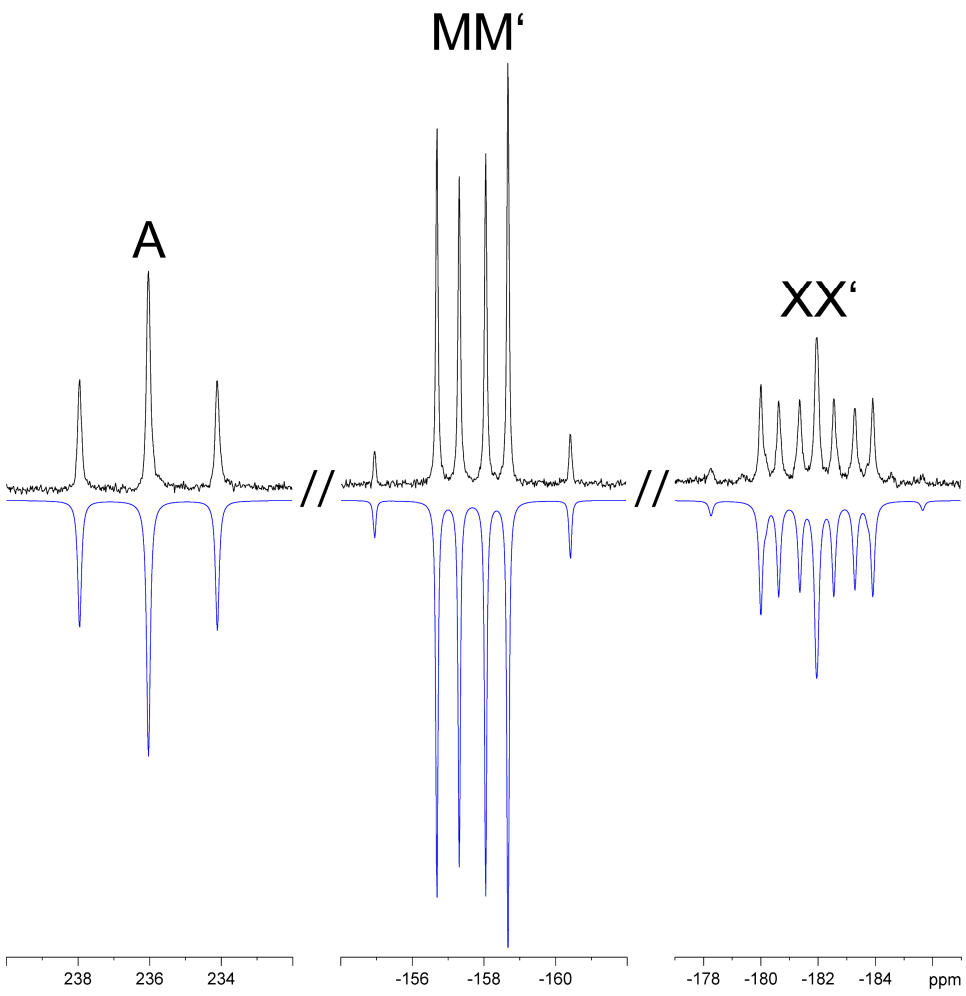


Figure S6: $^{31}P\{^{1}H\}$ NMR spectrum of **2b** in C_6D_6 at 293 K (measured top (black) and simulated bottom (blue)).

Table S3: Coupling constants obtained from the simulation in Figure **S5**.

	J [Hz]		δ [ppm]
$^{1}J_{P_AP_X} = {}^{1}J_{P_AP_X'}$	312.04	P_A	236.0
$^{1}J_{P_MP_X} = {}^{1}J_{P_M'P_X'}$	323.11	$P_{M/M'}$	-157.7
$^{1}J_{P_MP_M'}$	-384.20	$P_{X/X'}$	-181.9
$^{1}J_{P_XP_X'}$	2.63		
$^{2}J_{P_AP_M} = {}^{2}J_{P_AP_M'}$	2.82		
$^{2}J_{P_MP_X'} = {}^{2}J_{P_M'P_X}$	-0.87		
R-factor [%]	0.82		

5.4.2.3 [(Cp'''Co)(Cp'''Ni)(μ,η³:η³-P₃] (3)

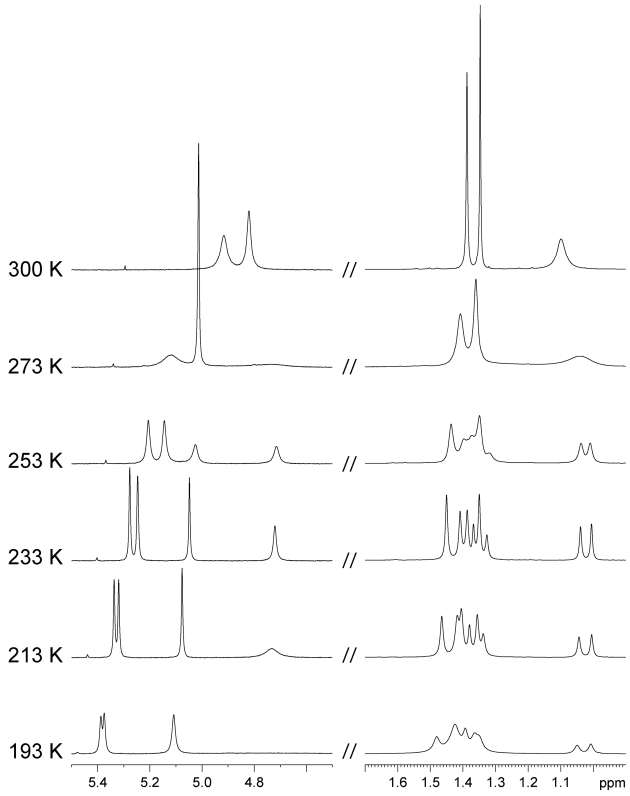


Figure S7:^{1}H NMR spectra of **3** in toluene-d_8 at different temperatures between 183 and 300 K (left part zoomed in).

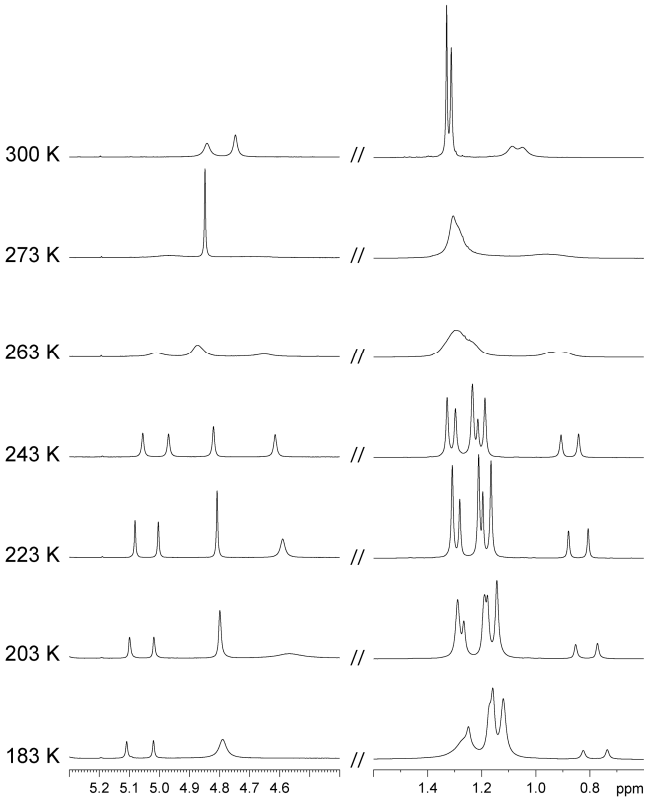


Figure S8:^{1}H NMR spectra of **3** in CD_2Cl_2 at different temperatures between 183 and 300 K (left part zoomed in).

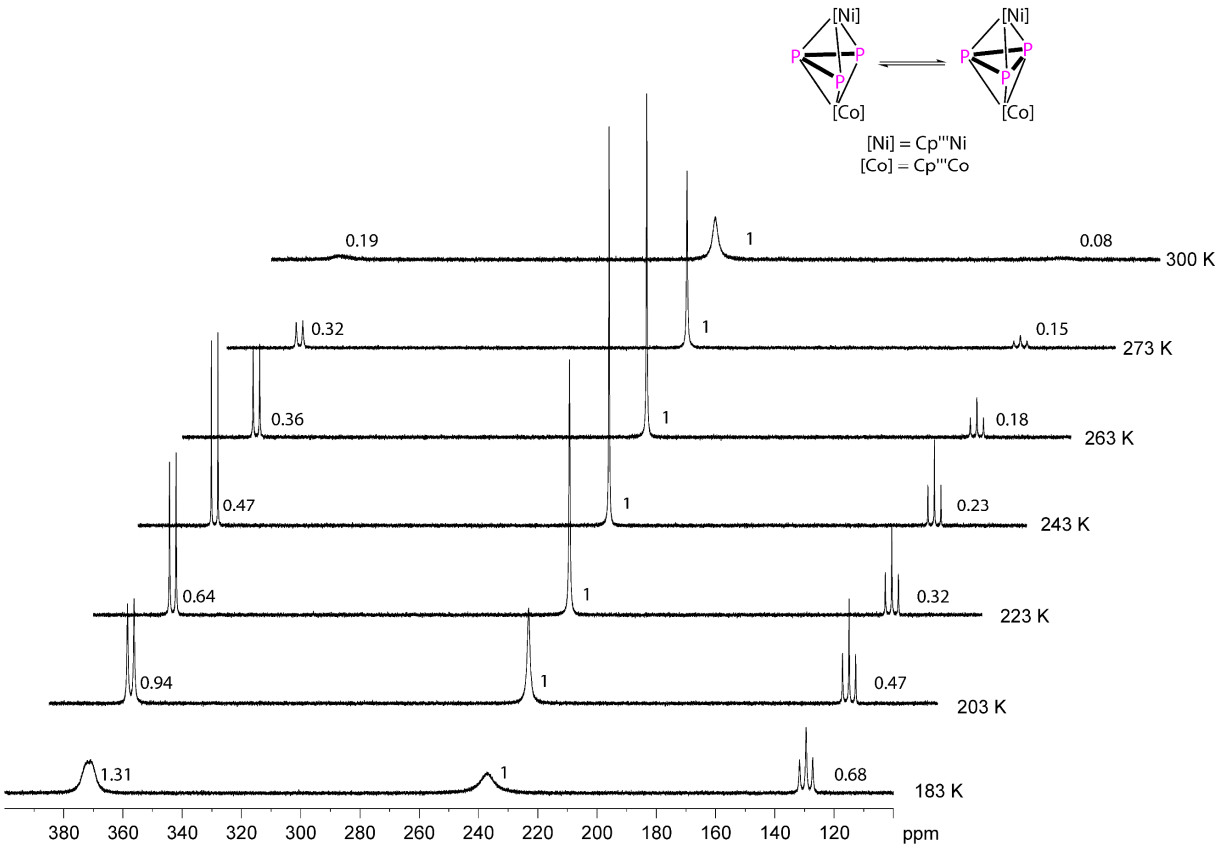


Figure S9:$^{31}P\{^{1}H\}$ NMR spectra of **3** in toluene-d_8 at different temperatures between 183 and 300 K and the proposed temperature dependent equilibrium (integrals given in the spectra).

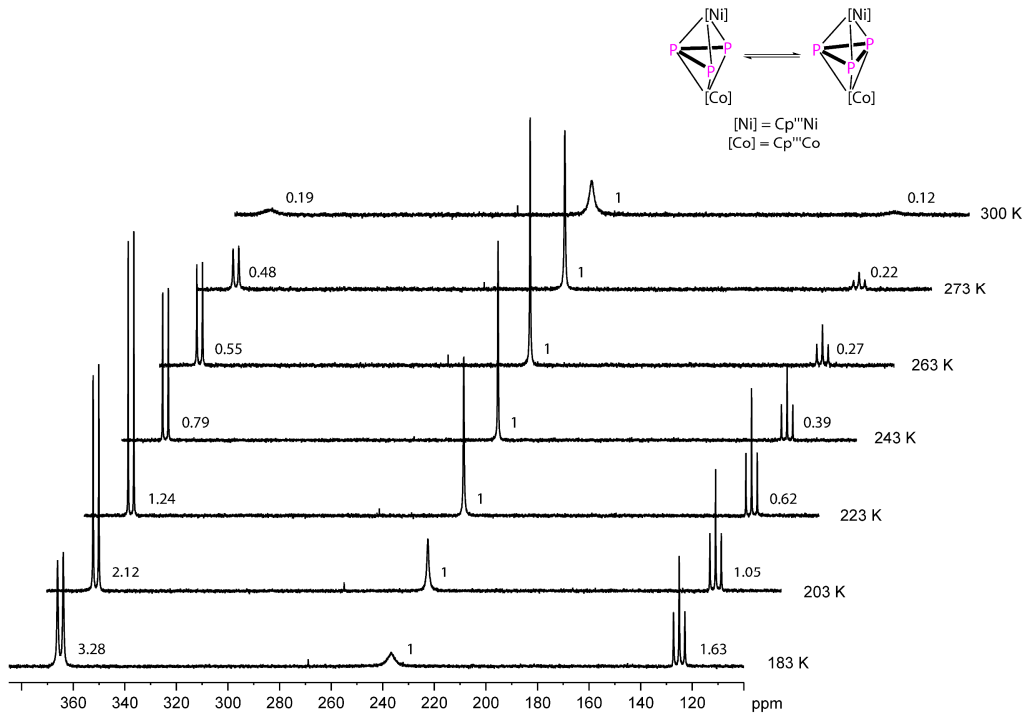


Figure S10:$^{31}P\{^{1}H\}$ NMR spectra of **3** in CD_2Cl_2 at different temperatures between 183 and 300 K and the proposed temperature dependent equilibrium (integrals given in the spectra).

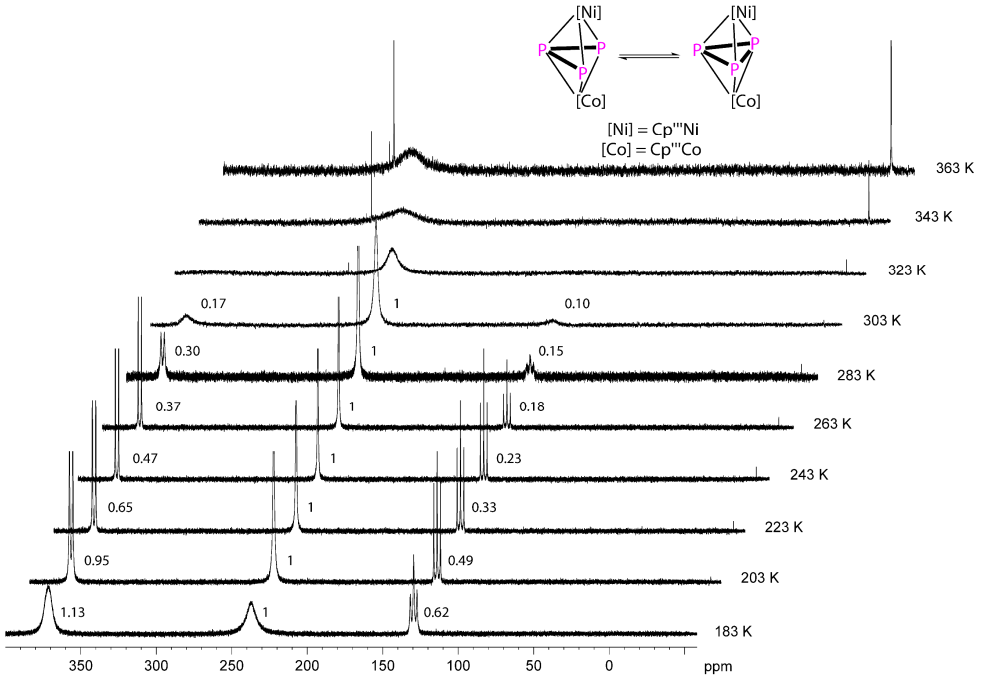


Figure S11:$^{31}P\{^{1}H\}$ NMR spectra of **3** in toluene-d_8 at different temperatures between 183 and 363 K and the proposed temperature dependent equilibrium (integrals given in the spectra).

5.4.2.4 [(Cp'''Co)(Cp'''Ni)(μ_3,η^3:η^2:η^1-P_3){$W(CO)_5$}] (4)

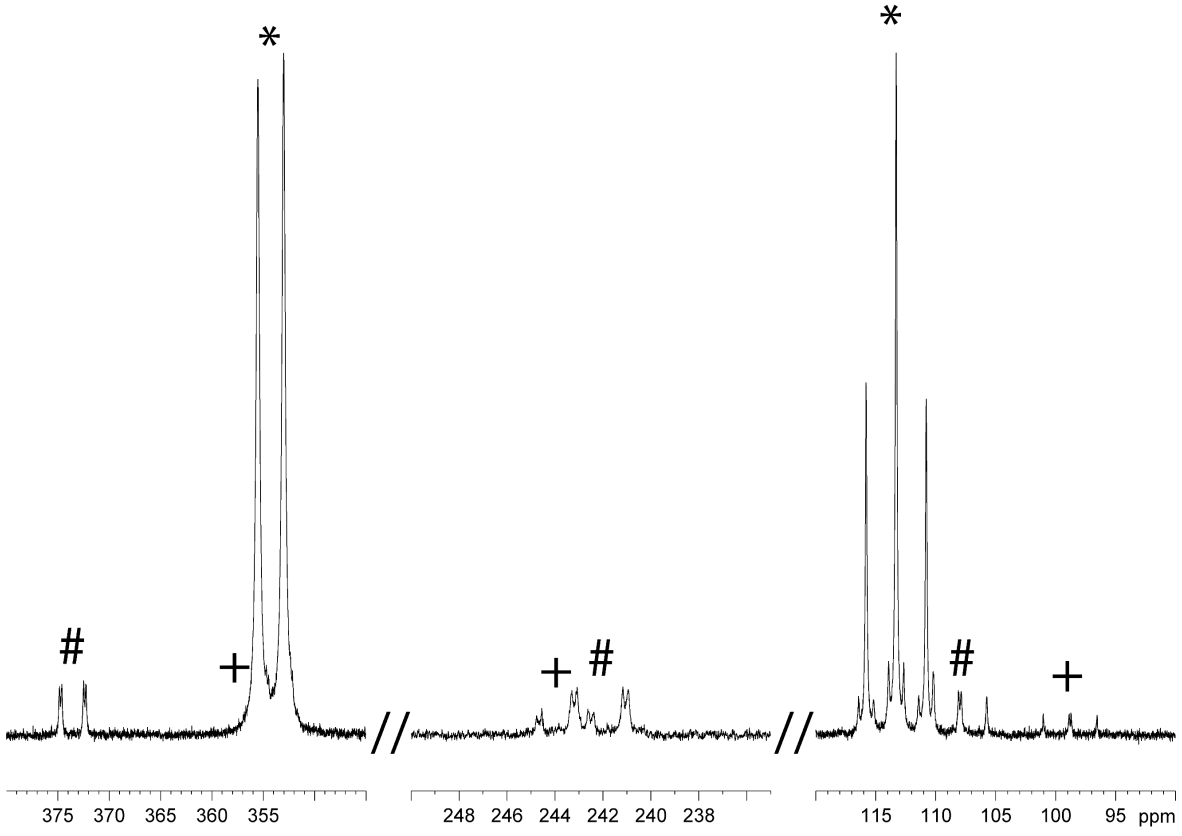


Figure S12: $^{31}P\{^{1}H\}$ NMR spectrum of the crude reaction mixture from the reaction of **3** with $[W(CO)_5(thf)]$ in C_6D_6 at 293 K. Signals marked with * belong to **4**, marked with # belong to isomer **I4-C** and + to isomer **I4-B**.

Compound **4**:

$^{31}P\{^{1}H\}$ NMR (C_6D_6, 293 K): δ [ppm] = 354.3 (d, $^{1}J_{PP}$ = 404 Hz, 2P, P_A), 113.3 (d, $^{1}J_{PP}$ = 406 Hz, $^{1}J_{PW}$ = 199 Hz, 1P, P_X).

Compound **I4-C**:

$^{31}P\{^{1}H\}$ NMR (C_6D_6, 293 K): δ [ppm] = 373.5 (dd, $^{1}J_{PP}$ = 386 Hz, $^{2}J_{PP}$ = 36 Hz, 0.1P, P_A), 242.1 (dd, $^{1}J_{PP}$ = 344 Hz, $^{2}J_{PP}$ = 36 Hz, 0.1P, P_M), 108.0 (dd, $^{1}J_{PP}$ = 386 Hz, $^{1}J_{PP}$ = 344 Hz 0.1P, P_X).

Compound **I4-B**:

$^{31}P\{^{1}H\}$ NMR (C_6D_6, 293 K): δ [ppm] = approx. 353 (overlapped by signal of **4**), 243.6 (dd, $^{1}J_{PP}$ = 345 Hz, $^{2}J_{PP}$ = 33 Hz, 0.04P, P_M), 98.8 (dd, $^{1}J_{PP}$ = 380 Hz, $^{1}J_{PP}$ = 345 Hz 0.04P, P_X).

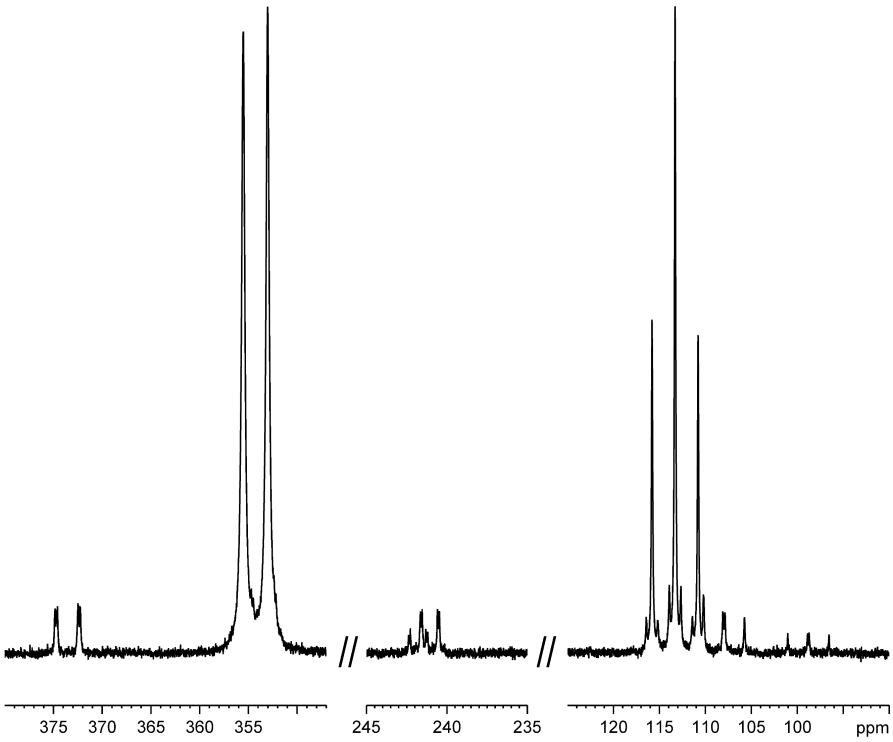


Figure S13: $^{31}P\{^{1}H\}$ NMR spectrum of **4** in C_6D_6 at 293 K.

5.4.3 Details on single crystal X-ray structure analysis

The X-ray diffraction experiments were performed on either an Gemini Ultra diffractometer (Oxford diffraction) with an AtlasS2 detector Mo radiation (λ = 0.71073 Å) (**1**), a GV 50 diffractometer (Rigaku, formerly Agilent Technologies) with TitanS2 detector from applying applying Cu-K*α* radiation (λ = 1.54178 Å) (**2a**) or Cu-K*β* radiation (λ = 1.39222 Å) (**3**) or SuperNova (Agilent Technologies) with an Atlas detector applying Cu-K*α* radiation (λ = 1.54178 Å) (**2b**, **4**, **5**). All measurements were performed at 123 K. An analytical numeric absorption correction[29] using a multifaceted crystal model based on expressions derived by R.C. Clark & J.S. Reid using spherical harmonicsas implemented in SACLE3 ABSPACK was applied (**1**, **2a**, **3**, **4**, **5**).[30] A numerical absorption correction based on gaussian integration over a multifaceted crystal model using *CrysAlisPro* using spherical harmonicsas implemented in SACLE3 ABSPACK was applied (**2b**). All structures were solved by direct methods with ShelXT[31] and Olex2[32] and refined by full-matrix least-squares method against F^2 in anisotropic approximation using ShelXL[33]. Hydrogen atoms were refined in calculated positions using riding on pivot atom model.

CCDC-1965029 (**1**), CCDC-1965030 (**2a**), CCDC-1965031 (**2b**), CCDC-1965032 (**3**), CCDC-1965033 (**4**) and CCDC-1965034 (**5**), contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: + 44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

5.4.3.1 [(Cp*Fe)(Cp'''Co)(μ,η^5:η^4-P$_5$)] (1)

Compound **1** crystallizes from a concentrated solution in ortho-difluoro benzene layered with hexane at -30 °C in the triclinic space group $P\bar{1}$ as dark violet plates. The asymmetric unit contains five molecules **1** while three of them are heavily disordered. The P_5 ligand of two molecules is disordered over two positions (occupancy of 0.95 and 0.05) and of one molecule disordered over four positions (occupancy of 0.40, 0.35, 0.15 and 0.10) and two ^{t}Bu groups of the latter molecule is disordered over two positions (occupancy of 0.50 and 0.50). The restrains SADI, SIMU and ISOR were applied to describe the disorder. Bond lengths and distances are given of one non-disordered molecule. The complete structure in solid state is depicted in Figure S14 and S15.

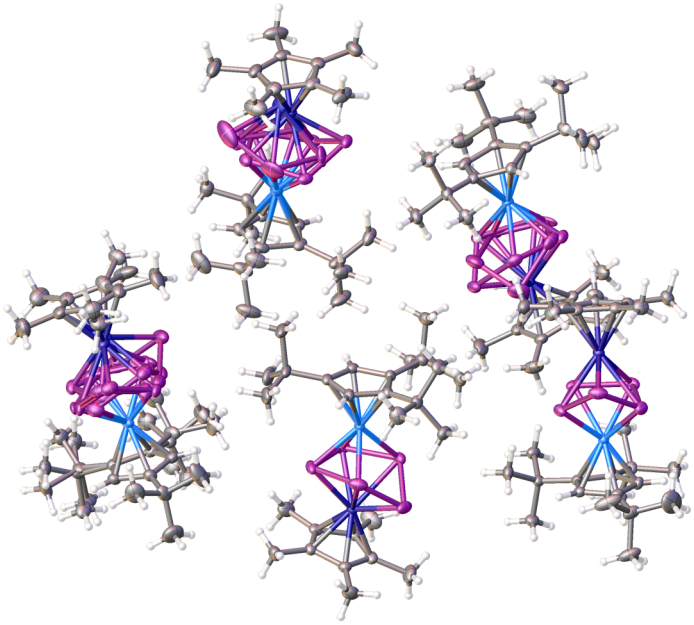


Figure S14: Molecular structure of **1** in solid state. Thermal ellipsoids are drawn with 50 % probability level.

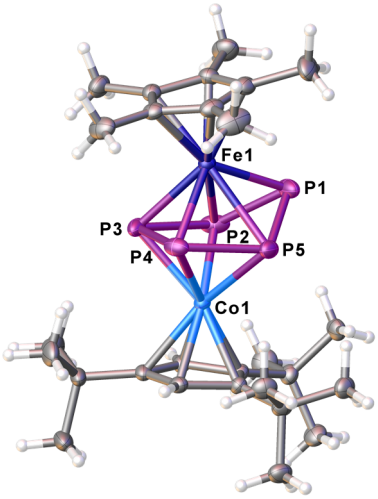


Figure S15: Molecular structure of **1** in solid state. Thermal ellipsoids are drawn with 50 % probability level. Depicted is one of the non-disordered molecules within the asymmetric unit. Selected bond lengths [Å] and angles [°]: P1-P2 2.1519(11), P2-P3 (2.2307(11), P3-P4 2.1266(10), P4-P5 2.2459(10), P1-P5 2.1505(11), Co1-P1 3.3325(8), Co1-P2 2.2991(8), Co1-P3 2.3228(7), Co1-P4 2.3159(7), Co1-P5 2.3088(7), Fe1-P1 2.2697(8), Fe1-P2 2.5299(8), Fe1-P3 2.3481(7), Fe1-P4 2.3396(7), Fe1-P5 2.5056(7), P1-P2-P3 112.96(4), P2-P3-P4 100.27(4), P3-P4-P5 100.06(4), P4-P5-P1 112.90(4), P2-P1-P5 85.37(4), Cp*-Fe-Co-Cp''' 13.161 (166.839).

5.4.3.2 [(Cp*Fe)(Cp'''Co)(μ$_3$,η^5:η^4:η^1-P$_5$){W(CO)$_5$}] (2a)

Compound **2a** crystallized from a concentrated solution in pentane at -30 °C in the monoclinic space group $P2_1/n$ as black blocks. The asymmetric contains one molecule of **2a**. The structure in solid state is given in Figure S16.

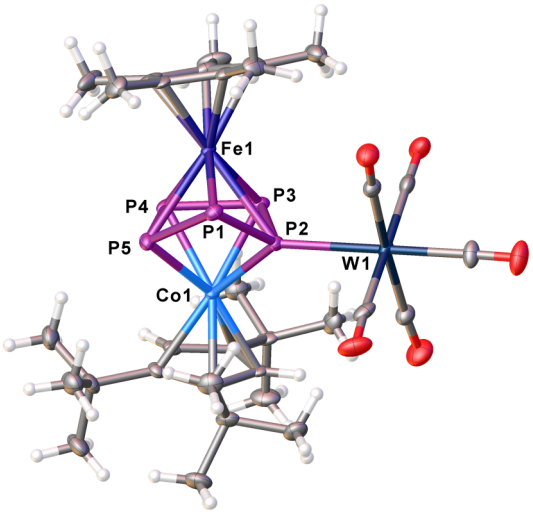


Figure S16: Molecular structure of **1** in solid state. Thermal ellipsoids are drawn with 50 % probability level. Selected bond lengths [Å] and angles [°]: P1-P2 2.1350(13), P2-P3 2.2476(14), P3-P4 2.1269(16), P4-P5 2.2504(16), P1-P5 2.1720(16), P2-W1 2.5537(10), P1-P2-P3 112.60(6), P2-P3-P4 98.52(6). P3-P4-P5 101.18(6), P1-P5-P4 111.68(6), P2-P1-P5 84.61(5), Cp*-Fe-Co-Cp''' 22.276 (157.724), P2-P4-P5-P1 34.695, P2-P3-P5-P1 34.110.

5.4.3.3 [(Cp*Fe)(Cp'''Co)(μ$_4$,η^5:η^4:η^1:η^1-P$_5$){W(CO)$_5$}$_2$] (2b)

Compound **2b** crystalizes from a concentrated solution in toluene while the solvent is slowly removed *in vacuo* in the orthorhombic space group $Pca2_1$ as dark brown plates. The asymmetric unit contains two molecules of **2b**. A refinement as an inverse twin was carried out. The restraint ISOR was applied to two carbon atoms. The structure in solid state is shown in Figure S17 and S18.

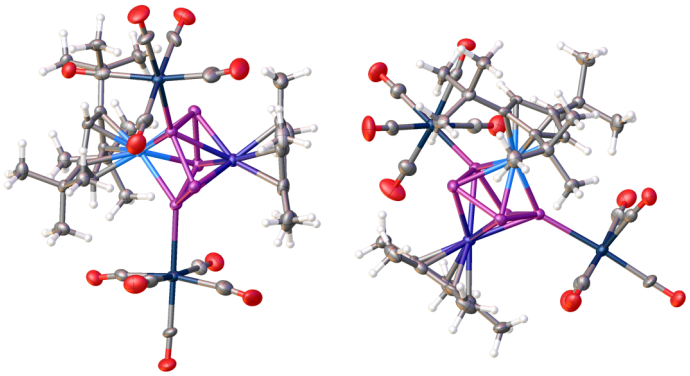


Figure S17: Molecular structure of **2a** in solid state. Thermal ellipsoids are drawn with 50 % probability level.

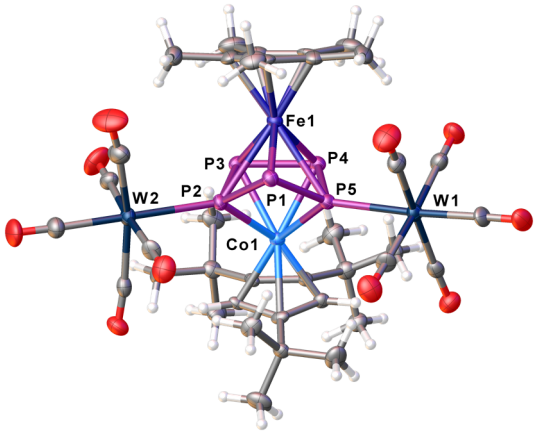


Figure S18: Molecular structure of **2a** in solid state. Thermal ellipsoids are drawn with 50 % probability level. Selected bond lengths [Å] and angles [°]: P1-P2 2.148(4), P2-P3 2.236(4), P3-P4 2.136(4), P4-P5 2.263(4), P1-P5 2.154(4), P2-W2 2.564(3), P5-W1 2.551(2), P1-P2-P3 110.79(15), P2-P3-P4 100.04(15), P3-P4-P5 98.68(15), P1-P5-P4 111.13(15), P2-P1-P5 83.62(13), Cp*-Fe-Co-Cp''' 25.659 (154.341), P2-P4-P5-P1 37.833, P2-P3-P5-P1 36.159.

5.4.3.4 [(Cp'''Co)(Cp'''Ni)(μ,η^3:η^3-P$_3$)] (3)

Compound **3** crystallizes from a concentrated solution in ortho-difluoro benzene layered with acetonitrile at -30 °C in the monoclinic space group $P2_1/c$ as dark brown needles. The asymmetric unit contains one molecule **3**. The structure in solid state is shown in figure S19.

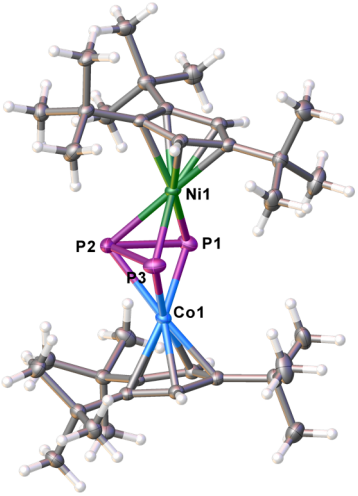


Figure S19: Molecular structure of **3** in solid state. Thermal ellipsoids are drawn with 50 % probability level. Selected bond lengths [Å] and angles [°]: P1-P2 2.1895(6), P2-P3 2.1945(6), P1-P3 2.7619(6), Co1-Ni1 3.3941(5), Ni1-P1 2.1826(5), Ni1-P2 2.3538(5), Ni1-P3 2.1931(5), Co1-P1 2.1965(5), Co1-P2 2.3457(4), Co1-P3 2.1849(5), Ni1-Co1 3.3941(5), P1-P2-P3 78.10(2), Ni1-P1-Co1 101.620(18), Ni1-P2-Co1 92.476(15), Ni1-P3-Co1 101.661(19), Cp'''-Ni-Co-Cp''' 18.064(161.936).

5.4.3.5 [(Cp'''Co)(Cp'''Ni)(μ$_3$,η^3:η^2:η^1-P$_3$){W(CO)$_5$}] (4)

Compound **4** crystallizes from a concentrated solution in CH_2Cl_2 layered with MeCN at room temperature in the triclinic space group $P\bar{1}$ in form of dark brown blocks. The asymmetric unit contains two molecules of **4**. The structure in solid state is shown in Figure S20 and S21.

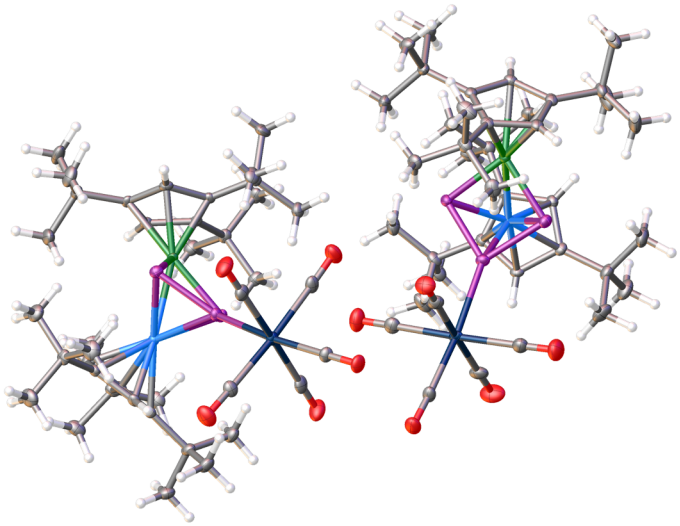


Figure S20: Molecular structure of **4** in solid state. Thermal ellipsoids are drawn with 50 % probability level.

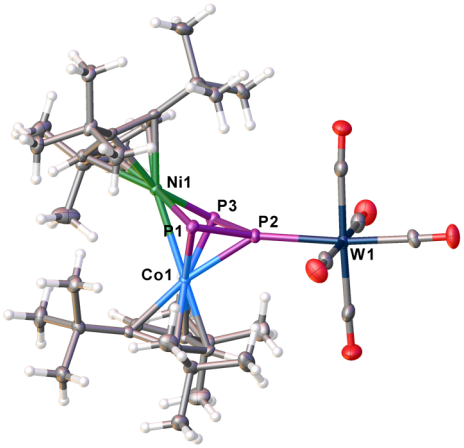


Figure S21: Molecular structure of **4** in solid state. Thermal ellipsoids are drawn with 50 % probability level. Selected bond lengths [Å] and angles [°]: P1-P2 2.1213(9), P2-P3 2.1238(10), P1-P3 3.0005(11), Ni1-P1 2.1928(8), Ni1-P2 3.0425(9), Ni1-P3 2.1882(8), Ni1-Co1 2.6182(6), Co1-P1 2.2397(8), Co1-P2 2.3277(8), Co1-P3 2.2362(8), W1-P2 2.4846(7), P1-P2-P3 89.95(4), Cp'''-Ni-Co-Cp''' 52.364.

5.4.3.6 [(Cp'''Ni)$_2$(μ,η^2:η^2-P$_2$)] (5)

Compound **5** crystallizes from a concentrated solution in hexane stored at -30 °C in the triclinic space group $P\bar{1}$ as red blocks. The asymmetric unit contains one molecule **5**. The structure in solid state is shown in figure S22.

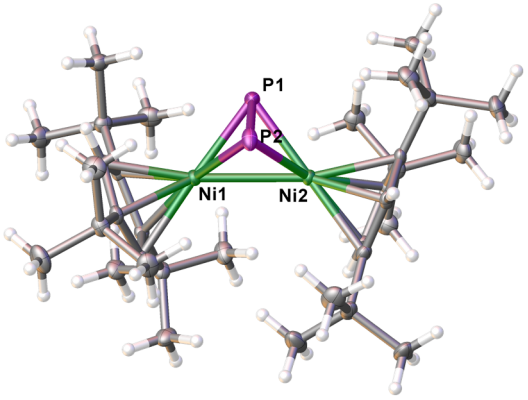


Figure S22: Molecular structure of **5** in solid state. Thermal ellipsoids are drawn with 50 % probability level. Selected bond lengths [Å] and angles [°]: Ni1-Ni2 2.5848(5), P1-P2 2.0805(8), Ni1-P1 2.1995(6), Ni1-P2 2.2066(6), Ni2-P1 2.1983(6), Ni2-P2 2.1987(6), Ni2-Ni1-P1 53.982(17), Ni2-Ni1-P2 53.933(16), Ni1-Ni2-P1 54.023(16), Ni1-Ni2-P2 54.216(16), P1-Ni1-P2 56.35(2), P1-Ni1-P2 56.48(2), Ni1-P1-P2 62.00(1), Ni1-P2-P1 61.65(2), Ni2-P1-P2 61.77(2), Ni2-P2-P1 61.75(2), Ni1-P1-Ni2 71.99(2), Ni1-P2-Ni2 71.851(19).

5.4.3.7 Crystallographic information

Table S4: Crystallographic data for all compounds

	1	2a	2b	3	4	5
CCDC	1965029	1965030	1965031	1965032	1965033	1965034
Formula	$C_{135}H_{220}Co_5Fe_5P_{25}$	$C_{32}H_{44}CoFeO_5P_5W$	$C_{74}H_{88}Co_2Fe_2O_{20}P_{10}W_4$	$C_{34}H_{58}CoNiP_3$	$C_{78}H_{116}Co_2Ni_2O_{10}P_6W_2$	$C_{34}H_{58}Ni_2P_2$
$D_{calc.}$/ g cm^{-3}	1.407	1.717	1.947	1.270	1.582	1.249
μ/mm^{-1}	1.312	14.455	17.120	7.061	9.910	2.371
Formula Weight	3191.25	962.15	2572.10	677.35	2002.50	646.16
Colour	dark black	dark black	clear brown	clear dark brown	clear dark brown	clear dark red
Shape	plate	block	block	needle	block	block
Size/mm^3	0.65×0.32×0.04	0.21×0.13×0.07	0.39×0.21×0.15	0.27×0.05×0.03	0.24×0.15×0.12	0.15×0.06×0.03
T/K	123.01(10)	123.00(10)	123.00(10)	123.02(13)	123.01(10)	123(1)
Crystal System	triclinic	monoclinic	orthorhombic	monoclinic	triclinic	triclinic
Flack Parameter			0.503(8)			
Hooft Parameter			0.498(5)			
Space Group	*P*-1	$P2_1/n$	$Pca2_1$	$P2_1/c$	*P*-1	*P*-1
a/Å	11.91379(19)	10.04893(15)	12.3918(3)	14.2229(5)	11.7671(3)	8.7286(5)
b/Å	22.7577(5)	31.8158(5)	40.0229(7)	19.1947(4)	11.8506(3)	12.1860(5)
c/Å	29.2373(5)	11.94872(18)	17.6945(4)	14.6893(5)	35.0039(6)	17.2330(9)
α/°	107.5943(17)	90	90	90	83.149(2)	81.990(4)
β/°	94.0464(14)	102.9845(15)	90	117.956(4)	84.296(2)	88.160(4)
γ/°	90.3095(15)	90	90	90	60.283(2)	71.242(4)
V/Å^3	7534.5(3)	3722.50(10)	8775.7(3)	3542.3(2)	4204.39(18)	1718.57(16)
Z	2	4	4	4	2	2
Z'	1	1	1	1	1	1
Wavelength/Å	0.71073	1.54184	1.54184	1.39222	1.54184	1.54184
Radiation type	Mo K_α	Cu K_α	Cu K_α	Cu K_β	Cu K_α	Cu K_α
θ_{min}/°	3.339	4.043	3.734	3.713	3.820	3.867
θ_{max}/°	30.508	73.909	73.679	74.009	73.824	76.583
Measured Refl.	94291	13945	18946	24385	47322	11343
Independent Refl.	45861	7242	12534	9639	16650	6907
Reflections with I > 2(I)	36206	6591	12153	7922	15916	6103
R_{int}	0.0292	0.0485	0.0310	0.0347	0.0251	0.0415
Parameters	1814	421	1038	370	937	361
Restraints	144	0	13	0	0	0
Largest Peak	1.937	1.547	1.822	0.373	0.999	0.451
Deepest Hole	-0.760	-3.036	-1.254	-0.432	-0.658	-0.478
GooF	1.051	1.070	1.068	1.016	1.121	1.018
wR_2 (all data)	0.1211	0.1018	0.0899	0.0815	0.0593	0.1170
wR_2	0.1113	0.0986	0.0891	0.0759	0.0585	0.1107
R_1 (all data)	0.0661	0.0465	0.0356	0.0434	0.0299	0.0487
R_1	0.0480	0.0422	0.0341	0.0325	0.0273	0.0431

5.4.4 Computational Details

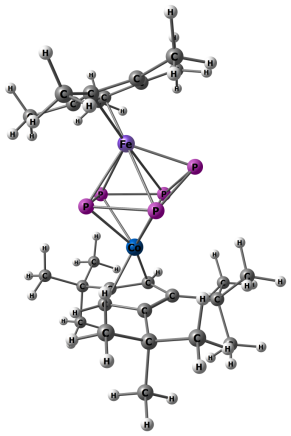
Gaussian 09 program package was used throughout.[34] Density functional theory (DFT) in form of Becke's three-parameter hybrid functioncal B3LYP[35] with def2-SVP all electron basis set[36] was employed. The Natural Bond Orbital (NBO) analysis has been performed with the NBO3.1 program implemented in Gaussian 09 program package. The figures for the energy schemata were created using OLEX2.[32] The figures for the supporting information concerning the DFT calculations were created with Chemcraft.[37]

5.4.4.1 Computations for [(Cp*Fe)(Cp'''Co)(μ,η^5:η^4-P$_5$] (1) and the reaction with [W(CO)$_5$(thf)]

Table S5: Total energies for all optimized geometries (B3LYP/def2-SVP level of theory).

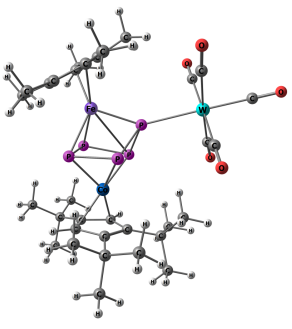
	total energy [Ha]
1 [(Cp*Fe)(Cp'''Co)(μ,η^5:η^4-P$_5$]	-5407.2923483
[W(CO)$_5$(thf)]	-865.7468723
thf	-232.2786488
I2a [(Cp*Fe)(Cp'''Co)(μ$_3$,η^5:η^4:η^1-P$_5$){W(CO)$_5$}]	-6040.7694041
2a [(Cp*Fe)(Cp'''Co)(μ$_3$,η^5:η^4:η^1-P$_5$){W(CO)$_5$}]	-6040.7694595
2b [(Cp*Fe)(Cp'''Co)(μ$_4$,η^5:η^4:η^1:η^1-P$_5$){W(CO)$_5$}$_2$]	-6674.2315986

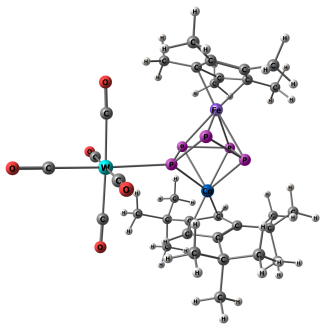
Table S6: Optimized geometries of **1** (left), [W(CO)$_5$(thf)] (middle) and thf (right). XYZ coordinated in angstroms. B3LYP/def2-SVP level of theory.



C	4.278226000	-0.413393000	-0.943268000	H	-5.404207000	-1.448600000	1.281596000	W	1.603117000	2.337707000	0.651551000	H	-1.554550000	0.701872000	0.072534000
C	4.090072000	0.968651000	-0.605668000	H	-4.996592000	-0.160167000	2.433822000	C	2.670206000	4.022345000	0.585305000	O	0.424896000	0.505342000	0.680570000
C	3.924161000	1.062103000	0.818337000	C	-2.526943000	-1.092275000	3.214594000	O	3.289051000	4.999227000	0.546999000	C	1.008258000	-0.785702000	0.547777000
C	3.980655000	-0.269075000	1.356288000	H	-2.840608000	-1.784091000	4.011968000	C	3.306423000	1.306739000	1.251011000	C	-0.159254000	-1.774905000	0.458258000
C	4.213687000	-1.178836000	0.271203000	H	-2.739455000	-0.075859000	3.574413000	O	4.267990000	0.769036000	1.582154000	C	-1.220182000	-1.070459000	1.313617000
C	4.458671000	-2.652751000	0.407048000	H	-1.439093000	-1.194510000	3.091486000	C	2.092034000	1.995139000	-1.339133000	C	-0.965896000	0.399717000	0.962133000
H	5.527218000	-2.847573000	0.609660000	C	-3.260995000	-1.687169000	-1.699773000	O	2.386946000	1.842036000	-2.440829000	H	1.657812000	-0.801659000	-0.344159000
H	4.185933000	-3.198641000	-0.506387000	C	-2.347687000	-2.928991000	-1.642192000	C	-0.078309000	3.402929000	0.050399000	H	1.645551000	-1.003722000	1.428413000
H	3.882726000	-3.087587000	1.237056000	H	-1.318175000	-2.668517000	-1.922705000	O	-0.987268000	4.023395000	-0.284638000	H	0.101206000	-2.782462000	0.816188000
C	3.901571000	-0.645904000	2.806173000	H	-2.710902000	-3.688428000	-2.354082000	C	1.155405000	2.745516000	2.639637000	H	-0.507821000	-1.866248000	-0.584237000
H	4.911407000	-0.714374000	3.248303000	H	-2.311219000	-3.391834000	-0.652518000	O	0.930297000	3.008866000	3.736952000	H	-1.027843000	-1.249354000	2.384897000
H	3.411761000	-1.620779000	2.944975000	C	-3.175375000	-1.159312000	-3.151785000	H	-1.682819000	0.772799000	0.682919000	H	-2.249798000	-1.393363000	1.097403000
H	3.332730000	0.091939000	3.389535000	H	-2.162816000	-0.809543000	-3.404027000	O	0.354506000	0.365764000	0.729898000	H	-1.224848000	1.091325000	1.782100000
C	3.783776000	2.329140000	1.606502000	H	-3.884794000	-0.339134000	-3.340586000	C	0.788996000	-0.899005000	0.180426000				
H	4.775768000	2.750377000	1.847102000	H	-3.424980000	-1.975167000	-3.847616000	C	-0.455461000	-1.782674000	0.193042000				
H	3.255193000	2.161384000	2.555969000	C	-4.736332000	-2.094666000	-1.468365000	C	-1.222789000	-1.248813000	1.410543000				
H	3.223642000	3.097204000	1.052375000	H	-5.400814000	-1.216723000	-1.510505000	C	-0.955977000	0.251720000	1.329657000				
C	4.151530000	2.116942000	-1.568881000	H	-4.890501000	-2.586340000	-0.499553000	H	1.196914000	-0.715604000	-0.823981000				
H	5.197831000	2.425334000	-1.742387000	H	-5.059485000	-2.800575000	-2.250881000	H	1.594405000	-1.299193000	0.820104000				
H	3.604544000	2.993703000	-1.194478000	C	-2.637259000	3.224383000	-0.154339000	H	-0.207593000	-2.851395000	0.268099000				
H	3.717426000	1.851541000	-2.543997000	C	-2.058780000	3.745660000	-1.483471000	H	-1.041663000	-1.634239000	-0.728241000				
C	4.591365000	-0.941253000	-2.312140000	H	-1.001630000	3.465957000	-1.602629000	H	-0.805537000	-1.663692000	2.342322000				
H	5.678566000	-0.897645000	-2.503918000	H	-2.125475000	4.844969000	-1.516590000	H	-2.296806000	-1.483650000	1.386422000				
H	4.094889000	-0.353721000	-3.098354000	H	-2.616387000	3.359716000	-2.351215000	H	-0.931597000	0.755067000	2.306834000				
H	4.272500000	-1.986005000	-2.429141000	C	-1.883159000	3.873618000	1.022003000								
C	-2.592000000	1.700517000	-0.076255000	H	-0.815423000	3.609753000	1.009423000								
C	-2.659615000	0.781101000	-1.162109000	H	-2.298746000	3.565064000	1.993934000								
H	-2.590597000	1.067312000	-2.206193000	H	-1.965405000	4.971087000	0.964789000								
C	-2.881934000	-0.566730000	-0.699248000	C	-4.131081000	3.630499000	-0.074956000								
C	-2.876256000	-0.482790000	0.762815000	H	-4.585538000	3.296597000	0.871012000								
C	-2.683987000	0.907644000	1.092669000	H	-4.708442000	3.186247000	-0.901210000								
H	-2.643033000	1.295909000	2.105752000	H	-4.235937000	4.726585000	-0.136155000								
C	-3.284101000	-1.442203000	1.909694000	Co	-1.013337000	0.191930000	-0.035003000								
C	-3.049989000	-2.943776000	1.668037000	Fe	2.408661000	-0.144459000	-0.026642000								
H	-3.335173000	-3.500305000	2.574880000	P	0.830617000	1.625493000	-0.338055000								
H	-1.991129000	-3.159046000	1.466002000	P	0.698436000	0.548745000	1.530759000								
H	-3.655022000	-3.342732000	0.845846000	P	0.329167000	-1.550704000	0.798647000								
C	-4.796403000	-1.209190000	2.165959000	P	1.346152000	-1.889035000	-1.106841000								
H	-5.142969000	-1.843800000	2.998411000	P	0.476056000	-0.020287000	-1.838419000								

Table S7: Optimized geometries of **I2a** (left), **2a** (right). XYZ coordinated in angstroms. B3LYP/def2-SVP level of theory.

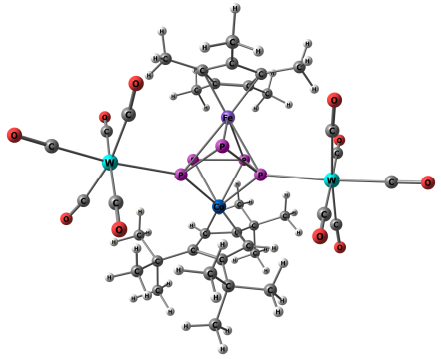




C	2.222874000	3.469066000	0.022890000	C	-2.278923000	-3.489662000	-0.334210000	C	0.658347000	4.639179000	0.927982000	C	4.853751000	-1.332589000	0.497089000
C	1.183512000	4.039885000	-0.785904000	C	-0.878511000	-3.574939000	0.303251000	C	1.500782000	4.591854000	-0.238917000	C	4.992461000	-0.219039000	1.555740000
C	0.125728000	4.473180000	0.091376000	H	-0.208176000	-2.831348000	-0.146633000	C	0.662111000	4.358451000	-1.380592000	H	4.691231000	0.754299000	1.144831000
C	0.488939000	4.114654000	1.428836000	H	-0.447165000	-4.571751000	0.119409000	C	-0.694846000	4.250157000	-0.914807000	H	6.050506000	-0.139687000	1.854407000
C	1.781791000	3.481389000	1.383839000	H	-0.879351000	-3.408858000	1.383080000	C	-0.700147000	4.455440000	0.503584000	H	4.401254000	-0.389888000	2.458260000
C	2.555658000	3.032841000	2.588438000	C	-2.093390000	-3.800653000	-1.838572000	C	-1.914146000	4.570596000	1.376370000	C	5.652846000	-0.835710000	-0.732343000
H	3.020559000	3.899978000	3.090730000	H	-1.460844000	-3.053402000	-2.339950000	H	-2.261133000	5.619419000	1.397582000	H	5.192663000	0.054314000	-1.187942000
H	3.359950000	2.332638000	2.331916000	H	-3.054299000	-3.865694000	-2.371883000	H	-1.703567000	4.270808000	2.412142000	H	5.759909000	-1.610718000	-1.506003000

H	1.907293000	2.538824000	3.327782000	H	-1.592112000	-4.774371000	-1.944928000	H	-2.747275000	3.954122000	1.014931000	H	6.666710000	-0.553912000	-0.409554000
C	-0.268434000	4.441149000	2.681933000	C	-3.197890000	-4.598920000	0.232664000	C	-1.902206000	4.066621000	-1.786426000	C	5.558159000	-2.622051000	0.987601000
H	0.107713000	5.379234000	3.127090000	H	-4.203593000	-4.548439000	-0.214563000	H	-2.246895000	5.040582000	-2.177879000	H	5.471698000	-3.429011000	0.242723000
H	-0.160076000	3.652080000	3.440723000	H	-3.309109000	-4.542205000	1.322549000	H	-2.740405000	3.617195000	-1.237394000	H	5.148561000	-2.992534000	1.935819000
H	-1.343138000	4.570322000	2.491945000	H	-2.774524000	-5.588267000	-0.003014000	H	-1.686491000	3.423979000	-2.652586000	H	6.630203000	-2.422367000	1.146130000
C	-1.098081000	5.230608000	-0.328616000	C	-5.085032000	0.616159000	-1.799009000	C	1.093199000	4.307372000	-2.815777000	C	1.263760000	-2.816491000	-2.873374000
H	-0.874387000	6.308668000	-0.412283000	C	-4.526702000	0.693093000	-3.231888000	H	0.923508000	5.280163000	-3.309845000	C	1.688162000	-1.859140000	-4.003352000
H	-1.920051000	5.118331000	0.393151000	H	-3.522282000	1.141628000	-3.245700000	H	0.531129000	3.549496000	-3.382798000	H	1.300425000	-0.843280000	-3.835898000
H	-1.469365000	4.895141000	-1.308449000	H	-5.185710000	1.314931000	-3.858170000	H	2.161679000	4.067637000	-2.916114000	H	1.293114000	-2.219869000	-4.966115000
C	1.258649000	4.280741000	-2.264872000	H	-4.470547000	-0.299776000	-3.704546000	C	2.977565000	4.853385000	-0.256879000	H	2.783162000	-1.798976000	-4.103590000
H	1.770830000	5.235974000	-2.479424000	C	-5.251500000	2.039122000	-1.234072000	H	3.177315000	5.938600000	-0.301158000	C	-0.268130000	-2.936096000	-2.853851000
H	0.259884000	4.332388000	-2.721171000	H	-4.286615000	2.564089000	-1.185721000	H	3.465888000	4.390181000	-1.125946000	H	-0.738644000	-1.974428000	-2.608443000
H	1.816919000	3.485395000	-2.779512000	H	-5.691355000	2.032121000	-0.224550000	H	3.471429000	4.463576000	0.645332000	H	-0.612272000	-3.684821000	-2.125846000
C	3.573321000	3.058193000	-0.477124000	H	-5.926848000	2.622276000	-1.880105000	C	1.110842000	4.933870000	2.328165000	H	-0.636147000	-3.247847000	-3.843879000
H	4.239016000	3.939250000	-0.511600000	C	-6.475207000	-0.071060000	-1.841719000	H	1.071156000	6.018861000	2.531571000	C	1.872766000	-4.215657000	-3.150094000
H	3.530254000	2.641957000	-1.492171000	H	-6.924133000	-0.131059000	-0.837856000	H	2.145390000	4.603467000	2.499556000	H	1.589204000	-4.936851000	-2.367657000
H	4.051442000	2.314606000	0.171372000	H	-6.402563000	-1.094721000	-2.241594000	H	0.475884000	4.436010000	3.075492000	H	2.972681000	-4.172994000	-3.189599000
C	-4.213103000	-0.254181000	-0.899856000	H	-7.161398000	0.499575000	-2.488630000	C	1.814508000	-2.372496000	-1.521705000	H	1.511626000	-4.603313000	-4.116739000
C	-3.432479000	-1.375540000	-1.296494000	Co	-2.195327000	-0.149028000	-0.170818000	C	3.061939000	-1.729244000	-1.306814000	Co	1.547847000	-0.657194000	-0.230190000
H	-3.231034000	-1.645933000	-2.327076000	Fe	0.384814000	2.387345000	0.213570000	H	3.673710000	-1.308356000	-2.096089000	Fe	0.503318000	2.776749000	-0.009362000
C	-2.965238000	-2.114806000	-0.152200000	P	-1.426722000	1.790503000	-1.420301000	C	3.406790000	-1.717356000	0.079542000	P	2.161745000	1.511447000	-0.883072000
C	-3.462620000	-1.385480000	1.022445000	P	-1.702053000	1.879451000	0.857873000	C	2.277119000	-2.342263000	0.793261000	P	0.241803000	0.800148000	-1.675390000
C	-4.193309000	-0.256334000	0.521576000	P	-0.393623000	0.212991000	1.467710000	C	1.336486000	-2.727626000	-0.226606000	P	-0.617880000	-0.058159000	0.188345000
H	-4.685370000	0.483821000	1.144178000	P	1.100748000	0.275556000	-0.216484000	H	0.407080000	-3.254675000	-0.037929000	P	-0.246830000	1.440762000	1.725454000
C	-3.553254000	-1.702527000	2.535468000	P	-0.475794000	-0.159793000	-1.705483000	C	2.057912000	-2.851173000	2.237451000	P	1.908249000	1.162494000	1.348162000
C	-2.401260000	-2.528980000	3.134294000	W	3.167181000	-1.365038000	-0.199897000	C	2.808440000	-2.084637000	3.339989000	W	-3.074079000	-1.000538000	0.182706000
H	-2.559719000	-2.627126000	4.219557000	C	4.725935000	-2.652311000	-0.259895000	H	2.516517000	-2.491371000	4.320696000	C	-4.992354000	-1.636916000	0.283928000
H	-1.428114000	-2.040829000	2.984257000	O	5.614950000	-3.388618000	-0.294652000	H	2.549908000	-1.015654000	3.334100000	O	-6.087305000	-1.997533000	0.342468000
H	-2.349727000	-3.545158000	2.727793000	C	3.979367000	-0.282448000	-1.772804000	H	3.897689000	-2.183502000	3.265346000	C	-3.768265000	0.952265000	0.287233000
C	-4.885425000	-2.472256000	2.742653000	O	4.436142000	0.311959000	-2.646174000	C	2.494304000	-4.339698000	2.270829000	O	-4.199496000	2.019176000	0.334433000
H	-5.028900000	-2.691963000	3.813259000	C	4.228718000	-0.236536000	1.164635000	H	2.335995000	-4.758433000	3.277953000	C	-3.209530000	-0.905877000	-1.888685000
H	-4.900585000	-3.425924000	2.197056000	O	4.861785000	0.358355000	1.923396000	H	3.557099000	-4.463620000	2.017409000	O	-3.312608000	-0.853881000	-3.032514000
H	-5.746188000	-1.876678000	2.400955000	C	2.328743000	-2.418775000	1.384610000	H	1.907844000	-4.941686000	1.559638000	C	-2.463421000	-2.973798000	0.082081000
C	-3.636376000	-0.398846000	3.366781000	O	1.874522000	-3.002008000	2.265439000	C	0.559512000	-2.787253000	2.614594000	O	-2.146686000	-4.081787000	0.041135000
H	-3.687541000	-0.656225000	4.435742000	C	2.197266000	-2.588712000	-1.577948000	H	0.423095000	-3.181141000	3.633649000	C	-2.942517000	-1.086958000	2.258461000
H	-4.532020000	0.197231000	3.141330000	O	1.705328000	-3.296814000	-2.338556000	H	-0.077610000	-3.389363000	1.953154000	O	-2.888233000	-1.149360000	3.404121000
H	-2.752520000	0.238586000	3.218937000					H	0.190038000	-1.751829000	2.604884000				

Table S8: Optimized geometries of **2b.** XYZ coordinated in angstroms. B3LYP/def2-SVP level of theory.



C	1.375171000	-3.919624000	1.244115000	C	1.850228000	3.671031000	-2.057620000
C	1.106936000	-3.405522000	2.558889000	H	2.249551000	2.658803000	-1.923095000
C	-0.312546000	-3.393161000	2.741094000	H	2.490160000	4.373095000	-1.502142000
C	-0.920956000	-3.888133000	1.536787000	H	1.936932000	3.917167000	-3.126365000
C	0.127678000	-4.215935000	0.609205000	C	-0.035402000	5.243271000	-1.832040000
C	-0.050179000	-4.880142000	-0.724273000	H	0.541275000	5.900952000	-1.162222000
H	-0.033887000	-5.978440000	-0.608523000	H	-1.100017000	5.430879000	-1.653159000
H	0.749290000	-4.608040000	-1.427639000	H	0.182077000	5.548174000	-2.868062000
H	-1.005542000	-4.607614000	-1.191905000	C	2.028259000	3.073768000	3.231881000
C	-2.372947000	-4.215070000	1.369516000	C	3.387649000	2.424800000	2.913681000
H	-2.562223000	-5.242314000	1.730123000	H	3.285043000	1.354250000	2.685455000
H	-2.690118000	-4.178050000	0.320353000	H	4.057322000	2.519416000	3.783007000
H	-3.020653000	-3.546142000	1.948623000	H	3.887159000	2.913115000	2.064201000
C	-1.031335000	-3.033182000	4.007213000	C	1.425156000	2.432530000	4.496059000
H	-1.086180000	-3.910158000	4.676245000	H	1.221320000	1.362241000	4.348635000
H	-2.060047000	-2.697262000	3.816039000	H	0.486334000	2.923170000	4.796566000
H	-0.517917000	-2.231652000	4.558483000	H	2.128379000	2.531417000	5.337910000
C	2.141094000	-3.105878000	3.603908000	C	2.261438000	4.583351000	3.505725000
H	2.402780000	-4.028303000	4.152370000	H	1.320367000	5.095478000	3.760710000
H	1.780789000	-2.376582000	4.343646000	H	2.694794000	5.086666000	2.627270000
H	3.068185000	-2.707710000	3.167761000	H	2.958881000	4.712016000	4.349524000
C	2.735313000	-4.271886000	0.725961000	Co	0.063079000	1.488208000	0.836333000
H	3.086946000	-5.190565000	1.228656000	Fe	0.179803000	-2.156104000	1.091627000
H	3.480299000	-3.492830000	0.929664000	P	1.115592000	-0.308483000	2.049640000
H	2.728792000	-4.470690000	-0.351399000	P	-1.068256000	-0.180987000	2.126927000
C	1.062666000	3.011486000	2.050167000	P	-1.565598000	0.012076000	-0.034966000
C	1.384980000	3.082039000	0.662550000	P	-0.174254000	-1.335448000	-1.070099000
H	2.390210000	2.985901000	0.270524000	P	1.456177000	-0.175737000	-0.178366000
C	0.224275000	3.377666000	-0.139053000	W	-4.081165000	-0.489998000	-0.855083000
C	-0.894963000	3.410129000	0.800792000	C	-5.858138000	-1.092263000	-1.590194000
C	-0.344537000	3.146171000	2.105876000	O	-6.869626000	-1.451749000	-2.014203000
H	-0.931721000	3.106629000	3.017705000	C	-3.604270000	0.456524000	-2.648889000
C	-2.348738000	3.921559000	0.730171000	O	-3.354047000	0.989725000	-3.634852000
C	-3.053313000	3.753478000	-0.624089000	C	-3.385826000	-2.287298000	-1.618722000
H	-4.096678000	4.089580000	-0.536395000	O	-3.121136000	-3.310007000	-2.077275000
H	-3.068026000	2.702550000	-0.936686000	C	-4.503279000	-1.331426000	0.989560000
H	-2.590026000	4.344071000	-1.420763000	O	-4.750955000	-1.765931000	2.026175000
C	-2.301701000	5.432653000	1.084337000	C	-5.132876000	1.176068000	-0.205466000
H	-3.324235000	5.843566000	1.095315000	O	-5.840519000	2.025455000	0.114057000
H	-1.713214000	6.008276000	0.356147000	W	3.880226000	-0.336585000	-1.250902000

H	-1.860623000	5.597400000	2.079695000	C	5.695601000	-0.572795000	-2.105635000
C	-3.218363000	3.218896000	1.800831000	C	4.500714000	1.548269000	-0.673418000
H	-4.264238000	3.539728000	1.695014000	C	4.600783000	-1.073855000	0.544214000
H	-2.909353000	3.468796000	2.825543000	C	3.393267000	-2.218636000	-1.987158000
H	-3.191396000	2.124732000	1.693709000	C	3.123154000	0.418778000	-3.039408000
C	0.369198000	3.762272000	-1.631149000	O	6.733836000	-0.718711000	-2.587132000
C	-0.421669000	2.838088000	-2.580754000	O	4.901226000	2.590255000	-0.385829000
H	-0.062778000	1.801362000	-2.499650000	O	5.002639000	-1.468014000	1.549165000
H	-0.276940000	3.160945000	-3.623941000	O	3.168287000	-3.241824000	-2.461680000
H	-1.496474000	2.835280000	-2.382030000	O	2.724901000	0.817732000	-4.039714000

5.5.4.2 Computations for the reaction of [(Cp'''Co)(Cp'''Ni)(μ,η³:η³-P₃] (3) and [W(CO)₅(thf)]

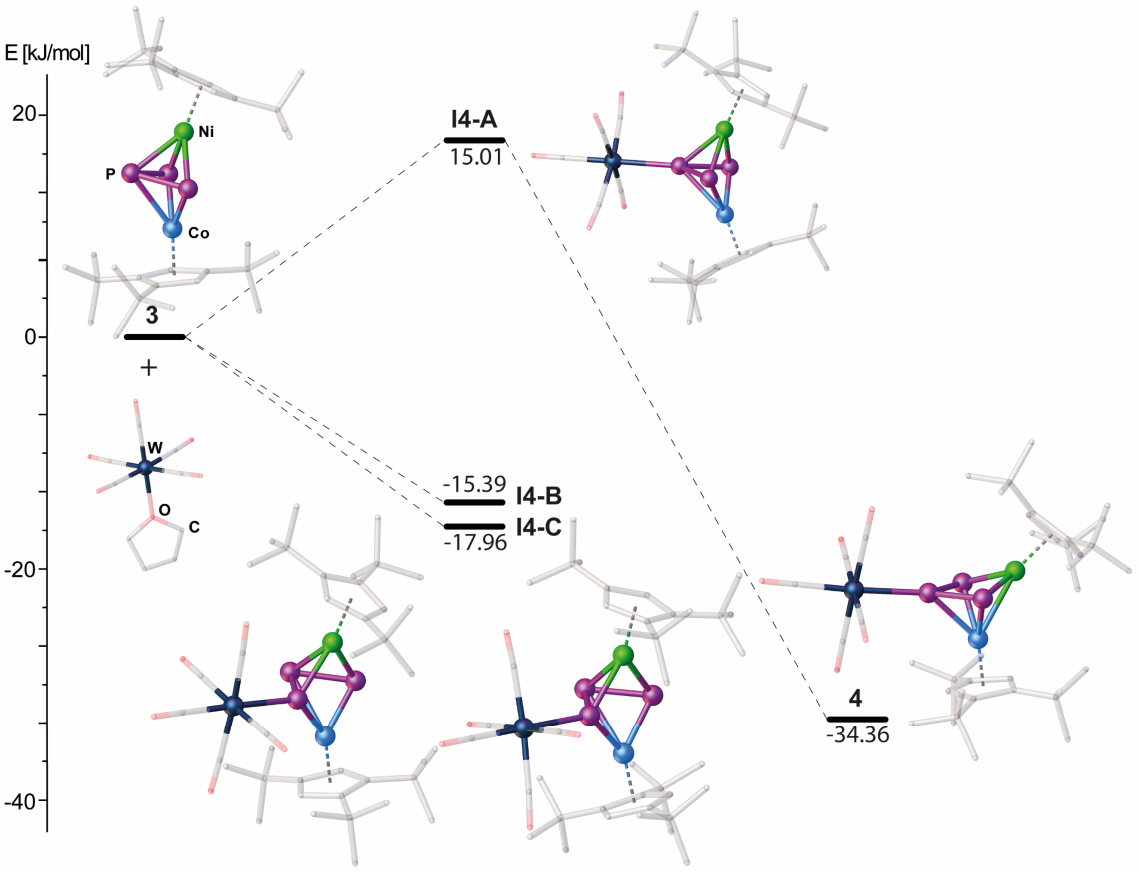


Figure S23: Energetic profile of the reaction of **3** and [W(CO)₅(thf)].

Table S9: Total energies for all optimized geometries (B3LYP/def2-SVP level of theory).

	total energy [Ha]
3 [(Cp'''Co)(Cp'''Ni)(μ,η³:η³-P₃]	-5244.2879391
4 [Cp'''CoCp'''Ni(μ₃,η³:η²:η¹-P₃){W(CO)₅}]	-5877.7692497
I4-A	-5877.7504461
I4-B	-5877.7620250
I4-C	-5877.7630013
[Cp'''NiCp'''Co(μ₃,η³:η²:η¹-P₃){W(CO)₅}] (position of Co and Ni exchanged)	-5877.7519902

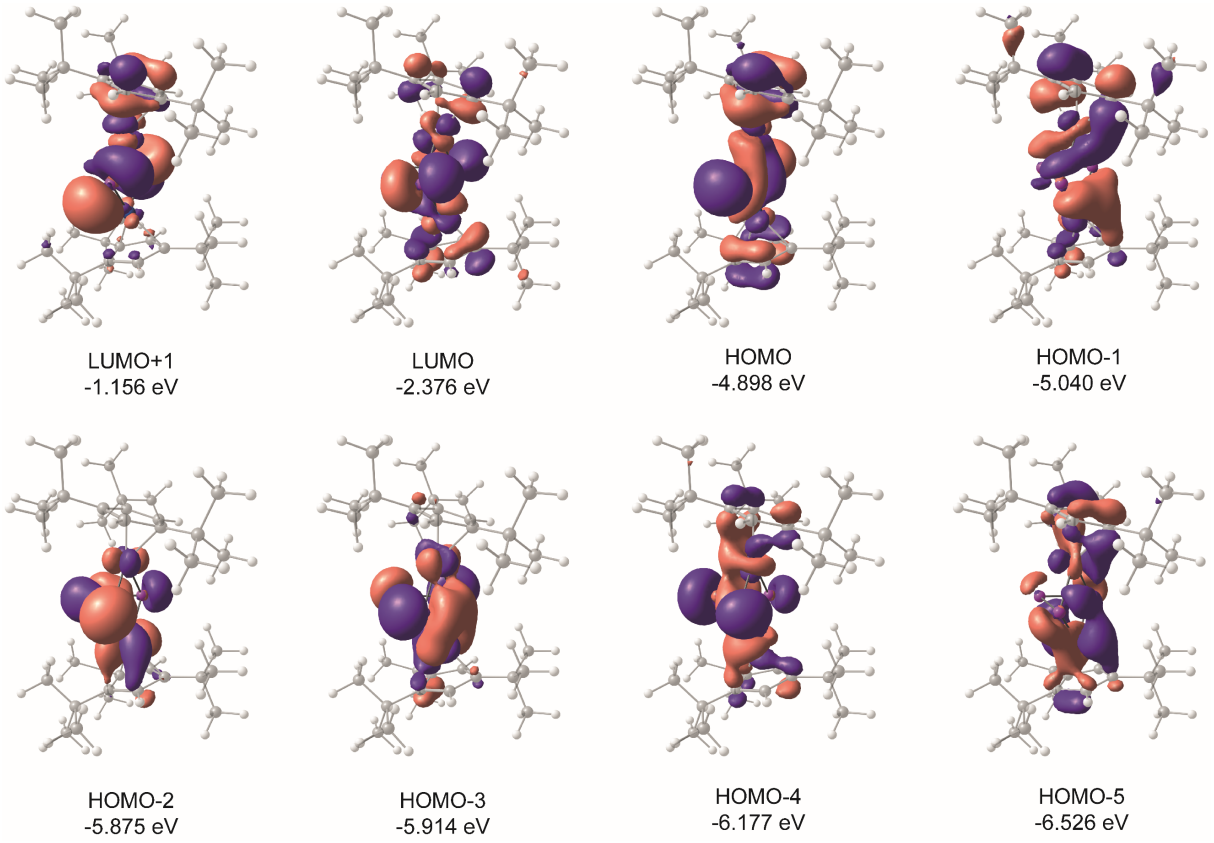


Figure S24: Frontier orbitals of **3** (B3LYP/def2-SVP level of theory).

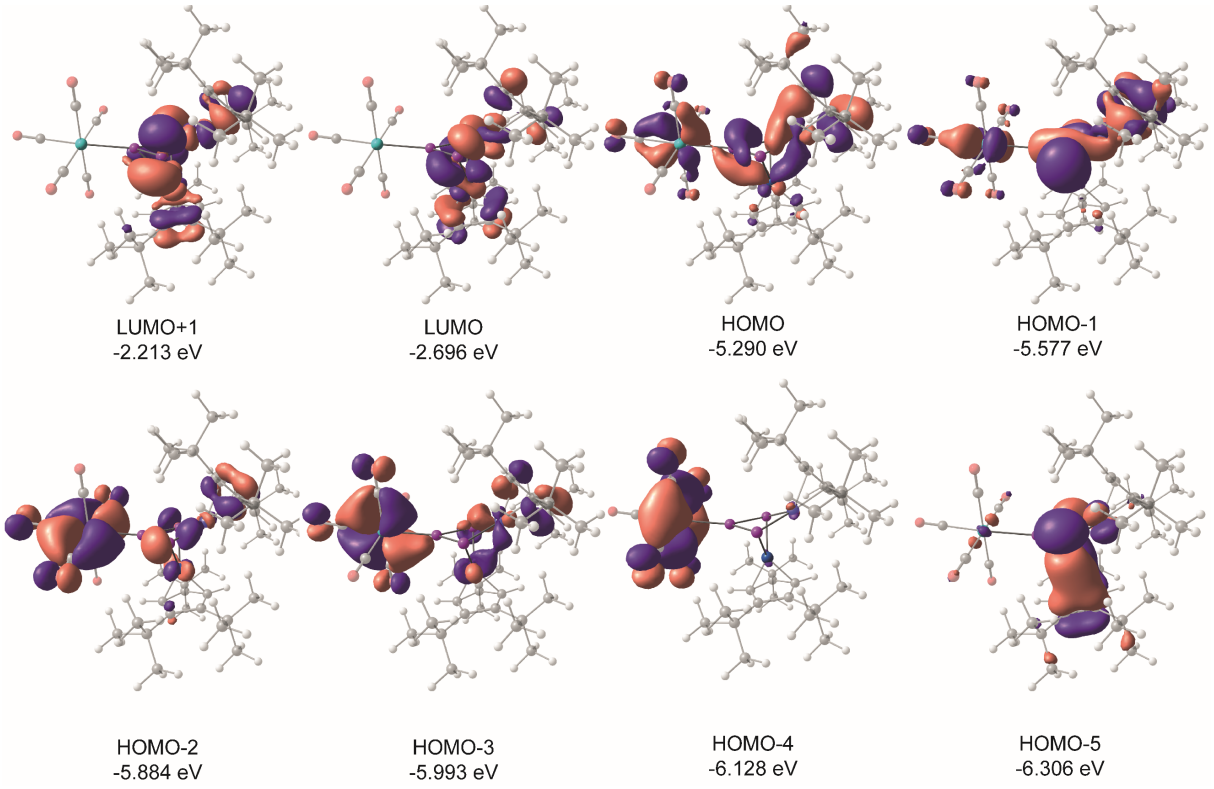
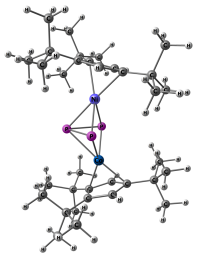
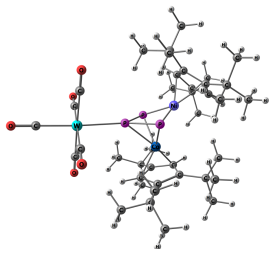


Figure S25: Frontier orbitals of **4** (B3LYP/def2-SVP level of theory).

Table S10: Optimized geometries of **3** (left) and **4** (right)**.** XYZ coordinated in angstroms. B3LYP/def2-SVP level of theory.

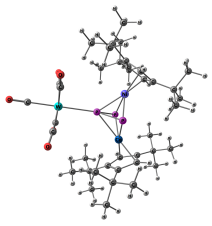


Ni	1.654055000	0.043408000	-0.059502000	H	-3.762722000	-4.089090000	1.670398000
Co	-1.735203000	0.092584000	0.045493000	H	-2.000148000	-1.946002000	-2.593762000
P	-0.032924000	0.056960000	1.418957000	H	-3.308290000	-3.003483000	-3.177997000
P	0.056081000	-1.627553000	-0.030659000	H	-2.793738000	-3.067976000	-1.480311000
P	-0.124309000	0.088991000	-1.434047000	H	-5.450179000	-2.669334000	-1.053263000
C	-3.619021000	-0.700074000	0.665609000	H	-5.719714000	-2.413348000	-2.783863000
C	-3.650876000	-0.427984000	-0.785026000	H	-6.163994000	-1.142518000	-1.618297000
C	-3.353313000	0.959686000	-0.931951000	H	-4.835550000	0.387453000	-3.193747000
C	-3.141095000	1.574898000	0.343126000	H	-4.351094000	-1.029196000	-4.150380000
C	-3.342245000	0.545586000	1.309209000	H	-3.108027000	0.061418000	-3.513285000
C	-3.959625000	-1.933575000	1.534818000	H	-2.840005000	2.910473000	2.802172000
C	-5.489213000	-1.931991000	1.787212000	H	-2.146283000	4.397107000	2.127504000
C	-3.264428000	-1.831039000	2.914802000	H	-1.266911000	2.851169000	1.972110000
C	-3.536015000	-3.291999000	0.944571000	H	-1.170860000	3.298682000	-0.615397000
C	-4.008757000	-1.293271000	-2.019320000	H	-2.054106000	4.819309000	-0.307101000
C	-2.967775000	-2.393721000	-2.324509000	H	-2.678805000	3.654776000	-1.490483000
C	-5.414078000	-1.915823000	-1.849230000	H	-4.927206000	3.536300000	-0.284663000
C	-4.077589000	-0.405805000	-3.285051000	H	-4.331856000	4.767729000	0.859407000
C	-2.971072000	3.065412000	0.610587000	H	-4.992534000	3.226279000	1.466613000
C	-2.264259000	3.315289000	1.955287000	H	3.217734000	0.749948000	-2.364972000
C	-2.171476000	3.744167000	-0.517335000	H	3.125737000	1.514904000	1.895065000
C	-4.390499000	3.683916000	0.665782000	H	6.218077000	-0.887119000	1.700933000
C	3.673285000	-0.349308000	0.785740000	H	5.633241000	-2.444199000	1.075729000
C	3.700348000	-0.606625000	-0.655587000	H	5.825488000	-2.215230000	2.820645000
C	3.298089000	0.611556000	-1.291735000	H	3.435542000	-2.943857000	3.166677000
C	3.016931000	1.626231000	-0.326595000	H	3.012303000	-3.054958000	1.445372000
C	3.244481000	1.010406000	0.942629000	H	2.086173000	-1.985105000	2.509217000
C	4.068195000	-1.193859000	2.022619000	H	3.035913000	0.071202000	3.509859000
C	5.516942000	-1.716264000	1.887488000	H	4.737614000	0.535595000	3.224939000
C	3.095112000	-2.365415000	2.291379000	H	4.350324000	-0.923254000	4.162321000
C	4.043364000	-0.315848000	3.296664000	H	6.042773000	-2.476913000	-2.426006000
C	4.160553000	-1.794209000	-1.532101000	H	6.252409000	-1.749774000	-0.814738000
C	5.689816000	-1.675502000	-1.755396000	H	5.942739000	-0.709395000	-2.219520000
C	3.830149000	-3.189739000	-0.969158000	H	2.748823000	-3.305327000	-0.799469000
C	3.481141000	-1.725343000	-2.922700000	H	4.351450000	-3.409694000	-0.030750000
C	2.790853000	3.109879000	-0.592961000	H	4.139582000	-3.958527000	-1.695231000
C	2.051083000	3.333464000	-1.924987000	H	3.750855000	-2.618562000	-3.507555000
C	1.989109000	3.761118000	0.549387000	H	3.804178000	-0.852747000	-3.508808000
C	4.183729000	3.783953000	-0.675840000	H	2.384445000	-1.691905000	-2.835116000
H	-3.278813000	1.481059000	-1.879745000	H	1.063897000	2.847345000	-1.920577000
H	-3.252914000	0.682617000	2.381660000	H	2.618159000	2.933709000	-2.779987000
H	-6.064269000	-2.031487000	0.856789000	H	1.905430000	4.411022000	-2.103977000
H	-5.803694000	-0.996257000	2.275249000	H	1.008542000	3.277813000	0.672334000
H	-5.766570000	-2.769444000	2.448755000	H	1.823638000	4.830087000	0.339423000
H	-3.471570000	-2.743273000	3.495557000	H	2.521692000	3.695590000	1.510885000
H	-3.632104000	-0.984668000	3.512700000	H	4.081818000	4.865499000	-0.865789000
H	-2.173051000	-1.732493000	2.814473000	H	4.786325000	3.349916000	-1.489238000
H	-2.454326000	-3.321864000	0.743981000	H	4.744096000	3.653672000	0.263331000
H	-4.066515000	-3.543850000	0.019336000				

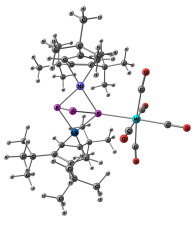


W	-3.644355000	-1.114928000	0.041640000	H	4.524911000	2.982809000	-1.619184000
Ni	1.922319000	-0.698321000	0.233965000	H	3.544809000	1.724914000	-0.818921000
Co	0.314353000	1.356558000	0.087355000	C	-0.278188000	3.302693000	2.807325000
P	0.303920000	-0.257958000	1.656640000	C	-0.495514000	4.831151000	2.954976000
P	-1.128736000	-0.529890000	0.077683000	H	0.401126000	5.393131000	2.648925000
P	0.454998000	-0.364598000	-1.373676000	H	-0.716717000	5.085659000	4.004270000
O	-2.791162000	-4.042020000	-1.040331000	H	-1.338710000	5.176477000	2.336539000
O	-3.365721000	-2.148752000	3.090503000	C	-1.558316000	2.573751000	3.257363000
O	-4.441474000	1.812307000	1.123841000	H	-2.437711000	2.872181000	2.667945000
O	-3.942027000	-0.105302000	-3.007673000	H	-1.774033000	2.813624000	4.310688000
O	-6.702426000	-1.996880000	0.034890000	H	-1.446431000	1.481982000	3.176336000
C	-3.092285000	-3.002131000	-0.657022000	C	0.891179000	2.880255000	3.712789000
C	-3.457741000	-1.779609000	2.007064000	H	1.085558000	1.800659000	3.636474000
C	-4.160957000	0.762920000	0.739166000	H	0.652394000	3.106598000	4.763914000
C	-3.826779000	-0.462394000	-1.920442000	H	1.819399000	3.418441000	3.465647000
C	-5.593617000	-1.678886000	0.037605000	C	4.270396000	-1.703732000	-2.203333000
C	-0.285115000	3.092842000	-1.015975000	C	3.233321000	-1.375626000	-3.297310000
C	1.148298000	3.118894000	-0.750153000	H	2.379638000	-2.060410000	-3.307607000
C	1.295967000	3.075598000	0.688418000	H	3.711919000	-1.418513000	-4.289517000
H	2.249873000	3.091230000	1.205562000	H	2.838073000	-0.358820000	-3.161558000
C	0.029162000	3.060768000	1.332062000	C	5.380547000	-0.632827000	-2.329446000
C	-0.922634000	3.006965000	0.273481000	H	5.001157000	0.381873000	-2.143086000
H	-1.994599000	2.944204000	0.424849000	H	5.783139000	-0.648597000	-3.353999000
C	3.689972000	-1.710847000	-0.764413000	H	6.219144000	-0.821978000	-1.642289000
C	2.775649000	-2.630641000	-0.062371000	C	4.954387000	-3.058291000	-2.506182000
C	2.821274000	-2.244015000	1.323184000	H	5.698996000	-3.305371000	-1.732964000
H	2.294472000	-2.755932000	2.121959000	H	5.479339000	-3.002776000	-3.473662000
C	3.702560000	-1.136754000	1.512117000	H	4.243457000	-3.890060000	-2.568850000
C	4.210260000	-0.824689000	0.228532000	C	2.061332000	-3.949658000	-0.443222000
H	4.919662000	-0.028159000	0.030630000	C	1.520010000	-4.015593000	-1.882819000
C	-1.141675000	3.295903000	-2.294281000	H	0.817536000	-3.192079000	-2.081128000
C	-0.811327000	4.674497000	-2.917719000	H	0.972822000	-4.960776000	-2.024105000
H	-0.890366000	5.478845000	-2.169194000	H	2.309466000	-3.986394000	-2.642481000
H	-1.527562000	4.896016000	-3.724761000	C	0.842964000	-4.187043000	0.483352000
H	0.193736000	4.715431000	-3.354725000	H	1.129773000	-4.330881000	1.535011000
C	-2.643451000	3.341579000	-1.926721000	H	0.314414000	-5.099736000	0.168413000
H	-2.983823000	2.406910000	-1.461250000	H	0.130698000	-3.351326000	0.433722000
H	-3.235154000	3.481120000	-2.843858000	C	3.051475000	-5.120024000	-0.208009000
H	-2.882384000	4.174768000	-1.248535000	H	3.944278000	-5.044068000	-0.842973000
C	-0.991321000	2.184040000	-3.353731000	H	2.561015000	-6.083013000	-0.426443000
H	0.043937000	2.016443000	-3.663188000	H	3.388777000	-5.142928000	0.839975000
H	-1.575270000	2.448273000	-4.250193000	C	4.191924000	-0.558662000	2.837248000
H	-1.380619000	1.229059000	-2.975770000	C	4.321474000	0.974653000	2.753834000
C	2.392900000	3.413477000	-1.615120000	H	5.029676000	1.281575000	1.968450000
C	2.339811000	2.872637000	-3.054077000	H	4.689659000	1.383385000	3.708788000
H	2.159924000	1.787802000	-3.065087000	H	3.349268000	1.437949000	2.533319000
H	3.305094000	3.059105000	-3.550374000	C	5.587287000	-1.165323000	3.126559000
H	1.568760000	3.354732000	-3.664953000	H	5.536746000	-2.264132000	3.182670000
C	2.580636000	4.952948000	-1.645406000	H	5.981129000	-0.792997000	4.087210000
H	1.728678000	5.466237000	-2.110392000	H	6.308913000	-0.902195000	2.337431000
H	3.487105000	5.212336000	-2.216661000	C	3.246388000	-0.928039000	3.995253000
H	2.697573000	5.354712000	-0.626751000	H	2.222679000	-0.564334000	3.819580000
C	3.657178000	2.807476000	-0.964886000	H	3.608033000	-0.484629000	4.936641000
H	3.895868000	3.262285000	0.007087000	H	3.195731000	-2.017767000	4.145795000

Table S11: Optimized geometries of **I4-A** (left) and **I4-B** (right)**.** XYZ coordinated in angstroms. B3LYP/def2-SVP level of theory.



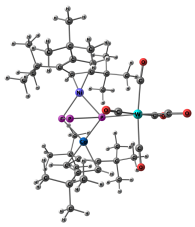
Ni	2.286873549	-2.040665455	-1.482162575	H	-5.086895451	-4.497421455	-4.206523575
Co	-1.102384451	-1.991489455	-1.377167575	H	-5.531175451	-3.226591455	-3.040957575
P	0.599894549	-2.027113455	-0.003703575	H	-4.202731451	-1.696620455	-4.616407575
P	0.688899549	-3.711626455	-1.453319575	H	-3.718275451	-3.113269455	-5.573040575
P	0.508509549	-1.995082455	-2.856707575	H	-2.475208451	-2.022655455	-4.935945575
C	-2.986202451	-2.784147455	-0.757051575	H	-2.207186451	0.826399545	1.379511425
C	-3.018057451	-2.512057455	-2.207686575	H	-1.513464451	2.313033545	0.704843425

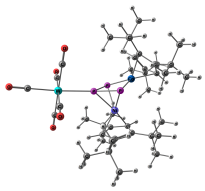


Ni	1.604396000	-1.127041000	-0.433380000	H	-6.354637000	0.322699000	-2.598906000
Co	-1.713703000	-0.999935000	0.063839000	H	-6.487875000	-0.404156000	-0.980774000
P	-0.205992000	-2.472423000	-0.528053000	H	-5.264054000	1.776290000	-0.298603000
P	-0.152671000	-0.755107000	-1.899478000	H	-5.063971000	2.195851000	-2.013175000
P	-0.021475000	0.415100000	-0.001325000	H	-3.645360000	2.125344000	-0.958164000
C	-3.569844000	-2.071939000	-0.193790000	H	-1.895800000	-2.728118000	3.645221000
C	-3.816944000	-0.635624000	-0.396843000	H	-1.319363000	-1.505635000	4.792490000

C	-2.720494451	-1.124387455	-2.354611575	H	-0.634092451	0.767095545	0.549449425	C	-3.418050000	0.024936000	0.806096000	H	-0.596170000	-1.606521000	3.166114000
C	-2.508276451	-0.509175455	-1.079534575	H	-0.538041451	1.214608545	-2.038057575	C	-2.911237000	-0.916709000	1.752360000	H	-1.134726000	0.936060000	2.889854000
C	-2.709426451	-1.538487455	-0.113451575	H	-1.421287451	2.735235545	-1.729761575	C	-3.013879000	-2.193688000	1.118961000	H	-1.828767000	0.893741000	4.528995000
C	-3.326806451	-4.017648455	0.112157425	H	-2.045986451	1.570702545	-2.913143575	C	-3.977963000	-3.349162000	-0.968403000	H	-2.793257000	1.513638000	3.175689000
C	-4.856394451	-4.016064455	0.364551425	H	-4.294387451	1.452226545	-1.707323575	C	-5.469581000	-3.639942000	-0.656970000	H	-4.667391000	-0.151735000	3.680153000
C	-2.631609451	-3.915112455	1.492141425	H	-3.699037451	2.683655545	-0.563253575	C	-3.182151000	-4.578817000	-0.466482000	H	-3.726134000	-0.708319000	5.087911000
C	-2.903196451	-5.376072455	-0.478089575	H	-4.359715451	1.142205545	0.043952425	C	-3.760891000	-3.284993000	-2.492453000	H	-4.302137000	-1.883457000	3.876949000
C	-3.375938451	-3.377344455	-3.441980575	H	3.850552549	-1.334125455	-3.787632575	C	-4.443869000	0.162677000	-1.568176000	H	2.993172000	-3.299504000	-1.711160000
C	-2.334956451	-4.477794455	-3.747169575	H	3.758555549	-0.569169455	0.472404425	C	-3.577556000	0.149001000	-2.847939000	H	3.820976000	0.742764000	-0.449496000
C	-4.781259451	-3.999896455	-3.271890575	H	6.850895549	-2.971192455	0.278272425	C	-5.863990000	-0.360343000	-1.887449000	H	5.598523000	-1.237258000	2.415124000
C	-3.444770451	-2.489878455	-4.707711575	H	6.266059549	-4.528272455	-0.346931575	C	-4.609634000	1.647434000	-1.174027000	H	4.366440000	-2.155951000	3.314540000
C	-2.338253451	0.981338545	-0.812073575	H	6.458306549	-4.299303455	1.397984425	C	-2.578969000	-0.676362000	3.220383000	H	4.889321000	-0.573818000	3.905151000
C	-1.631440451	1.231215545	0.532626425	H	4.068360549	-5.027930455	1.744016425	C	-1.537203000	-1.690442000	3.728725000	H	2.448184000	0.099710000	3.983038000
C	-1.538657451	1.660093545	-1.939995575	H	3.645121549	-5.139031455	0.022711425	C	-2.055574000	0.749285000	3.460899000	H	1.842459000	-1.372051000	3.191608000
C	-3.757680451	1.599842545	-0.756878575	H	2.718991549	-4.069178455	1.086556425	C	-3.898438000	-0.867412000	4.010852000	H	1.498136000	0.210795000	2.481332000
C	4.306103549	-2.433381455	-0.636920575	H	3.668731549	-2.012871455	2.087198425	C	3.368771000	-1.078769000	0.789983000	H	3.333197000	1.651351000	1.470189000
C	4.333166549	-2.690698455	-2.078247575	H	5.370432549	-1.548478455	1.802278425	C	3.103014000	-2.449065000	0.360359000	H	5.021902000	1.086757000	1.501535000
C	3.930907549	-1.472517455	-2.714395575	H	4.983142549	-3.007327455	2.739660425	C	3.172193000	-2.431634000	-1.085201000	H	4.179282000	1.487007000	3.014278000
C	3.649749549	-0.457842455	-1.749255575	H	6.675591549	-4.560986455	-3.848666575	C	3.530593000	-1.151481000	-1.571109000	H	4.509743000	-5.266475000	1.829419000
C	3.877299549	-1.073667455	-0.480031575	H	6.885227549	-3.833847455	-2.237398575	C	3.590382000	-0.316295000	-0.424755000	H	5.038373000	-3.583121000	2.046088000
C	4.701013549	-3.277932455	0.599958425	H	6.575557549	-2.793468455	-3.642180575	C	3.566078000	-0.426388000	2.182029000	H	5.083111000	-4.321907000	0.433533000
C	6.149760549	-3.800337455	0.464827425	H	3.381641549	-5.389400455	-2.222129575	C	4.665463000	-1.151046000	2.993814000	H	1.201293000	-3.482383000	2.214955000
C	3.727930549	-4.449488455	0.868718425	H	4.984268549	-5.493767455	-1.453410575	C	2.262153000	-0.377326000	3.007308000	H	2.670889000	-3.177068000	3.171889000
C	4.676182549	-2.399921455	1.874003425	H	4.772400549	-6.042600455	-3.117891575	C	4.052608000	1.032022000	2.020333000	H	2.194282000	-4.837640000	2.803808000
C	4.793371549	-3.878282455	-2.954761575	H	4.383673549	-4.702635455	-4.930215575	C	3.049452000	-3.813639000	1.088759000	H	2.363551000	-5.847866000	0.745452000
C	6.322634549	-3.759575455	-3.178056575	H	4.436996549	-2.936820455	-4.931468575	C	4.507569000	-4.263834000	1.370606000	H	3.046046000	-5.108877000	-0.706732000
C	4.462967549	-5.273812455	-2.391818575	H	3.017263549	-3.775978455	-4.257776575	C	2.234892000	-3.815504000	2.395166000	H	1.418242000	-4.638357000	-0.156136000
C	4.113959549	-3.809416455	-4.345360575	H	1.696715549	0.763271545	-3.343237575	C	2.430158000	-4.904811000	0.181121000	H	2.162876000	-1.843896000	-3.906632000
C	3.423671549	1.025805545	-2.015621575	H	3.250977549	0.849635545	-4.202647575	C	3.868421000	-0.786250000	-3.012836000	H	3.654934000	-2.818369000	-3.836103000
C	2.683901549	1.249390545	-3.347647575	H	2.538248549	2.326948545	-3.526637575	C	3.259679000	-1.803215000	-3.997038000	H	3.504005000	-1.518671000	-5.032701000
C	2.621927549	1.677044545	-0.873273575	H	1.641360549	1.193739545	-0.750326575	C	3.367064000	0.624334000	-3.374883000	H	2.272319000	0.695251000	-3.280565000
C	4.816547549	1.699879545	-2.098500575	H	2.456456549	2.746013545	-1.083237575	C	5.411513000	-0.820664000	-3.148594000	H	3.634443000	0.864611000	-4.416553000
H	-2.645994451	-0.603014455	-3.302405575	H	3.154510549	1.611516545	0.088224425	H	-3.484812000	1.092254000	0.977390000	H	3.813757000	1.397577000	-2.734363000
H	-2.620095451	-1.401456455	0.958999425	H	4.714636549	2.781425545	-2.288449575	H	-2.716494000	-3.130126000	1.578377000	H	5.714011000	-0.577361000	-4.180618000
H	-5.431450451	-4.115560455	-0.565871575	H	5.419143549	1.265842545	-2.911898575	H	-6.139102000	-2.843231000	-1.002249000	H	5.810328000	-1.817498000	-2.902067000
H	-5.170875451	-3.080330455	0.852588425	H	5.376914549	1.569598545	-1.159329575	H	-5.622878000	-3.759085000	0.427055000	H	5.886211000	-0.090876000	-2.474146000
H	-5.133751451	-4.853517455	1.026094425	W	0.991569591	-6.479707207	-1.746781320	H	-5.779700000	-4.577978000	-1.146340000	W	0.166855000	3.068435000	0.033861000
H	-2.838751451	-4.827346455	2.072896425	C	0.964999227	-8.464003048	-1.408357087	H	-3.480383000	-5.462493000	-1.051392000	C	0.249465000	5.085966000	-0.026621000
H	-2.999285451	-3.068741455	2.090039425	O	0.916973271	-9.580102765	-1.200424262	H	-3.389509000	-4.812420000	0.588110000	O	0.294617000	6.238763000	-0.070888000
H	-1.540232451	-3.816566455	1.391812425	C	1.127982230	-6.130719688	0.276334550	H	-2.096909000	-4.447570000	-0.587106000	C	2.110240000	3.079373000	-0.682954000
H	-1.821507451	-5.405937455	-0.678679575	O	1.213997363	-5.940254011	1.384806901	H	-2.710577000	-3.063503000	-2.736523000	O	3.196040000	3.175893000	-1.054958000
H	-3.433696451	-5.627923455	-1.403324575	C	-1.030698687	-6.705837532	-1.567263202	H	-4.394583000	-2.538577000	-2.984470000	C	-0.582354000	3.029982000	-1.906356000
H	-3.129903451	-6.173163455	0.247737425	O	-2.138276174	-6.947189237	-1.685730394	H	-4.009633000	-4.260925000	-2.938483000	O	-1.007535000	3.013250000	-2.973938000
H	-1.367329451	-4.030075455	-4.016422575	C	0.831325923	-6.847767086	-3.782979511	H	-2.637542000	0.694785000	-2.689369000	C	-1.734152000	3.287422000	0.811770000
H	-2.675471451	-5.087556455	-4.600657575	O	0.739302213	-7.079205019	-4.867197911	H	-4.117651000	0.654155000	-3.665200000	O	-2.773291000	3.493724000	1.266731000
H	-2.160919451	-5.152049455	-2.902971575	C	3.010112811	-6.680085825	-1.855498983	H	-3.323203000	-0.860092000	-3.187901000	C	0.869027000	3.081047000	1.987448000
H	-4.817360451	-4.753407455	-2.475923575	O	4.118105351	-6.903596775	-1.911335506	H	-5.858135000	-1.355453000	-2.347361000	O	1.236889000	3.117946000	3.076881000

Table S12: Optimized geometries of **I4-C** (left) and [Cp'''NiCp'''Co(μ_3,η^3:η^2:η^1-P_3){$W(CO)_5$}] (position of Co and Ni exchanged) (right)**.** XYZ coordinated in angstroms. B3LYP/def2-SVP level of theory.



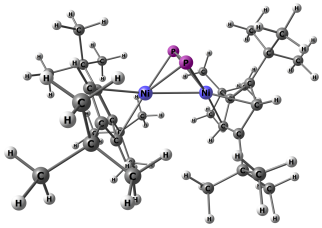


Ni	1.630781000	-0.985922000	0.032633000	H	-4.453851000	-5.056477000	2.172452000	W	-3.571909000	-1.236548000	0.045119000	H	4.316405000	3.193102000	-1.658890000
Co	-1.675525000	-1.119070000	-0.395467000	H	-5.287946000	-3.960049000	1.045382000	Co	2.029998000	-0.714324000	0.242231000	H	3.393676000	1.900979000	-0.845334000
P	0.050647000	-2.465639000	-0.574949000	H	-3.697005000	-5.042903000	-0.647562000	Ni	0.190559000	1.360779000	0.093888000	C	-0.438263000	3.275333000	2.824538000
P	0.302845000	-0.695270000	-1.848765000	H	-2.804910000	-5.875490000	0.639994000	P	0.367180000	-0.368154000	1.638044000	C	-0.717298000	4.787931000	3.020598000
P	-0.152295000	0.424847000	0.038552000	H	-1.929746000	-4.826394000	-0.490729000	P	-1.099683000	-0.551102000	0.066853000	H	0.150141000	5.395930000	2.718109000
C	-3.488507000	-1.040746000	0.680355000	H	-3.595217000	1.452963000	-2.804923000	P	0.527496000	-0.441035000	-1.355357000	H	-0.932059000	5.003029000	4.080174000
C	-3.182888000	-2.422954000	0.276914000	H	-3.222693000	0.958252000	-4.467381000	O	-2.575154000	-4.124597000	-1.016986000	H	-1.583762000	5.115078000	2.424944000
C	-3.131572000	-2.409755000	-1.156932000	H	-1.988743000	0.792822000	-3.194888000	O	-3.219068000	-2.215169000	3.104018000	C	-1.677120000	2.475234000	3.269720000
C	-3.404224000	-1.106714000	-1.664482000	H	-1.760368000	-1.747473000	-3.841175000	O	-4.531245000	1.649636000	1.112811000	H	-2.579542000	2.759151000	2.708585000
C	-3.616184000	-0.277944000	-0.533642000	H	-2.964601000	-1.409944000	-5.106598000	O	-3.949129000	-0.281931000	-3.014062000	H	-1.882042000	2.663060000	4.335771000
C	-3.913900000	-0.390801000	2.016111000	H	-3.238734000	-2.737443000	-3.964040000	O	-6.577553000	-2.297036000	0.069802000	H	-1.516979000	1.394272000	3.139614000
C	-5.450052000	-0.566308000	2.144009000	H	-5.496390000	-1.793813000	-3.244732000	C	-2.927785000	-3.098301000	-0.640728000	C	0.760650000	2.875774000	3.701586000
C	-3.623554000	1.125111000	1.992391000	H	-5.278621000	-0.538178000	-4.492745000	C	-3.337970000	-1.865506000	2.016953000	H	0.993081000	1.806572000	3.591764000
C	-3.227495000	-0.942374000	3.277608000	H	-5.652935000	-0.072763000	-2.813231000	C	-4.191669000	0.617378000	0.731724000	H	0.529216000	3.065020000	4.761734000
C	-3.096827000	-3.762839000	1.054500000	H	3.483188000	0.999350000	1.041254000	C	-3.802721000	-0.616733000	-1.924048000	H	1.663611000	3.456136000	3.456158000
C	-1.946893000	-3.840239000	2.083613000	H	2.478709000	-3.166948000	1.627443000	C	-5.490105000	-1.914206000	0.060874000	C	4.330661000	-1.572121000	-2.242732000
C	-4.449652000	-4.036438000	1.755844000	H	5.908980000	-3.499775000	-0.067251000	C	-0.498463000	3.133193000	-0.991492000	C	3.263856000	-1.335410000	-3.331945000
C	-2.869776000	-4.935544000	0.070586000	H	5.819869000	-2.811940000	-1.703647000	C	0.949734000	3.202016000	-0.744488000	H	2.449525000	-2.065732000	-3.307506000
C	-3.573483000	-0.725241000	-3.131106000	H	5.648233000	-4.559020000	-1.474396000	C	1.119060000	3.158436000	0.682655000	H	3.732798000	-1.385794000	-4.328413000
C	-3.064665000	0.701987000	-3.407677000	H	3.512150000	-4.461290000	-2.775017000	H	2.074525000	3.222518000	1.191912000	H	2.813844000	-0.338038000	-3.224992000
C	-2.839545000	-1.715260000	-4.055921000	H	3.379669000	-2.696387000	-2.904030000	C	-0.146211000	3.078924000	1.339266000	C	5.362665000	-0.429367000	-2.395820000
C	-5.091782000	-0.787237000	-3.435346000	H	2.079765000	-3.623331000	-2.137271000	C	-1.117894000	3.047602000	0.298249000	H	4.914202000	0.559838000	-2.224331000
C	3.522285000	-2.160140000	-0.089605000	H	2.327594000	-4.717744000	0.080240000	H	-2.187039000	2.987946000	0.467399000	H	5.758289000	-0.434432000	-3.423174000
C	3.874530000	-0.762849000	-0.275056000	H	3.914521000	-4.767215000	0.900844000	C	3.775284000	-1.598582000	-0.794871000	H	6.216973000	-0.547838000	-1.711815000
C	3.370377000	-0.065313000	0.872798000	H	3.679233000	-5.605830000	-0.645938000	C	2.927220000	-2.548691000	-0.053787000	C	5.101666000	-2.883464000	-2.527137000
C	2.765901000	-0.968460000	1.806548000	H	6.816420000	0.560263000	-1.573216000	C	3.013564000	-2.163012000	1.340458000	H	5.866445000	-3.066967000	-1.755789000
C	2.837365000	-2.245046000	1.183475000	H	6.596658000	-1.052832000	-0.853411000	H	2.525371000	-2.694477000	2.151205000	H	5.614258000	-2.812674000	-3.500201000
C	3.865493000	-3.452203000	-0.876120000	H	6.315338000	0.400308000	0.128351000	C	3.795825000	-0.996607000	1.492548000	H	4.445673000	-3.761162000	-2.567848000
C	5.398759000	-3.577069000	-1.040625000	H	3.547425000	-0.491914000	-3.113239000	C	4.216085000	-0.652629000	0.171064000	C	2.270369000	-3.905148000	-0.400250000
C	3.170879000	-3.551289000	-2.254427000	H	4.991717000	-1.515493000	-2.903933000	H	4.825051000	0.216091000	-0.058514000	C	1.729347000	-4.031703000	-1.835282000
C	3.415882000	-4.699925000	-0.078329000	H	5.168726000	0.158014000	-3.435300000	C	-1.365974000	3.294099000	-2.266385000	H	0.987834000	-3.248475000	-2.053054000
C	4.711128000	0.008443000	-1.321979000	H	4.837603000	2.012597000	-2.159929000	C	-1.083982000	4.665404000	-2.926687000	H	1.226529000	-5.004646000	-1.950049000
C	6.196452000	-0.030080000	-0.878186000	H	4.493353000	2.026723000	-0.427948000	H	-1.198433000	5.486724000	-2.201430000	H	2.515562000	-3.985471000	-2.597438000
C	4.593129000	-0.504030000	-2.769414000	H	3.208324000	1.595023000	-1.582636000	H	-1.802339000	4.836808000	-3.744158000	C	1.069417000	-4.184028000	0.537035000
C	4.281679000	1.493785000	-1.363961000	H	1.169351000	1.095517000	2.833181000	H	-0.078479000	4.732371000	-3.358925000	H	1.361462000	-4.270635000	1.593438000

C	2.365872000	-0.690937000	3.251735000	H	2.864756000	1.452856000	3.238216000	C	-2.866164000	3.298637000	-1.891199000	H	0.601355000	-5.139523000	0.255210000
C	2.015617000	0.790949000	3.465550000	H	1.733674000	0.967277000	4.515577000	H	-3.172842000	2.358423000	-1.413314000	H	0.306320000	-3.397519000	0.456075000
C	1.161298000	-1.556567000	3.666527000	H	0.284247000	-1.333927000	3.040214000	H	-3.466765000	3.409628000	-2.806531000	C	3.324773000	-5.014106000	-0.146690000
C	3.581661000	-1.051316000	4.142068000	H	0.895837000	-1.361910000	4.717943000	H	-3.127212000	4.131312000	-1.220658000	H	4.207886000	-4.899589000	-0.789839000
H	-2.902057000	-3.269296000	-1.776496000	H	1.376028000	-2.632779000	3.576730000	C	-1.184758000	2.158224000	-3.295706000	H	2.887047000	-6.006292000	-0.344482000
H	-3.848103000	0.780199000	-0.577872000	H	3.352643000	-0.860743000	5.203538000	H	-0.150906000	2.037863000	-3.630184000	H	3.669011000	-4.999463000	0.899229000
H	-5.748028000	-1.621930000	2.195718000	H	4.463560000	-0.449678000	3.871297000	H	-1.808556000	2.359150000	-4.181673000	C	4.275760000	-0.348699000	2.787098000
H	-5.968649000	-0.113057000	1.285098000	H	3.852795000	-2.113606000	4.037029000	H	-1.505045000	1.196443000	-2.873921000	C	4.268797000	1.187607000	2.668607000
H	-5.809723000	-0.066558000	3.058287000	W	-0.092199000	3.092488000	0.023585000	C	2.167651000	3.535529000	-1.633332000	H	4.928060000	1.538126000	1.859031000
H	-3.870985000	1.564512000	2.970443000	C	-0.129674000	5.106945000	-0.106907000	C	2.117857000	2.966675000	-3.062229000	H	4.624745000	1.647157000	3.604750000
H	-4.216688000	1.662486000	1.240148000	O	-0.157198000	6.258230000	-0.192004000	H	1.971683000	1.876478000	-3.049305000	H	3.254681000	1.560732000	2.466839000
H	-2.561607000	1.316577000	1.794292000	C	1.858780000	3.275392000	0.691205000	H	3.071430000	3.175719000	-3.572143000	C	5.726674000	-0.826199000	3.041505000
H	-2.132624000	-0.864213000	3.203725000	O	2.922609000	3.464645000	1.091307000	H	1.325545000	3.411684000	-3.673882000	H	5.772332000	-1.922956000	3.131851000
H	-3.490635000	-1.985055000	3.488689000	C	0.553182000	2.970863000	-1.951038000	C	2.298973000	5.080344000	-1.691610000	H	6.120941000	-0.390123000	3.974562000
H	-3.545033000	-0.349451000	4.149347000	O	0.916568000	2.913581000	-3.039519000	H	1.419977000	5.554775000	-2.147385000	H	6.396467000	-0.528946000	2.219033000
H	-0.971234000	-3.825420000	1.578072000	C	-2.068943000	3.130107000	-0.585544000	H	3.183756000	5.363174000	-2.285505000	C	3.399050000	-0.771909000	3.980083000
H	-2.021025000	-4.785749000	2.645512000	O	-3.171399000	3.224771000	-0.908687000	H	2.420610000	5.501812000	-0.681584000	H	2.345651000	-0.487982000	3.834108000
H	-1.954496000	-3.020829000	2.806897000	C	-0.685988000	3.193790000	2.008648000	C	3.463299000	2.986950000	-0.994310000	H	3.756486000	-0.289096000	4.903548000
H	-4.643154000	-3.344812000	2.584904000	O	-0.994390000	3.278891000	3.113848000	H	3.693678000	3.454310000	-0.026454000	H	3.436650000	-1.860134000	4.145082000

5.4.4.3 Computations for [(Cp'''Ni)$_2$(μ,η^2:η^2-P$_2$)] (5)

Table S13: Optimized geometries of **5**. XYZ coordinated in angstroms. B3LYP/def2-SVP level of theory.



Ni	-1.290409000	0.089755000	-0.548508000	H	-0.265027000	-1.731334000	1.842038000	H	-4.689771000	3.057200000	1.089838000	H	6.341424000	-0.284688000	-2.254623000
Ni	1.231106000	0.212902000	-0.370127000	H	-1.289211000	-3.105331000	1.416506000	C	-2.239658000	3.759768000	0.009010000	H	6.016127000	-0.789858000	-0.579753000
P	0.046023000	0.937036000	-2.107544000	H	-0.904240000	-2.804088000	3.122746000	H	-1.238635000	3.532124000	-0.385323000	H	5.874754000	0.921362000	-1.029393000
P	0.120827000	-1.129807000	-1.759631000	C	-3.597352000	-2.192040000	2.773350000	H	-2.199400000	3.677415000	1.106047000	C	3.901260000	0.679827000	-2.916183000
C	-2.658614000	-0.600849000	1.016383000	H	-4.473015000	-1.534332000	2.892941000	H	-2.475277000	4.808903000	-0.232903000	H	4.494715000	0.398622000	-3.800084000
C	-3.137352000	-1.000061000	-0.298714000	H	-3.396744000	-2.665871000	3.748189000	C	-3.340699000	3.034998000	-2.122742000	H	4.170852000	1.717019000	-2.670409000
C	-3.314219000	0.222337000	-1.047345000	H	-3.869037000	-2.990455000	2.072638000	H	-4.137908000	2.441045000	-2.596361000	H	2.838854000	0.659177000	-3.200177000
H	-3.662573000	0.268367000	-2.073829000	C	-3.642209000	-2.326361000	-0.914869000	H	-2.384771000	2.762388000	-2.595496000	C	4.004106000	-1.717949000	-2.346518000
C	-3.010065000	1.362662000	-0.249609000	C	-2.852183000	-3.585742000	-0.513716000	H	-3.545247000	4.093691000	-2.349278000	H	4.614018000	-1.825485000	-3.257546000
C	-2.573763000	0.842789000	0.996627000	H	-1.787303000	-3.484063000	-0.771778000	C	3.188023000	-2.190239000	1.134195000	H	2.952483000	-1.887319000	-2.623847000
H	-2.261813000	1.451201000	1.838357000	H	-3.249605000	-4.455585000	-1.060666000	C	2.761281000	-2.356192000	2.612244000	H	4.310268000	-2.516255000	-1.661609000
C	2.925482000	-0.736181000	0.664491000	H	-2.931081000	-3.819125000	0.554113000	H	3.314549000	-1.675845000	3.277845000	C	1.974575000	2.827651000	1.689137000
C	3.342559000	0.021408000	-0.521537000	C	-5.130990000	-2.499526000	-0.514568000	H	2.973493000	-3.386369000	2.938380000	C	0.691623000	2.672366000	2.525144000
C	2.973596000	1.396758000	-0.275237000	H	-5.548238000	-3.408073000	-0.979968000	H	1.686399000	-2.185073000	2.756705000	H	-0.157283000	2.397545000	1.884515000
H	3.170810000	2.215720000	-0.958752000	H	-5.729890000	-1.640031000	-0.854511000	C	4.700904000	-2.509180000	1.098812000	H	0.450880000	3.616521000	3.040323000
C	2.325859000	1.528115000	0.975089000	H	-5.261628000	-2.586275000	0.572570000	H	5.275822000	-1.761127000	1.667561000	H	0.800923000	1.896027000	3.298587000
C	2.272306000	0.206340000	1.522164000	C	-3.592024000	-2.264079000	-2.461616000	H	5.106684000	-2.545817000	0.081475000	C	3.150416000	3.177118000	2.635133000
H	1.841806000	-0.036642000	2.488318000	H	-2.575771000	-2.054018000	-2.827116000	H	4.884572000	-3.494071000	1.557913000	H	4.089541000	3.297596000	2.072384000
C	-2.359842000	-1.388305000	2.313021000	H	-4.272671000	-1.506821000	-2.876350000	C	2.402451000	-3.247280000	0.326060000	H	3.307922000	2.386151000	3.385474000
C	-2.023456000	-0.414592000	3.466912000	H	-3.906814000	-3.234463000	-2.875963000	H	2.639547000	-4.258228000	0.697957000	H	2.950202000	4.119774000	3.171618000
H	-1.128648000	0.186663000	3.250232000	C	-3.296451000	2.820290000	-0.597869000	H	2.630861000	-3.220322000	-0.744708000	C	1.791290000	3.976404000	0.680263000
H	-1.820075000	-0.991705000	4.382385000	C	-4.683803000	3.173118000	-0.005474000	H	1.319921000	-3.089321000	0.434988000	H	1.015286000	3.736247000	-0.061558000
H	-2.856245000	0.270680000	3.687416000	H	-5.468623000	2.518568000	-0.416570000	C	4.205861000	-0.307138000	-1.761645000	H	2.724327000	4.191640000	0.136612000
C	-1.137537000	-2.317437000	2.161062000	H	-4.952630000	4.216770000	-0.239869000	C	5.696011000	-0.107828000	-1.378139000	H	1.495514000	4.900931000	1.201254000

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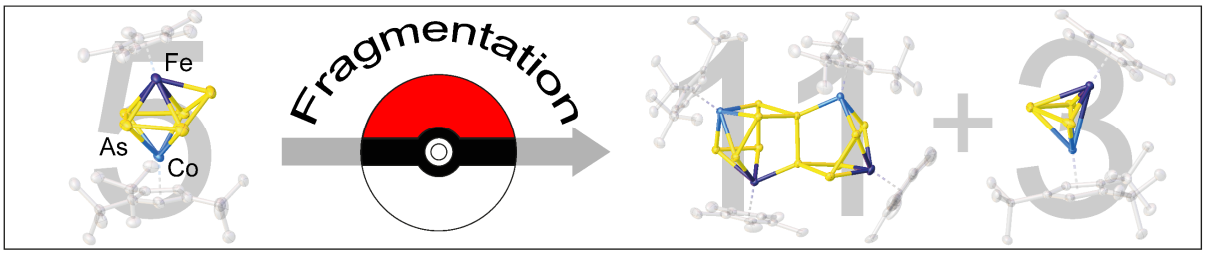
6. Synthesis of a novel Heterobimetallic Arsenic Triple-Decker Complex and its versatile Fragmentation Chemistry

Martin Piesch and Manfred Scheer



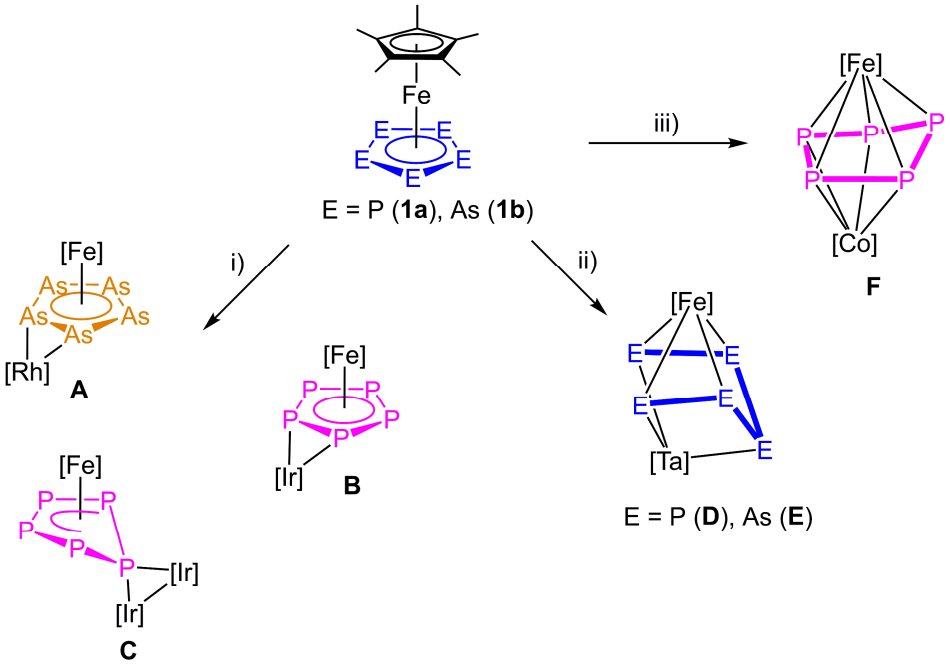
- Synthesis and characterization of all compounds was performed by Martin Piesch
- DFT calculations were performed by Martin Piesch
- X-ray measurements and calculations were done by Martin Piesch and finally checked by Michael Seidl
- Manuscript was written by Martin Piesch
- Figures were made by Martin Piesch

6.1 Introduction

Abstract: *The synthesis of the metastable triple-decker complex [(Cp*Fe)(Cp'''Co)(μ,η^5:η^4-As$_5$)] (**3**) (Cp* = pentamethyl-cyclopentadienyl, Cp''' = 1,2,4-tritertbutyl-cyclopentadienyl) is reported. **3** is unstable towards thermal stress and in solutions of acetonitrile, which converts **3** selectively into [(Cp*Fe)(Cp'''Co)(μ,η^3:η^3-As$_3$)] (**4**) and [(Cp*Fe)$_2$(Cp'''Co)$_2$(μ$_4$,η^4:η^4:η^3-As$_{11}$)] (**5**). Harsher reaction conditions lead to a further fragmentation into [Cp*Fe(η^5-As$_5$)] (**1b**), [(Cp'''Co)$_2$(μ,η^2:η^2-As$_2$)$_2$] (**6**) and [(Cp*Fe)$_2$(Cp'''Co)(μ$_3$,η^2:η^2:η^2-As$_3$)$_2$] (**7**) and which can be completed by long reaction times or very high temperatures. The fragmentation was investigated by VT and time dependent NMR spectroscopy and a finetuning of the selectivity can be achieved by applying different reaction conditions. All compounds have been fully characterized and their electronic structure elucidated by DFT calculations.*

The activation of white phosphorus and yellow arsenic in the coordination sphere of transition metal complexes has been widely investigated in the last decades yielding a plethora of polypnictogen (E_n) ligand complexes.[1] Most reactions proceed by thermolysis of carbonyl complexes like [(Cp^{R}M(CO)$_n$)$_2$] (e.g. M = Mo,[2] Fe,[3,4] Co,[5] Ni[6]) or photolysis of [Cp^{R}M(CO)$_4$] (e.g. M = V,[7] Nb,[8,9] Ta[9]) with P_4 and As_4, respectively, under harsh reaction conditions yielding the thermodynamically most stable products. In these reactions mono- or multinuclear homometallic E_n ligand complexes can be obtained, like e.g. pentaphospha- and pentaarsaferrocene [Cp*Fe(η^5-E$_5$)] (E = P (**1a**), As (**1b**), Scheme 1). To get access to heterometallic complexes different synthetic routes have to be applied. One way would be the photolysis or thermolysis of suitable polypnictogen ligand complexes with other transition metal carbonyl compounds. Thermolysis of [Cp^{R}Co(CO)]$_2$ or [Cp^{R}Co(CO)$_2$] with **1a,b** yielded a set of homometallic and heterometallic compounds with E_n (n = 1, 2, 4, 5, 6) ligands.[10,11] The selectivity of these reactions can hardly be controlled. Similar reactions involving heavier and much more expensive metals of group 9 (Rh, Ir) proceed under milder conditions more selectively but the isolated compounds still contain carbonyl ligands (**A**-**C**, cf. Scheme 1).[12,13] On the other hand, the thermolysis of **1a,b** with [Cp''Ta(CO)$_4$] proceeds quite selectively and [(Cp*Fe)(Cp'''Ta)(μ,η^4:η^3-E$_5$)] (E = P (**D**), As (**E**), Scheme 1) is formed as the only isolatable product.[12,14] But all the mentioned thermolysis reactions yield thermodynamic stable products and in the case of polyarsenic (As_n) complexes their formation cannot be monitored by NMR spectroscopy and no futher reactivity of these products is observed. Therefore, a suitable heterometallic E_n ligand complex is needed which is accessible under mild conditions and reactive enough that a further fragmentation or rearrangement could take place. We recently reported that the labile cobalt toluene triple-decker complex [(Cp'''Co)$_2$(μ,η^4:η^4-C$_7$H$_8$)] (**2**) can

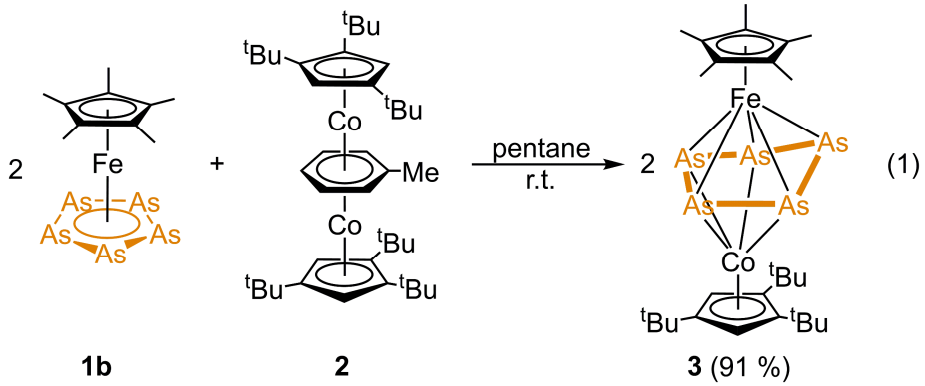
be reacted with **1a** to the heterobimetallic [(Cp*Fe)(Cp'''Co)(μ,η^5:η^4-P$_5$)] (**F**) under very mild conditions (Scheme 1).[15] But **F** proofed to be thermally stable and to be not suitable for subsequent reactivity studies. But what about the analog arsenic compound? Due to the in general lower E-E bond energy for the heavier homologs of group 15 elements, an enhanced reactivity can be expected. Therefore, we decided to synthesize the arsenic derivative of **F** by a similar approach and study its reactivity.



Scheme 1: Reaction of [Cp*Fe(η^5-E$_5$)] (E = P (**1a**), As (**1b**)) with i) [Cp*Ir(CO)$_2$] and [Cp*Rh(CO)]$_2$, ii) [(Cp''Ta(CO)$_4$] and iii) [(Cp'''Co)$_2$(μ,η^4:η^4-C$_7$H$_8$)] (**2**).

6.2 Results and Discussion

The reaction of [(Cp'''Co)$_2$(μ,η^4:η^4-C$_7$H$_8$)] (**2**) with pentaarsaferrocene ([Cp*Fe(η^5-As$_5$)] (**1b**)) in pentane at room temperature leads to the formation of the heterobimetallic triple-decker complex [(Cp*Fe)(Cp'''Co)(μ,η^5:η^4-As$_5$)] (**3**) in 91 % isolated yield (Eq. 1). Compound **3** can be obtained as a dark green air and moisture sensitve solid.



Crystals of **3** suitable for single crystal X-ray structure analysis are obtained from a concentrated solution in CH_2Cl_2 layered with acetonitrile at -30 °C.

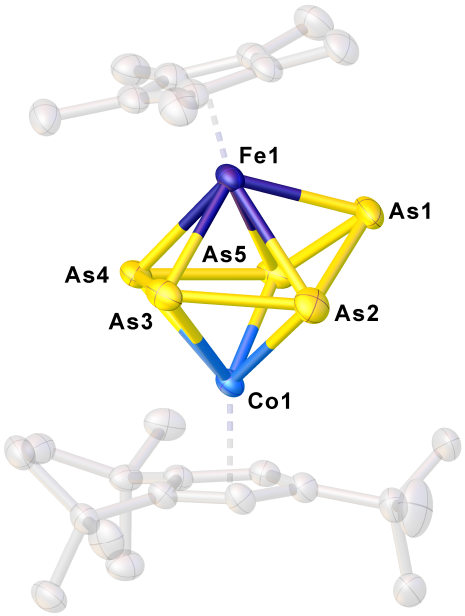
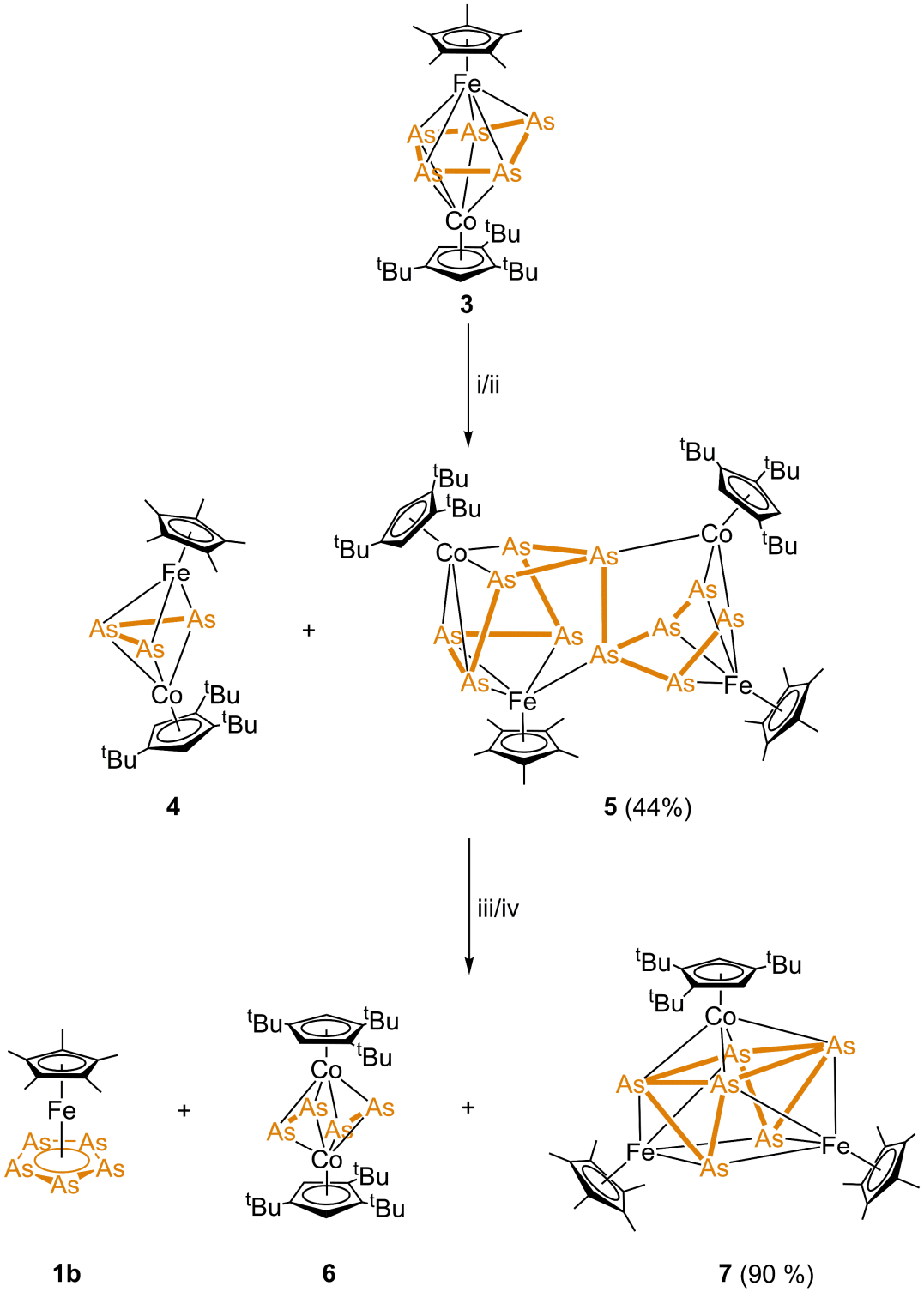


Figure 1: Molecular structure of one independent molecule of **3** in the solid state. Thermal ellipsoids are drawn with 50 % probability level. Hydrogen atoms are omitted for clarity.

The crystal structure analysis of **3** (Figure 1) reveals a dinuclear complex bearing a *cyclo*-As_5 ligand in an envelope conformation, which coordinates in a η^4 fashion to the {Cp'''Co} fragment and in η^5 mode to the {Cp*Fe} fragment. Both {CpM} fragments are tilted approx. 15 ° to each other (Cp*Fe-CoCp'''). The *cyclo*-As_5 ligand shows three shorter bonds (As1-As2 2.3716(6) Å, As1-As5 2.3682(5) Å, As3-As4 2.3401(5) Å) and two longer bonds (As2-As3 2.4383(6) Å, As4-As5 2.4627(5) Å). All bonds are in the range of As-As single bonds.[16] This is also in agreement with the Wiberg Bond Indices (WBIs) obtained from DFT calculations (0.77 and 0.78 for the longer, 1.00 and 1.08 for the shorter bonds). All bonds are elongated compared to the starting material **1b**. In contrast to the thermolysis of **1b** with $[\{Cp^*Co(CO)\}_2]$ the reaction with the cobalt toluene triple-decker complex **2** proceeds without fragmentation (the thermolysis of **1b** with $[\{Cp^*Co(CO)\}_2]$ leads to the formation of As_6 and As_4 ligand containing compounds).[11] In the LIFDI-MS spectrum beside the molecular ion peak traces of decomposition products (fragments of $[M+As]^+$, $[M-As]^-$ and $[M-2As]^-$) can be detected giving a first hint for the subsequent reactivity of **3**. Although single crystals can be obtained from layering a concentrated solution in CH_2Cl_2 with acetonitrile, compound **3** is unstable towards acetonitrile for longer time. A solution of **3** in a mixture of CH_2Cl_2 and MeCN leads after three days to a partial conversion of **3** into $[(Cp^*Fe)(Cp'''Co)(\mu,\eta^3{:}\eta^3\text{-}As_3)]$ (**4**) and $[(Cp^*Fe)_2(Cp'''Co)_2(\mu_4,\eta^4{:}\eta^4{:}\eta^3\text{-}As_{11})]$ (**5**). After column chromatographic workup a combined green fraction of **3** and **4** in a 1:4 ratio and a brown fraction of **5** can be obtained, the latter after crystallization in a yield of 44 % (cf. Scheme 2). Unfortunately, compound **4** cannot be separated from **3** by chromatographic workup (silica or alumina, column or thin layer

chromatography) or fractionized crystallization. A concentrated solution of a mixture of **3** and **4** in hexane was stored at -30 °C yielding after a few days slightly differently shaped green crystals of **3** and **4**. One of the single crystals of **4** was investigated by X-ray diffractions. After separation of the dried crystals under the microscope in the glove box, a small amount of analytically pure **4** was obtained.



Scheme 2: i) Reaction of **3** with acetonitrile for 72 h, ii) thermolysis in toluene at 60 °C ≤ 1 h, iii) thermolysis in toluene at 60 °C > 1h, at 115 °C 1<t<45 h or in xylene at 140 °C ≤ 45 h, each mixtures of **1b**, **4**, **5**, **6** and **7**, iv) thermolysis in xylene at 140 °C ≥ 45 h or in decalin at 190 °C ≥ 3h, selective formation of **1b**, **6** and **7**.

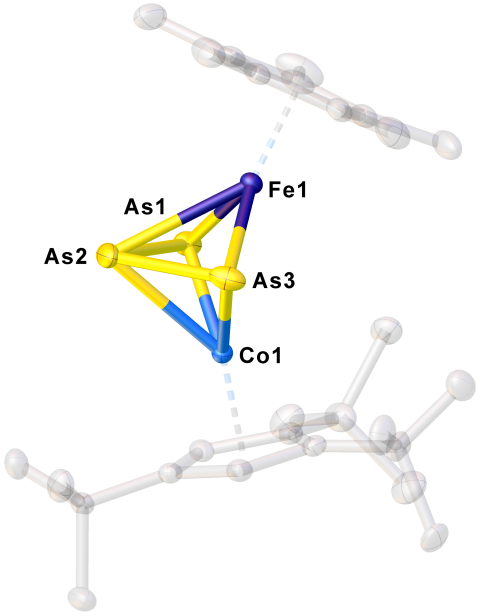


Figure 2: Molecular structure of **4** in the solid state. Thermal ellipsoids are drawn with 50 % probability level. Hydrogen atoms are omitted for clarity.

The structure of **4** in solid state (Figure 2) reveals a dinuclear triple-decker complex bearing an allylic As_3 ligand as middle deck. The As1-As2 (2.3933(3) Å) and As2-As3 (2.3879(3) Å) are in the range of single bonds (WBIs of 0.96 and 0.99).[16] The As1-As3 distance is 3.5112(3) Å, which is too long to be considered as an As-As bond. Since the distance is still below the sum of the van der Waals radii (Σ_{vdW} = 3.76 Å) an interaction between the two atoms can be expected, which is confirmed by a WBI of 0.17. The CpM fragments are tilted to each other with approx. 38 ° and a Fe-Co interaction is present (2.7744(4) Å, WBI of 0.20). Compound **4** represents the second complex known bearing an allylic As_3 ligand within a triple-decker complex (first example $[(Cp'''Co)_2(\mu,\eta^3{:}\eta^3\text{-}As_3)]^-$).[17] In the ^1H NMR spectrum in C_6D_6 four singlets centered at δ = 5.31, 1.60, 1.30 and 0.66 ppm with an integral ratio of 2:15:18:9 can be assigned to the Cp* and the Cp''' ligand, respectively. In the LIFDI-MS spectrum only the molecule ion peak can be detected. Crystals suitable for single crystal X-ray structure analysis of $[(Cp^*Fe)_2(Cp'''Co)_2(\mu_4,\eta^4{:}\eta^4{:}\eta^4{:}\eta^3\text{-}As_{11})]$ (**5**) can be obtained by layering a concentrated solution in CH_2Cl_2 with acetonitrile at room temperature. The structure of **5** (Figure 3) in solid state reveals a tetranuclear cage complex consisting of two {Cp*Fe} and two {Cp'''Co} fragments linked by an As_{11} ligand. The As ligand consists of a *cyclo*-As_5 subunit in an envelope conformation (As1-As5) linked with a *cyclo*-As_6 subunit in a chain conformation. All As-As bonds except As2-As3 and As8-As9 are in the range of elongated or slightly shortened single bonds (WBIs in the range of 0.82 and 1.02).[16] The As8-As9 bond (2.5816(5) Å) is elongated which is also underlined by an lower WBI of 0.55. The As2-As3 distance of 2.7746(5) Å is even more elongated and does not represent an As-As bond. Since the distance

is still below the sum of van der Waals radii (Σ_{vdW} = 3.76 Å), an interaction between As2 and As3 can be expected. Indeed, a WBI of 0.39 confirms the interaction.

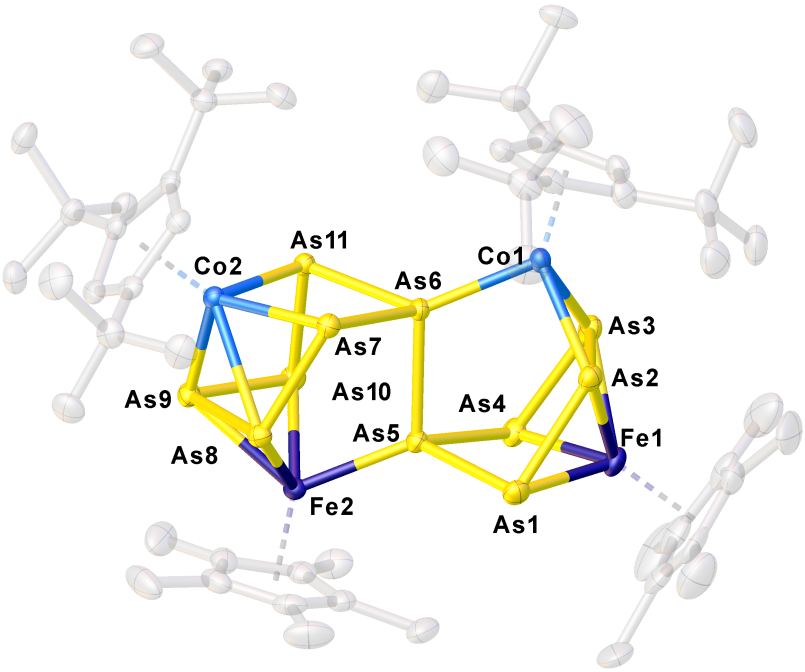


Figure 3: Molecular structure of **5** in the solid state. Thermal ellipsoids are drawn with 50 % probability level. Hydrogen atoms and solvent molecules are omitted for clarity.

Compound **5** shows the largest As_n ligand incorporated in a neutral heterometallic complex known and the second largest neutral compound at all (only $[(Cp'''Co)_3(\mu_3,\eta^4{:}\eta^3{:}\eta^3\text{-}As_{12})]$ bigger).[18] In the ^1H NMR spectrum in C_6D_6 at room temperature several broad and partially strongly shifted signals centered at δ = 9.84, 4.27, 2.36, 1.53, -0.51, -1.14 and -18.25 ppm with an integral ratio of 2:2:36:9:9:15:15 can be detected. The paramagnetism of **5** was investigated with Evans method revealing an effective magnetic moment of 2.27 μ_B corresponding to about one unpaired electron. The EPR spectra in the solid state (r.t. and 77 K) show a strong rhombic resonance with g values near to 2, indicating one unpaired electron (77 K: g_x = 2.29632, g_y = 2.16718, g_z = 2.07149, g_{iso} = 2.17833, cf. SI). DFT calculations reveal that the spin density is strongly located on the Fe1 atom (cf. Figure S39). In the LIFDI-MS the molecule ion peak cannot be detected, but the fragments $[M\text{-}Cp^*FeAs_5]^+$, $[M\text{-}Cp'''CoAs_5]^+$, $[M\text{-}Cp^*FeCp'''CoAs_4]^+$, $[M\text{-}Cp^*FeCp'''CoAs_5]^+$ and $[M\text{-}Cp^*FeCp'''CoAs_6]^+$. The fragmentation caused by acetonitrile can also be achieved under thermolytic conditions. Depending on the temperature and the duration of the reaction a different outcome was observed. To get a better insight into the fragmentation behavior, systematic studies were performed conducting the thermolysis of **3** at 60°C, 115 °C (toluene) and at 140 °C (xylene) for 93h by monitoring the transformation processes by recording NMR spectra after 1, 4, 7, 25, 45, 69 and 93 hours (cf. SI). The thermolysis in toluene at 60 °C after one hour shows a selective fragmentation of **3** into **4** and **5** which is not complete**.** Increasing the reaction time leads to a further fragmentation into

$[(Cp^*Fe)_2(Cp'''Co)(\mu_3,\eta^2:\eta^2\text{-}As_3)_2]$ (**7**), $[Cp^*Fe(\eta^5\text{-}As_5)]$ (**1b**) and $[(Cp'''Co)_2(\mu,\eta^2:\eta^2\text{-}As_2)_2]$ (**6**) (cf. Scheme 2), while **3**, **4** and **5** are also present. After 93 hours **3** and **5** were completely vanished. Conducting the thermolysis in boiling toluene leads to a similar observation. Already after 1h all subsequent products **4**, **5**, **6**, **7** and **1b** can be detected. The higher temperature causes **5** only to appear in the spectrum after 1h. After 93 hours a similar mixture like after thermolysis at 60 °C for 93h is observed. In contrast the ^{1}H NMR spectra of the thermolysis in xylene at 140 °C show no signals for **5** at all and **3** disappears already after 7h and **4** after 45 h completely. Finally, a mixture of **1b**, **6** and **7** is obtained. Conducting the thermolysis in decalin at 190 °C for 3 hours also leads to a selective fragmentation of **3** into **1b**, **6** and **7**. The latter reaction was also performed in bigger preparative scale. After column chromatographic workup a first green fraction containing both **1b** and **6** and a second brown fraction of **7** can be eluted. Compound **7** can be obtained as a dark brown solid in crystalline yields of 90 %. Crystals suitable for X-ray single crystal structure analysis can be obtained from a concentrated solution in toluene layered with acetonitrile at room temperature. The structure of **7** (Figure 4) reveals a trinuclear complex with an As_6 prism as ligand coordinating two {Cp*Fe} and one {Cp'''Co} fragments. The prismatic shaped ligand consists of two *cyclo*-As_3 subunits which are connected with each other via two shorter (2.7544(12) and 2.7570(12) Å) and one longer contact (2.9347(12) Å). All three distances are too long to be considered as bonds, but still below the sum of van-der-Waals radii and an interaction between these atoms can be expected. Indeed, WBIs of 0.27, 0.35 and 0.41 confirm this view.[19]

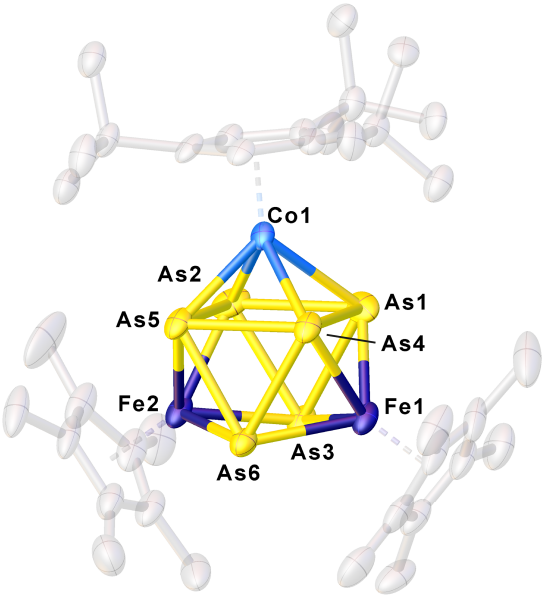


Figure 4: Molecular structure of **7** in the solid state. Thermal ellipsoids are drawn with 50 % probability level. Hydrogen atoms and solvent molecules are omitted for clarity.

The *cyclo*-As_3 units show each two shorter bonds for the edges coordinated to the iron fragments which are in the range of 2.5270(12) and 2.5446(13) Å and one longer bond for the

side-on coordination to the cobalt fragment (2.5853(11) and 2.6224(15) Å). All bonds are in the range of elongated As-As single bonds, confirmed by WBIs in the range of 0.61 and 0.68.[16] Compound **7** is isoelectronic to the homonuclear compound $[(Cp^*Co)_3(\mu_3,\eta^2:\eta^2:\eta^2\text{-}As_3)_2]^{2+}$ reported by *von Hänisch et al.* which is highly symmetric and not distorted showing short As-As bonds of 2.564(1) Å for the *cyclo*-As_3 subunit and long As-As distances between them with 2.854(1) Å.[20] The geometry of **7** is distorted due to two different metals and Cp ligands and represents the first compound with a Fe_2CoAs_6 scaffold since the analog Cp* substituted compound $[(Cp^*Fe)_2(Cp^*Co)(\mu_3,\eta^2:\eta^2:\eta^2\text{-}As_3)_2]$ was published by *Scherer et al*. in 1996, assigning erroneously one metal as cobalt instead of iron. Therefore the right composition of this compound is $[(Cp^*Fe)_3(\mu_3,\eta^2:\eta^2:\eta^2\text{-}As_3)_2]$.[11,20] In the ^{1}H NMR spectrum of **7** in C_6D_6 four singlets centered at δ = 5.13, 1.84, 1.54 and 1.39 ppm with an integral ratio of 2:30:18:9 can be assigned to two equivalent Cp* and one Cp''' ligand. In the LIFDI-MS in toluene, the molecule ion peak is detected. The reaction energy of the complete thermolysis of three equivalents of **3** to each one equivalent of **1b**, **6** and **7** is exothermic by -140.74 kJ·mol^{-1} (BP86/def2-TZVP level of theory).

6.3 Conclusion

In conclusion, a novel metastable heterobimetallic triple-decker complex with a folded *cyclo*-As_5 middle deck was synthesized. $[(Cp^*Fe)(Cp'''Co)(\mu,\eta^5:\eta^4\text{-}As_5)]$ (**3**) can be selectively converted yielding unprecedented mixed-metal polyarsenic complexes. The first fragmentation step delivers $[(Cp^*Fe)(Cp'''Co)(\mu,\eta^3:\eta^3\text{-}As_3)]$ (**4**) representing the second reported triple-decker complex bearing an allylic As_3 ligand[17] and $[(Cp^*Fe)_2(Cp'''Co)_2(\mu_4,\eta^4:\eta^4:\eta^4:\eta^3\text{-}As_{11})]$ (**5**) which is the compound with largest polyarsenic ligand incorporated in a heterometallic scaffold and the second largest neutral derivative at all.[18] This reaction proceeds stoichiometrically (five molecules **3** are converted into one molecule **4** and two molecules **11**). Under harsher reaction conditions a subsequent conversion of **4** and **5** into the thermodynamic stable compounds $[Cp^*Fe(\eta^5\text{-}As_5)]$ (**1b**), $[(Cp'''Co)_2(\mu,\eta^2:\eta^2\text{-}As_2)_2]$ (**6**) and $[(Cp^*Fe)_2(Cp'''Co)\ (\mu_3,\eta^2:\eta^2:\eta^2\text{-}As_3)_2]$ (**7**) occurs. The latter represents the first heterometallic complex comprising a prism shaped As_6 ligand. The complete conversion of **3** into **1b**, **6** and **7** proceeds stoichiometrically (three equivalents **3** give each one molecule **1b**, **6** and **7**). This reaction is exothermic by -140.74 kJ·mol^{-1}. Therefore, **3** displays a unique platform for in the investigation of thermolytic reactions and their pathway. Here several intermediates can be isolated and fully characterized and the selectivity can be easily controlled by finetuning of the reaction conditions.

6.4 Supporting Information

6.4.1 Synthetic procedures and experimental details

Synthetic Procedures: All manipulations were performed under an atmosphere of dry argon using standard glove-box and Schlenk techniques. All solvents were degassed and purified by standard procedures. The compounds $[(Cp'''Co)_2(\mu,\eta^4{:}\eta^4\text{-}C_7H_8)]$ (**2**)[21], $[Cp^*Fe(\eta^5\text{-}As_5)]$ (**1b**)[3] and $[(Cp'''CoCl)_2]$[22] were prepared according to literature procedures.

The NMR spectra were recorded with a Bruker Avance 400 spectrometer (^{1}H: 400.13 MHz, ^{31}P: 161.976 MHz). The chemical shifts are given in ppm referenced to external $SiMe_4$ (^{1}H) and H_3PO_4 (^{31}P). Elemental analyses were determined with an Elementar Vario EL III apparatus. All mass spectra were recorded with a Finnigan MAT 95 mass spectrometer (LIFDI-MS). The X-Band EPR measurements were carried out with a MiniScope MS400 device with a frequency of 9.44 GHz and a rectangular resonator TE102 of the company Magnettech GmbH.

6.4.1.1 Synthesis of $[(Cp^*Fe)(Cp'''Co)(\mu,\eta^5{:}\eta^4\text{-}As_5)]$ (3)

A solution of $[(Cp'''Co)_2(\mu,\eta^4{:}\eta^4\text{-}C_7H_8)]$ (**2**) (598 mg, 0.884 mmol, 1 eq) in 50 mL pentane was added dropwise to a stirred solution of $[Cp^*Fe(\eta^5\text{-}As_5)]$ (**1b**) (1.00 g, 1.768 mmol, 2 eq) in 200 mL pentane. The color changed to dark green after one hour. The ^{1}H NMR spectrum of the reaction mixture reveals the clean formation of **3** beside unused **1b** in a ratio of 91:9. Further **2** (51 mg, 0.075 mmol) in pentane was added and stirred for another hour. The solvent was removed *in vacuo*. **3** can be obtained as a dark green solid. Very few crystals of **3** suitable for X-ray single crystal structure analysis can be obtained from a concentrated solution in CH_2Cl_2 layered with acetonitrile at -30 °C after a few days beside decomposition products (vide infra).

Yield: 1.373 g (91 %).

^{1}H NMR (C_6D_6, 293 K): δ [ppm] = 3.67 (s, 2H, $C_5H_2{}^tBu_3$), 1.43 (s, 18H, $C_5H_2{}^tBu_3$), 1.40 (s, 15H, C_5Me_5), 1.33 (s, 9H, $C_5H_2{}^tBu_3$).

LIFDI-MS (toluene): *m/z* = 932.6 (4 %, $[M+As]^+$), 857.7 (100 %, $[M]^+$), 782.8 (4 %, $[M-As]^+$), 707.9 (15 %, $[M-2As]^+$).

EA: $C_{27}H_{44}CoFeAs_5$: calc [%]: C: 37.79; H: 5.17; found [%]: C: 37.32; H: 5.17.

6.4.1.2 Synthesis of [(Cp*Fe)(Cp'''Co)(μ,η³:η³-As₃)] (4) and [(Cp*Fe)₂(Cp'''Co)₂(μ₄,η⁴:η⁴:η⁴:η³-As₁₁)] (5)

10 mL MeCN were added to a solution of **3** (1.00 g, 1.166 mmol) in 50 mL CH_2Cl_2 and stirred for three days. The color changed from dark green to brown green. The ^{1}H NMR spectrum reveals a mixture of **3**, [(Cp*Fe)(Cp'''Co)(μ,η³:η³-As₃)] (**4**) and [(Cp*Fe)₂(Cp'''Co)₂(μ₄,η⁴:η⁴:η⁴:η³-As₁₁)] (**5**). The solvent was removed *in vacuo*. The residue was dissolved in CH_2Cl_2, SiO_2 added and dried *in vacuo*. The preabsorbed crude mixture was purified by column chromatography (SiO_2, pentane, 25 x 3 cm). Using pentane a dark green fraction can eluted containing a mixture of **3** and **4** in a ratio of 22:78 which cannot be separated further from each other (using alumina for column chromatography and using thin layer chromatography with silica and alumina, respectively were not successful). Using toluene, a strong dark brown fraction of **5** can be eluted. The solvent was removed *in vacuo*, the residue dissolved in CH_2Cl_2 and layered with MeCN at room temperature. After a few days **3** can be obtained as dark brown blocks. The supernatant was decanted off and the remaining crystals dried *in vacuo*. The mixture of **3** and **4** was dissolved in hexane and stored at -30 °C. After a few days two kind of slightly different shaped crystals were obtained, which were separated under the microscope yielding a few mg on analytically pure **4**.

Compound **4**:

Yield: 10 mg

^{1}H NMR (C_6D_6, 293 K): δ [ppm] = 5.31 (s, 2H, $C_5H_2{}^t$Bu$_3$), 1.60 (s, 15H, C_5Me_5), 1.30 (s, 18H, $C_5H_2{}^tBu_3$), 0.66 (s, 9H, $C_5H_2{}^tBu_3$).

LIFDI-MS (toluene): *m/z* = 708.0 (100 %, $[M]^+$).

EA: $C_{27}H_{44}CoFeAs_3$: calc [%]: C: 45.79; H: 6.26; found [%]: C: 45.62; H: 6.05.

Compound **5:**

Yield : 366 mg (0.204 mmol, 44 % related to **3** using the stoichiometry of 5 [(Cp*Fe)(Cp'''Co)As$_5$] → [(Cp*Fe)(Cp'''Co)As$_3$ + 2 [(Cp*Fe)$_2$(Cp'''Co)$_2$As$_{11}$]).

^{1}H NMR (C_6D_6, 293 K): δ [ppm] = 9.84 (br, 2H, $C_5H_2{}^t$Bu$_3$), 4.27 (s, 2H, $C_5H_2{}^t$Bu$_3$), 2.36 (br, 36H, $C_5H_2{}^tBu_3$), 1.53 (s, 9H, $C_5H_2{}^tBu_3$), -0.51 (br, 9H, $C_5H_2{}^tBu_3$), -1.14 (br, 15H, C_5Me_5), -18.25 (br, 15H, C_5Me_5).

Evans-NMR (C_6D_6, 293 K): μ_{eff} = 2.27 μ_B corresponding to 1.48 unpaired electrons.

LIFDI-MS (toluene): *m/z* = 1224.9 (20 %, [M-Cp*Fe-5As]$^+$), 1123.9 (11 %, [M-Cp'''Co-5As]$^+$), 1007.7 (7 %, [M-Cp*Fe-Cp'''Co-4As]$^+$), 932.8 (70 %, [M-Cp*Fe-Cp'''Co-5As]$^+$), 857.9 (100 %, [M-Cp*Fe-Cp'''Co-6As]$^+$).

EA: $C_{54}H_{88}Co_2Fe_2As_{11}$ x 0.85 CH_2Cl_2: calc [%]: C: 35.38; H: 4.85; found [%]: C: 35.44; H: 4.66.

EPR (X-band): (solid, 77 K) g_x = 2.29632, g_y = 2.16718, g_z = 2.07149, g_{iso} = 2.17833.

6.4.1.3 Synthesis of [(Cp*Fe)$_2$(Cp'''Co)(μ$_3$,η^2:η^2-As$_3$)$_2$] (7)

A solution of **3** (1.05 g, 1.2237 mmol) in decaline was stirred under reflux for 3 h while the color changed to brown-green. The ^{1}H NMR of the reaction mixture reveals [Cp*Fe(η^5-As$_5$)] (**1b**), [(Cp'''Co)$_2$(As$_2$)$_2$] (**6**) and [(Cp*Fe)$_2$(Cp'''Co)(μ$_3$,η^2:η^2-As$_3$)$_2$] (**7**). The solvent was removed *in vacuo*. The residue was dissolved in CH_2Cl_2, SiO_2 was added and the solvent removed *in vacuo*. The preabsorbed crude mixture was purified by column chromatography (SiO_2, hexane, 16x3 cm). Using hexane, a first dark green fraction (**6**) and a bright green fraction (**1b**) can be eluted. Using CH_2Cl_2, a dark brown fraction (**7**) can be eluted. **1b** and **6** were disposed. The solvent was removed *in vacuo*. Compound **7** was dissolved in toluene and layered with acetonitrile at room temperature. After a few days, **7** can be obtained as dark brown blocks. The supernatant was decanted off and dried *in vacuo*.

Compound **7**:

Yield: 203 mg (90 % related to **1** using the stoichiometry of 3 [(Cp*Fe)(Cp'''Co)As$_5$] → [Cp*FeAs$_5$] + [(Cp'''Co)$_2$(As$_2$)$_2$] + [(Cp*Fe)$_2$(Cp'''Co)As$_6$]).

^{1}H NMR (C_6D_6, 293 K): δ [ppm] = 5.13 (s, 2H, $C_5H_2{}^t$Bu$_3$), 1.84 (s, 30H, C_5Me_5), 1.54 (s, 18H, $C_5H_2{}^tBu_3$), 1.39 (s, 9H, $C_5H_2{}^tBu_3$).

LIFDI-MS (toluene): *m/z* = 1123.9 (100 %, [M]$^+$).

EA: $C_{37}H_{59}CoFe_2As_6$: calc [%]: C: 39.54; H: 5.29; found [%]: C: 39.79; H: 5.17.

6.4.1.4 Thermolysis reactions of [(Cp*Fe)(Cp’’’Co)(μ,η^5:η^4-As$_5$)] (3)

a-c): A solution of 50 mg **3** were dissolved in toluene (a, b) and xylene (c), respectively, and stirred for 93 h at a) 60 °C, b) 115 °C and c) 140 °C. Samples were each taken after 1, 4, 7, 25, 45, 69 and 93 hours, the solvent was removed *in vacuo* and taken up in C_6D_6 for NMR investigations. Selected spectra and graphs are depicted in chapter 2.6-2.8.

6.4.2 NMR spectroscopic investigations

6.4.2.1 [(Cp*Fe)(Cp’’’Co)(μ,η^5:η^4-As$_5$)] (3)

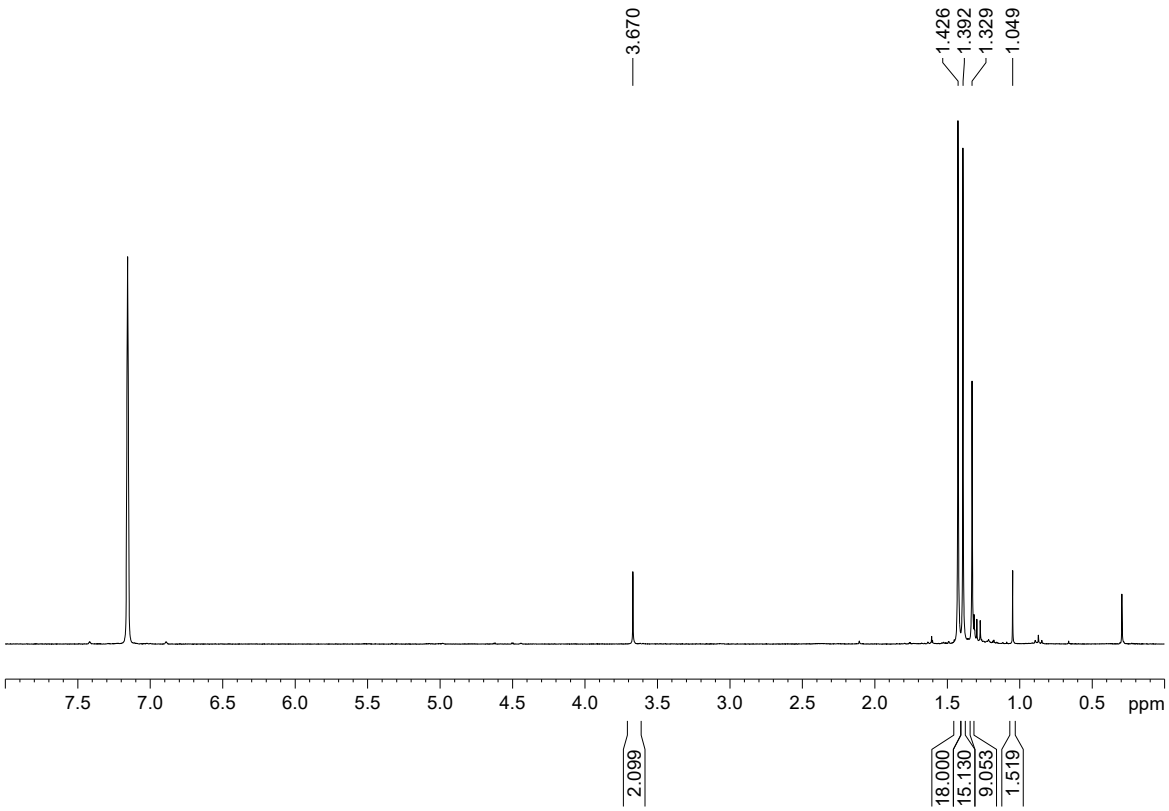


Figure S1: ^{1}H NMR spectrum in C_6D_6 at room temperature. Stoichiometric reaction of **1b** and **2**.

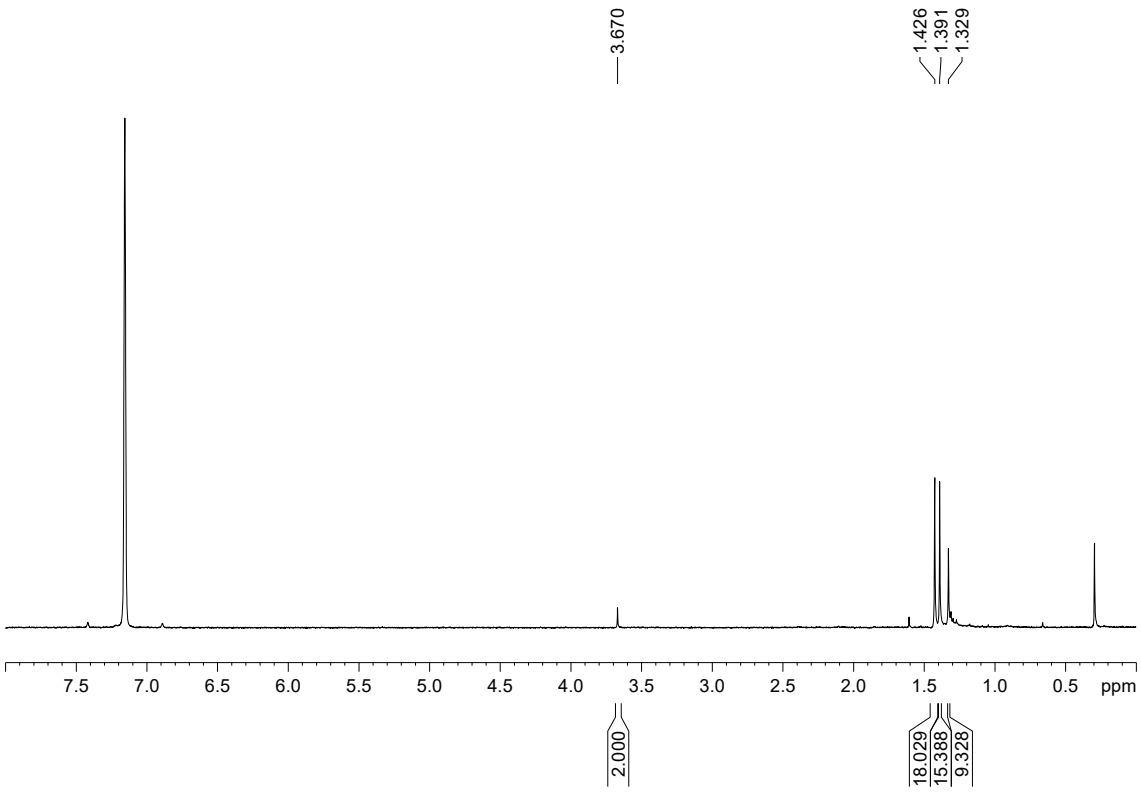


Figure S2: ^{1}H NMR spectrum of isolated dark green solid in C_6D_6 at room temperature.

6.4.2.1 [(Cp*Fe)(Cp’’’Co)(μ,η^3:η^3-As$_3$)] (4)

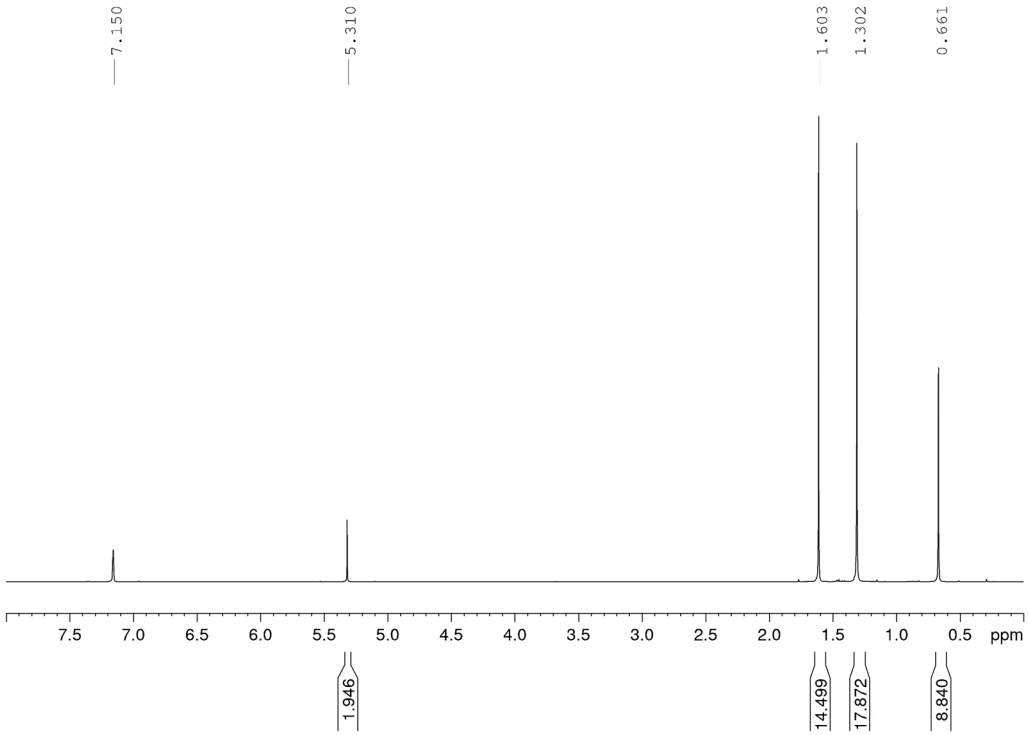


Figure S3: ^{1}H NMR spectrum of **4** in C_6D_6 at room temperature.

6.4.2.3 $[(Cp^*Fe)_2(Cp'''Co)_2(\mu_4,\eta^4:\eta^4:\eta^3\text{-}As_{11})]$ (5)

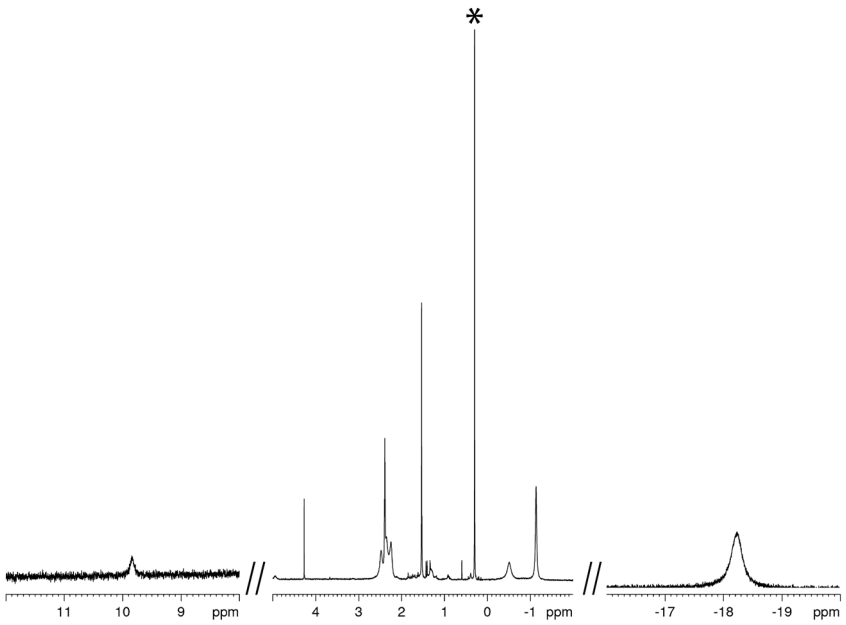


Figure S4: ^{1}H NMR spectrum of **5** in C_6D_6 at room temperature. Left and right part magnified for overview. Impurity of silicon grease (*).

6.4.2.4 $[(Cp^*Fe)_2(Cp'''Co)(\mu_3,\eta^2:\eta^2\text{-}As_3)_2]$ (7)

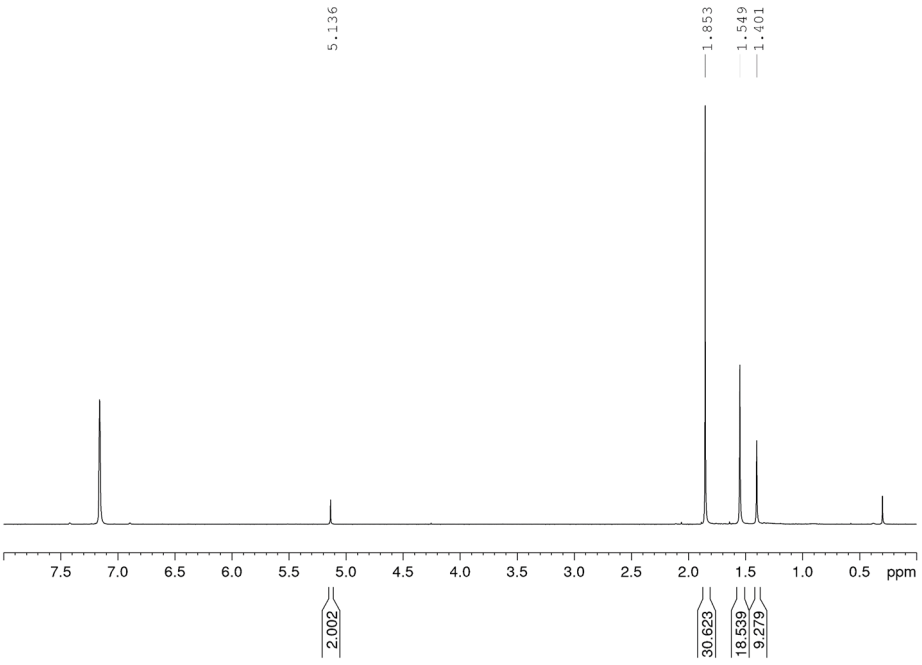


Figure S5: 1H NMR spectrum of **7** in C_6D_6 at room temperature.

6.4.2.5 Fragmentation of 3 with acetonitrile

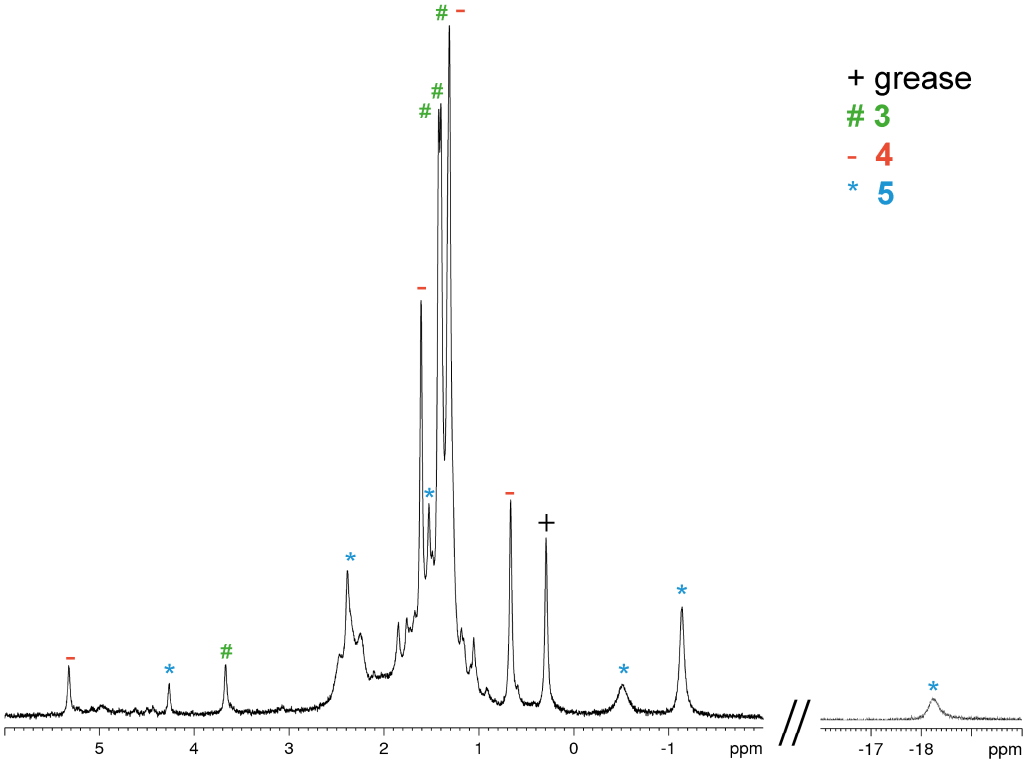


Figure S6: ^{1}H NMR spectrum of the reaction mixture three days after the addition of MeCN in C_6D_6 at room temperature.

6.4.2.6 Thermolysis of 3 in toluene at 60 °C

Since **1b** is the only compound which is present in all spectra, it was chosen to be the reference.

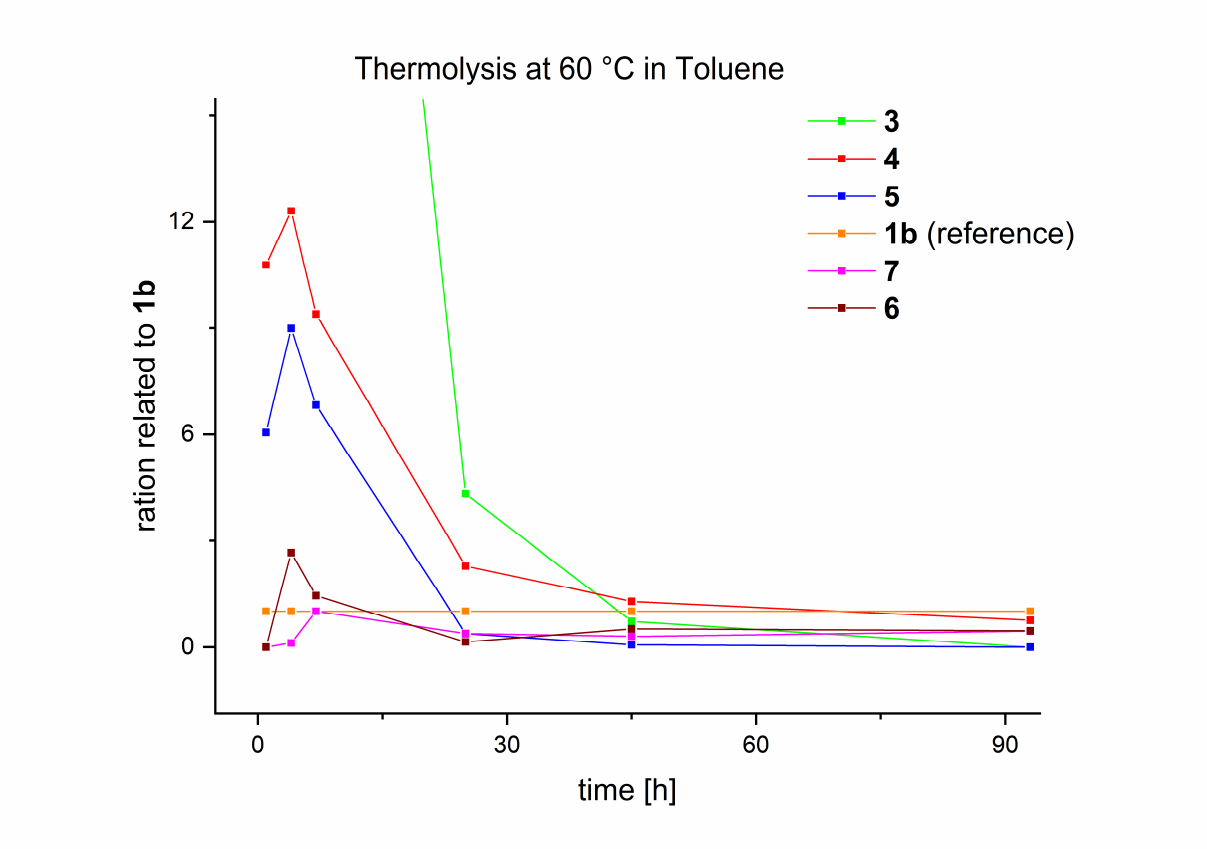


Figure S7: Plotted relative integrals for all compounds referenced to **1b**.

Table S1: Integral ratios of all compounds related to **1b**.

Time [h]	**3**	**4**	**5**	**7**	**1b**	**6**
1	131.579	10.789	6.053	0	1	0
4	96.154	12.308	8.99	0.115	1	2.663
7	43.478	9.391	6.822	1	1	1.435
25	4.329	2.281	0.377	0.381	1	0.146
45	0.715	1.276	0.061	0.299	1	0.511
93	0	0.745	0	0.445	1	0.454

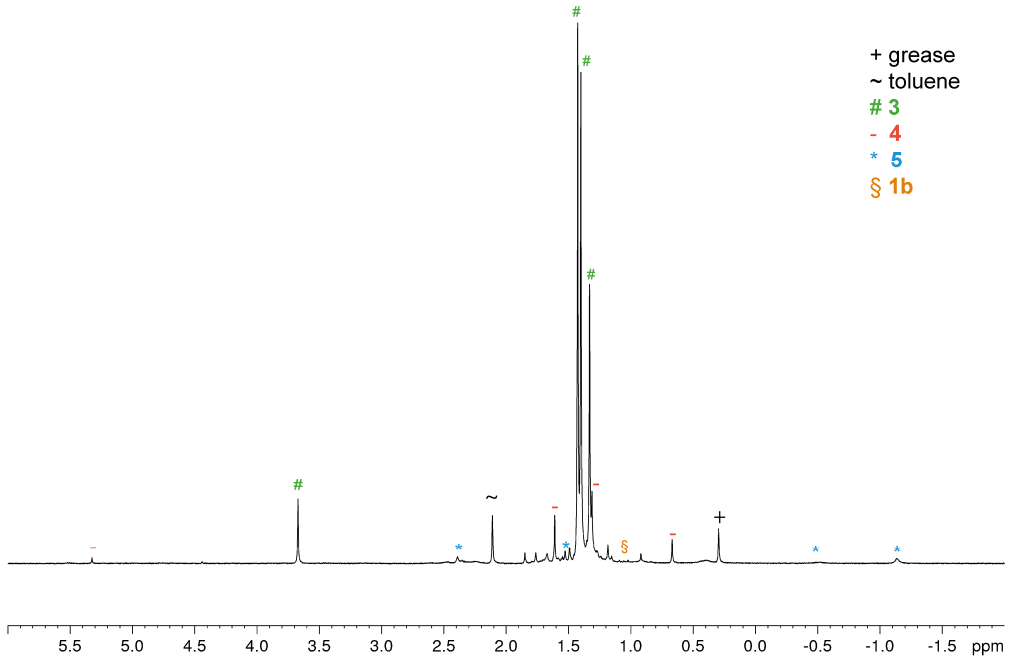


Figure S8: ^{1}H NMR spectrum of the reaction mixture in C_6D_6 at room temperature after 1h.

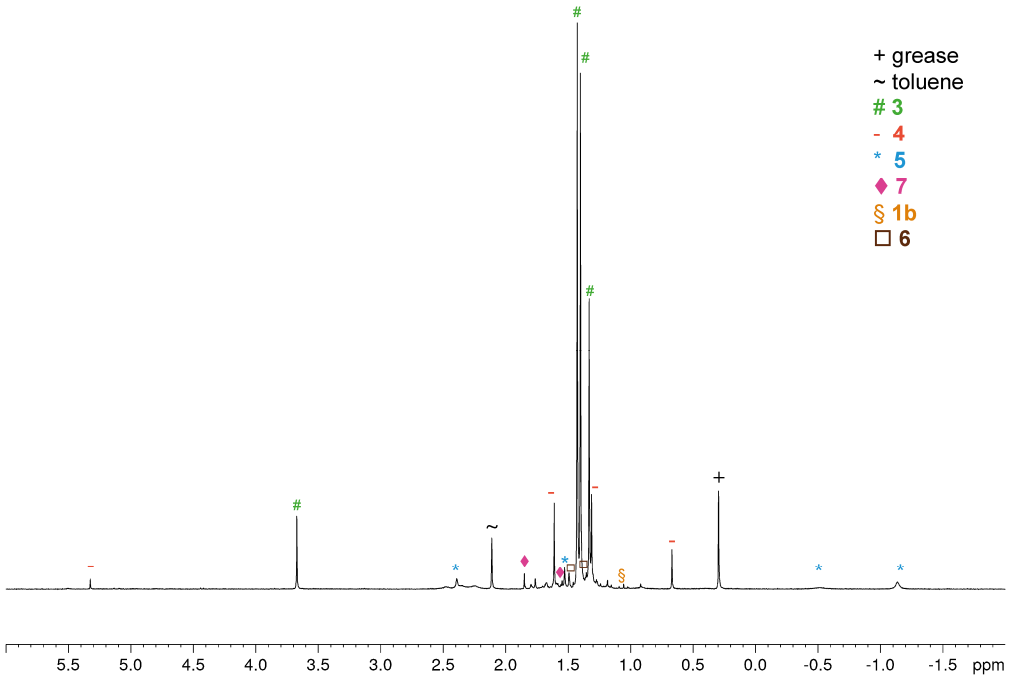


Figure S9: ^{1}H NMR spectrum of the reaction mixture in C_6D_6 at room temperature after 4h.

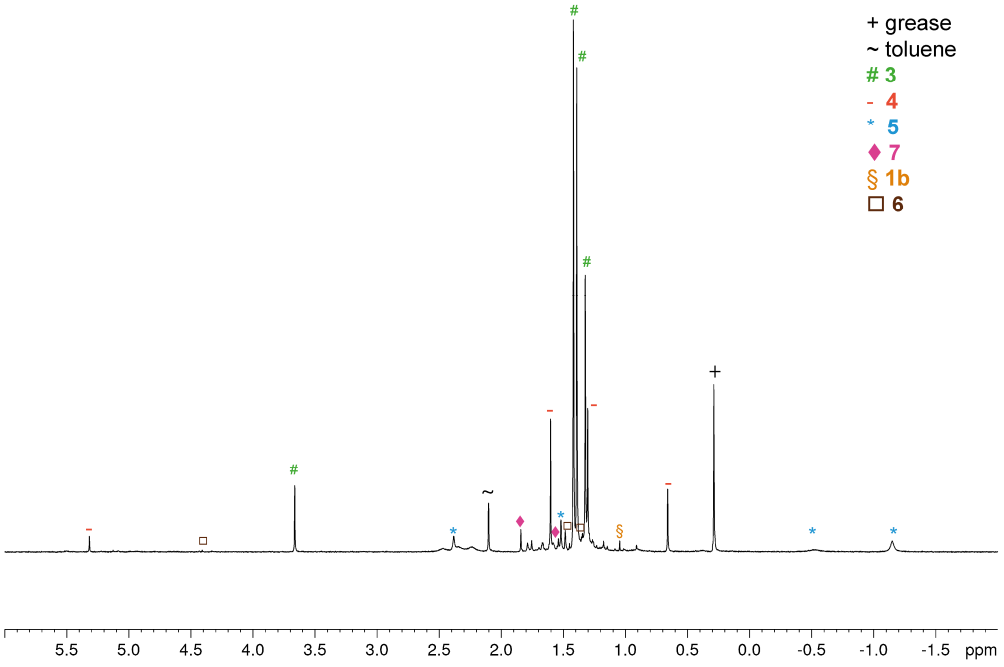


Figure S10: ^{1}H NMR spectrum of the reaction mixture in C_6D_6 at room temperature after 7h.

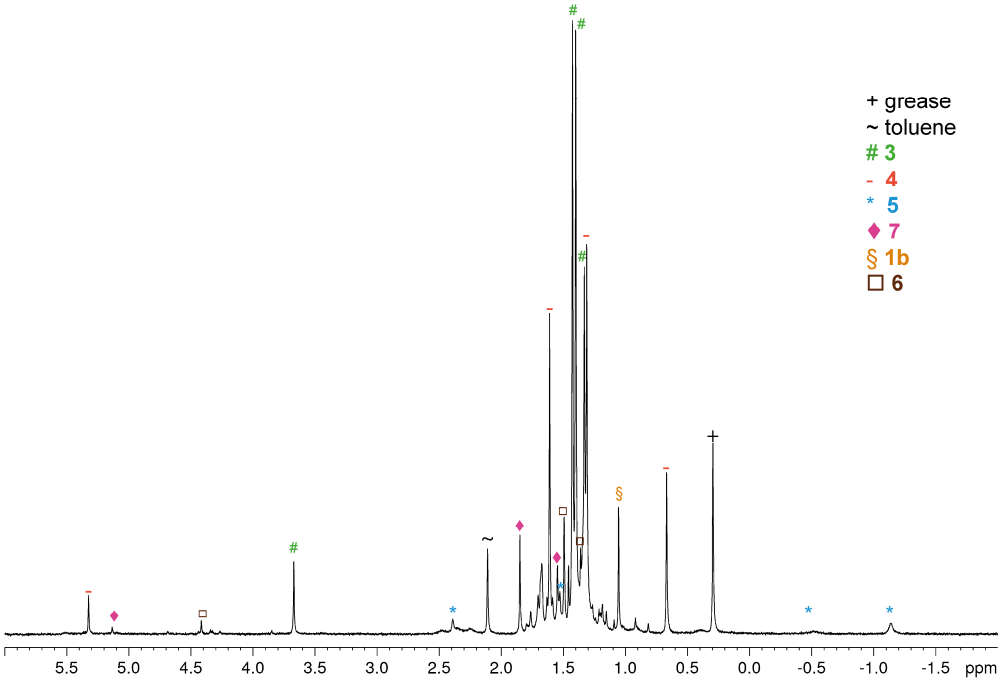


Figure S11: ^{1}H NMR spectrum of the reaction mixture in C_6D_6 at room temperature after 25h.

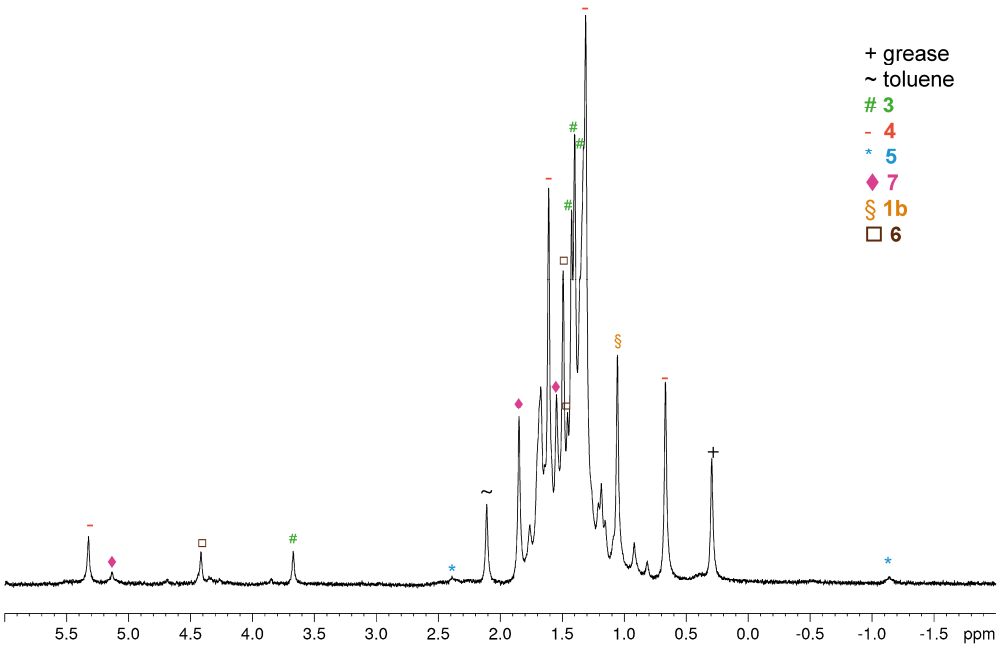


Figure S12: ^{1}H NMR spectrum of the reaction mixture in C_6D_6 at room temperature after 45h.

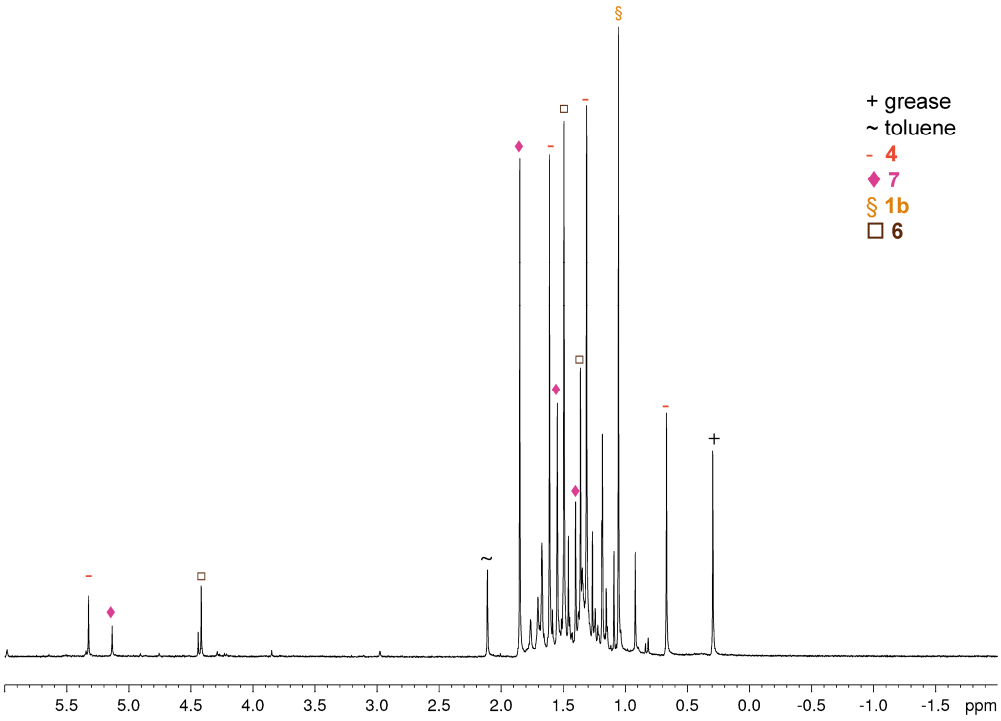


Figure S13: ^{1}H NMR spectrum of the reaction mixture in C_6D_6 at room temperature after 93h.

6.4.2.7 Thermolysis of 3 in toluene at 115 °C

Since **1b** is the only compound which is present in all spectra, it was chosen to be the reference.

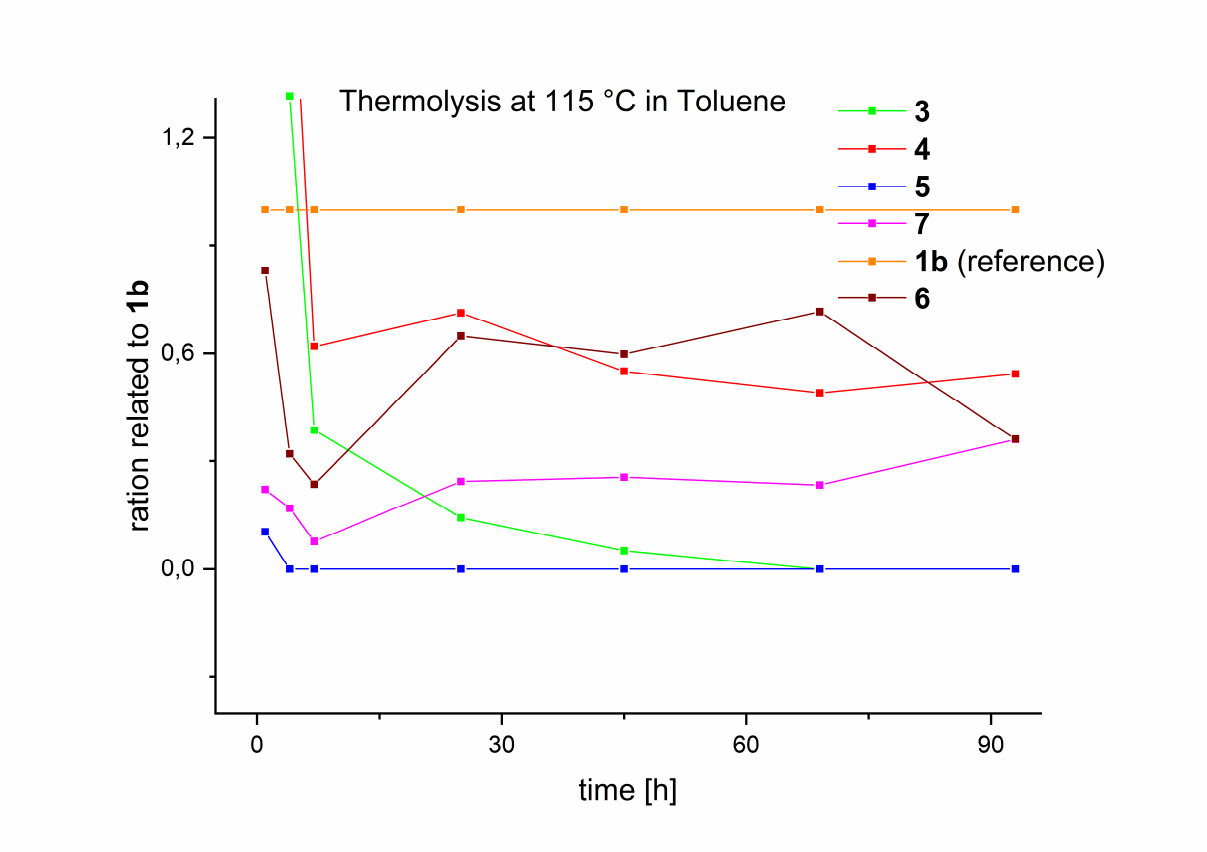


Figure S14: Plotted relative integrals for all compounds referenced to **1b**.

Table S2: Integral ratios of all compounds related to **1b**.

Time [h]	**3**	**4**	**5**	**7**	**1b**	**6**
1	4.329	3.281	0.103	0.221	1	0.831
4	1.316	1.845	0	0.168	1	0.32
7	0.386	0.62	0	0.077	1	0.235
25	0.142	0.712	0	0.243	1	0.649
45	0.051	0.551	0	0.255	1	0.598
69	0	0.4894	0	0.2331	1	0.7154
93	0	0.5438	0	0.3601	1	0.361

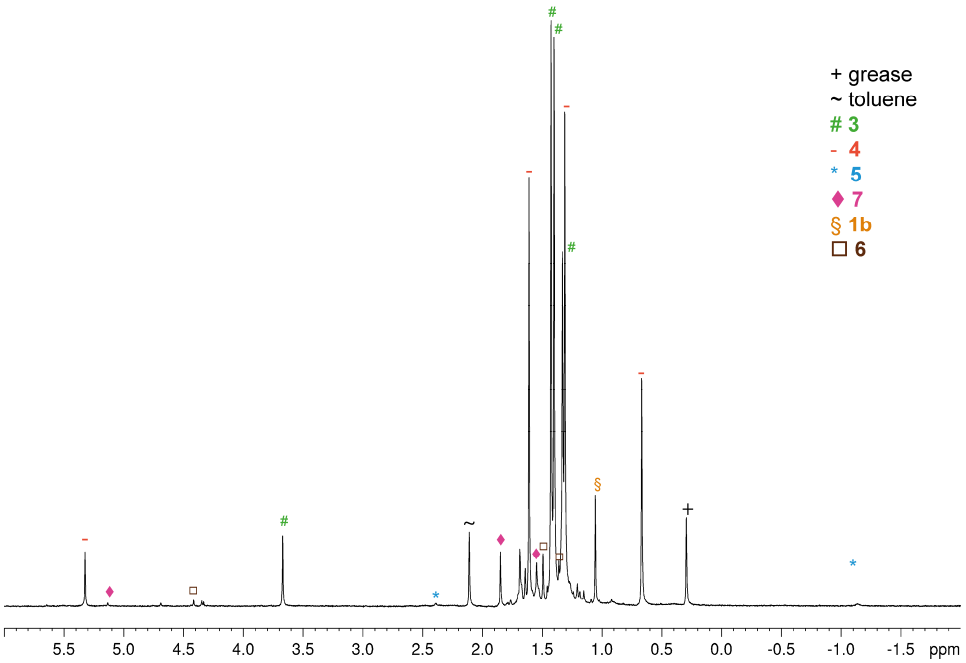


Figure S15: ^{1}H NMR spectrum of the reaction mixture in C_6D_6 at room temperature after 1h.

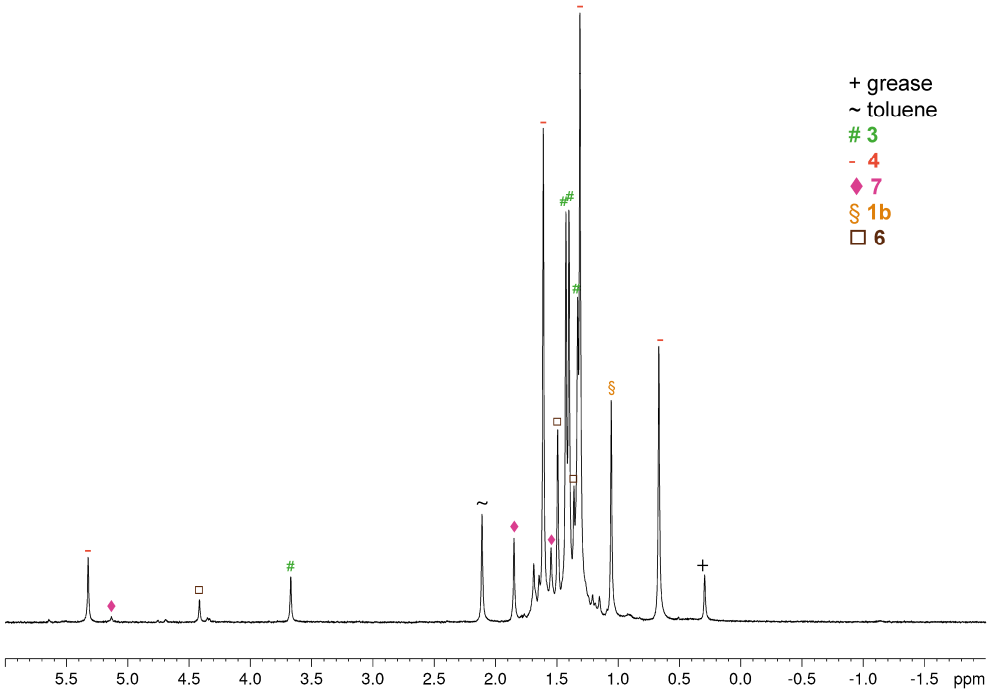


Figure S16: ^{1}H NMR spectrum of the reaction mixture in C_6D_6 at room temperature after 4h.

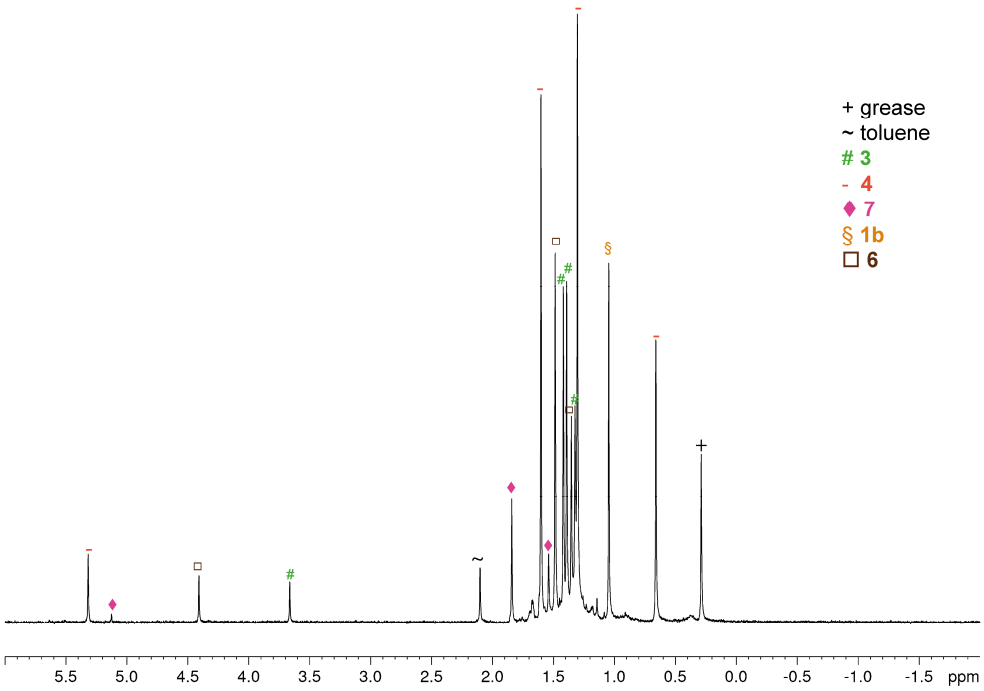


Figure S17: ^{1}H NMR spectrum of the reaction mixture in C_6D_6 at room temperature after 7h.

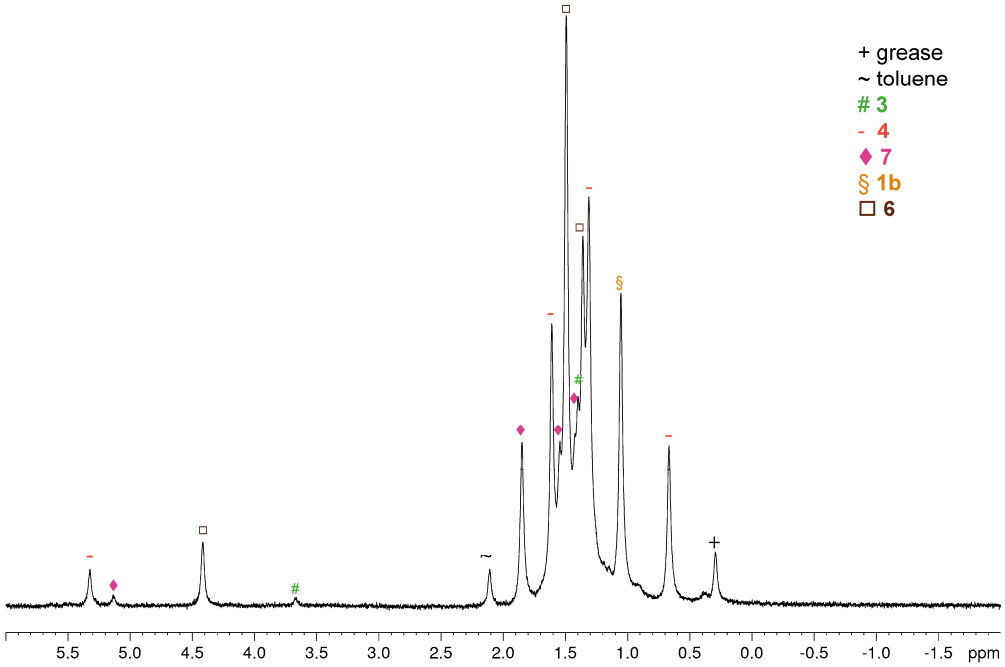


Figure S18: ^{1}H NMR spectrum of the reaction mixture in C_6D_6 at room temperature after 25h.

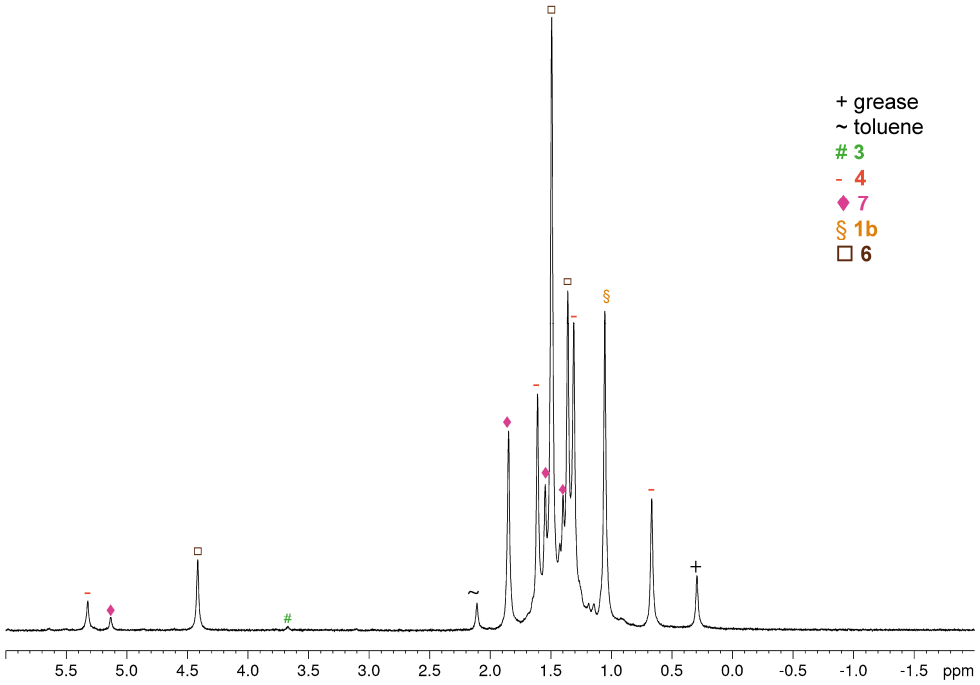


Figure S19: ^{1}H NMR spectrum of the reaction mixture in C_6D_6 at room temperature after 45h.

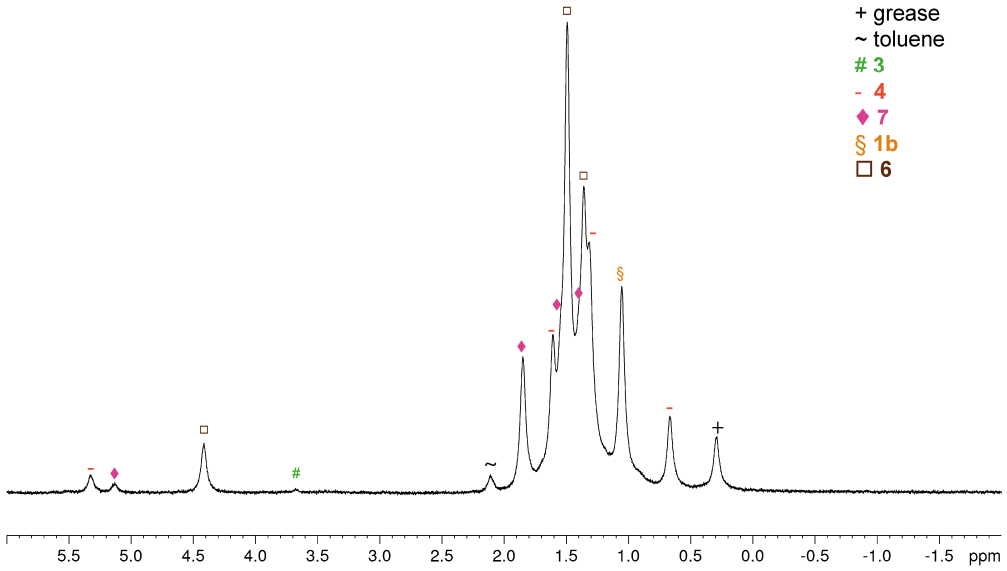


Figure S20: ^{1}H NMR spectrum of the reaction mixture in C_6D_6 at room temperature after 69h.

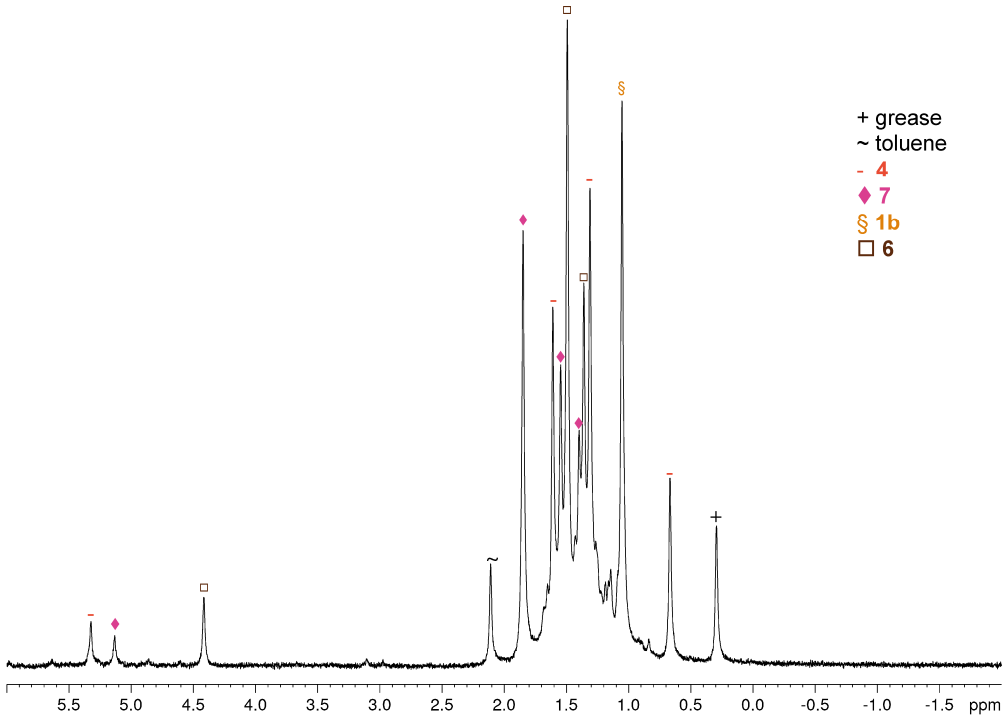


Figure S21: ^{1}H NMR spectrum of the reaction mixture in C_6D_6 at room temperature after 93h.

6.4.2.8 Thermolysis of 3 in xylene at 140 °C

Since **1b** is the only compound which is present in all spectra, it was chosen to be the reference.

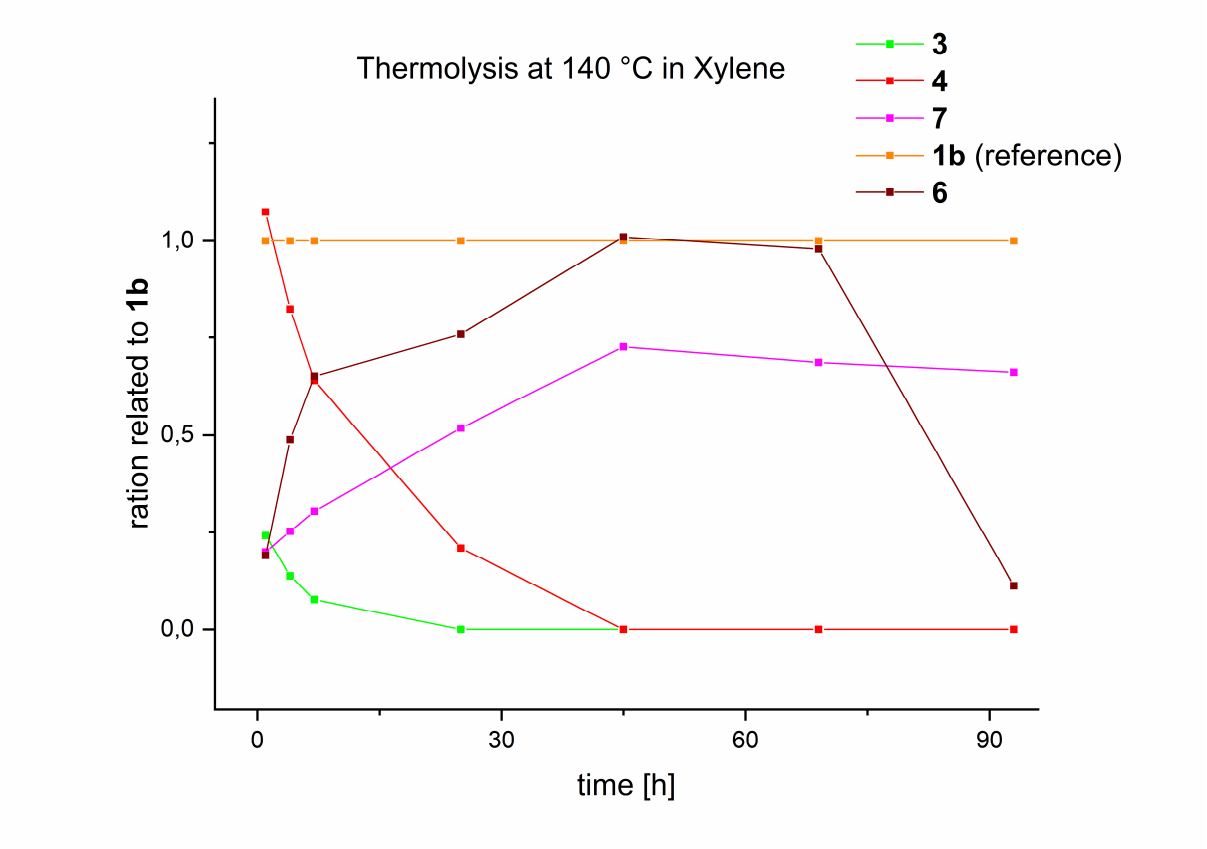


Figure S22: Plotted relative integrals for all compounds referenced to **1b**.

Table S3: Integral ratios of all compounds related to **1b**.

Time [h]	**3**	**4**	**5**	**7**	**1b**	**6**
1	0.241	1.073	0	0.198	1	0.189
4	0.137	0.823	0	0.252	1	0.488
7	0.077	0.64	0	0.304	1	0.651
25	0	0.208	0	0.518	1	0.758
45	0	0	0	0.726	1	1.01
69	0	0	0	0.686	1	0.9782
93	0	0	0	0.6606	1	0.112

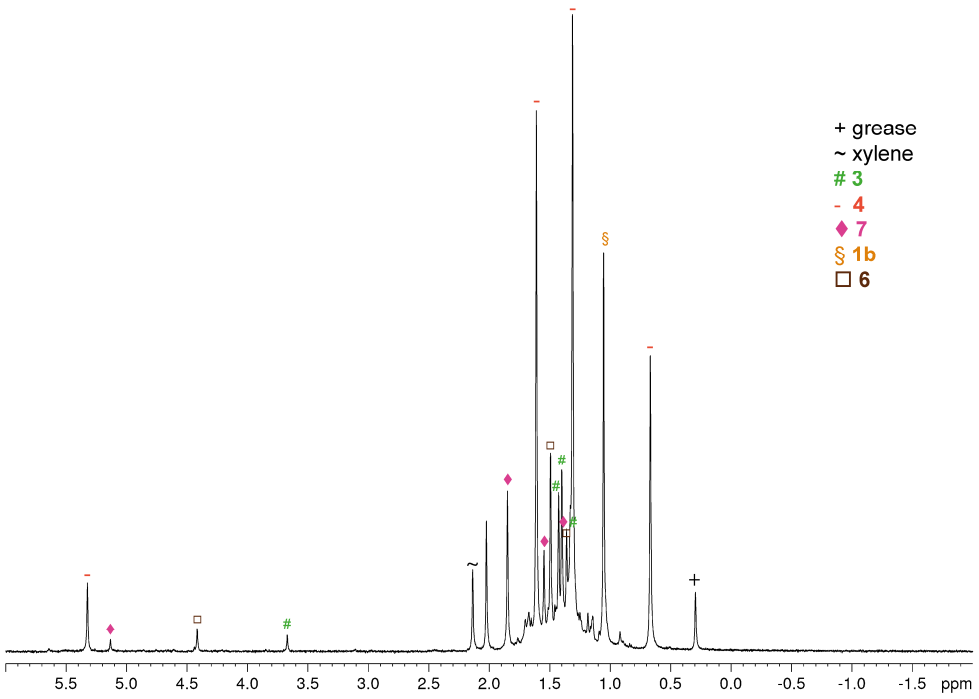


Figure S23: ^{1}H NMR spectrum of the reaction mixture in C_6D_6 at room temperature after 1h.

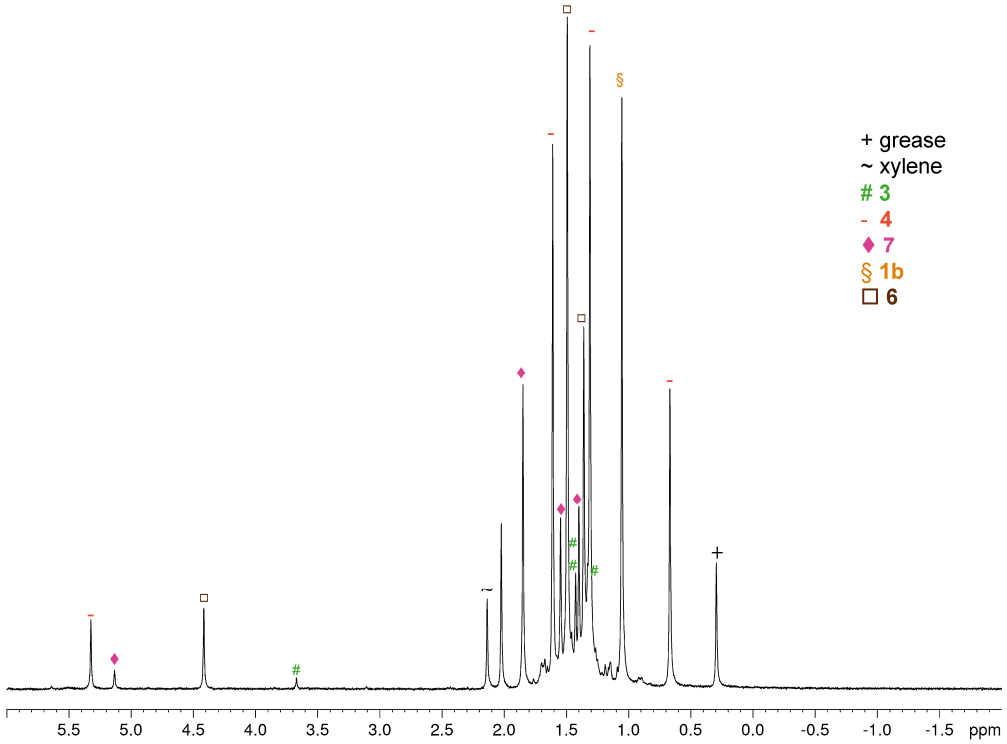


Figure S24: ^{1}H NMR spectrum of the reaction mixture in C_6D_6 at room temperature after 4h.

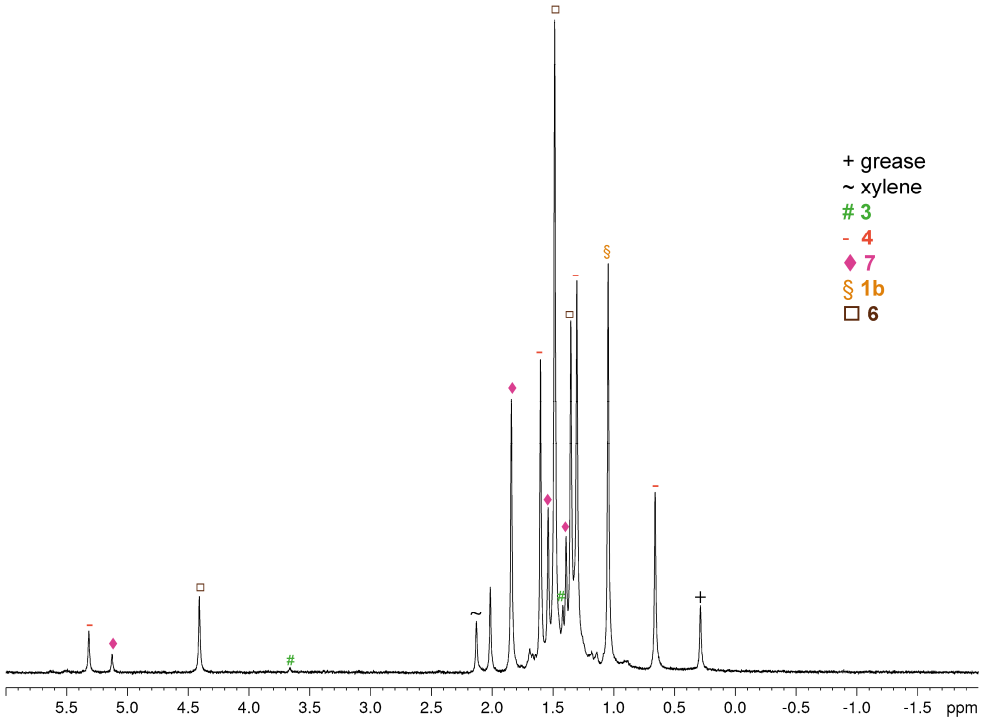


Figure S25: ^{1}H NMR spectrum of the reaction mixture in C_6D_6 at room temperature after 7h.

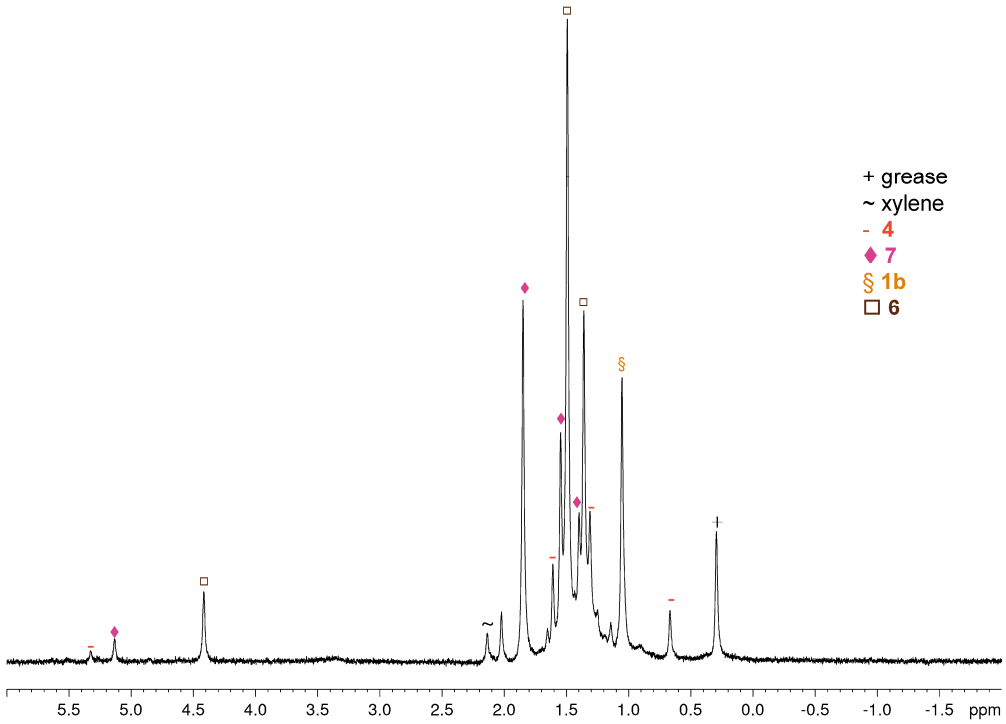


Figure S26: ^{1}H NMR spectrum of the reaction mixture in C_6D_6 at room temperature after 25h.

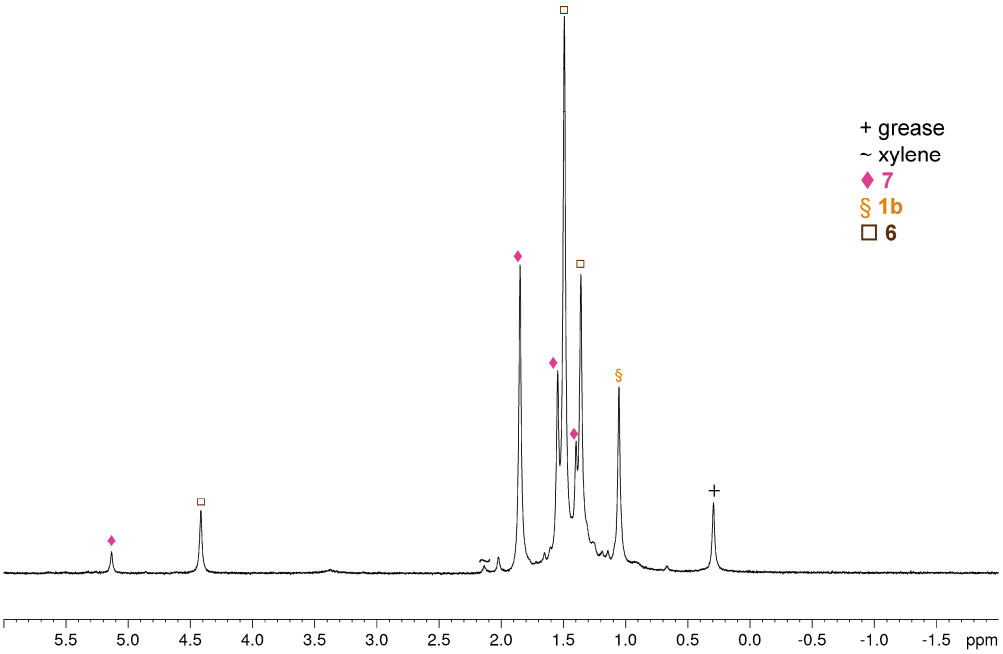


Figure S27: ^{1}H NMR spectrum of the reaction mixture in C_6D_6 at room temperature after 45h.

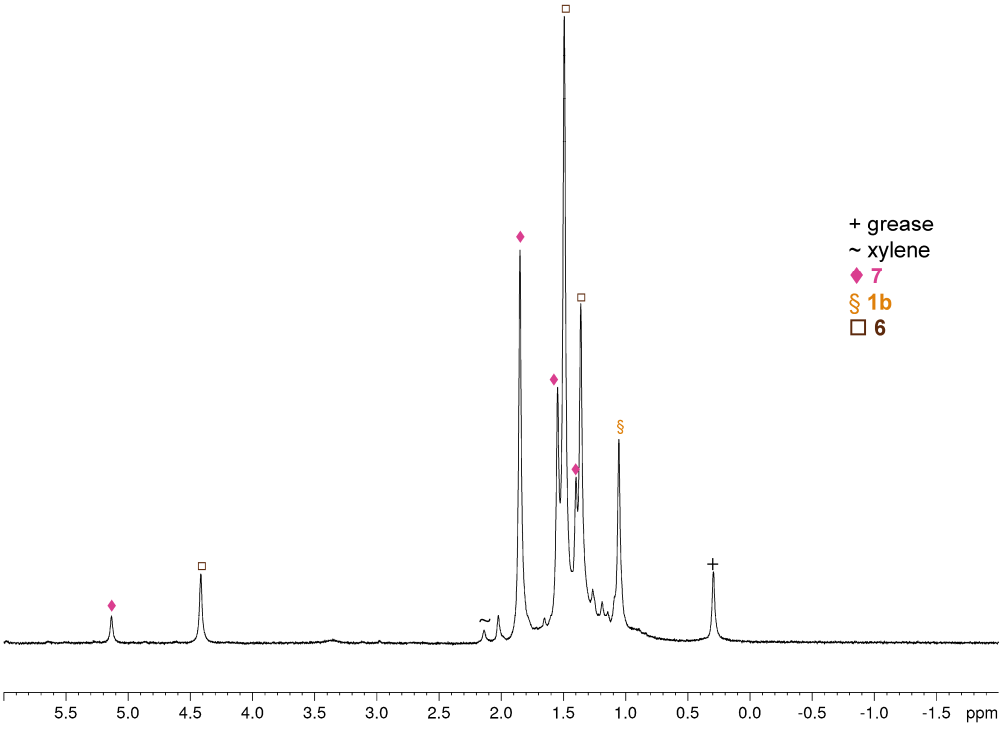


Figure S28: ^{1}H NMR spectrum of the reaction mixture in C_6D_6 at room temperature after 69h.

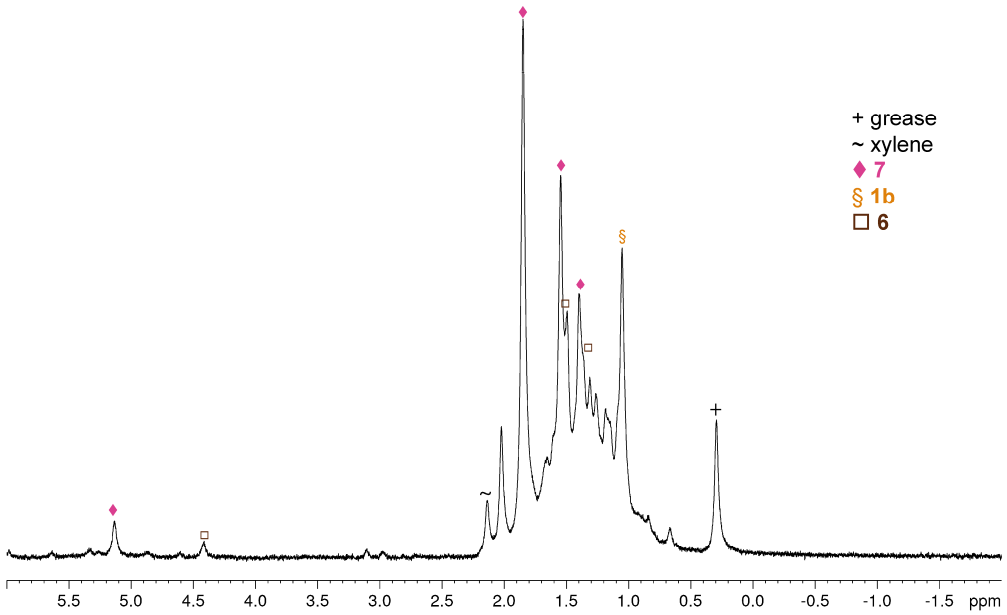


Figure S29: ^{1}H NMR spectrum of the reaction mixture in C_6D_6 at room temperature after 93h.

6.4.3 EPR spectroscopic investigations

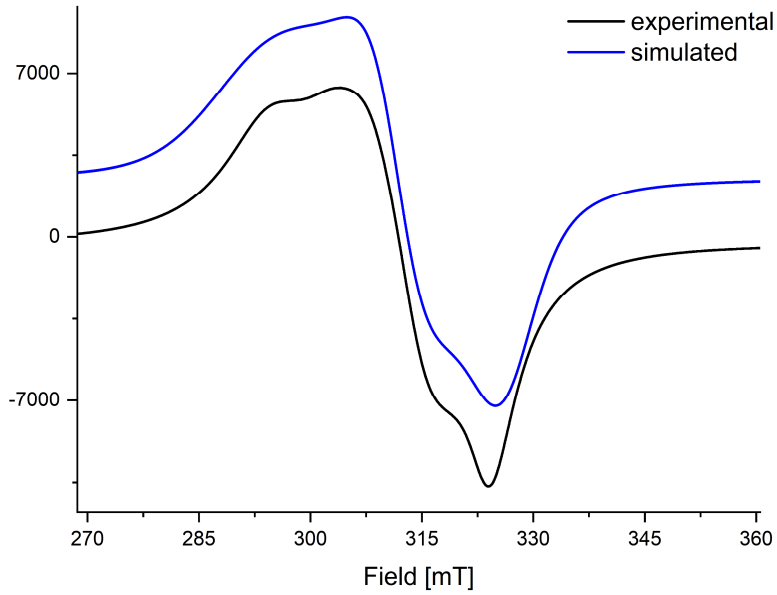


Figure S30: X-band EPR spectrum of **5** (crystalline solid at 77 K) experimental (black) and simulated (blue) g_x = 2.29632, g_y = 2.16718, g_z = 2.07149, g_{iso} = 2.17833.

The simulation has been performed using the EasySpin program.[23]

```
Sys.S = 1/2;
Sys.g = [ 2.16718 2.29632 2.07149];
Sys.lwpp = [ 4.3 4.3 ];
Sys.HStrain = [ 80 469 99  ];
Exp.mwFreq = 9.440920;
Exp.Range = [264.0235 364.8285];
Exp.nPoints = 4096;
Exp.Temperature = 77;
Exp.ModAmp = 0.2;
```

6.4.4 Details on single crystal X-ray structure analysis

The X-ray diffraction experiments were performed on either an Gemini Ultra diffractometer (Oxford diffraction) with an AtlasS2 detector Mo radiation (λ = 0.71073 Å) (**5**), a GV 50 diffractometer (Rigaku, formerly Agilent Technologies) with TitanS2 detector from applying applying Cu-K*α* radiation (λ = 1.54178 Å) (**4**) or Cu-K*β* radiation (λ = 1.39222 Å) (**3, 7**). All measurements were performed at 123 K. For the compounds (**3**, **4**, **5**, **7**) a numerical absorption correction based on gaussian integration over a multifaceted crystal model and an empirical absorption correction using spherical harmonics as implemented in SCALE3 ABSPACK was applied. All structures were solved by direct methods with ShelXT[24] and Olex2[25] and refined by full-matrix least-squares method against F^2 in anisotropic approximation using ShelXL[24]. Hydrogen atoms were refined in calculated positions using riding on pivot atom model.

6.4.4.1 [(Cp*Fe)(Cp’’’Co)(μ,η^5:η^4-As$_5$)] (3)

Compound **3** crystallizes from a concentrated solution in CH_2Cl_2 layered with acetonitrile at -30 °C in the triclinic space group $P\bar{1}$ as dark green blocks. The asymmetric unit contains five molecules **3** while four of them are heavily disordered (in one case even four times). Bond lengths and distances are given for the one non-disordered molecule. The structure in solid state is depicted in Figure S31 and S32.

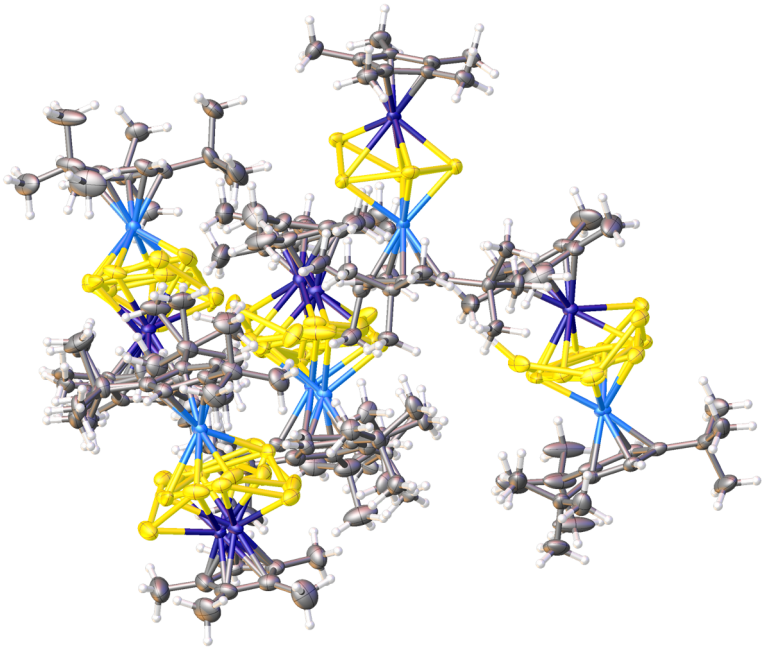


Figure S31: Molecular structure of **3** in solid state. Thermal ellipsoids are drawn with 50 % probability level.

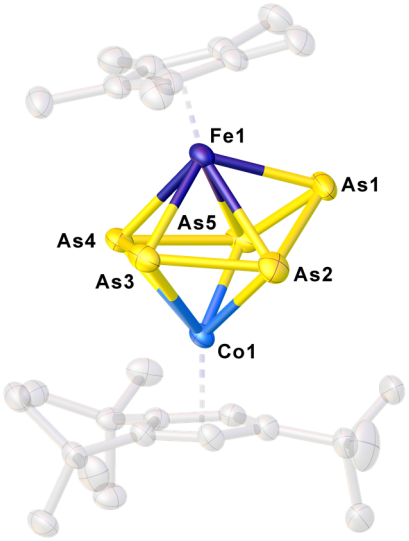


Figure S32: Molecular structure of one independent molecule **3** in solid state. Thermal ellipsoids are drawn with 50 % probability level. Selected bond lengths [Å] and angles [°]: Co1-Fe1 3.4241(5), As1-As2 2.3716(6), As2-As3 2.4383(6), As3-As4 2.3401(5), As4-As5 2.4627(5), As1-As5 2.3682(5), Co1-As1 3.6236(5), Co1-As2 2.4259(5), Co1-As3 2.4694(5), Co1-As4 2.4421(6), Co1-As5 2.4383(6), Fe1-As1 2.4095(6), Fe1-As2 2.7108(6), Fe1-As3 2.5026(5), Fe1-As4 2.4824(5), Fe1-As5 2.6514(5), As5-As1-As2-As3 130.722, Cp*Fe-Cp'''Co 164.996.

6.4.4.2 [(Cp*Fe)(Cp'''Co)(μ,η^3:η^3-As$_3$)] (4)

Compound **4** crystallizes from a concentrated solution in CH_2Cl_2 layered with acetonitrile at -30 °C in the monoclinic space group *I2$_1$/a* as dark green blocks. The asymmetric unit contains one molecule **4**. Two ^{t}Bu groups of the Cp''' ligand are disordered over two positions. The structure in solid state is depicted in Figure S33 and S34.

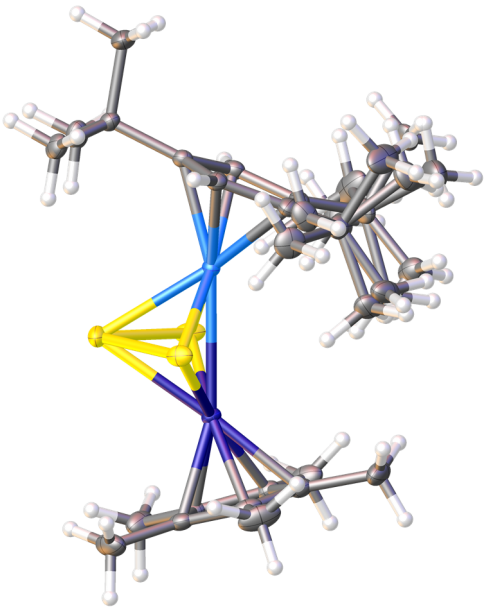


Figure S33: Molecular structure of **4** in solid state. Thermal ellipsoids are drawn with 50 % probability level.

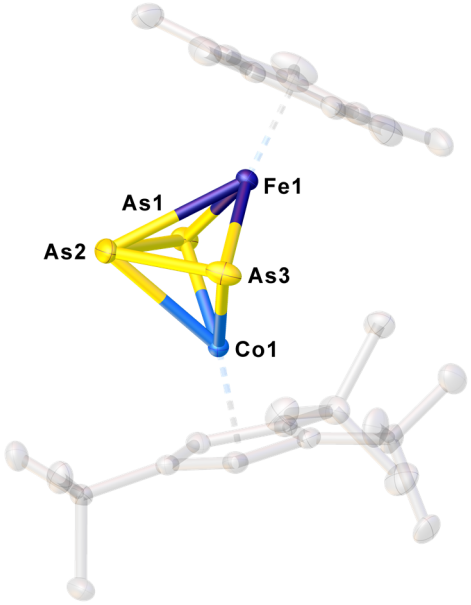


Figure S34: Molecular structure of **4** in solid state. Thermal ellipsoids are drawn with 50 % probability level. Depicted is the part of highest occupation. Selected bond lengths [Å] and angles [°]: As1-As2 2.3933(3), As2-As3 2.3879(3), As1-As3 3.5123(3), Fe1-Co1 2.7744(4), Fe1-As1 2.2632(3), Fe1-As2 2.5757(3), Fe1-As3 2.2652(3), Co1-As1 2.3131(3), Co1-As2 2.4739(3), Co1-As3 2.3251(3), Cp*Fe-Cp'''Co 141.827.

6.4.4.3 $[(Cp^*Fe)_2(Cp'''Co)_2(\mu_4,\eta^4{:}\eta^4{:}\eta^3\text{-}As_{11})]$ (5)

Compound **5** crystallizes from a concentrated solution in CH_2Cl_2 layered with acetonitrile at -30 °C in the monoclinic space group *P2₁/c* as dark brown blocks. The asymmetric unit contains one molecule **5** and 0.85 molecules CH_2Cl_2. One Cp* and one Cp''' ligand are disordered over two positions, the CH_2Cl_2 molecule is disordered over four positions The structure in solid state is depicted in Figure SX and SX.

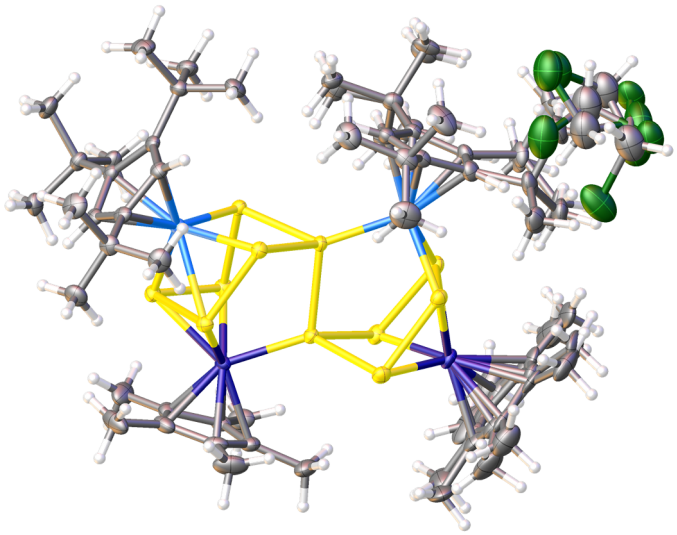


Figure S35: Molecular structure of **5** in solid state. Thermal ellipsoids are drawn with 50 % probability level.

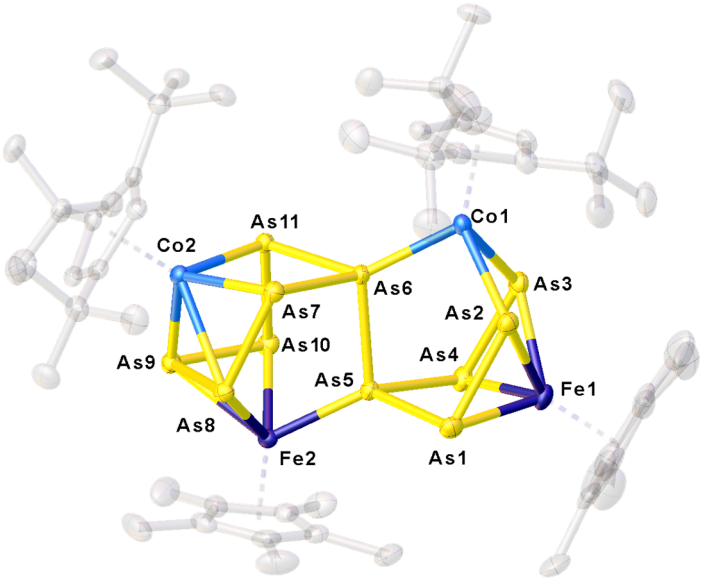


Figure S36: Molecular structure of **5** in solid state. Thermal ellipsoids are drawn with 50 % probability level. Depicted is the part of highest occupation. Solvent molecules are omitted for clarity. Selected bond lengths [Å] and angles [°]: As1-As2 2.3812(5), As2-As3 2.7746(5), As3-As4 2.3915(5). As4-As5 2.4316(4), As1-As5 2.4404(5). As5-As6 2.4123(4), As6-As7 2.4208(8), As7-As8 2.3843(4), As8-As9 2.5816(5), As9-As10 2.3812(5), As10-As11 2.4563(4), As6-As11 2.4628(4), Fe1-As1 2.4198(6), Fe1-As2 2.4539(6). Fe1-As3 2.4445(6), Fe1-As4 2.4231(6), Fe2-As5 2.2952(5), Fe2-As8 2.3842(5), Fe2-As9 2.4620(5), Fe2-As10 2.4648(5), Co1-As2 2.35802(5), Co1-As3 2.3646(5), Co1-As6 2.2793(5), Co2-As7 2.4126(5), Co2-As8 2.5740(5), Co2-As9 2.4053(5), Co2-As11 2.4175(5).

6.4.4.4 $[(Cp^*Fe)_2(Cp'''Co)(\mu_3,\eta^2:\eta^2\text{-}As_3)_2]$ (7)

Compound **7** crystallizes from a concentrated solution in toluene layered with acetonitrile at room temperature in the monoclinic space group *Cc* as dark brown blocks. The asymmetric unit contains one molecule **7**. The Cp'''Co fragment disordered over two positions. The structure in solid state is depicted in Figure SX and SX.

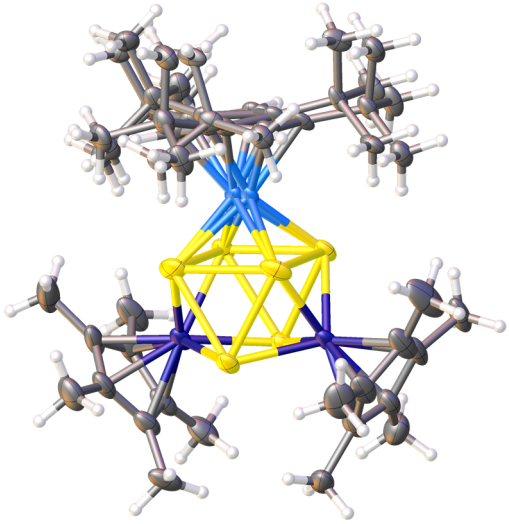


Figure S37: Molecular structure of **7** in solid state. Thermal ellipsoids are drawn with 50 % probability level.

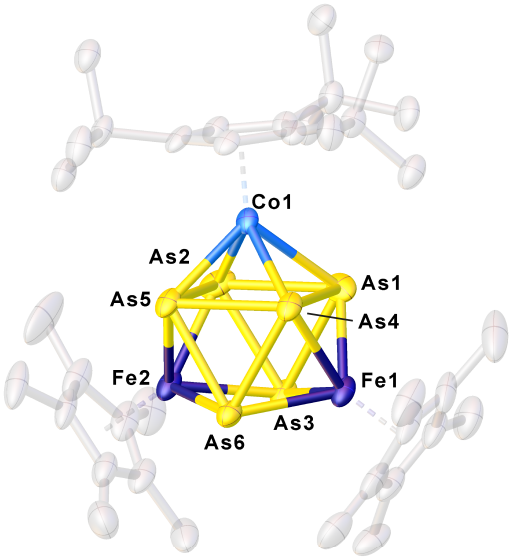


Figure S38: Molecular structure of **7** in solid state. Thermal ellipsoids are drawn with 50 % probability level. Depicted is the part of **7** with the highest occupation (70 %). Selected bond lengths [Å] and angles [°]: As1-As2 2.6224(15), As2-As3 2.5446(13), As1-As3 2.5285(13), As1-As4 2.7570(12), As2-As5 2.7544(13), As3-As6 2.9347(12), As4-As5 2.5853(11), As5-As6 2.5270(12), As4-As6 2.5334(12).

6.4.4.5 Crystallographic information

Table S4: Crystallographic data for all compounds

	3	**4**	**5**	**7**
Formula	$C_{135}H_{220}As_{25}Co_5Fe_5$	$C_{27}H_{44}As_3CoFe$	$C_{54.85}H_{89.7}As_{11}Cl_{1.7}Co_2Fe_2$	$C_{37}H_{59}As_6CoFe_2$
$D_{calc.}$/ g cm^{-3}	1.845	1.644	1.862	1.877
μ/mm^{-1}	10.647	12.547	6.455	11.146
Formula Weight	4290.00	708.193	1863.11	1123.99
Colour	clear dark green	clear dark green	clear dark brown	clear dark brown
Shape	block	block	block	block
Size/mm^3	0.14×0.13×0.08	0.35×0.21×0.13	0.62×0.43×0.32	0.31×0.23×0.14
T/K	122.95(16)	296.78(10)	123(1)	123(1)
Crystal System	triclinic	monoclinic	monoclinic	monoclinic
Flack Parameter				0.035(5)
Hooft Parameter				0.051(4)
Space Group	*P*-1	*I*2/*a*	$P2_1/c$	*Cc*
a/Å	12.02431(7)	17.54679(9)	12.8284(2)	19.6842(4)
b/Å	22.74711(14)	9.14890(5)	14.5804(2)	15.7329(2)
c/Å	29.66301(15)	35.63932(17)	35.7022(6)	12.8445(2)
α/°	72.6118(5)	90	90	90
β/°	86.0155(5)	90.5219(4)	95.551(2)	91.174(2)
γ/°	89.9742(5)	90	90	90
V/Å^3	7722.14(8)	5721.08(5)	6646.54(18)	3976.97(11)
Z	2	8	4	4
Z'	1	1	1	1
Wavelength/Å	1.39222	1.54184	0.71073	1.39222
Radiation type	Cu K_β	Cu K_α	Mo K_α	Cu K_β
θ_{min}/°	3.520	4.96	3.364	3.247
θ_{max}/°	73.857	67.07	32.251	74.066
Measured Refl.	129880	56873	38659	23082
Independent Refl.	41988	5105	20993	7704
Reflections with I > 2(I)	36616	5088	16754	7476
R_{int}	0.0458	0.0430	0.0232	0.0350
Parameters	2427	364	921	606
Restraints	471	0	552	128
Largest Peak	1.322	0.4739	0.875	1.441
Deepest Hole	-0.962	-0.4008	-0.700	-2.008
GooF	1.072	1.0695	1.085	1.050
wR_2 (all data)	0.1087	0.0461	0.0801	0.1117
wR_2	0.1040	0.0460	0.0744	0.1104
R_1 (all data)	0.0510	0.0195	0.0561	0.0416
R_1	0.0435	0.0194	0.0386	0.0405

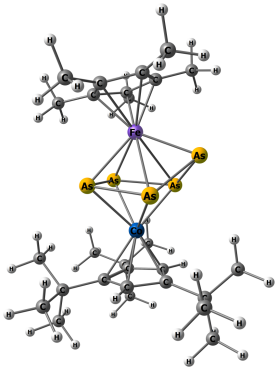
6.4.5 Computational Details

Gaussian 09 program[26] was used throughout. Density functional theory (DFT) in form of or BP86[27] (Becke's exchange and Perdew 86 correlation functional) with def2-TZVP all electron basis set was employed. The Natural Bond Orbital (NBO) analysis has been performed with the NBO6 program.[28] The long range dispersion correction GD3BJ was applied.[29] The figures for the supporting information concerning the DFT calculations were created with Chemcraft.[30]

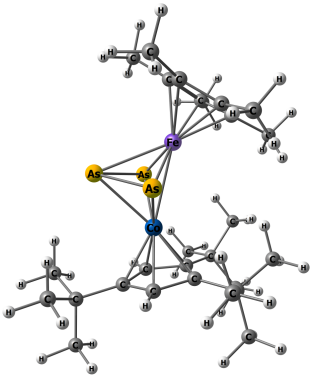
Table S5: Total energies for all optimized geometries (BP86/def2-TZVP level of theory).

	total energy [Ha]
3 [(Cp*Fe)(Cp'''Co)(μ,η^5:η^4-As_5]	-14884.0016082
4 [(Cp*Fe)(Cp'''Co) (μ,η^3:η^3-As_3)]	-10411.5930462
5 [$(Cp^*Fe)_2(Cp'''Co)_2(\mu_4,\eta^4:\eta^4:\eta^3$-$As_{11})$]	-32004.3018793
7 [$(Cp^*Fe)_2(Cp'''Co)(\mu_3,\eta^2:\eta^2$-$As_3)_2$]	-18774.5846073
1b [$Cp^*Fe(\eta^5$-$As_5)$]	-12835.2862475
6 [$(Cp'''Co)_2(As_2)_2$]	-13042.1875737

Table S6: Optimized geometry of **3** (left) and **4** (right). XYZ coordinates in angstroms. BP86/def2-TZVP level of theory.



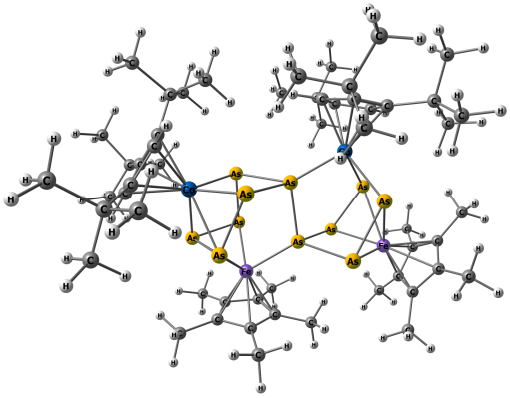
As	0.218192000	-1.641109000	0.759697000	H	-4.177513000	4.760600000	-0.150543000
As	0.373068000	0.636110000	1.757512000	H	-4.459330000	3.368776000	0.929006000
As	0.349522000	-1.072025000	-1.525790000	C	-2.651194000	-0.961403000	3.210185000
As	0.536605000	1.388250000	-1.333877000	H	-1.573961000	-1.131958000	3.072201000
As	1.817853000	2.120174000	0.554779000	H	-2.992481000	-1.594453000	4.042858000
Co	-1.170987000	0.200117000	-0.068432000	H	-2.794259000	0.082748000	3.516120000
Fe	2.152227000	-0.227620000	-0.002322000	C	-4.943729000	-1.042625000	2.211430000
C	-3.059299000	-0.577739000	-0.692111000	H	-5.098910000	0.022544000	2.437307000
C	-2.791698000	0.733096000	-1.229303000	H	-5.291527000	-1.632014000	3.074426000
H	-2.710234000	0.962466000	-2.285434000	H	-5.570644000	-1.296886000	1.345873000
C	-3.036203000	-0.436690000	0.759963000	C	-2.642229000	3.207073000	-0.296512000
C	3.312547000	-1.941418000	-0.325169000	C	-2.607754000	-3.006321000	-1.498014000
C	-2.768702000	0.955715000	1.028117000	H	-1.584949000	-2.815325000	-1.850099000
H	-2.704108000	1.388464000	2.020612000	H	-3.041359000	-3.798483000	-2.128399000
C	-2.645600000	1.695675000	-0.180679000	H	-2.535114000	-3.386169000	-0.478220000
C	-3.446527000	-1.331823000	1.938335000	C	4.681373000	1.462850000	-1.187578000
C	3.642891000	-0.918504000	-1.282625000	H	4.114801000	1.748666000	-2.084982000
C	3.545252000	-1.410678000	0.992985000	H	5.728434000	1.293822000	-1.492248000
C	4.118073000	0.227167000	-0.560124000	H	4.660317000	2.313980000	-0.495212000
C	-3.462917000	-1.731481000	-1.623114000	C	3.379894000	-2.143968000	2.284643000
C	4.061968000	-0.079335000	0.848292000	H	3.083324000	-1.463640000	3.094631000
C	-3.254183000	-2.841303000	1.743936000	H	4.324045000	-2.631800000	2.581124000
H	-3.894175000	-3.252331000	0.955600000	H	2.608678000	-2.922289000	2.208009000
H	-3.516090000	-3.357691000	2.679876000	C	-3.341152000	-1.286653000	-3.096715000
H	-2.205309000	-3.075748000	1.511691000	H	-4.021106000	-0.456219000	-3.335848000
C	-4.952657000	-2.057519000	-1.371865000	H	-3.603238000	-2.132137000	-3.749495000
H	-5.121909000	-2.476411000	-0.372759000	H	-2.311923000	-0.982688000	-3.339046000
H	-5.305164000	-2.794591000	-2.110024000	C	4.564079000	0.769691000	1.972786000
H	-5.569069000	-1.151005000	-1.467505000	H	4.604008000	1.829978000	1.693884000

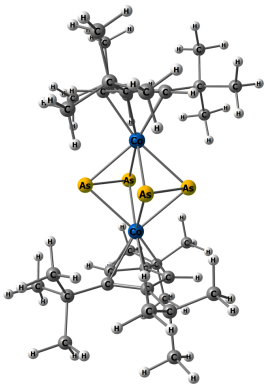


As	-0.547065000	-0.619783000	-1.777318000	H	-5.309904000	-1.558841000	-1.487888000
As	-0.530104000	-0.649245000	1.775850000	H	-3.946586000	-2.515921000	-0.860712000
As	-0.563681000	-2.284831000	-0.022959000	C	-2.541498000	3.163660000	-0.184693000
Fe	-1.814759000	-0.038632000	0.016625000	H	-1.866358000	3.465180000	0.627295000
Co	0.907055000	-0.279392000	0.002171000	H	-3.428294000	3.819738000	-0.135162000
C	-2.947140000	1.731302000	-0.065660000	H	-2.035164000	3.363102000	-1.136978000
C	-3.184117000	1.027861000	1.166670000	C	-3.322630000	1.245756000	-2.602857000
C	-3.304940000	0.867873000	-1.155371000	H	-2.539231000	1.978998000	-2.839340000
C	2.604438000	-0.194605000	-1.159136000	H	-4.292904000	1.695382000	-2.874847000
H	2.669038000	-0.535271000	-2.185179000	H	-3.167139000	0.372438000	-3.251403000
C	2.631475000	-0.188511000	1.121872000	C	4.904638000	-2.346036000	-0.024037000
H	2.723684000	-0.519554000	2.149686000	H	5.263100000	-1.805387000	-0.912564000
C	2.840926000	-1.019626000	-0.018734000	H	5.348137000	-3.353633000	-0.030040000
C	-3.729158000	-0.392326000	-0.602384000	H	5.266584000	-1.814472000	0.868526000
C	2.243689000	1.139294000	0.717621000	C	0.585823000	2.811098000	-1.824632000
C	3.359022000	-2.442069000	-0.021577000	H	-0.122690000	2.051462000	-2.182786000
C	-3.666584000	-0.290511000	0.839027000	H	0.543198000	3.677657000	-2.504010000
C	-3.050730000	1.607040000	2.540170000	H	0.244778000	3.126312000	-0.837524000
H	-2.833611000	0.829462000	3.286008000	C	2.276172000	1.676408000	-3.217462000
H	-3.982922000	2.112634000	2.845668000	H	3.309902000	1.319499000	-3.334617000
H	-2.240126000	2.347827000	2.587774000	H	2.108606000	2.474294000	-3.955782000
C	2.222944000	1.135468000	-0.754590000	H	1.586243000	0.852955000	-3.455014000
C	2.902816000	-3.203878000	1.233151000	C	1.817010000	1.670267000	3.160110000
H	3.253652000	-2.715669000	2.154052000	H	0.850966000	1.144454000	3.159541000
H	3.311098000	-4.225661000	1.220285000	H	1.757596000	2.495276000	3.885315000
H	1.806204000	-3.267168000	1.275847000	H	2.586950000	0.974936000	3.520307000
C	2.898786000	-3.199655000	-1.277373000	C	1.066204000	3.301169000	1.476564000
H	1.801685000	-3.255039000	-1.321091000	H	1.296938000	3.919731000	0.602465000
H	3.299607000	-4.224361000	-1.264977000	H	0.967265000	3.976490000	2.339736000

C	3.600180000	-1.048598000	-2.770964000	H	5.579593000	0.452354000	2.265859000	H	3.254364000	-2.713139000	-2.197385000	H	0.100311000	2.802242000	1.310679000
H	2.858861000	-1.794153000	-3.088876000	H	3.918234000	0.682516000	2.857798000	C	2.146254000	2.249837000	1.768214000	C	3.539638000	2.916811000	1.881163000
H	4.582788000	-1.360470000	-3.163897000	C	-1.740513000	3.839505000	0.774843000	C	-4.102813000	-1.344672000	1.806271000	H	4.295411000	2.172473000	2.173146000
H	3.333822000	-0.094216000	-3.245703000	H	-2.059622000	3.557466000	1.788870000	H	-3.896546000	-2.352298000	1.419497000	H	3.517310000	3.702696000	2.652152000
C	2.880950000	-3.333687000	-0.647452000	H	-1.780227000	4.937128000	0.704699000	H	-5.186693000	-1.275404000	2.002422000	H	3.861846000	3.370225000	0.937071000
H	2.271204000	-3.766324000	0.157949000	H	-0.698170000	3.516274000	0.648680000	H	-3.579327000	-1.248250000	2.767358000	C	3.031459000	3.379167000	-1.580178000
H	3.760321000	-3.983315000	-0.791455000	C	-2.195873000	3.672045000	-1.690240000	C	2.014542000	2.238671000	-1.804343000	H	2.810153000	3.962054000	-0.678459000
H	2.280509000	-3.370817000	-1.567610000	H	-1.161085000	3.366467000	-1.903646000	C	-4.212602000	-1.580111000	-1.371381000	H	3.004562000	4.071306000	-2.435680000
C	-4.104401000	3.664743000	-0.069174000	H	-2.246887000	4.769464000	-1.751872000	H	-3.766226000	-1.614737000	-2.374473000	H	4.054116000	2.983236000	-1.492285000
H	-4.776770000	3.217204000	-0.816554000	H	-2.843437000	3.262089000	-2.479479000								

Table S7: Optimized geometry of **5** (left) and **6** (right). XYZ coordinates in angstroms. BP86/def2-TZVP level of theory.





As	0.464584000	-1.578908000	-0.157848000	H	-7.054593000	1.310497000	3.397060000	As	1.619009000	-0.369156000	0.795032000	As	-1.619009000	0.369156000	-0.795032000
As	0.176207000	0.826944000	-0.211085000	C	1.854099000	4.406438000	-4.042891000	As	-0.049965000	1.062148000	1.493360000	As	0.049965000	-1.062148000	-1.493360000
As	-1.339882000	0.856664000	1.694588000	H	1.881935000	5.431081000	-3.642722000	Co	0.681485000	1.210684000	-0.816153000	Co	-0.681485000	-1.210684000	0.816153000
As	-1.949460000	0.889200000	-1.494213000	H	1.394967000	4.437432000	-5.042925000	C	1.903719000	1.604581000	-2.473461000	C	-1.903719000	-1.604581000	2.473461000
As	-2.236553000	-1.382221000	1.549188000	H	2.890135000	4.056582000	-4.159325000	C	2.491877000	2.115909000	-1.278504000	C	-2.491877000	-2.115909000	1.278504000
As	-3.532598000	-1.557738000	-0.714064000	C	0.006186000	4.524077000	2.036590000	C	1.633431000	3.086117000	-0.655939000	C	-1.633431000	-3.086117000	0.655939000
As	-1.725241000	-1.443722000	-2.296998000	H	-0.323359000	5.304600000	1.335868000	C	0.425687000	3.161497000	-1.485402000	C	-0.425687000	-3.161497000	1.485402000
As	3.073462000	0.603096000	1.323771000	H	-0.298619000	4.826361000	3.049554000	C	0.637092000	2.250610000	-2.587431000	C	-0.637092000	-2.250610000	2.587431000
As	2.386287000	-1.832121000	-1.654715000	H	-0.521704000	3.588226000	1.800934000	C	2.601267000	0.733050000	-3.497924000	C	-2.601267000	-0.733050000	3.497924000
As	2.018123000	-1.529047000	1.740459000	C	5.756004000	-1.888939000	-0.667703000	C	3.606215000	1.648818000	-4.239064000	C	-3.606215000	-1.648818000	4.239064000
As	3.377183000	0.351797000	-1.426169000	C	-0.184531000	-4.672453000	-2.538968000	C	3.373302000	-0.414115000	-2.823926000	C	-3.373302000	0.414115000	2.823926000
Co	-3.389279000	0.574904000	0.410449000	H	-0.740110000	-4.184851000	-3.352064000	C	1.604102000	0.160488000	-4.516411000	C	-1.604102000	-0.160488000	4.516411000
Co	2.106111000	1.988707000	-0.314054000	H	-0.048084000	-5.733306000	-2.810134000	C	2.199337000	3.925439000	0.498424000	C	-2.199337000	-3.925439000	-0.498424000
Fe	-1.466670000	-2.770114000	-0.234121000	H	0.809153000	-4.203204000	-2.495257000	C	3.188750000	3.085248000	1.337505000	C	-3.188750000	-3.085248000	-1.337505000
Fe	3.873651000	-1.392460000	0.197440000	C	5.358706000	-1.878065000	1.629287000	C	2.993483000	5.087424000	-0.149294000	C	-2.993483000	-5.087424000	0.149294000
C	-5.277594000	1.253596000	-0.324948000	C	-3.351042000	-4.622099000	-2.120797000	C	1.176620000	4.509121000	1.482066000	C	-1.176620000	-4.509121000	-1.482066000
C	-4.194171000	2.174538000	1.509271000	H	-4.314162000	-4.192017000	-1.813600000	C	-0.803792000	4.079735000	-1.454721000	C	0.803792000	-4.079735000	1.454721000
H	-3.625337000	2.853074000	2.135979000	H	-3.520340000	-5.680207000	-2.380772000	C	-1.667821000	3.951939000	-0.184573000	C	1.667821000	-3.951939000	0.184573000
C	-4.476120000	2.392356000	0.114431000	H	-3.031499000	-4.098858000	-3.034014000	C	-0.340753000	5.541835000	-1.646529000	C	0.340753000	-5.541835000	1.646529000
C	-5.437969000	0.408573000	0.833674000	C	1.163782000	-4.732109000	0.342447000	C	-1.739281000	3.745595000	-2.637140000	C	1.739281000	-3.745595000	2.637140000
H	-5.969667000	-0.535363000	0.837136000	H	1.803184000	-4.263974000	-0.418824000	H	3.461018000	1.817071000	-0.894242000	H	-3.461018000	-1.817071000	0.894242000
C	-0.902678000	-4.540004000	-1.234709000	H	1.389035000	-5.812300000	0.357660000	H	-0.084427000	2.050813000	-3.370847000	H	0.084427000	-2.050813000	3.370847000
C	-0.287302000	-4.525418000	0.063485000	H	1.451634000	-4.315398000	1.315657000	H	3.088456000	2.493479000	-4.717369000	H	-3.088456000	-2.493479000	4.717369000
C	-4.812874000	0.975254000	1.973116000	C	-0.405006000	3.970972000	-3.056850000	H	4.135484000	1.080300000	-5.019390000	H	-4.135484000	-1.080300000	5.019390000
C	-2.325405000	-4.504015000	-1.039697000	H	-1.025502000	3.309742000	-2.436005000	H	4.354199000	2.057789000	-3.543734000	H	-4.354199000	-2.057789000	3.543734000
C	-6.085750000	0.984333000	-1.603829000	H	-0.844347000	3.979711000	-4.065597000	H	4.096919000	-0.038585000	-2.086247000	H	-4.096919000	0.038585000	2.086247000
C	1.979519000	3.916207000	0.596875000	H	-0.461247000	4.990799000	-2.646722000	H	3.929323000	-0.990576000	-3.578754000	H	-3.929323000	0.990576000	3.578754000
C	-5.234516000	0.832566000	-2.877306000	C	5.071780000	-3.107136000	-0.325219000	H	2.683657000	-1.092807000	-2.301928000	H	-2.683657000	1.092807000	2.301928000
H	-4.589009000	1.691555000	-3.072378000	C	1.847279000	3.273388000	3.084125000	H	0.844197000	-0.463018000	-4.022270000	H	-0.844197000	0.463018000	4.022270000
H	-5.896122000	0.699653000	-3.747585000	H	1.262318000	2.360220000	2.901578000	H	2.133700000	-0.465330000	-5.250114000	H	-2.133700000	0.465330000	5.250114000
H	-4.591844000	-0.056208000	-2.805132000	H	1.570920000	3.662593000	4.077158000	H	1.089196000	0.960687000	-5.068603000	H	-1.089196000	-0.960687000	5.068603000
C	1.025432000	3.762859000	-0.469748000	H	2.902682000	2.987943000	3.110128000	H	2.707483000	2.180174000	1.735589000	H	-2.707483000	-2.180174000	-1.735589000
H	-0.046724000	3.850566000	-0.342622000	C	4.829599000	-3.103029000	1.088457000	H	3.544400000	3.688187000	2.185922000	H	-3.544400000	-3.688187000	-2.185922000
C	1.669905000	3.522507000	-1.729866000	C	2.157516000	5.691249000	2.383345000	H	4.073749000	2.782566000	0.761935000	H	-4.073749000	-2.782566000	-0.761935000
C	-3.729103000	0.751054000	4.253478000	H	3.243646000	5.634307000	2.517402000	H	3.479933000	5.690959000	0.632992000	H	-3.479933000	-5.690959000	-0.632992000
H	-2.927573000	0.067837000	3.939573000	H	1.725026000	6.050337000	3.330113000	H	2.340742000	5.747972000	-0.735705000	H	-2.340742000	-5.747972000	0.735705000
H	-3.946285000	0.556586000	5.314962000	H	1.949177000	6.441559000	1.605708000	H	3.773826000	4.699532000	-0.820261000	H	-3.773826000	-4.699532000	0.820261000
H	-3.349417000	1.779791000	4.171029000	C	-1.090638000	-4.454381000	2.538464000	H	0.579477000	3.713103000	1.949810000	H	-0.579477000	-3.713103000	-1.949810000
C	-1.314364000	-4.449811000	1.060488000	H	-0.168367000	-3.915552000	2.800179000	H	0.498496000	5.228310000	1.010929000	H	-0.498496000	-5.228310000	-1.010929000
C	3.050210000	3.468486000	-1.425896000	H	-1.004498000	-5.484773000	2.922963000	H	1.714092000	5.041602000	2.281147000	H	-1.714092000	-5.041602000	-2.281147000
H	3.834210000	3.284513000	-2.152472000	H	-1.918863000	-3.965520000	3.069998000	H	-2.118595000	2.950522000	-0.139434000	H	2.118595000	-2.950522000	0.139434000
C	-2.580013000	-4.447237000	0.382839000	C	4.725458000	3.972848000	0.441217000	H	-2.480573000	4.694267000	-0.220730000	H	2.480573000	-4.694267000	0.220730000
C	-5.425194000	-0.934887000	3.493917000	C	1.071707000	2.047325000	-3.705140000	H	-1.107938000	4.104657000	0.739830000	H	1.107938000	-4.104657000	-0.739830000
H	-6.390728000	-1.104243000	2.994405000	H	2.096526000	1.650848000	-3.747929000	H	0.233280000	5.912870000	-0.789177000	H	-0.233280000	-5.912870000	0.789177000
H	-5.537489000	-1.236109000	4.546270000	H	0.656752000	2.050150000	-4.725327000	H	-1.216713000	6.196706000	-1.771785000	H	1.216713000	-6.196706000	1.771785000
H	-4.668412000	-1.581583000	3.025781000	H	0.477821000	1.353290000	-3.093590000	H	0.288964000	5.636415000	-2.543915000	H	-0.288964000	-5.636415000	2.543915000
C	-6.887567000	-0.328503000	-1.459955000	C	5.701131000	3.181240000	-0.454938000	H	-1.252075000	3.908896000	-3.609495000	H	1.252075000	-3.908896000	3.609495000
H	-6.224611000	-1.192726000	-1.307191000	H	5.413792000	2.122619000	-0.506959000	H	-2.622416000	4.399505000	-2.590173000	H	2.622416000	-4.399505000	2.590173000
H	-7.455795000	-0.500618000	-2.385942000	H	6.718677000	3.247535000	-0.043437000	H	-2.091559000	2.704528000	-2.585579000	H	2.091559000	-2.704528000	2.585579000
H	-7.606321000	-0.282681000	-0.628603000	H	5.735098000	3.576307000	-1.479273000								
C	-4.998170000	0.539371000	3.413553000	C	6.775660000	0.092591000	0.705228000								
C	-4.115866000	3.752463000	-0.496829000	H	6.925339000	0.605226000	-0.251499000								
C	-4.030550000	3.824653000	-2.027692000	H	7.771403000	-0.173730000	1.099600000								
H	-3.293388000	3.108232000	-2.413645000	H	6.319279000	0.805369000	1.404432000								
H	-3.698930000	4.833764000	-2.314895000	C	6.253049000	-1.522801000	-2.027903000								
H	-4.990281000	3.642769000	-2.521280000	H	5.562631000	-1.872152000	-2.809377000								
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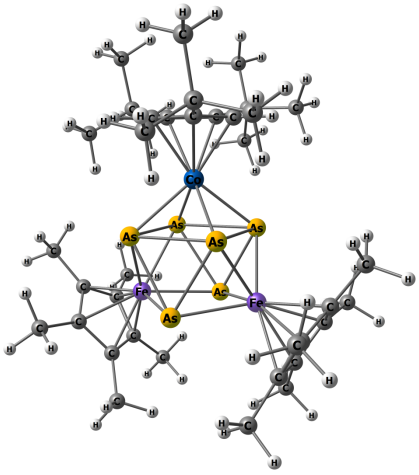
C	-2.740351000	4.194152000	0.035646000	H	6.338221000	-0.433231000	-2.139158000								
H	-2.738380000	4.351806000	1.120453000	C	5.018376000	5.478527000	0.221654000								
H	-2.438334000	5.138202000	-0.440111000	H	4.838820000	5.756805000	-0.827257000								
H	-1.988694000	3.427402000	-0.198571000	H	6.072242000	5.693344000	0.459089000								
C	-5.177661000	4.764022000	-0.000771000	H	4.387289000	6.116120000	0.852794000								
H	-6.184250000	4.494936000	-0.348857000	C	5.037548000	3.594456000	1.895621000								
H	-4.941656000	5.772164000	-0.375956000	H	4.472847000	4.190957000	2.619507000								

H	-5.198488000	4.800355000	1.098269000	H	6.107287000	3.762740000	2.092827000
C	1.045808000	3.471434000	-3.116213000	H	4.815281000	2.532566000	2.080573000
C	1.534238000	4.329456000	2.007082000	C	4.803808000	-4.239511000	-1.263152000
C	-7.131643000	2.111270000	-1.766987000	H	3.966866000	-4.863126000	-0.922338000
H	-7.747302000	2.197940000	-0.858999000	H	5.693927000	-4.887317000	-1.341249000
H	-7.798063000	1.878159000	-2.611659000	H	4.560936000	-3.880022000	-2.271932000
H	-6.676440000	3.088806000	-1.959530000	C	5.381140000	-1.490250000	3.071275000
C	-3.919201000	-4.483038000	1.044391000	H	5.353123000	-0.397241000	3.185178000
H	-3.914820000	-3.908376000	1.982012000	H	6.289668000	-1.864253000	3.573075000
H	-4.208096000	-5.519672000	1.285072000	H	4.510049000	-1.896887000	3.604739000
H	-4.696186000	-4.051651000	0.397762000	C	4.297800000	-4.241591000	1.896745000
C	5.950154000	-1.141333000	0.547086000	H	3.680740000	-3.892050000	2.735309000
C	-6.131942000	1.425869000	3.985143000	H	5.133762000	-4.827375000	2.316306000
H	-5.847193000	2.488423000	3.967680000	H	3.689750000	-4.920387000	1.287792000
H	-6.345944000	1.142931000	5.027669000				

Table S8: Optimized geometry of **7** (left) and **1b** (right). XYZ coordinates in angstroms. BP86/def2-TZVP level of theory.



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Co	1.714070000	-0.348517000	0.165292000	H	0.086583000	3.782077000	2.951762000
Fe	-1.854476000	-1.643983000	-0.252439000	H	-0.200697000	5.442011000	2.382395000
Fe	-1.217274000	2.022632000	0.186358000	H	1.046525000	4.436075000	1.613737000
C	3.231203000	-1.305623000	1.322056000	C	2.718672000	-3.570855000	2.313126000
C	3.607237000	0.550993000	-0.083780000	H	1.665345000	-3.525273000	2.001266000
C	3.235789000	-1.743313000	-0.035947000	H	2.778708000	-4.171958000	3.232675000
H	3.088696000	-2.769468000	-0.350386000	H	3.289968000	-4.095478000	1.532838000
C	3.499754000	-0.639480000	-0.928024000	C	2.541300000	-1.499829000	3.742885000
C	-0.981272000	3.920730000	1.083076000	H	2.950834000	-0.503414000	3.963270000
C	3.424689000	0.100383000	1.273544000	H	2.647266000	-2.113835000	4.650130000
H	3.460458000	0.743384000	2.146401000	H	1.470026000	-1.385556000	3.525268000
C	-2.754537000	-3.279744000	0.680741000	C	0.161114000	4.702287000	-1.137439000
C	-3.772594000	-2.359079000	0.254605000	H	1.123078000	4.660404000	-0.609814000
C	-0.929528000	4.052618000	-0.346466000	H	-0.072630000	5.764394000	-1.323944000
C	-2.009974000	-3.689590000	-0.485655000	H	0.297861000	4.214408000	-2.112997000
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C	-2.246472000	3.336047000	1.433324000	H	4.230286000	-3.053930000	-2.169205000
C	3.282901000	-2.163916000	2.570181000	H	3.795868000	-2.546636000	-3.814721000
C	-2.581696000	-3.024261000	-1.632217000	H	2.529220000	-2.668091000	-2.573887000
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C	-4.584580000	-1.396594000	-2.033532000	H	-4.548979000	2.064306000	-0.842705000
H	-5.017037000	-0.551764000	-1.479474000	H	-5.113260000	3.410358000	0.172028000
H	-5.417999000	-2.018608000	-2.402245000	H	-4.611580000	1.878132000	0.921013000
H	-4.059606000	-0.984657000	-2.906630000	C	5.326613000	-0.629295000	-2.615751000
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C	3.818721000	-0.897925000	-2.408019000	H	-2.821152000	-3.947628000	-3.563590000
C	-0.903781000	-4.698070000	-0.516195000	H	-1.139355000	-3.550527000	-3.144261000
H	-0.195519000	-4.487682000	-1.330166000	C	-2.548359000	3.585002000	-2.330159000
H	-1.296954000	-5.717876000	-0.667666000	H	-1.697028000	3.342994000	-2.983004000
H	-0.334535000	-4.695745000	0.423905000	H	-2.915645000	4.586131000	-2.613040000
C	4.084402000	1.997267000	-0.288830000	H	-3.342597000	2.859740000	-2.550920000
C	-2.561678000	-3.768082000	2.081631000	C	4.782144000	-2.292933000	2.936593000
H	-1.555485000	-4.183382000	2.227047000	H	5.351171000	-2.748421000	2.112408000
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H	-2.689578000	-2.954564000	2.811078000	H	5.219764000	-1.306341000	3.149048000
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H	-3.502471000	2.314615000	2.856633000	H	2.235195000	2.943467000	0.391290000
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C	-4.824882000	-1.755348000	1.129071000	C	5.579244000	2.025284000	0.117592000
H	-4.440247000	-1.542818000	2.136405000	H	5.712550000	1.689902000	1.156239000
H	-5.684767000	-2.438952000	1.232824000	H	5.975145000	3.049014000	0.031124000
H	-5.197918000	-0.809889000	0.711161000	H	6.179656000	1.369381000	-0.528611000
C	3.948747000	2.587271000	-1.698723000	As	-1.773908000	0.394363000	-1.496396000
H	4.552681000	2.057696000	-2.443155000	As	0.370076000	1.012701000	1.638675000
H	4.297002000	3.631155000	-1.678257000	As	-0.066227000	-1.542461000	1.304267000
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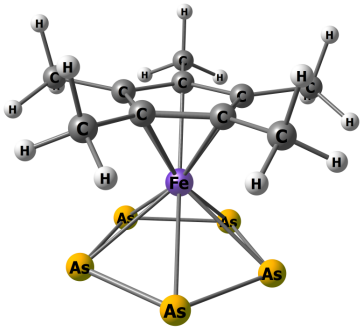

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C	-0.723479000	8.661957000	-0.157329000	C	-0.003538000	7.098965000	1.408450000
C	-2.586087000	7.329549000	1.099423000	C	1.159877000	7.689081000	0.802654000
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H	-2.906716000	6.505319000	0.440163000	H	2.883779000	6.473197000	0.420225000
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H	-2.563487000	9.694274000	-0.580860000	H	2.559587000	9.673469000	-0.604506000
H	-1.803948000	8.914863000	-1.991477000	H	1.779914000	8.901506000	-2.008270000
As	1.195548000	9.100025000	3.954434000				

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7. Functionalization of Heterobimetallic E_n Triple-Decker Complexes (E = P, As)

Martin Piesch and Manfred Scheer

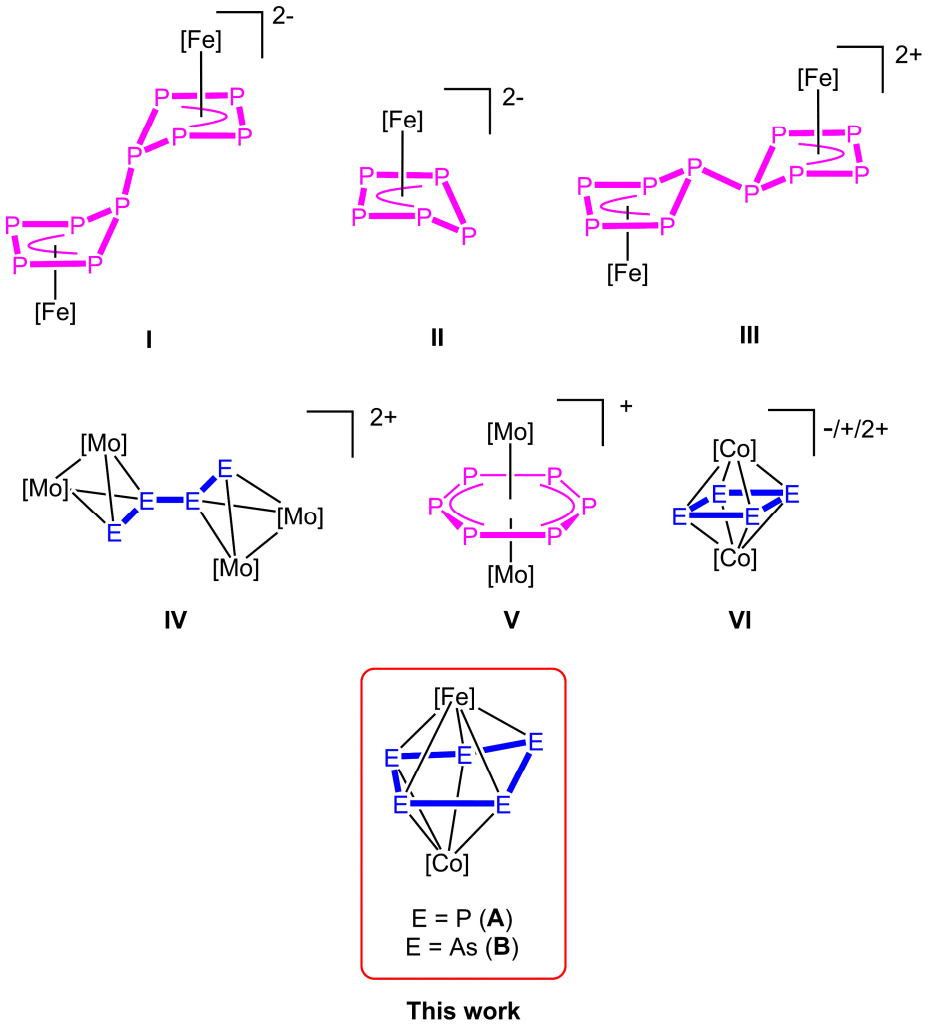
- Synthesis and characterization of all compounds was performed by Martin Piesch
- DFT calculations were performed by Martin Piesch
- X-ray measurements and calculations were done by Martin Piesch and finally checked by Michael Seidl
- Manuscript was written by Martin Piesch
- Figures were made by Martin Piesch
- The cyclic voltammograms were recorded by Martin Weber and Felix Riedelberger

7.1 Introduction

Abstract: *The redox chemistry of the heterobimetallic triple-decker complexes [(Cp*Fe)(Cp'''Co)(μ,η⁵:η⁴-E₅)] (E = P (**A**), As (**B**)) was investigated. After initial cyclic voltammetry studies the synthesis of the monocations [(Cp*Fe)(Cp'''Co)(μ,η⁵:η⁵-E₅)][FAl] (E = P (**1**), As (**2**)), the dications [(Cp*Fe)(Cp'''Co)(μ,η⁵:η⁵-E₅)][FAl] (E = P (**3**), As (**4**)), and the monoanions [K(2,2,2-crypt)][(Cp*Fe)(Cp'''Co)(μ,η⁴:η³-P₅)] (**5**), [K(2,2,2-crypt)] [(Cp*Fe)(Cp'''Co)(μ,η⁴:η⁴-As₆)] (**7**), were realized. The in situ prepared doubly reduced species of **A** and **B** were quenched with the electrophile [(Cp'''CoCl)₂] to give the cluster complexes [(Cp*Fe)(Cp'''Co)₃(μ₄,η⁴:η²:η²:η²-E₄)(μ₃-E)] (E = P (**8**), As (**9**)). **A** was also functionalized with the main group-based nucleophile KPPh₂ to give [K(2,2,2-crypt)][(Cp*Fe)(Cp'''Co)(μ,η⁴:η³-P₆Ph₂)] (**10**), which was afterwards quenched with MeI to yield [(Cp*Fe)(Cp'''Co)(μ,η⁴:η³-P₆Ph₂Me)] (**11**). All compounds have been fully characterized and their electronic structure were elucidated by DFT calculations.*

Ferrocene as one the most famous organometallic complexes plays still an important role in recent research. The redox couple $[Cp_2Fe]/[Cp_2Fe]^+$ is widely used as a reference system for electrochemical investigation methods like cyclic voltammetry.[1] According to the isolobal relationship of CH and P, the *cyclo*-P_5 ligand can formally replace the cyclopentadienyl ligand (Cp). The pentaphosphaferrocene $[Cp^*Fe(\eta^5\text{-}P_5)]$ as the first example for this was synthesized by *Scherer et al.* in 1987.[2] Its redox chemistry was investigated by spectroelectrochemical methods by *Winter* and *Geiger*[3], while the chemical oxidation and reduction has been realized by our group.[4] One oxidized and two reduced species could be isolated. Depending on the reducing agent one or two electrons can be transferred to $[Cp^*Fe(\eta^5\text{-}P_5)]$. When potassium hydride is used a single electron transfer occurs leading to the proposed intermediate $[Cp^*FeP_5]^{-\cdot}$ which dimerizes to the dinuclear complex $[(Cp^*Fe)_2(\mu,\eta^4\text{:}\eta^4\text{-}P_{10})]^{2-}$ (**I**) (Scheme 1).[5] When instead elemental potassium is used in excess the reaction leads to the dianionic species $[Cp^*Fe(\eta^4\text{-}P_5)]^{2-}$ (**II**). On the other hand, using thianthrenium hexafluoroantimonate as a strong oxidation agent the dinuclear compound $[(Cp^*Fe)_2(\mu,\eta^4\text{:}\eta^4\text{-}P_{10})]^{2+}$ (**III**) can be isolated. In these reactions the phosphorus ligand in $[Cp^*Fe(\eta^5\text{-}P_5)]$ responds to the withdrawal or addition of one electron in either in folding of the P_5 ring and in the formation of a new P-P bond.[4] A similar behavior upon oxidation with the formation of E-E bond has been reported for the complexes $[\{CpMo(CO)_2\}_2(\mu,\eta^2\text{:}\eta^2\text{-}E_2)]$ (E = P, As, Sb, Bi) (**IV**).[6] Not only sandwich complexes with an E_n ligands as an end-deck show an interesting redoxchemistry but also homometallic tripple-decker compounds were investigated. $[(Cp^RMo)_2(\mu,\eta^6\text{:}\eta^6\text{-}P_6)]$ as an example can be easily oxidized to $[(Cp^RMo)_2(\mu,\eta^6\text{:}\eta^6\text{-}P_6)]^+$ (**V**) which retains its initial triple-decker geometry in solid state.[7] The *cyclo*-P_6 ligand in **V** is only slightly distorted showing a

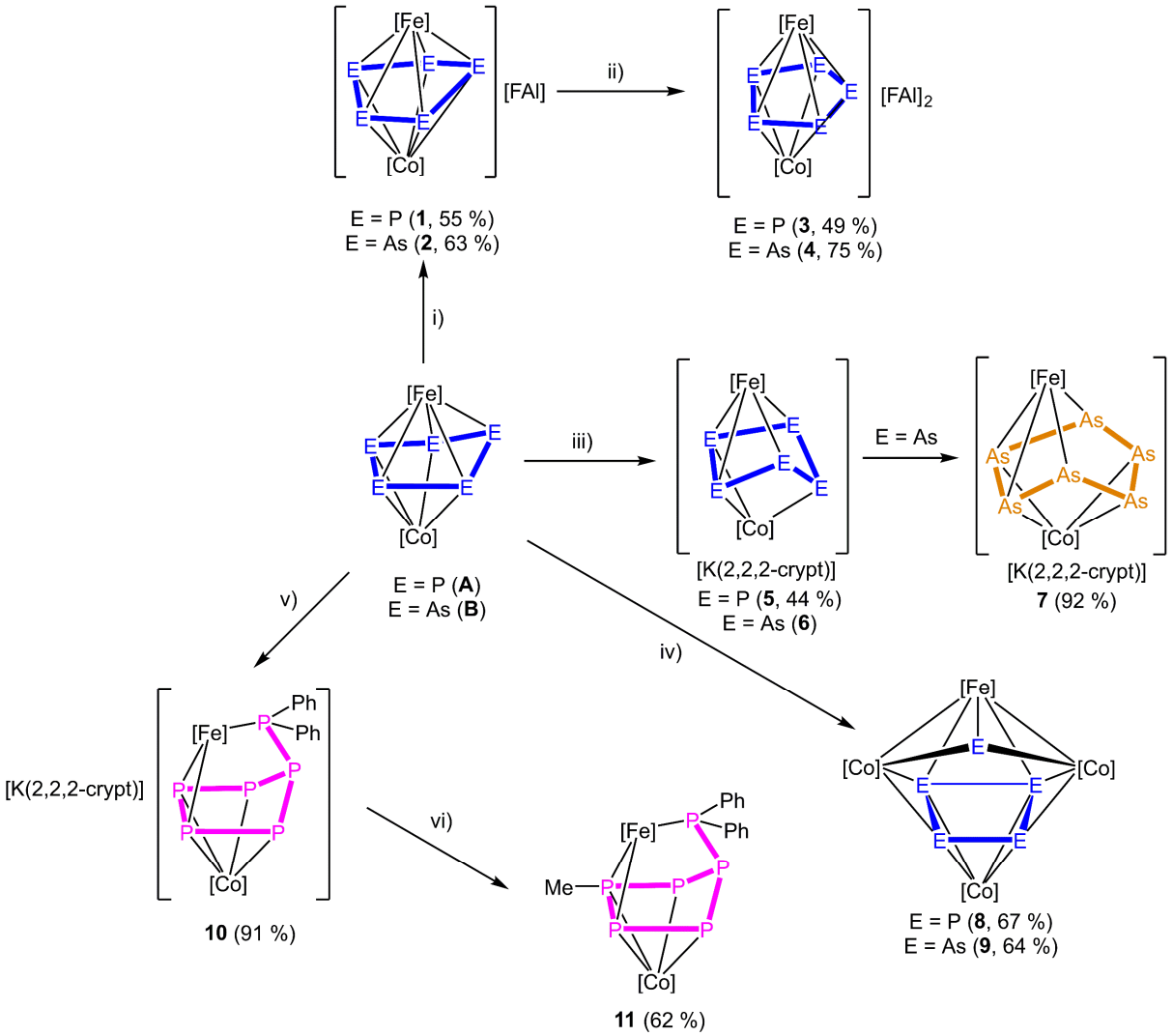
bis-allylic distortion (Scheme 1). Also, homometallic triple-decker complexes with two separated E_2 units in $[(Cp'''Co)_2(\mu,\eta^2{:}\eta^2\text{-}E_2)_2]$ (E = P, As) have been investigated yielding isostructural cationic, dicationic and anionic complexes of the type $[(Cp'''Co)_2(\mu,\eta^4{:}\eta^4\text{-}E_4)]^{+/2+/-}$ (**VI**).[8]



Scheme 1. Selected examples of oxidized and reduced polypnictogen ligand complexes and the heterometallic triple-decker complexes **A** and **B** ([Fe] = Cp*Fe, [Mo] = Cp*Mo, [Co] = Cp'''Co).

Intrigued by the diversity of the structural changes upon oxidiation and/or reduction of the E_n ligand complexes we investigated the redox properties of the heterobimetallic triple-decker complexes $[(Cp^*Fe)(Cp'''Co)(\mu,\eta^5{:}\eta^4\text{-}E_5)]$ (E = P (**A**), As (**B**)) which can be easily synthesized by the reaction of the cobalt toluene complex $[(Cp'''Co)_2(\mu,\eta^4{:}\eta^4\text{-}C_7H_8)]$ with $[Cp^*Fe(\eta^5\text{-}E_5)]$ (E = P, As)] in gram scale (cf. chapter 5 and 6). Compound **A** can also be obtained from the reaction of **I** wit $[(Cp'''CoCl)_2]$ in lower yields. The question arose whether it is possible to transfer this principle to the reaction of the reduced species of **A** and **B** with $[(Cp'''CoCl)_2]$ to build up larger cluster compounds.

7.2 Results and Discussion



Scheme 2: Overview over the reactivity of **A** and **B** with i) Ag[FAl], ii) Ag[FAl], iii) KC_8, iv) KC_8 + $[(Cp'''CoCl)_2]$, v) $KPPh_2$ and vi) MeI ([Fe] = Cp*, [Cp] = Cp'''Co).

To get a first insight in the reactivity of **A** and **B** the molecular frontier orbitals have been computed (Figure 1, BP86/def2-TZVP level of theory). They reveal, that both HOMO and LUMO are mainly located on the E_5 ligand with a rather low contribution of both metal atoms and in the case of the LUMO also the Cp* ligand. Therefore, the redox chemistry and the nucleophilic attack should be ligand centered. To get a first overview if redox processes are accessible, cyclic voltammetry measurements were performed (Figure 2). For **A** two electrochemically quasi-reversible oxidation processes (at -869 and -185 mV against $[Cp_2Fe]/[Cp_2Fe]^+$) and one reduction process (at -2289 mV against $[Cp_2Fe]/[Cp_2Fe]^+$) in thf can be detected. The cyclic voltammogram of **B** in CH_2Cl_2 reveals also two electrochemically quasi-reversible oxidation processes (at 269 and 1032 mV against $[Cp_2Fe]/[Cp_2Fe]^+$) and one reduction process (at -663 mV against $[Cp_2Fe]/[Cp_2Fe]^+$). For the chemical oxidation we choose Ag^+ as a suitable oxidant, due to the low oxidation potentials of **A** and **B**.[9]

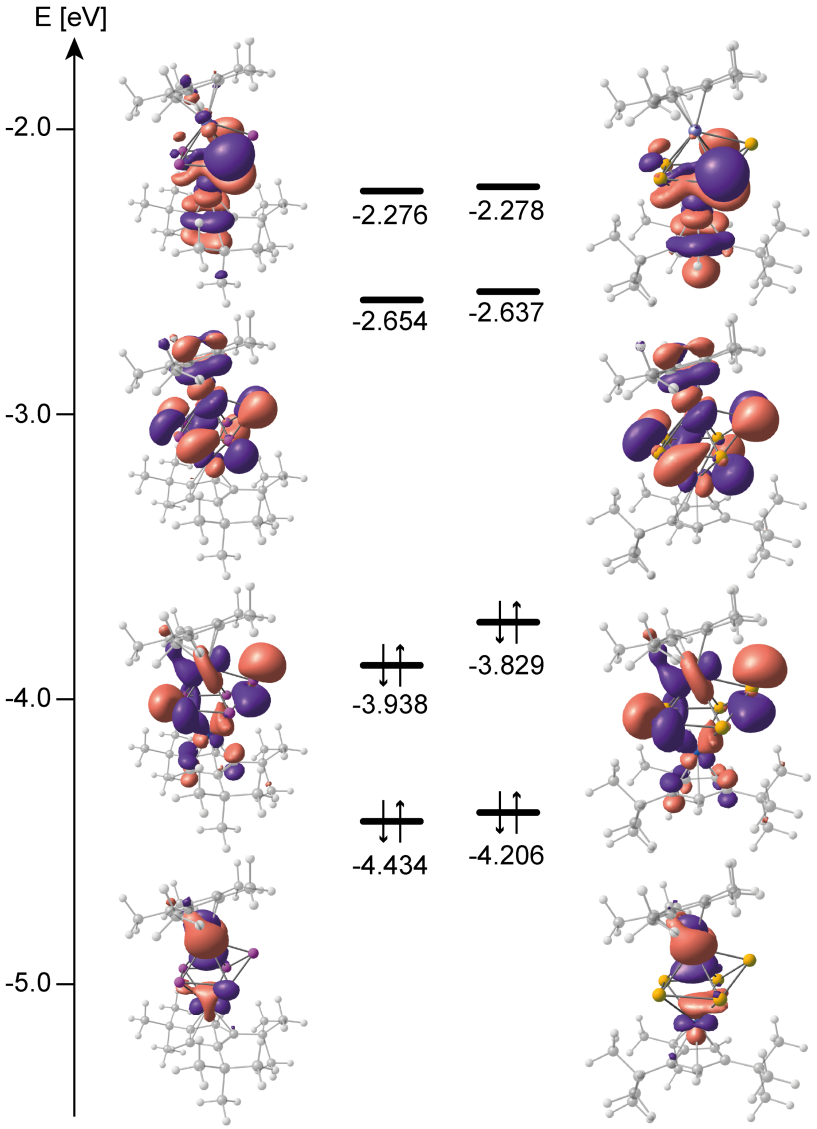


Figure 1. Frontier molecular orbitals of **A** (left) and **B** (right), BP86/def2-TZVP level of theory.

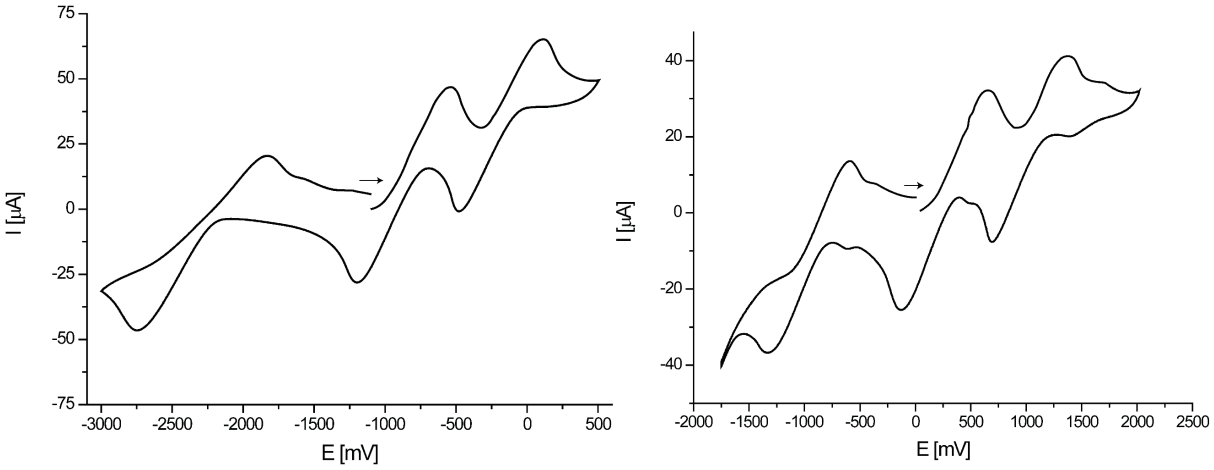
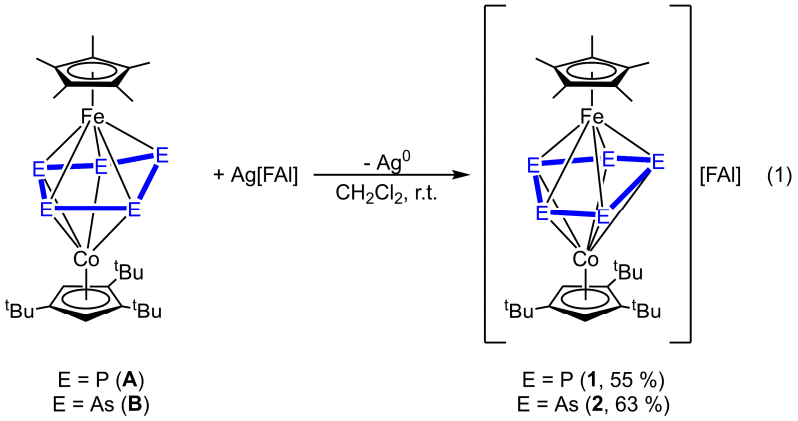


Figure 2. Cyclic voltammograms of **A** in thf (left) and **B** in CH_2Cl_2 (right) against $[Cp_2Fe]/[Cp_2Fe]^+$ (electrolyte $^nBu_4NPF_6$, scan rate: 100 mV/s. temperature: r.t.).

Both compounds can be oxidized using one equivalent of the Ag(I) salt containing the weakly coordinating anion $[FAl]^-$ ($[FAl\{OC_6F_{10}(C_6F_5)\}_3]^-$) leading to the isostructural compounds

[(Cp*Fe)(Cp'''Co)(μ,η^5:η^5-E$_5$)][FAl] (E = P (**1**), As (**2**)) isolated in crystalline yields of 55 and 63 %, respectively (Eq. 1). Compound **1** can be obtained as green, **2** as brown air- and moisture sensitive solids.



Crystals suitable for single crystal X-ray structure analysis were obtained from concentrated solutions in CH_2Cl_2 layered with hexane at -30°C.

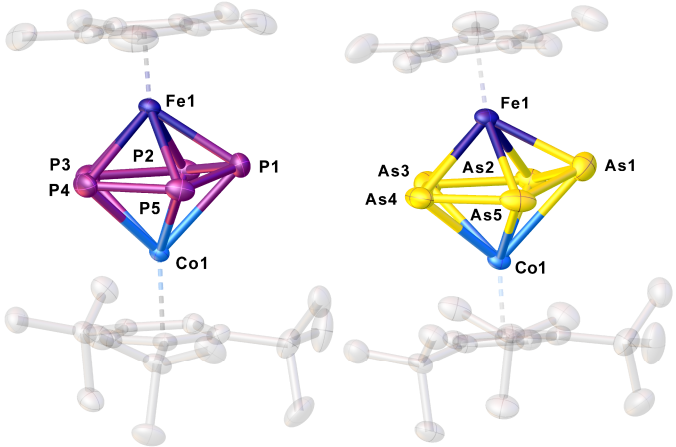


Figure 3: Molecular structure of the cations in **1** and **2** in the solid state. Thermal ellipsoids are drawn with 50 % probability level. Hydrogen atoms, anions and solvent molecules are omitted for clarity.

The structures in the solid state (Figure 3) reveal dinuclear triple-decker complexes with a folded *cyclo*-E$_5$ ligand as middle deck while the ligand planarized compared to the starting materials. The E$_5$ ligand coordinates to both iron and cobalt fragments in a η^5 fashion, while E1 is bent out of the plane (fold angle E2-E4-E5-E1) by ca. 9.4 ° (**1**) and 13.6 ° (**2**), respectively (35.0 ° in **A**, 37.9 ° in **B**). All E-E bonds are shortened compared to **A** and **B**, respectively. For **1** very similar P-P distances between 2.1214(9) to 2.1601(9) Å are present, while **A** shows three shorter distances (P1-P2 2.1459(10) Å, P3-P4 2.1283(10) Å, P1-P5 2.1498(10) Å) and two longer ones (P2-P3 2.2244(11) Å, P4-P5 2.2407(10) Å). All P-P bond lengths became almost equivalent, indicated also by Wiberg Bond Indices (WBIs) in the range of 0.97 and 1.06 for **1** in contrast to those in **A** (0.81 to 1.09). For the analog arsenic compound **2** the situation is similar. All As-As distances are in the range between 2.3224(8) and 2.3619(8) Å and shortened compared to **B**, while in **B** three shorter distances (As1-As2 2.3682(5) Å, As3-As4

2.3401(5) Å, As1-As5 2.3716(6) Å) and two longer ones (As2-As3 2.4627(5) Å, As4-As5 2.4383(6) Å). All As-As bonds became almost equivalent, indicated also by WBIs in the range of 0.91 and 1.01 for **2** in contrast to the range of 0.77 and 1.08 for **B.** The Fe1-Co1 distance is in both cases shortened compared to **A** and **B**, respectively (3.1539(5) Å (**1**), 3.3303(4) Å (**A**), 3.2188(6) Å (**2**), 3.4241(5) Å (**B**)). Compounds **1** and **2** are paramagnetic. The ^{1}H NMR spectrum of **1** in CD_2Cl_2 reveals four strongly broadened and shifted signals centered at δ = 5.66, 3.76, 3.29 and -65.22 ppm with an integral ratio of 15:9:18:2, while the signal at 5.66 ppm can be assigned to the Cp* ligand and the other three singlets correspond to the Cp''' ligand. The ^{31}P{^{1}H} NMR spectrum shows one broad singlet at δ = 275.1 ppm. The ^{1}H NMR of **2** in CD_2Cl_2 reveals three strongly broadened and shifted signals centered at δ = 3.84, 2.74 and -1.09 ppm with an integral ratio of 9:18:15, while the signals at 3.84 and 2.74 ppm can be assigned to the ^{t}Bu groups of the Cp''' ligands and the singlet at -1.09 ppm of the Cp* ligand. No signal for the C-H groups of the Cp''' ligand can be detected between +125 and -125 ppm. The Evans NMR reveals an effective magnetic moment of 2.04 μ_B for **1** and 1.90 μ_B for **2** corresponding to about one unpaired electron each. The EPR spectrum of **1** at 77 K (frozen o-$C_6H_4F_2$ solution) shows a strong rhombic resonance with hyperfine coupling to Co with *g* value of about 2 (g_x = 2.155, g_y = 2.035, g_z = 1.948, A_x = 290.125, A_Y = 55.125, A_Z = 120.125 MHz, Figure 4).

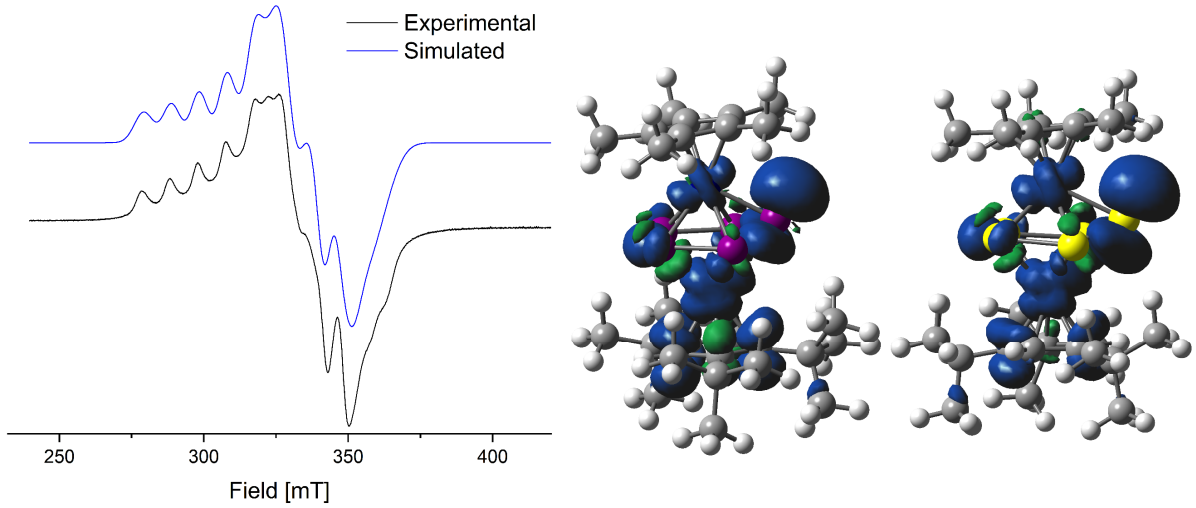
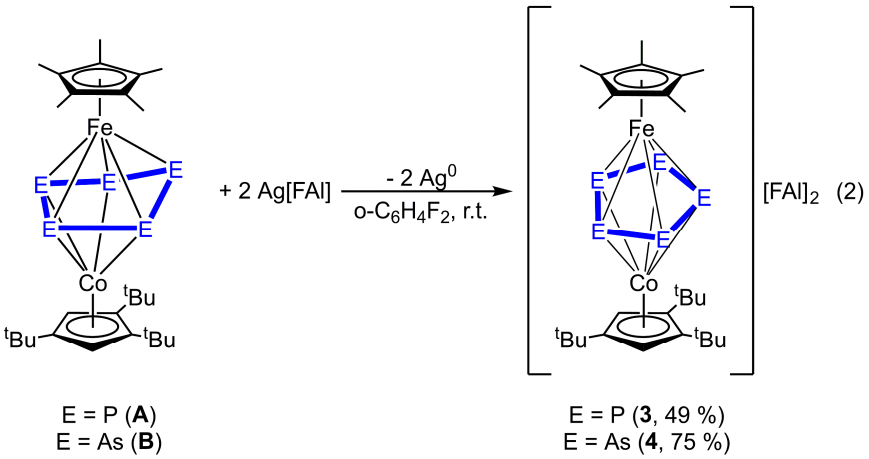


Figure 4. Experimental (black) and simulated (blue) X-band EPR spectrum of **1** in frozen o-$C_6H_4F_2$ solution (left) and the iso-surfaces of the spin density in **1** (middle) and **2** (right).

DFT calculations show that the spin density is distributed over both metal atoms, the E_5 and the Cp''' ligands (Figure 4). For **2** all EPR spectra (cf. SI) show resonances with weak rhombic character similarly to **1**. DFT calculations show that the spin density is mainly distributed over Fe, Co and As1 what is the explanation for a not well resolved hyperfine coupling to the Co atom (77 K, solid: g_x = 2.235, g_y = 1.952, g_z = 1.896, Figure 4). Using two equivalents of Ag[FAl] in the oxidation of **A** and **B**, respectively, gives the dicationic compounds

[(Cp*Fe)(Cp'''Co)(μ,η^5:η^5-E$_5$)][FAl]$_2$ (E = P (**3**), As (**4**)) in crystalline yields of 49 and 75 %, respectively (Eq. 2).



Both compounds can be obtained as air- and moisture sensitive brown solids. Crystals suitable for X-ray single crystal structure analysis were obtained from concentrated solutions in o-$C_6H_4F_2$ layered with hexane (**3**) and toluene (**4**) at -30 °C, respectively. The structures in the solid state (Figure 5) reveal dinuclear triple-decker complexes with a planar *cyclo*-E_5 ligand as middle deck.

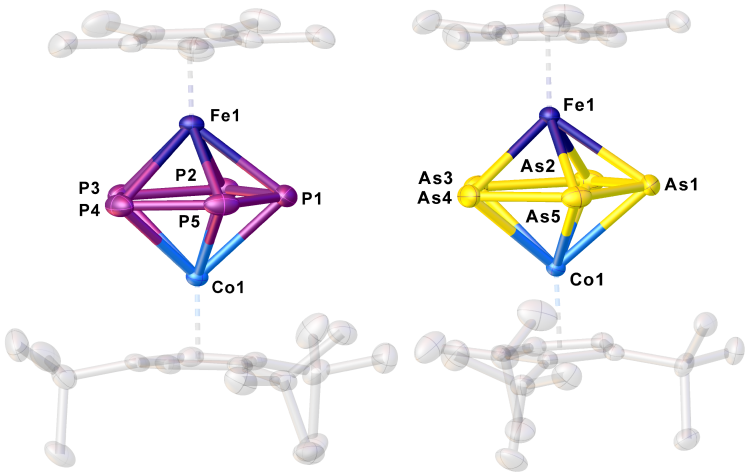
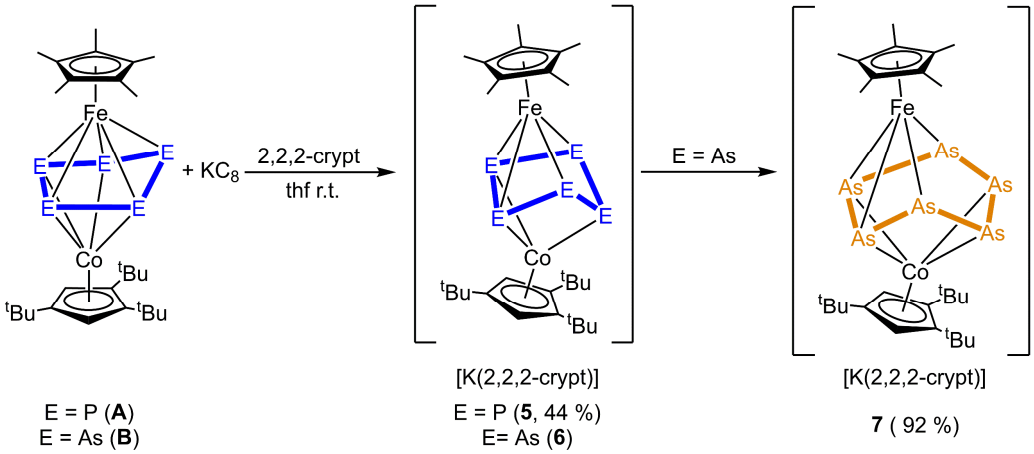


Figure 5: Molecular structure of the cations in **3** and **4** in the solid state. Thermal ellipsoids are drawn with 50 % probability level. Hydrogen atoms, anions and solvent molecules are omitted for clarity.

In compounds **3** and **4** the E_5 ligand coordinates to both iron and cobalt fragment in η^5 fashion and is completely planar while is folded slightly in the monocations **1** and **2** or strongly in **A** and **B**. For **3** all P-P distances are between 2.1425(16) and 2.1521(16) Å and are in the range between P-P single and double bonds.[10,11] They are only slightly longer than in [Cp*Fe(η^5-P$_5$)] showing distances in the range of 2.1158(15) and 2.1268(16) Å for **3**.[12] For **4** the As-As distances are in the range of 2.3390(6) and 2.3515(8) Å and also in the region between single and double bonds.[10,11] Compared to [Cp*Fe(η^5-As$_5$)] the As-As bonds are only slightly elongated (2.317(1) – 2.330(1) Å in **4**).[13] The Fe-Co distance is in both cases further shortened than for the mono cations **1** and **2** (**3**: 3.0644(10) Å, **4**: 3.0898(10) Å). The dicationic

compounds **3** and **4** are isostructural and isoelectronic to the monocationic homo- and heterobimetallic complexes $[(Cp^{R}M)(Cp^{R'}M')(\mu,\eta^5{:}\eta^5\text{-}E_5)]^+$ (M = Fe, Ru, M' = Fe, Ru, E = P, As).[14] The ^{1}H NMR spectrum of **3** in CD_2Cl_2 shows four singlets centered at δ = 3.69, 1.49, 1.39 and 1.21 ppm with an integral ratio of 2:18:9:15. In the $^{31}P\{^1H\}$ spectrum of **3** a sharp singlet at δ = 52.7 ppm is monitored. In the ^{1}H NMR spectrum of **4** four singlets centered at δ = 4.20, 1.25, 1.18 and 0.86 ppm with an integral ratio of 2:18:9:15 are detected.

Compound **A** can be reduced using potassium graphite in the presence of a 2,2,2-cryptand to yield [K(2,2,2-crypt][(Cp*Fe)(Cp'''Co)(μ,η^4:η^3-P$_5$)] (**5**) in crystalline yields of 44 % (Scheme 3). Compound **5** can be isolated as an extremely air- and moisture sensitive dark green solid.



Scheme 3: Reactivity of **A** and **B** with KC_8 in the presence of 2,2,2-cryptand and the subsequent reaction of **6** to **7**.

Crystals of **5** suitable for X-ray single crystal structure analysis can be obtained from a concentrated solution in thf layered with hexane at -30 °C.

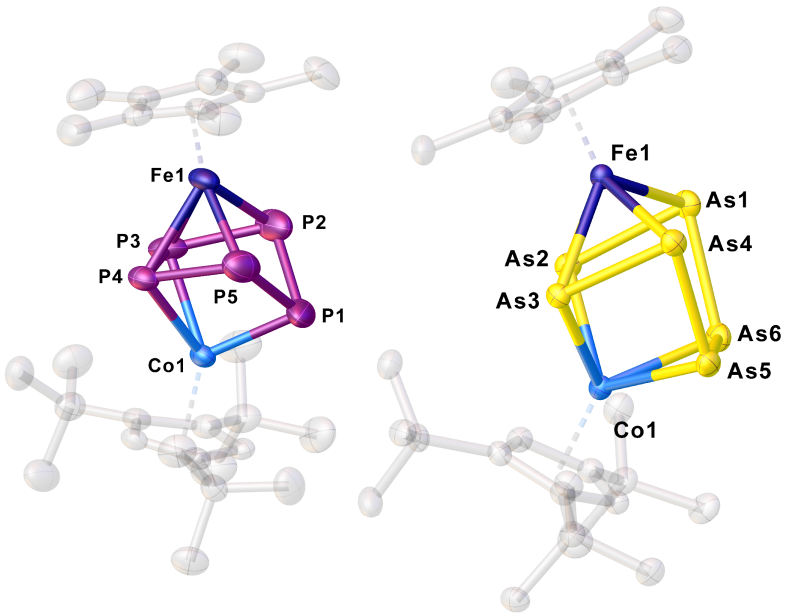


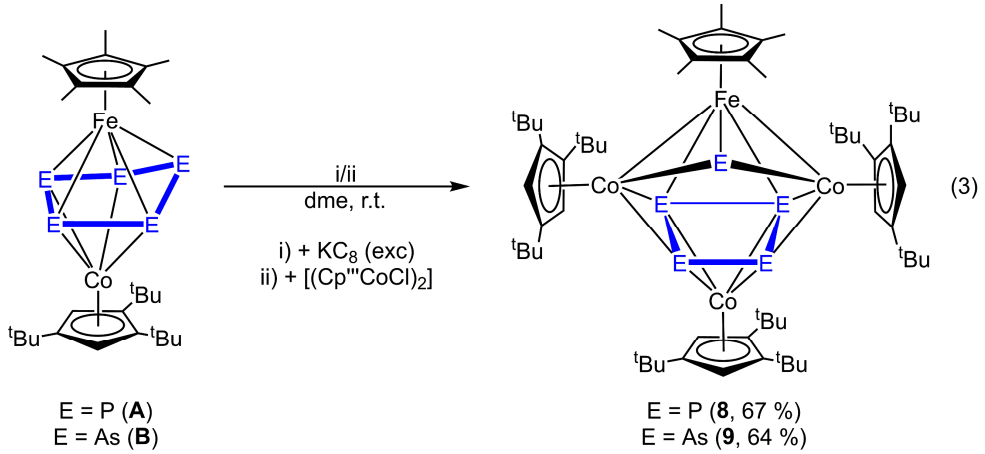
Figure 6: Molecular structure of the anions in **5** and **7** in the solid state. Thermal ellipsoids are drawn with 50 % probability level. Hydrogen atoms, cations and solvent molecules are omitted for clarity.

The structure of **5** in the solid state (Figure 6) reveals a dinuclear triple-decker complex with a strongly folded *cyclo*-P_5 middle deck. The P_5 ligand coordinates to the iron fragment in η^4 and to cobalt fragment in η^3 fashion. One P atom (P1) is bent out of the plane by ca. 44.5 °. There are two short (P2-P3 2.1741(12) Å, P4-P5 2.1773(13) Å), two slightly longer (P1-P2 2.1952(10) Å, P1-P5 2.2081(11) Å) and one longer P-P bond in the backbone (P3-P4 2.2454(13) Å). The Fe-Co distance increased compared to **A** (3.6617(6) Å in **5**). Compound **5** is paramagnetic. The ^{1}H NMR spectrum in thf-d_8 shows three broad and strongly shifted signals for the ^{t}Bu and Me groups of the Cp ligands, while no signal for the H atoms attached directly the Cp''' ligand can be detected. The effective magnetic moment was determined to be 2.01 μ_B by Evans method corresponding to about one unpaired electron. The EPR spectra show an isotropic resonance with *g* values near to 2 indicating also one unpaired electron (293 K, solid, g_{iso} = 2.060, cf. SI). The folding of the P_5 ligand in **A** is clearly dependent on the oxidation state. The oxidation to the mono cation **1** and dication **3** leads to a successive planarization of the P_5 ligand while the reduction inverts the folding and P1 turns from the coordination to Fe1 to Co1 accompanied by an increase of the folding angle.

For the reduction of the arsenic complex **B** potassium graphite in the presence of 2,2,2-cryptand was used. Regardless of numerous attempts to get crystals of the analog arsenic complex [K(2,2,2-crypt)][(Cp*Fe)(Cp'''Co)(μ,η^4:η^3-As_5)] (**6**) were not successful yielding always only brown oily residues. But the presence of **6** was proofed by paramagnetic signals in the ^{1}H NMR spectrum of the reaction mixture (mixture of **6**, **7** and unknown compound, cf. SI) and a strong isotropic resonance in the EPR spectra of the precipitated solid of reaction mixture with *g* values near to 2 (77 K, solid: g_{iso} = 2.123, r.t, solid: g_{iso} = 2.109). Leaving the schlenk with the oily residues of the crystallization at room temperature for a few weeks, a large amount of crystalline [K(2,2,2-crypt)][(Cp*Fe)(Cp'''Co)(μ,η^4:η^4-As_6)] (**7**) could be obtained in isolated yields of 92 % (Scheme 3). The formation of **7** is reproducible. The ^{1}H NMR spectrum of the mother liquor reveals [(Cp*Fe)(Cp'''Co)(μ,η^3:η^3-As_3)] as a side product (cf. chapter 6). The structure of **7** in solid state is shown in Figure 5. The molecular structure reveals a dinuclear triple-decker complex with a newly formed bent *cyclo*-As_6 ligand as middle deck. All As-As bonds except As2-As3 are in the range of single bonds (2.3441(5) - 2.4420(5) Å). The As2-As3 distance of 2.6907(5) Å displays a strongly elongated As-As single bond indicated by a WBI of 0.52.[11] The Fe-Co distance is significantly increased compared to **B** (3.8384(6) Å in **7**, 3.4241(5) Å in **B**). The structural motif of **7** is reminiscent of the cobalt complex [(Cp^+Co)$_2$(μ,η^4:η^4-As_6)], which is isoelectronic to **7**.[15] The ^{1}H NMR spectrum of **7** in thf-d_8 shows four singlets centered at δ = 4.14, 1.61, 1.53 and 1.35 ppm with an integral ratio of 2:15:18:9.

Compound **A** and **B** can both be *in situ* reduced to the formal dianions (attempts to isolate the dianionic species yielded only the related monoanions **5** and **7**) using an excess of KC_8 (> 2

eq) with subsequent electrophilic quenching with $[(Cp'''CoCl)_2]$ to yield the tetranuclear cluster $[(Cp^*Fe)(Cp'''Co)_3(\mu_4,\eta^4{:}\eta^2{:}\eta^2\text{-}E_4)(\mu_3\text{-}E)]$ (E = P (**8**), As (**9**)) in crystalline yields of 67 and 64 %, respectively after workup (Eq. 3).



E = P (**A**)
E = As (**B**)

E = P (**8**, 67 %)
E = As (**9**, 64 %)

Crystals suitable for X-ray single crystal structure analysis can be obtained from concentrated solutions in CH_2Cl_2 layered with acetonitrile at -30 °C (**8**) or room temperature (**9**).

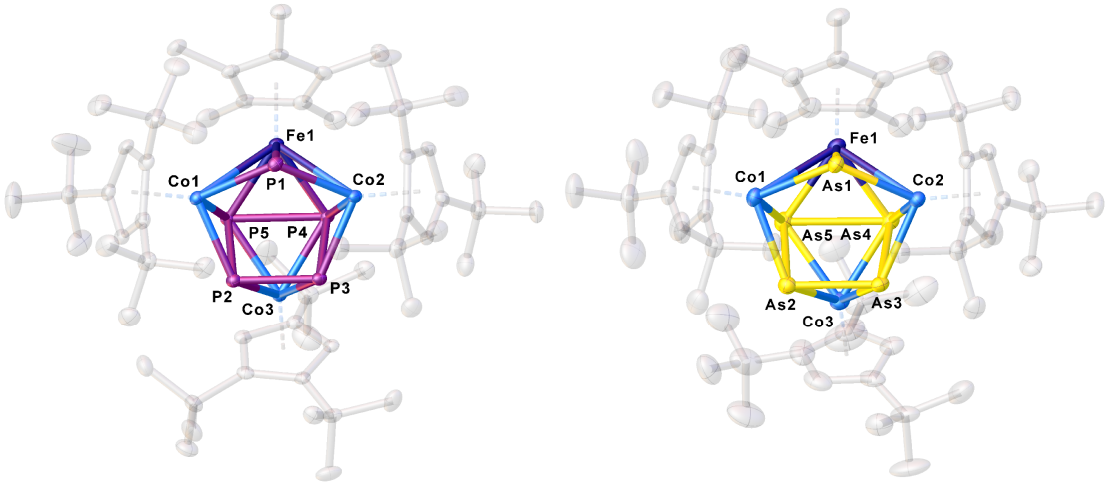


Figure 7: Molecular structures of **8** (left) and **9** (right) in the solid state. Thermal ellipsoids are drawn with 50 % probability level. Hydrogen atoms and solvent molecules are omitted for clarity.

The molecular structures of **8** and **9** in the solid state (Figure 7) reveal tetranuclear cluster, consisting of three {Cp'''Co} fragments, one {Cp*Fe} fragments coordinated by a trapezoid shaped E_4 ligand and a single E atom. The *cyclo*-E_4 ligands shows one short E2-E3 bond (**8**: 2.1295(10), **9**: 2.3565(4) Å), which is in the range of an elongated double bond.[10,11] This is also in line with WBIs of 1.14 (**8**) and 1.07 (**9**), respectively. The other E-E distances are longer than single bonds (**8**: P2-P5 2.4726(9), P3-P4 2.5045(9), P4-P5 2.4688(10), **9**: As2-As5 2.6300(4), As3-As4 2.7097(4), As4-As5 2.7102(4) Å), what is also in line with the WBIs in the range of 0.49-0.52 (**8**) and 0.45-0.56 (**9**), respectively. The Fe1-Co1 (**8**: 2.7735(5), **9**: 2.9006(6) Å) and Fe1-Co2 distances (**8**: 2.7638(5), **9**: 2.9339(5) Å) are in the range of elongated single bonds, what is also underlined by WBIs of 0.20 (**8**) and 0.20-0.21 (**9**). The Fe1-Co1 and Fe1-Co2 distances of **8** are comparable with those in the trinuclear complex $[\{Co(CO)_3\}\{Fe(CO)_3\}_2$

(μ_3-PPh)(μ_2-PHPh)] (Fe-Co distances of 2.713(2) and 2.724(2) Å).[16] In the case of the arsenic compound **9** the Fe1-Co1 (2.9006(6) Å) and Fe1-Co2 (2.9339(5) Å) distances are longer by ca. 0.2 Å than in **8** and clearly longer than reported Fe-Co bonds in arsenic bridged complexes (e.g. 2.702(3) Å in [{Fe(CO)$_3$}{Co(CO)$_3$}(μ-AsMe$_2$)]).[17] The ^{1}H NMR spectrum of **8** in C_6D_6 reveals eight singlets centered at δ = 5.49, 4.78, 4.45, 1.73, 1.64, 1.62, 1.59 and 1.33 with an integral ratio of 2:2:2:18:18:33:9:18. The ^{31}P{^{1}H} NMR spectrum shows three singlets centered δ = 1309.0, 563.0 and 111.9 ppm with an integral ratio of 1:2:2, while the signal at 1309.0 ppm can be assigned to the P1 atom. The other two singlets can be assigned to the P2/P3 (δ = 563.0 ppm) and to the P4/P5 (δ = 111.9 ppm) atoms, respectively. The strong low field shift of the signal for P2/P3 can be explained by the coordination to four metal units. Theoretically, a $^1J_{PP}$ coupling between P2 and P5, and P3 and P4, respectively should be present. Due to the long P-P distances the value of the coupling constant should be rather small can therefore not be observed since the singlets centered at δ = 563.0 and 111.9 ppm are broadened. For **9**, the ^{1}H NMR spectrum in C_6D_6 shows six broadened singlet centered at δ = 5.44, 4.74, 4.18, 1.77, 1.63 and 1.31 ppm with an integral ratio of 2:2:2:18:60:18. The potential of subsequent redox chemistry of **8** and **9** was investigated by cyclic voltammetry. The CV of **8** in CH_2Cl_2 (Figure 8) shows one electrochemically reversible reduction process at -1131 mV and two electrochemically reversible oxidation processes at 81 and 724 mV against [Cp_2Fe]/[Cp_2Fe]$^+$. The CV of **9** in CH_2Cl_2 shows one electrochemically reversible reduction process at -1077 mV and three electrochemically reversible oxidation processes at 85, 755 and 1547 mV against [Cp_2Fe]/[Cp_2Fe]$^+$.

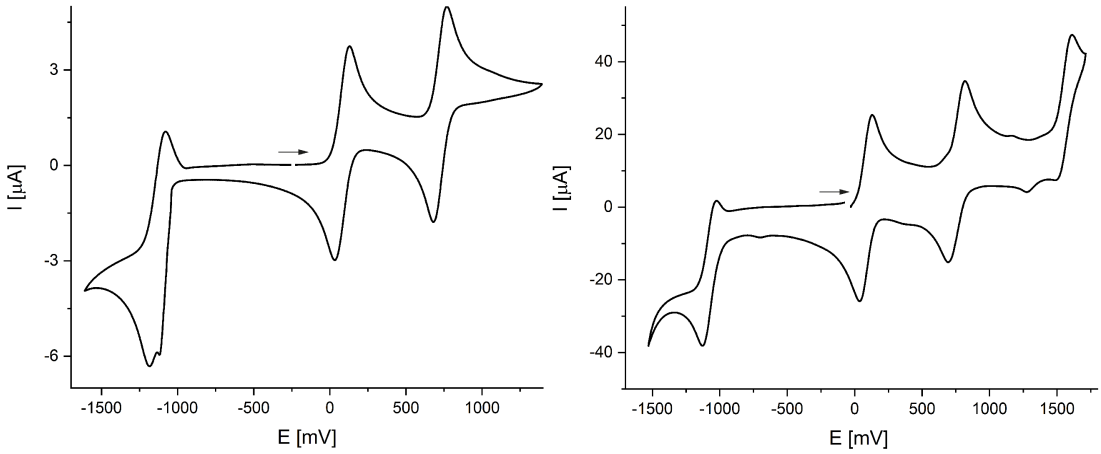
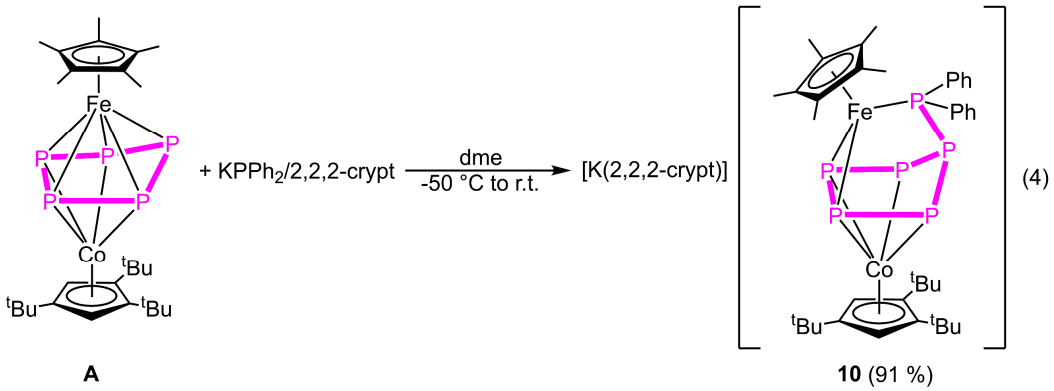


Figure 8. Cyclic voltammogram of **8** (left) and **9** (right) in CH_2Cl_2 against [Cp_2Fe]/[Cp_2Fe]$^+$ (electrolyte ^{n}Bu$_4$NPF$_6$, scan rate: 100 mV/s. temperature: r.t.).

The redox chemistry of **8** was started to be investigated (oxidation with Ag[FAl] and reduction with KC_8) and looks quite promising. But no characterizable products could be obtained so far. Compound **A** is reacted with $KPPh_2$ at -50 °C in dme in the presence of 2,2,2-cryptand to yield [K(2,2,2-crypt)][(Cp*Fe)(Cp'''Co)(μ,η^4:η^3-P$_6$Ph$_2$)] (**10**) in crystalline yields of 91 % (Eq. 4).



A **10** (91 %)

Crystals suitable for X-ray single crystal structure analysis can be obtained from a concentrated solution in dme layered with hexane at -30°C. The structure in solid state is depicted in Figure 9. The structure in solid state reveals a bent triple-decker complex with a P_6Ph_2 ligand as middle deck. The PPh_2^- (P1) nucleophile binds to the P atom which is bent out of the plane of the middle deck (P2). The P_6Ph_2 ligand coordinates in η^4 fashion to the {Cp'''Co} and in η^3 fashion to the {Cp*Fe} fragment. The Fe1-Co1 distance is 3.7537(4) Å long. The P-P bond lengths are in the range of single bonds (P1-P2 2.2429(7), P2-P3 2.2242(7), P2-P6 2.2013 Å, WBIs in the range of 0.81 and 0.98) or elongated double bonds (P3-P4 2.1634(7), P5-P6 2.1633(7) Å, WBI of 1.11) except the P4-P5 distance which is considerably longer than a P-P single bond (2.5886(7) Å).[10,11] This kind of P-P bond elongation was reported for $[(Cp'''Co)_3P_8]$ which shows a similar P_6 structural motif as **10** in the subunit of the P_8 ligand.[18] The $^{31}P\{^1H\}$ NMR spectrum in thf-d_8 shows four multipletts centered at δ = 187.5, 153.4, 49.2 and -155.0 ppm with an integral ratio of 1:2:1:2, indicating an ABB'MXX' spin system. Although the P4-P5 distance is longer than a P-P single bond, it can be considered as a P-P bond, indicated by a WBI of 0.39 and a $^1J_{PP}$ coupling constant of 106 Hz (cf. SI).

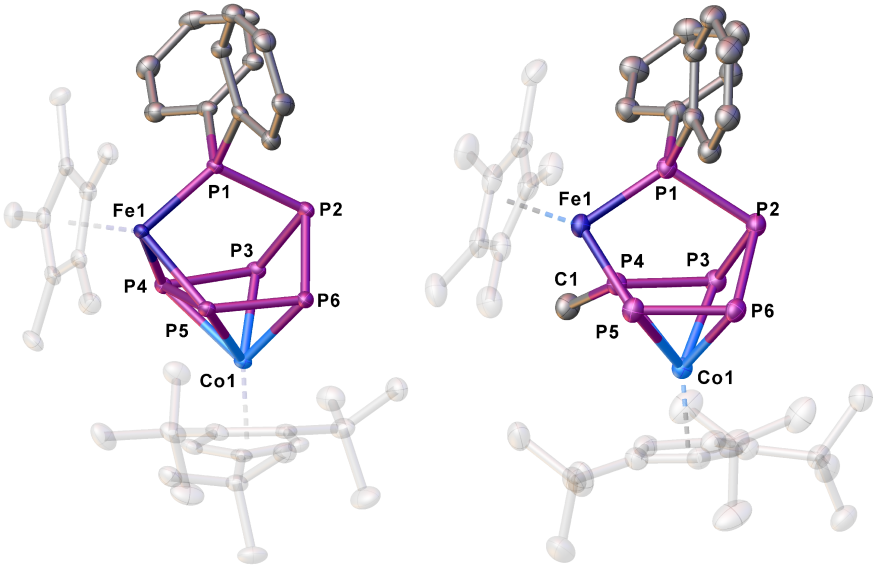
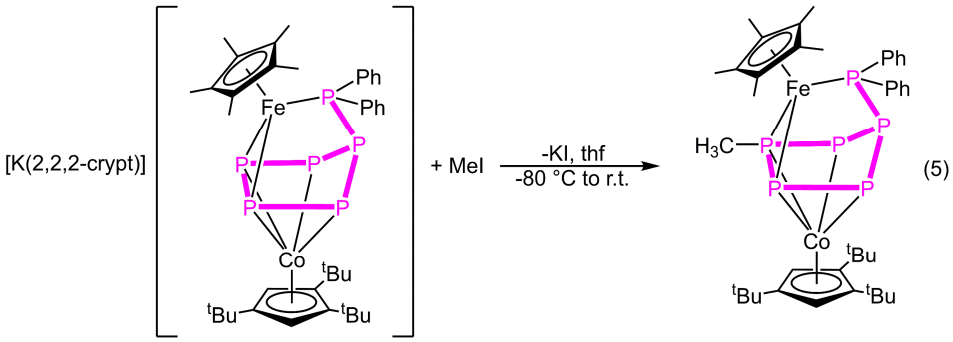


Figure 9: Molecular structures of the anion in **10** (left) and **11** (right) in the solid state. Thermal ellipsoids are drawn with 50 % probability level. Hydrogen atoms, cations and solvent molecules are omitted for clarity.

Compound **10** can quenched with the electrophile MeI under the release of KI to yield [(Cp*Fe)(Cp'''Co)(μ,η^4:η^3-P_6Ph_2Me)] (**11**) in crystalline yields of 62 % after workup (Eq. 5).



9 **11** (62 %)

Crystals suitable for X-ray single crystal structure analysis can be obtained from a concentrated solution of **11** in CH_2Cl_2 layered with MeCN at -30 °C. The structure in solid state (Figure 9) reveals a P_6Ph_2Me middle deck, while the methylation of **10** took place at P4. P4 represents a stereo center and **11** is obtained in a racemic mixture (centrosymmetric space group *P2₁/c*). All P-P bond lengths are comparable with those in **10**. The $^{31}P\{^1H\}$ NMR spectrum shows six multipletts at δ = 199.3, 111.7, 59.4, 28.3, -122.4 and -246.6 ppm with an integral ratio of 1:1:1:1:1:1 indicating an AMNOSX spin system. In the proton coupled spectrum a broadening of three signals can be observed. The use of the analog arsenic nucleophile $KAsPh_2$ gives in the presence of 2,2,2-cryptand yields only **5** under the formation of As_2Ph_4.

7.3 Conclusion

It could be shown that the heterobimetallic triple-decker complexes [(Cp*Fe)(Cp'''Co)(μ,η^5:η^4-E_5)] (E = P (**A**), As (**B**)) exhibit a versatile redox chemistry over several oxidation stages. Both **A** and **B** can each be oxidized two times with Ag[FAl] (formation of **1**, **2**, **3** and **4**) while a planarization of the folded E_5 middle-decks to a planar *cyclo*-E_5 takes place. On the other hand, reduction lead to an opposite change in the geometry of the E_5 middle decks. One E atom is turned to the other side of the E_5 ligand and coordinated to Co instead of iron (formation of **5** and **6**). In the case of **B**, a further fragmentation into complexes containing As_6 and As_3 ligands is observed (formation of **7**). Both **A** and **B** can be *in situ* reduced formally twice and quenched with the electrophile [(Cp'''$CoCl)_2$] to yield two novel cluster complexes (**8**, **9**). Their possible redox properties were investigated by cyclic voltammetry, revealing a set of redox processes which might be of interest for further research. **A** can be functionalized with $KPPh_2$ (formation of **10**) and subsequently quenched with the electrophile MeI (formation of **11**). The use of other main group nucleophiles and electrophiles might be the scope of further research.

7.4 Supporting Information

7.4.1 Synthetic procedures and experimental details

Synthetic Procedures: All manipulations were performed under an atmosphere of dry argon using standard glove-box and Schlenk techniques. All solvents were degassed and purified by standard procedures. The compounds [(Cp*Fe)(Cp'''Co)(μ,η^5:η^4-E$_5$)] (E = P (**A**), As (**B**)),[19,20] [KC$_8$][21], Ag[FAl][22] and [(Cp'''CoCl)$_2$][23] were prepared according to literature procedures. MeI, 2,2,2-cryptand were purchased commercially. KPPh$_2$ was synthesized by the reaction of KH with PPh$_2$H in dme and stored as a stock solution in dme.

The NMR spectra were recorded with a Bruker Avance 400 spectrometer (^{1}H: 400.13 MHz, ^{31}P: 161.976 MHz). The chemical shifts are given in ppm referenced to external SiMe$_4$ (^{1}H) and H$_3$PO$_4$ (^{31}P). Elemental analyses were determined with an Elementar Vario EL III apparatus. The X-Band EPR measurements were carried out with a MiniScope MS400 device with a frequency of 9.44 GHz and a rectangular resonator TE102 of the company Magnettech GmbH. The LIFDI-MS spectra were recorded with a Finnigan MAT 95 mass spectrometer. The ESI-MS spectra were acquired on a ThermoQuest Finnigan MAT TSQ 7000 mass spectrometer.

7.4.1.1 Synthesis of [(Cp*Fe)(Cp'''Co)(μ,η^5:η^5-P$_5$)][FAl] (1)

A solution of Ag[FAl] (233.8 mg, 0.157 mmol, 1 eq) in CH_2Cl_2 was added to a stirred solution of **A** (100 mg, 0.157 mmol, 1 eq) in CH_2Cl_2 at room temperature, while the color changed from dark red to brown-green and a dark precipitate (Ag^0) was obtained. After stirring for 1 h, the reaction mixture was filtered over diatomaceous earth. The solvent of the green solution reduced, layered with hexane and stored at -30 °C. After a few days **1** can be obtained as green plates. The supernatant was decanted off, washed with hexane and dried *in vacuo*.

Yield: 174 mg (55 %).

^{1}H NMR (CD_2Cl_2, 25 °C): δ [ppm] = 5.66 (br, $\omega_{1/2}$ = 13 Hz, 15H, C_5Me_5), 3.76 (br, $\omega_{1/2}$ = 45 Hz 9H, $C_5H_2{}^tBu_3$), 3.29 (br, $\omega_{1/2}$ = 42 Hz 18H, $C_5H_2{}^tBu_3$), -65.22 (br, $\omega_{1/2}$ = 622 Hz, 2H, $C_5H_2{}^tBu_3$).

^{19}F{^{1}H} NMR (CD_2Cl_2, 25 °C): δ [ppm] = -112.6 (d, J_{F-F} = 285 Hz, 6F), -117.1 (d, J_{F-F} = 279 Hz, 6F), -121.8 (d, J_{F-F} = 279 Hz, 3F), -127.9 (s, 6F), -130.6 (d, J_{F-F} = 274 Hz, 6F), -137.2 (d, J_{F-F} = 276 Hz, 6F), -141.2 (d, J_{F-F} = 274 Hz, 3F), -154.3 (t, J_{F-F} = 22 Hz, 6F), -165.0 (t, J_{F-F} = 18 Hz, 6F), -172.0 (s, AlF, 1F).

^{31}P{^{1}H} NMR (CD_2Cl_2, 25 °C): δ [ppm] = 275.1 (br, $\omega_{1/2}$ = 2600 Hz, P_5).

^{31}P NMR (CD_2Cl_2, 25 °C): δ [ppm] = 275.1 (br, $\omega_{1/2}$ = 2600 Hz, P_5).

Evans-NMR (CD_2Cl_2, 25 °C): μ_{eff} = 2.04 μ_B corresponding to 1.27 unpaired electrons.

ESI-MS (CH_2Cl_2): *m/z* = 638.1 (100 %, $[M]^+$), 607.1 (1 %, $[M\text{-}P]^+$).

EA $C_{63}H_{44}O_3AlF_{46}P_5FeCo$: calc [%]: C 37.47; H 2.20; found [%]: C 37.46; H 2.31.

X-band EPR (77 K, liquid) g_x = 2.155, g_y = 2.035, g_z = 1.948, A_x = 290.125, A_Y = 55.125, A_Z = 120.125 MHz, (77 K, solid) (overall shape similar to (77 K, liquid), but coupling not resolved).

7.4.1.2 Synthesis of [(Cp*Fe)(Cp'''Co)(μ,η^5:η^5-As$_5$)][FAl] (2)

A solution of Ag[FAl] (173.5 mg, 0.1165 mmol, 1 eq) in CH_2Cl_2 was added to a stirred solution of **B** (100 mg, 0.1165 mmol, 1 eq) in CH_2Cl_2 at room temperature, while the color changed from dark green to brown-green and a dark precipitate (Ag^0) was obtained. After stirring for 1 h, the reaction mixture was filtered over diatomaceous earth. The solvent of the brown-green solution reduced, layered with hexane and stored at -30 °C. After a few days **1** can be obtained as brown plates. The supernatant was decanted off, washed with hexane and dried *in vacuo*.

Yield: 165 mg (63 %).

^{1}H NMR (CD_2Cl_2, 25 °C): δ [ppm] = 3.84 (br, $\omega_{1/2}$ = 167 Hz, 9H, $C_5H_2{}^tBu_3$), 2.74 (br, $\omega_{1/2}$ = 119 Hz, 18H, $C_5H_2{}^tBu_3$), -1.09 (br, $\omega_{1/2}$ = 40 Hz, 15H, C_5Me_5).

^{19}F{^{1}H} NMR (CD_2Cl_2, 25 °C): δ [ppm] = -112.6 (d, $J_{F\text{-}F}$ = 285 Hz, 6F), -117.1 (d, $J_{F\text{-}F}$ = 279 Hz, 6F), -121.8 (d, $J_{F\text{-}F}$ = 279 Hz, 3F), -127.9 (s, 6F), -130.6 (d, $J_{F\text{-}F}$ = 274 Hz, 6F), -137.2 (d, $J_{F\text{-}F}$ = 276 Hz, 6F), -141.2 (d, $J_{F\text{-}F}$ = 274 Hz, 3F), -154.3 (t, $J_{F\text{-}F}$ = 22 Hz, 6F), -165.0 (t, $J_{F\text{-}F}$ = 18 Hz, 6F), -172.0 (s, AlF, 1F).

Evans-NMR (CD_2Cl_2, 25 °C): μ_{eff} = 1.90 μ_B corresponding to 1.14 unpaired electrons.

ESI-MS (CH_2Cl_2): *m/z* = 857.9 (100 %, $[M]^+$), 782.9 (67 %, $[M\text{-}As]^+$), 708.0 (13 %, $[M\text{-}2As]^+$).

EA $C_{63}H_{44}O_3AlF_{46}As_5FeCo$: calc [%]: C 33.79; H 1.98; found [%]: C 34.06; H 2.01.

X-band EPR (77 K, solid) g_x = 2.235, g_y = 1.952, g_z = 1.896, (77 K, liquid) g_{iso} = 2.04, (r.t, liquid) g_{iso} = 2.06, (r.t, solid) g_{iso} = 2.04.

7.4.1.3 Synthesis of [(Cp*Fe)(Cp'''Co)(μ,η^5:η^5-P$_5$)][FAl]$_2$ (3)

A solution of Ag[FAl] (238 mg, 0.160 mmol, 2.05 eq) in o-$C_6H_4F_2$ was added to a stirred solution of **A** (50 mg, 0.078 mmol, 1 eq) in o-$C_6H_4F_2$ at room temperature, while the color changed from dark red to brown and a dark precipitate (Ag^0) was obtained. After stirring for 1 h, the reaction

mixture was filtered over diatomaceous earth. The solvent of the brown solution reduced, layered with toluene and stored at -30 °C. After a few days **1** can be obtained as brown blocks. The supernatant was decanted off, washed with hexane and dried *in vacuo*.

Yield: 131 mg (49 %).

^{1}H NMR (o-$C_6H_4F_2$ + C_6D_6 capillary, 25 °C): *δ* [ppm] = 4.81 (s, 2H, $C_5H_2{}^tBu_3$), 1.42 (s, 18H, $C_5H_2{}^tBu_3$), 1.12 (s, *9*H, $C_5H_2{}^tBu_3$), 1.03 (s, 15H, C_5Me_5).

^{19}F{^{1}H} NMR (o-$C_6H_4F_2$ + C_6D_6 capillary, 25 °C): *δ* [ppm] = -112.6 (d, J_{F-F} = 285 Hz, 6F), -117.1 (d, J_{F-F} = 279 Hz, 6F), -121.8 (d, J_{F-F} = 279 Hz, 3F), -127.9 (s, 6F), -130.6 (d, J_{F-F} = 274 Hz, 6F), -137.2 (d, J_{F-F} = 276 Hz, 6F), -141.2 (d, J_{F-F} = 274 Hz, 3F), -154.3 (t, J_{F-F} = 22 Hz, 6F), -165.0 (t, J_{F-F} = 18 Hz, 6F), -172.0 (s, AlF, 1F).

^{31}P{^{1}H} NMR (o-$C_6H_4F_2$ + C_6D_6 capillary, 25 °C): *δ* [ppm] = 52.7 (s, P_5).

^{31}P NMR (o-$C_6H_4F_2$ + C_6D_6 capillary, 25 °C): *δ* [ppm] = 52.7 (s, P_5).

ESI-MS (CH_2Cl_2): *m/z* = 638.1 (100 %, $[M]^+$).

ESI-MS (o-$C_6H_4F_2$): *m/z* = 638.1 (100 %, $[M]^+$), 319.0 (7 %, $[M]^{2+}$).

EA $C_{99}H_{44}O_6Al_2F_{92}P_5FeCo$ x $C_6H_4F_2$: calc [%]: C 35.88; H 1.37; found [%]: C 35.58; H 1.42.

[(Cp*Fe)(Cp'''Co)(μ,η^5:η^5-P$_5$)][TEF]$_2$

^{1}H NMR (CD_2Cl_2, 25 °C): *δ* [ppm] = 4.69 (s, 2H, $C_5H_2{}^tBu_3$), 1.49 (s, 18H, $C_5H_2{}^tBu_3$), 1.39 (s, *9*H, $C_5H_2{}^tBu_3$), 1.21 (s, 15H, C_5Me_5).

^{19}F{^{1}H} NMR (CD_2Cl_2, 25 °C): *δ* [ppm] = -75.5 (s, [TEF]).

^{31}P{^{1}H} NMR (CD_2Cl_2, 25 °C): *δ* [ppm] = 54.7 (s, P_5).

^{31}P NMR (CD_2Cl_2, 25 °C): *δ* [ppm] = 54.7 (s, P_5).

ESI-MS (o-$C_6H_4F_2$): *m/z* = 319.0 (100 %, $[M]^{2+}$).

EA $C_{59}H_{44}O_8Al_2F_{72}P_5FeCo$ x 0.5 $C_6H_4F_2$: calc [%]: C 28.32; H 1.76; found [%]: C 28.26; H 1.65.

7.4.1.4 Synthesis of [(Cp*Fe)(Cp'''Co)(μ,η^5:η^5-As$_5$)][FAl]$_2$ (4)

A solution of Ag[FAl] (375 mg, 0.2518 mmol, 2 eq) in o-$C_6H_4F_2$ was added to a stirred solution of **B** (108 mg, 0.1259 mmol, 1 eq) in o-$C_6H_4F_2$ at room temperature, while the color changed from dark green to brown and a dark precipitate (Ag^0) was obtained. After stirring for 4 h, the reaction mixture was filtered over diatomaceous earth. The solvent of the brown solution

reduced, layered with toluene and stored at -30 °C. After a few days **4** can be obtained as brown blocks. The supernatant was decanted off, washed with hexane and dried *in vacuo*.

Yield: 344 mg (75 %).

^{1}H NMR (o-$C_6H_4F_2$ + C_6D_6 capillary, 25 °C): δ [ppm] = 4.20 (s, 2H, $C_5H_2{}^t$Bu$_3$), 1.25 (s, 18H, $C_5H_2{}^tBu_3$), 1.18 (s, 9H, $C_5H_2{}^tBu_3$), 0.86 (s, 15H, C_5Me_5).

^{19}F{^{1}H} NMR (o-$C_6H_4F_2$ + C_6D_6 capillary, 25 °C): δ [ppm] = -112.6 (d, $J_{F\text{-}F}$ = 285 Hz, 6F), -117.1 (d, $J_{F\text{-}F}$ = 279 Hz, 6F), -121.8 (d, $J_{F\text{-}F}$ = 279 Hz, 3F), -127.9 (s, 6F), -130.6 (d, $J_{F\text{-}F}$ = 274 Hz, 6F), -137.2 (d, $J_{F\text{-}F}$ = 276 Hz, 6F), -141.2 (d, $J_{F\text{-}F}$ = 274 Hz, 3F), -154.3 (t, $J_{F\text{-}F}$ = 22 Hz, 6F), -165.0 (t, $J_{F\text{-}F}$ = 18 Hz, 6F), -172.0 (s, AlF, 1F).

ESI-MS (o-$C_6H_4F_2$): *m/z* = 857.8 (56 %, $[M]^+$), 428.9 (100 %, $[M]^{2+}$).

EA $C_{99}H_{44}O_6Al_2F_{92}P_5FeCo$: calc [%]: C 32.84; H 1.22; found [%]: C 32.55; H 1.46.

7.4.1.5 Synthesis of [K(2,2,2-crypt)][(Cp*Fe)(Cp’’’Co)(μ,η^4:η^3-P$_5$)] (5)

A suspension of KC_8 (25 mg, 0.188, 1. 2 eq) in dme was added to a stirred solution of **A** (100 mg, 0.1567 mmol, 1 eq) and 2,2,2-crypt (59 mg, 0.1567 mmol, 1 eq) in dme, while the color changed from dark red to brown green. After stirring for 3 h it was filtered over diatomaceous earth. The solvent was reduced and layered with hexane at room temperature. **5** can be obtained as dark green blocks. The supernatant was decanted off and the crystals dried in vacuo.

Yield: 88 mg (44 %)

^{1}H NMR (thf-d_8, 25 °C): δ [ppm] = 6.24 (br, 9H, $C_5H_2{}^tBu_3$), 4.15 (br, 15H, C_5Me_5), 3.70 (br, 12H, crypt), 3.66 (br, 12H, cypt), 3.44 (br, 18H, $C_5H_2{}^tBu_3$), 2.66 (br, 12 H, crypt).

EA $C_{45}H_{80}O_6N_2P_5FeCoK$: calc [%]: C 51.29; H 7.65; N 2.66; found [%]: C 51.21; H 7.35; N 2.57.

Evans-NMR (thf-d_8, 25 °C): μ_{eff} = 2.01 μ_B corresponding to 1.24 unpaired electrons.

X-band EPR (77 K, solid) g_{iso} = 2.047, (77 K, liquid) g_{iso} = 2.041, (r.t, liquid) g_{iso} = 2.078, (r.t, solid) g_{iso} = 2.060.

7.4.1.6 Reaction of [(Cp*Fe)(Cp’’’Co)(μ,η^5:η^4-As)] (B) with KC_8

B (100 mg, 0.1166 mmol, 1 eq), KC_8 (19 mg, 0.1399, 1.2 eq) and 2,2,2-crypt (43.9 mg, 0.1166 mmol, 1 eq) were weighed in together and dimethoxyethane was added, while to color changed from dark green to brown. After stirring for 5 minutes, it was filtered over diatomaceous earth and the solvent was reduced. An excess of hexane was used for precipitation. The

microcrystalline solid was washed with hexane (slight brown to green color) and dried *in vacuo*. The ^{1}H NMR spectrum in thf-d_8 reveals the formation of **7** beside the paramagnetic compound [K(2,2,2-crypt)][(Cp*Fe)(Cp'''Co)(μ,η^4:η^3-As$_5$)] (**6**) (cf. Figure S10). X-Band EPR measurement of the obtained solid reveals a strong isotropic resonance.

Compound **6**:

X-band EPR (77 K, solid) g_{iso} = 2.123, (r.t, solid) g_{iso} = 2.109.

7.4.1.7 Synthesis of [K(2,2,2-crypt)][(Cp*Fe)(Cp'''Co)(μ,η^4:η^4-As$_6$)] (7)

B (500 mg, 0.5827 mmol, 1 eq), KC_8 (88 mg, 0.651, 1.12 eq) and 2,2,2-crypt (219.5 mg, 0.5827 mmol, 1 eq) were weighed in together and dimethoxyethane was added. After stirring overnight (color change from green to brown) it was filtered over diatomaceous earth. The solvent was reduced and layered with hexane at room temperature. After a few days an oily solid was observed at the Schlenk wall. Leaving it for a few weeks, crystalline solid (needles) of **7** were obtained. The supernatant was decanted off, washed with hexane and the crystals dried *in vacuo*. The ^{1}H NMR spectrum of the brown-green mother liquor reveals [(Cp*Fe)(Cp'''Co)(μ,η^3:η^3-As$_3$)][20] as a major compound.

Yield: 481 mg (92 %).

^{1}H NMR (thf-d_8, 25 °C): *δ* [ppm] = 4.14 (s, 2H, $C_5H_2{}^tBu_3$), 3.61 (s, 12H, $C_{18}H_{36}N_2O_6$), 3.57 (overlapped with solvent signal, $C_{18}H_{36}N_2O_6$), 2.56 (t, $^3J_{HH}$ = 4.4 Hz, 12H, $C_{18}H_{36}N_2O_6$), 1.61 (s, 15H, C_5Me_5), 1.53 (s, 18H, $C_5H_2{}^tBu_3$), 1. 35 (s, 9H, $C_5H_2{}^tBu_3$).

ESI-MS (dme): *m/z* = 932.9 (100 %, [M]$^-$).

EA $C_{45}H_{80}O_6N_2As_6FeCoK$: calc [%]: C 40.08; H 5.98; N 2.08; found [%]: C 40.60; H 6.12; N 1.94.

7.4.1.8 Synthesis of [(Cp*Fe)(Cp'''Co)$_3$(μ$_4$,η^4:η^2:η^2-P$_4$)(μ$_3$-P)] (8)

A suspension of KC_8 (500 mg, 3.699 mmol, 2.4 eq) in thf was added to a stirred solution of **A** (1.0 g, 1.567 mmol, 1 eq) in thf while the color changed from red to brown green. After a few minutes a solution of [(Cp'''CoCl)$_2$] (1.03 g, 1.567 mmol, 1 eq) was added and a brown green solution was obtained. After stirring for 2 h, silica was added and the solvent removed *in vacuo*. The reaction mixtures was purified by column chromatography (SiO_2, hexane, 15 x 5 cm). Using hexane a strong brown green fraction was eluted. The solvent was removed *in vacuo*. The residue was dissolved in CH_2Cl_2 and layered with acetonitrile and stored at -30 °C. After

a few days **8** can be obtained as large brown blocks. The supernatant was decanted off and the crystals dried *in vacuo*.

Yield: 1.29 g (67 %).

^{1}H NMR (C_6D_6, 25 °C): *δ* [ppm] = 5.49 (s, 2H, $C_5H_2{}^tBu_3$), 4.78 (s, 2H, $C_5H_2{}^tBu_3$), 4.45 (s, 2H, $C_5H_2{}^tBu_3$), 1.73 (s, 18H, $C_5H_2{}^tBu_3$), 1.64 (s, 18H, $C_5H_2{}^tBu_3$), 1.62 (s, 33H, $C_5H_2{}^tBu_3$+ C_5Me_5), 1.59 (s, 9H, $C_5H_2{}^tBu_3$), 1.33 (s, 18H, $C_5H_2{}^tBu_3$).

^{31}P{^{1}H} NMR (C_6D_6, 25 °C): *δ* [ppm] = 1309.0 (s, 1P, *P*), 563.0 (s, 2P, P_4), 111.9 (s, 2P, P_4).

LIFDI-MS (toluene): *m/z* = 1222.5 (100 %, $[M]^+$).

EA $C_{61}H_{102}P_5FeCo_3$: calc [%]: C 59.91; H 8.41; found [%]: C 60.28; H 8.47.

7.4.1.9 Synthesis of [(Cp*FeCp'''Co)$_3$(μ$_4$,η^4:η^2:η^2:η^2-As$_4$)(μ$_3$-As)] (9)

A suspension of KC_8 (118 mg, 0.874 mmol, 2.5 eq) in thf was added to a stirred solution of **B** (300 mg, 0.3496 mmol, 1 eq) and [(Cp'''CoCl)$_2$] (229 mg, 0.3496 mmol, 1 eq) in thf, while the color changed from dark green to brown. The ^{1}H NMR spectrum in C_6D_6 reveals the clean formation of **9**. The solvent was removed *in vacuo*. The residue was extracted with hexane and filtered over diatomaceous earth. The solvent was removed *in vacuo*. The obtained solid was dissolved in CH_2Cl_2 and layered with MeCN. After storage at room temperature for a few days, **9** can be obtained as dark brown blocks. The supernatant was decanted off and the crystals dried *in vacuo*.

Yield: 323 mg (64 %).

^{1}H NMR (C_6D_6, 25 °C): *δ* [ppm] = 5.44 (s, 2H, $C_5H_2{}^tBu_3$), 4.74 (s, 2H, $C_5H_2{}^tBu_3$), 4.18 (s, 2H, $C_5H_2{}^tBu_3$), 1.77 (s, 18H, $C_5H_2{}^tBu_3$), 1.63 (s, 60H, $C_5H_2{}^tBu_3$+ C_5Me_5),1.31 (s, 18H, $C_5H_2{}^tBu_3$).

LIFDI-MS (toluene): *m/z* = 1442.2 (100 %, $[M]^+$).

EA $C_{61}H_{102}As_5FeCo_3$: calc [%]: C 50.78; H 7.13; found [%]: C 50.96; H 7.11.

7.4.1.10 Synthesis of [K(2,2,2-crypt)][(Cp*Fe)(Cp'''Co)(μ,η^4:η^3-P$_6$Ph$_2$)] (10)

A solution of $KPPh_2$ in dme (2.77 mL, 0.113 mol/L, 0.313 mmol, 1 eq) was added to a stirred solution of **A** (200 mg, 0.313 mmol, 1 eq) and 2,2,2-cryptand (118 mg, 0.313 mmol, 1 eq) at -50 °C. The color changed from dark red to brown. The reaction mixture was warmed to room temperature, while the color changed to green. The solvent was reduced, layered with

pentane and stored at -30 °C. After a few days, **10** can be obtained as dark green blocks. The supernatant was decanted off, the crystals washed with hexane and dried *in vacuo*.

Yield: 354 mg (91 %).

^{1}H NMR (thf-d_8, 25 °C): *δ* [ppm] = 7.29 (m, 4H, P_6*Ph*$_2$), 6.94 (m, 6H, P_6*Ph*$_2$), 4.38 (s, 2H, C_5*H*$_2$^{t}Bu$_3$), 3.60 (s, 12H, crypt), 3.56 (t, ^{3}*J*$_{HH}$ = 4.7 Hz, 12H, crypt), 3.43 (s, 1.6H, dme), 3.27 (s, 2.28H, dme), 2.57 (t, ^{3}*J*$_{HH}$ = 4.7 Hz, 12H, crypt), 1.60 (s, 15H, C_5*Me*$_5$), 1.45 (s, 18H, C_5H_2*t*Bu$_3$), 1.21 (s, 18H, C_5H_2*t*Bu$_3$).

^{31}P{^{1}H} NMR (thf-d_8, 25 °C): *δ* [ppm] = 186.2 (m, 1P, *P*$_A$), 153.4 (m, 2P, *P*$_{BB'}$), 49.2 (m, 1P, *P*$_M$), -155.0 (m, 2P, *P*$_{XX'}$). (Coupling constants given in Table S1 obtained from simulation in Figure S1).

^{31}P NMR (thf-d_8, 25 °C): *δ* [ppm] = 186.2 (m, 1P, *P*$_A$), 153.4 (m, 2P, *P*$_{BB'}$), 49.2 (m, 1P, *P*$_M$), -155.0 (m, 2P, *P*$_{XX'}$). (Coupling constants same as ^{31}P{^{1}H}).

ESI-MS (dme): *m/z* = 823.1 (10 %, [M]$^-$), 841.1 (10 %, [M+H_2O]$^-$), 855,1 (100 %, [M+2O]$^-$).

EA $C_{57}H_{90}O_6N_2P_6KFeCo$: calc [%]: C 55.25; H 7.32; N 2.26 found [%]: C 55.29; H 7.22; N 2.02.

7.4.1.11 Synthesis of [(Cp*Fe)(Cp’’’Co)(μ,η^4:η^3-P_6Ph_2Me)] (11)

A solution of MeI in dme (0.177 mL, 0.161 mmol, 0.914 mol/L, 1 eq) was added to a stirred solution of **10** (mit 18-c-6) (200 mg, 0.161 mmol, 1 eq) in thf at -80 °C. The color changed from brown-green to dark green. The reaction mixture was warmed to room temperature. The solvent was removed *in vacuo*. The residue was extracted with hexane, filtered over diatomaceous earth and the solvent removed *in vacuo*. The residue was dissolved in CH_2Cl_2, layered with acetonitrile and stored at -30 °C. After a few days, **11** can be obtained as dark green rods. The supernatant was decanted off and the crystals dried *in vacuo*.

Yield: 84 mg (62 %).

^{1}H NMR (C_6D_6, 25 °C): *δ* [ppm] = 7.80 (m, 2H, P_6*Ph*$_2$Me), 7.54 (m, 2H, P_6*Ph*$_2$Me), 7.09 (m, 3H, P_6*Ph*$_2$), 6.89 (m, 3H, P_6*Ph*$_2$), 4.12 (d, ^{3}*J*$_{HH}$ = 2.4 Hz, 1H, C_5*H*$_2$^{t}Bu$_3$), 3.84 (d, ^{3}*J*$_{HH}$ = 2.4 Hz, 1H, C_5*H*$_2$^{t}Bu$_3$), 2.07 (t, ^{3}*J*$_{PH}$ = 6.8 Hz, 3H, P_6Ph_2*Me*), 1.74 (s, 9H, C_5H_2*t*Bu$_3$), 1.62 (s, 15H, C_5*Me*$_5$), 1.39 (s, 9H, C_5H_2*t*Bu$_3$), 1.31 (s, 18H, C_5H_2*t*Bu$_3$).

^{31}P{^{1}H} NMR (C_6D_6, 25 °C): *δ* [ppm] = 199.3 (m, 1P, P_A), 111.7 (m, 1P, P_M), 59.4 (m, 1P, P_N), 28.3 (m, 1P, P_O), -112.4 (m, 1P, P_S) , -246.6 (m, 1P, P_X).

^{31}P NMR (C_6D_6, 25 °C): δ [ppm] = 199.3 (m, 1P, P_A), 111.7 (m, 1P, P_M), 59.4 (m, 1P, P_N), 28.3 (m, 1P, P_O), -112.4 (m, 1P, P_S), -246.6 (m, 1P, P_X).

LIFDI-MS (toluene): *m/z* = 838.2 (100 %, $[M]^+$).

7.4.2. EPR studies

7.4.2.1 [(Cp*Fe)(Cp'''Co)(μ,η^5:η^5-P$_5$)][FAl] (1)

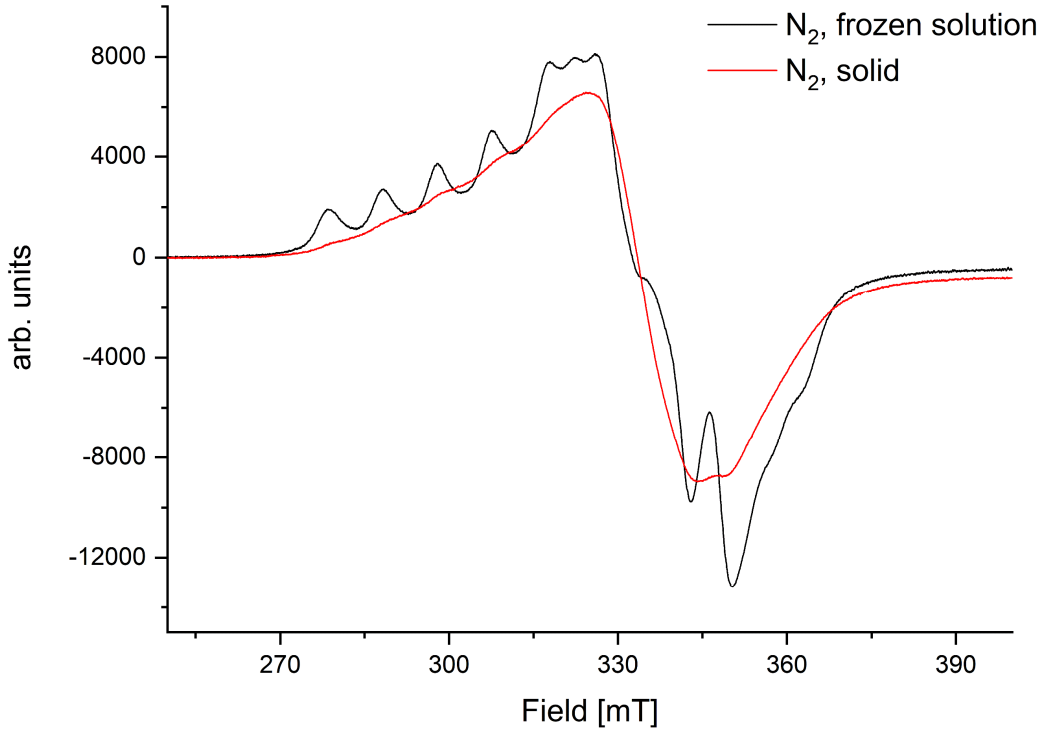


Figure S1: EPR spectra of **1** in solid state and frozen solution (o-$C_6H_4F_2$) at 77 K.

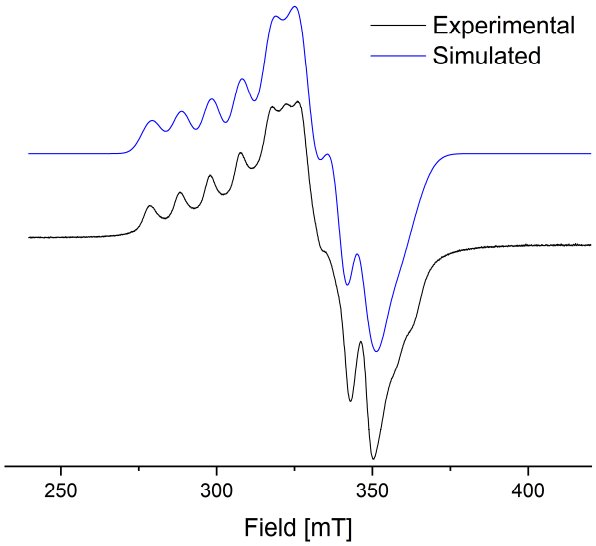


Figure S2: EPR spectra of **1** in solution (o-$C_6H_4F_2$) at 77 K (experimental (black) and simulated (blue). Parameters for the fitting: g_x = 2.155, g_y = 2.035, g_z = 1.948, A_x = 290.125, A_Y = 55.125, A_Z = 120.125.

```
The simulation has been performed with the EasySpin program.[24]
SysCo.Nucs = 'Co';
SysCo.S = 7/2;
SysCo.g = [ 2.15525 2.03525 1.948];
SysCo.lw = [ 5 ];
SysCo.A = [ 290.125 55.125 120.125];
SysCo.HStrain = [ 180.25 150.25 150.25  ];
SysCo.AStrain = [ 40.25 40.25 80.25  ];
Exp.mwFreq = 9.440920;
Exp.Range = [239.6630 420.2450];
Exp.nPoints = 4096;
Exp.Temperature = 77;
Exp.ModAmp = 0.2;
```

7.4.2.2 [(Cp*Fe)(Cp'''Co)(μ,η^5:η^5-As$_5$)][FAl] (2)

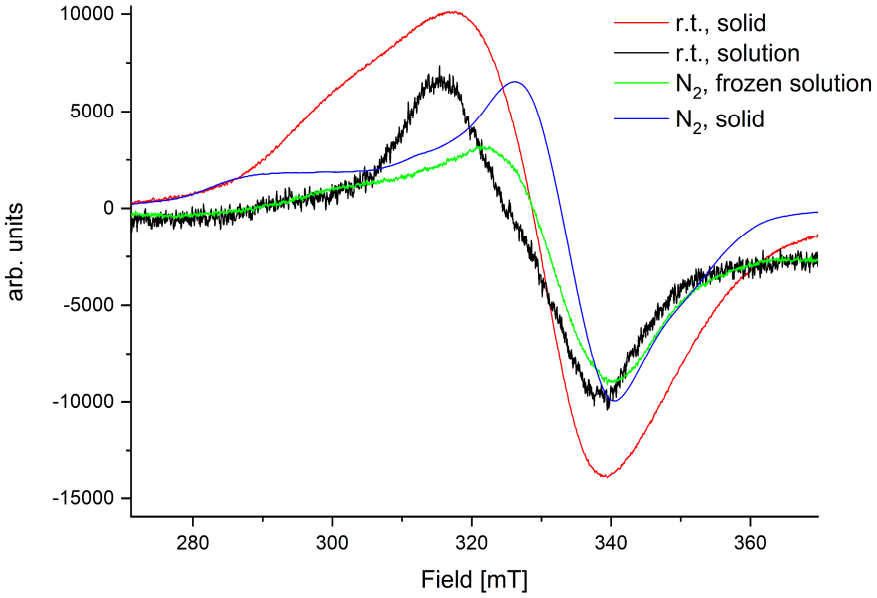


Figure S3: EPR spectra of **2** in solid state (r.t. (red), liquid nitrogen (blue) and in CH_2Cl_2 solution (r.t. (black), fozen solution in liquid nitrogen (green)).

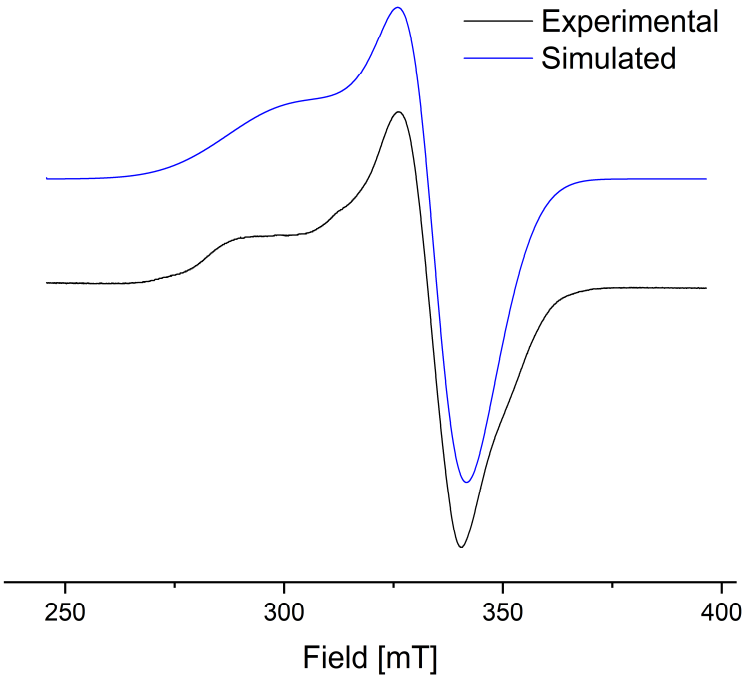


Figure S4: EPR spectra of **2** in solid state at 77 K (experimental (black) and simulated (blue). Parameters for the fitting: g_x = 2.235, g_y = 1.952, g_z = 1.896.

The simulation has been performed with the EasySpin program.[24]
Sys.S = 1/2;
Sys.g = [2.23533 1.9518 1.89552];
SysCo.lw = [20];
Sys.HStrain = [1239 412 639];

Exp.mwFreq = 9.440920;
Exp.Range = [239.6630 420.2450];
Exp.nPoints = 4096;
Exp.Temperature = 77;
Exp.ModAmp = 0.2;

7.4.2.3 [K(18-cr-6)(thf)$_2$][(Cp*Fe)(Cp'''Co)(μ,η^4:η^3-P$_5$)] (5)

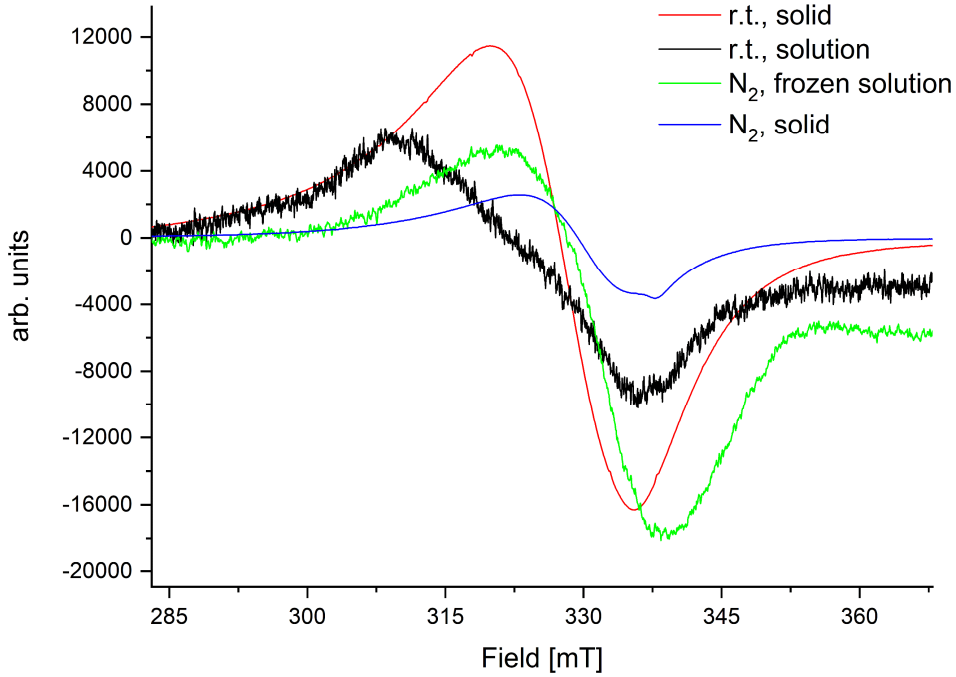


Figure S5: EPR spectra of **5** in solid state (r.t. (red), liquid nitrogen (blue) and in CH_2Cl_2 solution (r.t. (black), frozen solution in liquid nitrogen (green)).

7.4.2.4 [(Cp*Fe)(Cp'''Co)(μ,η^5:η^4-As$_5$)] + KC$_8$ (precipitated crude reaction mixture)

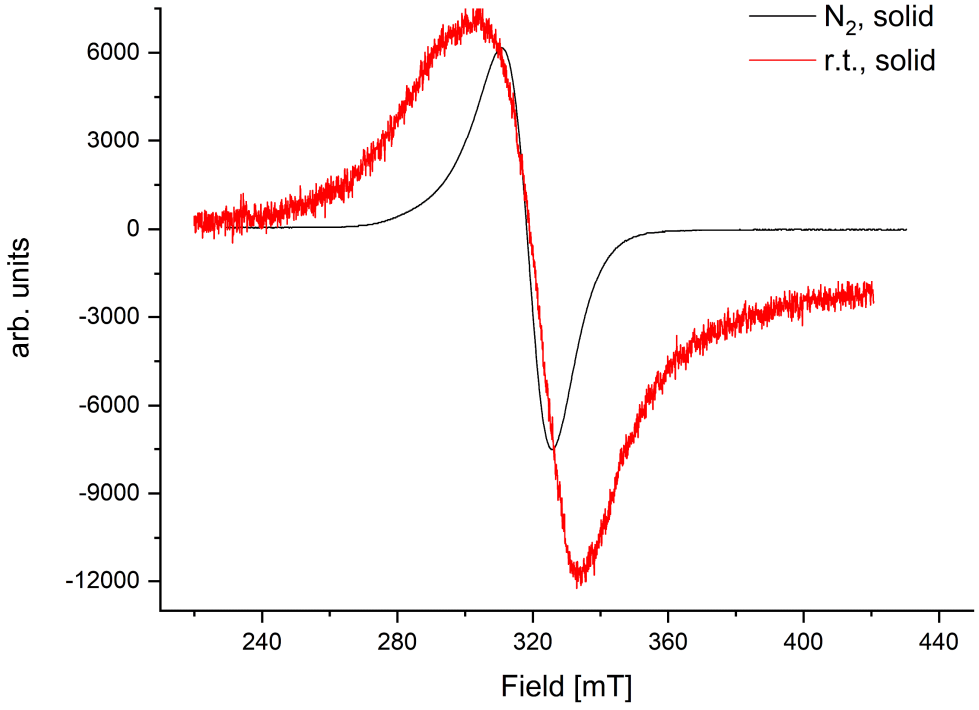


Figure S6: EPR spectra of precipitated solid obtained from the reaction of **B** with KC_8 in solid state (r.t. (black), liquid nitrogen (red).

7.4.3 NMR spectroscopic investigations

7.4.3.1 Reaction of B with KC_8

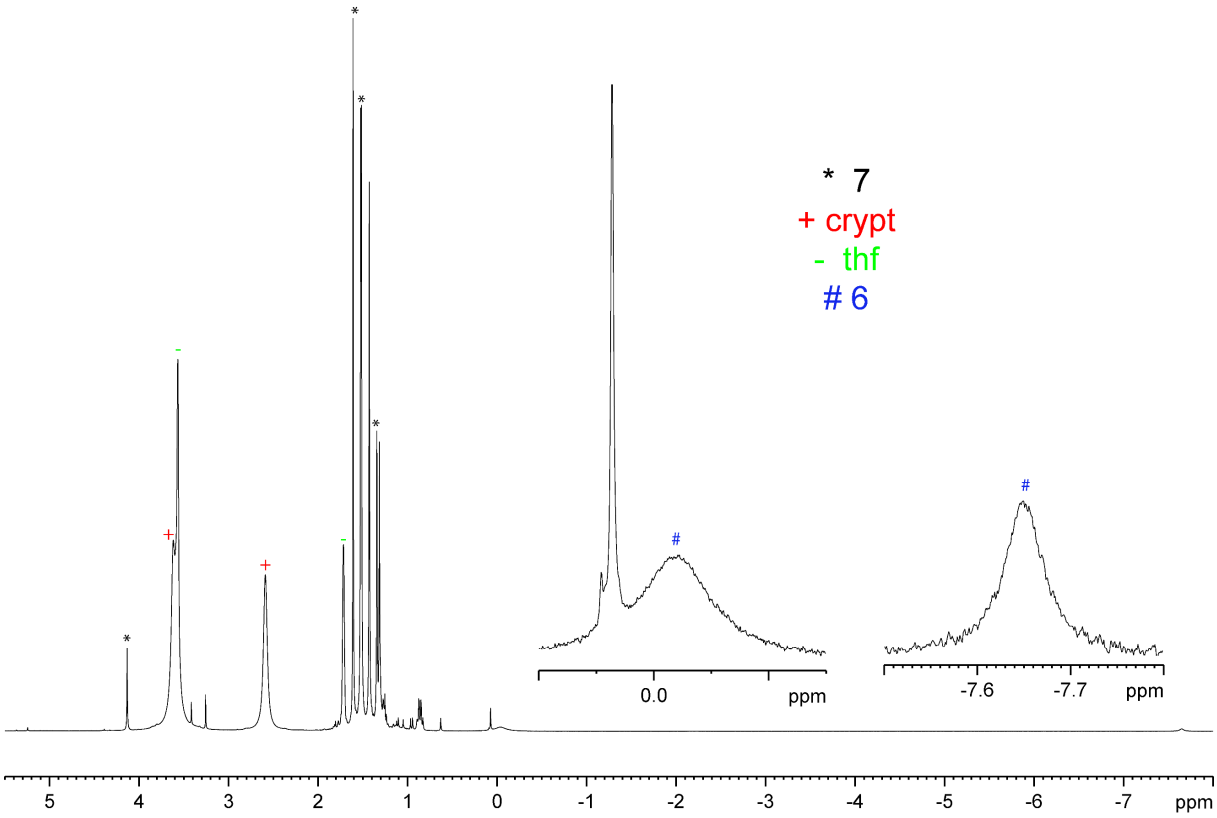


Figure S7: ^{1}H NMR spectrum in thf-d_8 of precipitated solid obtained from the reaction of **B** with KC_8.

7.4.3.2 [K(2,2,2-crypt)][(Cp*Fe)(Cp'''Co)(μ,η⁴:η³-P₆Ph₂)] (10)

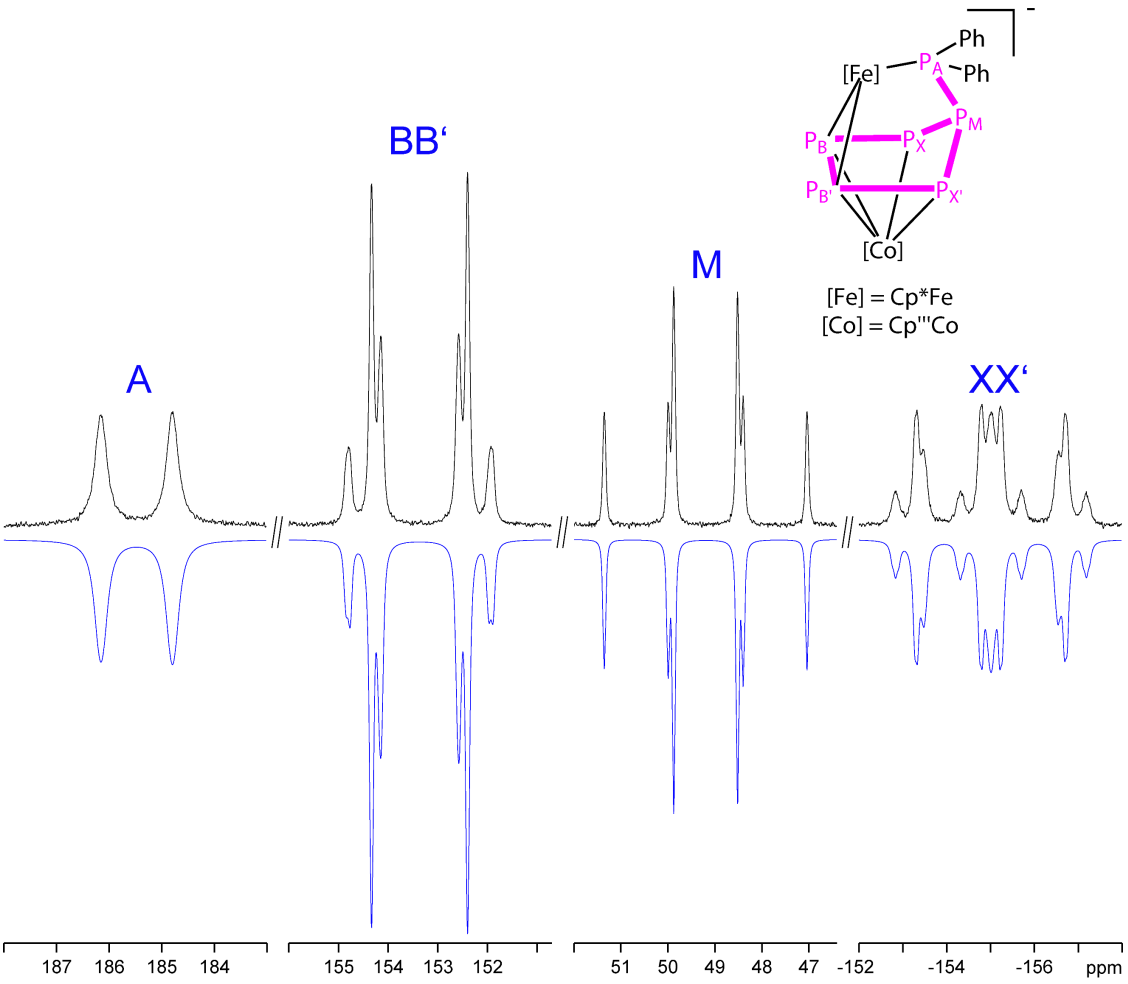


Figure S8: $^{31}P\{^1H\}$ NMR spectrum of **10** in thf-d_8 at room temperature (measured top (black) and simulated bottom (blue)).

Table S1: Coupling constants obtained from the simulation in Figure **S8**.

J [Hz]		δ [ppm]	
$^1J_{P_AP_M}$	220.05	P_A	187.47
$^1J_{P_BP_{B'}}$	105.86	$P_{BB'}$	153.37
$^1J_{P_BP_X} = {}^1J_{P_{B'}P_{X'}}$	328.77	P_M	49.19
$^1J_{P_MP_X} = {}^1J_{P_BP_{X'}}$	239.41	$P_{XX'}$	-155.01
$^2J_{P_AP_X} = {}^2J_{P_AP_{X'}}$	10.51		
$^2J_{P_BP_M} = {}^2J_{P_{B'}P_M}$	4.53		
$^2J_{P_{B'}P_X} = {}^2J_{P_{B'}P_X}$	-15.44		
$^2J_{P_XP_{X'}}$	10.56		
$^3J_{P_AP_B} = {}^3J_{P_AP_{B'}}$	-4.67		
R-factor [%]	0.20		

7.4.3.3 [(Cp*Fe)(Cp'''Co)(μ,η⁴:η³-P₆Ph₂Me)] (11)

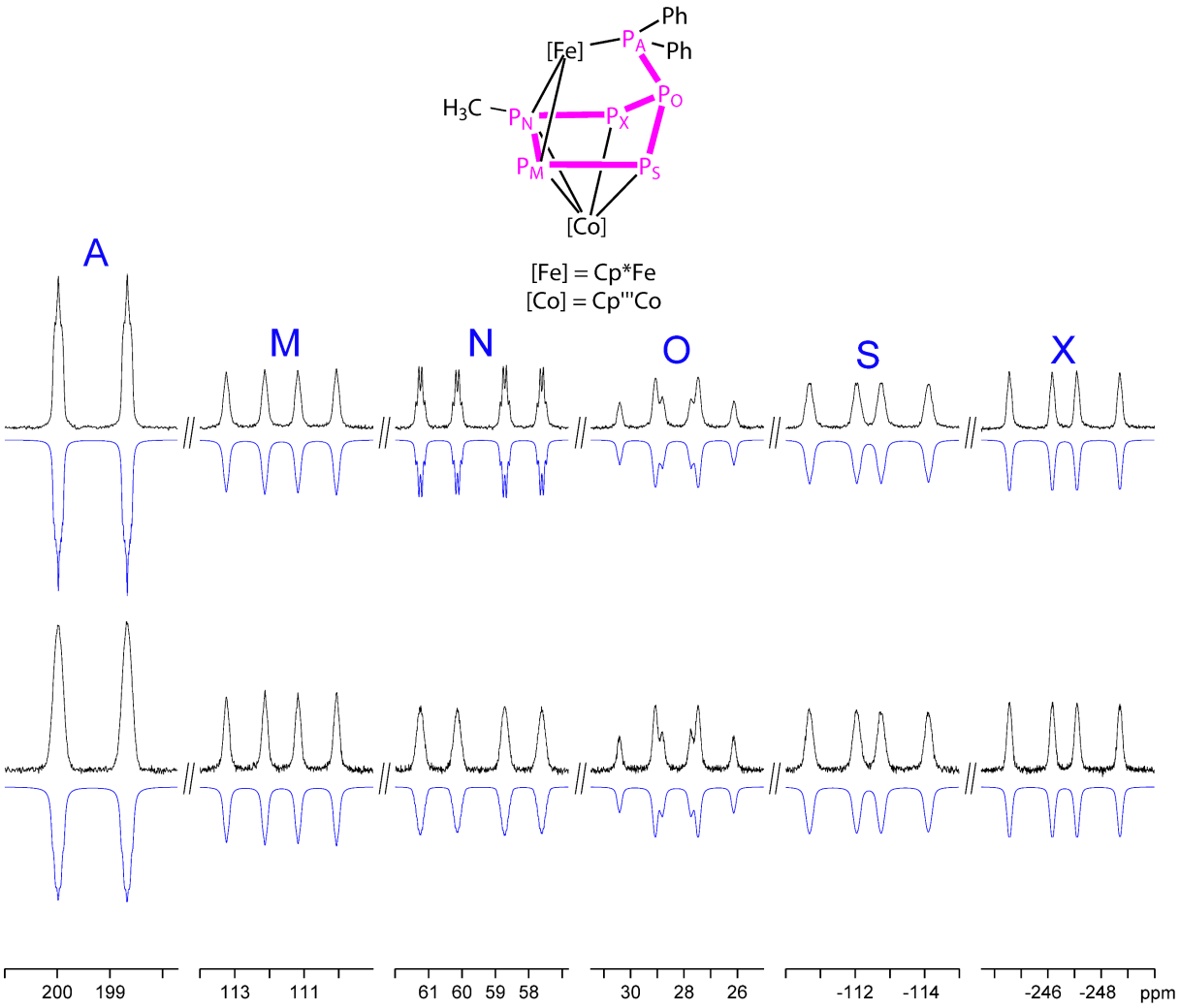


Figure S9: $^{31}P\{^{1}H\}$ (top) and ^{31}P (bottom) NMR spectra of **11** in C_6D_6 at room temperature (measured (black) and simulated (blue)).

Table S2: Coupling constants and chemical shifts obtained from the simulation of the $^{31}P\{^{1}H\}$ NMR spectrum of **11**.

coupling constants [Hz]		chemical shifts [ppm]	
$^{1}J_{P_AP_O}$	212.37	P_A	199.33
$^{1}J_{P_MP_N}$	179.66	P_M	111.65
$^{1}J_{P_MP_S}$	334.31	P_N	59.43
$^{1}J_{P_NP_X}$	409.78	P_O	28.26
$^{1}J_{P_OP_S}$	220.49	P_S	-112.39
$^{1}J_{P_OP_X}$	259.84	P_X	-246.63
$^{2}J_{P_AP_S}$	4.92		
$^{2}J_{P_AP_X}$	9.46	R-factor [%]	0.30
$^{2}J_{P_MP_O}$	12.20		
$^{2}J_{P_MP_X}$	8.98		

$^{2}J_{P_N P_O}$	12.51
$^{2}J_{P_N P_S}$	16.65
$^{2}J_{P_S P_X}$	-12.65
$^{3}J_{P_A P_N}$	15.04

Table S3: Coupling constants and chemical shifts obtained from the simulation of the ^{31}P NMR spectrum of **11**.

coupling constants [Hz]		chemical shifts [ppm]	
$^{1}J_{P_A P_O}$	212.24	P_A	199.33
$^{1}J_{P_M P_N}$	179.63	P_M	111.64
$^{1}J_{P_M P_S}$	334.12	P_N	59.43
$^{1}J_{P_N P_X}$	409.80	P_O	28.27
$^{1}J_{P_O P_S}$	220.30	P_S	-112.39
$^{1}J_{P_O P_X}$	259.98	P_X	-246.63
$^{2}J_{P_A P_S}$	7.64		
$^{2}J_{P_A P_X}$	10.91	R-factor [%]	0.44
$^{2}J_{P_M P_O}$	9.63		
$^{2}J_{P_M P_X}$	-1.91		
$^{2}J_{P_N P_O}$	12.81		
$^{2}J_{P_N P_S}$	17.27		
$^{2}J_{P_S P_X}$	-11.23		
$^{3}J_{P_A P_N}$	16.55		
$^{2}J_{P_N H}$	7.97		
$^{3}J_{P_M H}$	-1.91		
$^{3}J_{P_X H}$	3.97		

7.4.4 Details on single crystal X-ray structure analysis

The X-ray diffraction experiments were performed on either an Gemini Ultra diffractometer (Oxford diffraction) with an AtlasS2 detector Mo radiation (λ = 0.71073 Å) (**4**, **5**, **7**, **8**, **9**) or a GV 50 diffractometer (Rigaku, formerly Agilent Technologies) with TitanS2 detector from applying Cu-K*α* radiation (λ = 1.54178 Å) (**3**, **10**) or Cu-K*β* radiation (λ = 1.39222 Å) (**11**). All measurements were performed at 123 K. Data collection and reduction were performed with CrysAlispro (Version 171.37.34 (**3**), 171.38.43 (**4**, **8**, **10**),171.40.14a (**5**, **7**, **9**, **11**)). For the compounds (**4**, **5**, **8**, **10**) an analytical numeric absorption correction using a multifaceted crystal model based on expressions derived by R.C.Clark & J.S. Reid was applied.[25] For the compounds (**3**, **7**, **9**, **11**) a gaussian absorption correction based on gaussian integration over a multifaceted crystal model was applied. All structures were solved by direct methods with ShelXT[26] and Olex2[27] and refined by full-matrix least-squares method against F^2 in anisotropic approximation using ShelXL[26]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined in calculated positions using riding on pivot atom model.

7.4.4.1 [(Cp*Fe)(Cp'''Co)(μ,η^5:η^5-P$_5$)][FAl] (1)

Compound **1** crystallizes from a concentrated solution in CH_2Cl_2 layered with hexane at -30 °C in the triclinic space group $P\bar{1}$ as dark green blocks. The asymmetric unit contains one cation **1**, one [FAL] counterion and 2.5 molecules CH_2Cl_2. A solvent mask was calculated and 193 electrons were found in a volume of 820 Å^3 in two voids. This is consistent with the presence of 2.5 CH_2Cl_2 per asymmetric unit which account for 210 electrons per unit cell. The structure in solid state is depicted in Figure S10 and S11.

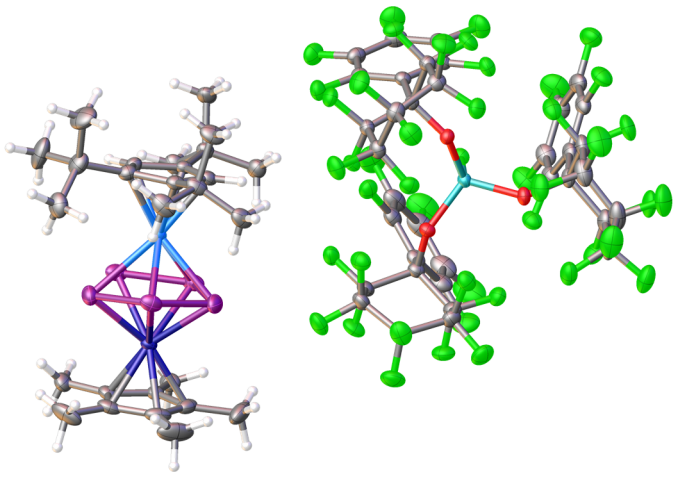


Figure S10: Molecular structure of **1** in the solid state. Thermal ellipsoids are drawn with 50 % probability level.

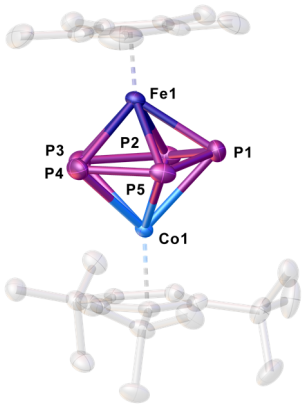


Figure S11: Molecular structure of the cation in **1** in the solid state. Thermal ellipsoids are drawn with 50 % probability level. Selected bond lengths [Å] and angles [°]: Co1-Fe1 3.1539(4), P1-P2 2.1215(9), P2-P3 2.1601(9), P3-P4 2.1226(9), P4-P5 2.1518(9), P1-P5 2.1400(8), P2-P4-P5-P1 9.363, (Cp*-centroid)FeCo(Cp'''-centroid) 176.043.

7.4.4.2 [(Cp*Fe)(Cp'''Co)(μ,η^5:η^5-As$_5$)][FAl] (2)

Compound **2** crystallizes from a concentrated solution in CH_2Cl_2 layered with hexane at -30 °C in the triclinic space group $P\bar{1}$ as dark brown plates. The asymmetric unit contains one cation **1**, one [FAL] counterion and 2.5 molecules CH_2Cl_2. A solvent mask was calculated and 206 electrons were found in a volume of 808 Å^3 in two voids. This is consistent with the presence of five CH_2Cl_2 per unit cell. The structure in solid state is depicted in Figure S12 and S13.

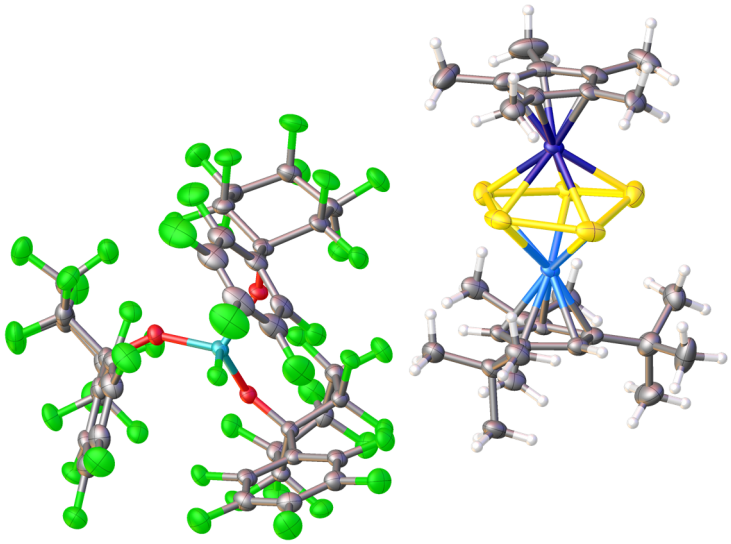


Figure S12: Molecular structure of **2** in the solid state. Thermal ellipsoids are drawn with 50 % probability level.

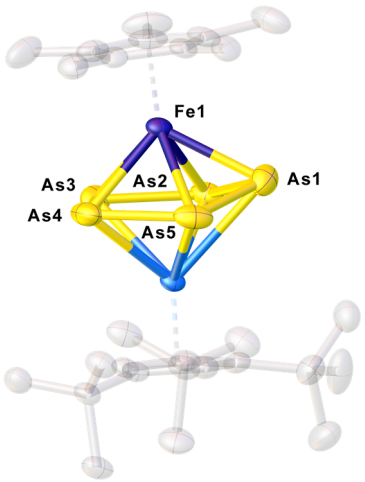


Figure S13: Molecular structure of the cation in **2** in the solid state. Thermal ellipsoids are drawn with 50 % probability level. Selected bond lengths [Å] and angles [°]: Co1-Fe1 3.2188(6), As1-As2 2.3392(7), As2-As3 2.3596(7), As3-As4 2.3252(8), As4-As5 2.3619(8), As1-As5 2.3224(8), As2-As4-As5-As1 13.611, (Cp*-centroid)FeCo(Cp'''-centroid) 174.958.

7.4.4.3 [(Cp*Fe)(Cp'''Co)(μ,η^5:η^5-P$_5$)][FAl]$_2$ (3)

Compound **3** crystallizes from a concentrated solution in *o*-$C_6H_4F_2$ layered with toluene at -30 °C in the monoclinic space group $P2_1$ as dark brown blocks. The asymmetric unit contains one dication **3**, two [FAL] counterions 3 molecules *o*-$C_6H_4F_2$ and 0.5 molecule toluene. The toluene molecule (0.5) share the position with 0.5 molecules *o*-$C_6H_4F_2$. The restraints SADI, SIMU, FLAT were applied to describe the solvent molecules appropriate. The structure in solid state is depicted in Figure S14 and S15.

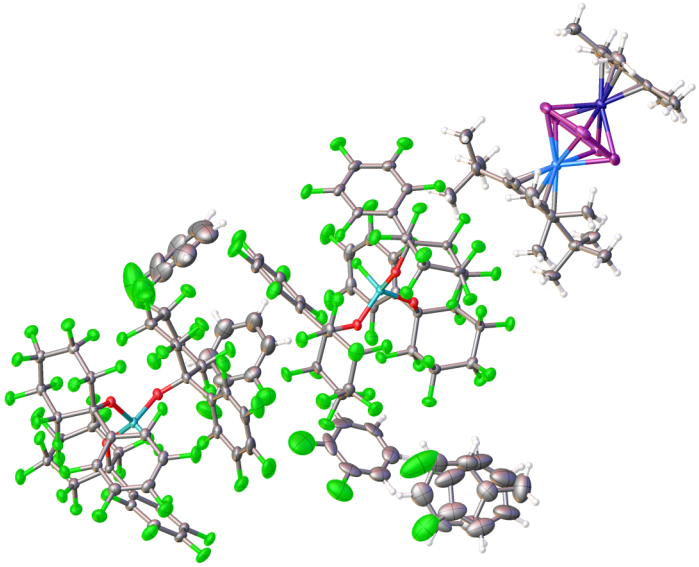


Figure S14: Molecular structure of **3** in the solid state. Thermal ellipsoids are drawn with 50 % probability level.

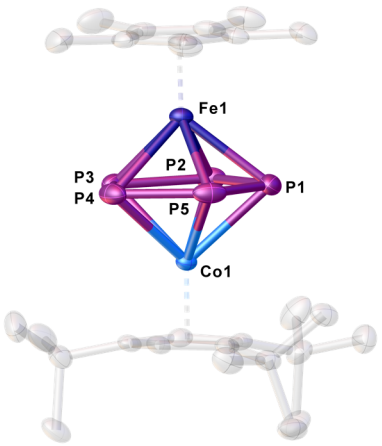


Figure S15: Molecular structure of the dication in **3** in the solid state. Thermal ellipsoids are drawn with 50 % probability level. Selected bond lengths [Å] and angles [°]: Fe1-Co1 3.0637(8), P1-P2 2.1449(12), P2-P3 2.1440(12), P3-P4 2.1439(12), P4-P5 2.1422(13), P1-P5 2.1523(13), P2-P4-P5-P1 -0.841, (Cp*-centroid)FeCo(Cp'''-centroid).

7.4.4.4 [(Cp*Fe)(Cp'''Co)(μ,η^5:η^5-As$_5$)][FAl]$_2$ (4)

Compound **4** crystallizes from a concentrated solution in *o*-$C_6H_4F_2$ layered with toluene at -30 °C in the monoclinic space group $P2_1$ as dark brown blocks. The asymmetric unit contains one dication of **4**, two [FAL] counterions 3.5 molecules *o*-$C_6H_4F_2$. A solvent mask was calculated and 298 electrons were found in a volume of 1198 Å^3 in one void. This is consistent with the presence of seven molecules *o*-$C_6H_4F_2$ per unit cell. A twin refinement (BASF of 0.216) was applied. The structure in solid state is depicted in Figure S16 and S17.

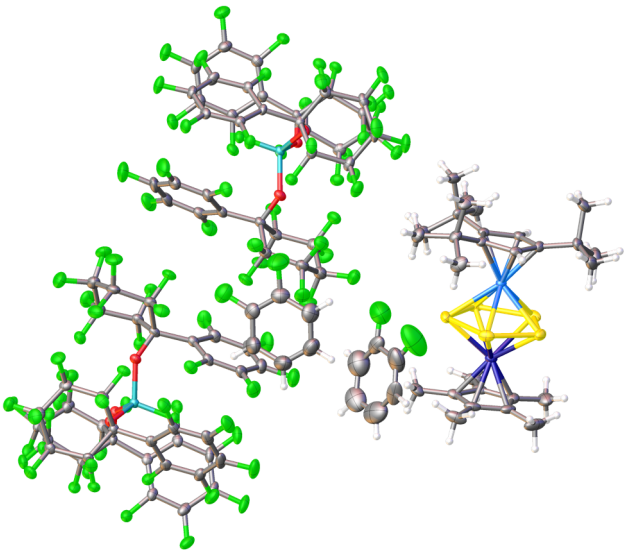


Figure S16: Molecular structure of **4** in the solid state. Thermal ellipsoids are drawn with 50 % probability level.

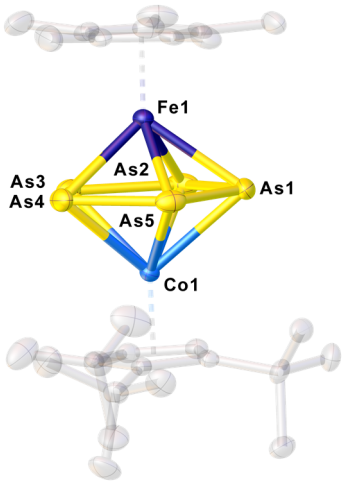


Figure S17: Molecular structure of the dication **4** in the solid state. Thermal ellipsoids are drawn with 50 % probability level. Selected bond lengths [Å] and angles [°]: Fe1-Co1 3.0891(9), As1-As2 2.3518(6), As2-As3 2.3418(6), As3-As4 2.3380(6), As4-As5 2.3493(6), As1-As5 2.3410(7), As2-As4-As5-As1 1.419, (Cp*-centroid)FeCo(Cp'''-centroid) 177.368.

7.4.4.5 [K(18-c-6)(thf)$_2$][(Cp*Fe)(Cp'''Co)(μ,η^4:η^3-P$_5$)] (5a)

Compound **5a** crystallizes from a concentrated solution in thf layered with hexane at -30 °C in the monoclinic space group *C2/c* as dark green blocks. The asymmetric unit contains one anion of **5a**, a potassium counterion chelated by 18-c-6 and two thf molecules and 1.4 thf molecules . Both thf molecules and the Cp* ligand are each disordered over two positions. The restraints SIMU, SADI and ISOR were applied to describe the disorder appropriate. A solvent mask was calculated and 428 electrons were found in a volume of 2668 Å^3 in eight voids. This is consistent with the presence of 11.2 molecules thf per unit cell. The structure in solid state is depicted in Figure S18 and S19.

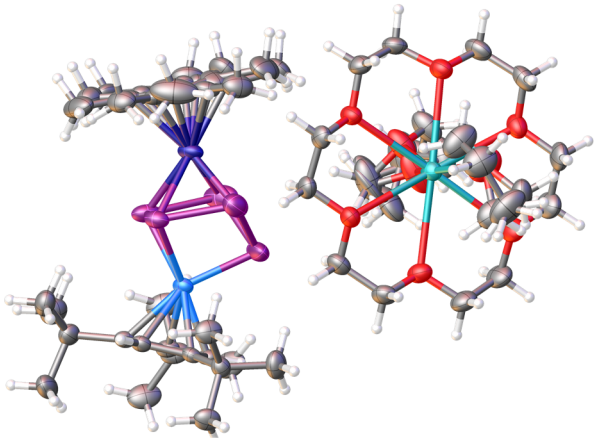


Figure S18: Molecular structure of **5a** in the solid state. Thermal ellipsoids are drawn with 50 % probability level.

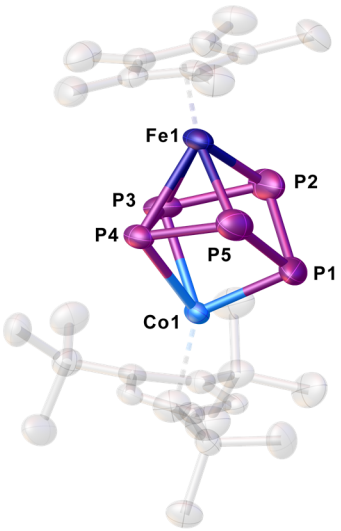


Figure S19: Molecular structure of the anion in **5a** in the solid state. Thermal ellipsoids are drawn with 50 % probability level. Selected bond lengths [Å] and angles [°]: Fe1-Co1 3.6683(7), P1-P2 2.194(2), P2-P3 2.1701(18), P3-P4 2.2285(13), P4-P5 2.1689(15), P1-P5 2.202(2), P2-P4-P5-P1 -43.946, (Cp*-centroid)FeCo(Cp'''-centroid) 156.989.

7.4.4.6 [K(2,2,2-crypt)][(Cp*Fe)(Cp'''Co)(μ,η^4:η^3-P$_5$)] (5b)

Compound **5b** crystallizes from a concentrated solution in dme layered with hexane at -30 °C in the triclinic space group $P\bar{1}$ as dark green blocks. The asymmetric unit contains two anions of **5b**, two potassium counterions chelated by 2,2,2-cryptand and 0.45 molecules hexane. Both cations are disordered over two positions, one anion is disordered over two positions, the Cp* ligand of the other anion is disordered over three positions. The restraints SIMU, SADI and RIGU were applied to describe the disorder appropriate. A solvent mask was calculated and 44 electrons in a void of 152 Å^3 was found. This is consistent with the presence of 0.9 molecules hexane per unit cell. The structure in solid state is depicted in Figure S20 and S21.

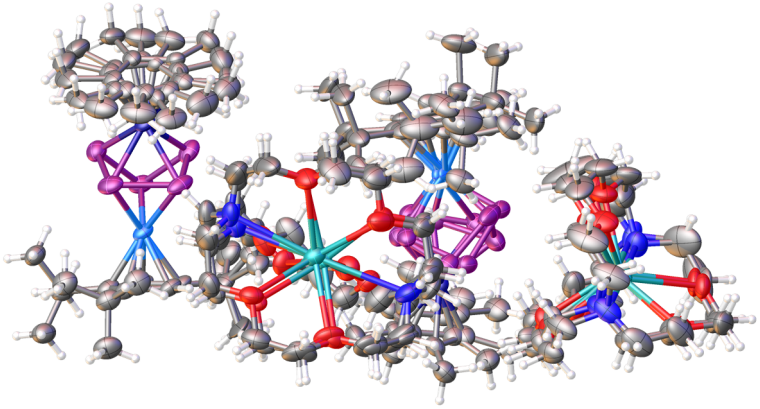


Figure S20: Molecular structure of **5b** in solid state. Thermal ellipsoids are drawn with 50 % probability level.

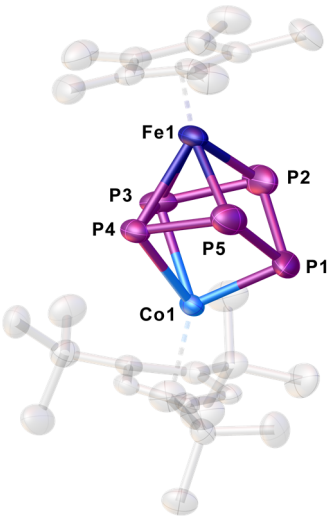


Figure S21: Molecular structure of the non-disordered anion (P_5 ligand) in **5b** in the solid state. Thermal ellipsoids are drawn with 50 % probability level. Selected bond lengths [Å] and angles [°]: Fe1-Co1 3.6620(6), P1-P2 2.1952(9), P2-P3 2.1741(12), P3-P4 2.2456(13), P4-P5 2.1770(12), P1-P5 2.2083(11), P2-P4-P5-P1 -44.456, (Cp*-centroid)FeCo(Cp'''-centroid) 152.772.

7.4.4.7 [K(2,2,2-crypt)][(Cp*Fe)(Cp'''Co)(μ,η⁴:η⁴-As₆)] (7)

Compound **7** crystallizes from a concentrated solution in dme layered with hexane at room temperature in the triclinic space group $P\bar{1}$ as dark brown plates. The asymmetric unit contains one anion of **7** and one potassium ion chelated by 2,2,2-cryptand. The structure in solid state is depicted in Figure S22 and S23.

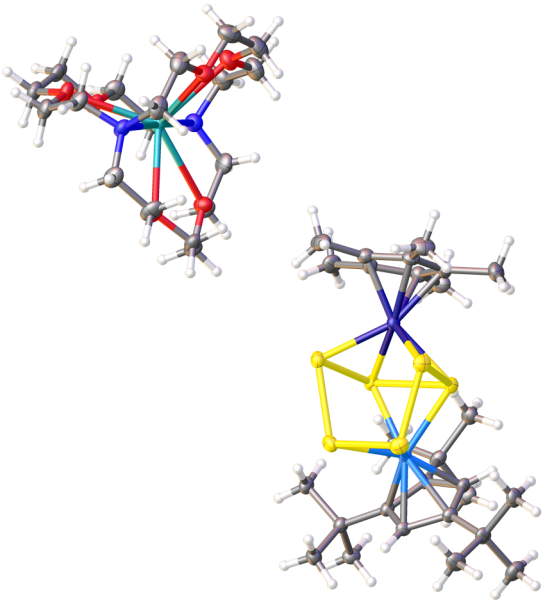


Figure S22: Molecular structure of **7** in solid state. Thermal ellipsoids are drawn with 50 % probability level.

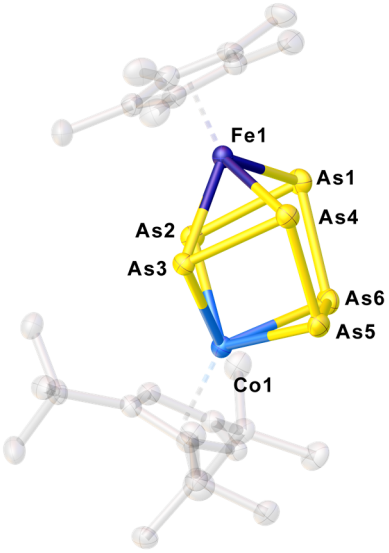


Figure S23: Molecular structure of the anion in **7** in the solid state. Thermal ellipsoids are drawn with 50 % probability level. Selected bond lengths [Å] and angles [°]: Fe1-Co1 3.8385(6), As1-As2 2.3871(5), As2-As3 2.6901(7), As3-As4 2.3843(5), As4-As5 2.4420(5), As5-As6 2.3441(5), As1-As6 2.4406(6), (Cp*-centroid)FeCo(Cp'''-centroid) 129.762.

7.4.4.8 [(Cp*Fe)(Cp'''Co)$_3$(μ_4,η^4:η^2:η^2-P$_4$)(μ_3-P)] (8)

Compound **8** crystallizes from a concentrated solution in CH_2Cl_2 layered with acetonitrile at -30 °C in the monoclinic space group *P2$_1$* as dark brown blocks. The asymmetric unit contains two molecules **8**. One ^{t}Bu group is disordered over two positions. The restraints SADI and SIMU were applied to describe the disorder. The structure in solid state is depicted in Figure S24 and S25.

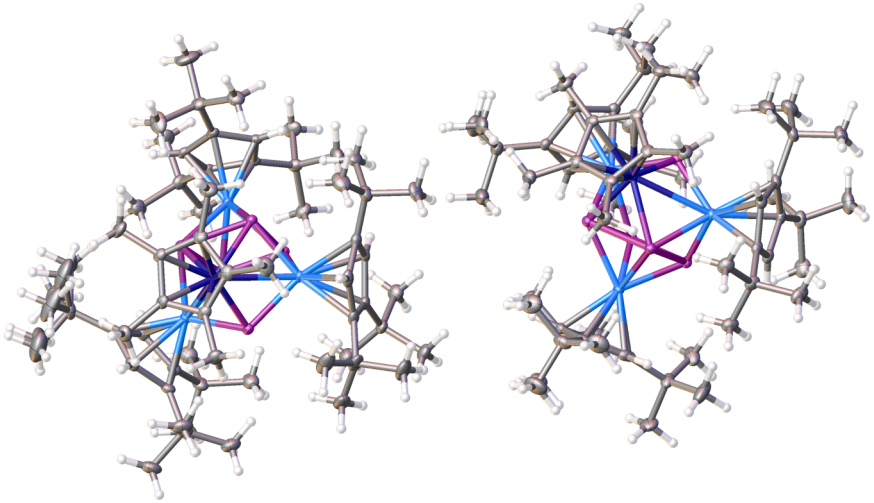


Figure S24: Molecular structure of **8** in the solid state. Thermal ellipsoids are drawn with 50 % probability level.

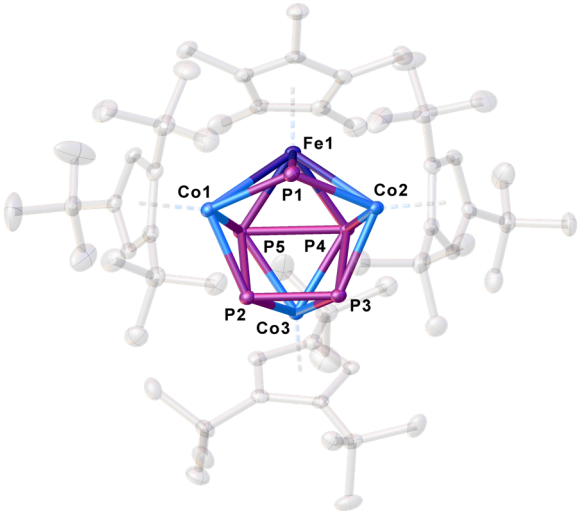


Figure S25: Molecular structure of one independent molecule **8** in the solid state. Thermal ellipsoids are drawn with 50 % probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Fe1-Co1 2.7735(5), Fe1-Co2 2.7638(5), P1-P2 3.1957(9), P1-P3 3.1541(9), P1-P4 3.3057(11), P1-P5 3.3178(9), P2-P3 2.1295(10), P2-P5 2.4726(9), P3-P4 2.5045(9), P4-P5 2.4688(10).

7.4.4.9 [(Cp*Fe)(Cp'''Co)$_3$(μ_4,η^4:η^2:η^2-As$_4$)(μ_3-As)] (9)

Compound **9** crystallizes from a concentrated solution in CH_2Cl_2 layered with acetonitrile at -30 °C in the monoclinic space group *P2$_1$/c* as dark brown blocks. The asymmetric unit contains one molecule **9** and 0.75 molecules toluene. The structure in solid state is depicted in Figure S26 and S27.

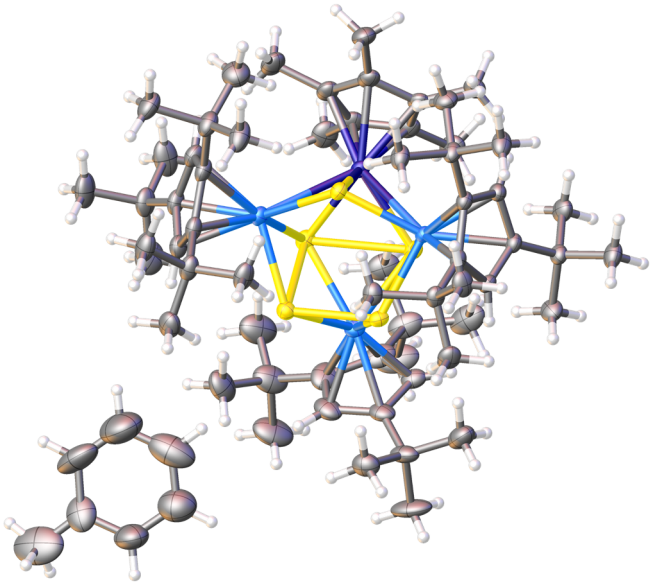


Figure S26: Molecular structure of **9** in the solid state. Thermal ellipsoids are drawn with 50 % probability level.

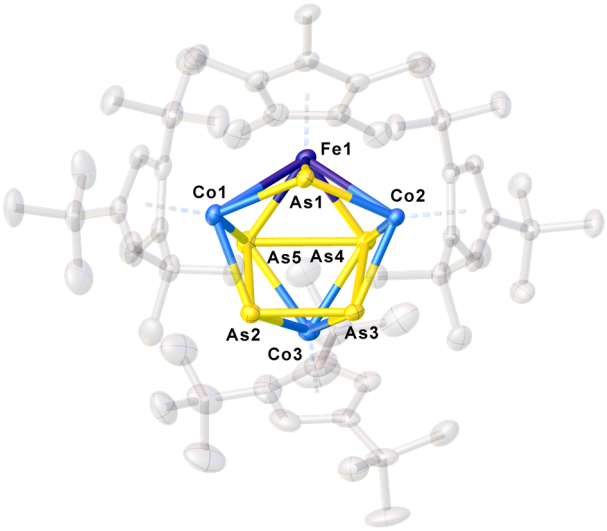


Figure S27: Molecular structure of **9** in the solid state. Thermal ellipsoids are drawn with 50 % probability level. Hydrogen atoms and solvent molecules are omitted for clarity. Selected bond lengths [Å] and angles [°]: Fe1-Co1 2.9006(6), Fe1-Co2 2.9339(5), As1-As2 3.4134(4)), As1-As3 3.3178(4), As1-As4 3.4709(4), As1-As5 3.4989(3), As2-As3 2.3565(4), As2-As5 2.6300(4), As3-As4 2.7097(4), As4-As5 2.7102(4).

7.4.4.10 [K(2,2,2-crypt)][(Cp*Fe)(Cp'''Co)(μ,η^4:η^3-P_6Ph_2)] (10)

Compound **10** crystallizes from a concentrated solution in dme layered with pentane at -30 °C in the triclinic space group $P\bar{1}$ as dark green blocks. The asymmetric unit contains one anion **10**, one potassium counterion chelated by 2,2,2-cryptand and 0.8 dme molecules. The dme molecule is disordered over three positions. A solvent mask was calculated and 56 electrons were found in one void of 422Å^3 per unit cell. This is consistent with the presence of 1.1 molecules dme which account for 55 electrons. The structure in solid state is depicted in Figure S28 and S29.

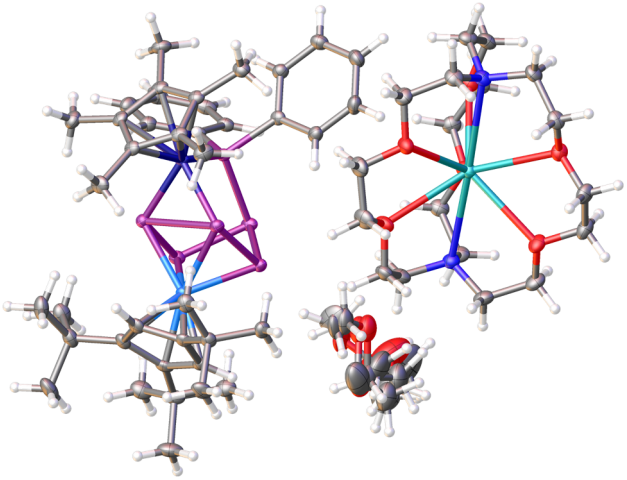


Figure S28: Molecular structure of **10** in the solid state. Thermal ellipsoids are drawn with 50 % probability level.

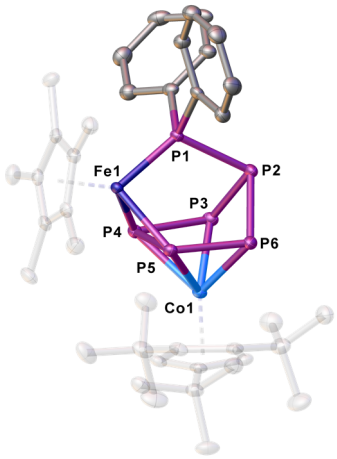


Figure S29: Molecular structure of the anion in **10** in the solid state. Thermal ellipsoids are drawn with 50 % probability level. Hydrogen atoms, counterion and solvent molecules are omitted for clarity. Selected bond lengths [Å] and angles [°]: Co1-Fe1 3.7537(4), P1-P2 2.2429(7), P2-P3 2.2242(7), P2-P6 2.2013(7), P3-P4 2.1634(7), P4-P5 2.5886(7), P5-P6 2.1633(7), P3-P5-P6-P2 46.296, (Cp*-centroid)FeCo(Cp'''-centroid) 104.296.

7.4.4.12 [(Cp*Fe)(Cp'''Co)(μ,η^4:η^3-P$_6$Ph$_2$Me)] (11)

Compound **11** crystallizes from a concentrated solution in CH_2Cl_2 layered with acetonitrile at -30 °C in the monoclinic space group *P2$_1$/c* as dark green rods. The asymmetric unit contains one molecule of **11** and one CH_2Cl_2 molecule. A solvent mask was calculated and 160 electrons were found two voids in a volume of 708 Å^3. This is consistent with the presence of four CH_2Cl_2 molecules per unit cell which account for 168 electrons. The structure in solid state is depicted in Figure S30.

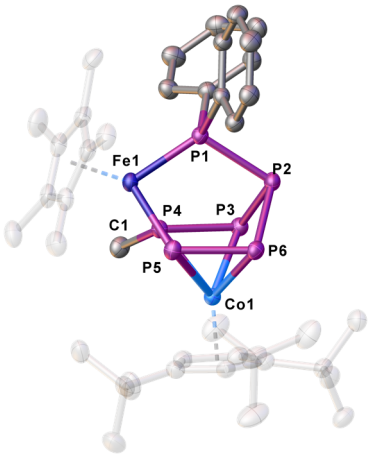


Figure S30: Molecular structure of **11** in the solid state. Thermal ellipsoids are drawn with 50 % probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Co1-Fe1 3.7496(4), P1-P2 2.2368(5), P2-P3 2.2024(5), P2-P6 2.2122(6), P3-P4 2.1534(5), P4-P5 2.5600(5), P5-P6 2.1406(5), P4-C1 1.8357(16) ,P3-P5-P6-P2 43.949, (Cp*-centroid)FeCo(Cp'''-centroid) 114.580.

7.4.4.13 Crystallographic information

Table S4: Crystallographic data for all compounds.

	1	**2**	**3**	**4**	**5 (18-c-6)**	**5 (2,2,2-crypt)**
Formula	$AlC_{63}CoF_{46}FeH_{49}O_3P_5$ · 2.5 CH_2Cl_2	$AlAs_5C_{63}CoF_{46}FeH_{49}O_3$ · 2.5 CH_2Cl_2	$C_{99}H_{44}Al_2CoF_{92}FeO_6P_5$ · 3 $C_6H_4F_2$ + 0.5 C_7H_8	$Al_2As_5C_{99}CoF_{92}FeH_{44}O_6$ · 3.5 $C_6H_4F_2$	$C_{47}CoFeH_{84}KO_8P_5$ · 1.4 C_4H_8O	$C_{90}Co_2Fe_2H_{160}K_2N_4O_{12}P_{10}$ · 0.45 C_6H_{14}
$D_{calc.}$/ g cm^{-3}	1.781	1.934	1.834	1.941	1.277	1.291
μ/mm^{-1}	6.822	8.031	4.219	1.622	6.082	5.113
Formula Weight	2231.90	2451.65	3789.27	4020.00	1215.65	2146.45
Colour	clear dark green	clear dark brown	clear dark brown	dark brown	clear dark green	clear dark green
Shape	block	plate	block	block	block	block
Size/mm^3	0.29×0.16×0.10	0.57×0.46×0.18	0.38×0.31×0.21	0.30×0.22×0.15	0.68×0.22×0.11	0.42×0.31×0.23
T/K	123.00(10)	123	123.01(10)	123(1)	123	123.0(3)
Crystal System	triclinic	triclinic	monoclinic	monoclinic	monoclinic	triclinic
Flack Parameter			0.0062(8)	0.216(4)		
Hooft Parameter			0.0020(6)	0.249(2)		
Space Group	*P*-1	*P*-1	$P2_1$	$P2_1$	*C*2/*c*	*P*-1
a/Å	13.4750(3)	13.4946(4)	17.5277(2)	17.5971(2)	20.8141(3)	16.1521(6)
b/Å	18.3242(3)	18.4836(4)	19.54690(10)	19.5391(2)	19.2297(3)	17.2031(6)
c/Å	19.9317(5)	20.0500(3)	21.7863(2)	21.7687(3)	32.0404(4)	20.0003(6)
α/°	116.796(2)	117.102(2)	90	90	90	86.912(2)
β/°	104.727(2)	104.793(2)	113.1770(10)	113.2570(10)	99.6310(10)	84.332(3)
γ/°	93.3840(10)	93.649(2)	90	90	90	89.021(3)
V/Å^3	4161.88(17)	4209.21(18)	6861.84(12)	6876.57(15)	12643.4(3)	5521.8(3)
Z	2	2	2	2	8	2
Z'	1	1	1	1	1	1
Wavelength/Å	1.54184	1.54184	1.54184	0.71073	1.54184	1.39222
Radiation type	Cu K_α	CuK_α	Cu K_α	MoK_α	Cu K_α	Cu K_β
θ_{min}/°	3.462	3.464	3.555	3.271	3.968	3.380
θ_{max}/°	73.479	72.918	73.712	32.428	72.962	74.590
Measured Refl.	46279	25697	78688	62619	21209	50007
Independent Refl.	16041	16118	27038	39669	12145	29142
Reflections with I > 2(I)	14851	14021	26513	34588	9414	21916
R_{int}	0.0289	0.0361	0.0236	0.0255	0.0295	0.0415
Parameters	1095	1095	2221	1942	731	2134
Restraints	0	0	297	1	267	527
Largest Peak	0.428	1.403	0.583	0.523	0.918	0.701
Deepest Hole	-0.312	-0.889	-0.326	-0.358	-0.477	-0.668
GooF	1.018	1.038	1.053	0.995	1.030	1.021
wR_2 (all data)	0.0929	0.1439	0.0721	0.0830	0.1583	0.1490
wR_2	0.0909	0.1382	0.0716	0.0790	0.1481	0.1327
R_1 (all data)	0.0390	0.0577	0.0271	0.0477	0.0704	0.0725
R_1	0.0360	0.0516	0.0265	0.0392	0.0545	0.0541

	7	**8**	**9**	**10 (18-c-6)**	**10 (2,2,2-crypt)**	**11**
Formula	$C_{45}H_{80}As_6CoFeKN_2O_6$	$C_{122}H_{204}Co_6Fe_2P_{10}$	$C_{68}H_{110}As_5Co_3Fe$	$C_{112}H_{181}Co_2Fe_2K_2O_{17}P_{12}$	$C_{63}CoFeH_{105}KN_2O_9P_6$	$C_{41}H_{59}Cl_2CoFeP_6$
$D_{calc.}$/ g cm^{-3}	1.633	1.282	1.517	1.322	1.265	1.392
μ/mm^{-1}	4.279	1.158	3.420	6.407	5.593	6.695
Formula Weight	1348.51	2445.82	1534.79	2478.96	1374.18	923.38
Colour	clear dark brown	clear dark brown	clear dark black	clear dark green	clear dark green	clear dark green
Shape	plate	block	needle	needle	block	needle
Size/mm^3	0.53×0.23×0.06	0.50×0.23×0.19	0.42×0.12×0.10	0.23×0.05×0.04	0.35×0.28×0.14	0.27×0.08×0.06
T/K	123(1)	123(1)	123(1)	123.0(2)	123.01(10)	123.00(13)
Crystal System	triclinic	monoclinic	monoclinic	monoclinic	triclinic	monoclinic
Flack Parameter		-0.010(3)				
Hooft Parameter		-0.014(3)				
Space Group	*P*-1	$P2_1$	$P2_1/c$	$P2_1/n$	*P*-1	$P2_1/c$
a/Å	10.4742(2)	13.5503(3)	14.05910(10)	21.6225(3)	14.0000(5)	13.2818(2)
b/Å	13.8238(4)	36.9635(5)	20.5359(2)	25.7116(3)	14.0766(5)	20.1996(2)
c/Å	19.3001(4)	14.0766(3)	23.2902(2)	23.0651(3)	19.0799(9)	17.3172(3)
α/°	91.715(2)	90	90	90	83.548(3)	90
β/°	100.138(2)	116.051(3)	91.7020(10)	103.7350(10)	87.970(3)	108.552(2)
γ/°	93.830(2)	90	90	90	74.955(3)	90
V/Å^3	2742.27(11)	6334.2(3)	6721.29(10)	12456.3(3)	3608.2(3)	4404.55(12)
Z	2	2	4	4	2	4
Z'	1	1	1	1	1	1
Wavelength/Å	0.71073	0.71073	0.71073	1.54184	1.54184	1.39222
Radiation type	Mo K_α	Mo K_α	Mo K_α	Cu K_α	Cu K_α	Cu K_β
θ_{min}/°	3.437	3.343	3.291	2.519	3.808	3.132
θ_{max}/°	32.387	32.282	32.286	74.028	75.420	74.449
Measured Refl.	26611	73979	38331	71013	43186	26252
Independent Refl.	17246	38311	21286	24499	13968	11896
Reflections with I > 2(I)	13244	35284	17127	21174	13406	11063
R_{int}	0.0369	0.0270	0.0217	0.0641	0.0185	0.0283
Parameters	573	1355	905	1459	681	529
Restraints	0	25	222	93	0	87
Largest Peak	1.535	0.576	0.640	0.855	0.743	0.806
Deepest Hole	-2.036	-0.302	-0.612	-0.734	-0.540	-0.720
GooF	1.031	1.027	1.025	1.015	1.036	1.056
wR_2 (all data)	0.1349	0.0664	0.0795	0.1330	0.1096	0.0969
wR_2	0.1207	0.0639	0.0733	0.1263	0.1079	0.0947
R_1 (all data)	0.0718	0.0378	0.0517	0.0583	0.0422	0.0383
R_1	0.0518	0.0320	0.0358	0.0500	0.0406	0.0356

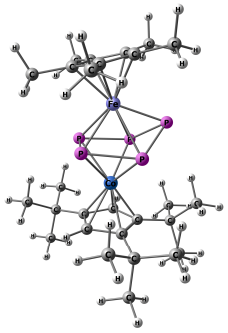
7.4.5 Computational Details

Gaussian 09 program[28] was used throughout. Density functional theory (DFT) in form of or BP86[29] (Becke's exchange and Perdew 86 correlation functional) with def2-TZVP all electron basis set was employed. For solvents effects has been accounted by using continuous polarizable continuum model (CPM).[30] The dielectric constant of dichloromethane (ε = 8.93) has been used in the calculations of the cations (**1**, **2**, **3**, **4**) and the dielectric constant of thf (ε = 7.4257) has been used in the calculations of the anions (**5**, **6**, **7**). The Natural Bond Orbital (NBO) analysis has been performed with the NBO6 program.[31] The long range dispersion correction GD3BJ was applied.[32] The figures for the supporting information concerning the DFT calculations were created with Chemcraft.[33]

Table S5: Total energies for all optimized geometries (BP86/def2-TZVP level of theory).

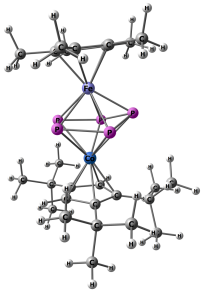
	total energy [Ha]
A [(Cp*Fe)(Cp'''Co)(μ,η^5:η^5-P_5)]	-5410.19002426
B [(Cp*Fe)(Cp'''Co)(μ,η^5:η^5-As_5)]	-14884.0016082
1 [(Cp*Fe)(Cp'''Co)(μ,η^5:η^5-P_5)]$^+$	-5410.03741142
2 [(Cp*Fe)(Cp'''Co)(μ,η^5:η^5-As_5)][FAl]	-14883.8485530
3 [(Cp*Fe)(Cp'''Co)(μ,η^5:η^5-P_5)]$^{2+}$ singlet	-5409.85428357
3 [(Cp*Fe)(Cp'''Co)(μ,η^5:η^5-P_5)]$^{2+}$ triplet	-5409.82485235
4 [(Cp*Fe)(Cp'''Co)(μ,η^5:η^5-As_5)]$^{2+}$ singlet	-14883.6731821
4 [(Cp*Fe)(Cp'''Co)(μ,η^5:η^5-As_5)]$^{2+}$ triplet	-14883.6509294
5 [(Cp*Fe)(Cp'''Co)(μ,η^4:η^3-P_5)]$^-$	-5410.29374369
6 [(Cp*Fe)(Cp'''Co)(μ,η^4:η^3-As_5)]$^-$	-14884.1104474
7 [(Cp*Fe)(Cp'''Co)(μ,η^4:η^4-As_6)]$^-$	-17120.3321848
8 [(Cp*Fe)(Cp'''Co)$_3$(μ$_4$,η^4:η^2:η^2:η^2-P_4)(μ$_3$-P)]	-9507.63354204
9 [(Cp*Fe)(Cp'''Co)$_3$(μ$_4$,η^4:η^2:η^2:η^2-As_4)(μ$_3$-As)]	-18981.4520850
10 [(Cp*Fe)(Cp'''Co)(μ,η^4:η^3-P_6Ph_2)]$^-$	-6215.26886391
11 [(Cp*Fe)(Cp'''Co)(μ,η^4:η^3-P_6Ph_2Me)]	-6255.08738192

Table S6: Optimized geometries of **A** (left) and **B** (right). XYZ coordinated in angstroms. BP86/def2-TZVP level of theory.



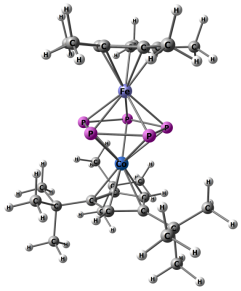
Co	-0.983296000	0.225091000	-0.031174000	H	3.070522000	3.035374000	1.166298000		As	0.218197000	-1.641108000	0.759689000	H	-4.177526000	4.760593000	-0.150567000
Fe	2.282592000	-0.126427000	-0.018176000	H	4.610793000	2.667568000	1.977758000		As	0.373061000	0.636106000	1.757517000	H	-4.459341000	3.368772000	0.928986000
P	0.813077000	1.679508000	-0.291484000	H	3.078717000	2.039979000	2.631379000		As	0.349524000	-1.072017000	-1.525797000	C	-2.651206000	-0.961381000	3.210191000
P	0.331130000	-1.493644000	0.731881000	C	-2.143537000	-2.932490000	-1.578560000		As	0.536610000	1.388256000	-1.333869000	H	-1.573971000	-1.131931000	3.072216000
P	0.664404000	0.590882000	1.548140000	H	-1.133499000	-2.632715000	-1.885458000		As	1.817854000	2.120171000	0.554794000	H	-2.992496000	-1.594425000	4.042867000
P	1.360171000	-1.879705000	-1.140956000	H	-2.484978000	-3.731146000	-2.255674000		Co	-1.170987000	0.200117000	-0.068434000	H	-2.794281000	0.082773000	3.516114000
P	0.484612000	0.001280000	-1.775707000	H	-2.068840000	-3.350080000	-0.572870000		Fe	2.152226000	-0.227617000	-0.002321000	C	-4.943733000	-1.042623000	2.211424000
C	-2.555449000	1.689945000	-0.108888000	C	3.696548000	2.169504000	-1.474625000		C	-3.059296000	-0.577745000	-0.692111000	H	-5.098919000	0.022547000	2.437289000
C	-2.652573000	0.913954000	1.073854000	H	3.556278000	1.926677000	-2.451563000		C	-2.791699000	0.733089000	-1.229309000	H	-5.291531000	-1.632005000	3.074426000
H	-2.606830000	1.315533000	2.080018000	H	5.034737000	2.501813000	-1.642332000		H	-2.710235000	0.962453000	-2.285441000	H	-5.570643000	-1.296897000	1.345868000
C	-2.795670000	-0.588706000	-0.702867000	H	3.433282000	3.017133000	-1.061693000		C	-3.036203000	-0.436688000	0.759963000	C	-2.642238000	3.207070000	-0.296528000
C	-2.617508000	0.759018000	-1.188397000	C	-4.566464000	-2.189031000	-1.457328000		C	3.312545000	-1.941421000	-0.325148000	C	-2.607740000	-3.006328000	-1.497998000
H	-2.532349000	1.030378000	-2.234236000	H	-4.714739000	-2.653055000	-0.474826000		C	-2.768705000	0.955718000	1.028110000	H	-1.584947000	-2.815335000	-1.850118000
C	3.956822000	0.990048000	-0.558084000	H	-4.847312000	-2.928279000	-2.223594000		H	-2.704112000	1.388471000	2.020604000	H	-3.041359000	-3.798510000	-2.128349000
C	-2.564140000	3.201767000	-0.202736000	H	-5.255479000	-1.334357000	-1.535269000		C	-2.645605000	1.695673000	-0.180689000	H	-2.535066000	-3.386145000	-0.478195000
C	-2.806005000	-0.485606000	0.759066000	C	4.424248000	-0.855469000	-2.336966000		C	-3.446529000	-1.331816000	1.938338000	C	4.681356000	1.462836000	-1.187625000
C	4.138707000	-0.380228000	-0.948578000	H	4.107918000	-1.896927000	-2.476533000		C	3.642883000	-0.918524000	-1.282624000	H	4.114774000	1.748633000	-2.085030000
C	3.825855000	-0.329126000	1.358544000	H	5.504390000	-0.793531000	-2.552583000		C	3.545261000	-1.410659000	0.992995000	H	5.728415000	1.293810000	-1.492301000
C	3.787480000	1.025446000	0.871005000	H	3.898489000	-0.243842000	-3.083042000		C	4.118068000	0.227160000	-0.560146000	H	4.660299000	2.313977000	-0.495273000
C	-3.164802000	-1.443491000	1.903449000	C	-1.807422000	3.833017000	0.978148000		C	-3.462912000	-1.731494000	-1.623106000	C	3.379906000	-2.143924000	2.284668000
C	-3.105693000	-1.734770000	-1.675567000	H	-2.248434000	3.540502000	1.942150000		C	4.061977000	-0.079319000	0.848275000	H	3.083342000	-1.463579000	3.094644000
C	-2.400349000	-1.059437000	3.190901000	H	-1.850566000	4.930688000	0.910174000		C	-3.254175000	-2.841298000	1.743950000	H	4.324055000	-2.631755000	2.581154000
H	-1.313610000	-1.137603000	3.046403000	H	-0.751453000	3.526896000	0.979633000		H	-3.894153000	-3.252333000	0.955608000	H	2.608685000	-2.922242000	2.208052000
H	-2.687244000	-1.753326000	3.997698000	C	4.287637000	-2.672055000	0.315377000		H	-3.516093000	-3.357681000	2.679889000	C	-3.341155000	-1.286879000	-3.096711000
H	-2.632194000	-0.043178000	3.534886000	H	3.669780000	-3.131519000	1.099350000		H	-2.205296000	-3.075738000	1.511722000	H	-4.021112000	-0.456247000	-3.335846000
C	4.065025000	-1.195477000	0.237492000	H	5.343472000	-2.886680000	0.552784000		C	-4.952649000	-2.057540000	-1.371850000	H	-3.603244000	-2.132168000	-3.749483000
C	-4.679370000	-1.255437000	2.167587000	H	4.043500000	-3.166570000	-0.633124000		H	-5.121894000	-2.476443000	-0.372749000	H	-2.311928000	-0.982715000	-3.339051000
H	-4.902344000	-0.211392000	2.431901000	C	-3.002729000	-1.230706000	-3.131498000		H	-5.305158000	-2.794605000	-2.110016000	C	4.564107000	0.769721000	1.972751000
H	-4.998836000	-1.899544000	3.001840000	H	-3.732425000	-0.436903000	-3.348535000		H	-5.569065000	-1.151027000	-1.467477000	H	4.604031000	1.830005000	1.693835000
H	-5.278171000	-1.514145000	1.283473000	H	-3.206599000	-2.068550000	-3.814303000		C	3.600170000	-1.048645000	-2.770961000	H	5.579626000	0.452386000	2.265809000
C	-1.950980000	3.684807000	-1.527262000	H	-1.992730000	-0.855527000	-3.356241000		H	2.858864000	-1.794221000	-3.088858000	H	3.918278000	0.682556000	2.857775000
H	-0.901275000	3.370807000	-1.617555000	C	-4.046880000	3.642638000	-0.147775000		H	4.582783000	-1.360507000	-3.163889000	C	-1.740527000	3.839511000	0.774826000
H	-1.988041000	4.783539000	-1.577704000	H	-4.617599000	3.202522000	-0.979082000		H	3.333795000	-0.094276000	-3.245717000	H	-2.059639000	3.557478000	1.788853000
H	-2.503837000	3.293583000	-2.394036000	H	-4.122275000	4.739147000	-0.218466000		C	2.880947000	-3.333696000	-0.647406000	H	-1.780244000	4.937134000	0.704675000
C	-2.882974000	-2.932985000	1.666229000	H	-4.516063000	3.323260000	0.794463000		H	2.271227000	-3.766329000	0.158016000	H	-0.698182000	3.516283000	0.648667000
H	-3.469742000	-3.349787000	0.840877000	C	3.697638000	-0.758436000	2.784171000		H	3.760318000	-3.983319000	-0.791429000	C	-2.195883000	3.672038000	-1.690259000
H	-3.152095000	-3.492964000	2.574792000	H	3.032826000	-0.087079000	3.344980000		H	2.280479000	-3.370837000	-1.567546000	H	-1.161093000	3.366464000	-1.903662000
H	-1.815603000	-3.106393000	1.470697000	H	4.679808000	-0.761211000	3.286056000		C	-4.104412000	3.664737000	-0.069195000	H	-2.246903000	4.769456000	-1.751896000
C	3.626419000	2.253887000	1.703568000	H	3.278337000	-1.771035000	2.855719000		H	-4.776777000	3.217193000	-0.816574000	H	-2.843444000	3.262073000	-2.479495000

Table S7: Optimized geometries of **1** (left) and **2** (right). XYZ coordinated in angstroms. BP86/def2-TZVP level of theory.

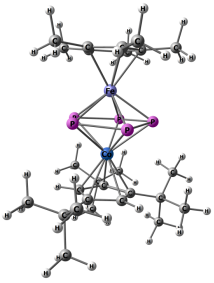


Fe	2.228631000	-0.103493000	-0.010914000	H	-3.164172000	-3.606241000	2.397351000		As	0.337492000	-0.434764000	1.875125000	C	-3.446975000	-1.654166000	-1.667212000
Co	-0.910362000	0.209971000	-0.006155000	H	-1.808083000	-3.203778000	1.328804000		As	0.292486000	-1.866791000	-0.066982000	C	-2.777673000	-1.459187000	-3.044573000
P	0.411708000	-1.627342000	0.637800000	C	-2.376695000	-1.224758000	3.146323000		As	0.484509000	-0.378940000	-1.912096000	H	-2.989527000	-0.478783000	-3.489398000
P	0.630542000	0.793386000	-1.674084000	H	-1.290709000	-1.345434000	3.029520000		As	0.629608000	1.796550000	-0.924031000	H	-3.161825000	-2.221767000	-3.736974000
P	0.885192000	1.780883000	0.263427000	H	-2.710898000	-1.935999000	3.914804000		As	1.324715000	1.659474000	1.346595000	H	-1.687788000	-1.583685000	-2.977655000
P	0.947022000	-1.324873000	-1.432516000	H	-2.574631000	-0.215949000	3.528957000		Co	-1.100400000	0.193222000	-0.049883000	C	-4.974646000	-1.467834000	-1.862024000
P	0.699841000	0.236270000	1.749090000	C	-2.182939000	-2.863134000	-1.736919000		Fe	2.118063000	-0.164277000	-0.031201000	H	-5.525840000	-1.588018000	-0.921087000
C	-2.586765000	0.864586000	1.125424000	H	-1.208839000	-2.599661000	-2.170434000		C	-3.004201000	-0.566356000	-0.682382000	H	-5.347695000	-2.214432000	-2.579156000
H	-2.535219000	1.215562000	2.149641000	H	-2.618411000	-3.661654000	-2.355925000		C	-2.927494000	-0.477303000	0.777516000	H	-5.194997000	-0.466591000	-2.259861000
C	-2.547581000	0.797886000	-1.145722000	H	-2.004091000	-3.265088000	-0.737699000		C	-2.677366000	0.914795000	1.094347000	C	-3.155961000	-3.101572000	-1.248609000
H	-2.482133000	1.121471000	-2.178263000	C	-3.996644000	3.574255000	-0.246725000		H	-2.581898000	1.308416000	2.099336000	H	-2.079922000	-3.258540000	-1.082120000
C	-2.751146000	-0.521812000	0.737810000	H	-4.392537000	3.166260000	-1.188115000		C	-2.617109000	1.692670000	-0.087744000	H	-3.467104000	-3.774023000	-2.061214000
C	-2.476057000	1.687379000	-0.013342000	H	-4.100636000	4.669215000	-0.273400000		C	-2.761236000	0.760039000	-1.169514000	H	-3.700512000	-3.406484000	-0.349351000
C	-2.777651000	-0.550809000	-0.730484000	H	-4.604649000	3.185606000	0.582728000		H	-2.726863000	1.035404000	-2.217773000	C	-3.287373000	-1.461765000	1.902769000
C	-2.503043000	3.198538000	-0.061013000	C	-3.119637000	-1.639866000	-1.753992000		C	3.592936000	-1.508869000	0.577848000	C	-4.775125000	-1.847919000	1.724398000
C	3.987265000	-0.397474000	-1.113584000	C	-4.640656000	-1.311918000	2.084017000		C	3.928573000	-0.183325000	1.021693000	H	-5.401311000	-0.951416000	1.607249000
C	3.993308000	0.902274000	-0.495017000	H	-4.839303000	-0.280478000	2.408527000		C	4.041913000	0.661242000	-0.141344000	H	-5.116943000	-2.391818000	2.617277000
C	4.117893000	2.206306000	-1.209517000	H	-4.977874000	-1.995564000	2.877293000		C	3.780065000	-0.144150000	-1.302331000	H	-4.937425000	-2.495756000	0.855953000
H	3.656409000	2.163138000	-2.204801000	H	-5.236733000	-1.506489000	1.183162000		C	3.517112000	-1.488541000	-0.859309000	C	-2.415644000	-2.729466000	1.989931000
H	5.180804000	2.464673000	-1.342737000	C	-4.585734000	-2.075420000	-1.523653000		C	3.437474000	-2.705218000	1.457201000	H	-2.266035000	-3.226247000	1.029295000
H	3.643890000	3.022666000	-0.648994000	H	-4.717877000	-2.614120000	-0.578455000		H	4.423955000	-3.145124000	1.676421000	H	-2.893231000	-3.446309000	2.674487000
C	3.887433000	-1.385283000	-0.070595000	H	-4.898937000	-2.745943000	-2.337755000		H	2.824120000	-3.481711000	0.980888000	H	-1.426594000	-2.491751000	2.404888000
C	-3.124920000	-1.529706000	1.829739000	H	-5.256454000	-1.203685000	-1.517812000		H	2.967148000	-2.441171000	2.414274000	C	-3.172972000	-0.766918000	3.277376000
C	3.914284000	0.716715000	0.929832000	C	-3.039430000	-1.060984000	-3.183097000		C	4.208399000	0.205164000	2.436349000	H	-2.152986000	-0.399914000	3.467070000
C	-1.990413000	3.810619000	1.251427000	H	-3.765264000	-0.251090000	-3.344725000		H	4.100721000	1.286433000	2.593514000	H	-3.411910000	-1.498642000	4.062060000
H	-2.600355000	3.494326000	2.109621000	H	-3.266267000	-1.861474000	-3.901371000		H	5.241797000	-0.071535000	2.701854000	H	-3.875303000	0.072762000	3.376842000
H	-2.038421000	4.907432000	1.193321000	H	-2.031055000	-0.685125000	-3.412294000		H	3.536312000	-0.310971000	3.135694000	C	-2.698186000	3.202808000	-0.168754000
H	-0.946112000	3.525223000	1.444953000	C	3.890210000	-2.867107000	-0.249258000		C	4.444072000	2.098942000	-0.156287000	C	-2.323724000	3.725570000	-1.563562000
C	-1.703709000	3.757092000	-1.250047000	H	3.258517000	-3.362987000	0.500046000		H	3.962062000	2.643655000	-0.979278000	H	-1.288548000	3.466502000	-1.831077000
H	-0.627016000	3.567182000	-1.138299000	H	4.914049000	-3.257548000	-0.133218000		H	5.534444000	2.183342000	-0.292578000	H	-2.412063000	4.821227000	-1.584159000
H	-1.847924000	4.845526000	-1.310106000	H	3.531593000	-3.158126000	-1.244865000		H	4.184038000	2.603195000	0.783779000	H	-2.990223000	3.320977000	-2.338657000
H	-2.032831000	3.323855000	-2.205138000	C	3.947681000	1.796482000	1.958721000		C	3.868495000	0.315592000	-2.720391000	C	-4.191481000	3.532624000	0.097029000
C	3.832740000	-0.696405000	1.191293000	H	3.544288000	2.740795000	1.569262000		H	3.226310000	-0.279473000	-3.383367000	H	-4.841337000	3.029634000	-0.633808000
C	4.119423000	-0.659446000	-2.576931000	H	4.986747000	1.981945000	2.274760000		H	4.904630000	0.214840000	-3.082708000	H	-4.349962000	4.618185000	0.014471000
H	3.697666000	-1.633599000	-2.855192000	H	3.372024000	1.521645000	2.852583000		H	3.580867000	1.370305000	-2.824245000	H	-4.492144000	3.212277000	1.104884000
H	5.183323000	-0.657735000	-2.863836000	C	3.777438000	-1.338878000	2.537214000		C	3.289458000	-2.669891000	-1.742071000	C	-1.841774000	3.892949000	0.904512000
H	3.613933000	0.114417000	-3.170312000	H	3.272624000	-0.698564000	3.272861000		H	2.670920000	-3.433227000	-1.251422000	H	-2.055904000	3.505190000	1.910533000
C	-2.873370000	-3.010859000	1.519687000	H	4.799142000	-1.527141000	2.905140000		H	4.254920000	-3.136411000	-1.996207000	H	-2.053742000	4.972106000	0.907786000
H	-3.457296000	-3.377643000	0.669714000	H	3.252802000	-2.302709000	2.505345000		H	2.799461000	-2.388028000	-2.683442000	H	-0.768986000	3.759080000	0.711732000

Table S8: Optimized geometries of **3** (singlet, left) and **3** (triplet, right). XYZ coordinated in angstroms. BP86/def2-TZVP level of theory.

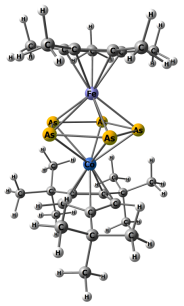


Co	-0.852881000	0.229224000	0.016424000	H	-4.305548000	3.114709000	1.213700000
Fe	2.143114000	-0.086706000	-0.002543000	C	-3.093359000	-1.553775000	-1.793196000
P	0.661039000	0.086404000	-1.831984000	C	-2.896993000	-3.041712000	-1.479969000
P	0.905042000	1.811094000	-0.542054000	H	-1.837015000	-3.284005000	-1.318763000
P	0.488127000	-1.669329000	-0.572277000	H	-3.234342000	-3.621685000	-2.350097000
P	0.788672000	1.139761000	1.511783000	H	-3.477711000	-3.383882000	-0.618163000
P	0.599806000	-1.014777000	1.492317000	C	4.129881000	1.361030000	2.125677000
C	-2.679714000	-0.550329000	0.753998000	H	3.797235000	2.386816000	1.922523000
C	-3.028755000	-1.618783000	1.789412000	H	5.202376000	1.405437000	2.375648000
C	-2.391392000	1.682078000	0.022253000	H	3.600985000	0.992186000	3.014094000
C	3.936596000	0.468113000	0.946352000	C	-2.447282000	3.186947000	0.024926000
C	-2.689802000	-0.547492000	-0.716315000	C	-4.607911000	-1.268992000	-2.017221000
C	-2.468261000	0.820474000	-1.130150000	H	-5.197983000	-1.444015000	-1.109672000
H	-2.398266000	1.157623000	-2.141113000	H	-4.975185000	-1.941176000	-2.805831000
C	-2.459430000	0.815701000	1.157695000	H	-4.772739000	-0.232078000	-2.341709000
H	-2.381485000	1.143499000	2.188399000	C	-2.002082000	3.779456000	-1.320286000
C	-2.179526000	-2.905515000	1.735669000	H	-0.957760000	3.523944000	-1.552269000
H	-1.969460000	-3.254717000	0.723518000	H	-2.076047000	4.874396000	-1.277767000
H	-2.710701000	-3.705739000	2.269819000	H	-2.636714000	3.434734000	-2.148525000
H	-1.221027000	-2.753988000	2.249035000	C	-1.646456000	3.808995000	1.179340000
C	3.782166000	-0.963834000	0.983657000	H	-1.912872000	3.372212000	2.151491000
C	3.708952000	-1.437849000	-0.374731000	H	-1.861182000	4.885325000	1.228145000
C	3.963058000	0.877694000	-0.433687000	H	-0.564441000	3.693940000	1.029972000
C	-2.887592000	-1.052060000	3.217817000	C	3.805692000	-1.814331000	2.208970000
H	-1.863318000	-0.709990000	3.428376000	H	3.450138000	-1.270504000	3.093269000
H	-3.117364000	-1.854076000	3.932043000	H	4.842881000	-2.128116000	2.410305000
H	-3.586840000	-0.226684000	3.411349000	H	3.205127000	-2.725708000	2.092722000
C	3.625531000	-2.864614000	-0.801618000	C	3.874776000	-0.339251000	-2.740433000
H	3.110139000	-3.486781000	-0.059158000	H	3.348462000	-1.211206000	-3.148536000
H	4.643616000	-3.268819000	-0.922565000	H	4.925985000	-0.405267000	-3.064535000
H	3.110484000	-2.975114000	-1.764638000	H	3.448458000	0.567460000	-3.189381000
C	-4.529279000	-1.950622000	1.572925000	C	-2.363202000	-1.279825000	-3.125754000
H	-5.139727000	-1.036805000	1.543991000	H	-2.524768000	-0.266616000	-3.513047000
H	-4.874394000	-2.567765000	2.414370000	H	-2.749055000	-1.977607000	-3.880718000
H	-4.700639000	-2.514531000	0.649763000	H	-1.282625000	-1.456525000	-3.038478000
C	3.820591000	-0.300108000	-1.250547000	C	4.202582000	2.263542000	-0.931270000
C	-3.958147000	3.493130000	0.242100000	H	3.772307000	2.423307000	-1.927927000
H	-4.573197000	3.044677000	-0.549926000	H	5.288290000	2.435758000	-1.010457000
H	-4.100987000	4.582837000	0.219906000	H	3.799578000	3.024127000	-0.249794000

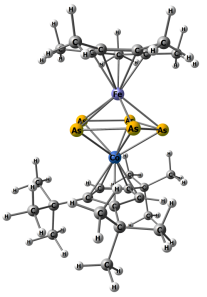


Co	-0.727825000	0.217782000	0.007120000	H	-4.263149000	3.078389000	1.266674000
Fe	2.043982000	-0.082868000	0.008128000	C	-3.035366000	-1.519052000	-1.823924000
P	0.699699000	0.155302000	-1.869357000	C	-2.839370000	-3.008281000	-1.514302000
P	0.896222000	1.848728000	-0.519924000	H	-1.781957000	-3.247105000	-1.330400000
P	0.440846000	-1.678076000	-0.588725000	H	-3.153177000	-3.587383000	-2.394041000
P	0.748724000	1.056709000	1.588272000	H	-3.434617000	-3.358241000	-0.665835000
P	0.663930000	-1.123868000	1.532400000	C	4.090252000	1.309846000	2.162582000
C	-2.684014000	-0.541661000	0.743659000	H	3.756944000	2.341268000	1.995546000
C	-3.066754000	-1.624180000	1.755708000	H	5.169977000	1.342624000	2.383443000
C	-2.353688000	1.683699000	0.012156000	H	3.585131000	0.915717000	3.053360000
C	3.874837000	0.451863000	0.964703000	C	-2.421309000	3.189649000	0.058047000
C	-2.641732000	-0.517786000	-0.737252000	C	-4.548238000	-1.240717000	-2.069457000
C	-2.473091000	0.862310000	-1.125570000	H	-5.148352000	-1.404276000	-1.166268000
H	-2.437662000	1.214797000	-2.149991000	H	-4.906279000	-1.924470000	-2.852567000
C	-2.438331000	0.793577000	1.153850000	H	-4.711038000	-0.208660000	-2.409168000
H	-2.383637000	1.124039000	2.185216000	C	-1.993446000	3.817284000	-1.276349000
C	-2.189501000	-2.893098000	1.734280000	H	-0.949948000	3.571197000	-1.524985000
H	-1.954871000	-3.253506000	0.730609000	H	-2.071386000	4.911092000	-1.210621000
H	-2.708922000	-3.698613000	2.272662000	H	-2.632918000	3.485474000	-2.106025000
H	-1.240906000	-2.714446000	2.260005000	C	-1.605417000	3.786559000	1.215651000
C	3.731230000	-0.983074000	0.964920000	H	-1.862873000	3.330078000	2.181805000
C	3.650390000	-1.422264000	-0.405476000	H	-1.814391000	4.862759000	1.289938000
C	3.898856000	0.896295000	-0.404456000	H	-0.524637000	3.670964000	1.052916000
C	-2.984864000	-1.058866000	3.189241000	C	3.803023000	-1.868077000	2.160229000
H	-1.970292000	-0.714420000	3.439060000	H	3.425617000	-1.375399000	3.064423000
H	-3.242535000	-1.859114000	3.896196000	H	4.859829000	-2.126541000	2.340367000
H	3.690564000	-0.231842000	3.350617000	H	3.254060000	-2.806399000	2.013644000
C	3.585679000	-2.836424000	-0.866740000	C	3.844002000	-0.267930000	-2.738488000
H	3.104381000	-3.489489000	-0.128453000	H	3.329347000	-1.131493000	-3.176800000
H	4.612350000	-3.208098000	-1.018626000	H	4.905165000	-0.327910000	-3.031678000
H	3.054668000	-2.934544000	-1.821912000	H	3.432187000	0.649427000	-3.178128000
C	-4.550178000	-1.991226000	1.498140000	C	-2.288946000	-1.243824000	-3.147186000
H	-5.179499000	-1.090270000	1.470257000	H	-2.405267000	-0.216397000	-3.511947000
H	-4.904955000	-2.634324000	2.316245000	H	-2.694357000	-1.910311000	-3.920402000
H	-4.688045000	-2.539270000	0.559988000	H	-1.216258000	-1.464420000	-3.057242000
C	3.759001000	-0.262051000	-1.252279000	C	4.157775000	2.287534000	-0.868151000
C	-3.927299000	3.491378000	0.304953000	H	3.753751000	2.469774000	-1.871337000
H	-4.550885000	3.068783000	-0.494855000	H	5.248154000	2.443031000	-0.918904000
H	-4.073051000	4.581000000	0.325081000	H	3.750273000	3.039276000	-0.180559000

Table S9: Optimized geometries of **4** (singlet, left) and **4** (triplet, right). XYZ coordinated in angstroms. BP86/def2-TZVP level of theory.

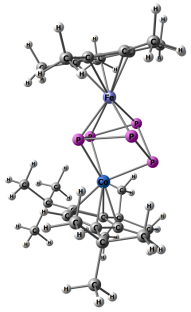


As	-0.459866000	-1.124861000	1.636599000	C	3.301489000	-1.524260000	-1.785767000
As	-0.685384000	1.234952000	1.649795000	C	4.806638000	-1.178745000	-1.988550000
As	-0.824200000	1.953285000	-0.608874000	H	4.933624000	-0.135912000	-2.310696000
As	-0.532773000	0.060390000	-2.016107000	H	5.213964000	-1.834875000	-2.770881000
As	-0.301604000	-1.854316000	-0.623917000	H	5.389749000	-1.328982000	-1.072324000
Co	0.994760000	0.226559000	0.012537000	C	3.165710000	-3.018963000	-1.471710000
Fe	-2.029112000	-0.129262000	-0.010656000	H	3.749885000	-3.333423000	-0.601731000
C	2.842000000	-0.531291000	-0.715111000	H	3.538004000	-3.586533000	-2.335943000
C	2.829974000	-0.529800000	0.754491000	H	2.115900000	-3.309709000	-1.320726000
C	2.586662000	0.834066000	1.153652000	C	2.588491000	-1.286513000	-3.134063000
H	2.514460000	1.165205000	2.183310000	H	1.518733000	-1.528977000	-3.077528000
C	2.518777000	1.696854000	0.015683000	H	3.034410000	-1.954931000	-3.882670000
C	2.600409000	0.832601000	-1.116416000	H	2.697237000	-0.263003000	-3.512986000
H	2.545705000	1.168548000	-2.145647000	C	3.228723000	-1.578779000	1.794703000
C	-3.680578000	-0.761198000	1.123603000	C	2.447618000	-2.907327000	1.747429000
C	-3.566653000	-1.561251000	-0.067598000	H	1.485693000	-2.809206000	2.268568000
C	-3.664839000	-0.684275000	-1.204482000	H	3.023299000	-3.680781000	2.275022000
C	-3.845969000	0.658123000	-0.716466000	H	2.247994000	-3.263459000	0.735704000
C	-3.849643000	0.611248000	0.722092000	C	4.743012000	-1.840521000	1.579173000
C	-3.731847000	-1.276332000	2.523008000	H	4.940143000	-2.405127000	0.661612000
H	-4.779012000	-1.482014000	2.797749000	H	5.119308000	-2.431630000	2.425916000
H	-3.338891000	-0.547663000	3.243981000	H	5.307525000	-0.897986000	1.539994000
H	-3.172853000	-2.215062000	2.635120000	C	3.066787000	-1.016234000	3.222463000
C	-3.470578000	-3.049106000	-0.109703000	H	3.737009000	-0.167212000	3.415388000
H	-3.013799000	-3.406361000	-1.041834000	H	3.323373000	-1.808904000	3.938225000
H	-4.482392000	-3.481911000	-0.051825000	H	2.031903000	-0.708058000	3.432184000
H	-2.894302000	-3.446118000	0.736177000	C	2.622974000	3.200861000	0.014461000
C	-3.698203000	-1.111886000	-2.633752000	C	1.822799000	3.861470000	1.147033000
H	-3.386778000	-0.306601000	-3.311429000	H	0.742270000	3.824005000	0.954764000
H	-4.729086000	-1.390455000	-2.906179000	H	2.107959000	4.919802000	1.222588000
H	-3.061439000	-1.987530000	-2.816955000	H	2.019170000	3.393044000	2.121401000
C	-4.102529000	1.863384000	-1.558117000	C	4.139031000	3.452121000	0.265184000
H	-3.832674000	2.792826000	-1.040338000	H	4.444727000	3.076847000	1.251799000
H	-5.177856000	1.919497000	-1.792861000	H	4.328048000	4.534454000	0.228672000
H	-3.559976000	1.824934000	-2.512195000	H	4.756463000	2.963710000	-0.501504000
C	-4.090146000	1.769213000	1.631578000	C	2.236114000	3.802264000	-1.344382000
H	-3.655619000	1.605287000	2.626202000	H	2.887073000	3.436021000	-2.150458000
H	-5.174459000	1.913888000	1.764372000	H	2.338904000	4.895005000	-1.303074000
H	-3.679809000	2.702049000	1.223506000	H	1.193784000	3.574806000	-1.611916000



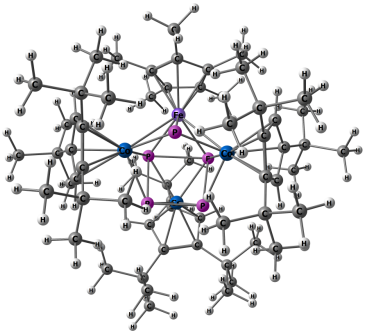
As	-0.618696000	-1.349870000	1.625741000	C	3.255989000	-1.424473000	-1.866776000
As	-0.598361000	1.043970000	1.765235000	C	4.756706000	-1.062382000	-2.072893000
As	-0.791014000	2.020383000	-0.481762000	H	4.873519000	-0.011831000	-2.372223000
As	-0.530388000	0.225827000	-2.034881000	H	5.166131000	-1.698311000	-2.870856000
As	-0.245144000	-1.825940000	-0.702400000	H	5.345302000	-1.227105000	-1.162084000
Co	0.881907000	0.208779000	0.005117000	C	3.137033000	-2.931758000	-1.615953000
Fe	-1.921954000	-0.104518000	-0.021100000	H	3.735501000	-3.276816000	-0.767598000
C	2.799920000	-0.484495000	-0.747314000	H	3.499040000	-3.460368000	-2.508945000
C	2.813914000	-0.565000000	0.725859000	H	2.091475000	-3.237274000	-1.462432000
C	2.557235000	0.758274000	1.182570000	C	2.520243000	-1.140913000	-3.194268000
H	2.507729000	1.051025000	2.225180000	H	1.467132000	-1.450795000	-3.143973000
C	2.509348000	1.693060000	0.075624000	H	2.993758000	-1.734094000	-3.988515000
C	2.631402000	0.913392000	-1.085924000	H	2.559040000	-0.090628000	-3.507967000
H	2.625501000	1.303930000	-2.096406000	C	3.207990000	-1.670447000	1.710937000
C	-3.666966000	-0.736775000	1.047084000	C	2.413854000	-2.989328000	1.609874000
C	-3.530079000	-1.496746000	-0.169065000	H	1.442649000	-2.900973000	2.116805000
C	-3.578526000	-0.579078000	-1.275926000	H	2.972069000	-3.782522000	2.127603000
C	-3.740953000	0.750875000	-0.743747000	H	2.228626000	-3.321097000	0.586642000
C	-3.777925000	0.654040000	0.692397000	C	4.718543000	-1.943506000	1.498071000
C	-3.849591000	-1.295923000	2.415870000	H	4.922261000	-2.437126000	0.541259000
H	-4.929897000	-1.422281000	2.597664000	H	5.078985000	-2.604037000	2.299666000
H	-3.462542000	-0.626009000	3.193903000	H	5.295070000	-1.008185000	1.535741000
H	-3.379905000	-2.280627000	2.529900000	C	3.038605000	-1.172601000	3.162413000
C	-3.496157000	-2.982304000	-0.264165000	H	3.709015000	-0.334083000	3.396879000
H	-3.009005000	-3.324752000	-1.185888000	H	2.286298000	-1.996072000	3.846162000
H	-4.530885000	-3.362178000	-0.276331000	H	2.002095000	-0.868668000	3.374668000
H	-2.987552000	-3.436616000	0.595692000	C	2.623914000	3.195213000	0.179504000
C	-3.619118000	-0.962424000	-2.715207000	C	1.778412000	3.786294000	1.318877000
H	-3.327622000	-0.133846000	-3.372258000	H	0.706100000	3.773830000	1.078304000
H	-4.652313000	-1.244211000	-2.976753000	H	2.065310000	4.834734000	1.480151000
H	-2.977029000	-1.826476000	-2.930473000	H	1.925322000	3.250867000	2.267280000
C	-3.989704000	1.962047000	-1.544486000	C	4.125827000	3.437868000	0.503245000
H	-3.733398000	2.894521000	-0.992021000	H	4.401961000	2.988802000	1.467808000
H	-5.064608000	2.033219000	-1.783939000	H	4.308606000	4.520610000	0.560225000
H	-3.442133000	1.979073000	-2.495374000	H	4.772141000	3.014160000	-0.278165000
C	-4.035243000	1.775815000	1.638232000	C	2.281620000	3.882437000	-1.150356000
H	-3.582145000	1.595204000	2.621418000	H	2.953618000	3.560955000	-1.958541000
H	-5.122748000	1.875116000	1.788710000	H	2.386886000	4.970642000	-1.041169000
H	-3.665375000	2.733574000	1.252069000	H	1.246485000	3.676013000	-1.462086000

Table S10: Optimized geometries of **5** (left) and **6** (right). XYZ coordinated in angstroms. BP86/def2-TZVP level of theory.



Co	1.137536000	0.260565000	-0.183374000	H	5.115071000	-2.981501000	-1.962093000	Co	1.368169000	0.263097000	-0.064031000	H	5.310019000	-3.040160000	-1.843706000
Fe	-2.438767000	-0.098311000	-0.072900000	H	4.697351000	-2.850605000	-0.242063000	Fe	-2.362083000	-0.104385000	0.118035000	H	4.906476000	-2.891867000	-0.120994000
P	0.066195000	0.483096000	-2.154432000	C	-4.364517000	-0.504566000	-0.783155000	As	0.306597000	0.545249000	-2.155128000	C	-4.299102000	-0.717327000	-0.390335000
P	-1.158461000	1.698368000	-0.743767000	C	-3.991625000	-1.425471000	0.260328000	As	-1.278655000	1.861591000	-0.765444000	C	-3.764442000	-1.518158000	0.680503000
P	-0.674799000	0.684867000	1.148684000	C	-3.707143000	-0.655796000	1.449603000	As	-0.489428000	0.906865000	1.304363000	C	-3.443783000	-0.633991000	1.777345000
P	-1.303977000	-1.192925000	-1.701617000	C	-3.922203000	0.735953000	1.138387000	As	-1.331023000	-1.256858000	-1.742225000	C	-3.800383000	0.709075000	1.381282000
P	-0.486168000	-1.417197000	0.316690000	C	-4.313094000	0.825892000	-0.243051000	As	-0.297479000	-1.494039000	0.407998000	C	-4.314059000	0.653671000	0.039224000
C	3.070049000	-0.535721000	-0.555607000	C	-4.808703000	-0.873996000	-2.163493000	C	3.282372000	-0.585704000	-0.432208000	C	-4.845233000	-1.238937000	-1.682362000
C	2.813443000	-0.580350000	0.877139000	H	-4.580348000	-0.075407000	-2.882965000	C	3.019677000	-0.636558000	1.001762000	H	-4.733490000	-0.504631000	-2.492147000
C	2.968975000	0.857607000	-0.934409000	H	-5.898357000	-1.053346000	-2.194859000	C	3.222820000	0.810960000	-0.800856000	H	-5.920034000	-1.476872000	-1.588139000
H	3.090210000	1.228827000	-1.944959000	H	-4.306248000	-1.786346000	-2.513123000	H	3.365968000	1.188675000	-1.806602000	H	-4.323184000	-2.154291000	-1.993981000
C	2.581869000	0.781055000	1.296962000	C	-3.932342000	-2.915087000	0.133038000	C	2.819623000	0.724062000	1.429908000	C	-3.599998000	-3.005330000	0.656539000
H	2.338185000	1.077432000	2.311326000	H	-3.595941000	-3.211454000	-0.871641000	H	2.583393000	1.020801000	2.446009000	H	-3.229179000	-3.345929000	-0.322946000
C	2.689266000	1.675728000	0.198950000	H	-4.917412000	-3.382596000	0.308138000	C	2.949399000	1.625124000	0.336660000	H	-4.553172000	-3.526858000	0.853360000
C	2.916916000	-1.674392000	1.948876000	H	-3.223022000	-3.343162000	0.855544000	C	3.103193000	-1.737218000	2.069880000	H	-2.872905000	-3.333139000	1.412484000
C	3.466823000	-1.600569000	-1.587559000	C	-3.326646000	-1.209163000	2.786988000	C	3.668145000	-1.650784000	-1.468097000	C	-2.917086000	-1.045465000	3.115974000
C	2.613256000	3.189180000	0.227269000	H	-2.784819000	-2.159512000	2.680956000	C	2.921205000	3.140703000	0.370943000	H	-2.260460000	-1.922553000	3.026559000
C	2.357233000	-2.642936000	-1.828578000	H	-4.213915000	-1.394332000	3.417444000	C	2.557414000	-2.692065000	-1.707379000	H	-3.733181000	-1.298488000	3.815339000
H	2.077678000	-3.184267000	-0.921312000	H	-2.667796000	-0.515784000	3.329351000	H	2.271847000	-3.228253000	-0.799074000	H	-2.320005000	-0.240020000	3.567238000
H	2.689395000	-3.375248000	-2.582966000	C	-3.784444000	1.894077000	2.074788000	H	2.892291000	-3.428941000	-2.456036000	C	-3.700737000	1.944781000	2.219048000
H	1.450848000	-2.140651000	-2.195754000	H	-3.154127000	1.636551000	2.937146000	H	1.653202000	-2.192034000	-2.082802000	H	-2.994478000	1.806823000	3.049328000
C	3.725476000	-0.933464000	-2.955956000	H	-4.765097000	2.224546000	2.459427000	C	3.921649000	-0.983761000	-2.837460000	H	-4.679004000	2.221459000	2.649594000
H	2.819782000	-0.434469000	-3.332013000	H	-3.317085000	2.755734000	1.573456000	H	3.017267000	-0.474892000	-3.204762000	H	-3.345289000	2.802077000	1.625818000
H	4.014183000	-1.706661000	-3.684086000	C	-4.692704000	2.085448000	-0.957074000	H	4.196279000	-1.758376000	-3.569519000	C	-4.866295000	1.812463000	-0.730426000
H	4.539675000	-0.195192000	-2.904260000	H	-4.106170000	2.941790000	-0.594917000	H	4.743298000	-0.253515000	-2.792179000	H	-4.330777000	2.741343000	-0.488374000
C	4.375036000	-1.673251000	2.467931000	H	-5.761139000	2.320697000	-0.803553000	C	4.551893000	-1.734144000	2.615642000	H	-5.934945000	1.969202000	-0.497549000
H	5.085867000	-1.923277000	1.668105000	H	-4.521850000	2.001739000	-2.039445000	H	5.276300000	-1.976062000	1.825128000	H	-4.779967000	1.653455000	-1.814232000
H	4.492963000	-2.410593000	3.278843000	C	1.707008000	3.670167000	1.372796000	H	4.659015000	-2.478004000	3.422073000	C	2.125588000	3.650979000	1.582696000
H	4.643199000	-0.681248000	2.861454000	H	0.687190000	3.277757000	1.247740000	H	4.810764000	-0.744511000	3.020707000	H	1.084267000	3.298220000	1.537065000
C	2.543044000	-3.095035000	1.498198000	H	1.664415000	4.770749000	1.383818000	C	2.749303000	-3.160433000	1.610927000	H	2.122696000	4.752130000	1.596323000
H	1.512868000	-3.118514000	1.114651000	H	2.086490000	3.339293000	2.351171000	H	1.722357000	-3.199230000	1.220124000	H	2.566026000	3.304511000	2.529700000
H	2.602412000	-3.772497000	2.364674000	C	4.044035000	3.733652000	0.448527000	H	2.810124000	-3.839094000	2.476333000	C	4.382148000	3.637975000	0.476829000
H	2.216045000	-3.489586000	0.729604000	H	4.460899000	3.363667000	1.398067000	H	3.432577000	-3.544954000	0.846428000	H	4.860825000	3.250038000	1.389042000
C	1.984749000	-1.344014000	3.136812000	H	4.038314000	4.835442000	0.480178000	C	2.145997000	-1.416875000	3.240449000	H	4.415271000	4.739118000	0.511023000
H	2.272886000	-0.416494000	3.649586000	H	4.713774000	3.415328000	-0.364962000	H	2.407624000	-0.482520000	3.754590000	H	4.973332000	3.301410000	-0.388318000
H	2.035981000	-2.158419000	3.875591000	C	2.066370000	3.731958000	-1.104312000	H	2.196283000	-2.227639000	3.983343000	C	2.288237000	3.702009000	-0.914461000
H	0.941787000	-1.246157000	2.800186000	H	2.698277000	3.432682000	-1.953505000	H	1.107050000	-1.338546000	2.885176000	H	2.836462000	3.374660000	-1.810104000
C	4.789231000	-2.282551000	-1.175074000	H	2.035328000	4.832586000	-1.078480000	C	4.992029000	-2.333403000	-1.060418000	H	2.302408000	4.803209000	-0.893472000
H	5.582193000	-1.531797000	-1.034526000	H	1.047343000	3.355860000	-1.281780000	H	5.787421000	-1.582866000	-0.933227000	H	1.244976000	3.364949000	-1.009964000

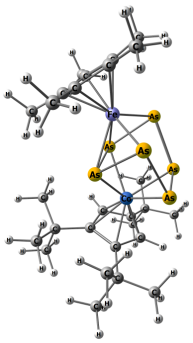
Table S11: Optimized geometries of **8** (left) and **9** (right). XYZ coordinated in angstroms. BP86/def2-TZVP level of theory.

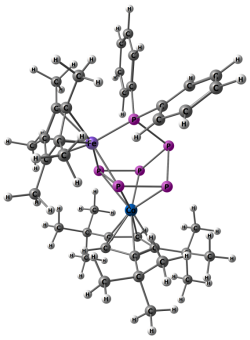


Co	1.129195000	-1.809108000	-0.234702000	C	-1.253204000	-4.807058000	0.347270000	As	-2.041335000	-0.252323000	-0.029946000	C	-0.003036000	4.694437000	-2.743253000
Co	0.565979000	2.023081000	-0.057664000	H	-1.571308000	-3.792262000	0.625804000	As	0.348399000	1.280454000	1.624785000	H	0.344914000	3.668908000	-2.925393000
Co	-2.290219000	-0.380331000	-0.000177000	H	-1.874029000	-5.531977000	0.895085000	As	0.856452000	1.381008000	-1.080193000	H	0.708036000	5.387546000	-3.217754000
Fe	0.999813000	0.050123000	1.769912000	H	-1.443668000	-4.948321000	-0.725518000	As	0.779321000	-1.052272000	1.741960000	H	-0.977945000	4.833255000	-3.233106000
P	1.916772000	0.254939000	-0.203033000	C	0.675237000	-6.413570000	0.215069000	As	1.203803000	-1.300552000	-0.869094000	C	-3.856716000	3.942239000	3.116655000
P	-0.653754000	-1.124913000	-1.386181000	H	0.548988000	-6.513617000	-0.873021000	Co	-1.171633000	1.904080000	-0.057342000	H	-3.709499000	4.972890000	2.760219000
P	-0.988990000	0.983739000	-1.287519000	H	0.073948000	-7.194718000	0.706603000	Co	-0.703160000	-2.147491000	0.227563000	H	-3.997438000	3.975368000	4.208179000
P	-0.967615000	1.034860000	1.212364000	H	1.735017000	-6.589985000	0.452287000	Co	2.300999000	0.388677000	0.537633000	H	-4.783080000	3.560079000	2.676189000
P	-0.589613000	-1.407027000	1.117017000	C	0.735638000	3.450969000	-3.150240000	Fe	-0.674524000	-0.231374000	-1.896118000	C	-5.363346000	3.955605000	-0.100571000
C	2.989459000	-2.846768000	-0.832300000	C	1.089938000	2.100612000	-3.790465000	C	-1.052023000	3.785941000	0.861043000	H	-5.313387000	4.433204000	0.885497000
C	2.019554000	-2.893547000	-1.905681000	H	1.066222000	2.187415000	-4.888365000	H	-0.248778000	4.072106000	1.530118000	H	-6.421090000	3.750717000	-0.331342000
C	0.870543000	-3.574105000	-1.366531000	H	0.348271000	1.345362000	-3.495082000	C	0.031784000	-1.031732000	-3.766152000	H	-4.981796000	4.673154000	-0.842423000
H	-0.038239000	-3.769096000	-1.922314000	H	2.073437000	1.733021000	-3.494268000	C	-1.480832000	0.719223000	-3.681846000	C	2.728462000	1.646200000	4.222638000
C	1.100793000	-4.006964000	-0.035775000	C	1.575788000	4.587642000	-3.774874000	C	-2.291187000	3.183000000	1.289708000	H	1.693566000	1.404747000	3.939882000
C	2.386790000	-3.511660000	0.300778000	H	2.653799000	4.407159000	-3.702908000	C	-1.268695000	-1.569104000	-3.486199000	H	2.701545000	2.289701000	5.115238000
H	2.873700000	-3.662165000	1.255201000	H	1.355892000	5.548368000	-3.285283000	C	-2.204962000	-0.489169000	-3.432009000	H	3.236642000	0.710893000	4.498311000
C	0.897185000	3.484781000	-1.619647000	H	1.325322000	4.682912000	-4.842839000	C	-0.102785000	0.388737000	-3.899309000	C	2.739435000	3.681210000	2.741532000
C	2.046529000	3.491437000	-0.736024000	C	-0.731734000	3.740930000	-3.538116000	C	-2.624307000	3.070231000	2.785727000	H	3.270993000	4.241316000	1.958499000
C	1.559726000	3.867015000	0.570237000	H	-1.411057000	2.989073000	-3.112129000	C	-3.076552000	2.993034000	0.086656000	H	2.683100000	4.320091000	3.635831000
H	2.193736000	3.990706000	1.438312000	H	-0.822235000	3.696815000	-4.633591000	C	3.750528000	1.888177000	0.499178000	H	1.717257000	3.478647000	2.991953000
C	0.168187000	4.144892000	0.531938000	H	-1.055687000	4.741186000	-3.213529000	H	3.578985000	2.897513000	0.144228000	C	-4.232968000	-3.035259000	-1.021915000
C	-0.233501000	3.833320000	-0.790933000	C	3.557282000	3.434192000	-0.988584000	C	-0.247855000	-3.846343000	1.373656000	H	-3.676998000	-2.137659000	-1.318323000
H	-1.249355000	3.920570000	-1.156857000	C	3.994488000	2.542062000	-2.160033000	H	0.619487000	-3.907751000	2.020196000	H	-5.307896000	-2.835104000	-1.139899000
C	-3.960470000	-1.099003000	-1.161009000	H	3.607959000	1.522330000	-2.028860000	C	-0.088730000	4.969604000	-1.239004000	H	-3.977435000	-3.853394000	-1.709471000
C	-4.207326000	0.280629000	-0.765043000	H	5.093746000	2.491086000	-2.185054000	C	-4.548307000	2.640561000	-0.154156000	C	3.902545000	0.088137000	1.871850000
C	-4.166574000	0.308247000	0.671997000	H	3.663080000	2.922638000	-3.131046000	C	-2.281117000	3.493130000	-1.008540000	H	3.859522000	-0.538712000	2.755026000
H	-4.303750000	1.199095000	1.275323000	C	4.049706000	4.882865000	-1.224633000	H	-2.609371000	3.514462000	-2.039374000	C	-4.485420000	-4.810084000	0.708637000
C	-3.950228000	-0.995158000	1.194071000	H	5.142875000	4.888234000	-1.361401000	C	-2.834272000	1.620727000	3.252038000	H	-4.010363000	-5.544501000	0.041101000
C	-3.790279000	-1.845047000	0.062619000	H	3.808530000	5.517986000	-0.359049000	H	-3.572568000	1.081461000	2.654388000	H	-5.570682000	-4.822063000	0.518558000
H	-3.575802000	-2.905178000	0.113420000	H	3.590770000	5.335448000	-2.112438000	H	-3.155357000	1.603763000	4.305392000	H	-4.313620000	-5.134873000	1.742313000
C	1.945370000	1.255299000	3.345664000	C	4.280138000	2.898307000	0.261600000	H	-1.886541000	1.072738000	3.174522000	C	0.739552000	-5.249807000	-0.577610000
C	2.808297000	0.159273000	3.040409000	H	4.189080000	3.581014000	1.117220000	C	-1.542171000	-3.366276000	1.800567000	C	4.293617000	-0.367730000	0.563272000
C	2.093370000	-1.046462000	3.321357000	H	5.352983000	2.782426000	0.048573000	C	-1.053690000	4.032221000	-0.537119000	C	-2.871164000	-4.109958000	3.809014000
C	0.787706000	-0.694100000	3.793707000	H	3.872591000	1.917671000	0.539968000	C	-0.642947000	6.398827000	-1.020860000	H	-3.867552000	-3.951544000	3.384485000
C	0.693053000	0.735757000	3.811613000	C	-0.688428000	4.955532000	1.490787000	H	-1.653798000	6.495515000	-1.444416000	H	-2.957307000	-4.015696000	4.902607000
C	2.440967000	2.646624000	3.543513000	C	-0.166952000	4.944286000	2.928865000	H	0.010265000	7.140910000	-1.506597000	H	-2.562895000	-5.141210000	3.579424000
H	3.256310000	2.889253000	2.853791000	H	-0.245447000	3.941795000	3.363827000	H	-0.700339000	6.636287000	0.051566000	C	3.860896000	0.168164000	-2.789831000
H	2.845740000	2.733905000	4.568739000	H	-0.769091000	5.626283000	3.548401000	C	-2.400247000	-3.466378000	0.637728000	H	3.950452000	-0.903002000	-2.602646000
H	1.653820000	3.393492000	3.439943000	H	0.877894000	5.283418000	2.985202000	C	0.920671000	1.335686000	-4.446846000	H	4.229446000	0.375030000	-3.807714000
C	4.287341000	0.294273000	2.833012000	C	-0.632862000	6.413469000	0.967903000	H	1.348773000	1.996859000	-3.676413000	H	2.795406000	0.428050000	-2.752861000
H	4.804554000	-0.647054000	3.055056000	H	0.400915000	6.790650000	0.970537000	H	0.468684000	1.974792000	-5.220418000	C	-4.664017000	-2.369069000	1.312182000
H	4.689024000	1.061272000	3.513322000	H	-1.244981000	7.070226000	1.606282000	H	1.755070000	0.790794000	-4.905445000	H	-4.617844000	-2.598107000	2.380867000
H	4.561932000	0.590005000	1.812901000	H	-1.014426000	6.476436000	-0.061350000	C	-1.467883000	3.641180000	3.637352000	H	-5.726227000	-2.356302000	1.024314000

C	2.694907000	-2.399940000	3.494196000	C	-2.149258000	4.481415000	1.486876000	H	-0.534228000	3.084113000	3.475310000	H	-4.254078000	-1.362797000	1.150502000
H	1.981907000	-3.197078000	3.267682000	H	-2.606355000	4.596163000	0.495917000	H	-1.732222000	3.550171000	4.701397000	C	-3.698437000	-0.634757000	-3.453592000
H	2.997535000	-2.523085000	4.549721000	H	-2.740888000	5.079380000	2.197161000	H	-1.288702000	4.705468000	3.423855000	H	-4.157728000	-0.592006000	-2.458422000
H	3.588650000	-2.538385000	2.878890000	H	-2.216842000	3.420408000	1.770464000	C	3.599230000	1.474330000	1.856537000	H	-3.982740000	-1.597352000	-3.901672000
C	-0.166187000	-1.652308000	4.427700000	C	-4.077733000	-1.838770000	-2.505437000	C	-5.155167000	1.609954000	0.809690000	H	-4.154741000	0.162024000	-4.058090000
H	-1.159212000	-1.213483000	4.563809000	C	-3.688129000	-3.320248000	-2.320072000	H	-4.570436000	0.680135000	0.789828000	C	4.902477000	2.692848000	3.528736000
H	0.213093000	-1.953711000	5.419472000	H	-2.655378000	-3.402060000	-1.951739000	H	-6.181054000	1.375564000	0.486721000	H	5.449496000	1.773712000	3.785539000
H	-0.294716000	-2.563209000	3.831153000	H	-3.746111000	-3.831603000	-3.292175000	H	-5.212128000	1.965085000	1.842887000	H	4.885989000	3.346667000	4.414835000
C	-0.413129000	1.536844000	4.421809000	H	-4.357001000	-3.846434000	-1.624189000	C	-1.823157000	-3.099747000	3.288237000	H	5.456190000	3.206568000	2.728679000
H	-1.084722000	1.957321000	3.654240000	C	-3.185084000	-1.324492000	-3.651353000	C	-0.552147000	-3.349394000	4.131301000	C	0.370129000	-6.670221000	-0.082999000
H	-0.007653000	2.365773000	5.020407000	H	-3.313490000	-0.264961000	-3.870203000	H	-0.206898000	-4.391092000	4.050814000	H	0.391699000	-6.719111000	1.015503000
H	-1.028319000	0.913528000	5.083890000	H	-3.416969000	-1.891670000	-4.566730000	H	-0.784005000	-3.153082000	5.188651000	H	1.084846000	-7.409843000	-0.477746000
C	4.476844000	-2.486845000	-0.796343000	H	-2.128116000	-1.489668000	-3.403689000	H	0.269822000	-2.680451000	3.838292000	H	-0.640453000	-6.950810000	-0.415318000
C	4.866251000	-2.135922000	0.647584000	C	-5.562980000	-1.797903000	-2.932255000	C	1.320173000	4.886380000	-0.630971000	C	4.258968000	-2.709955000	1.475838000
H	4.863721000	-3.019244000	1.301359000	H	-6.211211000	-2.173116000	-2.125837000	H	1.313971000	5.107694000	0.444801000	H	4.522495000	-2.440114000	2.507267000
H	4.159573000	-1.396505000	1.038881000	H	-5.715085000	-2.429983000	-3.821239000	H	1.985601000	5.613041000	-1.121069000	H	4.609080000	-3.738444000	1.307539000
H	5.878920000	-1.708550000	0.676696000	H	-5.889750000	-0.780628000	-3.183954000	H	1.739655000	3.880167000	-0.773388000	H	3.164411000	-2.692556000	1.391361000
C	4.889844000	-1.278861000	-1.650069000	C	-4.682625000	1.546784000	-1.488730000	C	-1.589844000	-4.008540000	-0.428074000	C	4.628028000	1.029245000	-1.774841000
H	4.739881000	-1.434488000	-2.722190000	C	-4.086562000	2.787740000	-0.796229000	H	-1.964068000	-4.234077000	-1.417998000	C	0.716405000	-5.242570000	-2.108067000
H	5.960958000	-1.078170000	-1.493880000	H	-4.366754000	3.696104000	-1.350721000	C	-0.284832000	-4.312425000	0.032376000	H	-0.269647000	-5.530654000	-2.500507000
H	4.323576000	-0.389011000	-1.339576000	H	-2.991612000	2.705698000	-0.774957000	C	-4.703430000	2.053857000	-1.567710000	H	1.452124000	-5.960561000	-2.501072000
C	5.282227000	-3.739418000	-1.216359000	H	-4.439771000	2.909154000	0.235261000	H	-4.547883000	2.814416000	-2.345220000	H	0.975253000	-4.247920000	-2.494180000
H	6.361586000	-3.536148000	-1.128397000	C	-6.223164000	1.591959000	-1.337274000	H	-5.718154000	1.652212000	-1.702846000	C	2.153960000	-4.906233000	-0.099622000
H	5.072762000	-4.039115000	-2.250249000	H	-6.698560000	0.726629000	-1.820015000	H	-3.981965000	1.241729000	-1.714935000	H	2.420743000	-3.885942000	-0.402008000
H	5.037670000	-4.589820000	-0.562239000	H	-6.622362000	2.507927000	-1.800905000	C	4.199096000	0.790764000	-0.321311000	H	2.886285000	-5.602451000	-0.536073000
C	2.079922000	-2.535849000	-3.397946000	H	-6.512149000	1.586128000	-0.276199000	C	-1.629617000	-3.006829000	-3.628158000	H	2.241567000	-4.971869000	0.993434000
C	2.162248000	-1.021412000	-3.638959000	C	-4.328784000	1.667448000	-2.974670000	H	-0.850031000	-3.661832000	-3.235001000	C	4.355019000	2.495571000	-2.173010000
H	1.247289000	-0.548051000	-3.263949000	H	-4.663420000	2.650094000	-3.340924000	H	-1.750249000	-3.243549000	-4.701096000	H	3.283702000	2.732263000	-2.090048000
H	2.244571000	-0.810202000	-4.716732000	H	-4.825157000	0.905892000	-3.586484000	H	-2.576202000	-3.242304000	-3.131419000	H	4.653379000	2.644775000	-3.221518000
H	3.006890000	-0.552309000	-3.127957000	H	-3.242510000	1.601651000	-3.123436000	C	3.457454000	2.365903000	3.076072000	H	4.925552000	3.205185000	-1.556518000
C	3.252440000	-3.270874000	-4.083572000	C	-4.080654000	-1.399836000	2.646019000	C	-3.919919000	-3.393400000	0.442644000	C	6.412386000	-1.633717000	0.824739000
H	3.191463000	-3.118269000	-5.172260000	C	-3.426420000	-2.765904000	2.902364000	C	1.232322000	-1.846560000	-4.127875000	H	6.954452000	-0.982895000	0.126098000
H	3.202536000	-4.352753000	-3.888069000	H	-3.923074000	-3.558390000	2.322858000	H	2.115521000	-1.216858000	-4.283337000	H	6.890569000	-2.626255000	0.811926000
H	4.233050000	-2.910639000	-3.755037000	H	-3.594772000	-3.031375000	3.967560000	H	1.044018000	-2.410209000	-5.057055000	H	6.520873000	-1.210332000	1.834046000
C	0.796399000	-3.018411000	-4.110284000	H	-2.364342000	-2.748259000	2.619441000	H	1.492994000	-2.569567000	-3.342617000	C	6.147991000	0.798177000	-1.907121000
H	0.675303000	-4.110068000	-4.043572000	C	-3.453313000	-0.329188000	3.550667000	C	-2.084710000	2.030664000	-4.051574000	H	6.698748000	1.409878000	-1.176941000
H	0.856802000	-2.749445000	-5.175321000	H	-3.965027000	0.638137000	3.443864000	H	-3.075039000	2.166870000	-3.607209000	H	6.484023000	1.081509000	-2.916961000
H	-0.098080000	-2.535470000	-3.691280000	H	-2.399850000	-0.169743000	3.287318000	H	-2.206078000	2.071920000	-5.149530000	H	6.423559000	-0.250657000	-1.745605000
C	0.230228000	-5.011111000	0.693768000	H	-3.520593000	-0.629135000	4.608082000	H	-1.447752000	2.870812000	-3.762549000	C	4.805443000	-2.431131000	-0.931505000
C	0.404510000	-4.920891000	2.211744000	C	-5.592851000	-1.500489000	2.957747000	C	-2.264295000	-1.656064000	3.570944000	H	3.761179000	-2.461346000	-1.273249000
H	1.445797000	-5.110635000	2.510959000	H	-6.093855000	-0.534781000	2.794388000	H	-1.441979000	-0.968330000	3.333057000	H	5.174632000	-3.465473000	-0.863837000
H	-0.229974000	-5.664565000	2.716777000	H	-5.748209000	-1.798558000	4.007031000	H	-2.514936000	-1.536262000	4.636774000	H	5.407832000	-1.921444000	-1.692013000
H	0.109165000	-3.922230000	2.559256000	H	-6.075656000	-2.248176000	2.311243000	H	-3.127668000	-1.350343000	2.976090000	C	4.915777000	-1.762900000	0.446045000

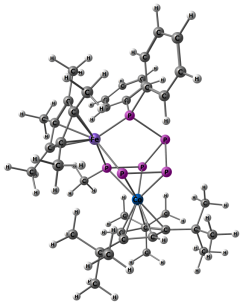
Table S12: Optimized geometries of **7** (left) and **10** (right). XYZ coordinated in angstroms. BP86/def2-TZVP level of theory.





As	0.358698000	-1.468328000	0.009185000	H	-0.552835000	-1.651560000	2.690726000	Fe	-1.544349000	-0.843116000	0.840907000	H	-2.457059000	0.837076000	3.975456000
As	0.490206000	0.806521000	1.356596000	H	-1.440023000	-2.677814000	3.846146000	Co	1.907462000	-0.050895000	-0.399930000	C	-4.222429000	-1.430252000	-3.487434000
As	1.618471000	-0.919904000	-1.967414000	H	-1.797272000	-0.944670000	3.747741000	P	-2.261986000	0.597677000	-0.523339000	H	-3.932111000	-2.155509000	-4.250731000
As	1.804138000	2.152200000	-0.154596000	C	-2.534584000	-2.907756000	-1.757324000	P	0.246777000	0.388161000	1.193757000	C	2.778391000	-3.862579000	0.227470000
As	-0.589362000	0.132635000	-2.358037000	H	-1.743345000	-2.358906000	-2.287946000	P	0.057162000	-1.538956000	-0.486745000	H	3.304267000	-3.738110000	1.186249000
As	-0.448670000	2.172597000	-1.166932000	H	-2.950230000	-3.668405000	-2.438220000	P	-0.735789000	1.466583000	-1.953027000	H	2.811724000	-4.930247000	-0.040110000
Co	-1.417645000	0.215484000	-0.066910000	H	-2.067017000	-3.420871000	-0.914511000	P	0.699699000	1.909269000	-0.307903000	H	1.728394000	-3.561682000	0.356668000
Fe	2.412570000	-0.141952000	0.157814000	C	-4.750901000	2.723406000	1.779745000	P	0.538085000	-0.319610000	-2.233338000	C	3.881185000	1.249761000	1.988760000
C	-2.745631000	-1.002916000	1.086558000	H	-5.571022000	2.216202000	1.249148000	C	-3.181272000	-2.157655000	1.181178000	C	-5.568741000	-1.068771000	-3.338518000
C	-3.426969000	0.519675000	-0.534198000	H	-5.067271000	3.754864000	2.002593000	C	-1.950098000	-2.828780000	1.459205000	H	-6.331451000	-1.511021000	-3.982418000
H	-3.760551000	0.942547000	-1.474672000	H	-4.583680000	2.199123000	2.732371000	C	3.352937000	-0.963462000	0.765567000	C	4.331001000	1.991242000	-1.500835000
C	-2.684037000	0.335598000	1.603236000	C	3.559919000	-3.150248000	-0.100909000	H	3.131330000	-1.507483000	1.675742000	C	4.914772000	-3.426349000	-1.015219000
H	-2.373601000	0.594476000	2.610321000	H	2.626086000	-3.601282000	0.265623000	C	3.636010000	0.450398000	0.897917000	H	5.405837000	-2.856869000	-1.818804000
C	-3.208442000	-0.887768000	-0.297456000	H	4.396274000	-3.783099000	0.244139000	C	-4.948922000	0.428470000	-1.533230000	H	4.999097000	-4.499765000	-1.249976000
C	-3.126060000	1.280064000	0.633401000	H	3.534194000	-3.192035000	-1.199127000	H	-5.241723000	1.155685000	-0.774118000	H	5.458957000	-3.233416000	-0.077801000
C	3.708880000	-1.745283000	0.389528000	C	-2.340098000	3.419408000	1.713478000	C	-2.503771000	2.639657000	1.375176000	C	-1.499812000	-4.116964000	0.848134000
C	3.279254000	-1.254976000	1.675517000	H	-2.114894000	2.875346000	2.642607000	H	-1.975726000	1.926283000	2.010668000	H	-1.884048000	-4.229725000	-0.176017000
C	3.705094000	0.115184000	1.788013000	H	-2.638755000	4.445033000	1.981997000	C	-2.841483000	2.245322000	0.071423000	H	-1.852504000	-4.979994000	1.439453000
C	4.388499000	0.471066000	0.571657000	H	-1.416307000	3.462744000	1.119465000	C	-3.270142000	-1.016814000	2.067643000	H	-0.403785000	-4.172868000	0.790184000
C	-3.463185000	2.731400000	0.919868000	C	2.594404000	-2.060432000	2.732802000	C	3.691918000	-0.472450000	-1.428161000	C	5.854439000	1.823577000	-1.718334000
C	4.388042000	-0.670819000	-0.295243000	H	2.004561000	-1.417482000	3.400571000	H	3.775502000	-0.579828000	-2.504472000	H	6.249390000	2.660356000	-2.316925000
C	-3.649756000	-1.934847000	-1.330820000	H	3.320708000	-2.616195000	3.351440000	C	3.845600000	0.764182000	-0.717635000	H	6.072087000	0.864429000	-2.248206000
C	-2.601595000	-2.164491000	2.084503000	H	1.901692000	-2.787376000	2.284262000	C	-2.819707000	3.919781000	1.838674000	H	6.392344000	1.803766000	-0.759256000
C	-3.741457000	3.510421000	-0.374080000	C	3.531192000	1.011600000	2.972553000	H	-2.545488000	4.211872000	2.854803000	C	3.597762000	0.359773000	3.219057000
H	-2.859745000	3.497668000	-1.031434000	H	3.287247000	2.038176000	2.658831000	C	-3.598464000	0.068234000	-1.670145000	H	4.263366000	-0.514987000	3.262757000
H	-3.986864000	4.557300000	-0.137306000	H	4.450901000	1.053464000	3.581545000	C	3.409593000	-1.544820000	-0.533569000	H	2.552707000	0.015779000	3.211745000
H	-4.592692000	3.079644000	-0.922834000	H	2.713997000	0.664295000	3.619228000	C	-2.096189000	-0.989107000	2.887005000	H	3.757944000	0.951606000	4.133195000
C	-4.130389000	-1.238976000	-2.622315000	C	-3.968347000	-2.297006000	2.801290000	C	-3.481222000	4.825228000	1.002732000	C	5.378175000	1.628948000	2.040957000
H	-5.008352000	-0.600836000	-2.443314000	H	-4.238030000	-1.353735000	3.298814000	H	-3.733226000	5.824353000	1.364279000	H	5.614375000	2.101064000	3.008151000
H	-4.416344000	-2.007429000	-3.356605000	H	-3.920942000	-3.091360000	3.563753000	C	-3.482877000	3.171724000	-0.770004000	H	5.657129000	2.331480000	1.245873000
H	-3.329276000	-0.627790000	-3.063396000	H	-4.770671000	-2.546932000	2.093137000	H	-3.720519000	2.891395000	-1.797794000	H	6.007115000	0.731789000	1.931914000
C	-2.213136000	-3.534815000	1.508923000	C	5.077933000	-0.767193000	-1.619158000	C	-1.265774000	-2.101856000	2.499925000	C	4.071910000	3.358270000	-0.854625000
H	-2.961544000	-3.933062000	0.815756000	H	4.550640000	-1.455316000	-2.295228000	C	3.427132000	-3.020830000	-0.881598000	H	4.609722000	3.488758000	0.091272000
H	-2.121181000	-4.251924000	2.339682000	H	6.112664000	-1.135136000	-1.502329000	C	-4.245661000	-2.637648000	0.245732000	H	2.996935000	3.501814000	-0.678008000
H	-1.242902000	-3.482781000	0.995050000	H	5.122539000	0.212625000	-2.114249000	H	-4.888327000	-1.814252000	-0.090519000	H	4.418481000	4.147061000	-1.540526000
C	-4.865418000	-2.709555000	-0.771715000	C	5.092359000	1.766611000	0.320110000	H	-4.894024000	-3.391208000	0.728317000	C	0.041059000	-2.473744000	3.128147000
H	-4.608719000	-3.322457000	0.100238000	H	5.157412000	1.987447000	-0.754179000	H	-3.812060000	-3.098521000	-0.654222000	H	0.668752000	-3.044271000	2.429459000
H	-5.270777000	-3.379813000	-1.546273000	H	6.120107000	1.734194000	0.722409000	C	-3.249703000	-0.872099000	-2.658401000	H	-0.101893000	-3.088870000	4.034177000
H	-5.661377000	-2.010735000	-0.471696000	H	4.570527000	2.607671000	0.799171000	H	-2.203744000	-1.175829000	-2.757404000	H	0.605416000	-1.574660000	3.415340000
C	-1.535346000	-1.829007000	3.151953000					C	-4.458816000	-0.116445000	2.201473000	C	3.638078000	2.031289000	-2.882391000
								H	-4.170581000	0.897729000	2.508073000	H	3.960499000	2.930376000	-3.429937000
								H	-5.166507000	-0.508309000	2.953247000	H	2.546160000	2.060269000	-2.758460000
								H	-5.004748000	-0.028485000	1.252210000	H	3.886194000	1.159639000	-3.502497000
								C	-5.926843000	-0.138654000	-2.358838000	C	2.996797000	2.496357000	2.173960000
								H	-6.973506000	0.147180000	-2.231608000	H	1.945449000	2.192927000	2.286728000
								C	-3.809636000	4.447958000	-0.305643000	H	3.053098000	3.198935000	1.340616000
								H	-4.314011000	5.154280000	-0.968749000	C	-1.796994000	-0.041122000	4.005143000
								C	2.709669000	-3.287815000	-2.215145000	H	-0.756974000	0.319134000	3.950959000
								H	1.645581000	-3.020757000	-2.134765000	H	-1.932519000	-0.523606000	4.988916000
								H	2.788501000	-4.354052000	-2.480064000	H	3.304595000	3.024501000	3.091455000
								H	3.150738000	-2.701285000	-3.034390000				

Table S13: Optimized geometries of **11.** XYZ coordinated in angstroms. BP86/def2-TZVP level of theory.



Co	-1.903070000	-0.009573000	0.189627000	H	2.106751000	1.804626000	-3.793408000	C	3.685012000	-0.972588000	4.003435000	H	-6.416881000	-1.345054000	-0.906492000
Fe	1.628468000	1.154778000	-0.295615000	C	4.902051000	0.930490000	-0.869801000	H	3.293853000	-0.743670000	4.996509000	H	-6.325046000	-1.720270000	-2.646751000
P	2.198220000	-0.853600000	0.188342000	H	5.262598000	0.537887000	0.088136000	C	5.013096000	-1.385980000	3.848717000	H	-6.007062000	-0.063480000	-2.064677000
P	0.526206000	-2.233935000	0.763472000	H	5.695290000	1.577202000	-1.281287000	H	5.664133000	-1.480624000	4.719657000	C	-3.695214000	-1.134976000	-3.057878000
P	-0.646014000	-0.760491000	1.954728000	H	4.772508000	0.084414000	-1.559033000	C	5.500101000	-1.679501000	2.572705000	H	-3.795921000	-0.077428000	-3.334195000
P	-0.048530000	1.170580000	1.184326000	C	3.855759000	2.255336000	1.859854000	H	6.534423000	-2.004288000	2.442220000	H	-4.171836000	-1.726261000	-3.853720000
P	-0.129387000	0.349275000	-1.206936000	H	3.128880000	2.351489000	2.677741000	C	4.667041000	-1.562718000	1.455903000	H	-2.630292000	-1.405978000	-3.033803000
P	-0.788221000	-1.700375000	-0.939826000	H	4.597056000	3.065479000	1.975830000	H	5.056251000	-1.803367000	0.466393000	C	-3.249118000	3.031963000	0.477142000
C	-0.714573000	0.903025000	-2.870350000	H	4.380435000	1.301877000	1.998251000	C	-4.154047000	-1.892272000	1.810071000	C	-4.656982000	3.594993000	0.170183000
H	-1.553354000	0.295340000	-3.221384000	C	1.371759000	4.090991000	1.143296000	C	-4.002968000	-1.453252000	3.283042000	H	-4.973746000	3.336463000	-0.851340000
H	0.124092000	0.815636000	-3.576051000	H	0.376526000	4.374390000	0.777337000	H	-2.969014000	-1.151616000	3.503329000	H	-4.656848000	4.692166000	0.264409000
H	-1.022456000	1.954534000	-2.814921000	H	1.957499000	5.014915000	1.283936000	H	-4.251395000	-2.304719000	3.933780000	H	-5.402140000	3.189288000	0.870551000
C	-3.794914000	-0.731107000	0.872609000	H	1.232238000	3.624092000	2.128953000	H	-4.683214000	-0.627065000	3.538548000	C	-2.241714000	3.595127000	-0.531938000
C	-3.827375000	-0.586088000	-0.577735000	C	0.930455000	3.935070000	-2.034415000	C	-3.255532000	-3.134442000	1.639632000	H	-1.245709000	3.184224000	-0.319821000
C	-3.512840000	0.792144000	-0.861424000	H	0.574752000	3.423321000	-2.937902000	H	-3.156034000	-3.459960000	0.602487000	H	-2.200675000	4.693594000	-0.466783000
H	-3.473358000	1.223480000	-1.855851000	H	1.485006000	4.829951000	-2.366812000	H	-3.666398000	-3.970263000	2.227668000	H	-2.510603000	3.329735000	-1.565213000
C	-3.335110000	1.526431000	0.346682000	H	0.057459000	4.282474000	-1.471878000	H	-2.245818000	-2.918828000	2.015914000	C	-2.835564000	3.448915000	1.896686000
C	-3.478768000	0.573671000	1.396726000	C	2.843864000	-1.933528000	-1.152698000	C	-5.644680000	-2.256470000	1.619093000	H	-3.565548000	3.104235000	2.644207000
H	-3.347954000	0.798041000	2.449015000	C	3.309959000	-3.239043000	-0.915954000	H	-6.279349000	-1.367474000	1.755139000	H	-2.783800000	4.546442000	1.963030000
C	2.801115000	2.159880000	-1.770768000	H	3.379718000	-3.614165000	0.106314000	H	-5.940831000	-3.005097000	2.369954000	H	-1.848489000	3.033788000	2.149218000
C	3.643304000	1.721491000	-0.700524000	C	3.665592000	-4.063749000	-1.984055000	H	-5.859102000	-2.674642000	0.629736000	C	2.708687000	-1.490496000	-2.475601000
C	3.186619000	2.334899000	0.525587000	H	4.028236000	-5.074866000	-1.788733000	C	-4.365245000	-1.474216000	-1.710894000	H	2.313980000	-0.487747000	-2.640897000
C	2.070422000	3.171328000	0.195220000	C	3.544777000	-3.604905000	-3.301101000	C	-4.194051000	-2.991352000	-1.544624000	C	3.338652000	-1.139739000	1.601224000
C	1.827321000	3.060842000	-1.217399000	H	3.819901000	-4.254956000	-4.133827000	H	-3.129774000	-3.252018000	-1.461937000	C	2.856186000	-0.843406000	2.890109000
C	3.042932000	1.930860000	-3.230111000	C	3.058219000	-2.318185000	-3.544998000	H	-4.594791000	-3.490437000	-2.440243000	H	1.827368000	-0.496916000	3.015097000
H	3.665116000	1.043402000	-3.403748000	H	2.945570000	-1.958717000	-4.569913000	H	-4.728222000	-3.395953000	-0.680265000				
H	3.570744000	2.793155000	-3.674279000					C	-5.871576000	-1.130666000	-1.834603000				

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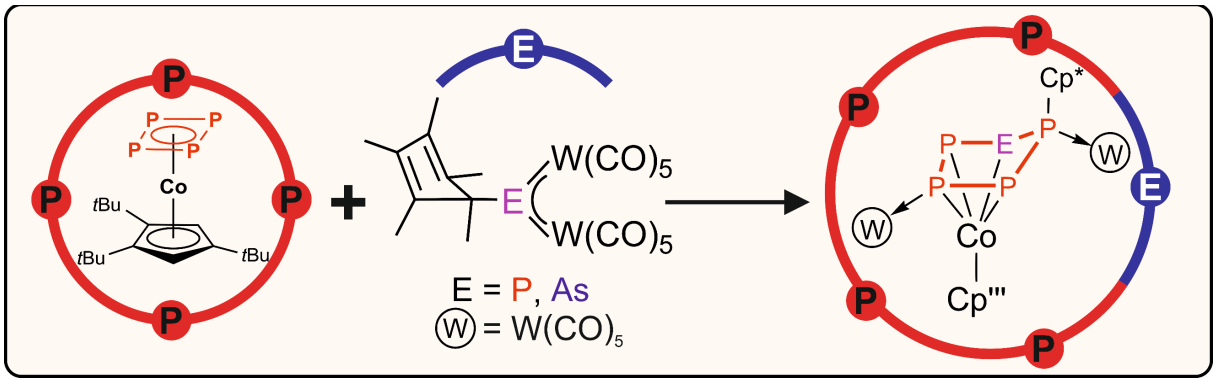
8. Ring Expansions of non-polar Polyphosphorus Rings

Martin Piesch, Michael Seidl, Markus Stubenhofer and Manfred Scheer



- Synthesis and characterization of **3** was performed by Markus Stubenhofer
- Synthesis and characterization of **5a**, **5b**, **6a**, **6b**, **6c** was performed by Martin Piesch
- DFT calculations were performed by Martin Piesch
- X-ray measurements and calculations were done by Markus Stubenhofer (**3**) and Martin Piesch (**5a**, **5b**, **6a**, **6b**, **6c**) and finally checked by Michael Seidl
- Manuscript was written by Michael Seidl
- Simulation of NMR spectra was performed by Michael Seidl
- Figures (DFT) were created by Martin Piesch and all other figures (X-ray, NMR, Chemdraw, etc.) were created by Michael Seidl
- This work was already published as:
  M. Piesch, M. Seidl, M. Stubenhofer, M. Scheer *Chem. Eur. J.* **2019**, *29*, 6311-6316.
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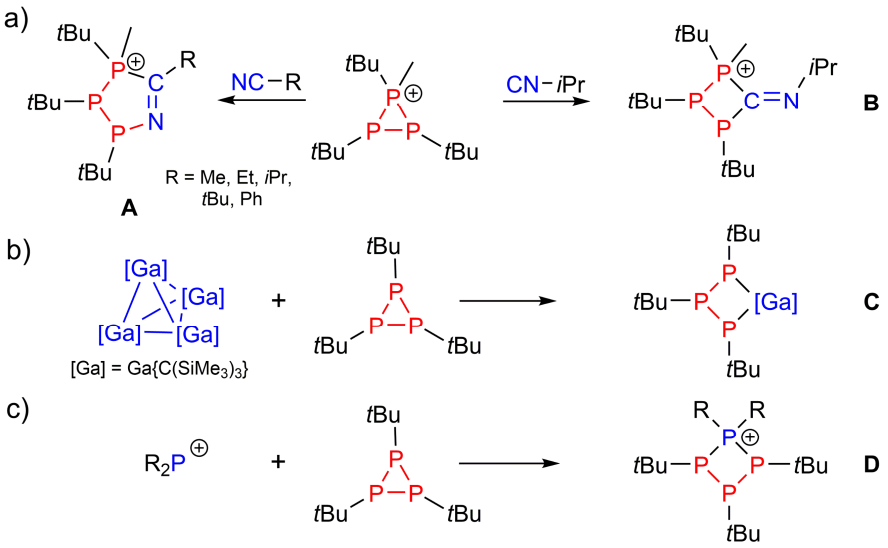
8.1. Introduction

*The reaction of the phosphinidene complex [Cp*P{W(CO)$_5$}$_2$] (**1a**) (Cp* = CpMe$_5$) with the anionic cyclo-P$_n$ ligand complex [(η^3-P$_3$)Nb(ODipp)$_3$]$^-$ (**2**) (Dipp = 2,6-diisopropylphenyl) results in the formation of [{W(CO)$_5$}$_2${μ_3,η^3:η^1:η^1-P$_4$Cp*}Nb(ODipp)$_3$]$^-$ (**3**), which represents an unprecedented example of a ring expansion of a polyphosphorus ligand complex initiated by a phosphinidene complex. Further, the reaction of the pnictinidene complexes [Cp*E{W(CO)$_5$}$_2$] (E = P (**1a**), As (**1b**)) with the neutral complex [Cp'''Co(η^4-P$_4$)] (Cp''' = 1,2,4-tBu$_3$C$_5$H$_2$) leads, by the insertion of the pentel atom into the cyclo-P$_4$ ligand, to a cyclo-P$_4$E ring (E = P, As). Starting from **1a**, the two isomers [Cp'''Co(μ_3,η^4:η^1:η^1-P$_5$Cp*){W(CO)$_5$}$_2$] (**5a**, **5b**), and from **1b,** the three isomers [Cp'''Co(μ_3,η^4:η^1:η^1-AsP$_4$Cp*){W(CO)$_5$}$_2$] (**6a**, **6b**, **6c**) with unprecedented cyclo-P$_4$E ligands (E = P, As) can be isolated. The complexes **6a**, **6b**, **6c** represent unique examples of ring expansions leading to new mixed five-membered cyclo-P$_4$As ligands. The possible reaction pathways for the formation of **5a**, **5b** and **6a**, **6b**, **6c** were investigated by a combination of temperature-dependent ^{31}P{^{1}H} NMR studies and DFT calculations.*

Ring expansions of strained rings (three- or four-membered) such as oxiranes, aziridines and oxetanes have attracted the interest in chemistry as an essential synthetic tool for heterocycle and natural products synthesis.[1] This synthetic tool is, however, not limited to carbon-containing rings, but can also be applied for homoatomic main group atom-based rings and also cage compounds[2,3] (the latter is not in the focus of this article). It has, for example, been used to convert strained three-or four-membered phosphorus cycles to expand them into four- or five-membered heterocycles (Scheme 1). In principle, reactions with reagents possessing multiple bonds to expand the initial ring by two atoms have to be distinguished from reactions with reagents possessing a single reactive atom to expand the ring by just one atom.[4,5] However, the first mentioned reaction principle can also proceed by a one-atom insertion at the ring as *Manners et al*. were recently able to show.[5] Thus, the three-membered *cyclo*-phosphinophosphonium rings undergo either the expected two-atom insertion in the case of nitriles (Scheme 1; product **A**) or a one-atom insertion by using isonitriles (product **B**). They were able to show that for such ring expansions the polarization of the P-P bond plays a decisive role.[5] On the other hand, it is known that very reactive low-valent main group compounds as for instance Al(I) species,[6] Ga(I) species,[7] silylenes[8] and germylenes[9] can insert into non-polar P-P bonds. For example, *Uhl et al.* reported the reaction of [Ga{C(SiMe$_3$)$_3$}]$_4$ (dissociates in solution to a reactive one-atomic species) with (*t*BuP)$_3$ (Scheme 1b), leading by the insertion of Ga{C(SiMe$_3$)$_3$} to a four-membered heteroatomic ring (**C**).[2]



Scheme 1. Examples for the ring expansion of homoatomic three-membered phosphorus cycles.

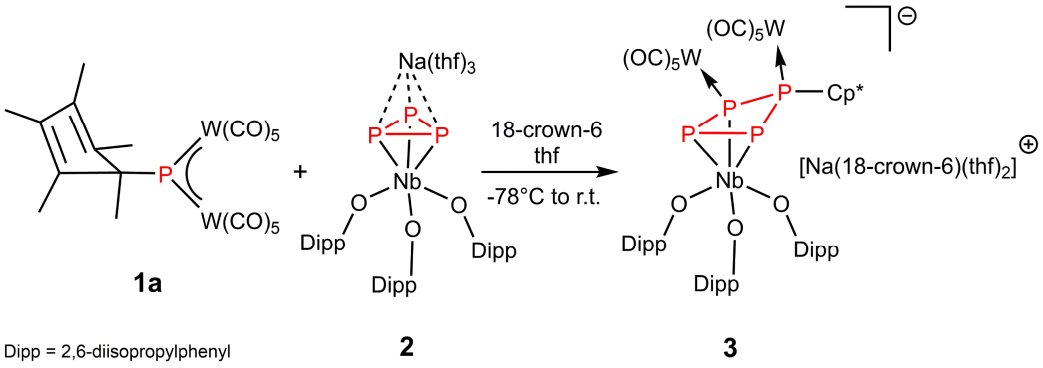
Burford et al. reported the formation of compound **D** by the reaction of the (*t*BuP)$_3$ with R_2P^+ (generated in situ from R_2PCl and Me_3SiOTf or $GaCl_3$).[10] The insertion of R_2P^+ is not limited to three membered rings, which was shown for the reaction with $(PhP)_5$ leading to monocationic compounds $[P_5Ph_4R_2]^+$ and, if a second R_2P^+ unit is inserted, to the dicationic compounds $[P_6Ph_4R_4]^{2+}$.[11] Also, the insertion of the in situ generated phosphinidene [{W(CO)$_5$}PMe] into a homoatomic C-C bond of 1,6-methano-[10]annulene was reported, which resulted in a phosphorus-containing 11-membered ring.[12] But, also stable phosphinidene complexes can deliver one P atom, however, in a multicomponent ring insertion reaction. Thus, the reaction of the phosphaalkyne MesC≡P with the phosphinidene complex [Cp*P{W(CO)$_5$}$_2$] (**1a**) leads to an insertion of the PC unit of the phosphaalkyne and of the P atom of the phosphinidene into the Cp* ring of the phosphinidene complex to form a 1,2-diphosphacyclooctatetraene ligand.[13]

8.2 Results and Discussion

Considering the state of research, the question arises whether it is possible to develop a neutral stable - non-transient – and selective monoatomic insertion reagent. And, if so, would such a reagent be able to insert into a non-polarised E-E bond? The pnictinidene complexes [Cp*E{W(CO)$_5$}$_2$] (E = P, As) are known to show a versatile reaction behavior. Thus, by Cp* migration, an intermediate with a W≡P triple bond is formed,[13,14] and the elimination of the Cp* substituents results in highly reactive radical species [·E{W(CO)$_5$}$_2$].[15] However, the pnictinidene complexes are also electrophilic and can react with nucleophiles to yield new heterocycles.[16] By focusing on the targeted ring expansion reactions, the used ring systems

should be similarly good nucleophiles. Therefore, they should either be charged or possess reactive lone pairs, opening the use of the pnictinidene complexes towards ring systems of group 15 or group 16 elements. Moreover, the successful use of these P- or As-moieties would open up a way to build up rare examples of heteroatomic ring systems. Herein, we report the successful use of the pnictinidene complexes [Cp*E{W(CO)$_5$}$_2$] (E = P (**1a**), As (**1b**)) in unprecedented ring expansion reactions with unsubstituted non-polar *cyclo*-P$_n$ rings serving as ligands in transition metal complexes.

Because of the negative charge and the strained three- membered ring, [Na(thf)$_3$][(η^3-P$_3$)Nb(ODipp)$_3$] (**2**),[17] reported by *Cummins et al.*, seemed to be a suitable starting compound for the targeted ring expansion reaction. It can be regarded as a P$_3^{3-}$ synthon,[18] as shown by its reactivity towards AsCl$_3$ leading to P$_3$As.[17] Reacting the phosphinidene complex [Cp*P{W(CO)$_5$}$_2$] (**1a**) with **2** at -78°C results immediately in a color change from dark blue to red-brown. After workup, the complex [Na(18-c-6)(thf)$_2$][{W(CO)$_5$}$_2${μ_3,η^3:η^1:η^1-P$_4$Cp*}Nb(ODipp)$_3$] (**3**) can be obtained in yields of up to 81% (Scheme 2). Complex **3** is the product of the formal insertion of the phosphinidene complex (**1a**) into a P-P bond of the *cyclo*-P$_3$ ligand followed by the migration of a {W(CO)$_5$} unit to one of the phosphorus atoms of the former *cyclo*-P$_3$ ring. Compound **3** is very air- and moisture-sensitive, but manageable under strictly inert conditions.



Scheme 2. Reaction of the pnictinidene complex **1a** with [Na(thf)$_3$][{ODipp}$_3$Nb(η^3-P$_3$)] (**2**).

The ^{31}P{^{1}H} NMR spectrum of **3** shows four different sets of signals at 105.7, 73.6, 38.1 and 4.3 ppm, respectively, which are all split up into doublets of doublets of doublets (cf. Figure S1). Compared to **2** (singlet at -204.8 ppm), the signals are shifted to low field. Further, the signals at 38.1 and 73.6 ppm show satellites for the P-W coupling with coupling constants of 237 and 138 Hz, respectively. The difference in the coupling constants is likely caused by the altered hybridization of the P1 (sp^3) and P2 (sp^2) atoms (for labeling cf. Figure 1).[19]

The main structural motif of **3** is a *cyclo*-P$_4$ ring with three phosphorus atoms η^3-coordinated to the Nb atom (Figure 1). The fourth phosphorus atom (P1) is located above the plane formed by the atoms P2-P3-P4. Further, the atom P1 is substituted by a Cp* ligand and coordinates

to a $\{W(CO)_5\}$ fragment. The second $\{W(CO)_5\}$ fragment is attached to the atom P2. The P-P bond distances range from 2.2105(15) Å to 2.2302(14) Å and can be regarded as P-P single bonds. However, compared with the starting compound $[Na(thf)_3][P_3Nb(ODipp)_3]$ (**2**) (2.194 Å to 2.205 Å),[17] they are only slightly elongated. The Nb1-P2 (2.6787(11) Å), Nb1-P3 (2.5927(10) Å) and Nb1-P4 bond lengths (2.6045(11) Å) are also elongated compared to **2** (2.512 Å to 2.525 Å).

The first step of the reaction between **1a** and **2** should be an adduct formation of one of the lone pairs of a phosphorus atom of the *cyclo*-P_3 unit with the acceptor p-orbital of the phosphinidene complex, as indicated by the color change from blue to red-brown. The next step might be the migration of one $\{W(CO)_5\}$ fragment to an adjacent phosphorus atom followed by the insertion of the phosphinidene unit into a P-P bond, which might be driven by the reduction of the ring strain caused by the expansion from a three- to a four-membered ring.

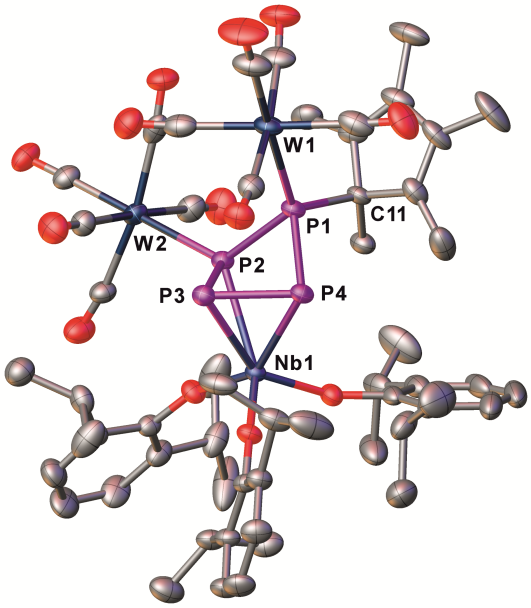
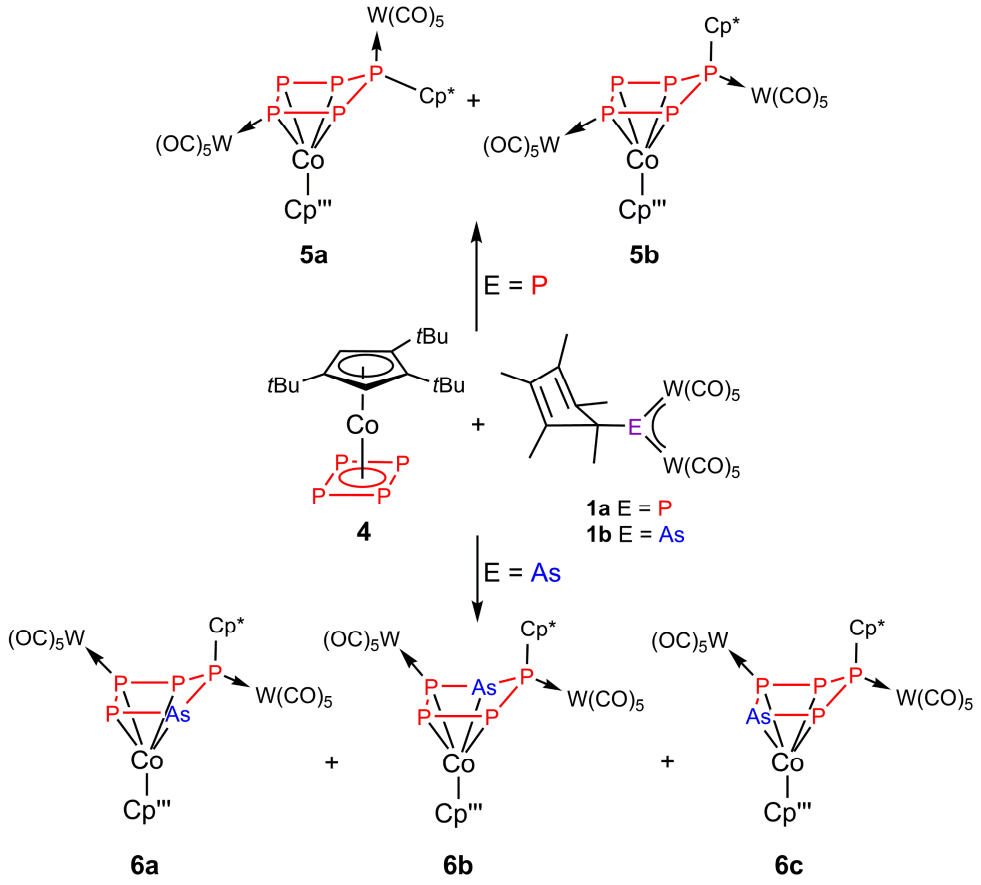


Figure 1. Molecular structure of **3** with ellipsoids at 50% probability level. The hydrogen atoms, the solvent molecules and the counter ion are omitted for clarity.

After the successful use of a charged polyphosphorus ring as a nucleophile for a ring expansion reaction, the question of a neutral ring suitable for the attack on the pnictinidene complexes (**1a**,**b**) was still open. To this effect, the *cyclo*-P_4 ligand in the neutral complex $[Cp'''Co(\eta^4\text{-}P_4)]$ (**4**) was chosen.[20] The reaction of the phosphinidene complex **1a** and $[Cp'''Co(\eta^4\text{-}P_4)]$ (**4**) already proceeds at -78°C and results in two isomeric complexes $[\{W(CO)_5\}_2(\mu_3,\eta^4{:}\eta^1{:}\eta^1\text{-}P_5Cp^*)CoCp''']$ (**5a**,**b**) (Scheme 3). Both products are the result of a ring expansion reaction from a *cyclo*-P_4 to a *cyclo*-P_5 ligand (substituted by a Cp* moiety), which is finally η^4-coordinated at the Cp'''Co fragment and donates towards two $\{W(CO)_5\}$ fragments.



Scheme 3. Reactions of the complex [Cp‴Co(η⁴-P₄)] (**4**) with the pnictinidene complexes [Cp*E{W(CO)₅}₂] (E = P (**1a**); As (1**b**)).

The complexes **5a** and **5b** differ only by the orientation of the Cp* substituents and the corresponding {W(CO)$_5$} fragments. In the case of **5a**, which is the main product of the reaction, the Cp* substituent is located below the P_4 plane (same side as the Cp‴Co fragment). The $^{31}P\{^1H\}$ NMR of the reaction mixture (Figure S2) indicates a practically clean reaction resulting in **5a** and **5b** as the main products with a ratio of 1 to 0.19, respectively. This was surprising since theoretical calculations (B3LYP/def2-SVP level of theory) predicted **5b** to be by 5 kJ/mol energetically more favored than **5a** (Figure S12). Therefore, **5a** can be seen as the kinetically preferred product. This was also proven by performing the reaction at different temperatures (-78°C, r.t., 65°C) leading to the progressive formation of **5b** with increasing temperature (**5a**:**5b**: -78°C: 1 : 0.19; r.t.: 1 : 0.33; 65°C: 1 : 0.45) (cf. Figure S5).

A separation of both isomers **5a** and **5b** was possible by preparative thin-layer chromatography resulting in a crystalline isolated yield of 33% and 2%, respectively. The $^{31}P\{^1H\}$ NMR spectra each show five signal sets, with the corresponding phosphorus-phosphorus couplings at 107.8, 75.2, 34.2, -44.2 and -60.2 ppm for **5a** and at 105.8, 90.2, 48.6, -27.0 and -41.9 ppm for **5b** (cf. Figure S3 (**5a**) and Figure S4 (**5b**)).

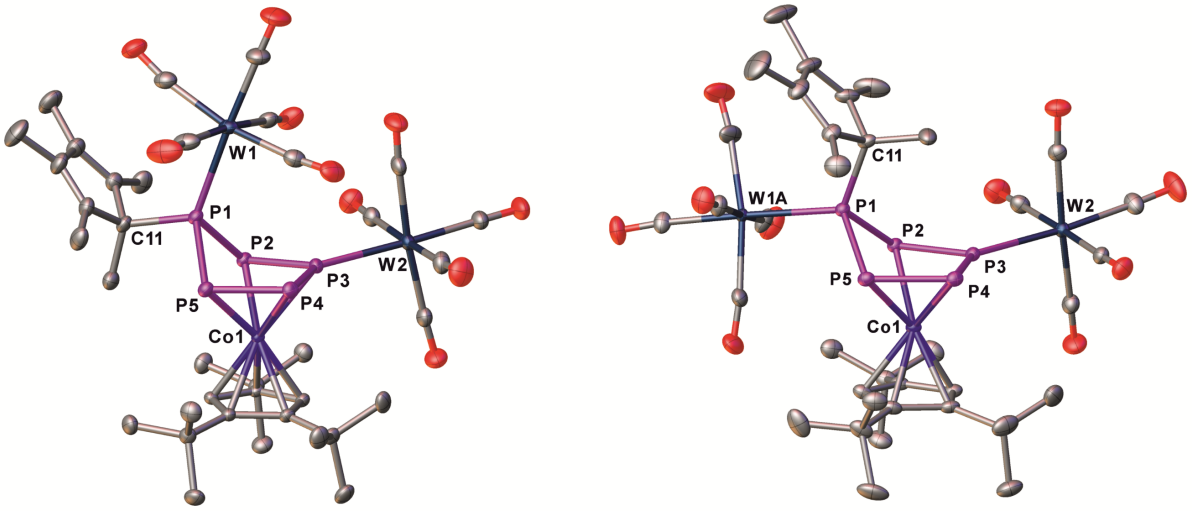


Figure 2. Molecular structure of **5a** (left) and **5b** (right) with ellipsoids at 50% probability level. The hydrogen atoms and the disorder of a $\{W(CO)_5\}$ fragment of **5b** are omitted for clarity.

By layering CH_2Cl_2 solutions of **5a** and **5b** with acetonitrile, it was possible to obtain crystals suitable for single crystal X-ray analysis. The molecular structures of **5a** and **5b** are depicted in Figure 2. Both compounds possess a *cyclo*-P_5 ring in an envelope conformation, η^4-coordinated to the Co atom, with a Cp* substituent attached to P1. Further, the P_5 ring coordinates to two $\{W(CO)_5\}$ units. The P-P distances of the phosphorus atoms in the P_4 plane (2.1222(6) Å to 2.1539(7) Å) are in the range between a single and a double P-P bond and shortened compared to the starting compound **4** (2.1557(18) Å - 2.1699(14) Å).[20] The P1-P2 and P1-P5 distances of both compounds (2.2016(7) Å - 2.2154(9) Å) are in the range of single bonds. The Co-P distances (2.2966(9) Å - 2.3152(9) Å) are comparable to complex **4**. Only the Co1-P2 bonds are an exception with 2.3335(8) Å for **5a** and 2.3857(5) Å for **5b**, which might be explained by the steric demand of the neighboring Cp* substituent and the $\{W(CO)_5\}$ fragments. The structural motif of the *cyclo*-P_5R ligand in **5a,b** is reminiscent of the one in the iron complex $[Cp^*Fe(\eta^4\text{-}P_5CH_2SiMe_3)]^-$[21] and, partially, $[(^{Mes}BIAN)Co(\eta^4\text{-}P_5R_2)]$ (R = *i*Pr, *t*Bu, Cy; ^{Mes}BIAN = bis(mesitylimino)acenaphthene diimine).[22]

To gain insight into the formation of **5a,b**, we applied variable temperature $^{31}P\{^1H\}$ NMR spectroscopy, however, already at -78°C, the signals of **5a** and **5b** were present and no further signals of possible intermediates were detected. Therefore, we investigated the reaction pathway by DFT by calculating the relative energies of the supposed intermediates. Accordingly, in the first reaction step, the adduct of **1a** and **4** is formed, followed by a shift of a $\{W(CO)_5\}$ fragment and the insertion of the phosphinidene unit into the *cyclo*-P_4 ring resulting in **5a** and **5b**. All reaction steps are exothermic except the adduct formation, which, however, is compensated by the exothermic $\{W(CO)_5\}$ shift and insertion steps (the energy diagram for this possible reaction pathway is depicted in Figure S 12).

Furthermore, the use of the arsenidene complex [Cp*As{W(CO)$_5$}$_2$] (**1b**) could also provide insight into the reaction pathway, especially as to where the inserted pnictogen atom is finally located in the product. Moreover, the desired *cyclo*-P$_4$As ligand complex would add to a largely unknown class of ligands, with so far only two known compounds with a *cyclo*-P$_4$As moiety: [(CyP)$_4$AsLi(TMEDA)(thf)][23] (Cy = cyclohexyl; TMEDA = tetramethylethylenediamine) and [Cp‴Fe(η^5-P$_4$As)].[24] During the reaction of the arsenidene complex [Cp*As{W(CO)$_5$}$_2$] (**1b**) and [Cp‴Co(η^4-P$_4$)] (**4**), at -40°C, a color change from dark blue to brown is monitored, changing, after some hours at room temperature, to red. The work-up resulted in dark red crystals of **6** turning out to be a mixture of the three isomers [Cp'''Co(μ$_3$,η^4:η^1:η^1-P$_4$AsCp*){W(CO)$_5$}$_2$] (**6a-c**), which all show the desired Cp*-substituted *cyclo*-P$_4$As ligand as the main structural motif (Scheme 3). The isomers only differ by the position of the arsenic atom within the ring.

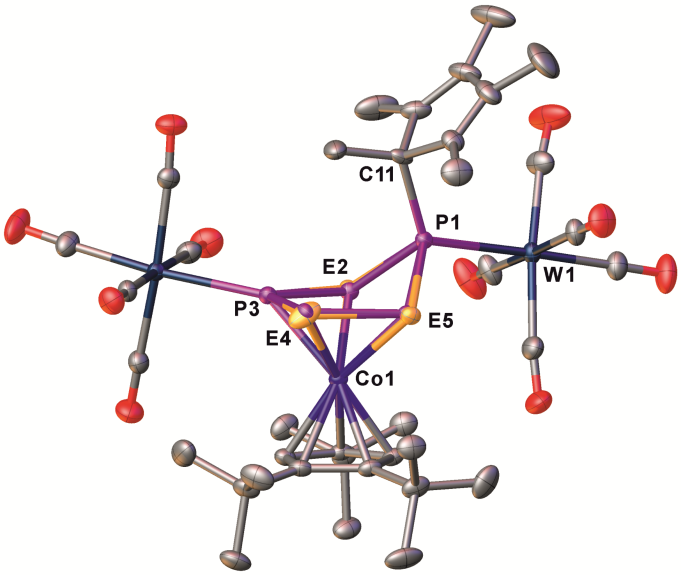


Figure 3. Molecular structures of **6** with ellipsoids at 50% probability level. The hydrogen atoms are omitted for clarity. The mixed phosphorus and arsenic positions are labelled with E originating from the three different isomers of **6**.

The molecular structures of the three isomers **6a**, **6b** and **6c** are depicted in Figure 3. The distribution of the different isomers in the crystal was crystallographically determined to be 0.46 (**6a**) to 0.44 (**6b**) to 0.1 (**6c**). A similar distribution is found in the ^{31}P{^{1}H} NMR spectra obtained from dissolved crystals of **6** or – interestingly - directly obtained from the reaction mixture. The P-P and P-As distances in all three isomers vary between 2.113(9) Å to 2.210(10) Å and 2.161(10) Å to 2.336(4) Å, respectively. The Co-P and Co-As distances are in the range of 2.3019(6) Å to 2.353(8) Å and 2.316(10) Å to 2.534(4) Å, whereas the Co-E2 (E = P, As) distances are elongated, compared to the other Co-E distances as observed for **5a**,**b**.

The ^{1}H and ^{31}P NMR spectra of **6** show both signal sets of the three isomers in the ratio 0.48 : 0.42 : 0.10 (**6a**:**6b**:**6c**). In the $^{31}P\{^{1}H\}$ NMR spectrum, the four signals for **6a** are observed at 98.9, 86.5, 69.7 and -17.6 ppm, the ones for **6b** at 128.8, 78.1, 40.9 and -10.3 ppm and the signals for **6c** are found at 114.9, 87.7, 0.9 and -51.4 ppm (cf. Figure S6-9).

To gain insight into the reaction pathway, the reaction of **1b** with **4** was performed at -78°C and monitored by ^{31}P NMR spectroscopy in increments of 20°C until room temperature was reached. Moreover, after 9 and 18 hours at room temperature, additional ^{31}P NMR spectra were recorded (Figure 4 I). At temperatures below 233 K, no reaction was observed. Only after reaching -40°C, the formation of two new intermediates **I-A** and **I-B** was detected. This is also in accordance with the observed color change from blue to brown at -40°C. In combination with the ^{31}P NMR study, we also performed DFT calculations (B3LYP/def2-SVP level of theory) to gain further insight into a possible reaction pathway (Figure 4 II).

The calculations predicted an adduct formation to be the first reaction step, although it is by 14.51 kJ/mol energetically less favored. However, the next steps, leading to the intermediates **I-A** and **I-B**, are energetically strongly favored and compensates the energy deficit for the formation of **I-1**. These processes involve shifts of $\{W(CO)_5\}$ fragments and the insertion of the arsenic atom into a P-P bond (cf. SI for a more detailed energy diagram). At 253 K, simultaneously with the decline of the $^{31}P\{^{1}H\}$ NMR signals of **I-B**, a new set of signals, stemming from the intermediate **I-C**, appears. The transformation of **I-B** to **I-C** occurs by a 1,2-$\{W(CO)_5\}$ shift, which is by 2.8 kJ/mol energetically favored. At 273 K, the signals for **I-B** have completely vanished and the intermediate **I-C** becomes the main product. Further, the signals for the intermediate **I-A** also decrease and new signals for **6b** and **6a** appear. The formation of **6b** can be explained by a 1,3-Cp* shift or a 1,2-$\{W(CO)_5\}$ shift at **I-A** or **I-C**, respectively, both rearrangements are exothermic by 30.8 or 28.1 kJ/mol. Further, the formation of **6a** can be explained by a 1,2-$\{W(CO)_5\}$ shift at **6b**, which is again energetically favored. At room temperature, only the signals for **I-C**, **6a** and **6b** in the ratio 0.36 : 0.36 : 0.28 are observed. After nine hours at room temperature, in addition to the previous signals, the signals for **6c** can be observed. **6c** is likely formed by a 1,2-Cp* shift at the isomer **I-C**, which is again favored by 23.7 kJ/mol. After another 9 hours, only the signals of the three isomers **6a-c** are observed.

8.3 Conclusion

In conclusion, we showed by the exemplified reactions of the anionic *cyclo*-P_3 complex $[Na(thf)_3][(\eta^3\text{-}P_3)Nb(ODipp)_3]$ (**2**) and the neutral *cyclo*-P_4 complex $[Cp'''Co(\eta^4\text{-}P_4)]$ (**4**) that the pnictinidene complexes $[Cp^*E\{W(CO)_5\}_2]$ (E = P, As) can be used as selective monoatomic insertion reagents into unpolarized P-P bonds. Thus, unprecedented ring expansion reactions

occur leading to new *cyclo*-P_4 and *cyclo*-P_4E complexes (E = P, As). By the combination of DFT calculations and ^{31}P NMR spectroscopy at variable temperatures, insight into a possible reaction pathway for the formation of the three isomers of **6** was gained, which should also be valid for the phosphinidene insertion reaction. Further, the reaction of the arsenidene complex **1b** with **4** opens a new synthesis route to achieve novel mixed-element ligands. The transfer of this synthesis route to other *cyclo*-P_n ligands (n>4) or especially to *cyclo*-As_n ligands will open a new chapter in this chemistry.

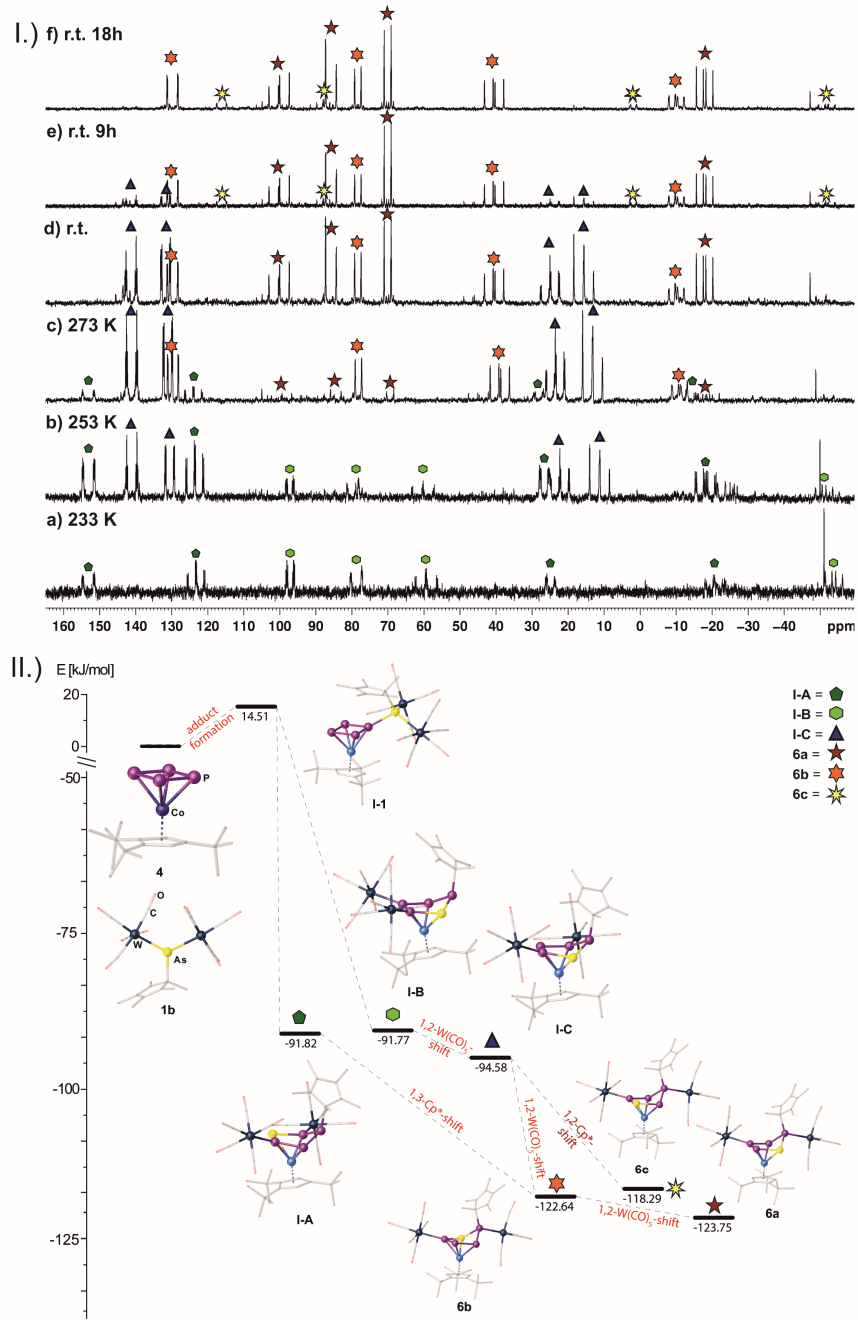


Figure 4. I) $^{31}P\{^1H\}$ NMR spectra (CD_2Cl_2) of the reaction of **1b** with **4** from 233K to room temperature and after 9 and 18 hours at room temperature. II) Part of the energetic profile of a proposed reaction pathway for the reaction between **1b** and **4**.

8.4 Supporting Information

8.4.1 Synthetic procedures and experimental details

All manipulations were carried out under an inert atmosphere of dried argon using standard Schlenk and glove box techniques. Solvents were dried using a MB SPS-800 device of the company MBRAUN. NMR spectra were recorded on a Bruker Avance III 400 MHz NMR spectrometer. Chemical shifts were measured at ambient temperature and are given in ppm; they are referenced to TMS for ^{1}H and ^{13}C, and 85% H_3PO_4 for ^{31}P as external standard. Spectrum simulations were performed with the simulation module “daisy“, embedded in the software *Bruker Topspin (V. 3.0)*.[25] LIFDI-MS spectra (LIFDI = liquid injection field desorption ionization) were measured on a JEOL AccuTOF GCX. Elemental analysis (CHN) was determined using a Vario micro cube instrument. The IR spectrum of compound **3** was recorded in CH_2Cl_2 solution using a Varian FTS-800 FT-IR spectrometer. The IR spectra of **5a**, **5b** and **6** were recorded as solids using a ThermoFisher Nicolet iS5 FT-IR spectrometer with an ITX Germanium crystal. The compounds [Cp*E{W(CO)$_5$}$_2$] (E = P (**1a**), As (**1b**)),[26] [Na(thf)$_3$][(η^3-P$_3$)Nb(ODipp)$_3$] (**2**)[17] and [Cp‴Co(η^4-P$_4$)][20] were synthetized according to literature procedures.

8.4.1.1 Synthesis of [(ODipp)$_3$Nb(μ^3,η^3:η^1:η^1-P$_4$Cp*){W(CO)$_5$}$_2$][Na(18-c-6)(thf)$_2$] (3)

A solution of [Cp*P{W(CO)$_5$}$_2$] (**1a**) (244 mg, 0.3 mmol, 1 eq) in thf (20 ml) is cooled to -78°C. To this solution a solution of [Na(thf)$_3$][P$_3$Nb(ODipp)$_3$] (**2**) (287 mg, 0.3 mmol, 1 eq) and 18-c-6 (79 mg, 0.3 mmol) in 10 ml thf is added. A colour change from blue to dark brown is, after the addition, immediately observed. The reaction is warmed to room temperature and stirred for 16 hours. Subsequent the solvent is removed and the resulting black oil is dissolved in 2 ml thf and layered by 10 ml of *n*-hexane. After few days some crystals, suited for X-ray analysis, could be obtained. Additionally to the crystals, also black oil has formed on the bottom of the Schlenk flask. The solvent was decanted and the black oil was dried in vaco and the obtained powder of **3** was isolated. (Yield: 430 mg, 0.24 mmol, 80%)

^{1}H NMR (thf-d$_8$, 27°C): δ [ppm] = 7.74 (d, $^3J_{H,H}$ = 8 Hz, 6H, C$_6$*H*$_3$), 6.79 (t, $^3J_{H,H}$ = 8 Hz, 3H, C$_6$*H*$_3$), 3.65 (m, 6H, C*H*(CH$_3$)$_2$), 3.61 (m, 8H, thf), 1.90 (s, 3H, C*H*$_3$), 1.75 (m, 8H, thf), 1.59 (s, 3H, C*H*$_3$), 1.57 (s, 3H, C*H*$_3$), 1.53 (s, 3H, C*H*$_3$), 1.51 (d, $^3J_{H,P}$ = 11 Hz, 3H, C*H*$_3$), 1.00 - 1.25 (36H, CH(C*H*$_3$)$_2$).

$^{31}P\{^{1}H\}$ NMR (thf-d_8, 27°C): δ [ppm] = 105.7 (ddd, $^{1}J_{P,P}$ = 192 Hz, $^{1}J_{P,P}$ = 199 Hz, $^{2}J_{P,P}$ = 32 Hz, 1P), 73.6 (ddd, $^{1}J_{P,P}$ = 199 Hz, $^{1}J_{P,P}$ = 146 Hz, $^{2}J_{P,P}$ = 32 Hz, $^{1}J_{P,W}$ = 138 Hz, 1P), 38.1 (ddd, $^{1}J_{P,P}$ = 192 Hz, $^{1}J_{P,P}$ = 146 Hz, $^{2}J_{P,P}$ = 19 Hz, $^{1}J_{P,W}$ = 237 Hz, 1P), 4.3 (ddd, $^{1}J_{P,P}$ = 199 Hz, $^{1}J_{P,P}$ = 199 Hz, $^{2}J_{P,P}$ = 19 Hz, 1P).

^{31}P NMR (thf-d_8, 27°C): δ [ppm] = 105.7 (ddd, $^{1}J_{P,P}$ = 192 Hz, $^{1}J_{P,P}$ = 199 Hz, $^{2}J_{P,P}$ = 32 Hz, 1P), 73.6 (ddd, $^{1}J_{P,P}$ = 199 Hz, $^{1}J_{P,P}$ = 146 Hz, $^{2}J_{P,P}$ = 32 Hz, $^{1}J_{P,W}$ = 138 Hz, 1P), 38.1 (ddd, $^{1}J_{P,P}$ = 192 Hz, $^{1}J_{P,P}$ = 146 Hz, $^{2}J_{P,P}$ = 19 Hz, $^{1}J_{P,W}$ = 237 Hz, 1P), 4.3 (ddd, $^{1}J_{P,P}$ = 199 Hz, $^{1}J_{P,P}$ = 199 Hz, $^{2}J_{P,P}$ = 19 Hz, 1P).

IR (CH_2Cl_2): v = 3059 (w, CH), 2962 (m, CH_3), 2869 (w, CH_3), 2067 (w, CO), 1932 (vs, CO), 1840 (sh, CO).

EA $C_{68}H_{90}NaNbO_{19}P_4W_2$: calc [%]: C 44.90; H 4.99; found [%]: C 44.47; H 5.00.

8.4.1.2 Synthesis of [(Cp’’’Co)(μ$_3$,η^4:η^1-P$_5$Cp*){W(CO)$_5$}$_2$] (5a and 5b)

[Cp*P{W(CO)$_5$}$_2$] (**1a**) (195 mg, 0.24 mmol, 1 eq) in 20 ml thf was added to a stirred solution of [Cp’’’Co(η^4-P$_4$)] (**4**) (100 mg, 0.24 mmol, 1 eq) in thf at -100 °C. The dark blue reaction mixture was allowed to warm to room temperature, while the color changed to red. The $^{31}P\{^{1}H\}$ NRM spectrum of the reaction mixture reveals two isomers of the product [(Cp’’’Co)(μ$_3$,η^4:η^1-P$_5$Cp*){W(CO)$_5$}$_2$] (**5a** and **5b**, ratio 5.5:1) beside small amounts of impurities. The solvent was removed *in vacuo*. The residue was dissolved in a small amount of CH_2Cl_2, SiO_2 was added and the solvent removed *in vacuo*. The preabsorbed crude mixture was purified by column chromatography (SiO_2, hexane, 12 x 2.5 cm). Using hexane two weak yellow to orange fractions were eluted and disposed. With hexane/toluene 1:1 a dark red fraction was eluted (mixture of **5a** and **5b** according to $^{31}P\{^{1}H\}$ NMR). After removing the solvent *in vacuo,* the residue was dissolved in CH_2Cl_2 and layered with acetonitrile. After a few days **5a** can be obtained in form of dark red plates (90 mg). The supernatant was decanted off and the crystals dried in vacuo. The $^{31}P\{^{1}H\}$ NMR spectrum of the mother liquid shows a ratio of the two isomers of 1.3:1 (**5a**:**5b**). To separate **5a** and **5b** the solvent of the mixture was removed *in vacuo* and the residue was dissolved in a small amount of CH_2Cl_2 and purified by preparative thin layer chromatography (SiO_2, 1mm 20x20 cm, hexane/toluene 10:1). The first weak yellow and fourth weak brown fraction were disposed. The second and third red fraction were scratched of the plate, extracted with CH_2Cl_2 and filtered over diatomaceous earth. The solvent was removed *in vacuo*, the residues were each dissolved in CH_2Cl_2, layered with acetonitrile and stored at r.t. After a few days, crystals of **5a** (fraction 3, 8 mg) and of **5b**

(fraction 2, 7 mg) can be obtained. The supernatant was decanted off and the crystals dried *in vacuo*.

Isomer 1 (**5a**): Yield: 90 mg + 8 mg = 98 mg (0.0797 mmol, 33 %).

^{1}H NMR (CD_2Cl_2, 27°C): δ [ppm] = 6.28 (d, 1H, $C_5H_2{}^tBu_3$), 4.93 (m, 1H, $C_5H_2{}^tBu_3$), 2.20 (s, 3H, C_5Me_5), 2.13 (d, $^3J_{P:H}$ = 10 Hz, 3H, C_5Me_5), 2.11 (s, 3H, C_5Me_5), 1.82 (d, $^4J_{P:H}$ = 3 Hz, 3H, C_5Me_5), 1.77 (d, $^4J_{P:H}$ = 3 Hz, 3H, C_5Me_5), 1.49 (s, 9H, $C_5H_2{}^tBu_3$), 1.43 (s, 9H, $C_5H_2{}^tBu_3$), 1.36 (s, 9H, $C_5H_2{}^tBu_3$).

^{31}P{^{1}H} NMR (CD_2Cl_2, 27°C): δ [ppm] = 107.8 (dddd, $^1J_{P,P}$ = 259 Hz, $^1J_{P,P}$ = 260 Hz, $^2J_{P,P}$ = 11 Hz, $^2J_{P,P}$ = 8 Hz, $^1J_{P,W}$ = 235 Hz, 1P), 75.2 (dddd, $^1J_{P,P}$ = 464 Hz, $^1J_{P,P}$ = 437 Hz, $^2J_{P,P}$ = 11 Hz, $^2J_{P,P}$ = 40 Hz, $^1J_{P,W}$ = 235 Hz, 1P), 34.2 (ddd, $^1J_{P,P}$ = 464 Hz, $^1J_{P,P}$ = 407 Hz, $^2J_{P,P}$ = 8 Hz, 1P), -44.2 (dddd, $^1J_{P,P}$ = 259 Hz, $^1J_{P,P}$ = 407Hz, $^2J_{P,P}$ = 22 Hz, $^1J_{P,P}$ = 40 Hz, 1P), -60.2 (ddd, $^1J_{P,P}$ = 260 Hz, $^1J_{P,P}$ = 437 Hz, $^2J_{P,P}$ = 22 Hz, 1P).

^{31}P NMR (CD_2Cl_2, 27°C): δ [ppm] = 107.8 (brdd, $^1J_{P,P}$ = 259 Hz, $^1J_{P,P}$ = 260 Hz, $^1J_{P,W}$ = 235 Hz, 1P), 75.2 (dddd, $^1J_{P,P}$ = 464 Hz, $^1J_{P,P}$ = 437 Hz, $^2J_{P,P}$ = 11 Hz, $^2J_{P,P}$ = 40 Hz, $^1J_{P,W}$ = 235 Hz, 1P), 34.2 (ddd, $^1J_{P,P}$ = 464 Hz, $^1J_{P,P}$ = 407 Hz, $^2J_{P,P}$ = 8 Hz, 1P), -44.2 (dddd, $^1J_{P,P}$ = 259 Hz, $^1J_{P,P}$ = 407Hz, $^2J_{P,P}$ = 22 Hz, $^1J_{P,P}$ = 40 Hz, 1P), -60.2 (ddd, $^1J_{P,P}$ = 260 Hz, $^1J_{P,P}$ = 437 Hz, $^2J_{P,P}$ = 22 Hz, 1P).

IR (Ge-ATR): ν [cm^{-1}] = 2071 (m, CO), 2062 (s, CO), 1994 (w, CO), 1976 (w, CO), 1939 (s, CO), 1921 (vs, CO), 1906 (vs, CO), 1884 (m, CO).

LIFDI-MS (toluene): *m/z* = 1229.93 (100 %, $[M]^+$), 1094.87 (22 %, $[M\text{-}C_5Me_5]^+$);

EA $C_{37}H_{44}O_{10}P_5CoW_2{\cdot}(C_7H_8)_{0.25}$: calc [%]: C: 37.14; H: 3.70; found [%]: C: 36.82; H: 3.59.

Isomer 2 (**5b**): Yield: 7 mg (0.0055 mmol, 2 %).

^{1}H NMR (CD_2Cl_2, 27°C): δ [ppm] = 6.54 (d, 1H, $C_5H_2{}^tBu_3$), 4.94 (m, 1H, $C_5H_2{}^tBu_3$), 1.79 (m, 6H, C_5Me_5), 1.67 (s, 6H, C_5Me_5), 1.51 (s, 9H, $C_5H_2{}^tBu_3$), 1.36 (s, 9H, $C_5H_2{}^tBu_3$), 1.29 (s, 9H, $C_5H_2{}^tBu_3$), 0.62 (d, $^3J_{P,H}$ = 11 Hz, 3H, C_5Me_5).

^{31}P{^{1}H} NMR (CD_2Cl_2, 27°C): δ [ppm] =105.8 (dddd, $^1J_{P,P}$ = 435 Hz, $^1J_{P,P}$ = 475 Hz, $^2J_{P,P}$ = 15 Hz, $^2J_{P,P}$ = 23 Hz, $^1J_{P,W}$ = 234 Hz, 1P), 90.2 (dddd, $^1J_{P,P}$ = 297 Hz, $^1J_{P,P}$ = 275 Hz, $^2J_{P,P}$ = 15 Hz, $^2J_{P,P}$ = 11 Hz, $^1J_{P,W}$ = 217 Hz, 1P), 48.6 (ddd, $^1J_{P,P}$ = 475 Hz, $^1J_{P,P}$ = 391 Hz, $^2J_{P,P}$ = 11 Hz,

1P), -27.0 (dddd, $^{1}J_{P,P}$ = 275 Hz, $^{1}J_{P,P}$ = 391 Hz, $^{2}J_{P,P}$ = 34 Hz, $^{2}J_{P,P}$ = 23 Hz, 1P), -41.9 (ddd, $^{1}J_{P,P}$ = 297 Hz, $^{1}J_{P,P}$ = 435 Hz, $^{2}J_{P,P}$ = 34 Hz, 1P).

^{31}P NMR (CD_2Cl_2, 27°C): δ [ppm] = 105.8 (dddd, $^{1}J_{P,P}$ = 435 Hz, $^{1}J_{P,P}$ = 475 Hz, $^{2}J_{P,P}$ = 15 Hz, $^{2}J_{P,P}$ = 23 Hz, $^{1}J_{P,W}$ = 234 Hz, 1P), 90.2 (brdd, $^{1}J_{P,P}$ = 297 Hz, $^{1}J_{P,P}$ = 275 Hz, $^{1}J_{P,W}$ = 217 Hz, 1P), 48.6 (ddd, $^{1}J_{P,P}$ = 475 Hz, $^{1}J_{P,P}$ = 391 Hz, $^{2}J_{P,P}$ = 11 Hz, 1P), -27.0 (dddd, $^{1}J_{P,P}$ = 275 Hz, $^{1}J_{P,P}$ = 391 Hz, $^{2}J_{P,P}$ = 34 Hz, $^{2}J_{P,P}$ = 23 Hz, 1P), -41.9 (ddd, $^{1}J_{P,P}$ = 297 Hz, $^{1}J_{P,P}$ = 435 Hz, $^{2}J_{P,P}$ = 34 Hz, 1P).

IR (Ge-ATR): ν [cm^{-1}] = 2072 (m, CO), 2063 (s, CO), 1994 (w, CO), 1963 (m, CO), 1933 (s, CO), 1917 (vs, CO), 1897 (s, CO).

8.4.1.3 Synthesis of [(Cp’’’Co)(μ$_3$,η^4:η^1:η^1-P$_4$AsCp*){W(CO)$_5$}$_2$] (6)

[Cp*As{W(CO)$_5$}$_2$] (**1b**) (274 mg, 0.32 mmol, 1 eq) in 20 ml thf was added to a stirred solution of [Cp’’’Co(η^4-P$_4$)] (**4**) (133 mg, 0.32mmol, 1 eq) in thf at -100 °C. The dark blue reaction mixture was allowed to warm to room temperature. At -40°C the color changed to brown and after 2 hours at room temperature it changed to red. The solvent was removed *in vacuo*. The residue was dissolved in CH_2Cl_2 and layered with acetonitrile. After a few days, [(Cp’’’Co)(μ$_3$,η^4:η^1:η^1-P$_4$AsCp*){(W(CO)$_5$)$_2$}] (**6**) can be obtained as dark red plates. The supernatant was decanted off and the crystalline solid dried *in vacuo*.

Yield: 147 mg (0.12 mmol, 36%).

Isomer 1 (**6a**):

^{1}H NMR (CD_2Cl_2, 27°C): δ [ppm] = 6.49 (d, 1H, C$_5$*H*$_2$^{t}Bu$_3$), 5.00 (m, 1H, C$_5$*H*$_2$^{t}Bu$_3$), 1.82 (s, 3H, C$_5$*Me*$_5$), 1.77 (s, 3H, C$_5$*Me*$_5$), 1.68 (s, 6H, C$_5$*Me*$_5$), 1.50 (s, 9H, C$_5$H$_2$^{t}*Bu*$_3$), 1.36 (s, 9H, C$_5$H$_2$^{t}*Bu*$_3$), 1.31 (s, 9H, C$_5$H$_2$^{t}*Bu*$_3$), 0.61 (d, $^{3}J_{P:H}$ = 12 Hz, 3H, C$_5$*Me*$_5$).

^{31}P{^{1}H} NMR (CD_2Cl_2, 27°C): δ [ppm] = 98.9 (ddd, $^{1}J_{P,P}$ = 482 Hz, $^{1}J_{P,P}$ = 432 Hz, $^{2}J_{P,P}$ = 14 Hz, $^{1}J_{P,W}$ = 231 Hz, 1P), 86.5 (ddd, $^{1}J_{P,P}$ = 482 Hz, $^{2}J_{P,P}$ = 4 Hz, $^{2}J_{P,P}$ = 14 Hz, 1P), 69.7 (ddd, $^{1}J_{P,P}$ = 311 Hz, $^{2}J_{P,P}$ = 14 Hz, $^{2}J_{P,P}$ = 14 Hz, $^{1}J_{P,W}$ = 213 Hz, 1P), -17.6 (ddd, $^{1}J_{P,P}$ = 311 Hz, $^{1}J_{P,P}$ = 432 Hz, $^{2}J_{P,P}$ = 4 Hz, 1P).

^{31}P NMR (CD_2Cl_2, 27°C): δ [ppm] = 98.9 (ddd, $^{1}J_{P,P}$ = 482 Hz, $^{1}J_{P,P}$ = 432 Hz, $^{2}J_{P,P}$ = 14 Hz, $^{1}J_{P,W}$ = 231 Hz, 1P), 86.5 (ddd, $^{1}J_{P,P}$ = 482 Hz, $^{2}J_{P,P}$ = 4 Hz, $^{2}J_{P,P}$ = 14 Hz, 1P), 69.7 (brd, $^{1}J_{P,P}$ = 311 Hz, $^{1}J_{P,W}$ = 213 Hz, 1P), -17.6 (ddd, $^{1}J_{P,P}$ = 311 Hz, $^{1}J_{P,P}$ = 432 Hz, $^{2}J_{P,P}$ = 4 Hz, 1P).

Isomer 2 (**6b**):

^{1}H NMR (CD_2Cl_2, 27°C): δ [ppm] = 6.46 (d, 1H, $C_5H_2{}^tBu_3$), 4.87 (m, 1H, $C_5H_2{}^tBu_3$), 1.82 (s, 3H, C_5Me_5), 1.74 (s, 3H, C_5Me_5), 1.68 (s, 6H, C_5Me_5), 1.50 (s, 9H, $C_5H_2{}^tBu_3$), 1.39 (s, 9H, $C_5H_2{}^tBu_3$), 1.28 (s, 9H, $C_5H_2{}^tBu_3$), 0.60 (d, $^{3}J_{P:H}$ = 12 Hz, 3H, C_5Me_5).

^{31}P{^{1}H} NMR (CD_2Cl_2, 27°C): δ [ppm] = 128.8 (ddd, $^{1}J_{P,P}$ = 474 Hz, $^{2}J_{P,P}$ = 28 Hz, $^{2}J_{P,P}$ = 7 Hz, $^{1}J_{P,W}$ = 220 Hz, 1P), 78.1 (ddd, $^{1}J_{P,P}$ = 290 Hz, $^{2}J_{P,P}$ = 7 Hz, $^{2}J_{P,P}$ = 13 Hz, $^{1}J_{P,W}$ = 215 Hz, 1P), 40.9 (ddd, $^{1}J_{P,P}$ = 474 Hz, $^{1}J_{P,P}$ = 390 Hz, $^{2}J_{P,P}$ = 13 Hz, 1P), -10.3 (ddd, $^{1}J_{P,P}$ = 290 Hz, $^{1}J_{P,P}$ = 390 Hz, $^{2}J_{P,P}$ = 28 Hz, 1P).

^{31}P NMR (CD_2Cl_2, 27°C): δ [ppm] = 128.8 (ddd, $^{1}J_{P,P}$ = 474 Hz, $^{2}J_{P,P}$ = 28 Hz, $^{2}J_{P,P}$ = 7 Hz, $^{1}J_{P,W}$ = 220 Hz, 1P), 78.1 (brd, $^{1}J_{P,P}$ = 290 Hz, $^{1}J_{P,W}$ = 215 Hz, 1P), 40.9 (ddd, $^{1}J_{P,P}$ = 474 Hz, $^{1}J_{P,P}$ = 390 Hz, $^{2}J_{P,P}$ = 13 Hz, 1P), -10.3 (ddd, $^{1}J_{P,P}$ = 290 Hz, $^{1}J_{P,P}$ = 390 Hz, $^{2}J_{P,P}$ = 28 Hz, 1P).

Isomer 3 (**6c**):

^{1}H NMR (CD_2Cl_2, 27°C): δ [ppm] = 6.52 (d, 1H, $C_5H_2{}^tBu_3$), 4.80 (m, 1H, $C_5H_2{}^tBu_3$), 1.81 (s, 3H, C_5Me_5), 1.77 (s, 3H, C_5Me_5), 1.68 (s, 6H, C_5Me_5), 1.52 (s, 9H, $C_5H_2{}^tBu_3$), 1.34 (s, 9H, $C_5H_2{}^tBu_3$), 1.29 (s, 9H, $C_5H_2{}^tBu_3$), 0.50 (d, $^{3}J_{P:H}$ = 11 Hz, 3H, C_5Me_5).

^{31}P{^{1}H} NMR (CD_2Cl_2, 27°C): δ [ppm] = 114.9 (ddd, $^{1}J_{P,P}$ = 438 Hz, $^{2}J_{P,P}$ = 13 Hz, $^{2}J_{P,P}$ = 21 Hz, 1P), 87.7 (ddd, $^{1}J_{P,P}$ = 299 Hz, $^{1}J_{P,P}$ = 275 Hz, $^{2}J_{P,P}$ = 13 Hz, 1P), 0.9 (ddd, $^{1}J_{P,P}$ = 275 Hz, $^{2}J_{P,P}$ = 37 Hz, $^{2}J_{P,P}$ = 21 Hz, 1P), -51.4 (ddd, $^{1}J_{P,P}$ = 299 Hz, $^{1}J_{P,P}$ = 438 Hz, $^{2}J_{P,P}$ = 37 Hz, 1P).

^{31}P NMR (CD_2Cl_2, 27°C): δ [ppm] = 114.9 (ddd, $^{1}J_{P,P}$ = 438 Hz, $^{2}J_{P,P}$ = 13 Hz, $^{2}J_{P,P}$ = 21 Hz, 1P), 87.7 (brdd, $^{1}J_{P,P}$ = 299 Hz, $^{1}J_{P,P}$ = 275 Hz, 1P), 0.9 (ddd, $^{1}J_{P,P}$ = 275 Hz, $^{2}J_{P,P}$ = 37 Hz, $^{2}J_{P,P}$ = 21 Hz, 1P), -51.4 (ddd, $^{1}J_{P,P}$ = 299 Hz, $^{1}J_{P,P}$ = 438 Hz, $^{2}J_{P,P}$ = 37 Hz, 1P).

LIFDI-MS (toluene): *m/z* = 1274.01 (100 %, $[M]^+$), 1138.92 (47 %, $[M\text{-}C_5Me_5]^+$).

IR (Ge-ATR): ν [cm^{-1}] = 2072 (w, CO), 2063 (m, CO), 1993 (w, CO), 192 (m, CO), 1931 (s, CO), 1917 (vs, CO), 1898 (vs, CO).

EA $C_{37}H_{44}O_{10}P_4AsCoW_2$: calc [%]: C: 34.88; H: 3.48; found [%]: C: 34.91; H: 3.36.

8.4.2 NMR spectroscopic investigations

8.4.2.1 $[(ODipp)_3Nb(\mu^3,\eta^3{:}\eta^1{:}\eta^1\text{-}P_4Cp^*)\{W(CO)_5\}_2][Na(18\text{-}c\text{-}6)(thf)_2]$ (3)

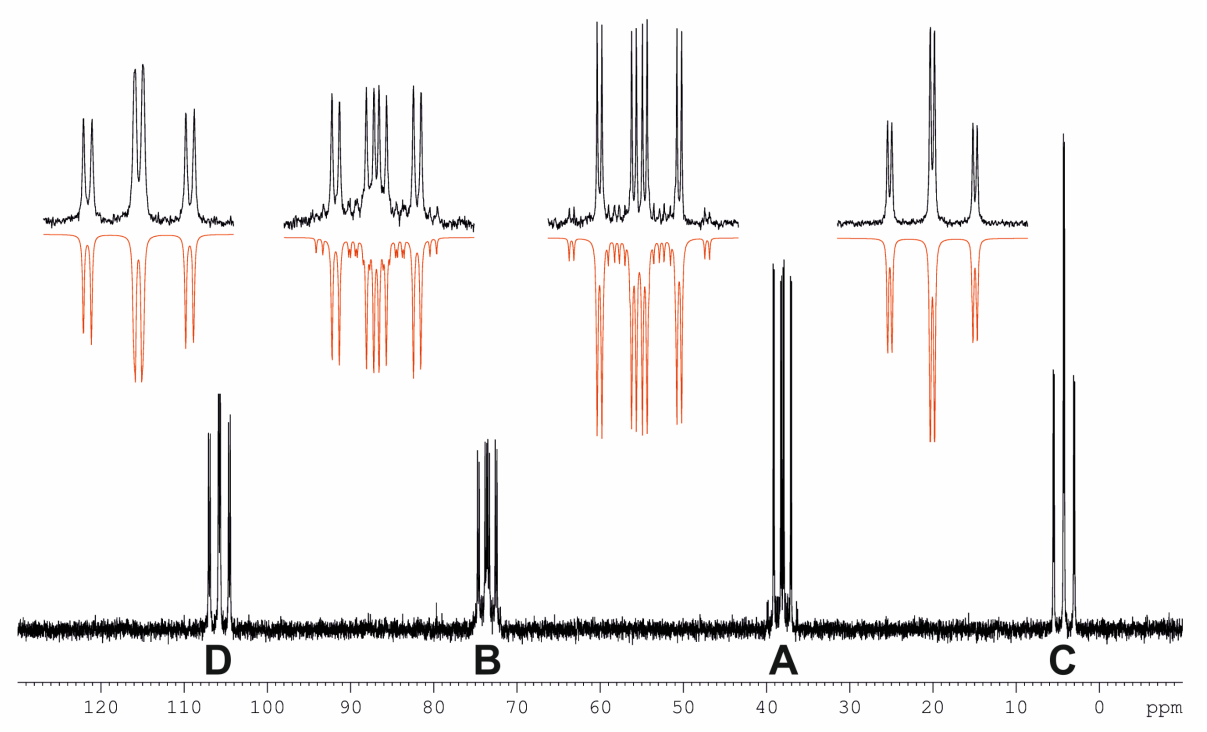


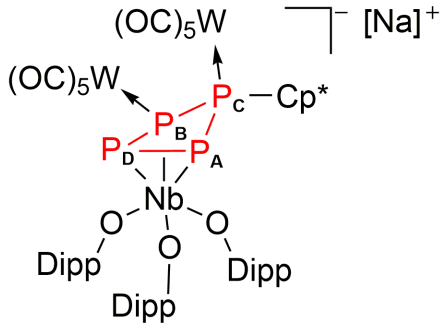
Figure S1. Experimental (black) and simulated (red) $^{31}P\{^1H\}$ NMR spectrum of compound **3**. $^{31}P\{^1H\}$ NMR chemical shifts and coupling constants for [Na][**3**] are obtained from the simulation.

P_D: 105.7 ppm ($^1J_{PD:PA}$ = 192 Hz; $^1J_{PD:PC}$ = 199 Hz; $^2J_{PD:PB}$ = 32 Hz)

P_B: 73.6 ppm ($^1J_{PB:PA}$ = 146 Hz; $^1J_{PB:PC}$ = 199 Hz; $^2J_{PB:PD}$ = 32 Hz; $^1J_{PB:W}$ = 138 Hz)

P_A: 38.1 ppm ($^1J_{PA:PB}$ = 146 Hz; $^1J_{PA:PD}$ = 192 Hz; $^2J_{PA:PC}$ = 20 Hz $^1J_{PC:W}$ = 237 Hz)

P_C: 4.3 ppm ($^1J_{PC:PB}$ = 199 Hz; $^1J_{PC:PD}$ = 199 Hz; $^2J_{PC:PA}$ = 20 Hz)



3

8.4.2.2 [(Cp'''Co)(μ$_3$,η^4:η^1-P$_5$Cp*){W(CO)$_5$}$_2$] (5a and 5b)

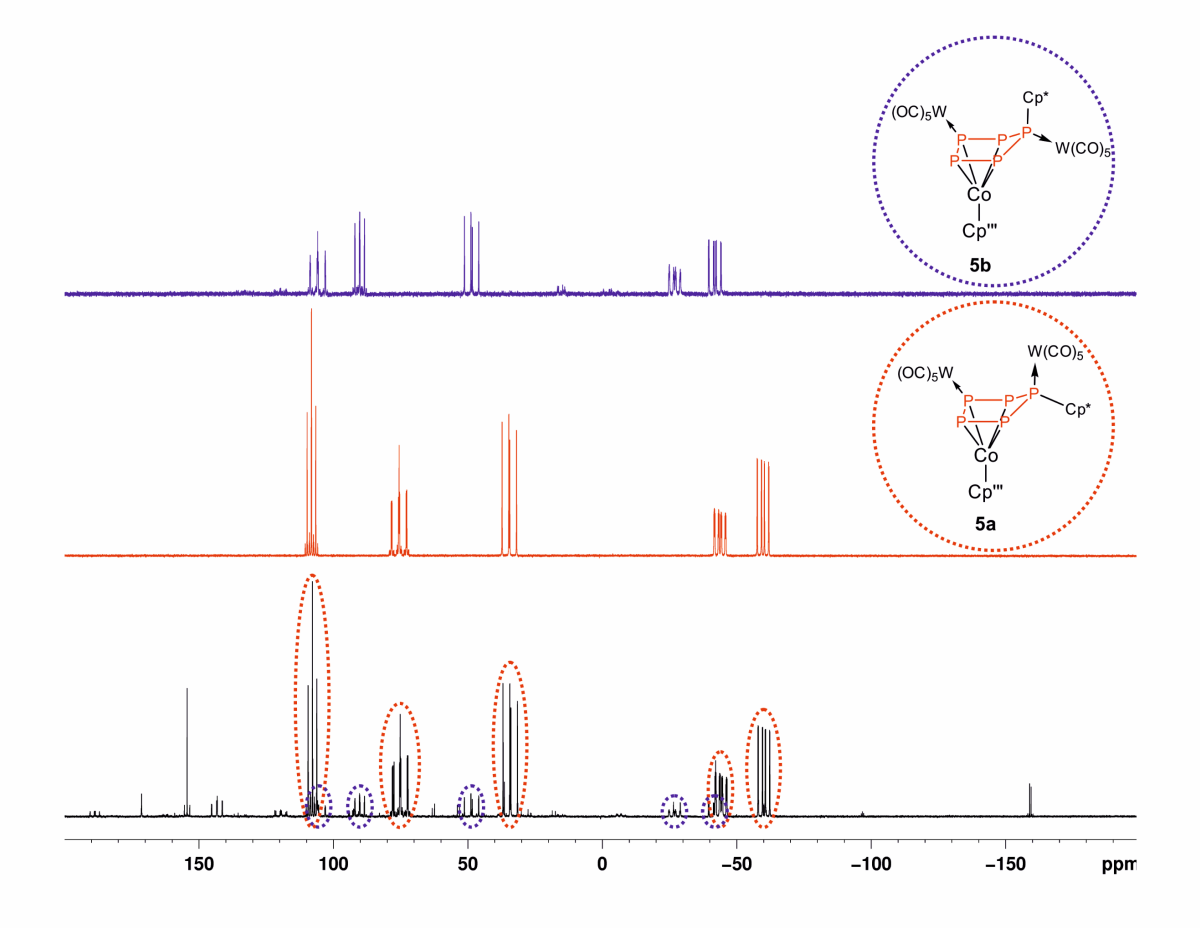


Figure S2. $^{31}P\{^1H\}$ NMR spectra of the reaction mixture of [Cp*P{W(CO)$_5$}$_2$] and [Cp'''Co(η^4-P$_4$)] (black) and of the isolated compounds **5a** (red) and **5b** (blue).

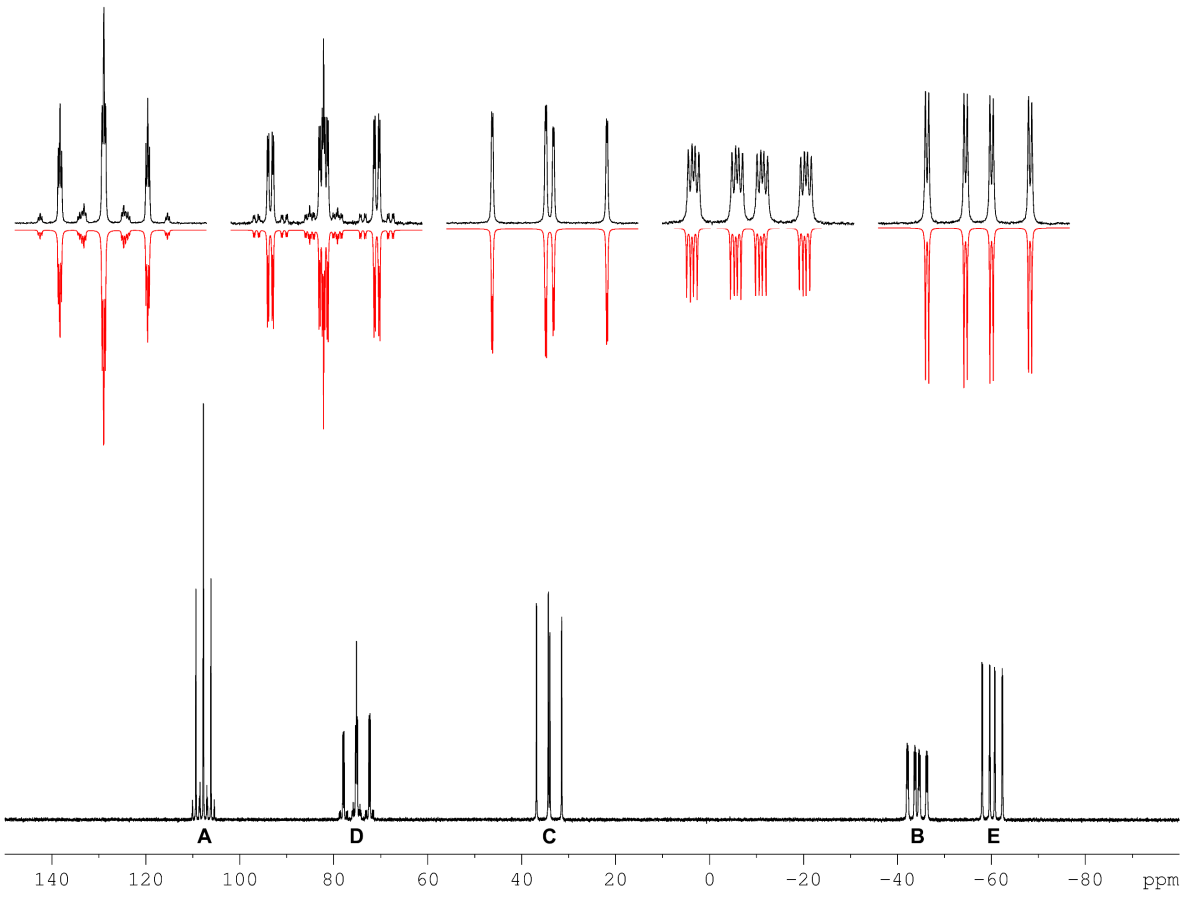
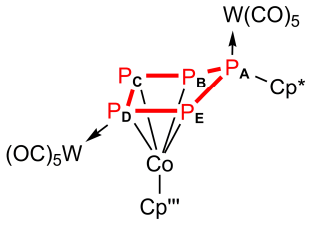


Figure S3. Experimental (black) and simulated (red) $^{31}P\{^{1}H\}$ NMR spectrum of compound **5a** in CD_2Cl_2. ^{31}P NMR chemical shifts and coupling constants for [**5a**] obtained from the simulation.



5a

P_A: 107.8 ppm ($^{1}J_{PA:PE}$ = 259 Hz; $^{1}J_{PA:PB}$ = 260 Hz; $^{2}J_{PA:PC}$ = 11 Hz; $^{2}J_{PA:PD}$ = 8 Hz $^{1}J_{PA:W}$ = 235 Hz)

P_D: 75.2 ppm ($^{1}J_{PC:PD}$ = 464 Hz; $^{1}J_{PC:PB}$ = 437 Hz; $^{2}J_{PC:PA}$ = 11 Hz; $^{2}J_{PC:PE}$ = 40 Hz; $^{1}J_{PC:W}$ = 235 Hz)

P_C: 34.2 ppm ($^{1}J_{PD:PC}$ = 464 Hz; $^{1}J_{PD:PE}$ = 407 Hz; $^{2}J_{PD:PA}$ = 8 Hz $^{2}J_{PD:PB}$ = 1 Hz)

P_B: -44.2 ppm ($^{1}J_{PE:PA}$ = 259 Hz; $^{1}J_{PE:PD}$ = 407 Hz; $^{2}J_{PE:PB}$ = 22 Hz; $^{2}J_{PE:PC}$ = 40 Hz)

P_E: -60.2 ppm ($^{1}J_{PB:PA}$ = 260 Hz; $^{1}J_{PB:PC}$ = 437 Hz; $^{2}J_{PB:PD}$ = 1 Hz; $^{2}J_{PB:PE}$ = 22 Hz)

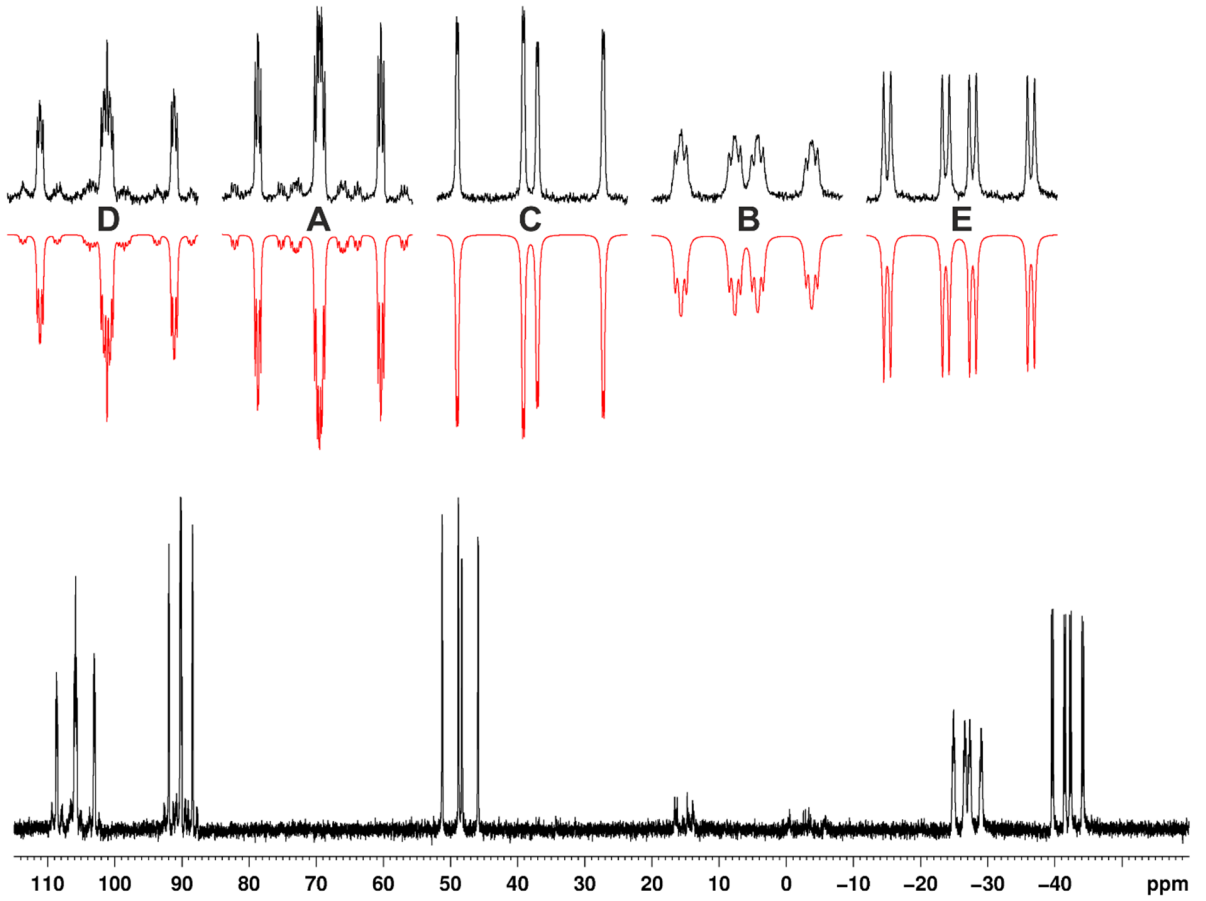
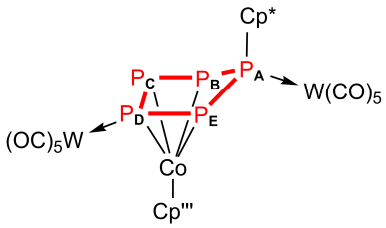


Figure S4. Experimental (black) and simulated (red) $^{31}P\{^{1}H\}$ NMR spectrum of compound **5b** in CD_2Cl_2. ^{31}P NMR chemical shifts and coupling constants for [**5b**] obtained from the simulation.



5b

P_D: 105.8 ppm ($^{1}J_{PC:PB}$ = 435 Hz; $^{1}J_{PC:PD}$ = 475 Hz; $^{2}J_{PC:PA}$ = 15 Hz; $^{2}J_{PC:PE}$ = 23 Hz $^{1}J_{PC:W}$ = 234 Hz)

P_A: 90.2 ppm ($^{1}J_{PA:PB}$ = 297 Hz; $^{1}J_{PA:PE}$ = 275 Hz; $^{2}J_{PA:PC}$ = 15 Hz; $^{2}J_{PA:PD}$ = 11 Hz; $^{1}J_{PA:W}$ = 217 Hz)

P_C: 48.6 ppm ($^{1}J_{PD:PC}$ = 475 Hz; $^{1}J_{PD:PE}$ = 391 Hz; $^{2}J_{PD:PA}$ = 11 Hz $^{2}J_{PD:B}$ = 1 Hz)

P_B: -27.0 ppm ($^{1}J_{PE:PA}$ = 275 Hz; $^{1}J_{PE:PD}$ = 391 Hz; $^{2}J_{PE:PB}$ = 34 Hz; $^{2}J_{PE:PC}$ = 23 Hz)

P_E: -41.9 ppm ($^{1}J_{PB:PA}$ = 297 Hz; $^{1}J_{PB:PC}$ = 435 Hz; $^{2}J_{PB:PD}$ = 1 Hz; $^{2}J_{PB:PE}$ = 34 Hz)

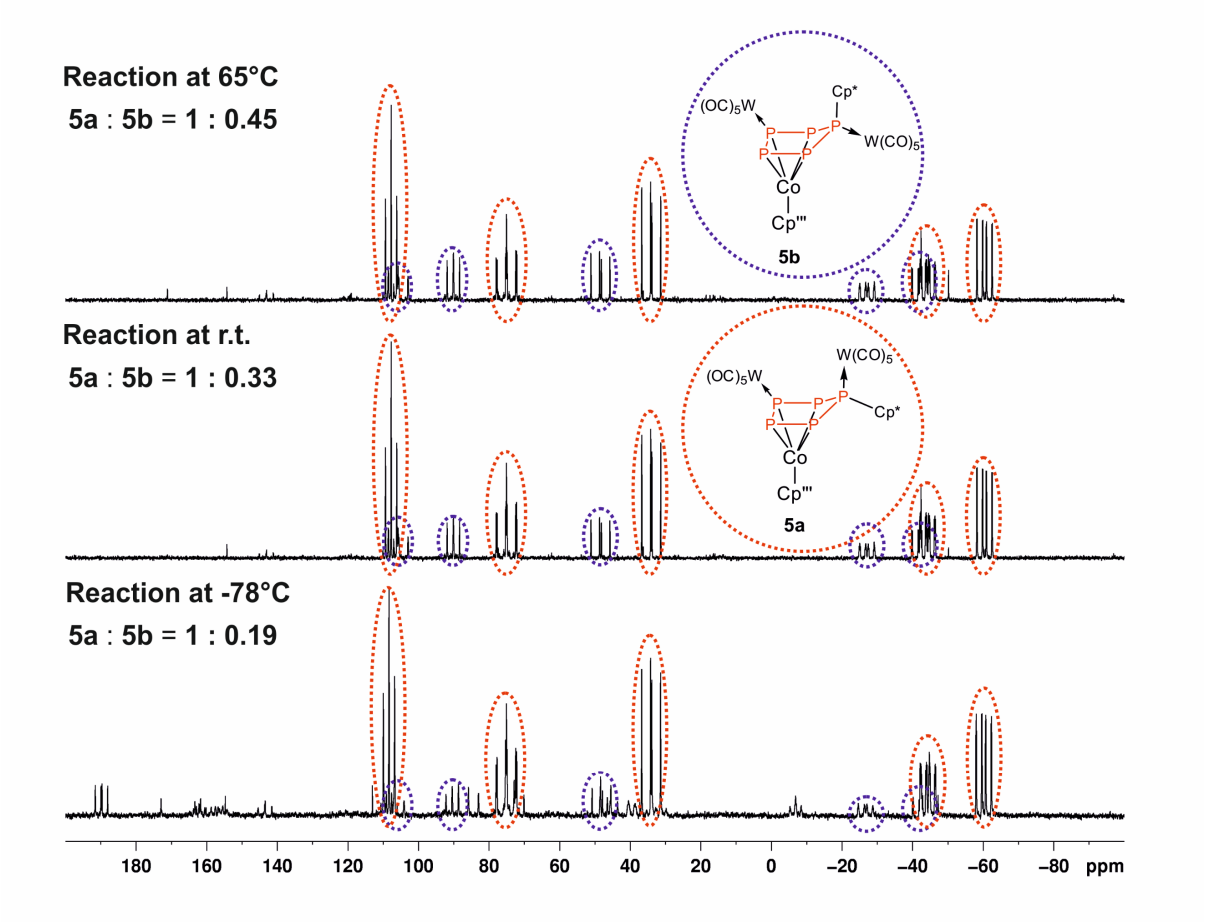
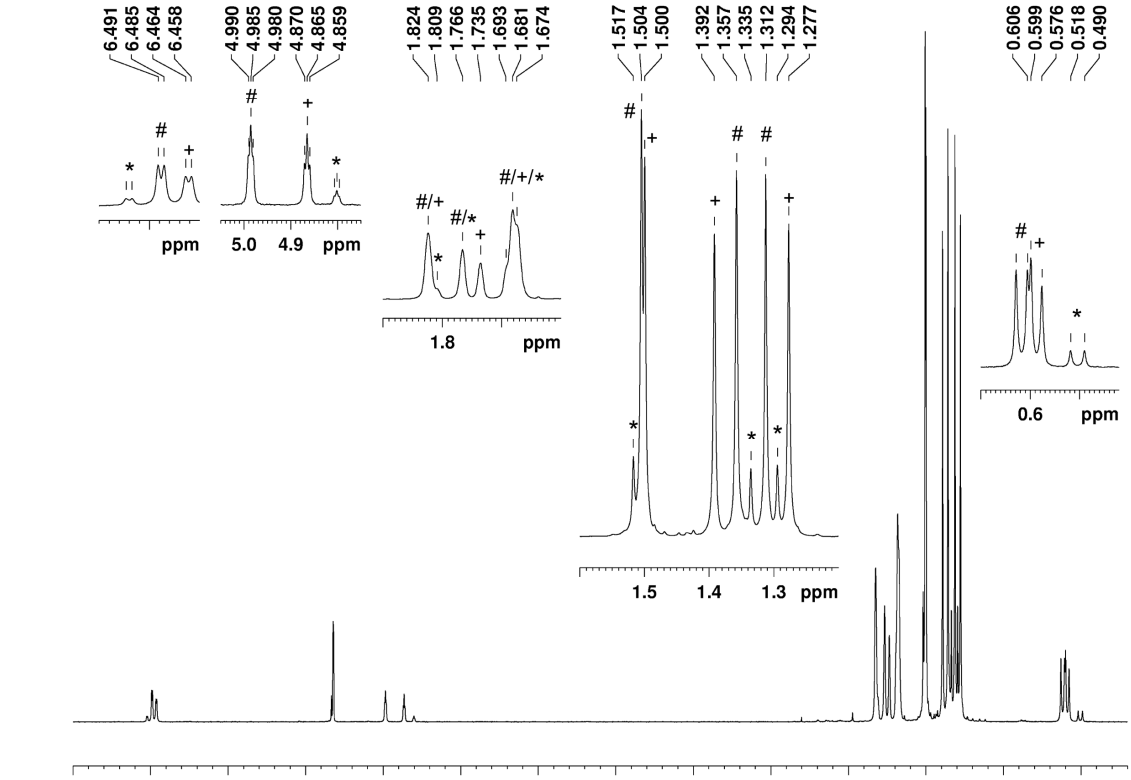


Figure S5. $^{31}P\{^{1}H\}$ NMR spectra at room temperature from the reaction mixtures of the reaction of **1a** and **4** performed at different temperatures.

8.4.2.3 [(Cp'''Co)(μ$_3$,η^4:η^1:η^1-P$_4$AsCp*){W(CO)$_5$}$_2$] (6)



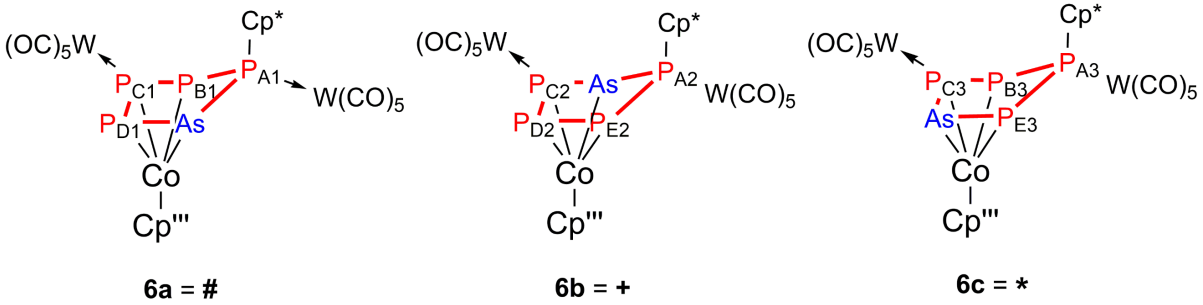


Figure S6. ^{1}H NMR spectrum of the three isomers of **6** in CD_2Cl_2.

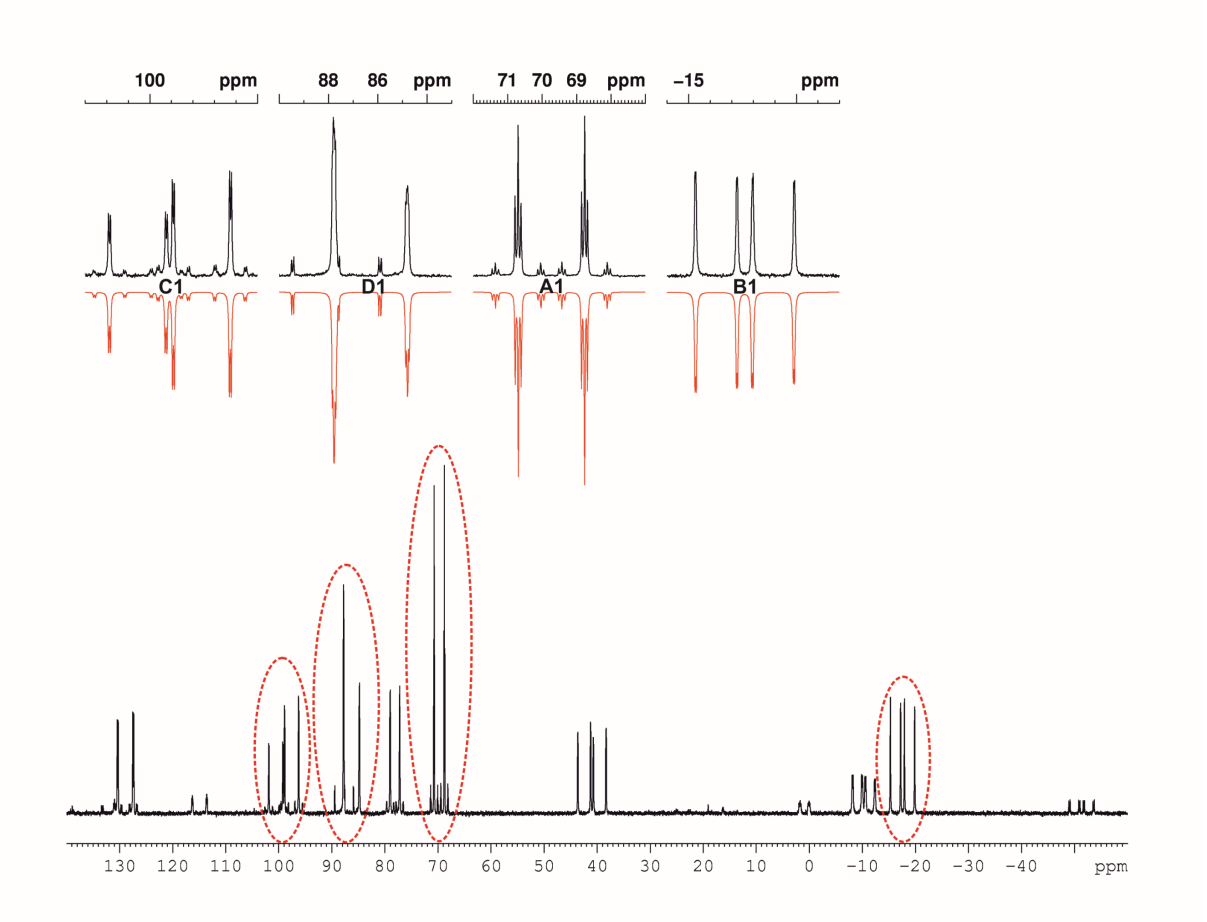
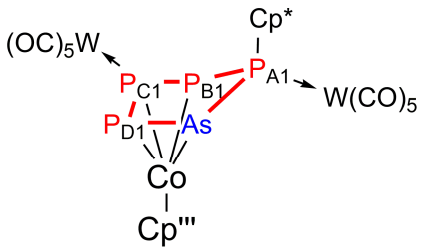


Figure S7. Experimental (black) and simulated (red) $^{31}P\{^{1}H\}$ NMR spectrum of compound **6a** in CD_2Cl_2. ^{31}P NMR chemical shifts and coupling constants for **6a** obtained from the simulation.



6a

P_{C1}: 98.9 ppm ($^{1}J_{PC1:PD1}$ = 482 Hz; $^{1}J_{PC1:PB1}$ = 432 Hz; $^{2}J_{PC1:PA1}$ = 14 Hz; $^{1}J_{PC1:W}$ = 231 Hz)

P_{D1}: 86.5 ppm ($^{1}J_{PD1:PC1}$ = 482 Hz; $^{2}J_{PD1:PB1}$ = 4 Hz; $^{2}J_{PD1:PA1}$ = 14 Hz)

P_{A1}: 69.7 ppm ($^{1}J_{PA1:PB1}$ = 311 Hz; $^{2}J_{PA1:PC1}$ = 14 Hz $^{2}J_{PA1:PD1}$ = 14 Hz; $^{1}J_{PA1:W}$ = 213 Hz)

P_{B1}: -17.6 ppm ($^{1}J_{PB1:PA1}$ = 311 Hz; $^{1}J_{PB1:PC1}$ = 432 Hz; $^{2}J_{PB1:PD1}$ = 4 Hz)

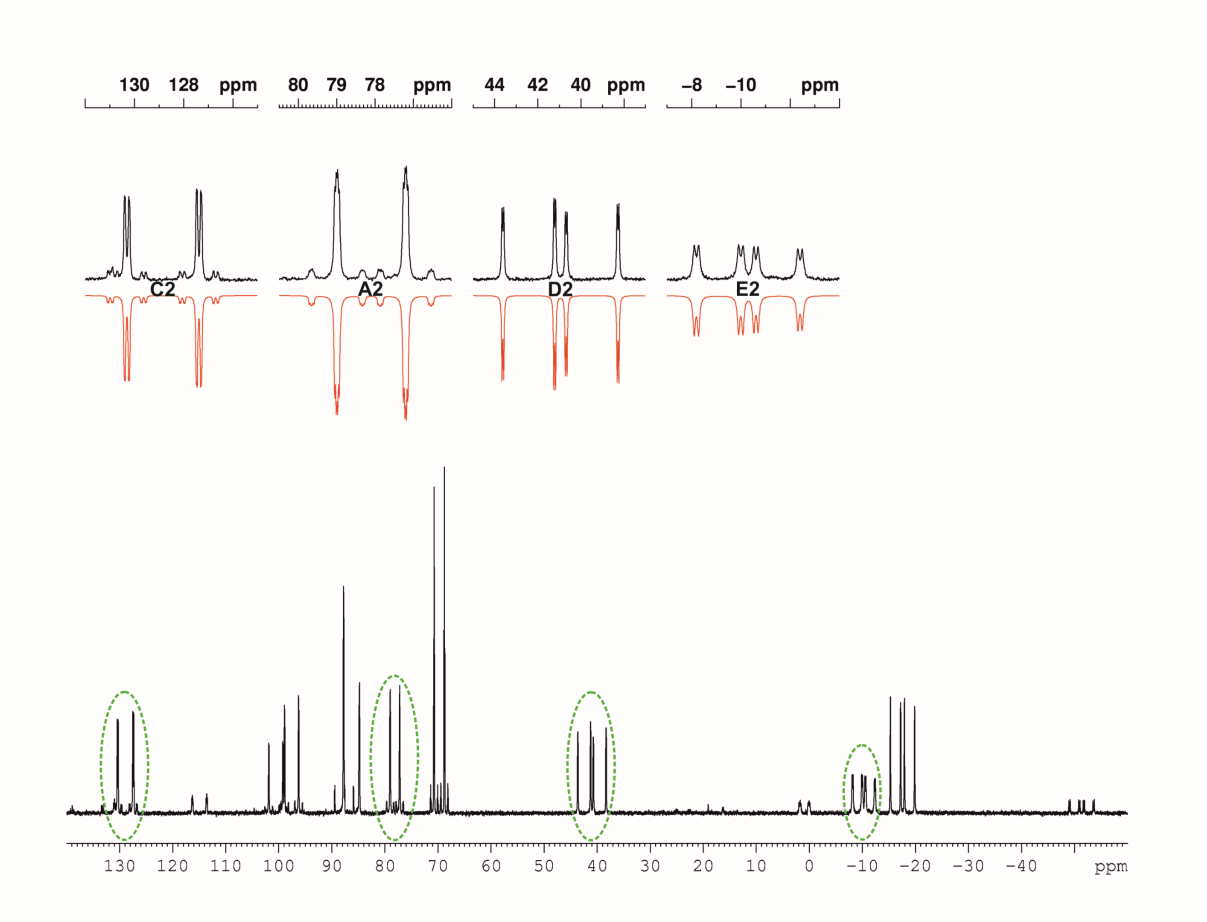
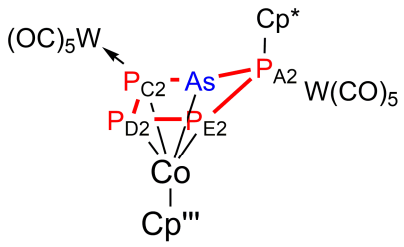


Figure S8. Experimental (black) and simulated (red) $^{31}P\{^{1}H\}$ NMR spectrum of compound **6b** in CD_2Cl_2. ^{31}P NMR chemical shifts and coupling constants for **6b** obtained from the simulation.



6b

P_{C2}: 128.8 ppm ($^{1}J_{PC2:PD2}$ = 474 Hz; $^{2}J_{PC2:PE2}$ = 28 Hz; $^{2}J_{PC2:PA2}$ = 7 Hz $^{1}J_{PC2:W}$ = 220 Hz)

P_{A2}: 78.1 ppm ($^{1}J_{PA2:PE1}$ = 290 Hz; $^{2}J_{PA2:PC2}$ = 7 Hz; $^{2}J_{PA2:PD2}$ = 13 Hz; $^{1}J_{PA2:W}$ = 215 Hz)

P_{D2}: 40.9 ppm ($^{1}J_{PD2:PC2}$ = 474 Hz; $^{1}J_{PD2:PE2}$ = 390 Hz; $^{2}J_{PD2:PA2}$ = 13 Hz)

P_{E2}: -10.3 ppm ($^{1}J_{PE2:PA2}$ = 290 Hz; $^{1}J_{PE2:PD2}$ = 390 Hz; $^{2}J_{PE2:PC2}$ = 28 Hz)

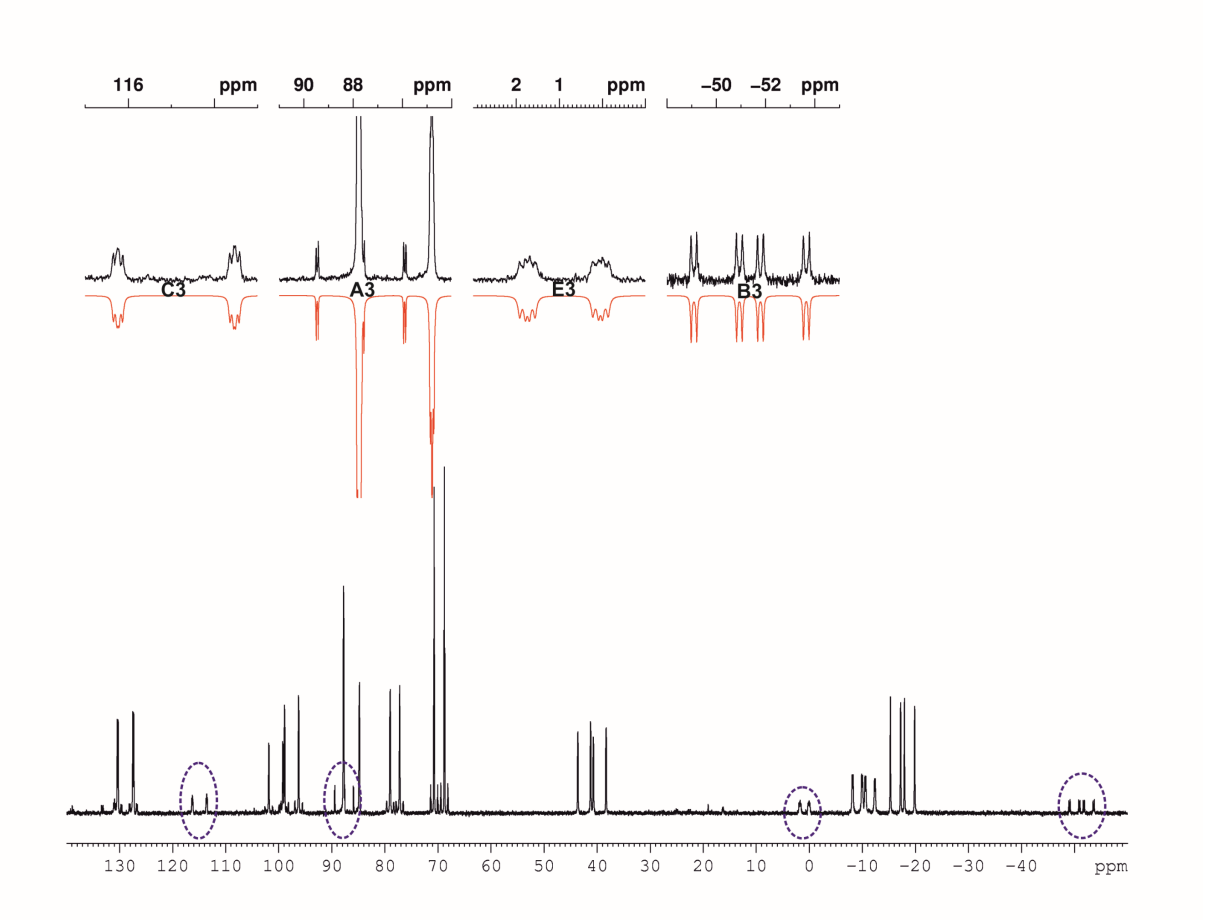
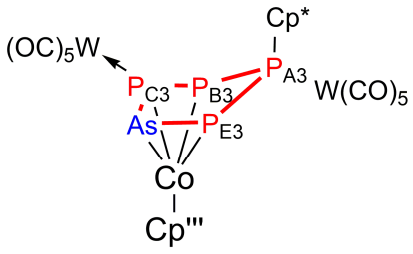


Figure S9. Experimental (black) and simulated (red) $^{31}P\{^{1}H\}$ NMR spectrum of compound **6c** in CD_2Cl_2. ^{31}P NMR chemical shifts and coupling constants for **6c** obtained from the simulation. The satellite signals for the $^{1}J_{P:W}$ could, due to the low concentration of **6c**, not be observed.



6c

P_{C3}: 114.9 ppm ($^{1}J_{PC3:PB3}$ = 438 Hz; $J_{PC3:PA3}$ = 13 Hz; $^{2}J_{PC3:PE3}$ = 21 Hz)

P_{A3}: 87.7 ppm ($^{1}J_{PA3:PB3}$ = 299 Hz; $^{1}J_{PA3:PE3}$ = 275 Hz; $^{2}J_{PA3:PC3}$ = 13 Hz)

P_{E3}: 0.9 ppm ($^{1}J_{PE3:PA3}$ = 275 Hz; $^{2}J_{PE3:PB3}$ = 37 Hz $^{2}J_{PE3:PC3}$ = 21 Hz)

P_{B3}: -51.4 ppm ($^{1}J_{PB3:PA3}$ = 299 Hz; $^{1}J_{PB3:PC3}$ = 438 Hz; $^{2}J_{PB3:PE3}$ = 37 Hz)

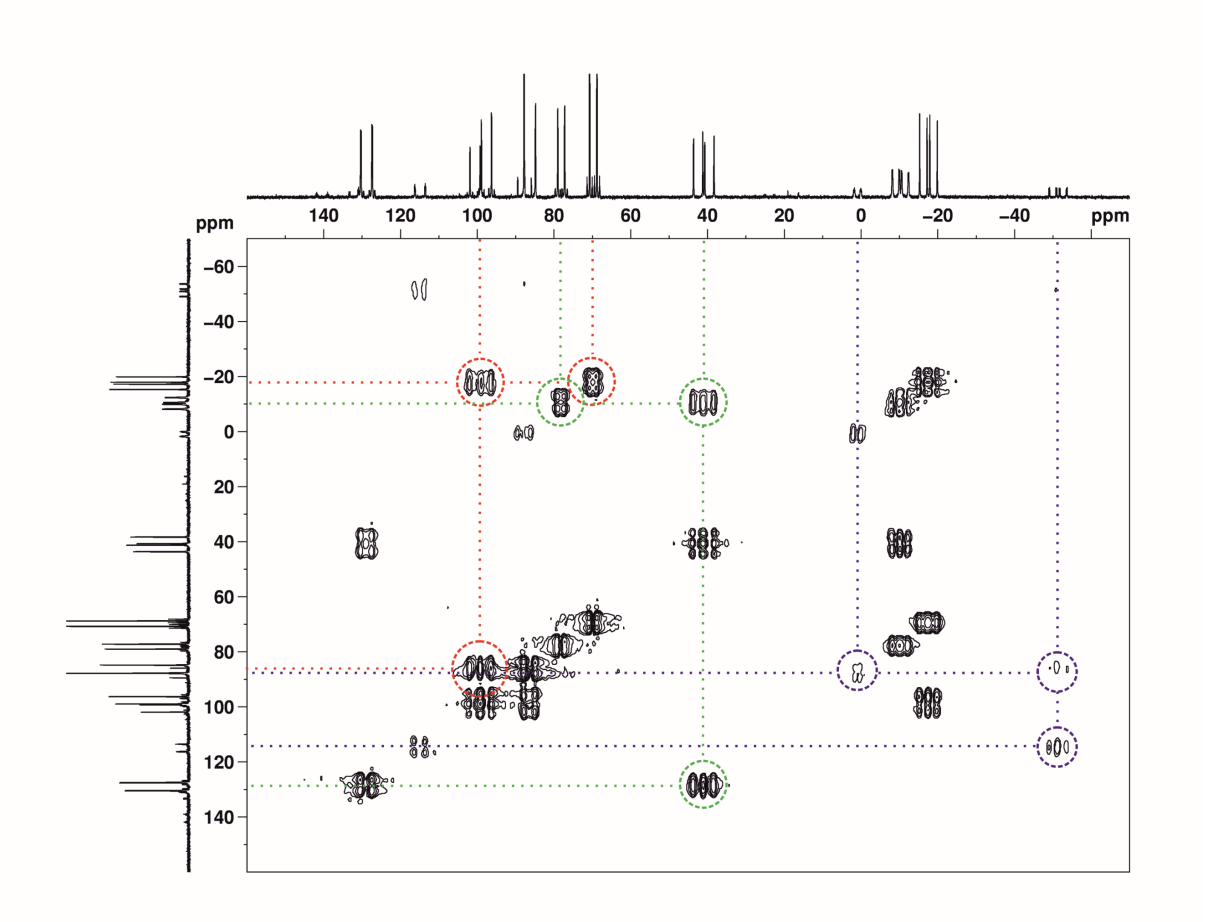
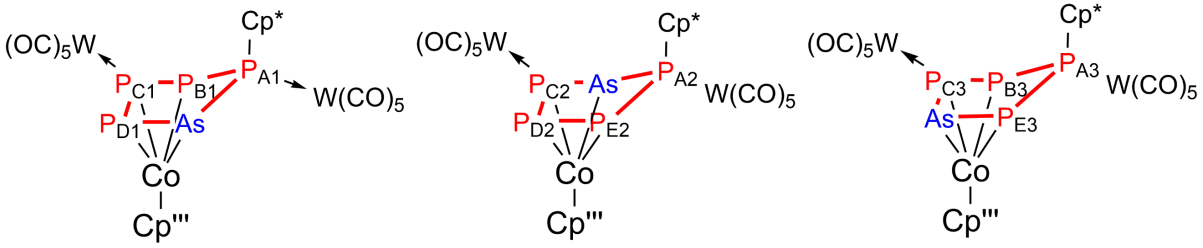


Figure S10. ^{31}P COSY NMR spectrum of compound **6** in CD_2Cl_2.



6a = **#** **6b** = **+** **6c** = *****

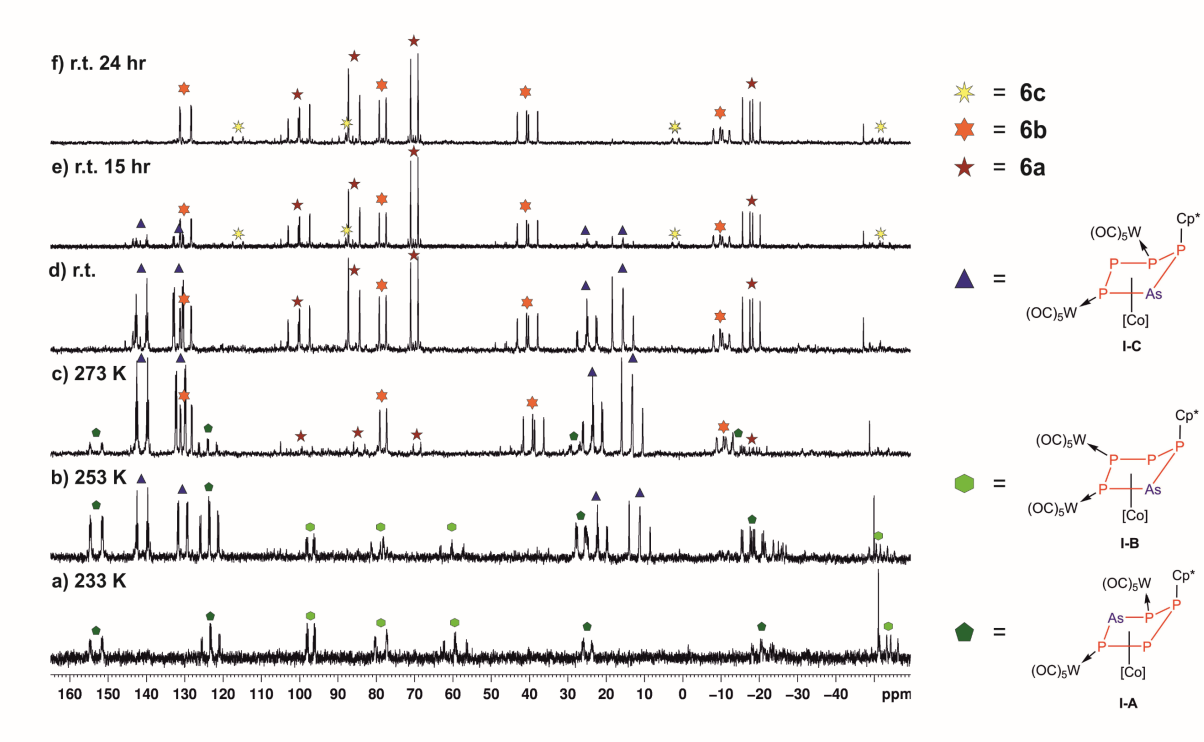


Figure S11. Temperature and time depending $^{31}P\{^{1}H\}$ NMR spectra (thf-d_8) of the reaction of **1b** and **4**.

8.4.3 Crystallographic Details

The crystals were selected and mounted on a Gemini Ultra diffractometer equipped with an AtlasS2 CCD detector (**5a**, **5b 6**) and a SuperNova diffractometer equipped with a Atlas CCD detector (**3**), respectively. All crystals (**3**, **5a**, **5b**, **6**) were kept at T = 123(1) K during data collection. Data collection and reduction were performed with **CrysAlispro** (Version 171.34.36 (**3**), 171.38.43 (**5a**), 171.40.14a (**5b**, **6**)).[27] For the compounds (**3**, **5a**, **5b**, **6**) an analytical numeric absorption correction using a multifaceted crystal model based on expressions derived by R.C. Clark & J.S. Reid.(Clark, R. C. & Reid, J. S. (1995). Acta Cryst. A51, 887-897) was applied. Using **Olex2**,[28] the structure of compound **3** was solved by **Superflip**[29] and the structures of **5a**, **5b** and **6** by **ShelXT**[30] respectively. A least-square refinement on F^2 was carried out with **ShelXL**[31] for all structures. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms at the carbon atoms were located in idealized positions and refined isotropically according to the riding model.

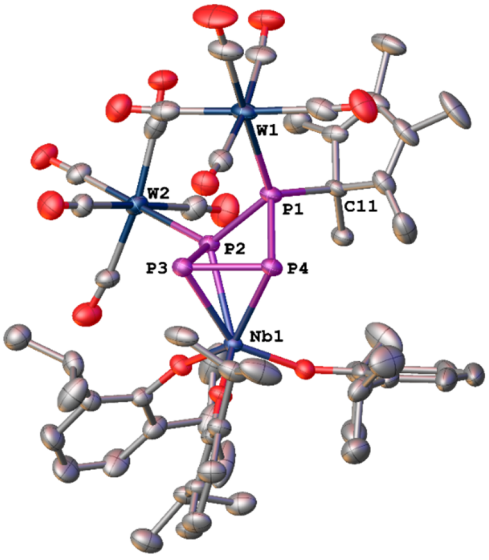
Compound **3**: The asymmetric unit contains a hexane molecule, which is disordered over two positions with a ratio of 60 to 40. Further, the 18-c-6 and the two thf molecules coordinating the potassium ion are heavily disordered. The 18-c-6 molecule shows a disorder over three positions with a distribution of 50 to 30 to 20. To describe this disorder the DFIX, SADI and SIMU restrains were applied.

Compound **5b**: The asymmetric unit contains one molecule of **5b**. One of the two $W(CO)_5$ units of **5b** is disordered over two positions with a distribution of 66 to 34. To describe this disorder the restrains SADI and SIMU were applied.

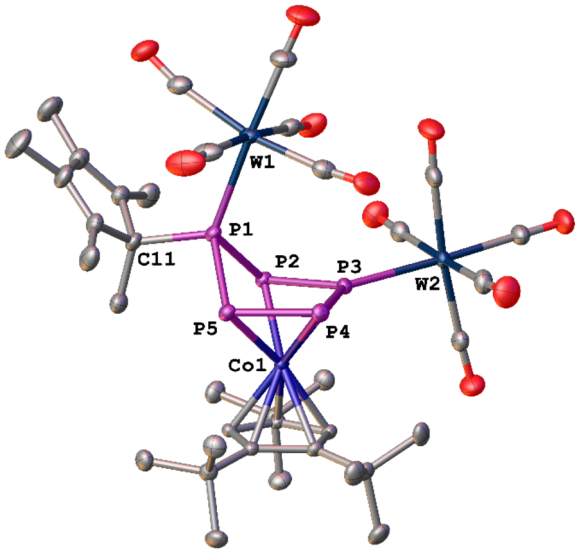
Compound **6**: Compounds **6** crystallize as a mixture of three individual compounds (**6a**, **6b** and **6c**) in the space group $P\bar{1}$ with one molecule in the asymmetric unit. The three isomers differ by the position of the arsenic atom. The distribution of the arsenic atom over the positions 2, 4 or 5 was determined to be 0.44 to 0.1 to 0.46. Further, three CO ligands of one $W(CO)_5$ unit are disordered over two positions (75:25). To describe these disorders the SIMU restraint was applied.

CCDC-1896430 (**3**), CCDC-1896431 (**5a**), CCDC-1896432 (**5b**) and CCDC-1896433 (**6**), contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: + 44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

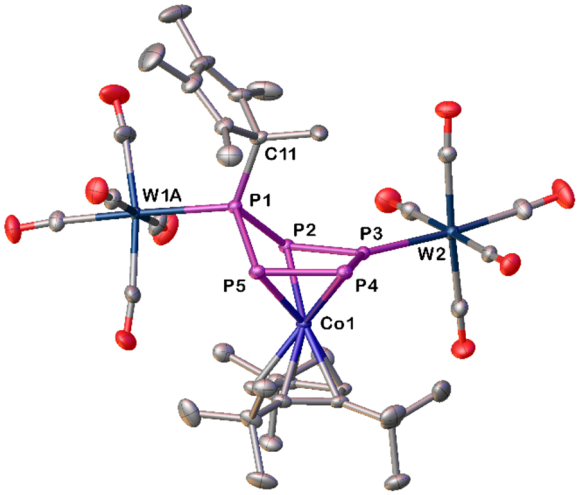
Compound	**3** (hexane)	**5a** 0.5(toluene)	**5b**	**6**
CCDC	1896430	1896431	1896432	1896433
Formula	$C_{82}H_{120}NaNbO_{21}P_4W_2$	$C_{40.5}H_{48}CoO_{10}P_5W_2$	$C_{37}H_{44}CoO_{10}P_5W_2$	$C_{37}H_{44}AsCoO_{10}P_4W_2$
$D_{calc.}$/ g cm^{-3}	1.507	1.804	1.851	1.916
μ/mm^{-1}	6.880	13.629	5.802	6.506
Formula Weight	2049.25	1276.27	1230.20	1274.15
Colour	brown	clear light orange	clear dark red	clear dark red
Shape	block	plate	plate	block
Size/mm^3	0.56×0.46×0.37	0.24×0.07×0.04	0.47×0.40×0.09	0.52×0.19×0.11
T/K	123(1)	123(1)	123(2)	123(1)
Crystal System	triclinic	triclinic	triclinic	triclinic
Space Group	*P*-1	*P*-1	*P*-1	*P*-1
a/Å	15.5700(3)	10.4770(2)	12.6456(3)	12.6194(2)
b/Å	16.0909(3)	11.4879(4)	13.3629(3)	13.4312(3)
c/Å	18.4744(3)	21.0415(5)	14.3474(3)	14.3370(3)
α/°	78.1980(10)	82.861(2)	67.893(2)	67.678(2)
β/°	86.1760(10)	84.604(2)	79.646(2)	79.592(2)
γ/°	87.0370(10)	69.455(2)	83.882(2)	83.686(2)
V/Å^3	4517.13(14)	2349.60(11)	2207.62(9)	2208.66(8)
Z	2	2	2	2
Z'	1	1	1	1
Wavelength/Å	1.54178	1.54184	0.71073	0.71073
Radiation type	CuK$_\alpha$	CuK$_\alpha$	MoK$_\alpha$	MoK$_\alpha$
Θ_{min}/°	2.807	4.130	3.294	3.416
Θ_{max}/°	74.100	73.000	37.745	37.830
Measured Refl.	48920	28482	65108	64366
Independent Refl.	17877	9110	22222	22293
Reflections with I > 2(I)	17176	8376	18896	18835
R_{int}	0.0561	0.0312	0.0282	0.0259
Parameters	1427	574	609	591
Restraints	2082	122	181	114
Largest Peak	1.749	0.906	2.235	3.081
Deepest Hole	-3.038	-1.029	-1.134	-2.640
GooF	1.104	1.064	1.049	1.039
wR_2 (all data)	0.1248	0.0565	0.0601	0.0629
wR_2	0.1234	0.0552	0.0564	0.0593
R_1 (all data)	0.0481	0.0264	0.0365	0.0381
R_1	0.0467	0.0233	0.0267	0.0279



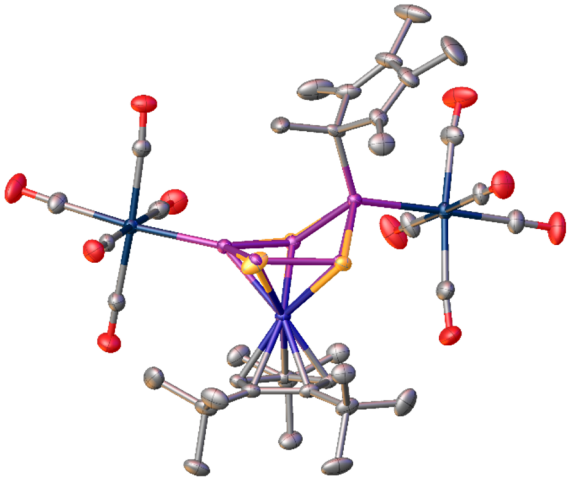
Molecular structure of 3 (ellipsoids are set at 50% probability level). All hydrogen atoms, solvent molecules and the counter ion have been omitted for clarity. Selected Bond Lengths (Å) and Angles (°): P1–P2 2.2302(14), P2–P3 2.2141(14), P3–P4 2.2105(15), P4–P1 2.2199(14), C11–P1 1.910(4), P1–W1 2.5829(11), P2–W2 2.5927(10), P2–Nb1 2.6787(11), P3–Nb1 2.5292(11), P4–Nb1 2.6045(11); P1–P2–P3 83.43(5), P2–P3–P4 82.46(5), P3–P4–P1 83.75(5), P4–P1–P2 81.89(5).



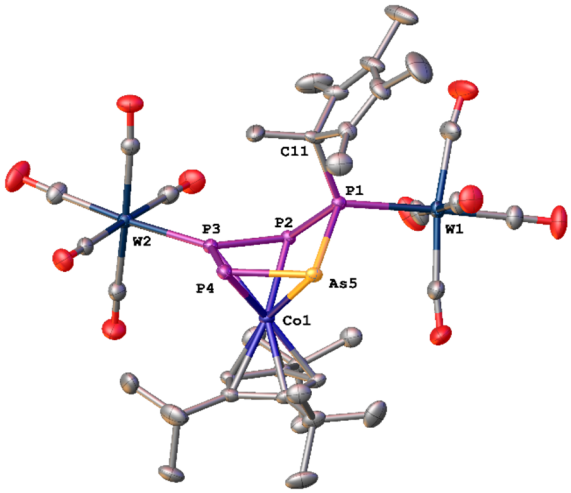
Molecular structure of 5a (ellipsoids are set at 50% probability level). All hydrogen atoms and the solvent molecule have been omitted for clarity. Selected Bond Lengths (Å) and Angles (°): P1–P2 2.2095(9), P2–P3 2.1227(10), P3–P4 2.1504(10), P4–P5 2.1316(10), P5–P1 2.2154(9), C11–P1 1.895(3), P1–W1 2.5274(8), P3–W2 2.4875(7), P2–Co1 2.3335(8), P3–Co1 2.2966(9), P4–Co1 2.3152(9), P5–Co1 2.3115(8); P1–P2–P3 97.69(4), P2–P3–P4 104.72(4), P3–P4–P5 98.78(4), P4–P5–P1 101.88(4), P5–P1–P2 85.99(3).



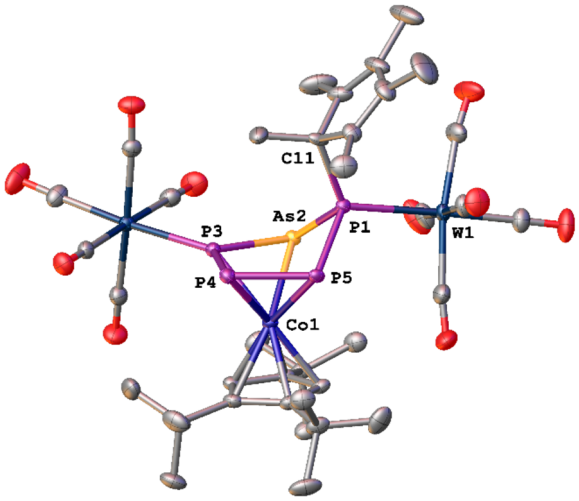
Molecular structure of 5b (ellipsoids are set at 50% probability level). All hydrogen atoms have been omitted for clarity. Selected Bond Lengths (Å) and Angles (°): P1–P2 2.2016(7), P2–P3 2.1222(6), P3–P4 2.1425(6), P4–P5 2.1539(7), P5–P1 2.2013(6), C11–P1 1.9154(18), P1–W1A 2.5637(6), P1–W1B 2.5388(13) P3–W2 2.4897(5), P2–Co1 2.3857(5), P3–Co1 2.3029(5), P4–Co1 2.3133(5), P5–Co1 2.3119(5); P1–P2–P3 103.94(2), P2–P3–P4 105.24(3), P3–P4–P5 99.41(2), P4–P5–P1 106.60(3), P5–P1–P2 87.82(2).



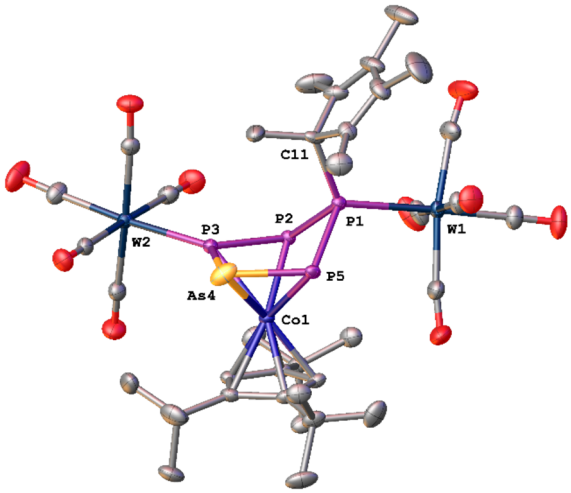
Molecular structure of 6 (ellipsoids are set at 50% probability level). **6** crystallises as a mixture of three individual isomers. The only difference is the position of the arsenic atom, which is distributed over the positions 2, 4 and 5. All hydrogen atoms have been omitted for clarity.



Molecular structure of 6a (isomer 1) (ellipsoids are set at 50% probability level). All hydrogen atoms have been omitted for clarity. Selected Bond Lengths (Å) and Angles (°): P1–P2 2.210(10), P2–P3 2.113(9), P3–P4 2.155(3), P4–As5 2.237(5), As5–P1 2.336(4), C11–P1 1.924(2), P1–W1 2.5562(5), P3–W2 2.4893(5), P2–Co1 2.353(8), P3–Co1 2.3019(6), P4–Co1 2.342(3), As5–Co1 2.437(5); P1–P2–P3 107.0(3), P2–P3–P4 104.1(2), P3–P4–As5 102.22(12), P4–As5–P1 102.71(16), As5–P1–P2 87.6(3).



Molecular structure of 6b (isomer 2) (ellipsoids are set at 50% probability level). All hydrogen atoms have been omitted for clarity. Selected Bond Lengths (Å) and Angles (°): P1–As2 2.313(5), As2–P3 2.240(4), P3–P4 2.155(3), P4–P5 2.205(11), P5–P1 2.179(9), C11–P1 1.924(2), P1–W1 2.5562(5), P3–W2 2.4893(5), As2–Co1 2.534(4), P3–Co1 2.3019(6), P4–Co1 2.342(3), P5–Co1 2.307(10); P1–As2–P3 99.52(14), As2–P3–P4 108.97(11), P3–P4–P5 96.8(2), P4–P5–P1 109.1(4), P5–P1–As2 88.8(3).



Molecular structure of 6c (isomer 3) (ellipsoids are set at 50% probability level). All hydrogen atoms have been omitted for clarity. Selected Bond Lengths (Å) and Angles (°):P1–P2 2.210(10), P2–P3 2.113(9), P3–As4 2.161(10), As4–P5 2.228(13), P5–P1 2.179(10), C11–P1 1.924(2), P1–W1 2.5562(5), P3–W2 2.4893(5), P2–Co1 2.353(8), P3–Co1 2.3019(6), As4–Co1 2.316(10), P5–Co1 2.307(10); P1–P2–P3 107.0(3), P2–P3–As4 104.7(3), P3–As4–P5 95.9(4), As4–P5–P1 110.3(5), P5–P1–P2 83.9 (4).

8.4.4 Computational Details

Gaussian 09 program package was used throughout.[32] Density functional theory (DFT) in form of Becke's three-parameter hybrid functioncal B3LYP[33] with def2-SVP all electron basis set[34] was employed. Basis sets were obtained from the EMSL basis exchange database.[35] The figures for energy schemata were created using OLEX2.[28] The figures for the supporting information concerning the DFT calculations were created with Chemcraft.[36]

9.4.4.1 Computations for the reaction of [Cp'''Co(η⁴-P₄)] and [Cp*P{W(CO)₅}₂]

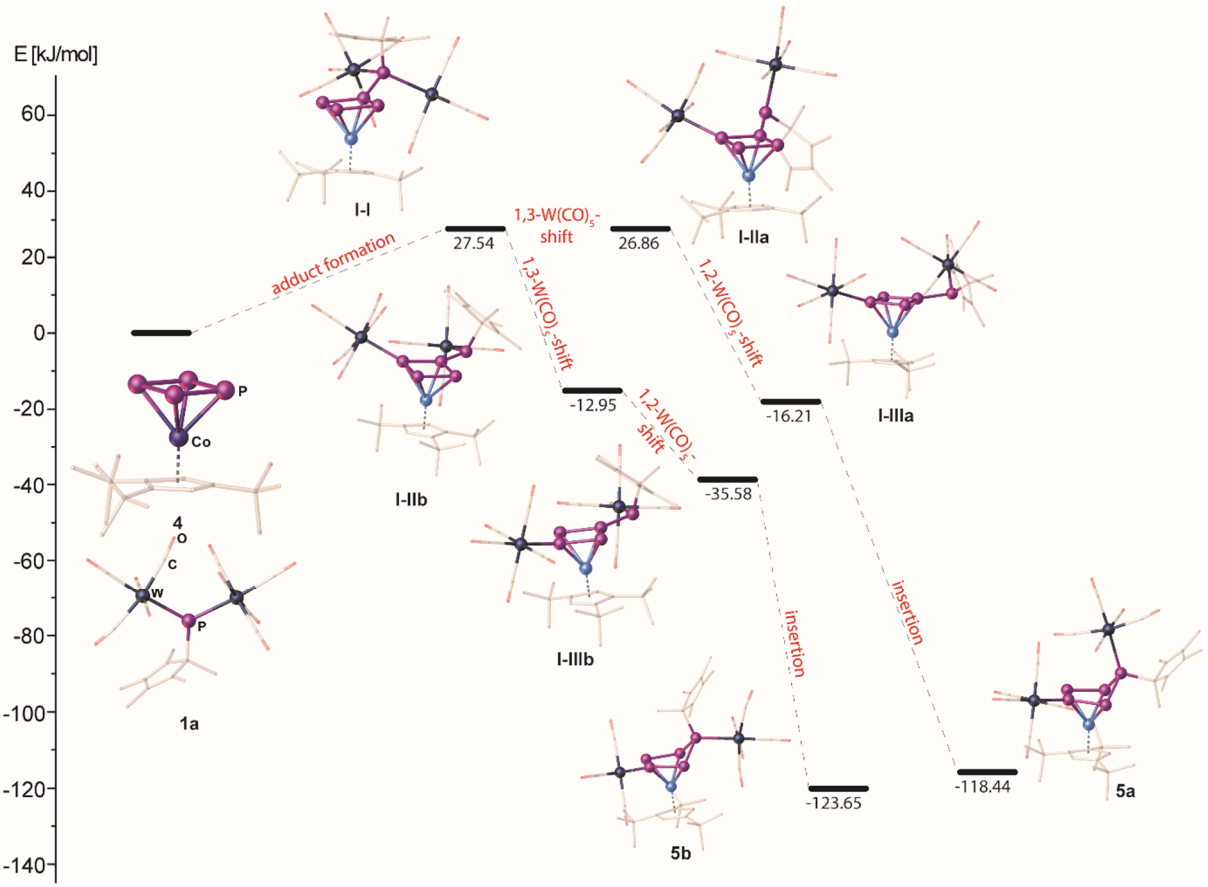
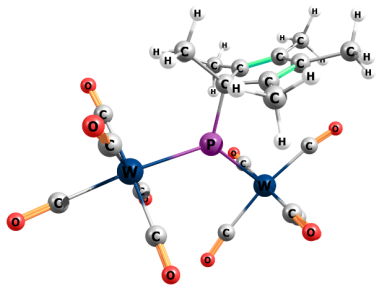


Figure S12. Energetic profile of the reaction of **1a** and **4**.

Table S1: Total energies for all optimized geometries (B3LYP/def2-SVP level of theory)

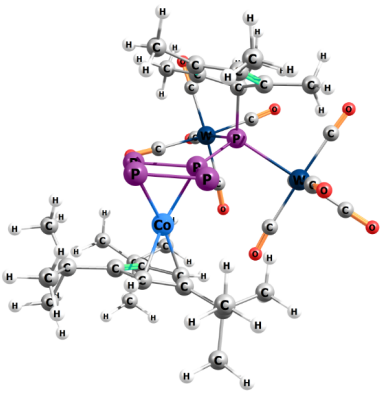
	total energy [Ha]		total energy [Ha]
1a ($Cp^*P(W(CO)_5)_2$)	-1997.9828540	**I-IIIa**	-5410.5536578
4 ($Cp'''CoP_4$)	-3412.5646307	**I-IIIb**	-5410.5610352
I-I	-5410.5369960	**5a**	-5410.5925969
I-IIa	-5410.5372526	**5b**	-5410.5945800
I-IIb	-5410.5524152		

Table S2: Optimized geometries of **1a** (left), **4** (right). XYZ coordinated in angstroms. B3LYP/def2-SVP level of theory.



W	2.935078000	4.595149000	7.198739000	C	-0.765534000	2.949588000	7.317758000	Co	-0.417673000	-0.552526000	-0.017096000	H	-1.724816000	3.859104000	-0.972235000
W	1.975590000	3.074788000	11.280722000	C	-0.754430000	2.566762000	6.005907000	P	-2.390055000	-1.787047000	0.367220000	H	-2.867905000	1.810735000	-2.042742000
P	1.589837000	3.155539000	8.797554000	C	0.204149000	1.465599000	5.820896000	P	-0.562784000	-2.440444000	1.372059000	H	-4.304971000	2.165743000	-1.064410000
C	4.116051000	5.817765000	6.039775000	C	0.790603000	1.162230000	7.017425000	P	0.414414000	-2.674813000	-0.576367000	H	-3.567782000	0.545883000	-1.000976000
O	4.778104000	6.502282000	5.395792000	C	-0.584882000	1.207779000	9.119594000	P	-1.412039000	-1.997598000	-1.579155000	H	-3.367728000	0.736056000	1.583954000
C	4.284055000	3.019758000	6.932707000	H	0.066132000	0.499188000	9.646113000	C	-1.094903000	1.428314000	0.083004000	H	-4.191059000	2.307954000	1.422023000
O	5.022760000	2.155315000	6.783035000	H	-1.355795000	0.625356000	8.589238000	C	-0.279393000	1.086675000	1.201141000	H	-2.652476000	2.209207000	2.297552000
C	2.008705000	4.089149000	5.405232000	H	-1.091328000	1.828174000	9.869106000	C	1.045737000	0.706010000	0.779275000	H	1.210021000	1.631222000	3.447543000
O	1.630015000	3.939927000	4.329091000	C	-1.619519000	4.001484000	7.963239000	C	1.045285000	0.786649000	-0.685839000	H	2.400580000	0.430991000	3.983780000
C	1.559526000	6.148673000	7.456925000	H	-1.954048000	3.695357000	8.967667000	C	-0.277476000	1.215012000	-1.063268000	H	0.794926000	-0.109362000	3.458794000
O	0.803958000	7.000426000	7.594729000	H	-2.519122000	4.209210000	7.365552000	C	-2.470496000	2.087558000	0.107644000	H	2.063102000	-1.705396000	2.069882000
C	4.077791000	5.328200000	8.763741000	H	-1.090713000	4.962059000	8.084391000	C	-2.224359000	3.612621000	-0.022022000	H	3.642350000	-0.995222000	2.469990000
O	4.770494000	5.799768000	9.550061000	C	-1.581674000	3.118277000	4.884891000	C	-3.347282000	1.621193000	-1.069890000	H	3.166393000	-1.211395000	0.773733000
C	2.439097000	3.139705000	13.296689000	H	-0.939705000	3.570710000	4.110208000	C	-3.206745000	1.813752000	1.431813000	H	3.799818000	1.462556000	0.717295000
O	2.703151000	3.182020000	14.413327000	H	-2.286032000	3.888870000	5.227046000	C	2.161548000	0.464175000	1.825354000	H	3.980425000	1.479743000	2.480270000
C	2.054045000	5.161891000	11.249899000	H	-2.163051000	2.323438000	4.387640000	C	1.595397000	0.617847000	3.256761000	H	2.804441000	2.562584000	1.697114000
O	2.070200000	6.307551000	11.257994000	C	0.432815000	0.803982000	4.496074000	C	2.795435000	-0.942810000	1.766162000	H	3.162158000	2.536514000	-1.037196000
C	-0.037915000	3.192351000	11.790094000	H	0.845716000	1.520844000	3.766288000	C	3.247735000	1.554594000	1.660777000	H	1.877098000	2.866239000	-2.219032000
O	-1.138952000	3.261297000	12.109369000	H	-0.511748000	0.427517000	4.068204000	C	2.136742000	0.723075000	-1.780596000	H	3.433102000	2.189768000	-2.761827000
C	1.870077000	1.002015000	11.421720000	H	1.132078000	-0.040382000	4.567365000	C	2.683454000	2.164569000	-1.954160000	H	3.986083000	-0.221872000	-2.386413000
O	1.823436000	-0.139682000	11.537159000	C	1.792622000	0.082522000	7.304779000	C	3.311552000	-0.234641000	-1.515827000	H	2.959906000	-1.267485000	-1.378572000
C	4.017174000	2.908471000	10.871842000	H	1.606506000	-0.397763000	8.279056000	C	1.522594000	0.286335000	-3.133285000	H	3.912684000	0.051019000	-0.644889000
O	5.137971000	2.786275000	10.667486000	H	2.828570000	0.460887000	7.330696000	H	-0.613545000	1.111875000	2.232301000	H	2.320411000	0.214683000	-3.888370000
C	0.183405000	2.049880000	8.088779000	H	1.763137000	-0.705500000	6.538103000	H	-0.605603000	1.361947000	-2.087217000	H	0.783716000	1.002187000	-3.520489000
								H	-1.591696000	3.985655000	0.798883000	H	1.037230000	-0.697521000	-3.056342000
								H	-3.181677000	4.157770000	0.010573000				

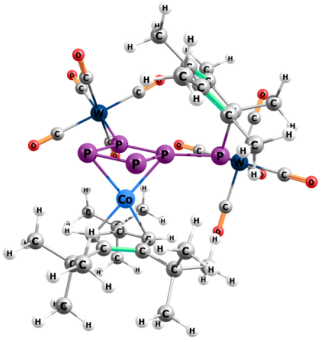
Table S3: Optimized geometries of **I-I** (left), **I-IIa** (right). XYZ coordinated in angstroms. B3LYP/def2-SVP level of theory.

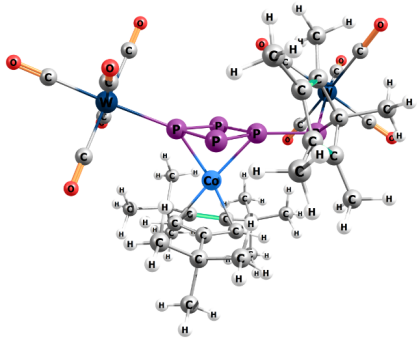


Co	2.995589000	0.098216000	0.231812000	H	1.143236000	-1.677133000	-1.891818000	Co	2.223968000	0.848470000	0.909094000	H	5.817351000	1.387406000	-2.302898000
P	0.762952000	-0.012485000	0.983193000	W	-2.377601000	-2.327188000	-0.408872000	P	-0.093708000	0.795018000	0.502316000	H	4.743323000	2.791596000	-2.488460000
P	1.944783000	1.551892000	1.878021000	W	-2.036520000	2.178670000	-0.971567000	P	0.545043000	1.261313000	2.560846000	H	4.883630000	1.598718000	-3.803033000
P	3.270781000	-0.060626000	2.533425000	P	-1.478788000	0.040371000	0.694284000	P	1.564728000	-0.654700000	2.593755000	H	3.775804000	-0.625879000	-3.648350000
P	2.060782000	-1.633041000	1.594686000	C	-3.196290000	-3.830518000	-1.462186000	P	0.891268000	-1.127160000	0.571784000	H	2.965042000	-1.163954000	-2.170850000
C	3.988582000	1.495598000	-1.016334000	O	-3.667891000	-4.683921000	-2.081691000	C	3.354673000	2.614795000	1.244931000	H	4.741281000	-1.032538000	-2.229679000
C	4.891029000	0.741350000	-0.212955000	C	-0.657029000	-3.460007000	-0.225457000	C	4.048953000	1.443651000	1.660795000	H	2.379309000	1.189410000	-3.853142000
C	4.804223000	-0.666249000	-0.507136000	O	0.257118000	-4.157394000	-0.137227000	C	4.289040000	0.556386000	0.555942000	H	2.226456000	2.495395000	-2.676150000
C	3.745027000	-0.804185000	-1.510822000	C	-3.144347000	-3.299367000	1.249817000	C	3.643352000	1.173998000	-0.606064000	H	1.477619000	0.922567000	-2.343142000
C	3.263458000	0.531186000	-1.774149000	O	-3.617616000	-3.922746000	2.094854000	C	3.067330000	2.412477000	-0.135943000	W	-3.897767000	0.226227000	0.581633000
C	4.004665000	3.010137000	-1.190729000	C	-4.195182000	-1.316848000	-0.511246000	C	3.206603000	3.900551000	2.051261000	W	0.499052000	-3.456779000	-0.466007000
C	4.973365000	3.283291000	-2.372053000	O	-5.226734000	-0.812216000	-0.532516000	C	4.395641000	4.800671000	1.620675000	P	-1.742798000	1.031737000	-0.883720000
C	2.618665000	3.572274000	-1.542834000	C	-1.720015000	-1.627680000	-2.247975000	C	1.891325000	4.630445000	1.741978000	C	-5.529686000	-0.484570000	1.523506000
C	4.539858000	3.721401000	0.065830000	O	-1.396455000	-1.348767000	-3.316254000	C	3.308674000	3.641396000	3.565367000	O	-6.465919000	-0.889451000	2.065795000
C	5.861061000	-1.642475000	0.070526000	C	-2.411960000	3.768803000	-2.142046000	C	5.244921000	-0.648797000	0.735620000	C	-2.786250000	-0.494096000	2.178324000
C	6.846886000	-0.886085000	0.993090000	O	-2.609545000	4.699758000	-2.797332000	C	5.736027000	-0.735914000	2.200538000	O	-2.233949000	-0.907222000	3.099966000
C	5.284703000	-2.798053000	0.916109000	C	-3.248382000	1.128608000	-2.295968000	C	4.610719000	-2.015703000	0.417189000	C	-4.126588000	2.037131000	1.564481000
C	6.705433000	-2.199058000	-1.103337000	O	-3.926356000	0.667377000	-3.100485000	C	6.503497000	-0.413619000	-0.135910000	O	-4.296785000	3.032061000	2.118690000
C	3.255827000	-1.960411000	-2.408438000	C	-3.806789000	2.581630000	0.051821000	C	3.665880000	0.902369000	-2.125458000	C	-5.198697000	0.847991000	-0.912403000
C	4.095918000	-1.894426000	-3.711973000	O	-4.826495000	2.801594000	0.534659000	C	4.850117000	1.717822000	-2.708064000	O	-5.981685000	1.143220000	-1.701999000

C	3.353668000	-3.375045000	-1.811509000	C	-0.861686000	3.465626000	0.150028000	C	3.803256000	-0.566464000	-2.549489000	C	-3.731479000	-1.573731000	-0.439417000
C	1.774531000	-1.746796000	-2.788096000	O	-0.227080000	4.255215000	0.698827000	C	2.362261000	1.412147000	-2.775535000	O	-3.689688000	-2.569232000	-1.013765000
H	5.570218000	1.175203000	0.511721000	C	-0.477986000	1.707087000	-2.227452000	H	4.375362000	1.260207000	2.677636000	O	-0.028894000	-5.321136000	-1.069082000
H	2.466290000	0.768059000	-2.471428000	O	0.324831000	1.466860000	-3.022970000	H	2.514906000	3.110018000	-0.758920000	O	-0.338879000	-6.378147000	-1.403191000
H	5.983908000	2.898347000	-2.162133000	C	-1.848719000	0.237058000	2.677332000	H	5.362089000	4.309146000	1.814532000	C	-1.165207000	-3.557958000	0.793458000
H	5.052358000	4.367653000	-2.550155000	C	-0.980757000	-0.718317000	3.497747000	H	4.376061000	5.746640000	2.185136000	O	-2.060647000	-3.705117000	1.492612000
H	4.615557000	2.812033000	-3.300640000	C	-0.230292000	0.008284000	4.371924000	H	4.347781000	5.043890000	0.547753000	C	-0.577673000	-2.636093000	-2.061724000
H	2.208461000	3.119557000	-2.456311000	C	-0.540924000	1.439970000	4.219468000	H	1.774721000	4.824589000	0.667627000	O	-1.125797000	-2.219269000	-2.977497000
H	2.690278000	4.657381000	-1.715957000	C	-1.492457000	1.600181000	3.255331000	H	1.869404000	5.602282000	2.259923000	C	2.134569000	-3.641354000	-1.724947000
H	1.903266000	3.413771000	-0.724489000	C	-3.356144000	-0.045195000	2.826364000	H	1.023330000	4.046865000	2.078590000	O	3.021140000	-3.846578000	-2.428877000
H	3.905089000	3.517610000	0.941261000	H	-3.968472000	0.670051000	2.257917000	H	2.515256000	2.962435000	3.911999000	C	1.654703000	-4.269545000	1.053620000
H	4.547140000	4.810025000	-0.097816000	H	-3.633063000	0.046029000	3.889578000	H	3.202875000	4.590615000	4.113090000	O	2.309561000	-4.730566000	1.877529000
H	5.572472000	3.423034000	0.305739000	H	-3.618702000	-1.057337000	2.494130000	H	4.282661000	3.211184000	3.846084000	C	-1.738477000	2.817700000	-1.660273000
H	7.412046000	-0.109682000	0.455183000	C	-1.053163000	-2.208967000	3.433041000	H	6.303556000	0.155900000	2.507316000	C	-1.146447000	3.976414000	-0.873062000
H	7.579233000	-1.601916000	1.395941000	H	-2.053910000	-2.579119000	3.709936000	H	6.408110000	-1.601337000	2.300689000	C	-0.283082000	4.646924000	-1.685450000
H	6.336443000	-0.422743000	1.850423000	H	-0.332875000	-2.672422000	4.120883000	H	4.904289000	-0.886272000	2.905098000	C	-0.168428000	3.945360000	-2.983923000
H	4.874505000	-2.415279000	1.863129000	H	-0.847494000	-2.598448800	2.424769000	H	3.823066000	-2.251867000	1.146159000	C	-0.968322000	2.846923000	-2.977281000
H	6.092146000	-3.502536000	1.172724000	C	0.734124000	-0.491389000	5.405380000	H	5.375536000	-2.805149000	0.490572000	C	-3.217683000	3.154334000	-1.984740000
H	4.495588000	-3.360267000	0.410708000	H	1.740791000	-0.064858000	5.253175000	H	4.174266000	-2.067691000	-0.581847000	H	-3.685698000	2.385350000	-2.615958000
H	6.134770000	-2.864335000	-1.761917000	H	0.833690000	-1.584885000	5.396188000	H	6.288745000	-0.446764000	-1.210823000	H	-3.246153000	4.107816000	-2.536168000
H	7.553901000	-2.777043000	-0.704422000	H	0.420161000	-0.192833000	6.420575000	H	7.251099000	-1.194250000	0.075615000	H	-3.821889000	3.261107000	-1.074621000
H	7.115587000	-1.382218000	-1.718023000	C	0.048910000	2.489943000	5.114330000	H	6.963631000	0.561989000	0.088046000				
H	5.166600000	-2.058497000	-3.524526000	H	1.149940000	2.428903000	5.133021000								
H	3.985912000	-0.917457000	-4.207666000	H	-0.288923000	2.361816000	6.158094000								
H	3.752319000	-2.669192000	-4.415813000	H	-0.221822000	3.506890000	4.800277000								
H	2.941508000	-4.093134000	-2.536654000	C	-2.277984000	2.852147000	3.023593000								
H	2.761038000	-3.469481000	-0.890624000	H	-2.501707000	3.023685000	1.967324000								
H	4.383306000	-3.687470000	-1.604774000	H	-1.746333000	3.737968000	3.396930000								
H	1.419994000	-2.601166000	-3.382965000	H	-3.250983000	2.807539000	3.546691000								
H	1.603792000	-0.846372000	-3.391948000												

Table S4: Optimized geometries of **I-IIb** (left), **I-IIIa** (right). XYZ coordinated in angstroms. B3LYP/def2-SVP level of theory.

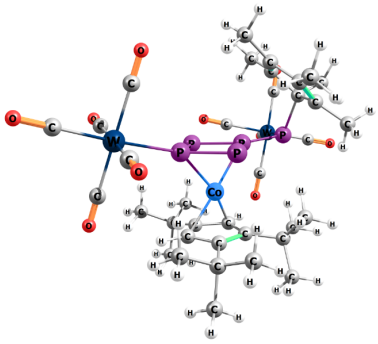


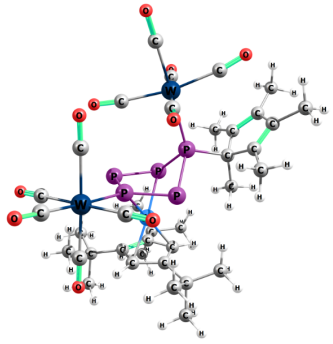


Co	1.211133000	1.971769000	-0.095287000	H	3.990132000	3.543472000	1.295356000	Co	-0.989051000	1.471719000	-0.280087000	H	2.151092000	2.786829000	0.237841000
P	-0.274021000	0.547753000	0.979061000	W	-3.478589000	-0.968599000	-1.183692000	P	0.860186000	-0.050972000	-0.469656000	W	4.395691000	-0.612117000	1.211458000
P	0.668391000	2.057422000	2.204040000	W	2.857726000	-2.609389000	-0.007111000	P	-0.855873000	-0.484372000	-1.691222000	W	-4.080415000	-1.812939000	0.702555000
P	2.591922000	1.178707000	1.656734000	P	-2.427906000	0.436443000	0.856845000	P	-1.895914000	-0.543541000	0.234224000	P	2.953848000	0.204005000	-0.928652000
P	1.665398000	-0.362747000	0.460562000	C	-4.404070000	-1.815200000	-2.763693000	P	-0.142430000	0.002723000	1.440899000	C	5.576799000	-1.006306000	2.795947000
C	1.592915000	2.200849000	-2.173139000	O	-4.931702000	-2.294024000	-3.672762000	C	-1.759803000	2.854677000	-1.674491000	O	6.252456000	-1.229040000	3.706070000
C	0.315632000	2.716697000	-1.809654000	C	-1.736191000	-1.976341000	-1.654196000	C	-2.612726000	2.735978000	-0.538864000	C	2.957792000	-1.937440000	1.905888000
C	0.442479000	3.793613000	-0.860498000	O	-0.780070000	-2.552500000	-1.939872000	C	-1.927665000	3.124996000	0.661798000	O	2.176222000	-2.691293000	2.286457000
C	1.878331000	3.910772000	-0.570954000	C	-4.091061000	-2.622372000	-0.077226000	C	-0.559410000	3.481086000	0.253934000	C	5.349709000	-2.195041000	0.271022000
C	2.531803000	2.904903000	-1.368209000	O	-4.458269000	-3.568495000	0.463431000	C	-0.497004000	3.280697000	-1.166689000	O	5.921697000	-3.086295000	-0.180720000
C	1.902282000	1.272229000	-3.337683000	C	-5.235883000	0.035449000	-0.687927000	C	-2.193570000	2.805088000	-3.134126000	C	5.822388000	0.697106000	0.450298000
C	1.900094000	2.160051000	-4.609826000	O	-6.209754000	0.585752000	-0.423592000	C	-2.771420000	4.209291000	-3.452850000	O	6.614032000	1.417343000	0.030675000
C	3.292465000	0.632724000	-3.183497000	C	-2.939275000	0.564683000	-2.448037000	C	-0.997303000	2.536937000	-4.061476000	C	3.597484000	0.918692000	2.352429000
C	0.827717000	0.182847000	-3.488196000	O	-2.658758000	1.383599000	-3.213891000	C	-3.290572000	1.752248000	-3.377037000	O	3.223549000	1.750149000	3.057537000
C	-0.787818000	4.676217000	-0.516477000	C	3.935875000	-4.322842000	-0.085683000	C	-2.710336000	3.268843000	1.992869000	C	-5.770114000	-2.905597000	0.986153000
C	-2.045735000	4.141015000	-1.238591000	O	4.558993000	-5.291051000	-0.120921000	C	-4.192836000	2.882381000	1.783925000	O	-6.729429000	-3.523251000	1.141546000
C	-1.154979000	4.734906000	0.980902000	C	4.611859000	-1.533124000	-0.293521000	C	-2.182787000	2.378173000	3.137380000	C	-3.790896000	-2.795402000	-1.110729000
C	-0.542706000	6.105871000	-1.058790000	O	5.591206000	-0.954757000	-0.457624000	C	-2.716107000	4.755271000	2.427033000	O	-3.635891000	-3.342285000	-2.108082000
C	2.749609000	4.967828000	0.147750000	C	3.152483000	-2.599604000	2.052010000	C	0.612422000	4.200773000	0.957554000	C	-2.960382000	-3.287814000	1.678778000
C	3.057781000	6.072973000	-0.899280000	O	3.314436000	-2.612755000	3.188692000	C	0.371332000	5.724547000	0.781234000	O	-2.358479000	-4.102321000	2.214111000
C	2.125130000	5.606076000	1.400221000	C	1.131843000	-3.751204000	0.263936000	C	0.790930000	3.883114000	2.451368000	C	-4.400329000	-0.884794000	2.535899000
C	4.110345000	4.374562000	0.586027000	O	0.215628000	-4.421256000	0.424330000	C	1.952393000	3.866457000	0.262696000	O	-4.603398000	-0.393591000	3.554311000
H	-0.623314000	2.373842000	-2.229212000	C	2.562790000	-2.725298000	-2.069230000	H	-3.646431000	2.411887000	-0.585211000	C	-5.164776000	-0.341310000	-0.267960000
H	3.602526000	2.728908000	-1.375153000	O	2.434014000	-2.845409000	-3.202745000	H	0.386511000	3.450502000	-1.773786000	O	-5.754492000	0.486044000	-0.809952000
H	0.917216000	2.629351000	-4.770882000	C	-2.764474000	-0.153618000	2.708518000	H	-3.649675000	4.433985000	-2.827741000	C	3.044512000	-0.783940000	-2.615320000
H	2.132101000	1.545939000	-5.494639000	C	-1.816085000	-1.246464000	3.173176000	H	-3.083910000	4.258209000	-4.508343000	C	2.374732000	-2.149406000	-2.633684000
H	2.654634000	2.959756000	-4.542895000	C	-1.069653000	-0.766787000	4.207056000	H	-2.022128000	4.998264000	-3.282638000	C	1.440338000	-2.162600000	-3.623896000
H	4.093462000	1.388370000	-3.176398000	C	-1.476978000	0.624337000	4.505751000	H	-0.246548000	3.340030000	-4.001648000	C	1.416293000	-0.844895000	-4.301323000
H	3.491095000	-0.047622000	-4.025260000	C	-2.461892000	1.001979000	3.644744000	H	-1.334031000	2.482255000	-5.108420000	C	2.322667000	-0.015964000	-3.714987000
H	3.363647000	0.049615000	-2.255119000	C	-4.249771000	-0.557988000	2.782360000	H	-0.503405000	1.587865000	-3.810861000	C	4.554373000	-0.878234000	-2.932728000
H	0.748863000	-0.428064000	-2.579219000	H	-4.913672000	0.251797000	2.441676000	H	-2.923506000	0.736048000	-3.169895000	H	5.036028000	0.112408000	-2.927019000
H	1.080719000	-0.488485000	-4.322430000	H	-4.506759000	-0.787239000	3.829667000	H	-3.614695000	1.785383000	-4.428986000	H	4.679873000	-1.314465000	-3.936971000
H	-0.161478000	0.613984000	-3.698759000	H	-4.465500000	-1.447592000	2.177536000	H	-4.181496000	1.926149000	-2.755129000	H	5.085433000	-1.516189000	-2.215521000
H	-1.941503000	4.145723000	-2.333422000	C	-1.808641000	-2.623576000	2.592452000	H	-4.696799000	3.540078000	1.059654000	C	2.765136000	-3.284011000	-1.740313000
H	-2.901251000	4.786221000	-0.987904000	H	-2.772024000	-3.138392000	2.753302000	H	-4.727127000	2.974885000	2.741078000	H	3.823068000	-3.566920000	-1.872103000
H	-2.300926000	3.122948000	-0.913435000	H	-1.024624000	-3.250960000	3.037958000	H	-4.307334000	1.843538000	1.447894000	H	2.159596000	-4.178871000	-1.939627000
H	-1.499281000	3.752322000	1.331292000	H	-1.648602000	-2.610083000	1.502666000	H	-2.334014000	1.315219000	2.902817000	H	2.643290000	-3.030500000	-0.675044000
H	-1.984346000	5.446729000	1.121564000	C	0.005667000	-1.473504000	4.977778000	H	-2.744735000	2.591304000	4.060500000	C	0.553711000	-3.296607000	-4.047445000
H	-0.329154000	5.050381000	1.623883000	H	0.981723000	-0.970168000	4.863415000	H	-1.119892000	2.524331000	3.346524000	H	-0.513775000	-3.033499000	-3.948555000
H	0.233737000	6.644680000	-0.502024000	H	0.135470000	-2.515255000	4.654119000	H	-1.727900000	5.116172000	2.734025000	H	0.725861000	-4.204237000	-3.453137000
H	-1.471464000	6.691617000	-0.975350000	H	-0.215643000	-1.485290000	6.058880000	H	-3.393410000	4.883377000	3.286032000	H	0.715658000	-3.557650000	-5.107508000
H	-0.253415000	6.087055000	-2.121474000	C	-0.880877000	1.416509000	5.631522000	H	-3.080027000	5.403446000	1.614113000	C	0.539534000	-0.573926000	-5.487348000
H	2.149525000	6.571537000	-1.261264000	H	0.215429000	1.497223000	5.532843000	H	-0.552281000	6.061379000	1.270483000	H	-0.527103000	-0.715397000	-5.242105000
H	3.581752000	5.654250000	-1.772381000	H	-1.071854000	0.932204000	6.605137000	H	0.306439000	5.995025000	-0.284333000	H	0.765002000	-1.272918000	-6.311362000
H	3.709895000	6.839525000	-0.450475000	H	-1.287988000	2.435944000	5.683767000	H	1.211275000	6.285666000	1.221537000	H	0.663499000	0.446057000	-5.875698000
H	2.860664000	6.277643000	1.869211000	C	-3.233779000	2.283555000	3.613333000	H	1.693722000	4.389896000	2.823387000	C	2.704614000	1.377062000	-4.105924000
H	1.845972000	4.843007000	2.142258000	H	-3.334821000	2.661549000	2.581722000	H	0.932136000	2.807923000	2.623023000	H	2.685780000	2.056498000	-3.236017000

H	1.238418000	6.209423000	1.175612000	H	-2.754829000	3.068430000	4.216252000	H	-0.047477000	4.230592000	3.064675000	H	2.036824000	1.785463000	-4.877427000
H	4.700163000	5.160582000	1.081379000	H	-4.260346000	2.151717000	4.001703000	H	2.776371000	4.346381000	0.811243000	H	3.733320000	1.419425000	-4.507483000
H	4.712955000	4.013949000	-0.259726000					H	1.998798000	4.239832000	-0.770467000				

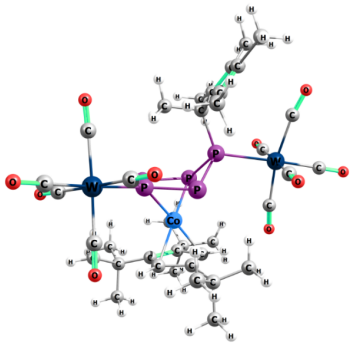
Table S5: Optimized geometries of **I-IIIb** (left), **5a** (right). XYZ coordinated in angstroms. B3LYP/def2-SVP level of theory.





Co	-0.705098000	-1.352394000	0.292037000	H	-3.822683000	-1.423877000	1.639749000	W	-3.281413000	-1.230420000	-0.762308000	H	3.889078000	-0.087152000	-1.887310000
P	0.752872000	0.433321000	0.502197000	W	4.458400000	0.192029000	-1.046699000	W	2.380783000	-2.886239000	0.329862000	H	5.216583000	0.214614000	-0.736946000
P	-0.989497000	0.494090000	1.791282000	W	-4.442911000	1.183938000	-0.814068000	Co	1.510039000	1.648237000	-0.082735000	C	-4.975219000	-0.878888000	0.388382000
P	-2.075638000	0.465488000	-0.107468000	P	2.830852000	0.534215000	1.094933000	P	-0.003684000	0.454982000	1.323380000	C	1.460105000	2.862779000	3.719323000
P	-0.320604000	0.366284000	-1.382948000	C	5.833324000	-0.268051000	-2.446711000	P	1.154370000	-0.662784000	-0.102297000	H	1.241885000	3.909442000	3.456299000
C	-0.733066000	-3.071373000	-0.930939000	O	6.623071000	-0.541573000	-3.244318000	P	0.878947000	0.402164000	-1.980478000	H	1.588930000	2.821507000	4.812100000
C	0.365551000	-3.091659000	-0.017113000	C	3.108531000	0.646189000	-2.554515000	P	-0.490283000	1.927862000	-1.308001000	H	0.586181000	2.247829000	3.462726000
C	-0.099138000	-3.082846000	1.344858000	O	2.409643000	0.908522000	-3.431395000	P	-1.865108000	0.813817000	0.098687000	C	-1.840450000	3.413696000	1.435176000
C	-1.563875000	-3.008744000	1.276890000	C	5.146799000	2.151306000	-1.168032000	O	-5.984114000	-0.815263000	0.938570000	H	-1.034988000	3.097231000	2.111339000
C	-1.901238000	-2.987579000	-0.122374000	O	5.571767000	3.211945000	-1.302556000	O	-0.215125000	-4.537257000	-0.681306000	H	-2.444699000	4.173546000	1.956076000
C	-0.696998000	-3.339184000	-2.431631000	C	5.860564000	-0.218594000	0.437536000	O	5.062423000	-1.452978000	1.383197000	H	-1.380225000	3.888227000	0.557037000
C	-0.862570000	-4.875311000	-2.581580000	O	6.646372000	-0.444305000	1.245193000	O	-2.027336000	-2.977810000	1.645598000	C	-1.797510000	-1.819391000	-2.081429000
C	-1.855632000	-2.640005000	-3.166589000	C	3.898361000	-1.789408000	-1.102271000	O	-1.050058000	-2.211282000	-2.864086000	C	3.926784000	3.234061000	3.463796000
C	0.641626000	-2.922338000	-3.065262000	O	3.639038000	-2.912253000	-1.192058000	O	3.750976000	-5.706258000	0.882274000	H	4.868617000	2.892586000	3.007088000
C	0.882935000	-3.304619000	2.520761000	C	-6.260900000	1.859691000	-1.421395000	O	1.225491000	-2.867389000	3.347130000	H	4.045787000	3.194393000	4.558557000
C	2.331797000	-3.417233000	1.995565000	O	-7.290339000	2.242369000	-1.767092000	O	3.551845000	-2.916486000	-2.678313000	H	3.771298000	4.285791000	3.175873000
C	0.889855000	-2.162609000	3.558600000	C	-5.191522000	0.944764000	1.111131000	O	-4.876781000	-3.762976000	-1.833818000	C	3.375117000	5.549467000	-1.752422000
C	0.553880000	-4.656851000	3.198833000	O	-5.626536000	0.823247000	2.167342000	C	3.503343000	1.815336000	0.572209000	H	3.848904000	5.811256000	-0.792956000
C	-2.706000000	-3.195351000	2.304200000	C	-3.892247000	3.140083000	-0.335217000	H	4.159221000	0.987238000	0.819106000	H	3.116688000	6.488080000	-2.268179000
C	-3.000698000	-4.718656000	2.365825000	O	-3.598934000	4.217143000	-0.069885000	O	-4.551438000	0.621216000	-3.080183000	H	4.120330000	5.031457000	-2.368409000
C	-2.445457000	-2.670913000	3.727234000	C	-3.725820000	1.444402000	-2.753340000	C	2.662707000	2.478748000	1.505686000	C	-3.916758000	2.741242000	0.172341000
C	-3.993542000	-2.494154000	1.815874000	O	-3.344770000	1.588135000	-3.825886000	C	1.975635000	3.478358000	0.752495000	C	-2.762097000	2.245255000	1.038797000
H	1.407516000	-3.134786000	-0.313941000	C	-4.977171000	-0.759609000	-1.292656000	H	1.243363000	4.161852000	1.166457000	C	-3.461254000	1.673883000	2.268720000
H	-2.913605000	-2.942468000	-0.509664000	O	-5.262970000	-1.842163000	-1.560376000	C	4.482568000	2.027709000	-1.786596000	C	1.471339000	4.326396000	-2.894288000
H	-0.052430000	-5.416621000	-2.068395000	C	2.725843000	2.312978000	1.938493000	C	5.788584000	2.787949000	-1.429883000	H	2.059659000	3.595414000	-3.453332000
H	-0.836153000	-5.154788000	-3.646926000	C	1.903423000	3.328750000	1.160417000	H	5.662992000	3.878111000	-1.485762000	H	1.381038000	5.230805000	-3.517247000
H	-1.821395000	-5.219333000	-2.162865000	C	0.847265000	3.716282000	1.929624000	H	6.589752000	2.502751000	-2.130674000	H	0.462316000	3.912627000	-2.762345000
H	-2.840683000	-2.949305000	-2.785728000	C	0.896298000	3.009567000	3.228186000	H	6.127829000	2.539918000	-0.412325000	C	4.121814000	2.309306000	-3.255135000
H	-1.824994000	-2.894728000	-4.237253000	C	1.979774000	2.184056000	3.253613000	C	3.252785000	-4.687333000	0.680990000	H	4.029869000	3.378019000	-3.478690000
H	-1.781964000	-1.545270000	-3.082778000	C	4.183322000	2.759376000	2.173274000	C	2.456825000	3.516282000	-0.607232000	H	3.189043000	1.803134000	-3.543798000
H	0.813840000	-1.840041000	-2.972797000	H	4.758054000	2.002794000	2.730401000	C	1.073616000	5.638267000	-0.838361000	H	4.923596000	1.916222000	-3.898908000
H	0.635777000	-3.168767000	-4.138434000	H	4.184479000	3.689311000	2.765311000	H	0.138937000	5.113507000	-0.593994000	C	-5.081119000	2.533110000	0.844181000
H	1.495967000	-3.446150000	-2.612976000	H	4.709799000	2.957146000	1.231786000	H	0.817277000	6.463012000	-1.520387000	C	-2.739352000	1.063448000	3.431201000
H	2.463611000	-4.254693000	1.294655000	C	2.281234000	3.833373000	-0.195573000	H	1.474871000	6.088567000	0.082316000	H	-3.412074000	0.926409000	4.289500000
H	3.006904000	-3.591618000	2.847018000	H	3.256446000	4.350057000	-0.183910000	C	3.005492000	0.895976000	3.466874000	H	-1.896312000	1.688572000	3.771281000
H	2.662392000	-2.490242000	1.507687000	H	1.538164000	4.542848000	-0.585308000	H	2.191060000	0.220546000	3.167428000	H	-2.315074000	0.072719000	3.192476000
H	1.278427000	-1.239478000	3.107275000	H	2.377585000	3.011625000	-0.924072000	H	3.089092000	0.849651000	4.563956000	C	-4.300600000	-2.843107000	-1.444934000
H	1.560800000	-2.429303000	4.391015000	C	-0.223822000	4.711758000	1.596654000	H	3.946957000	0.506855000	3.051953000	C	-3.727284000	3.444554000	-1.137573000
H	-0.095587000	-1.948579000	3.979393000	H	-1.230087000	4.261564000	1.640222000	C	-4.091843000	-0.033662000	-2.254232000	H	-3.070661000	4.326346000	-1.034546000
H	-0.410515000	-4.650818000	3.720752000	H	-0.099094000	5.139045000	0.592348000	C	4.098390000	-1.956939000	1.001091000	H	-4.686349000	3.795554000	-1.542921000
H	1.329761000	-4.892144000	3.944153000	H	-0.227566000	5.549411000	2.315704000	C	3.431136000	2.435062000	-0.724584000	H	-3.266406000	2.804436000	-1.907014000
H	0.538242000	-5.475883000	2.462203000	C	-0.097509000	3.261740000	4.322619000	C	2.732156000	2.345727000	3.025571000	C	-6.473498000	2.882957000	0.412955000
H	-2.142798000	-5.294003000	2.739044000	H	-1.131131000	3.089222000	3.977108000	C	0.686175000	-3.923219000	-0.329438000	H	-7.108290000	1.981343000	0.373346000
H	-3.263560000	-5.112469000	1.371909000	H	-0.053894000	4.310204000	4.665964000	C	2.093960000	4.706623000	-1.533435000	H	-6.499418000	3.352786000	-0.579579000
H	-3.852936000	-4.905499000	3.038850000	H	0.075251000	2.619612000	5.197585000	C	3.126700000	-2.896275000	-1.611718000	H	-6.954007000	3.574291000	1.126389000
H	-3.350907000	-2.827213000	4.333428000	C	2.491083000	1.355974000	4.390331000	C	-4.798269000	1.890490000	2.145739000	C	-5.878327000	1.578918000	3.136711000
H	-2.229719000	-1.592241000	3.724987000	H	2.833984000	0.367604000	4.041932000	C	1.624794000	-2.871384000	2.271552000	H	-6.589394000	0.844142000	2.725378000
H	-1.627239000	-3.190832000	4.236936000	H	1.724844000	1.198174000	5.163319000	C	-2.468477000	-2.360419000	0.781863000	H	-6.459555000	2.482317000	3.388510000
H	-4.774656000	-2.586738000	2.584935000	H	3.357901000	1.834018000	4.882843000	C	4.788902000	0.514741000	-1.702195000	H	-5.478900000	1.165749000	4.072941000
H	-4.400760000	-2.932414000	0.894718000					H	5.528816000	0.251604000	-2.473042000				

Table S6: Optimized geometries of **5b**. XYZ coordinated in angstroms. B3LYP/def2-SVP level of theory.



W	-3.995257000	0.320796000	0.595625000	H	4.169637000	1.263378000	-1.338650000
W	3.809507000	-2.039999000	0.281461000	H	4.934147000	2.128776000	0.016471000
Co	0.904930000	1.575762000	-0.235366000	C	-5.131115000	-1.415455000	0.399523000
P	0.008289000	-0.332714000	0.915998000	C	-0.487393000	2.399961000	3.407212000
P	1.743741000	-0.601574000	-0.341784000	H	-1.104246000	3.253661000	3.091352000
P	1.234443000	0.353293000	-2.217152000	H	-0.580720000	2.311404000	4.500706000
P	-0.798953000	0.977115000	-1.773979000	H	-0.909378000	1.488738000	2.961097000
P	-1.731063000	-0.595135000	-0.469296000	C	-0.458718000	-2.802021000	-1.942665000
O	-5.905712000	-2.265349000	0.369770000	C	-3.253671000	2.204963000	0.943665000
O	2.700891000	-4.471748000	-1.538067000	C	1.497870000	3.912766000	3.652129000
O	5.071726000	0.292917000	2.111270000	H	2.561340000	4.084990000	3.423572000
O	-4.930136000	1.224611000	-2.359108000	H	1.386834000	3.877516000	4.747789000
O	-2.978011000	3.301022000	1.184679000	H	0.924748000	4.776310000	3.279804000
O	6.230957000	-3.934167000	1.100237000	C	1.032779000	5.962089000	-1.689067000
O	2.144282000	-3.165800000	2.810648000	H	1.112810000	6.369074000	-0.668514000
O	5.519140000	-1.039886000	-2.266766000	H	0.471252000	6.688857000	-2.297266000
O	-6.656450000	1.494299000	1.867644000	H	2.044248000	5.895663000	-2.108743000
C	2.407178000	2.593126000	0.813992000	C	-2.202174000	-3.352402000	-0.221508000
H	3.300562000	2.140367000	1.230240000	C	-1.768700000	-2.346885000	-1.281881000
O	-2.992537000	-0.705088000	3.487916000	C	-2.905484000	-2.379479000	-2.295985000
C	1.184741000	2.754264000	1.520919000	C	0.235640000	4.032100000	-3.128543000
C	0.289333000	3.369304000	0.594785000	C	3.535485000	3.547553000	-2.802999000
H	-0.741518000	3.620687000	0.812659000	H	2.983509000	4.444025000	-3.106170000
C	3.651371000	3.394448000	-1.276921000	H	3.060925000	2.667199000	-3.259980000
C	4.311081000	4.670812000	-0.687449000	H	4.547161000	3.636613000	-3.227964000
H	3.691444000	5.565326000	-0.837337000	C	-3.362152000	-3.933947000	-0.630635000
H	5.283958000	4.846004000	-1.174574000	C	-2.897341000	-1.573301000	-3.559380000
H	4.490309000	4.562964000	0.393402000	C	-5.692012000	1.062337000	1.404246000
C	5.353785000	-3.249939000	0.800589000	C	-1.386483000	-3.673170000	0.993752000
C	0.967244000	3.686139000	-0.638417000	H	-0.334417000	-3.888653000	0.740538000
C	-1.171715000	4.897479000	-1.292452000	H	-1.782747000	-4.552020000	1.521119000
H	-1.770854000	3.980021000	-1.215279000	H	-1.367077000	-2.842744000	1.720788000
H	-1.632989000	5.528526000	-2.067321000	C	-4.123071000	-5.039061000	0.037378000
H	-1.246435000	5.442275000	-0.339702000	C	-5.043154000	-3.771442000	-2.618386000
C	1.826176000	1.423044000	3.592891000	H	-0.614333000	-3.810717000	-2.357281000
H	1.502826000	0.454240000	3.185001000	H	-0.151589000	-2.138994000	-2.763149000
H	1.704215000	1.379332000	4.686450000	H	0.366719000	-2.859351000	-1.222681000
H	2.900843000	1.543584000	3.389816000	H	-3.804527000	-1.749438000	-4.153755000
C	-3.343327000	-0.336244000	2.457196000	H	-2.838171000	-0.488414000	-3.371145000
C	4.613391000	-0.536333000	1.456999000	H	-2.031665000	-1.826104000	-4.197688000
C	2.331825000	3.187092000	-0.495103000	H	-5.931709000	-3.624186000	-1.981762000
C	0.990596000	2.586037000	3.025666000	H	-5.206937000	-3.223848000	-3.556626000
C	3.071351000	-3.594164000	-0.897102000	H	-5.002871000	-4.847328000	-2.860518000
C	0.291601000	4.601512000	-1.693054000	H	-5.136594000	-4.706890000	0.316599000
C	4.896300000	-1.376078000	-1.362008000	H	-4.246331000	-5.902691000	-0.638225000
C	-3.799802000	-3.328763000	-1.908209000	H	-3.624619000	-5.395538000	0.949144000
C	2.728684000	-2.752605000	1.913409000	H	1.194495000	3.653306000	-3.489557000
C	-4.590141000	0.904542000	-1.308919000	H	-0.496259000	3.215644000	-3.198279000
C	4.619530000	2.215909000	-1.031985000	H	-0.093685000	4.825175000	-3.819057000
H	5.532926000	2.362312000	-1.627492000				

8.4.4.2 Computations for the reaction of [Cp'''Co(η⁴-P₄)] and [Cp*As{W(CO)₅}₂]

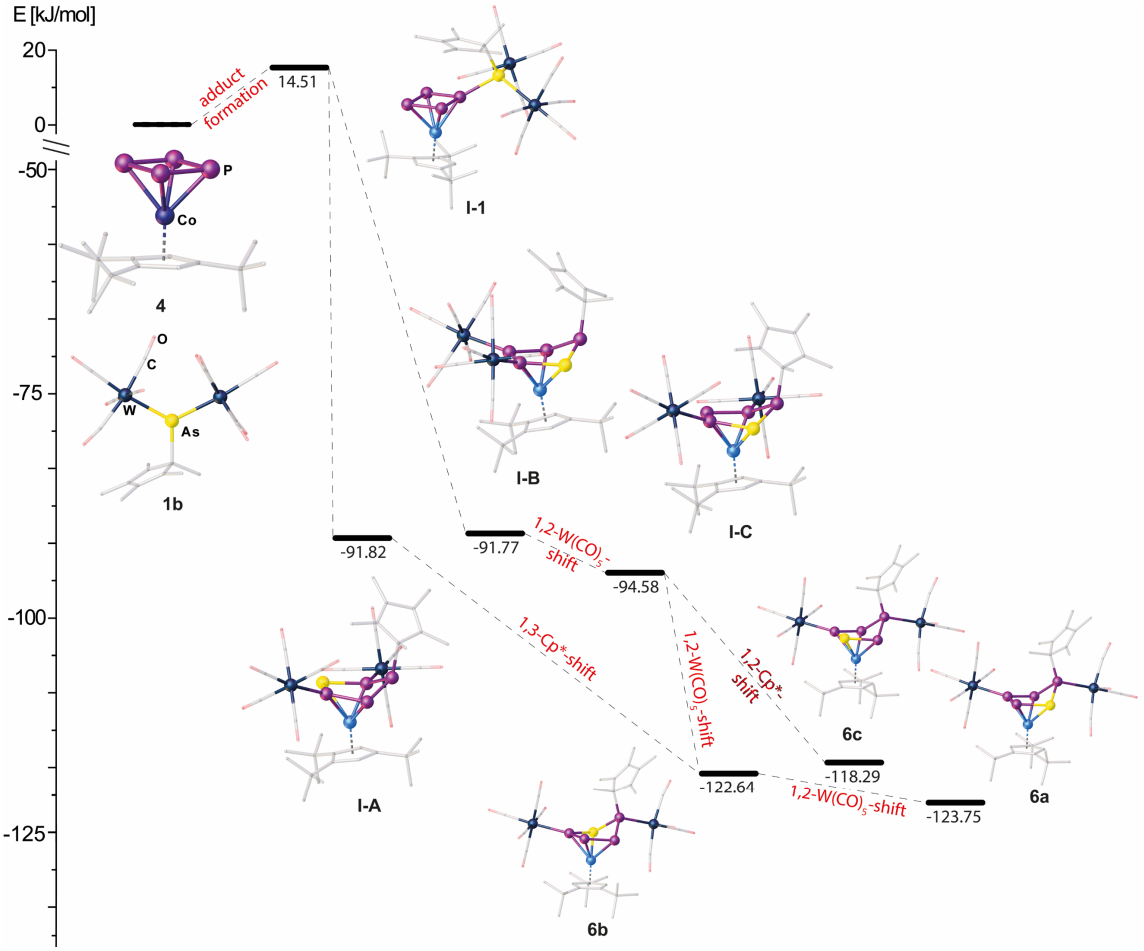
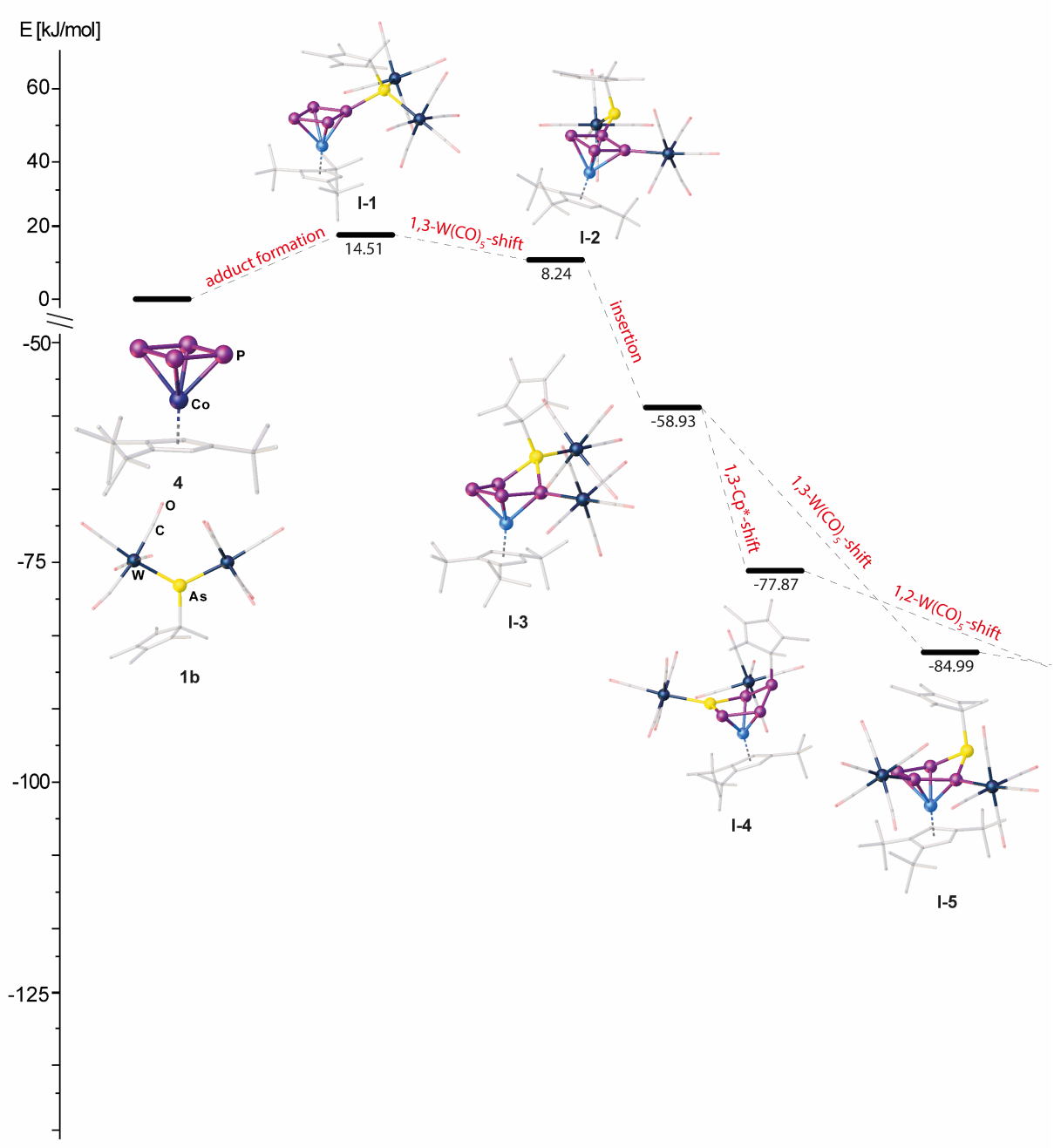


Figure S13. Part of the energetic profile of the reaction of **1b** and **4**.

Table S7: Total energies for all optimized geometries (B3LYP/def2-SVP level of theory)

	total energy [Ha]
1b ($Cp^*As(W(CO)_5)_2$)	-3892.3729602
4 ($Cp'''CoP_4$)	-3412.5646307
I-1	-7304.9320638
I-2	-7304.9344539
I-3	-7304.9600344
I-4	-7304.9672499
I-5	-7304.9699227
I-6	-7304.9435112
I-7	-7304.9760339
I-8	-7304.9775111

	total energy [Ha]
I-9	-7304.9707998
I-10	-7304.9616212
I-11	-7304.9672499
I-12	-7304.9686164
I-A	-7304.9725651
I-B	-7304.9725455
I-C	-7304.9736136
6a	-7304.9847264
6b	-7304.9843006
6c	-7304.9826438


E [kJ/mol]
60
40
20
0
-50
-75
-100
-125
adduct formation
1,3-W(CO)5-shift
insertion
1,3-Cp*-shift
1,3-W(CO)5-shift
1,2-W(CO)5-shift
14.51
8.24
-58.93
-77.87
-84.99
I-1
I-2
I-3
I-4
I-5
4
1b
P
Co
O
C
W
As

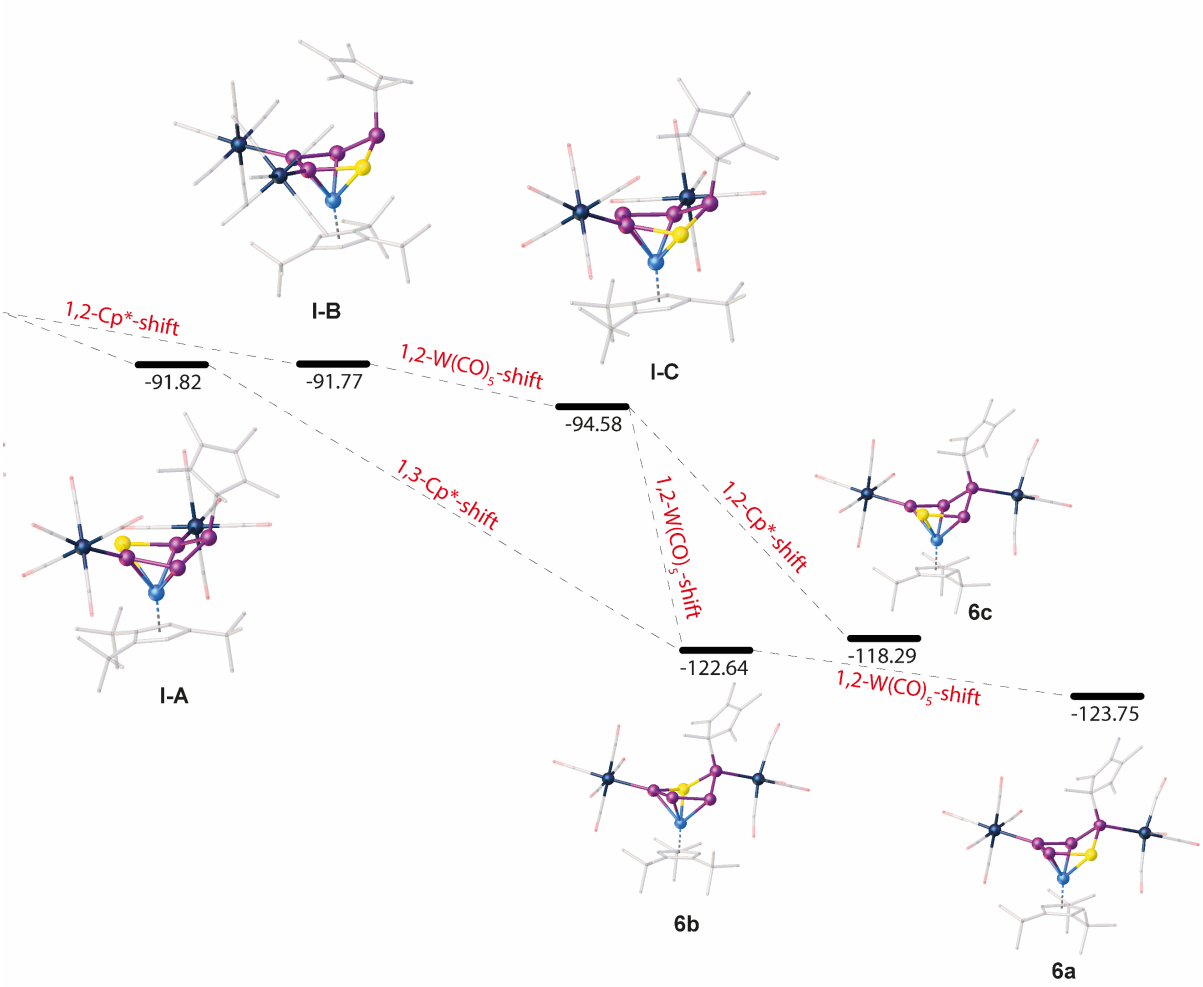


Figure S14. Energetic profile of the reaction of **1b** with **4**.

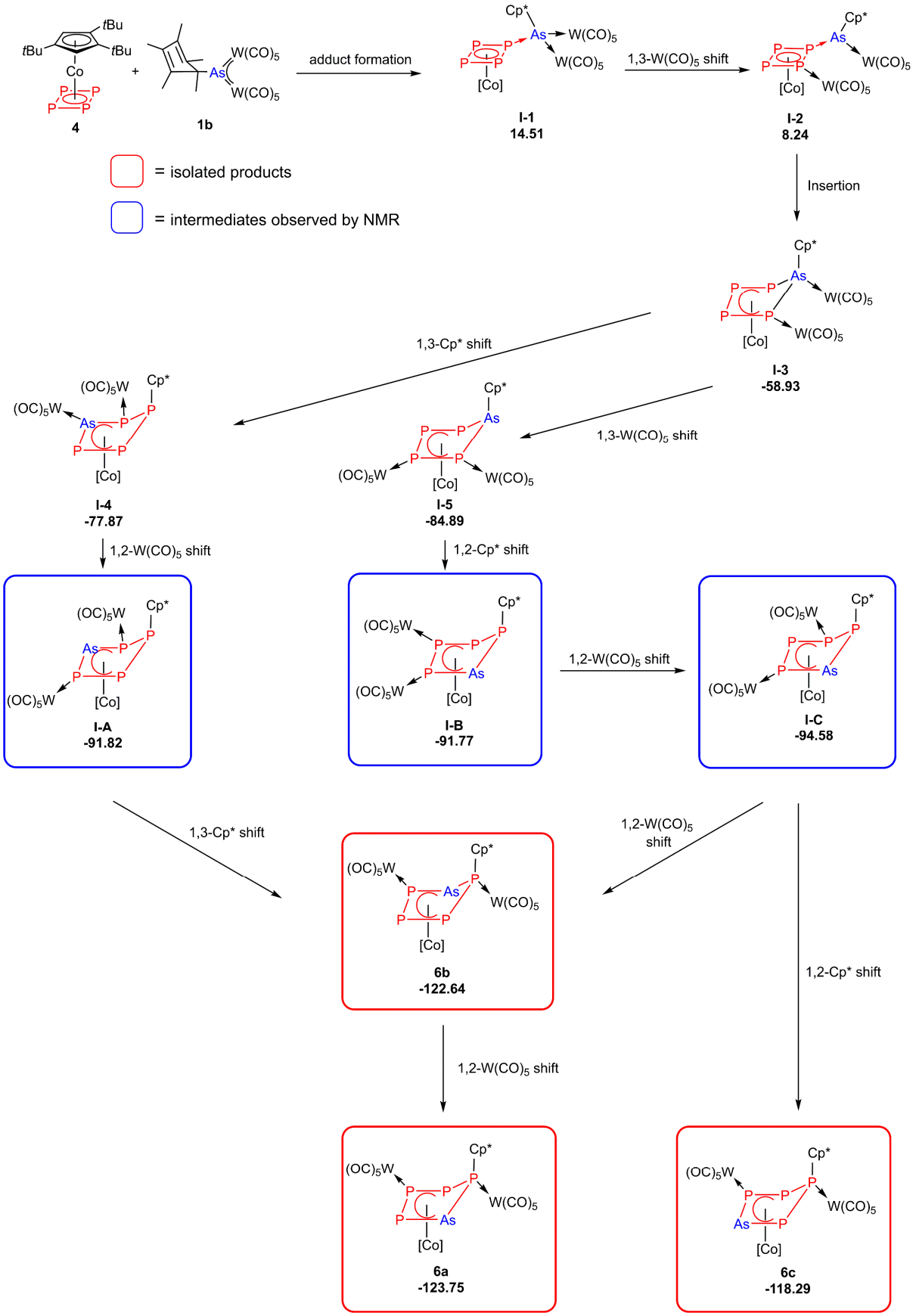


Figure S15. Possible reaction pathway for the reaction of **1b** and **4**.

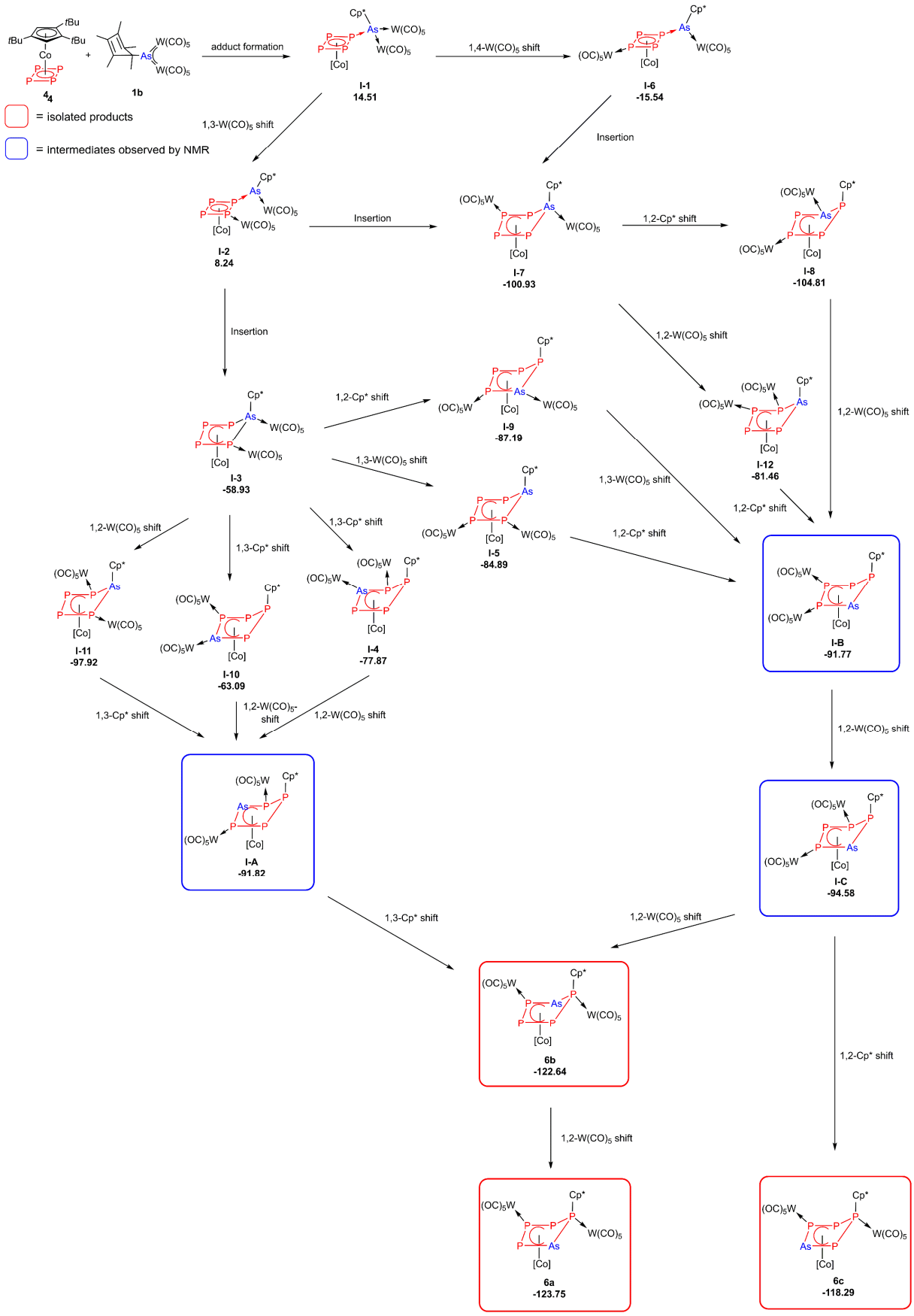
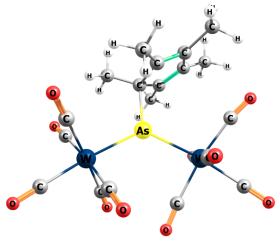
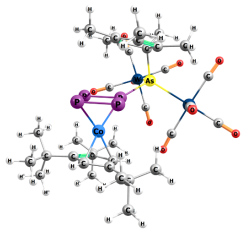


Figure S16. Extended possible reaction pathway for the reaction of **1b** and **4**.

Table S8: Optimized geometries of **1b** (left), **I-1** (right). XYZ coordinated in angstroms. B3LYP/def2-SVP level of theory.

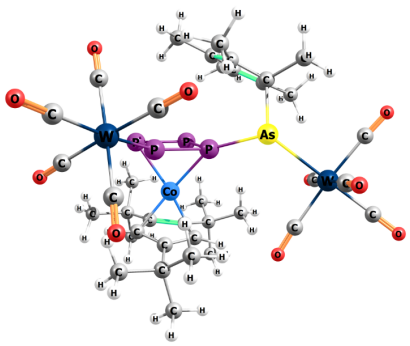


W	6.188297000	12.074673000	3.074164000	C	8.495076000	16.239082000	4.794028000
W	8.714888000	12.733478000	6.924010000	C	8.438879000	16.952331000	5.962735000
As	7.368278000	13.599321000	4.842721000	C	7.090223000	16.845510000	6.532210000
C	6.596708000	13.248550000	1.404771000	C	6.308824000	16.063162000	5.717669000
O	6.802672000	13.845932000	0.445924000	C	6.568117000	15.993512000	3.172879000
C	4.380063000	13.079583000	3.287200000	H	5.596739000	15.516476000	2.986860000
O	3.379592000	13.637400000	3.373042000	H	7.246227000	15.712727000	2.356017000
C	5.728568000	10.805278000	4.659661000	H	6.421233000	17.086016000	3.126386000
O	5.457292000	10.088208000	5.512750000	C	9.636274000	16.159703000	3.819674000
C	8.005693000	11.090170000	2.753374000	H	9.601044000	16.990477000	3.091101000
O	9.001115000	10.565408000	2.538041000	H	9.623167000	15.226723000	3.236036000
C	5.258364000	10.723502000	1.833170000	H	10.612236000	16.212697000	4.323943000
O	4.736184000	9.961575000	1.149834000	C	9.527820000	17.775627000	6.581008000
C	10.502902000	13.313593000	6.016522000	H	9.711052000	17.478080000	7.626539000
O	11.486361000	13.652004000	5.531983000	H	9.252947000	18.844727000	6.601824000
C	8.796538000	14.465619000	8.070903000	H	10.475195000	17.688385000	6.031043000
O	8.920786000	15.324422000	8.826230000	C	6.681738000	17.554569000	7.787383000
C	6.898765000	12.253687000	7.845807000	H	6.875121000	18.638111000	7.710062000
O	5.903036000	12.011792000	8.359763000	H	7.260288000	17.193092000	8.653499000
C	8.776714000	10.863804000	6.028308000	H	5.615973000	17.418330000	8.016429000
O	8.848255000	9.796420000	5.610353000	C	4.846511000	15.754911000	5.872263000
C	9.757694000	11.837916000	8.442464000	H	4.655493000	14.717073000	6.195405000
O	10.343964000	11.324879000	9.288478000	H	4.296972000	15.895131000	4.927071000
C	7.145797000	15.633054000	4.540100000	H	4.381027000	16.408780000	6.623161000

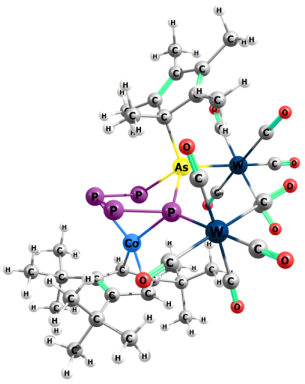


Co	3.134168000	0.086879000	0.236490000	H	1.182523000	-1.647194000	-1.854176000
P	0.912360000	-0.022511000	0.994992000	W	-2.381109000	-2.405857000	-0.423959000
P	2.110552000	1.528171000	1.894650000	W	-2.045790000	2.244852000	-1.032993000
P	3.440507000	-0.090480000	2.533173000	As	-1.479910000	0.044523000	0.637488000
P	2.209100000	-1.648155000	1.595927000	C	-3.185053000	-3.939326000	-1.446641000
C	4.084387000	1.495784000	-1.025303000	O	-3.646375000	-4.810615000	-2.047997000
C	5.015480000	0.726882000	-0.269534000	C	-0.635766000	-3.498279000	-0.212990000
C	4.908046000	-0.675843000	-0.577295000	O	0.303811000	-4.157015000	-0.103881000
C	3.809877000	-0.795080000	-1.541934000	C	-3.126860000	-3.325280000	1.276067000
C	3.325864000	0.546042000	-1.769437000	O	-3.585003000	-3.907516000	2.157420000
C	4.085930000	3.013369000	-1.168267000	C	-4.201821000	-1.405947000	-0.553282000
C	4.967654000	3.318209000	-2.408139000	O	-5.231070000	-0.897246000	-0.591406000
C	2.675570000	3.574724000	-1.407808000	C	-1.727941000	-1.700779000	-2.262296000
C	4.705565000	3.698112000	0.063962000	O	-1.396533000	-1.392488000	-3.319874000
C	5.973110000	-1.668075000	-0.044207000	C	-2.454724000	3.822886000	-2.211421000
C	6.998809000	-0.929542000	0.849093000	O	-2.673762000	4.742466000	-2.875051000
C	5.410369000	-2.820816000	0.814666000	C	-3.243404000	1.143408000	-2.326066000
C	6.770679000	-2.228295000	-1.248456000	O	-3.914131000	0.631540000	-3.105593000
C	3.280230000	-1.937969000	-2.433712000	C	-3.799125000	2.628023000	0.026006000
C	4.079940000	-1.868471000	-3.762431000	O	-4.806420000	2.832280000	0.540884000
C	3.383026000	-3.358870000	-1.852503000	C	-0.869525000	3.523520000	0.100494000
C	1.790139000	-1.707978000	-2.767804000	O	-0.225125000	4.288526000	0.670901000
C	5.723411000	1.147991000	0.434813000	C	-0.473534000	1.779506000	-2.276348000
H	2.503069000	0.797666000	-2.431135000	O	0.353060000	1.533590000	-3.045192000
H	5.991522000	2.932557000	-2.279779000	C	-1.839038000	0.263719000	2.758151000
H	5.030800000	4.406814000	-2.565650000	O	-0.940358000	-0.680883000	3.540148000
H	4.545662000	2.867498000	-3.319862000	C	-0.151591000	0.057439000	4.372452000
H	2.206242000	3.142208000	-2.302337000	C	-0.473537000	1.486926000	4.216545000
H	2.727475000	4.664525000	-1.556929000	C	-1.468433000	1.630018000	3.292625000
H	2.021824000	3.387445000	-0.544721000	C	-3.339932000	-0.033171000	2.890055000
H	4.135757000	3.470357000	0.977591000	H	-3.955923000	0.688671000	2.332775000
H	4.696654000	4.790274000	-0.073839000	H	-3.628061000	0.034322000	3.952985000
H	5.753687000	3.399727000	0.222729000	H	-3.594144000	-1.040951000	2.537008000
H	7.552708000	-0.154350000	0.297803000	C	-1.013825000	-2.172381000	3.482824000
H	7.737309000	-1.656389000	1.219647000	H	-2.012223000	-2.542819000	3.768223000
H	6.524811000	-0.468044000	1.728242000	H	-0.287468000	-2.633472000	4.165977000
H	5.035714000	-2.436842000	1.775855000	H	-0.814778000	-2.566323000	2.473848000
H	6.216581000	-3.536775000	1.041913000	C	0.857305000	-0.429904000	5.368366000
H	4.597804000	-3.370356000	0.333005000	H	1.854529000	0.002535000	5.176120000
H	6.170510000	-2.883731000	-1.890606000	H	0.964060000	-1.522877000	5.359294000
H	7.625443000	-2.818018000	-0.881579000	H	0.580940000	-0.129464000	6.394052000
H	7.169048000	-1.413040000	-1.872894000	C	0.157764000	2.551755000	5.064111000
H	5.154213000	-2.044975000	-3.610404000	H	1.258721000	2.507144000	5.012268000
H	3.964775000	-0.885786000	-4.245498000	H	-0.110259000	2.427261000	6.128372000
H	3.706434000	-2.633080000	-4.462132000	H	-0.147462000	3.562359000	4.760929000
H	2.942908000	-4.067105000	-2.570920000	C	-2.259618000	2.876144000	3.047875000
H	2.818412000	-3.456275000	-0.914428000	H	-2.483320000	3.032625000	1.987897000
H	4.415698000	-3.681362000	-1.679449000	H	-1.730595000	3.768899000	3.408313000
H	1.413869000	-2.551410000	-3.364855000	H	-3.232971000	2.836633000	3.570585000
H	1.609764000	-0.798498000	-3.355150000				

Table S9: Optimized geometries of **I-2** (left), **I-3** (right). XYZ coordinated in angstroms. B3LYP/def2-SVP level of theory.



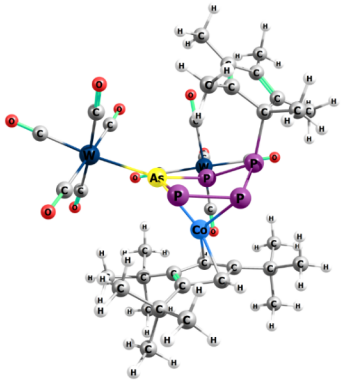
Co	-1.055445000	1.942534000	0.232184000	H	2.180173000	2.647764000	0.941818000
P	0.139017000	-0.022603000	0.753338000	W	4.156159000	-0.588220000	-1.049391000
P	-1.977527000	-0.298481000	0.368873000	W	-3.744689000	-1.916964000	-0.607639000

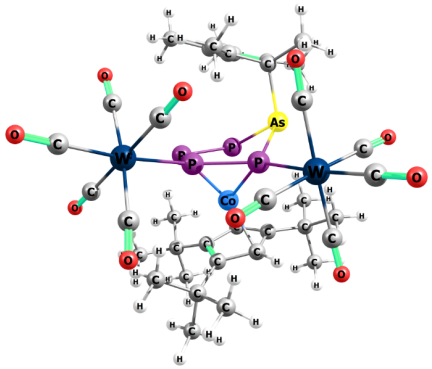


W	-0.895296000	3.221169000	0.115320000	C	-3.043873000	-2.016961000	4.150555000
W	3.148082000	-0.789121000	1.346665000	H	-3.502996000	-1.017839000	4.207442000
Co	-2.206676000	-1.271014000	-0.259128000	H	-2.578725000	-2.229785000	5.126428000

P	-2.397107000	1.094098000	1.972092000	As	1.826210000	-1.530697000	0.195978000	P	-0.718059000	0.631532000	-0.497164000	H	-3.846870000	-2.753843000	3.989171000
P	-0.265396000	1.365940000	2.384330000	C	5.753372000	-0.162422000	-2.196863000	P	-0.223621000	-2.466359000	-0.799990000	C	-6.830714000	-0.613111000	0.163255000
C	-1.330975000	2.688810000	-1.732496000	O	6.665463000	0.085168000	-2.861558000	P	-1.978888000	0.109647000	-2.162925000	H	-7.102369000	-1.400329000	-0.549977000
C	-2.265592000	3.234012000	-0.807560000	C	4.679868000	0.958713000	0.226046000	As	1.302147000	-0.639021000	-0.727441000	H	-7.608038000	0.164366000	0.099995000
C	-1.595492000	3.972089000	0.233648000	O	5.021488000	1.827331000	0.900862000	P	-1.607391000	-2.010998000	-2.395710000	H	-6.864558000	-1.037584000	1.179032000
C	-0.159101000	3.835606000	-0.030708000	C	5.396853000	-1.858492000	0.036714000	O	0.186357000	3.966520000	-2.831338000	C	-5.957043000	-4.014226000	-0.161349000
C	-0.046285000	3.020911000	-1.214472000	O	6.141625000	-2.526484000	0.604570000	O	-2.203826000	2.491205000	2.971282000	H	-5.553430000	-4.488920000	0.746738000
C	-1.634603000	2.070312000	-3.090790000	C	3.670323000	-2.133453000	-2.362237000	O	-3.785482000	3.618248000	-1.240227000	H	-6.487358000	-4.789578000	-0.737573000
C	-1.160323000	3.088457000	-4.159608000	O	3.421924000	-2.974691000	-3.103525000	O	2.084282000	3.446738000	1.332919000	H	-6.693348000	-3.264420000	0.151230000
C	-0.875528000	0.745655000	-3.298768000	C	3.080473000	0.745394000	-2.180956000	O	-1.101634000	6.310522000	0.806801000	C	-1.974657000	-2.090478000	3.029831000
C	-3.149295000	1.857146000	-3.255061000	O	2.542342000	1.528506000	-2.841848000	O	5.283181000	-1.022691000	3.671087000	C	1.156914000	0.027811000	-3.727717000
C	-2.411921000	4.858558000	1.206169000	C	-5.281268000	-3.164144000	-1.047563000	O	1.520404000	1.110574000	3.378789000	H	0.424717000	-0.762160000	-3.938610000
C	-3.928711000	4.659253000	0.975305000	O	-6.164179000	-3.866376000	-1.279057000	C	-2.769270000	3.408705000	-0.741298000	H	1.729133000	0.209687000	-4.653150000
C	-2.164651000	4.586034000	2.705348000	C	-3.552565000	-1.558032000	-2.648938000	C	-1.026144000	5.187696000	0.553520000	H	0.605493000	0.948269000	-3.488112000
C	-2.105769000	6.339935000	0.870019000	O	-3.490959000	-1.451096000	-3.790644000	C	-0.166432000	3.686547000	-1.773481000	C	-1.332108000	-3.488180000	3.057100000
C	1.116681000	4.521592000	0.508421000	C	-2.405641000	-3.487844000	-0.912759000	C	-1.715906000	2.748006000	1.960550000	H	-2.095052000	-4.282012000	3.021327000
C	1.364677000	5.753112000	-0.404657000	O	-1.709222000	-4.372193000	-1.129728000	C	2.057718000	0.439279000	2.615437000	H	-0.758218000	-3.623805000	3.985872000
C	1.091867000	4.984873000	1.975145000	C	-3.994762000	-2.468379000	1.383188000	C	1.025376000	3.301547000	0.912598000	H	-0.639267000	-3.637622000	2.217740000
C	2.331539000	3.577550000	0.375084000	O	-4.143314000	-2.808486000	2.469737000	C	4.505533000	-0.935870000	2.822422000	C	2.959835000	2.130837000	-2.249502000
H	-3.341095000	3.123701000	-0.884977000	C	-5.084311000	-0.341208000	-0.418802000	O	1.878603000	-3.472340000	2.585209000	H	2.456598000	2.588470000	-3.118412000
H	0.891187000	2.734191000	-1.680123000	O	-5.819793000	0.538884000	-0.341096000	C	2.150110000	-0.362878000	-2.628924000	H	3.882067000	2.696812000	-2.064284000
H	-1.657244000	4.063639000	-4.033743000	C	1.966871000	-2.319986000	2.164882000	C	-4.080361000	-2.377571000	-0.135678000	H	2.300357000	2.298024000	-1.383761000
H	-1.400507000	2.712155000	-5.166742000	C	2.405216000	-1.319077000	3.203017000	C	2.271409000	-2.497571000	2.115446000	C	4.379623000	-2.053629000	0.251002000
H	-0.072246000	3.247296000	-4.110246000	C	1.387598000	-1.143096000	4.096567000	C	-4.333708000	-0.985972000	0.240128000	C	-5.355892000	1.275233000	0.758768000
H	0.211782000	0.894715000	-3.257053000	C	0.250706000	-2.009670000	3.720838000	C	-3.435384000	-0.699194000	1.326844000	H	-5.530657000	1.034965000	1.818720000
H	-1.118364000	0.322357000	-4.285486000	C	0.575246000	-2.716444000	2.601361000	H	-3.371337000	0.255257000	1.837590000	H	-6.122722000	2.001487000	0.451068000
H	-1.148907000	0.004020000	-2.534946000	C	2.913888000	-3.519657000	2.001547000	C	-5.422406000	0.510748000	-1.605287000	H	-4.383756000	1.776019000	0.674006000
H	-3.556827000	1.212590000	-2.463462000	H	2.573379000	-4.211350000	1.214748000	H	-4.576233000	1.184516000	-1.784393000	C	4.234218000	-1.342596000	-3.032907000
H	-3.363804000	1.377057000	-4.220947000	H	2.944569000	-4.082863000	2.950067000	H	-6.343900000	1.076229000	-1.817945000	C	-5.398225000	-2.860562000	-2.340892000
H	-3.694830000	2.813588000	-3.229986000	H	3.940914000	-3.213878000	1.766185000	H	-5.353308000	-0.306752000	-2.329554000	H	-6.190216000	-2.120715000	-2.180974000
H	-4.242231000	4.966733000	-0.033743000	C	3.790674000	-0.761209000	3.275328000	C	-3.066359000	-2.855936000	0.763723000	H	-5.843806000	-3.688794000	-2.913380000
H	-4.485408000	5.281268000	1.692487000	H	4.517206000	-1.525980000	3.606618000	H	-2.662801000	-3.862444000	0.749670000	H	-4.616003000	-2.407140000	-2.967613000
H	-4.237873000	3.615982000	1.136882000	H	3.860804000	0.080724000	3.978921000	C	2.906773000	-1.640709000	-2.955986000	C	2.255434000	-2.958710000	-3.249192000
H	-2.582472000	3.610746000	2.995397000	H	4.135823000	-0.410034000	2.293535000	C	4.441962000	0.088327000	-2.724896000	H	1.907455000	-3.474605000	-2.336460000
H	-2.678831000	5.353048000	3.306372000	C	1.382375000	-0.291159000	5.331555000	C	-2.707537000	-1.863320000	1.715382000	H	2.952584000	-3.641518000	-3.755356000
H	-1.107984000	4.597272000	2.981928000	H	0.515740000	0.391701000	5.352683000	C	-4.816145000	-3.410192000	-1.026401000	H	1.371238000	-2.847901000	-3.898793000
H	-1.072394000	6.623963000	1.104557000	H	2.290699000	0.321607000	5.416208000	C	-5.450780000	0.022003000	-0.141340000	C	5.364048000	-2.250836000	-3.411691000
H	-2.770804000	6.996927000	1.452450000	H	1.313807000	-0.910644000	6.243389000	C	3.240677000	0.678695000	-2.477275000	H	5.018935000	-3.258743000	-3.679153000
H	-2.279592000	6.546972000	-0.197801000	C	-1.014281000	-2.080944000	4.522716000	C	-0.914188000	-1.010214000	3.278379000	H	6.080722000	-2.359404000	-2.581371000
H	0.545414000	6.484061000	-0.344209000	H	-1.477683000	-1.084953000	4.632444000	H	-0.155375000	-1.025261000	2.486112000	H	5.926571000	-1.845605000	-4.269980000
H	1.471540000	5.454341000	-1.458788000	H	-0.820753000	-2.447842000	5.546151000	H	-0.408854000	-1.180660000	4.241563000	C	5.798020000	0.726437000	-2.746639000
H	2.294802000	6.260260000	-0.102340000	H	-1.762135000	-2.744433000	4.067646000	H	-1.352690000	-0.002565000	3.310782000	H	5.767252000	1.780806000	-2.442532000
H	2.072538000	5.418792000	2.223340000	C	-0.194367000	-3.816052000	1.940644000	O	5.120429000	-2.785759000	-0.236715000	H	6.246651000	0.677736000	-3.754167000
H	0.922849000	4.140870000	2.659597000	H	-0.128880000	-3.754583000	0.843798000	C	-3.889809000	-4.591606000	-1.407673000	H	6.493982000	0.203686000	-2.068719000
H	0.341993000	5.759117000	2.173845000	H	-1.256719000	-3.804857000	2.223026000	H	-3.010641000	-4.259889000	-1.977416000	O	4.857413000	1.773269000	0.379521000
H	3.227966000	4.069053000	0.779899000	H	0.203694000	-4.808845000	2.221268000	H	-4.452032000	-5.293373000	-2.042146000	C	4.204605000	0.874432000	0.670922000
H	2.558292000	3.312671000	-0.665738000					H	-3.546260000	-5.163050000	-0.533771000				

Table S10: Optimized geometries of **I-4** (left), **I-5** (right). XYZ coordinated in angstroms. B3LYP/def2-SVP level of theory.

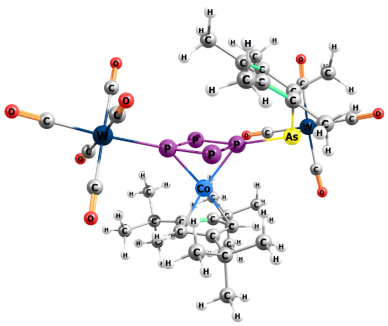


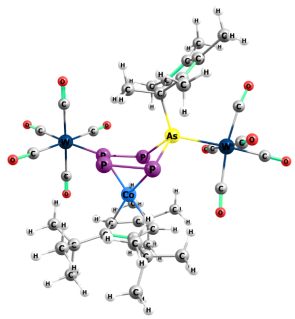


W	-2.398181000	-0.132636000	-2.021298000	C	-0.309356000	6.195712000	-0.585434000	W	-3.418439000	-0.913399000	0.543125000	C	3.732245000	3.980663000	-2.626921000
W	2.284276000	-2.798431000	-0.038178000	H	0.572475000	6.641421000	-0.098269000	W	1.412746000	-2.297012000	-1.992259000	H	3.221668000	3.717791000	-3.566374000
Co	0.843920000	1.984631000	0.667650000	H	-1.116584000	6.945668000	-0.579219000	Co	0.477970000	1.966730000	-0.170377000	H	4.814684000	4.021421000	-2.828889000
P	-0.116413000	1.958830000	2.840600000	C	0.531190000	-3.629610000	-0.794963000	P	0.947286000	-0.383772000	-0.219308000	H	3.402862000	4.989429000	-2.331532000
P	-1.004698000	0.523957000	0.140821000	H	-0.048696000	5.986550000	-1.634655000	P	1.512614000	1.926375000	1.998860000	C	-1.786487000	4.076713000	-3.679118000
P	1.536607000	0.610457000	2.507362000	C	4.949371000	4.159822000	0.252946000	P	-1.010590000	0.150118000	0.528396000	H	-2.165359000	4.900423000	-3.059891000
P	-2.010986000	1.235501000	1.961922000	H	5.208567000	3.695056000	-0.706913000	As	2.571168000	-0.066439000	1.438808000	H	-2.536642000	3.880305000	-4.461644000
As	0.947416000	-0.546386000	0.677390000	H	5.890976000	4.346890000	0.793246000	P	-0.629745000	1.716244000	1.932174000	H	-0.863962000	4.417773000	-4.175253000
O	-0.004505000	-1.691956000	-3.511032000	H	4.481289000	5.134860000	0.043404000	O	-4.755818000	2.005189000	0.854609000	C	-0.636069000	6.391717000	-0.973406000
O	-4.948466000	1.478075000	-0.873819000	C	3.329435000	3.337331000	-3.005190000	O	-2.139338000	-3.867155000	0.283191000	H	0.443663000	6.604923000	-0.939743000
O	-3.304974000	-2.913741000	-0.642994000	H	2.463813000	3.954416000	-3.291454000	O	-4.142286000	-0.883973000	-2.608407000	H	-1.165491000	7.264701000	-0.558730000
O	-1.576842000	2.484797000	-3.695838000	H	3.802341000	2.970312000	-3.930256000	O	-3.147824000	-1.031913000	3.749425000	H	-0.925104000	6.291298000	-2.029030000
O	-4.243552000	-0.967416000	-4.463996000	H	4.051660000	3.986734000	-2.490586000	O	-6.259922000	-2.257635000	0.974691000	C	3.438302000	2.939614000	-1.513254000
O	3.754504000	-5.565274000	-0.504519000	C	-0.774285000	4.909322000	0.148897000	O	2.127955000	-4.693717000	-3.946597000	C	0.168004000	-2.422048000	3.155802000
O	3.191980000	-1.975691000	-3.028227000	C	-1.107898000	-1.681958000	4.052111000	O	1.860730000	-0.281882000	-4.461131000	H	0.547558000	-3.457768000	3.201554000
C	-2.966697000	-1.909894000	-1.084334000	H	-1.241578000	-1.490237000	5.133025000	C	-3.827063000	-0.889639000	-1.505737000	H	-0.070084000	-2.231056000	2.096745000
C	-3.568207000	-0.663920000	-3.579373000	H	-0.261860000	-1.056769000	3.732240000	C	-5.228007000	-1.770297000	0.811537000	H	-0.773948000	-2.391854000	3.718335000
C	-0.832459000	-1.136184000	-2.937894000	H	-0.802430000	-2.731716000	3.945530000	C	-4.269246000	0.970192000	0.737519000	C	4.213363000	3.346916000	-0.246981000
C	-4.026844000	0.896613000	-1.238035000	C	-2.013487000	4.350013000	-0.570354000	C	-2.576948000	-2.809206000	0.364905000	H	3.959287000	4.365454000	0.085169000
C	2.840981000	-2.231472000	-1.966041000	H	-1.813433000	4.136127000	-1.629913000	C	1.698371000	-0.985100000	-3.561877000	H	5.294800000	3.332639000	-0.454008000
C	-1.863670000	1.559241000	-3.068953000	H	-2.827631000	5.090945000	-0.535946000	C	-3.206467000	-0.982063000	2.602084000	H	4.020646000	2.657129000	0.586826000
C	3.218813000	-4.557717000	-0.339980000	H	-2.375662000	3.430936000	-0.088655000	C	1.865882000	-3.821666000	-3.238667000	C	-0.140215000	-0.457690000	5.692807000
O	5.037589000	-1.573112000	1.114252000	C	-3.135925000	-3.768906000	2.718434000	O	4.556875000	-2.138731000	-1.280834000	H	-0.403707000	0.609409000	5.789638000
C	-2.362606000	-1.383881000	3.291945000	H	-3.185128000	-4.127607000	1.677058000	C	1.165205000	-1.448793000	3.700027000	H	0.064813000	-0.821582000	6.715217000
C	2.188797000	2.723715000	-0.886284000	H	-3.962864000	-4.258461000	3.261507000	C	-0.166781000	3.965122000	-0.778529000	H	-1.030326000	-0.981498000	5.321256000

C	4.048431000	-1.995652000	0.709341000	H	-2.193418000	-4.128710000	3.153689000	C	3.431615000	-2.173215000	-1.513286000	C	1.140891000	-3.697993000	-0.472626000
C	2.639054000	3.203500000	0.417646000	C	1.785831000	-3.481465000	1.861090000	C	-0.364902000	3.037725000	-1.889641000	C	-1.178187000	1.671230000	-3.867673000
C	1.525018000	3.915264000	0.980786000	C	3.896994000	3.954341000	2.495205000	C	0.916096000	2.434041000	-2.144053000	H	-0.328083000	1.940206000	-4.511689000
H	1.533037000	4.393389000	1.953644000	H	3.569120000	5.002121000	2.417836000	H	1.105009000	1.698620000	-2.916962000	H	-2.040182000	1.484394000	-4.524924000
C	4.701392000	1.906274000	1.383999000	H	4.882579000	3.957843000	2.984332000	C	-2.842175000	2.339211000	-2.173260000	H	-0.942358000	0.723500000	-3.361398000
H	4.139483000	1.331171000	2.131880000	H	3.203583000	3.416753000	3.159736000	H	-2.672278000	1.412465000	-1.614204000	C	3.245449000	-0.360478000	4.100443000
H	5.711903000	2.080054000	1.786835000	C	-4.306457000	-0.220178000	2.523188000	H	-3.613082000	2.137401000	-2.933019000	C	-2.513593000	4.954139000	-0.122391000
H	4.806241000	1.282381000	0.494795000	C	4.128643000	1.254831000	-1.851600000	H	-3.245056000	3.077117000	-1.477264000	H	-2.956690000	4.943506000	-1.125011000
C	0.826672000	3.166696000	-1.031698000	H	4.960948000	1.814204000	-1.409619000	C	1.227060000	3.880990000	-0.440044000	H	-2.955158000	5.810927000	0.409640000
H	0.217127000	2.982459000	-1.909174000	H	4.489618000	0.837481000	-2.803527000	H	1.699478000	4.463460000	0.343526000	H	-2.819538000	4.043359000	0.411118000
C	-2.939051000	0.010456000	3.151561000	H	3.885121000	0.408456000	-1.195041000	C	2.546798000	-1.290590000	3.135584000	C	3.291339000	-2.577838000	2.774125000
C	-4.458600000	-1.554558000	2.303459000	C	-3.024657000	0.767652000	4.493572000	C	2.335666000	0.035156000	5.041318000	H	2.730697000	-3.188576000	2.051515000
C	0.415643000	3.954700000	0.082806000	H	-2.035636000	0.888404000	4.961474000	C	1.926780000	2.989416000	-1.302654000	H	3.436389000	-3.186789000	3.682849000
C	2.897583000	2.133220000	-2.125228000	H	-3.662429000	0.194687000	5.186368000	C	-0.985475000	5.121924000	-0.150225000	H	4.283779000	-2.373107000	2.343568000
C	4.023006000	3.265670000	1.115067000	H	-3.467572000	1.769088000	4.375277000	C	-1.541747000	2.785910000	-2.859516000	C	4.708181000	-0.032383000	4.025910000
C	-3.254153000	-2.275159000	2.777380000	C	-5.311159000	0.876119000	2.337553000	C	1.049890000	-0.645137000	4.799178000	H	5.017433000	0.317017000	3.025798000
C	-1.147027000	5.278000000	1.596155000	H	-4.869157000	1.770310000	1.869409000	C	3.921933000	1.560400000	-1.989116000	H	5.330908000	-0.917666000	4.250382000
H	-1.494809000	4.401489000	2.160782000	H	-5.733493000	1.201360000	3.306491000	H	3.743137000	0.787857000	-1.228952000	H	4.983614000	0.750876000	4.746225000
H	-1.960017000	6.020822000	1.589442000	H	-6.151536000	0.556846000	1.705783000	H	5.005179000	1.592013000	-2.185041000	C	2.547274000	0.974663000	6.190163000
H	-0.301846000	5.725471000	2.141891000	C	-5.660695000	-2.263623000	1.755023000	H	3.430367000	1.253002000	-2.922766000	H	1.850312000	1.828847000	6.139853000
O	1.526590000	-3.896226000	2.900611000	H	-5.391657000	-2.906590000	0.901696000	O	1.025550000	-4.502944000	0.338349000	H	3.568557000	1.379233000	6.217390000
C	1.910341000	1.277966000	-2.950597000	H	-6.438557000	-1.563040000	1.420709000	C	-0.552423000	5.382284000	1.313014000	H	2.358897000	0.475072000	7.156234000
H	1.469284000	0.480066000	-2.338674000	H	-6.112744000	-2.923945000	2.516015000	H	-0.748476000	4.509297000	1.951846000	O	-1.645581000	-2.643780000	-2.948900000
H	2.442252000	0.800254000	-3.785986000	O	-0.417420000	-4.124298000	-1.209836000	H	-1.134033000	6.226617000	1.713144000	C	-0.571330000	-2.492622000	-2.569702000
H	1.095081000	1.870552000	-3.385996000					H	0.507746000	5.653876000	1.412466000				

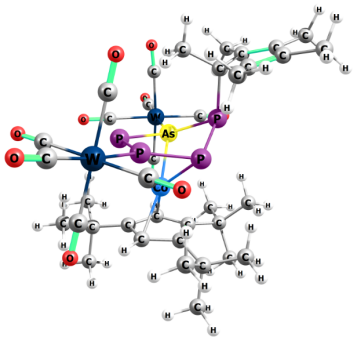
Table S11: Optimized geometries of **I-6** (left), **I-7** (right). XYZ coordinated in angstroms. B3LYP/def2-SVP level of theory.





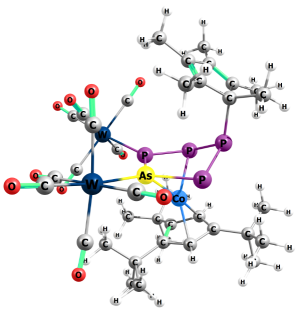
Co	-0.908475000	-1.386459000	0.524822000	H	2.216141000	-2.474070000	-0.252464000	W	-3.878661000	-2.068005000	0.321833000	C	-1.482707000	3.997877000	3.620171000
P	0.645653000	0.296093000	0.163163000	W	4.834883000	0.002381000	-0.753158000	W	4.052994000	0.405008000	0.627614000	H	-0.919899000	4.849349000	3.206614000
P	-1.031276000	0.862825000	1.385188000	W	-4.649457000	1.079163000	-0.767036000	Co	-1.026963000	1.590069000	-0.243724000	H	-1.327604000	3.985228000	4.710972000
P	-2.219355000	0.309808000	-0.353251000	As	2.778439000	0.773267000	0.954890000	P	0.657730000	1.037176000	-1.821598000	H	-2.553535000	4.172550000	3.431201000
P	-0.528333000	-0.289755000	-1.595980000	C	6.406328000	-0.730852000	-1.781460000	P	-0.140388000	-0.302592000	0.949330000	C	-1.272180000	5.963196000	-1.736690000
C	-1.180948000	-2.429441000	2.334411000	O	7.300965000	-1.163666000	-2.370574000	P	-1.355864000	0.350578000	-2.216201000	H	-2.293141000	5.877458000	-2.129030000
C	-2.245382000	-2.681310000	1.416661000	C	3.498391000	-0.839024000	-2.089305000	As	1.728583000	-0.571211000	-0.460093000	H	-0.740171000	6.696834000	-2.362897000
C	-1.755701000	-3.306307000	0.217089000	O	2.742655000	-1.288341000	-2.835888000	P	-1.840801000	-0.605350000	-0.330056000	H	-1.331553000	6.373374000	-0.716003000
C	-0.301669000	-3.410989000	0.375781000	C	4.951507000	1.689559000	-1.954499000	O	-2.740927000	-4.473757000	-1.512682000	C	-4.494269000	4.634514000	-0.621762000
C	0.004841000	-2.848115000	1.664803000	O	5.099029000	2.602895000	-2.639545000	O	-5.113088000	0.244561000	2.198483000	H	-4.634057000	4.538785000	0.466029000
C	-1.309745000	-2.049321000	3.805254000	C	6.117215000	0.933029000	0.590389000	O	-2.142589000	-3.182519000	2.807818000	H	-5.486548000	4.784105000	-1.077246000
C	-1.446714000	-3.391678000	4.572040000	O	6.833392000	1.451013000	1.327217000	O	-5.651186000	-1.085963000	-2.190572000	H	-3.897836000	5.538522000	-0.804951000
C	-0.058335000	-1.310885000	4.314528000	C	4.927463000	-1.696458000	0.429746000	O	-6.255371000	-4.000267000	1.182855000	C	-1.009929000	2.653965000	3.003061000
C	-2.563681000	-1.197724000	4.075021000	O	5.049869000	-2.634340000	1.087461000	O	6.685942000	1.673971000	1.854904000	C	0.446449000	-2.789377000	-2.090859000
C	-2.741028000	-3.855856000	-0.845540000	C	-6.508724000	1.851470000	-1.033607000	O	2.934302000	3.392811000	0.965909000	H	-0.407585000	-2.821144000	-1.402892000
C	-4.198684000	-3.626447000	-0.384719000	O	-7.561973000	2.293504000	-1.178818000	C	-2.753868000	-2.772631000	1.927157000	H	0.555217000	-3.792587000	-2.535953000
C	-2.598836000	-3.191846000	-2.231365000	C	-4.283386000	2.597089000	0.600290000	C	-5.394650000	-3.302038000	0.868131000	H	0.207390000	-2.083689000	-2.898651000
C	-2.573198000	-5.389732000	-0.973727000	O	-4.096792000	3.443594000	1.354737000	C	-3.129358000	-3.605140000	-0.869662000	C	-1.831221000	1.511046000	3.628968000
C	0.808262000	-4.154970000	-0.396902000	C	-3.914789000	2.280690000	-2.311735000	C	-4.669664000	-0.577517000	1.525522000	H	-2.911787000	1.635602000	3.461939000
C	0.815592000	-5.620946000	0.114975000	O	-3.510837000	2.945414000	-3.153839000	C	3.266619000	2.297116000	0.814493000	H	-1.669493000	1.493276000	4.718119000
C	0.687801000	-4.138978000	-1.931031000	C	-5.119732000	-0.394177000	-2.162016000	C	-5.006586000	-1.415018000	-1.298513000	H	-1.530816000	0.530148000	3.232637000
C	2.186369000	-3.553013000	-0.053529000	O	-5.432433000	-1.181396000	-2.937505000	C	5.730236000	1.205507000	1.408788000	C	2.988482000	-1.623510000	-3.571547000
H	-3.287304000	-2.450812000	1.610719000	C	-5.327891000	-0.118304000	0.782016000	O	2.991388000	-0.399441000	3.568793000	H	2.266107000	-2.006188000	-4.315547000
H	1.004133000	-2.773349000	2.081524000	O	-5.685977000	-0.784397000	1.649569000	C	1.749406000	-2.434960000	-1.374640000	H	3.984058000	-1.656114000	-4.035390000
H	-2.337605000	-3.950830000	4.245545000	C	2.419495000	2.862357000	1.004466000	C	-2.483835000	3.185265000	-0.474805000	H	2.739042000	-0.560859000	-3.414693000
H	-1.541871000	-3.200561000	5.652886000	C	1.574050000	3.385292000	-0.139646000	C	3.362101000	-0.109967000	2.520221000	C	5.150696000	-1.364509000	0.584549000
H	-0.566078000	-4.034188000	4.416375000	C	0.438708000	3.936620000	0.377823000	C	-1.131789000	3.697652000	-0.672168000	C	0.962619000	4.942770000	-1.404029000
H	0.850752000	-1.924068000	4.217320000	C	0.449839000	3.798832000	1.849408000	C	-0.405164000	3.401300000	0.538894000	H	1.055845000	5.499998000	-0.460089000
H	-0.175070000	-1.068543000	5.382299000	C	1.594945000	3.161580000	2.232997000	H	0.630387000	3.666636000	0.716201000	H	1.388329000	5.572877000	-2.199755000
H	0.107500000	-0.370223000	3.769028000	C	3.814496000	3.507446000	1.074981000	C	-0.487203000	4.038376000	-3.188996000	H	1.580922000	4.037588000	-1.334278000
H	-2.515249000	-0.232431000	3.550228000	H	4.417475000	3.110619000	1.906593000	H	0.268755000	3.246755000	-3.282679000	C	3.349306000	-0.943943000	-0.594934000
H	-2.648344000	-0.990591000	5.153180000	H	3.699782000	4.593219000	1.233918000	H	-0.213594000	4.837234000	-3.896969000	C	-3.766541000	3.498194000	-2.747191000
H	-3.488561000	-1.709579000	3.767844000	H	4.382340000	3.358378000	0.147437000	H	-1.445867000	3.623628000	-3.508528000	H	-3.235927000	4.397374000	-3.079110000
H	-4.421816000	-4.148896000	0.558136000	C	2.003031000	3.365877000	-1.572461000	C	-2.506682000	2.606986000	0.842716000	H	-4.792866000	3.569864000	-3.139093000
H	-4.885180000	-4.017053000	-1.150420000	H	2.934189000	3.935370000	-1.731788000	H	-3.380301000	2.150465000	1.295643000	H	-3.296811000	2.618233000	-3.210038000
H	-4.431337000	-2.562138000	-0.253627000	H	1.236835000	3.802154000	-2.228222000	C	2.122169000	-3.431467000	-0.296943000	C	1.195107000	-3.833095000	0.810583000
H	-2.855080000	-2.125171000	-2.179122000	H	2.204748000	2.342213000	-1.928580000	C	3.861028000	-3.314537000	-1.833303000	H	0.875611000	-2.978782000	1.431527000
H	-3.296953000	-3.662951000	-2.941097000	C	-0.679772000	4.614019000	-0.357267000	C	-1.261515000	2.791532000	1.504171000	H	1.664533000	-4.564061000	1.483279000
H	-1.589325000	-3.270019000	-2.644803000	H	-1.649382000	4.127158000	-0.157892000	C	-3.830640000	3.362574000	-1.216227000	H	0.270453000	-4.295199000	0.420614000
H	-1.627681000	-5.678910000	-1.446625000	H	-0.526166000	4.615576000	-1.445043000	C	-0.506788000	4.615960000	-1.755772000	C	4.104599000	-5.011204000	0.137625000
H	-3.386426000	-5.793416000	-1.596853000	H	-0.791268000	5.664027000	-0.035241000	C	2.945424000	-2.420381000	-2.301733000	H	3.559926000	-5.374496000	1.019811000
H	-2.630463000	-5.881763000	0.010078000	C	-0.630773000	4.361725000	2.724527000	C	0.481493000	2.465354000	3.327464000	H	5.086210000	-4.641102000	0.475814000
H	-0.116510000	-6.153966000	-0.111367000	H	-1.629503000	4.000301000	2.428831000	H	0.880336000	1.547403000	2.874258000	H	4.300096000	-5.879021000	-0.515715000
H	0.967949000	-5.656360000	1.204949000	H	-0.664976000	5.463037000	2.649468000	H	0.619896000	2.388156000	4.416947000	C	5.179646000	-3.688968000	-2.438809000
H	1.644529000	-6.172118000	-0.357215000	H	-0.481214000	4.108466000	3.783405000	H	1.088869000	3.312477000	2.976473000	H	5.394922000	-3.121182000	-3.354500000
H	1.559822000	-4.653273000	-2.362809000	C	2.071539000	2.873131000	3.622558000	O	5.885266000	-2.248328000	0.632411000	H	5.208493000	-4.761893000	-2.696119000
H	0.685261000	-3.112414000	-2.324521000	H	2.394385000	1.822332000	3.726825000	C	-4.768897000	2.170313000	-0.925807000	H	6.005196000	-3.513646000	-1.728974000
H	-0.203308000	-4.659264000	-2.298047000	H	1.289407000	3.061601000	4.371914000	H	-4.307626000	1.221529000	-1.227544000	O	5.047766000	1.063084000	-2.372768000
H	2.960957000	-4.028262000	-0.672347000	H	2.942088000	3.497435000	3.894806000	H	-5.700898000	2.288362000	-1.498396000	C	4.688458000	0.833773000	-1.305484000
H	2.478378000	-3.717204000	0.992525000					H	-5.052793000	2.095530000	0.132316000				

Table S12: Optimized geometries of **I-8** (left), **I-9** (right). XYZ coordinated in angstroms. B3LYP/def2-SVP level of theory.



W	-4.246939000	0.317431000	-1.257064000	C	-0.604657000	-5.625105000	0.229415000	W	-3.295384000	-1.392738000	0.267826000	C	3.444870000	4.271922000	-2.541224000
W	4.015063000	-0.529987000	-1.201982000	H	0.273366000	-5.823777000	0.863887000	W	2.163020000	-2.276230000	-1.456366000	H	3.146107000	3.797321000	-3.488866000
Co	-0.329802000	-1.086136000	0.873596000	H	-0.656723000	-6.415232000	-0.536825000	Co	0.187152000	2.045769000	-0.290197000	H	4.526000000	4.478615000	-2.591387000
P	0.939250000	2.039727000	1.123040000	H	-1.504507000	-5.702348000	0.859726000	As	1.085965000	-0.247998000	0.021946000	H	2.917234000	5.235697000	-2.462576000
P	-0.176265000	-0.502389000	-1.472750000	C	1.198225000	-2.671350000	4.901041000	P	0.918953000	2.345498000	1.970620000	C	-1.802625000	3.331987000	-4.314709000
P	-1.032625000	1.086830000	1.479122000	H	0.270077000	-2.445245000	5.440181000	P	-1.133824000	0.086003000	0.439645000	H	-2.382686000	4.151771000	-3.870353000
As	1.554088000	0.149239000	-0.145831000	H	2.030441000	-2.549540000	5.612361000	P	2.251980000	0.596555000	1.840517000	H	-2.393014000	2.925184000	-5.151093000
P	-1.822784000	0.270245000	-0.366538000	H	1.166993000	-3.730763000	4.600309000	P	-1.161514000	1.819125000	1.673777000	H	-0.875313000	3.756361000	-4.731337000
O	-3.518519000	3.237217000	-2.440284000	C	-2.454036000	-3.055058000	4.440695000	O	-5.131905000	1.247158000	0.003782000	C	-1.462068000	6.103124000	-1.785385000
O	-5.005631000	-2.591748000	-0.093538000	H	-2.804234000	-3.832989000	3.744888000	O	-1.473815000	-4.040904000	0.572501000	H	-0.447934000	6.504879000	-1.634893000
O	-3.277685000	-1.084118000	-4.001582000	H	-3.237545000	-2.904800000	5.200821000	O	-3.440520000	-1.815412000	-2.935249000	H	-2.181027000	6.907316000	-1.560042000
O	-5.274541000	1.704982000	1.470244000	H	-1.558074000	-3.437257000	4.949657000	O	-3.465230000	-1.131846000	3.475224000	H	-1.565442000	5.845689000	-2.849013000
O	-7.170344000	0.614376000	-2.480249000	C	-0.507501000	-4.232855000	-0.448748000	O	-5.889998000	-3.209041000	0.474713000	C	3.135512000	3.355370000	-1.326977000
O	6.856330000	-1.102007000	-2.477307000	C	2.997738000	6.178930000	2.035680000	O	3.551023000	-4.660297000	-3.016566000	C	0.179662000	-1.983809000	3.456827000
O	4.257389000	-3.389563000	0.258350000	H	2.799345000	7.250591000	1.861386000	O	2.559236000	-0.418339000	-4.054861000	H	0.734554000	-2.906186000	3.704023000
C	-3.609161000	-0.582671000	-3.023807000	H	4.010061000	5.963645000	1.667436000	C	-3.342969000	-1.651949000	-1.804058000	H	0.086604000	-1.967945000	2.359694000
C	-6.112637000	0.505428000	-2.036864000	H	3.004450000	6.036097000	3.130305000	C	-4.946734000	-2.551224000	0.393279000	H	-0.830541000	-2.087262000	3.874429000
C	-3.771476000	2.198017000	-2.021682000	C	-1.749613000	-4.023280000	-1.334321000	C	-4.473247000	0.309366000	0.094478000	C	3.625561000	4.054617000	-0.046060000
C	-4.735002000	-1.551563000	-0.506917000	H	-2.686768000	-4.104942000	-0.763337000	C	-2.111378000	-3.093391000	0.454057000	H	3.180115000	5.054127000	0.076952000
C	4.154458000	-2.349956000	-0.228710000	H	-1.779375000	-4.792456000	-2.121654000	C	2.414100000	-1.072608000	-3.116811000	H	4.717577000	4.188936000	-0.091853000
C	-4.897522000	1.209720000	0.504829000	H	-1.730331000	-3.040147000	-1.827023000	C	-3.381545000	-1.210203000	2.331149000	H	3.395124000	3.462628000	0.851121000
C	5.819023000	-0.899108000	-2.014181000	C	3.416872000	3.949406000	-0.228322000	C	3.043742000	-3.793016000	-2.450046000	C	-0.828881000	0.044631000	5.741154000
O	2.653187000	-2.085612000	-3.677986000	H	4.272144000	4.516886000	0.163623000	O	5.067114000	-1.398008000	-0.353120000	H	-1.311643000	1.036467000	5.730186000
C	1.958995000	5.316393000	1.383548000	H	3.380648000	4.113372000	-1.318487000	C	0.874519000	-0.770540000	3.987719000	H	-0.672375000	-0.214394000	6.803278000
C	-1.114918000	-2.042050000	2.623573000	H	3.643956000	2.881581000	-0.079589000	C	-0.654583000	3.826651000	-1.225447000	H	-1.546639000	-0.672301000	5.321786000
C	3.114947000	-1.523309000	-2.788614000	C	3.929101000	1.202370000	-2.351127000	C	4.026108000	-1.697829000	-0.736610000	C	1.925838000	-3.540792000	0.184649000
C	0.350094000	-2.085865000	2.610018000	C	2.834488000	-2.071072000	3.139558000	C	-0.535968000	2.765711000	-2.223681000	C	-0.824318000	1.054010000	-4.075022000
C	0.709316000	-2.796153000	1.405323000	H	2.969112000	-3.136517000	2.902784000	C	0.847684000	2.370649000	-2.228665000	H	0.068273000	1.379351000	-4.628906000
H	1.727414000	-3.006836000	1.100269000	H	3.577601000	-1.810719000	3.908209000	H	1.263526000	1.605274000	-2.873837000	H	-1.535523000	0.649671000	-4.810222000
C	1.459403000	-0.270698000	4.110666000	H	3.072868000	-1.481669000	2.242938000	C	-2.811020000	1.634258000	-2.733239000	H	-0.537190000	0.225593000	-3.409974000
H	1.776722000	0.374577000	3.279948000	C	-0.183715000	4.526504000	0.960224000	H	-2.594143000	0.846040000	-2.003673000	C	2.617604000	0.785187000	4.480809000
H	2.191615000	-0.149153000	4.924954000	C	-1.824461000	-0.638076000	4.735131000	H	-3.400258000	1.187790000	-3.548939000	C	-3.198265000	4.457938000	-1.020452000
H	0.498282000	0.104660000	4.469687000	H	-0.977528000	-0.916428000	5.372147000	H	-3.438221000	2.379665000	-2.241528000	H	-3.476883000	4.285777000	-2.066849000
C	-1.550064000	-2.702346000	1.422129000	H	-2.689053000	-0.489312000	5.400212000	C	0.666881000	4.017920000	-0.694779000	H	-3.843968000	5.269470000	-0.651000000
H	-2.589201000	-2.831927000	1.139577000	H	-1.607469000	0.326423000	4.255162000	H	0.917104000	4.746702000	0.068620000	H	-3.434434000	3.557197000	-0.436953000
C	0.525017000	5.425598000	1.703916000	C	-0.003375000	6.430920000	2.682434000	C	2.252487000	-0.349599000	3.536397000	C	3.284646000	-1.483107000	3.446927000
C	0.795162000	3.709523000	0.129890000	H	0.438499000	6.279902000	3.682565000	C	1.543551000	1.029984000	5.286314000	H	2.963758000	-2.272619000	2.751382000
C	-0.445768000	-3.223016000	0.692377000	H	-1.095019000	6.376234000	2.791169000	C	1.619228000	3.173851000	-1.334493000	H	3.412517000	-1.943609000	4.440464000
C	-2.181808000	-1.717530000	3.698743000	H	0.254616000	7.460685000	2.380231000	C	-1.728891000	4.882654000	-0.862784000	H	4.265732000	-1.116298000	3.108817000
C	1.422033000	-1.749946000	3.675915000	C	-1.674451000	4.423863000	0.838879000	C	-1.499652000	2.206548000	-3.295836000	C	3.965665000	1.441486000	4.497021000
C	2.139722000	4.353664000	0.436925000	H	-2.175017000	5.202233000	1.431630000	C	0.467606000	0.063659000	4.986849000	H	4.261838000	1.819611000	3.503564000
C	0.756761000	-4.194311000	-1.324076000	H	-2.072255000	3.452641000	1.178266000	C	3.892897000	2.029591000	-1.503772000	H	4.754648000	0.732315000	4.806618000
H	0.861053000	-3.227817000	-1.836274000	H	-2.000953000	4.547497000	-0.208216000	H	3.737901000	1.364020000	-0.643872000	H	3.994233000	2.289036000	5.196153000
H	0.697556000	-4.975007000	-2.098200000	C	0.447397000	3.571516000	-1.351539000	H	4.973643000	2.226426000	-1.582569000	C	1.413235000	2.073548000	6.354479000
H	1.671739000	-4.382053000	-0.742114000	H	1.210068000	2.998932000	-1.899256000	H	3.590684000	1.500929000	-2.418912000	H	0.571367000	2.754571000	6.141467000
O	3.902185000	2.118387000	-3.044895000	H	0.382849000	4.572681000	-1.809951000	O	1.827201000	-4.257828000	1.076115000	H	2.320108000	2.685742000	6.454281000
C	-3.508480000	-1.270657000	3.042726000	H	-0.519816000	3.069965000	-1.499732000	C	-1.567064000	5.360215000	0.601030000	H	1.205155000	1.617306000	7.337569000
H	-3.373445000	-0.362105000	2.440703000	O	5.458055000	0.939861000	1.285371000	H	-1.707723000	4.533199000	1.311708000	O	-0.667998000	-3.242855000	-2.659653000
H	-3.958755000	-2.046931000	2.410252000	C	4.932806000	0.428334000	0.400614000	H	-2.331797000	6.121734000	0.816733000	C	0.325368000	-2.881007000	-2.209666000
H	-4.241346000	-1.038305000	3.829989000					H	-0.592131000	5.826463000	0.800875000				

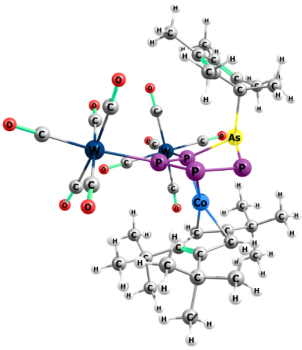
Table S13: Optimized geometries of **I-10** (left), **I-11** (right). XYZ coordinated in angstroms. B3LYP/def2-SVP level of theory.

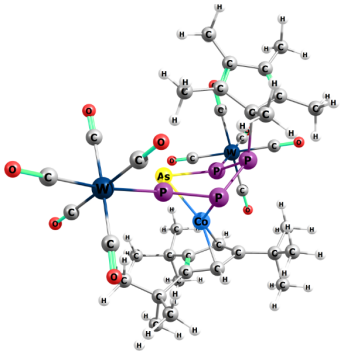


W	0.280966000	2.787745000	-1.857628000	C	3.941099000	-5.429001000	0.229548000	W	-2.398181000	-0.132636000	-2.021298000	C	-0.309356000	6.195712000	-0.585434000

W	-3.526556000	-0.758690000	0.664314000	H	3.168057000	-6.038896000	-0.263873000	W	2.284276000	-2.798431000	-0.038178000	H	0.572475000	6.641421000	-0.098269000
Co	1.406114000	-1.648662000	-0.132360000	H	4.511651000	-6.085236000	0.906485000	Co	0.843920000	1.984631000	0.667650000	H	-1.116584000	6.945668000	-0.579219000
P	0.549041000	-1.783203000	2.097360000	H	4.629605000	-5.060815000	-0.547056000	P	-0.116413000	1.958830000	2.840600000	H	-0.048696000	5.986550000	-1.634655000
P	2.586248000	0.281595000	0.676803000	C	0.307293000	-4.079246000	-3.962812000	P	-1.004698000	0.523957000	0.140821000	C	4.949371000	4.159822000	0.252946000
As	-0.793250000	-0.671295000	0.640783000	H	0.854127000	-3.413769000	-4.641386000	P	1.536607000	0.610457000	2.507362000	H	5.208567000	3.695056000	-0.706913000
P	2.247839000	-0.520773000	2.690452000	H	-0.570072000	-4.457332000	-4.510947000	P	-2.010986000	1.235501000	1.961922000	H	5.890976000	4.346890000	0.793246000
P	0.714360000	0.713173000	-0.305943000	H	0.954930000	-4.939982000	-3.732184000	As	0.947416000	-0.546386000	0.677390000	H	4.481289000	5.134860000	0.043404000
O	-1.436359000	1.175155000	-4.068028000	C	3.635282000	-2.600234000	-4.092528000	O	-0.004505000	-1.691956000	-3.511032000	C	3.329435000	3.337331000	-3.005190000
O	2.094777000	4.531487000	0.156780000	H	4.408166000	-3.100741000	-3.488419000	O	-4.948466000	1.478075000	-0.873819000	H	2.463813000	3.954416000	-3.291454000
O	-2.339764000	3.421910000	-0.082748000	H	4.135912000	-2.121471000	-4.949740000	O	-3.304974000	-2.913741000	-0.642994000	H	3.802341000	2.970312000	-3.930256000
O	2.890095000	2.571113000	-3.741177000	H	2.961396000	-3.373994000	-4.484152000	O	-1.576842000	2.484797000	-3.695838000	H	4.051660000	3.986734000	-2.490586000
O	-0.365303000	5.482527000	-3.405073000	C	3.314270000	-4.257114000	1.033875000	O	-4.243552000	-0.967416000	-4.463996000	C	-0.774285000	4.909322000	0.148897000
O	-6.664991000	-0.663883000	1.061465000	C	-0.625188000	1.215998000	4.167800000	O	3.754504000	-5.565274000	-0.504519000	C	-1.107898000	-1.681958000	4.052111000
O	-4.122286000	-3.368035000	-1.132100000	H	-0.778732000	1.009077000	5.243093000	O	3.191980000	-1.975691000	-3.028227000	H	-1.241578000	-1.490237000	5.133025000
C	-1.411570000	3.161327000	-0.705993000	H	-0.861467000	0.279854000	3.637285000	C	-2.966697000	-1.909894000	-1.084334000	H	-0.261860000	-1.056769000	3.732240000
C	-0.127145000	4.501969000	-2.847717000	H	-1.371366000	1.964777000	3.872617000	C	-3.568207000	-0.663920000	-3.579373000	H	-0.802430000	-2.731716000	3.945530000
C	-0.841481000	1.728422000	-3.256827000	C	4.446270000	-3.457154000	1.702574000	C	-0.832459000	-1.136184000	-2.937894000	C	-2.013487000	4.350013000	-0.570354000
C	1.445036000	3.886470000	-0.537831000	H	5.180980000	-3.092951000	0.967303000	C	-4.026844000	0.896613000	-1.238035000	H	-1.813433000	4.136127000	-1.629913000
C	-3.842648000	-2.451670000	-0.497087000	H	4.989362000	-4.102146000	2.411224000	C	2.840981000	-2.231472000	-1.966041000	H	-2.827631000	5.090945000	-0.535946000
C	1.969005000	2.593044000	-3.053967000	H	4.052661000	-2.592000000	2.254955000	C	-1.863670000	1.559241000	-3.068953000	H	-2.375662000	3.430936000	-0.088655000
C	-5.522024000	-0.701315000	0.912855000	C	0.352036000	4.175306000	3.412582000	C	3.218813000	-4.557717000	-0.339980000	C	-3.135925000	-3.768906000	2.718434000
O	-3.295045000	-2.604394000	3.305303000	H	0.625370000	4.688947000	2.476434000	O	5.037589000	-1.573112000	1.114252000	H	-3.185128000	-4.127607000	1.677058000
C	0.770204000	1.684994000	3.902041000	H	0.496333000	4.910194000	4.224390000	C	-2.362606000	-1.383881000	3.291945000	H	-3.962864000	-4.258461000	3.261507000
C	2.280057000	-2.249876000	-2.034865000	H	-0.720397000	3.940064000	3.365267000	C	2.188797000	2.723715000	-0.886284000	H	-2.193418000	-4.128710000	3.153689000
C	-3.359207000	-1.947451000	2.366332000	C	-3.471392000	0.967139000	1.829080000	C	4.048431000	-1.995652000	0.709341000	C	1.785831000	-3.481465000	1.861090000
C	1.069773000	-3.027231000	-1.797672000	C	-1.068100000	-4.378564000	-1.930153000	C	2.639054000	3.203500000	0.417646000	C	3.896994000	3.954341000	2.495205000
C	1.257158000	-3.680686000	-0.531883000	H	-0.557168000	-5.337043000	-1.751038000	C	1.525018000	3.915264000	0.980786000	H	3.569120000	5.002121000	2.417836000
H	0.528825000	-4.330576000	-0.059681000	H	-1.958014000	-4.586345000	-2.541186000	H	1.533037000	4.393389000	1.953644000	H	4.882579000	3.957843000	2.984332000
C	-1.038980000	-2.150589000	-3.024652000	H	-1.423942000	-3.988963000	-0.966617000	C	4.701392000	1.906274000	1.383999000	H	3.203583000	3.416753000	3.159736000
H	-1.470173000	-1.703134000	-2.118842000	C	3.157380000	1.746316000	3.912425000	H	4.139483000	1.331171000	2.131880000	C	-4.306457000	-0.220178000	2.523188000
H	-1.873706000	-2.470332000	-3.668149000	C	1.873758000	-0.803805000	-4.168711000	H	5.711903000	2.080054000	1.786835000	C	4.128643000	1.254831000	-1.851600000
H	-0.492677000	-1.368671000	-3.557169000	H	1.184340000	-1.489082000	-4.674304000	H	4.806241000	1.282381000	0.494795000	H	4.960948000	1.814204000	-1.409619000
C	3.141371000	-2.492535000	-0.904850000	H	2.418345000	-0.257084000	-4.953204000	C	0.826672000	3.166696000	-1.031698000	H	4.489618000	0.837481000	-2.803527000
H	4.135399000	-2.072885000	-0.793537000	H	1.282616000	-0.071436000	-3.604103000	H	0.217127000	2.982459000	-1.909174000	H	3.885121000	0.408456000	-1.195041000
C	1.978977000	0.798182000	4.078657000	C	1.978027000	0.017836000	5.406498000	C	-2.939051000	0.010456000	3.151561000	C	-3.024657000	0.767652000	4.493572000
C	2.670944000	2.988278000	3.633476000	H	1.120972000	-0.670987000	5.472063000	C	-4.458600000	-1.554558000	2.303459000	H	-2.035636000	0.888404000	4.961474000
C	2.561370000	-3.427927000	-0.005167000	H	1.909339000	0.726049000	6.248569000	C	0.415643000	3.954700000	0.082806000	H	-3.662429000	0.194687000	5.186368000
C	2.881341000	-1.527763000	-3.261456000	H	2.895939000	-0.576865000	5.529432000	C	2.897583000	2.133220000	-2.125228000	H	-3.467572000	1.769088000	4.375277000
C	-0.161948000	-3.367881000	-2.669783000	C	4.584900000	1.321719000	4.083091000	C	4.023006000	3.265670000	1.115067000	C	-5.311159000	0.876119000	2.337553000
C	1.192305000	2.951551000	3.629862000	H	4.871453000	0.518564000	3.381475000	C	-3.254153000	-2.275159000	2.777380000	H	-4.869157000	1.770310000	1.869409000
C	2.390570000	-4.851692000	2.111135000	H	4.774516000	0.927799000	5.097911000	C	-1.147027000	5.278000000	1.596155000	H	-5.733493000	1.201360000	3.306491000
H	1.927647000	-4.071913000	2.731408000	H	5.276002000	2.161063000	3.922841000	H	-1.494809000	4.401489000	2.160782000	H	-6.151536000	0.556846000	1.705783000
H	2.971787000	-5.512766000	2.773092000	C	3.446096000	4.250582000	3.400865000	H	-1.960017000	6.020822000	1.589442000	C	-5.660695000	-2.263623000	1.755023000
H	1.582594000	-5.458581000	1.673226000	H	3.245721000	4.659708000	2.397579000	H	-0.301846000	5.725471000	2.141891000	H	-5.391657000	-2.906590000	0.901696000
O	-3.529886000	1.913315000	2.476036000	H	4.530406000	4.096486000	3.490706000	O	1.526590000	-3.896226000	2.900611000	H	-6.438557000	-1.563040000	1.420709000
C	3.927664000	-0.478847000	-2.813744000	H	3.158089000	5.032493000	4.124674000	C	1.910341000	1.277966000	-2.950597000	H	-6.112744000	-2.923945000	2.516015000
H	3.507724000	0.245734000	-2.102942000	O	-3.832132000	1.040270000	-1.995639000	H	1.469284000	0.480066000	-2.338674000	O	-0.417420000	-4.124298000	-1.209836000
H	4.283366000	0.081304000	-3.690399000	C	-3.698588000	0.404746000	-1.048645000	H	2.442252000	0.800254000	-3.785986000	C	0.531190000	-3.629610000	-0.794963000
H	4.811247000	-0.936983000	-2.346769000					H	1.095081000	1.870552000	-3.385996000				

Table S14: Optimized geometries of **I-12** (left), **I-13** (right). XYZ coordinated in angstroms. B3LYP/def2-SVP level of theory.

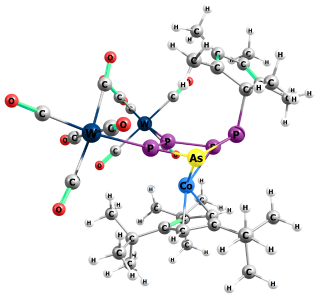


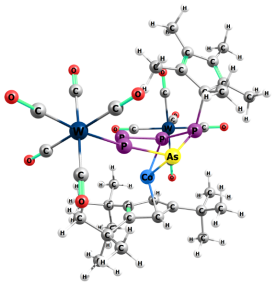


W	2.177170000	0.085202000	2.212866000	C	-0.632035000	6.081309000	0.688520000	W	-3.907898000	0.152413000	-0.997367000	C	-1.417515000	4.240223000	3.759677000
W	-1.920375000	-2.992564000	-0.061166000	H	-1.544454000	6.412881000	0.168116000	W	4.295706000	-1.224053000	-0.476909000	H	-0.420352000	4.630345000	4.018174000
Co	-1.166825000	1.768150000	-0.649364000	H	0.067740000	6.931631000	0.724595000	Co	0.333819000	1.440217000	0.642502000	H	-2.051680000	4.305370000	4.658424000
P	-0.145053000	1.881953000	-2.808665000	H	-0.905216000	5.822659000	1.723350000	P	0.977864000	-0.387494000	2.019397000	H	-1.851211000	4.897796000	2.990021000
P	0.799352000	0.537815000	-0.010332000	C	-5.539643000	3.397333000	-0.452283000	P	-1.457462000	-0.033539000	0.008887000	C	3.042491000	5.280576000	0.456589000
P	-1.540417000	0.281455000	-2.468889000	H	-5.787876000	2.882990000	0.484848000	P	1.902508000	-0.329532000	0.064787000	H	2.665283000	5.602756000	-0.521541000
As	1.935365000	1.453078000	-1.835942000	H	-6.466334000	3.469519000	-1.043551000	P	-1.071417000	-1.171815000	1.854891000	H	4.092024000	5.607219000	0.527732000
P	-0.888716000	-0.655359000	-0.660058000	H	-5.217483000	4.421248000	-0.204067000	As	0.293529000	0.037300000	-1.459667000	H	2.471779000	5.810825000	1.235401000
O	-0.021759000	-1.806481000	3.617366000	C	-4.017845000	2.763679000	2.877648000	O	-2.825456000	1.041100000	-3.902826000	C	-0.185570000	5.680677000	-1.188686000
O	4.499565000	2.028779000	1.096762000	H	-3.262874000	3.490617000	3.214714000	O	-5.140792000	-0.728500000	1.853266000	H	-1.060480000	5.807023000	-0.532267000
O	3.536643000	-2.522082000	0.868109000	H	-4.488296000	2.326451000	3.773173000	O	-3.804431000	-2.896673000	-2.053335000	H	-0.397833000	6.203540000	-2.135156000
O	0.939731000	2.554271000	3.857737000	H	-4.791423000	3.314003000	2.323849000	O	-4.416652000	3.235822000	-0.235552000	H	0.667857000	6.180129000	-0.710777000
O	4.042921000	-0.476224000	4.717623000	C	0.029246000	4.880041000	-0.039545000	O	-6.856964000	0.157218000	-2.170529000	C	-1.342712000	2.768822000	3.269439000
O	-3.043014000	-5.941323000	0.282604000	C	1.385723000	-1.585931000	-4.052370000	O	7.035672000	-2.696349000	-1.123179000	C	0.570787000	-3.923418000	0.035192000
O	-3.105207000	-2.412669000	2.887527000	H	1.525587000	-1.326162000	-5.117761000	O	4.833538000	0.857797000	-2.887422000	H	1.253619000	-4.503688000	0.682090000
C	3.034705000	-1.584810000	1.299575000	H	0.466952000	-1.072070000	-3.730401000	C	-3.783230000	-1.827738000	-1.634109000	H	1.020221000	-2.926252000	-0.072020000
C	3.361351000	-0.271740000	3.809758000	H	1.192007000	-2.665442000	-4.004364000	C	-5.783841000	0.158106000	-1.746650000	H	0.578302000	-4.396503000	-0.956526000
C	0.739370000	-1.136409000	3.075886000	C	1.296355000	4.474144000	0.731778000	C	-3.186137000	0.729020000	-2.856591000	C	-2.767084000	2.283721000	2.953526000
C	3.661726000	1.331321000	1.461474000	H	1.075430000	4.213937000	1.776684000	C	-4.675138000	-0.427404000	0.847007000	H	-3.264557000	2.924634000	2.211223000
C	-2.657350000	-2.566558000	1.842085000	H	2.006986000	5.315347000	0.748254000	C	4.634364000	0.129738000	-2.021640000	H	-3.379676000	2.309186000	3.868343000
C	1.373619000	1.680141000	3.241898000	H	1.800452000	3.619922000	0.258279000	C	-4.202856000	2.130596000	-0.488693000	H	-2.765074000	1.250814000	2.580006000
C	-2.635561000	-4.869704000	0.163584000	C	3.451120000	-3.514763000	-2.535158000	C	6.042960000	-2.159225000	-0.889601000	C	-2.034942000	-5.472644000	-0.967210000
O	-4.758914000	-2.172766000	-1.355569000	H	3.470149000	-3.829816000	-1.478354000	O	5.868169000	0.639617000	1.639526000	H	-2.849228000	-5.168264000	-1.643005000
C	2.580541000	-1.196442000	-3.239675000	H	4.326307000	-3.981687000	-3.019488000	C	-0.808224000	-3.855415000	0.608926000	H	-2.267276000	-6.497194000	-0.627254000
C	-2.680061000	2.327231000	0.829001000	H	2.548519000	-3.941103000	-2.994379000	C	0.318451000	3.502038000	-0.097209000	H	-1.110005000	-5.523154000	-1.558282000

C	-3.737685000	-2.436062000	-0.898616000	C	-1.250645000	-3.588649000	-1.935835000	C	5.288580000	-0.008345000	0.888165000	C	3.948131000	-2.596835000	1.044384000
C	-3.115699000	2.753157000	-0.497578000	C	-4.346460000	3.377055000	-2.631889000	C	1.480657000	3.329103000	0.768104000	C	3.714974000	3.434723000	1.967777000
C	-2.070289000	3.601555000	-1.000000000	H	-4.160334000	4.456022000	-2.520137000	C	0.974259000	2.852604000	2.023536000	H	3.314725000	4.008038000	2.817807000
H	-2.086077000	4.081468000	-1.971612000	H	-5.296154000	3.265488000	-3.176182000	H	1.591727000	2.615445000	2.882464000	H	4.774146000	3.709376000	1.855974000
C	-4.934731000	1.219143000	-1.592641000	H	-3.554042000	2.948271000	-3.263975000	C	3.743054000	3.031872000	-0.471104000	H	3.685005000	2.365670000	2.222286000
H	-4.251203000	0.727711000	-2.297625000	C	4.399696000	0.103328000	-2.402638000	H	3.778738000	1.954060000	-0.277975000	C	-2.604001000	-3.470419000	2.141724000
H	-5.927358000	1.267472000	-2.067964000	C	-4.447780000	0.601353000	1.669159000	H	4.779494000	3.403796000	-0.500781000	C	1.239495000	4.051288000	-2.483926000
H	-5.023977000	0.577295000	-0.714449000	H	-5.324643000	1.048231000	1.186988000	H	3.310641000	3.175408000	-1.463817000	H	2.146946000	4.581641000	-2.174418000
C	-1.394383000	2.936378000	1.048435000	H	-4.799190000	0.114455000	2.591025000	C	-0.829553000	3.152358000	0.698870000	H	0.922732000	4.494061000	-3.440614000
H	-0.812831000	2.822409000	1.956527000	H	-4.048546000	-0.183122000	1.012458000	H	-1.852824000	3.203407000	0.346031000	H	1.494178000	2.998326000	-2.675276000
C	3.061700000	0.224846000	-3.101760000	C	3.103718000	1.020883000	-4.414981000	C	-1.143142000	-3.112914000	1.886673000	C	-0.228234000	-3.520625000	3.062946000
C	4.624432000	-1.215143000	-2.137259000	H	2.115059000	1.076170000	-4.896001000	C	-3.028395000	-4.284761000	1.137965000	H	0.833935000	-3.333684000	2.844407000
C	-1.026762000	3.777143000	-0.042071000	H	3.795185000	0.524345000	-5.116910000	C	-0.451973000	2.805219000	2.029840000	H	-0.353000000	-4.599416000	3.251158000
C	-3.371851000	1.639167000	2.024657000	H	3.464823000	2.051191000	-4.266334000	C	0.090219000	4.178536000	-1.469261000	H	-0.483747000	-2.984172000	3.990611000
C	-4.457162000	2.649506000	-1.270564000	C	5.319959000	1.266546000	-2.181477000	C	2.967539000	3.745815000	0.649242000	C	-3.340831000	-3.054409000	3.378311000
C	3.493261000	-2.020178000	-2.649085000	H	4.826372000	2.102911000	-1.658622000	C	-1.911986000	-4.535379000	0.196796000	H	-3.262341000	-1.970900000	3.565089000
C	0.411681000	5.323298000	-1.462859000	H	5.697336000	1.671064000	-3.138737000	C	-0.744273000	1.905942000	4.395347000	H	-2.937670000	-3.560034000	4.275233000
H	0.877816000	4.506855000	-2.031849000	H	6.195231000	0.981582000	-1.581155000	H	-0.694861000	0.846301000	4.109115000	H	-4.409923000	-3.300118000	3.316578000
H	1.133651000	6.153164000	-1.410683000	C	5.836774000	-1.833843000	-1.507759000	H	-1.376479000	1.982403000	5.293871000	C	-4.377940000	-4.916171000	0.969978000
H	-0.459130000	5.683846000	-2.032043000	H	5.565864000	-2.456952000	-0.640671000	H	0.266854000	2.235326000	4.680215000	H	-4.818302000	-4.655716000	-0.007172000
O	-0.903527000	-3.973246000	-2.961229000	H	6.560354000	-1.079154000	-1.169241000	O	3.753203000	-3.363336000	1.877655000	H	-5.084159000	-4.604902000	1.752014000
C	-2.323768000	0.927913000	2.910783000	H	6.357306000	-2.496640000	-2.221329000	C	-1.165094000	3.604117000	-2.161388000	H	-4.310602000	-6.017703000	0.998450000
H	-1.714304000	0.226423000	2.326234000	O	0.839401000	-4.042615000	1.243631000	H	-1.066677000	2.524854000	-2.336521000	O	2.883118000	-3.186350000	-2.616481000
H	-2.832053000	0.352242000	3.697484000	C	-0.128109000	-3.632874000	0.782233000	H	-1.294692000	4.087381000	-3.141339000	C	3.372988000	-2.482672000	-1.852780000
H	-1.648107000	1.632232000	3.414472000					H	-2.088205000	3.783781000	-1.595493000				

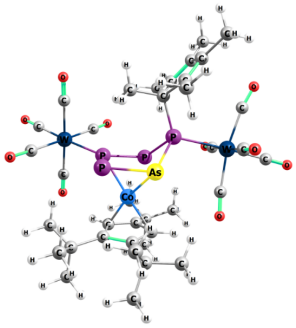
Table S15: Optimized geometries of **I-B** (left), **I-C** (right). XYZ coordinated in angstroms. B3LYP/def2-SVP level of theory.



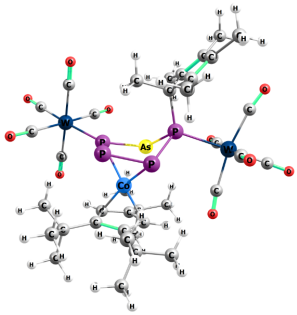


W	-2.065601000	-1.904735000	1.857310000	C	6.552495000	0.987019000	0.334990000	W	-3.833865000	0.208890000	-1.147502000	C	-1.444747000	4.408791000	3.559376000
W	-1.780190000	2.929511000	-0.974583000	H	6.406710000	2.016302000	0.698691000	W	4.197874000	-1.277712000	-0.651952000	H	-0.444827000	4.756434000	3.863675000
Co	2.058831000	0.181615000	0.361716000	H	7.487986000	0.960575000	-0.246670000	Co	0.340208000	1.464504000	0.600676000	H	-2.122008000	4.525432000	4.420664000
As	1.767353000	0.783659000	-2.028422000	H	6.678264000	0.332004000	1.211031000	As	0.977919000	-0.387492000	2.130422000	H	-1.803398000	5.068267000	2.753639000
P	1.532974000	-2.040660000	-0.360190000	C	2.729657000	2.838332000	4.152549000	P	-1.443637000	-0.008569000	-0.008251000	C	3.144303000	5.233113000	0.463132000
P	-0.020432000	0.998710000	-0.638689000	H	2.521269000	2.025538000	4.857739000	P	1.860473000	-0.340878000	0.026368000	H	2.793938000	5.561136000	-0.523368000
P	2.081055000	-1.482883000	-2.412031000	H	2.362024000	3.769766000	4.610959000	P	-1.200131000	-1.141112000	1.873325000	H	4.198464000	5.538769000	0.557066000
P	-0.141583000	-0.881971000	0.374674000	H	3.822139000	2.927154000	4.042967000	P	0.270036000	0.025619000	-1.339505000	H	2.566925000	5.775836000	1.228375000
O	-2.164114000	0.452210000	4.063730000	C	3.945008000	-0.517894000	4.563642000	O	-2.608775000	0.987916000	-4.029340000	C	-0.032057000	5.641215000	-1.387628000
O	-2.104932000	-4.430114000	-0.142859000	H	4.900122000	-0.741781000	4.063185000	O	-5.228111000	-0.554363000	1.660815000	H	-0.945238000	5.784861000	-0.789627000
O	-4.345366000	-0.443381000	0.103723000	H	3.872442000	-1.163669000	5.453838000	O	-3.764044000	-2.862701000	-2.137511000	H	-0.184269000	6.138182000	-2.359256000
O	-0.197897000	-3.673342000	3.800748000	H	3.980406000	0.524779000	4.905050000	O	-4.312376000	3.325609000	-0.515993000	H	0.792045000	6.153134000	-0.871462000
O	-4.501218000	-3.274128000	3.360351000	C	5.363496000	0.523709000	-0.551900000	O	-6.721992000	0.243262000	-2.462185000	C	-1.416257000	2.924461000	3.104310000
O	-4.041969000	5.029276000	-1.707790000	C	-0.972617000	-0.687728000	-4.276632000	O	6.871708000	-2.781243000	-1.479663000	C	0.464656000	-3.918832000	0.127280000
O	-0.292978000	5.417932000	0.433581000	H	-0.770883000	-0.504034000	-5.347954000	O	4.622015000	0.850705000	-3.045255000	H	1.120268000	-4.480491000	0.817301000
C	-3.494203000	-0.928552000	0.701657000	H	-0.523419000	0.156020000	-3.727834000	C	-3.730264000	-1.787980000	-1.734299000	H	0.918928000	-2.924274000	0.012205000
C	-3.614783000	-2.775504000	2.817510000	H	-2.059925000	-0.630216000	-4.137136000	C	-5.670502000	0.233978000	-1.987158000	H	0.512701000	-4.417758000	-0.850466000
C	-2.113248000	-0.358449000	3.252520000	C	5.658191000	-0.896510000	-1.067086000	C	-3.014381000	0.714813000	-2.989351000	C	-2.846390000	2.496223000	2.737395000
C	-2.067078000	-3.508557000	0.542725000	H	5.861018000	-1.598451000	-0.243155000	C	-4.704777000	-0.296753000	0.670620000	H	-3.282840000	3.140551000	1.960782000
C	-0.776394000	4.491526000	-0.045970000	H	6.555132000	-0.880272000	-1.706246000	C	4.466429000	0.103288000	-2.187283000	H	-3.494980000	2.571016000	3.624306000
C	-0.811640000	-3.010497000	3.089934000	H	4.822077000	-1.292223000	-1.661452000	C	-4.109098000	2.207626000	-0.717217000	H	-2.877920000	1.455445000	2.387277000
C	-3.216668000	4.270415000	-1.438885000	C	-2.602226000	-3.340107000	-3.517215000	C	5.903184000	-2.233534000	-1.178938000	C	-2.104752000	-5.460931000	-0.975072000
O	-0.288623000	3.682647000	-3.736428000	H	-2.920256000	-3.826644000	-2.581327000	O	5.911239000	0.517833000	1.412886000	H	-2.869831000	-5.146998000	-1.702049000
C	-0.425083000	-2.009784000	-3.838866000	H	-2.942828000	-3.992836000	-4.340680000	C	-0.937973000	-3.836302000	0.638493000	H	-2.382214000	-6.474254000	-0.635658000
C	2.950014000	0.068139000	2.354925000	H	-3.144949000	-2.388443000	-3.602818000	C	0.413819000	3.500198000	-0.206433000	H	-1.148135000	-5.542185000	-1.509390000
C	-0.805709000	3.400341000	-2.750652000	C	-2.938212000	1.530353000	-1.995200000	C	5.284182000	-0.105970000	0.679003000	C	3.913484000	-2.670650000	0.863670000
C	2.710273000	1.467277000	2.021898000	C	2.255155000	3.957582000	2.003217000	C	1.530306000	3.323919000	0.714922000	C	3.721855000	3.370286000	1.998654000
C	3.408803000	1.709445000	0.790984000	H	3.321041000	4.223656000	1.929089000	C	0.954891000	2.905112000	1.962772000	H	3.306897000	3.951756000	2.835852000
H	3.429595000	2.661738000	0.272498000	H	1.743925000	4.777474000	2.528202000	H	1.526413000	2.692024000	2.858721000	H	4.790774000	3.619073000	1.925607000
C	0.522230000	2.463031000	2.967772000	H	1.835711000	3.915855000	0.989743000	C	3.832761000	2.969059000	-0.435613000	H	3.655741000	2.300926000	2.247965000
H	0.011973000	2.453323000	1.995470000	C	1.112390000	-3.808442000	-3.503687000	H	3.809918000	1.888075000	-0.259930000	C	-2.803397000	-3.411519000	2.076194000
H	0.117921000	3.306025000	3.550432000	C	1.431268000	-0.540596000	4.380946000	H	4.884652000	3.294135000	-0.403707000	C	1.462278000	3.985960000	-2.558947000
H	0.258949000	1.541502000	3.492992000	H	1.375484000	0.463164000	4.816035000	H	3.461166000	3.146980000	-1.446315000	H	2.346069000	4.538978000	-2.220916000
C	3.795192000	-0.453750000	1.312252000	H	1.344800000	-1.257519000	5.211497000	C	-0.777632000	3.206056000	0.547009000	H	1.189100000	4.395906000	-3.543318000
H	4.173972000	-1.469483000	1.285950000	H	0.561626000	-0.681995000	3.727261000	H	-1.782593000	3.271061000	0.146826000	H	1.737528000	2.931432000	-2.706215000
C	1.053975000	-2.320492000	-3.818244000	C	1.764092000	-1.935893000	-5.131345000	C	-1.325271000	-3.079665000	1.893648000	C	-0.482857000	-3.510075000	3.115591000
C	-0.161876000	-4.262066000	-3.342316000	H	1.706836000	-0.852283000	-5.322082000	C	-3.186312000	-4.235069000	1.063388000	H	0.594195000	-3.354570000	2.948748000
C	4.150556000	0.558392000	0.378770000	H	1.279089000	-2.453869000	-5.974984000	C	-0.470721000	2.893648000	1.904929000	H	-0.646493000	-4.584413000	3.299173000
C	2.742646000	-0.793189000	3.621220000	H	2.827861000	-2.217965000	-5.117566000	C	0.260582000	4.132759000	-1.609760000	H	-0.769431000	-2.964224000	4.028840000
C	2.041926000	2.638761000	2.780252000	C	2.392632000	-4.586287000	-3.443658000	C	3.031272000	3.700496000	0.653731000	C	-3.598077000	-2.967676000	3.266362000
C	-1.114520000	-3.150131000	-3.555719000	H	3.070960000	-4.220802000	-2.652537000	C	-2.027877000	-4.510162000	0.181951000	H	-3.530603000	-1.879869000	3.430968000
C	5.249309000	1.489935000	-1.743364000	H	2.956321000	-4.516170000	-4.391174000	C	-0.911125000	2.061206000	4.274686000	H	-3.238561000	-3.451326000	4.193407000
H	4.485611000	1.164405000	-2.462981000	H	2.206825000	-5.652056000	-3.250138000	H	-0.932041000	0.991764000	4.022470000	H	-4.662640000	-3.217405000	3.159102000
H	6.212337000	1.535111000	-2.275999000	C	-0.608393000	-5.660848000	-3.038903000	H	-1.561979000	2.210060000	5.150610000	C	-4.533042000	-4.853953000	0.836474000
H	5.002122000	2.515030000	-1.426707000	H	-1.154072000	-5.702343000	-2.082671000	H	0.112075000	2.327933000	4.581156000	H	-4.919936000	-4.604162000	-0.165707000
O	-3.610488000	0.821128000	-2.597069000	H	0.235212000	-6.362086000	-2.975380000	O	3.752497000	-3.445441000	1.696713000	H	-5.274279000	-4.522455000	1.576676000
C	2.786476000	-2.299227000	3.264246000	H	-1.298583000	-6.035687000	-3.814218000	C	-0.949754000	3.527304000	-2.353564000	H	-4.480472000	-5.955596000	0.885471000
H	2.069709000	-2.561059000	2.474336000	O	-3.317454000	2.336537000	1.799080000	H	-0.822685000	2.447506000	-2.503903000	O	2.629878000	-3.192308000	-2.727597000
H	2.534915000	-2.894159000	4.153871000	C	-2.757237000	2.517516000	0.813085000	H	-1.035987000	3.992507000	-3.346973000	C	3.174624000	-2.502339000	-1.989607000
H	3.784649000	-2.622759000	2.934917000					H	-1.903721000	3.700639000	-1.839608000				

Table S16: Optimized geometries of **6a** (left), **6b** (right). XYZ coordinated in angstroms. B3LYP/def2-SVP level of theory.

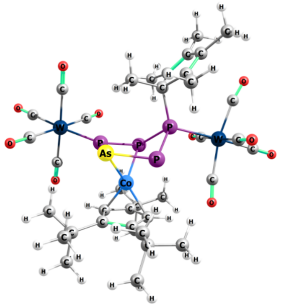


W	-3.773033000	-2.140597000	0.283039000	H	-1.464996000	3.653998000	4.898896000
W	3.987902000	0.323853000	0.668042000	H	-2.649859000	3.900097000	3.590446000
Co	-0.985738000	1.567693000	-0.179606000	C	-1.279026000	6.012616000	-1.444211000
P	-1.351356000	0.395623000	-2.199799000	H	-2.288624000	5.927214000	-1.864581000
P	1.759254000	-0.606950000	-0.459776000	H	-0.748139000	6.788109000	-2.018793000
P	-1.755696000	-0.630306000	-0.344936000	H	-1.370042000	6.367436000	-0.405369000
O	-2.608323000	-4.518277000	-1.571964000	C	-4.492227000	4.574523000	-0.473713000
O	-5.104669000	0.111549000	2.164170000	H	-4.655657000	4.418540000	0.603762000
O	-2.052502000	-3.245090000	2.784339000	H	-5.476099000	4.733510000	-0.944024000
O	-5.520734000	-1.140796000	-2.239566000	H	-3.906736000	5.495925000	-0.594304000
O	-6.131381000	-4.118875000	1.085206000	C	-1.058292000	2.444954000	3.120017000
O	6.596211000	1.532943000	2.014037000	C	0.505185000	-2.780862000	-1.981435000
O	2.883388000	3.282374000	1.218687000	H	-0.335712000	-2.838565000	-1.279697000
C	-2.657876000	-2.840662000	1.896873000	H	0.654665000	-3.784759000	-2.409943000
C	-5.276717000	-3.403844000	0.791895000	H	0.223589000	-2.098426000	-2.795335000
C	-2.998311000	-3.657267000	-0.919930000	C	-1.864847000	1.242976000	3.646636000
C	-4.619973000	-0.686355000	1.489991000	H	-2.945583000	1.359479000	3.475835000
C	3.197590000	2.193511000	0.992580000	H	-1.715383000	1.143913000	4.733107000
C	-4.886144000	-1.478658000	-1.343657000	H	-1.539342000	0.301621000	3.180193000
C	5.651138000	1.087690000	1.523888000	C	2.999656000	-1.566894000	-3.524081000
O	2.930287000	-0.734605000	3.530113000	H	2.130006000	-1.784837000	-4.169151000
C	1.804906000	-2.353597000	-1.284579000	H	3.904258000	-1.771402000	-4.113376000
C	-2.461702000	3.149519000	-0.357260000	H	2.980626000	-0.481037000	-3.331227000
C	3.297967000	-0.352511000	2.510525000	C	5.141222000	-1.403513000	0.497179000
C	-1.115488000	3.695609000	-0.496080000	C	0.967441000	5.021044000	-1.111985000
C	-0.409942000	3.345627000	0.713390000	H	1.025991000	5.534416000	-0.140768000
H	0.617438000	3.616571000	0.925958000	H	1.399650000	5.696301000	-1.866125000
C	-0.425370000	4.182640000	-2.975390000	H	1.603664000	4.126588000	-1.067267000
H	0.360891000	3.425206000	-3.100224000	C	3.384681000	-3.936999000	-0.591962000
H	-0.168250000	5.024939000	-3.637600000	C	-3.699185000	3.557689000	-2.637945000
H	-1.363265000	3.751180000	-3.332517000	H	-3.177240000	4.480880000	-2.912811000
C	-2.501669000	2.500855000	0.927759000	H	-4.716851000	3.631409000	-3.051388000
H	-3.375447000	2.005377000	1.336766000	H	-3.203138000	2.708797000	-3.130807000
C	2.205841000	-3.367820000	-0.220574000	C	1.343468000	-3.713954000	0.954757000
C	3.859345000	-3.323646000	-1.852366000	H	1.212921000	-2.867096000	1.650160000
C	-1.275116000	2.669171000	1.625384000	H	1.770654000	-4.544024000	1.534137000
C	-3.795816000	3.344759000	-1.117561000	H	0.328996000	-4.019208000	0.644460000
C	-0.486363000	4.683064000	-1.514435000	C	4.132248000	-5.039152000	0.095833000
C	2.970955000	-2.379320000	-2.265173000	H	3.614584000	-5.393390000	0.997621000
C	0.426952000	2.270772000	3.478115000	H	5.139321000	-4.705044000	0.395283000
H	0.852417000	1.372512000	3.010008000	H	4.270630000	-5.905175000	-0.573914000
H	0.535771000	2.162176000	4.568385000	C	5.128066000	-3.755512000	-2.523158000
H	1.029295000	3.138009000	3.170978000	H	5.314657000	-3.209980000	-3.458377000
O	5.915422000	-2.253985000	0.482166000	H	5.106659000	-4.832764000	-2.761332000
C	-4.724281000	2.127659000	-0.908958000	H	5.995482000	-3.596057000	-1.860817000
H	-4.249707000	1.202130000	-1.258219000	O	4.991962000	1.243797000	-2.257600000
H	-5.648898000	2.269491000	-1.488135000	C	4.629160000	0.917943000	-1.216309000
H	-5.023531000	1.990751000	0.138645000	P	-0.006344000	-0.345844000	0.893550000
C	-1.582629000	3.734738000	3.806275000	As	0.805934000	1.070697000	-1.823106000
H	-1.025126000	4.622652000	3.469009000				



W	-3.908320000	-2.009850000	0.243503000	H	-1.074397000	4.876562000	3.171389000
W	4.057808000	0.331494000	0.580368000	H	-1.583775000	4.024925000	4.651967000
Co	-0.926356000	1.572406000	-0.244075000	H	-2.710316000	4.177615000	3.279301000
P	0.811920000	0.927775000	-1.727059000	C	-0.939089000	5.941180000	-1.766938000
P	-1.212972000	0.294966000	-2.199900000	H	-1.943861000	5.881633000	-2.203742000
P	1.798070000	-0.633979000	-0.449393000	H	-0.356823000	6.652348000	-2.374216000
P	-1.800461000	-0.603814000	-0.324448000	H	-1.032844000	6.362889000	-0.753529000
O	-2.721449000	-4.444914000	-1.522962000	C	-4.290351000	4.669244000	-0.874852000
O	-5.184471000	0.369554000	2.002113000	H	-4.520514000	4.564310000	0.196579000
O	-2.352958000	-3.127419000	2.843535000	H	-5.238955000	4.844493000	-1.407686000
O	-5.534563000	-1.022077000	-2.364190000	H	-3.662999000	5.562994000	-0.997570000
O	-6.373321000	-3.877216000	0.989882000	C	-1.116035000	2.678672000	2.990293000
O	6.715834000	1.554061000	1.812759000	C	0.508469000	-2.847984000	-1.887570000
O	2.941710000	3.255765000	1.270736000	H	-0.290924000	-2.907149000	-1.138057000
C	-2.898673000	-2.718821000	1.919656000	H	0.656958000	-3.856588000	-2.305099000
C	-5.480266000	-3.202106000	0.716957000	H	0.166766000	-2.190735000	-2.698843000
C	-3.125667000	-3.570092000	-0.898987000	C	-1.969698000	1.531229000	3.561885000
C	-4.726106000	-0.480307000	1.374364000	H	-3.034822000	1.636333000	3.307018000
C	3.258650000	2.180203000	0.991624000	H	-1.895878000	1.525464000	4.660586000
C	-4.938661000	-1.352980000	-1.439612000	H	-1.626097000	0.549447000	3.203865000
C	5.752032000	1.105243000	1.364206000	C	2.872530000	-1.558337000	-3.585006000
O	3.131078000	-0.759174000	3.472748000	H	1.976237000	-1.798059000	-4.184674000
C	1.837995000	-2.378185000	-1.277735000	H	3.749561000	-1.732528000	-4.223634000
C	-2.315970000	3.194139000	-0.593999000	H	2.829298000	-0.475382000	-3.380774000
C	3.461244000	-0.369888000	2.442087000	C	5.229482000	-1.372387000	0.318585000
C	-0.941288000	3.676084000	-0.697687000	C	1.236580000	4.847639000	-1.291126000
C	-0.312639000	3.375684000	0.565019000	H	1.288700000	5.395043000	-0.338459000
H	0.714338000	3.613972000	0.814567000	H	1.731535000	5.469232000	-2.052608000
C	-0.120424000	3.992050000	-3.166741000	H	1.819363000	3.921809000	-1.191540000
H	0.550703000	3.122548000	-3.192767000	C	3.487469000	-3.936292000	-0.698377000
H	0.307788000	4.756359000	-3.834932000	C	-3.425695000	3.538520000	-2.950370000
H	-1.082487000	3.688295000	-3.584812000	H	-2.879944000	4.444959000	-3.235034000
C	-2.448071000	2.635367000	0.726531000	H	-4.419827000	3.604288000	-3.418626000
H	-3.364083000	2.208774000	1.121420000	H	-2.914344000	2.665174000	-3.379974000
C	2.330797000	-3.383334000	-0.243213000	C	1.569940000	-3.728191000	1.000834000
C	3.865964000	-3.310609000	-1.984873000	H	1.615075000	-2.925861000	1.758446000
C	-1.249951000	2.797884000	1.473809000	H	1.968694000	-4.635891000	1.475268000
C	-3.603349000	3.392060000	-1.429807000	H	0.500634000	-3.905948000	0.796615000
C	-0.217100000	4.570734000	-1.738071000	C	4.297824000	-5.027801000	-0.067488000
C	2.936832000	-2.379472000	-2.333030000	H	3.833459000	-5.415414000	0.849734000
C	0.346053000	2.517869000	3.440531000	H	5.306806000	-4.667810000	0.193511000
H	0.795364000	1.592857000	3.052081000	H	4.432270000	-5.875350000	-0.760921000
H	0.393834000	2.475518000	4.539793000	C	5.094969000	-3.715248000	-2.741590000
H	0.972138000	3.361248000	3.115290000	H	5.208334000	-3.158660000	-3.681868000
O	6.017794000	-2.207028000	0.249002000	H	5.076922000	-4.790679000	-2.988336000
C	-4.574849000	2.209282000	-1.222932000	H	6.001701000	-3.545151000	-2.136930000
H	-4.116311000	1.263030000	-1.536925000	As	0.001256000	-0.378299000	1.049356000
H	-5.475058000	2.364209000	-1.836240000	O	4.890677000	1.324972000	-2.377667000
H	-4.912345000	2.104287000	-0.183404000	C	4.588251000	0.972236000	-1.326685000
C	-1.655009000	4.021952000	3.552475000				

Table S17: Optimized geometries of **6c**. XYZ coordinated in angstroms. B3LYP/def2-SVP level of theory.



W	-3.758269000	-2.089228000	0.381424000	H	-2.512487000	3.987275000	3.565329000
W	4.029515000	0.315320000	0.663387000	C	-1.081839000	5.983615000	-1.518740000
Co	-0.881214000	1.566700000	-0.170132000	H	-2.097292000	5.916132000	-1.928423000
P	1.780354000	-0.579466000	-0.454756000	H	-0.534954000	6.729556000	-2.116971000

P	-1.721080000	-0.626609000	-0.296392000	H	-1.154283000	6.367267000	-0.488638000
O	-2.617372000	-4.503851000	-1.440314000	C	-4.324787000	4.637253000	-0.487885000
O	-5.034888000	0.221776000	2.229534000	H	-4.483661000	4.497777000	0.592440000
O	-2.032239000	-3.177579000	2.887354000	H	-5.307296000	4.819486000	-0.952454000
O	-5.510385000	-1.099951000	-2.140990000	H	-3.713335000	5.539516000	-0.623594000
O	-6.136244000	-4.021814000	1.235232000	C	-0.942767000	2.500531000	3.119870000
O	6.662456000	1.484696000	1.996174000	C	0.544233000	-2.754415000	-2.015651000
O	2.994228000	3.290329000	1.248832000	H	-0.298208000	-2.823642000	-1.316864000
C	-2.639042000	-2.778995000	1.998586000	H	0.712498000	-3.755656000	-2.443457000
C	-5.274734000	-3.322941000	0.923385000	H	0.254576000	-2.079367000	-2.832629000
C	-3.003926000	-3.632612000	-0.799812000	C	-1.768051000	1.322491000	3.670616000
C	-4.570917000	-0.598780000	1.568117000	H	-2.846221000	1.448834000	3.491168000
C	3.276704000	2.195508000	1.009891000	H	-1.625542000	1.248557000	4.760023000
C	-4.875025000	-1.436448000	-1.244502000	H	-1.452725000	0.365623000	3.229756000
C	5.708406000	1.053587000	1.510699000	C	2.995910000	-1.454973000	-3.555417000
O	2.987406000	-0.757979000	3.524688000	H	2.161255000	-1.720703000	-4.229058000
C	1.838973000	-2.306968000	-1.320844000	H	3.927665000	-1.580503000	-4.124065000
C	-2.333294000	3.163690000	-0.370003000	H	2.889526000	-0.379303000	-3.338157000
C	3.349883000	-0.369783000	2.505241000	C	5.172788000	-1.415365000	0.469383000
C	-0.976507000	3.684732000	-0.517982000	C	1.139032000	4.937208000	-1.172306000
C	-0.279979000	3.349385000	0.699337000	H	1.218621000	5.464125000	-0.209946000
H	0.750052000	3.610341000	0.910294000	H	1.583047000	5.589125000	-1.940020000
C	-0.282094000	4.092788000	-3.008251000	H	1.749672000	4.025584000	-1.120831000
H	0.466172000	3.294065000	-3.106778000	C	3.438989000	-3.895872000	-0.689875000
H	0.019417000	4.905671000	-3.688405000	C	-3.581749000	3.578330000	-2.647125000
H	-1.239269000	3.701581000	-3.361487000	H	-3.032203000	4.480655000	-2.936618000
C	-2.383406000	2.536890000	0.925235000	H	-4.601276000	3.681727000	-3.049426000
H	-3.264207000	2.060400000	1.341420000	H	-3.119697000	2.710208000	-3.139888000
C	2.265135000	-3.340072000	-0.284328000	C	1.425098000	-3.715439000	0.898215000
C	3.892664000	-3.246010000	-1.939592000	H	1.324822000	-2.891186000	1.625455000
C	-1.155655000	2.700097000	1.621392000	H	1.854121000	-4.570797000	1.438152000
C	-3.667928000	3.381504000	-1.123997000	H	0.399085000	-3.995267000	0.602287000
C	-0.325912000	4.631819000	-1.560431000	C	4.198059000	-5.016906000	-0.046762000
C	2.992885000	-2.297142000	-2.315720000	H	3.693196000	-5.401385000	0.849997000
C	0.539754000	2.310522000	3.480872000	H	5.208222000	-4.690319000	0.249967000
H	0.956177000	1.405948000	3.016692000	H	4.328813000	-5.860393000	-0.746167000
H	0.646007000	2.205842000	4.571764000	C	5.155128000	-3.649566000	-2.639496000
H	1.152176000	3.169296000	3.170382000	H	5.329583000	-3.068241000	-3.555260000
O	5.949702000	-2.263412000	0.442631000	H	5.133601000	-4.717022000	-2.918615000
C	-4.626458000	2.191835000	-0.893668000	H	6.029405000	-3.513268000	-1.980975000
H	-4.180953000	1.248674000	-1.234992000	O	5.019367000	1.245906000	-2.264751000
H	-5.552066000	2.351504000	-1.466569000	C	4.658824000	0.916997000	-1.224150000
H	-4.919991000	2.074098000	0.157832000	P	0.032543000	-0.360851000	0.929163000
C	-1.446858000	3.811628000	3.780948000	P	0.870150000	1.048934000	-1.699197000
H	-0.878208000	4.684569000	3.423943000	As	-1.240052000	0.382326000	-2.288018000
H	-1.326520000	3.751361000	4.874574000				

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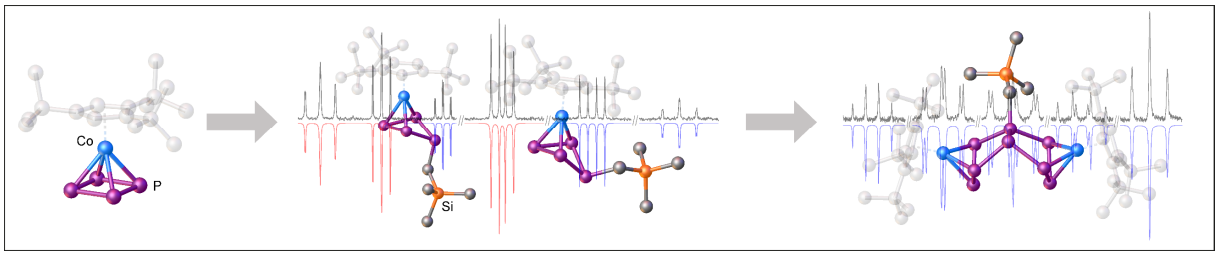
9. Transformation of the *cyclo*-P_4 Ligand in [Cp’’’Co(η^4-P_4)]

Martin Piesch, Michael Seidl and Manfred Scheer



- DFT calculations were performed by Martin Piesch
- All compounds have been synthesized and characterized by Martin Piesch
- X-Ray measurements and calculations were done by Martin Piesch and finally checked by Michael Seidl
- Manuscript was written by Martin Piesch
- Figures were made by Martin Piesch

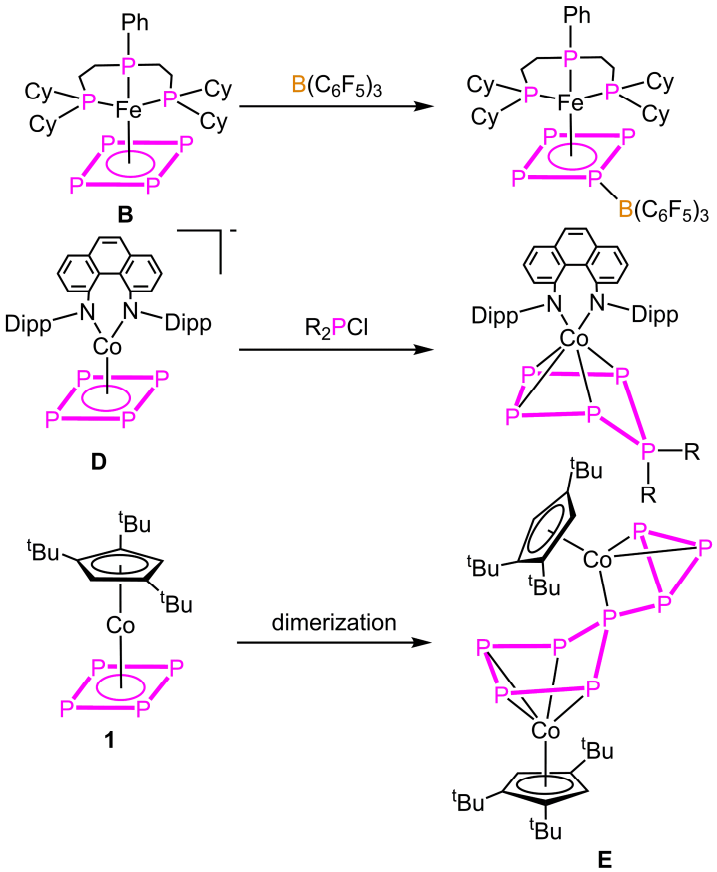
9.1 Introduction

Abstract: *The reactivity of the cyclo-P_4 ligand complex [Cp'''Co(η^4-P_4)] (**1**) (Cp''' = 1,2,4-tri-tertbutyl-cyclopentadienyl) towards reduction and main group nucleophiles was investigated. With K[CpFe(CO)$_2$] a selective reduction to the dianionic complex [(Cp'''Co)$_2$(μ,η^3:η^3-P_8)]$^{2-}$ (**2**) was achieved. The reaction of **1** with ^{t}BuLi and LiCH$_2$SiMe$_3$ as carbon-based nucleophiles yielded [Cp'''Co(η^3-P_4R)]$^-$ (R = ^{t}Bu (**4**), CH$_2$SiMe$_3$ (**7**)), which depending on the reaction conditions undergo subsequent reactions with another equivalent **1** to form [(Cp'''Co)$_2$(μ,η^3:η^3-P_8R)]$^-$ (R = ^{t}Bu (**5**), CH$_2$SiMe$_3$ (**8**)). In the case **4** a different pathway was observed, namely a dimerization followed by fragmentation into [Cp'''Co(η^3-$P_5{}^tBu_2$)]$^-$ (**6**) and [Cp'''Co(η^3-P_3)]$^-$ (**3**). With NaOH as an oxygen-based nucleophile the synthesis of [Cp'''Co(η^3-P_4(O)H]$^-$ (**9**) was achieved. All compounds were characterized by X-ray crystal structure analysis, NMR spectroscopy and mass spectrometry. Their electronic structures and reaction behavior were elucidated by DFT calculations.*

The transformation of the P_4 tetrahedron of white phosphorus in the coordination sphere of transition metal complexes yielding functionalized phosphorus compounds is a widely investigated field of research.[1] Most reactions proceed by thermolysis of carbonyl complexes like [(Cp^{R}M(CO)$_n$)$_2$] (e.g. M = Cr,[2] Mo,[3,4] W,[5] Fe,[6,7] Co,[8] Ni[9]) under harsh reaction conditions or photolysis of e.g. [Cp^{R}M(CO)$_4$] (M = V,[10] Nb,[11,12] Ta[12]) with P_4 yielding the thermodynamically most stable products. Complexes with cyclic polyphosphorus ligands possess a special aromatic character. While metal sandwich complexes with *cyclo*-P_3 ([Cp*Ni(η^3-P_3)[13]), *cyclo*-P_5 ([Cp*Fe(η^5-P_5)][6]) and *cyclo*-P_6 ([(Cp*Mo)$_2$(μ,η^6:η^6-P_6)][3]) ligands are known for decades, the *cyclo*-P_4 Co complex in this row was unknown for a long time. In 2017 we succeeded in the synthesis of [Cp'''Co(η^4-P_4)] (**1**).[14] This encouraged the synthesis of other complexes containing *cyclo*-P_4 ligands, for which few were recently reported as e.g based on group five metals, [Cp^{R}M(CO)$_2$(η^4-P_4)] (M = V, Nb, Ta (**A**)),[10,12] on iron, [^{Ph}PP$^{Cy}_2$Fe(η^4-P_4)] (**B**),[15] on molybdenum, [(Ar^{Dipp}CN)$_2$Mo(CO)$_2$(η^4-P_4)] (**C**)[16] and the anionic iron complex [Cp^{Ar}Fe(η^4-P_4)]$^-$[17] as well as the anionic cobalt complex [(PHDI)Co(η^4-P_4)]$^-$ (**D**).[18] The reactivity of these complexes was only barley investigated by the coordination chemistry of **A** and **B** towards coinage metal salts[15,19] and the reactivity of **B** towards Lewis acids like B(C_6F_5)$_3$ was investigated (Scheme 1).[15] The anionic compound **D** was quenched with phosphorus based electrophiles (R_2PCl) leading to neutral complexes with substituted *cyclo*-P_5R_2 ligands (Scheme 1).[18] Similar ring expansion reactions were also reported for **1** using the pnictogenidene complexes Cp*E{W(CO)$_5$}$_2$ (E = P, As) leading to neutral cobalt complexes with organo-substituted *cyclo*-P_5 and *cyclo*-P_4As ligands.[20] This shows that the reactions with electrophiles were investigated, but not the reactivity towards nucleophiles or reduction reactions in general. The former chemistry was studied for [Cp*Fe(η^5-P_5)] and [Cp*Ni(η^3-P_3)]

by our group,[21,22] for which organo-substituted anionic complexes of the type $[Cp^*Fe(\eta^4\text{-}P_5R)]^-$ and $[Cp'''Ni(\eta^2\text{-}P_3R)]^-$ were obtained. With this state of the art in mind the questions arose, how **1** will respond to redox reactions or to a nucleophilic attack. Will a dimerization by a P-P bond formation or a simple substitution occur, as it is known from the reactions of other *cyclo*-P_n ligand complexes? Is a structural rearrangement possible, which would include a reorganization process? In addition, control of the reactivity of **1** is a challenging task since it shows a high intrinsic tendency to dimerize irreversibly in solution to give a linked 5- and 3-membered P_8 ligand in $[(Cp'''Co)_2(\mu,\eta^4\text{:}\eta^3\text{-}P_8)]$ (**E**, Scheme 1).[14] The tendency to decrease the ring strain is rarely known as for example for the four-membered heterocycles the phosphetanes[23] (addition of nucleophiles) and the cobalt diphosphete complex $[Cp'''Co(\eta^4\text{-}P_2(C^tBu)_2)]$, which oxidation leads to $[Cp'''Co(\eta^5\text{-}P_3(C^tBu)_2]^+$ and $[Cp'''Co(\eta^3\text{-}P(C^tBu)_2]^+$, respectively.[24]

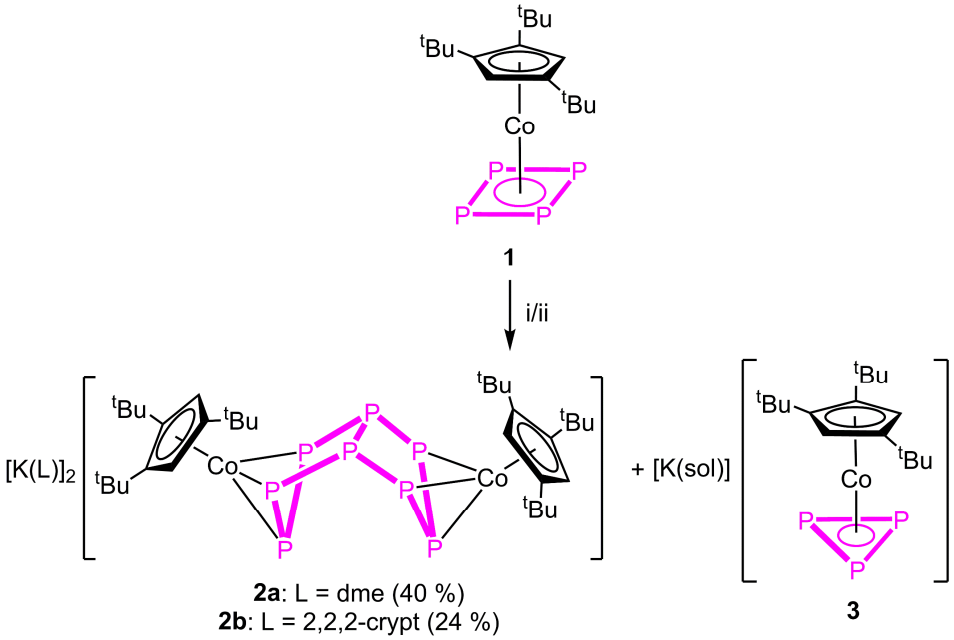
Herein we report on the unprecedented transformations of the *cylco*-P_4 ligand complex **1** upon reduction and reaction with main group nucleophiles.



Scheme 1. Reactivity of selected *cyclo*-P_4 ligand complexes.

9.2 Results and Discussion

To get a first insight in the reactivity of **1** the frontier molecular orbitals (cf. Figure S32) have been computed by DFT calculations. They reveal that both HOMO and LUMO are mainly located on the *cyclo*-P_4 ligand and hence **1** should react with both electrophiles as well as nucleophiles. The reactivity of **1** towards electrophiles has been shown by reactions with $Cp^*E\{W(CO)_5\}_2$, (E = P, As).[20] On the other hand the cyclic voltammogram (cf. Figure S18) of **1** reveals a weak irreversible oxidation process at +275 mV and a strong irreversible reduction process at -2081 mV against $[Cp_2Fe]/[Cp_2Fe]^+$ indicating the potential ligand centered redox activity of **1**. Due to the low reduction potential of **1** we used potassium, potassium graphite and potassium hydride for the chemical reduction. In all cases the formation of a mixture of $[(Cp'''Co)_2(\mu,\eta^3{:}\eta^3\text{-}P_8)]^{2-}$ (**2**) and $[Cp'''Co(\eta^3\text{-}P_3)]^-$ (**3**) [25] in a ca. 1:1 ratio (Scheme 2) is observed (cf. Figure S1). When the reaction is conducted in the presence of 18-c-6 or 2,2,2-cryptand only **3** can be detected in the $^{31}P\{^1H\}$ NMR spectrum. The selective synthesis of **2** can be achieved by using $K[CpFe(CO)_2]$ at low temperatures. Interestingly, $K[CpFe(CO)_2]$ should not be able to reduce **1** (its reduction potential of -1800 mV in thf against $[Cp_2Fe]/[Cp_2Fe]^+$ is higher than that of **1** (vide supra)).[26] After workup $[K(dme)]_2[(Cp'''Co)_2(\mu,\eta^3{:}\eta^3\text{-}P_8)]$ (**2a**) can be obtained as a dark green solid in crystalline yields of 40 % (Scheme 2). Although well diffracting single crystals of **2a** could be obtained, a satisfactory refinement of the X-ray data was not possible since the potassium counterions and dme molecules are severely disordered over several positions with side occupancies partially below 8 % (cf. SI). Addition of 2,2,2-cryptand to a crude reaction mixture of **2a** and recrystallization from a dme/acetonitrile mixture at -30 °C yielded single crystals of $[K(2,2,2\text{-cryptand})]_2[(Cp'''Co)_2(\mu,\eta^3{:}\eta^3\text{-}P_8)]$ (**2b**) suitable for X-ray diffractions in 24 % yield. Both **2a** and **2b** can be isolated as dark green extremely air and moisture sensitive solids. The structure in the solid state (Figure 1) shows a dianionic dinuclear complex with a P_8 ligand consisting of a *cis*-bicyclo[3.3.0]octane core which coordinates to two {Cp'''Co} fragments. Compound **2** displays the first compound with such a ligand. The structural motif is similar to the realgar-like P_8 cages (tricyclo[3.3.0.0]octane) as in $[(L_nM)_4(\mu_4,\eta^1{:}\eta^1{:}\eta^1{:}\eta^1{:}\eta^1{:}\eta^1{:}\eta^1{:}\eta^1\text{-}P_8)]$ (L_nM = nacnacGa,[27] nacnacFe,[28] $NN^{fc}Sc$,[29] Cp^*_2Sm[30]), $[(Cp^{Me}Fe(CO)_2)_2(Cp^{Me}Fe(CO))_2(\mu_4,\eta^1{:}\eta^1{:}\eta^1{:}\eta^1{:}\eta^1{:}\eta^1\text{-}P_8)]$,[31] $[(Cp^*Ir(CO))_2(\mu_5,\eta^1{:}\eta^1{:}\eta^1{:}\eta^1{:}\eta^1{:}\eta^1\text{-}P_8)\{Cr(CO)_5\}_3]$[32] or $[(Cp'''Ni)_2(\mu,\eta^2{:}\eta^2\text{-}P_8)]^{2-}$[22] with the difference that in **2b** one P-P bond is cleaved (P1-P5, Figure 1). In all mentioned complexes, the P_8 ligands coordinates either in $\eta^1{:}\eta^1$ (Ga, Fe, Sc, Sm, Ir) or η^2 (Ni) fashion to the metal fragments, while in **2b** two allylic P_3 subunits (P1-P2 2.1554(6), P1-P8 2.1577(6), P4-P5 2.1519(6), P5-P6 2.1580(6) Å) are coordinating to two {Cp'''Co} fragments in η^3 fashion. These P-P bond lengths are between single[33] and double[34] bond lengths, what is also in line with the calculated Wiberg Bond Indices (WBIs) of 1.11 and 1.12, respectively.



Scheme 2: Reaction of **1** with i) K, KH or KC_8. in thf at r.t, ii) $K[CpFe(CO)_2]$ in thf at -80 °C.

All other P-P distance are in the range of single bonds (2.1947(6) - 2.2247(6) Å) underlined by WBIs between 0.93 and 0.96.The ^{1}H NMR spectrum of **2a** in thf-d_8 shows three singlets centered at δ = 3.96, 1.31 and 1.22 ppm with an integral ratio of 4:36:18 indicating two equivalent free rotating Cp''' ligands. The $^{31}P\{^{1}H\}$ NMR spectrum in thf-d_8 shows three multiplets centered at δ = 96.2, 83.1 and -124.2 ppm with an integral ratio of 2:4:2 of an AA'MM'M''M'''XX' spin system.

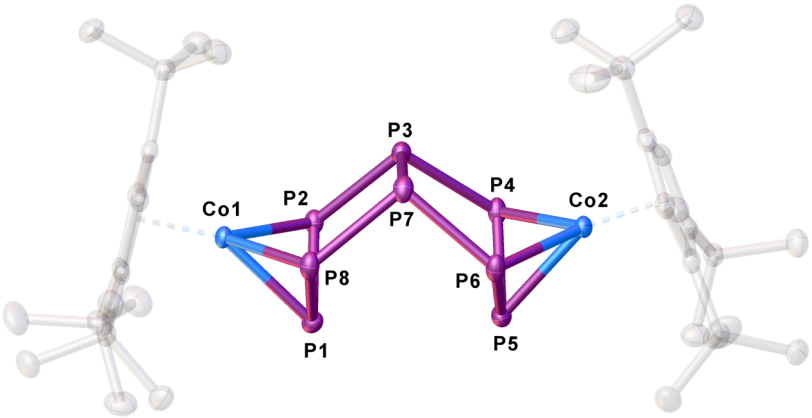
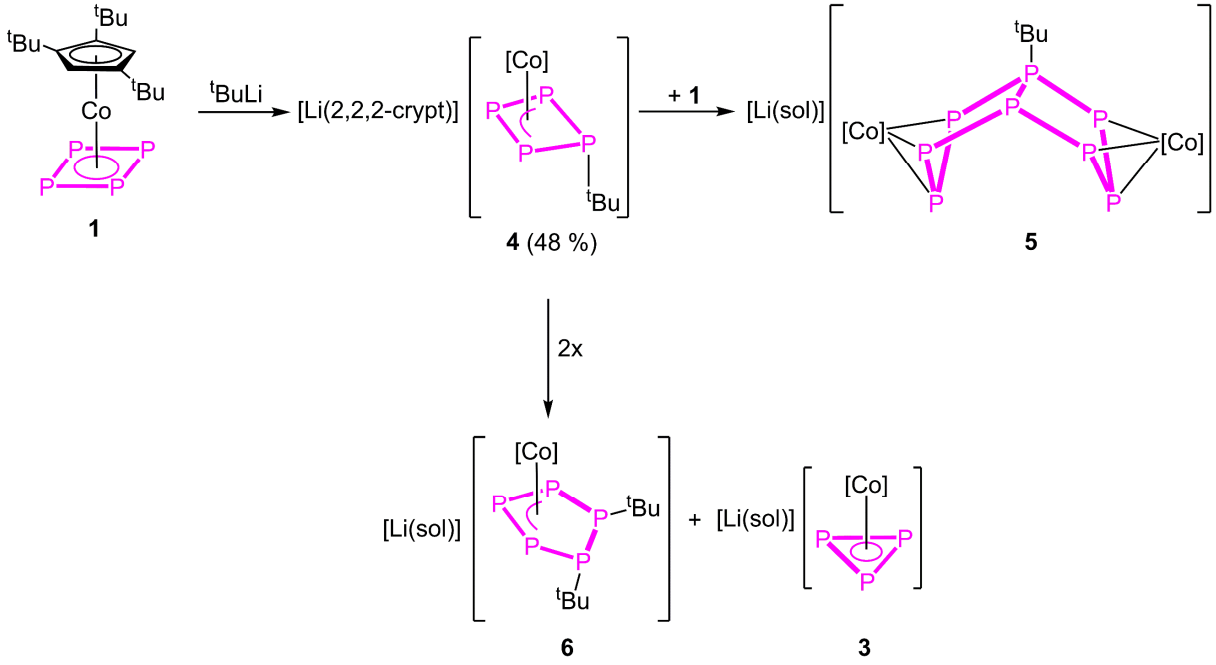


Figure 1: Structure of the dianion in **2b** in the solid state. Thermal ellipsoids are shown at 50 % probability level. Hydrogen atoms, cations and solvent molecules are omitted for clarity.

Instead of adding electrons to the system by reduction, nucleophiles can also serve as electron deliverers. We selected ^{t}BuLi as a strong carbon-based nucleophile with a higher steric demand to avoid side reactions. The reaction with **1** in thf at -100 °C proceeds instantly during the addition of ^{t}BuLi indicated by an immediate color change from red to brown. After warming

to room temperature, the ^{1}H and $^{31}P\{^{1}H\}$ NMR spectra reveal the selective formation of $[Cp'''Co(\eta^3\text{-}P_4{}^tBu)]^-$ (**4**) (Scheme 3). Pure **4** can be precipitated from the reaction mixture in a yield of 48 % after addition of the 2,2,2-cryptand.



Scheme 3: Reaction of **1** with tBuLi and subsequent reactions.

Regardless of numerous attempts to obtain single crystals suitable for X-ray diffractions we were only able to receive poorly diffracting ones (resolution < 1.20 Å). The atom connectivity can be determined unambiguously, however a discussion of the bond lengths and angles would not be appropriate. The structure in solid state (cf. Figure S22) reveals a folded *cyclo*-P_4 ligand with one P atom deviating from the former planar P_4 unit, to which the ^{t}Bu substituent is bond to in an endo position (isomer **4a**). Theoretically, a second isomer with the tBu substituent in exo position (**4b**) would be possible, however it could not be detected by NMR spectroscopy (vide infra; cf. Figure 4). According to DFT calculations the energy difference between the endo and exo isomers of **4** (i.e. **4a** and **4b**) is 11.91 kJ·mol^{-1}, **4a** being favored. During the optimization of the crystallization conditions we noticed that **4** is not stable in solution over the time (especially in absence of 2,2,2-cryptand) and is converted to $[(Cp'''Co)_2(\mu,\eta^3\text{:}\eta^3\text{-}P_8{}^tBu)]^-$ (**5**) or $[Cp'''Co(\eta^3\text{-}P_3)]^-$ (**3**) and $[Cp'''Co(\eta^3\text{-}P_5{}^tBu_2)]^-$ (**6**) (Scheme 3). This process has been monitored by $^{31}P\{^{1}H\}$ NMR spectroscopy and the products **5** and **6** could be isolated and characterized spectroscopically and by single crystal X-ray diffractions. For compound **5** very few single crystals suitable for X-ray diffractions could be obtained, while the quality of the crystals of **6** gave only very poor data indicating however the atom connectivity in **6** (cf. SI).The molecular structure of **5** (Figure 2) shows a binuclear complex with a substituted $P_8{}^tBu$ ligand coordinating to two {Cp'''Co} fragments each in a η^3 fashion similar to **2**.

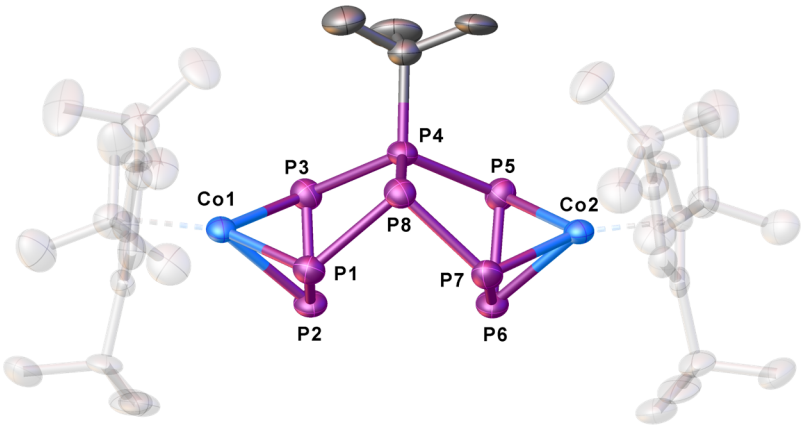


Figure 2: Molecular structure of the anion in **5** in the solid state. Thermal ellipsoids are shown at 50 % probability level. Hydrogen atoms, cations and solvent molecules are omitted for clarity.

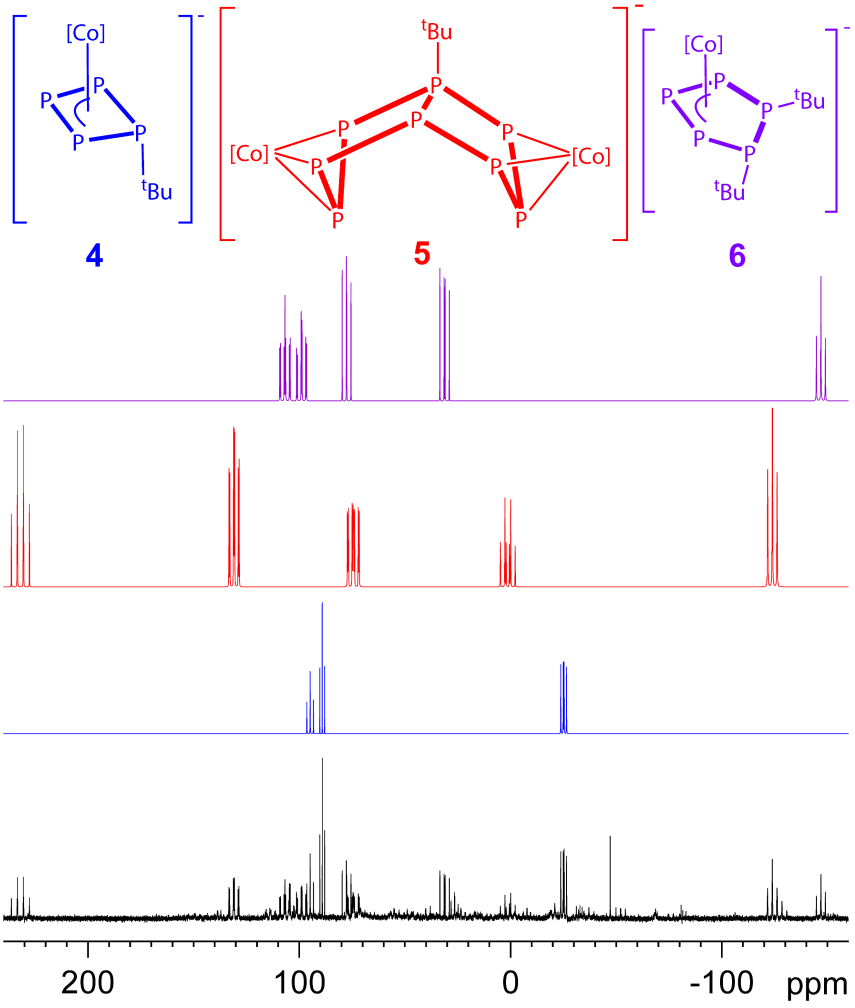
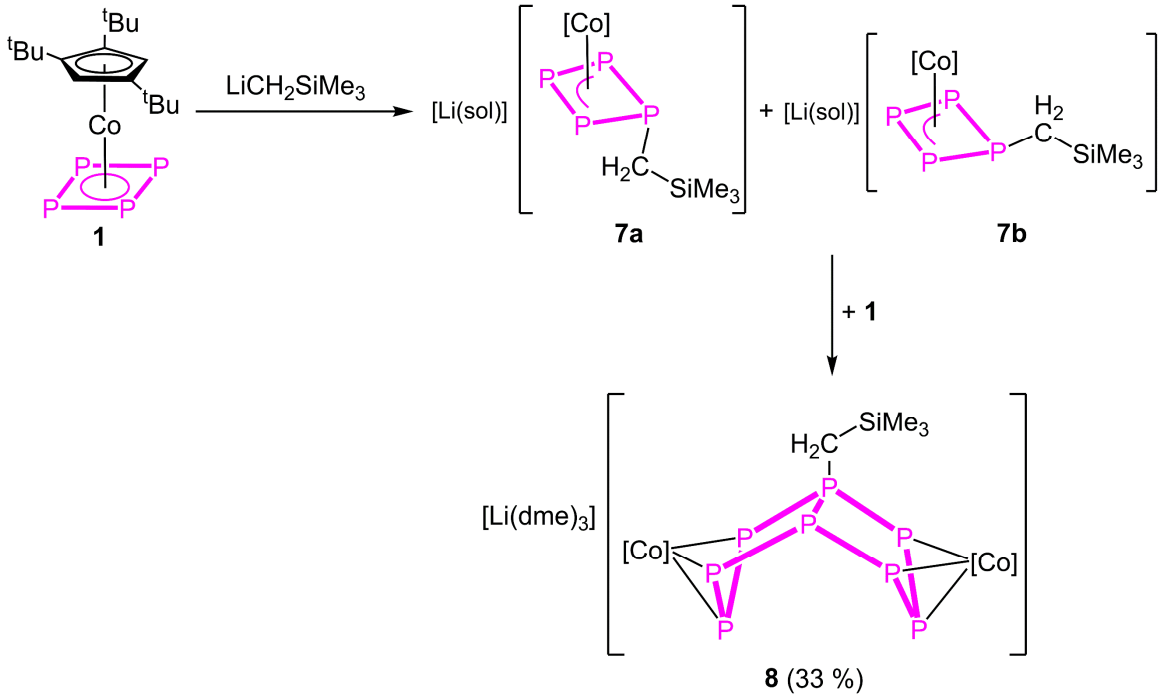


Figure 3: $^{31}P\{^{1}H\}$ NMR spectrum of the reaction of **1** with ^{t}BuLi at r.t. in thf-d_8 and the simulated spectra of **4**, **5** and **6** ([Co] = Cp'''Co).

All P-P distances are comparable to those in **2**. The identity of **3**, **5** and **6** was further proven by simulation of the related $^{31}P\{^{1}H\}$ NMR spectra. Performing the reaction of **1** with ^{t}BuLi at room temperature the $^{31}P\{^{1}H\}$ NMR spectrum of the reaction mixture in thf-d_8 reveals a mixture

of all four compounds **3**, **4**, **5** and **6** beside traces of unknown compounds (Figure 3). The $^{31}P\{^{1}H\}$ NMR spectra of **4**, **5** and **6** have been simulated separately from this spectrum since **3**, **5** and **6** could not be separated preparatively from each other. The formation of **5** can be explained by the reaction of **4** with another equivalent **1** which is energetically favored by 52.48 kJ·mol^{-1} (Figure 4) and probably driven by the decrease of the ring strain as the driving force. An alternative pathway for the release of ring strain would be the dimerization of two equivalents of **4** followed by a subsequent fragmentation to form **6** (containing an unprecedented disubstituted *cyclo*-P_5 ligand) and **3** (containing a *cyclo*-P_3 ligand). This reaction is exothermic by 161.09 kJ·mol^{-1}. Interestingly these subsequent reactions can be avoided or at least slowed down when the lithium counter ion is completely separated from the anion in **4** by i.e. addition of a 2,2,2-cryptand. Since the nucleophile ^{t}BuLi seems to be too strong and induces subsequent reactions, we employed $LiCH_2SiMe_3$ as a weaker and sterically less demanding carbon-based nucleophile in the reaction with **1**. The reaction of **1** with $LiCH_2SiMe_3$ in thf at -100 °C leads to the formation of $[Cp'''Co(\eta^3\text{-}P_3CH_2SiMe_3)]^-$ (**7**) and after warming to room temperature $[Li(dme)_3][(Cp'''Co)_2(\mu,\eta^3\text{:}\eta^3\text{-}P_8CH_2SiMe_3)]$ (**8**) which can be isolated in crystalline yields of 33 % after workup (Scheme 4). The formation of **7** and **8** can be detected by color changes from red (**1**) to brown (**7**) to green (**8**). The outcome of the reaction is independent whether 0.5 or 1 equivalents $LiCH_2SiMe_3$ are used.



Scheme 4: Reaction of **1** with $LiCH_2SiMe_3$ ([Co] = Cp'''Co).

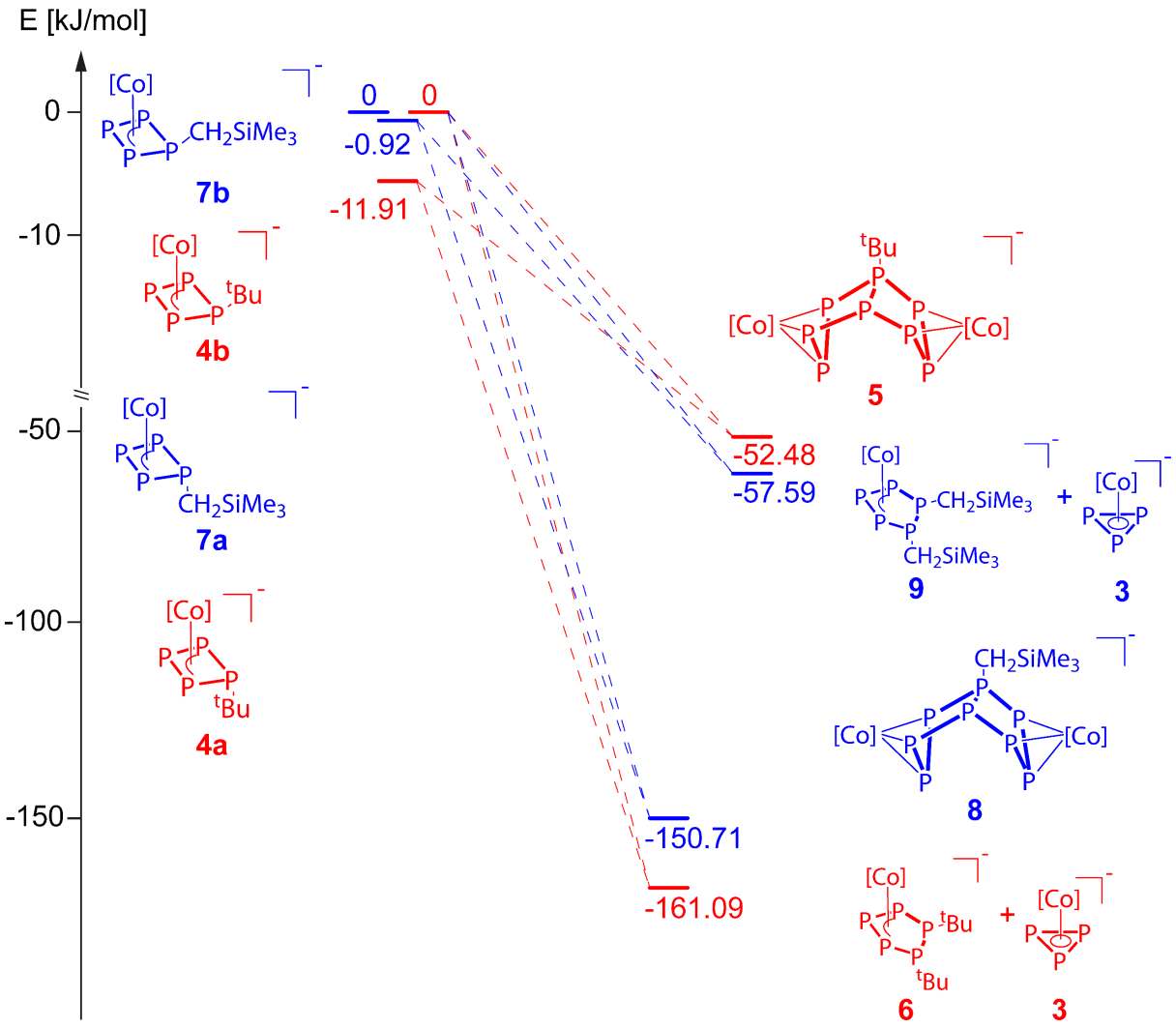


Figure 4: Energetic diagram of the isomers **4a,b** and **7a,b** and their subsequent reactions. **4b** and **7b** were each used as reference for the related calculations (0 kJ·mol^{-1}, [Co] = Cp'''Co).

The reaction can be stopped partially and the formation of **8** reduced when 12-c-4 or 2,2,2-cryptand is added directly after the addition of $LiCH_2SiMe_3$ at -80 °C. The crude $^{31}P\{^1H\}$ spectra of these reactions reveals two isomers of **7** being present in a ratio of 1:0.25 (2,2,2-crypt) and 1:1.33 (12-c-4), respectively, which can be assigned to complexes where the CH_2SiMe_3 substituent is located in an endo position (**7a**) or in an exo position (**7b**). The $^{31}P\{^1H\}$ NMR spectra reveal also the formation of **8** and **3** beside minor amounts of unknown side products, while the reaction in the presence of 2,2,2-cryptand seems to be much more selective to give **3**, **7a**, **7b** and **8** (cf. Figure S10 and S11). According to DFT calculations, the energy of the isomers **7a** and **7b** differ only by 0.92 kJ·mol^{-1} with **7a** being favored (Figure 4). Few crystals of the isomer **7a** were obtained from a concentrated solution of the mixture of isomers in thf layered with hexane at -30 °C. The molecular structure (Figure 5, left) shows a folded *cyclo*-P_4 ligand with one P atom bent out of the plane bearing the CH_2SiMe_3 substituent. The P1-P2 (2.2283(16) Å) and P1-P4 (2.2229(19) Å) distances are longer than the P2-P3 (2.1877(17) Å) and P3-P4 (2.1895(16) Å) bonds. All P-P bond lengths are elongated compared to **1**.[14] The

$^{31}P\{^{1}H\}$ NMR spectrum of **7** in thf-d_8 shows three multiplets of an AMXX' spin system (**7a**) centered at δ = 52.6, 46.0 and 18.8 ppm with an integral ratio of 1:1:2 and three multiplets of an AMM'X spin system (**7b**) centered at δ = 39.5, 3.94 and -78.0 ppm with an integral ratio of 1:2:1. The J_{PP} coupling constants obtained from the simulation (cf. SI) correlate nicely with the bond distances obtained from the X-ray structure determination.

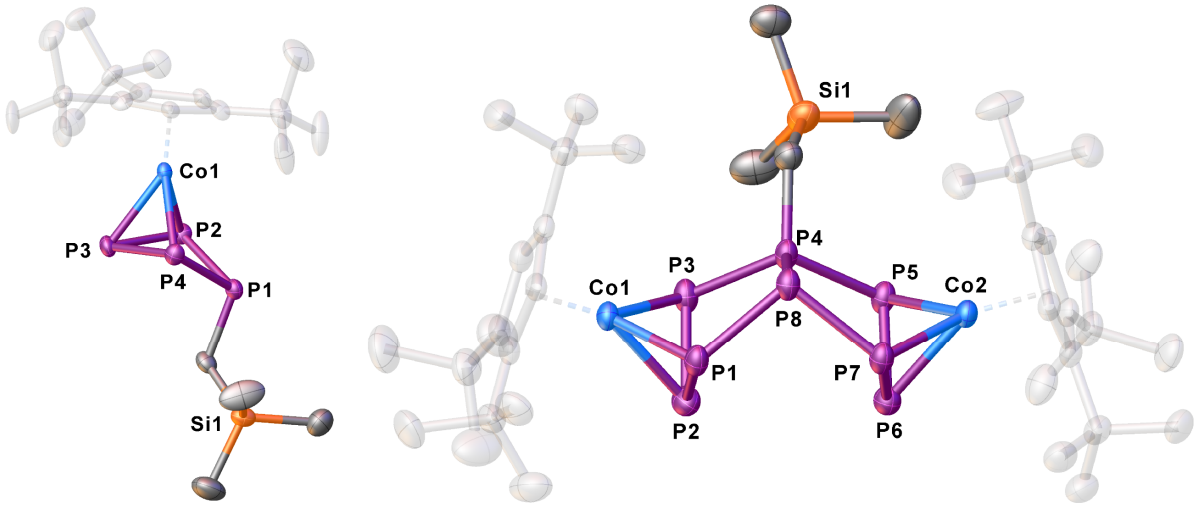
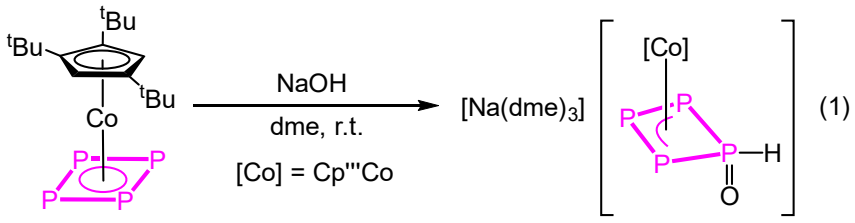


Figure 5. Molecular structure of the anions **7a** and **8** in the solid state. Thermal ellipsoids are shown at 50 % probability level. Hydrogen atoms, cations and solvent molecules are omitted for clarity.

When the reaction is conducted without the use of 12-c-4 or 2,2,2-cryptand a color change from initial red over brown (**7**) to dark green (**8**) is observed. Crystals of **8** suitable for single crystal X-ray diffraction were obtained from a concentrated solution in a mixture of hexane and dme stored at -30 °C. The structure of **8** (Figure 5, right) shows a dinuclear anionic complex with a substituted P_8 ligand. The P_8 structural motif is similar to that observed in the reduced complex **2** and analogous to that found in **5**. The P_8 ligand consists of two condensed five membered rings (bicyclo[3,3,0]octane) coordinating to the {Cp'''Co} fragments via the allylic P_3 subunits (P1-P2-P3 and P5-P6-P7). The bond distances (P1-P2 2.1643(11), P2-P3 (2.1574(11), P5-P6 2.1494(11), P6-P7 2.1575(11) Å) are in the range between single and double bonds, indicated by the WBIs between 1.09 and 1.11. All other P-P distances are in the range of single bonds. The $^{31}P\{^{1}H\}$ NMR spectrum of **8** in thf-d_8 shows five multiplets centered at δ = 187.9, 102.8, 74.4, 40.6 and -118.8 ppm with an integral ratio of 1:2:2:1:2 indicating an $AM_2N_2OX_2$ spin system. The simulation of the spectrum at 193 K was conducted to determine the coupling constants and chemical shifts (cf. Figure S13). The formation of **8** can be explained by the reaction of **7** with another equivalent **1**, what is energetically favored by -150.71 kJ·mol^{-1}. However, [Cp'''Co(η^3-$P_5(CH_2SiMe_3)_2$)]$^-$ (**9**) analog to **6** was never detected by NMR since the dimerization and subsequent fragmentation of **7** to **9** and **3** would be energetically favored by -57.59 kJ·mol^{-1}(Figure 4). The reaction of **1** with $LiCH_2SiMe_3$ was investigated by VT $^{31}P\{^{1}H\}$ NMR spectroscopy (cf. Figure S14-16). At 193 K the reaction is

already complete (absence of signals of **1**). The $^{31}P\{^{1}H\}$ NMR spectrum shows six broad multiplets which can be assigned to **7a**,**b**. Upon warming, these signals broaden and only two broad triplets remain (at 233 and 253 K). The formation of **8** can detected for the first time at 253 K. At room temperature **3**, **7a**,**b**, **8** and a second set of signals quite similar to those of **8** are observed. The latter might represent an isomer of **8**. After 24 hours at room temperature, the signals of **7a**,**b** disappeared completely.

The reaction of the oxygen-based nucleophile NaOH with **1** at room temperature yields $[Na(dme)_3][Cp'''Co(\eta^3\text{-}P_4(O)H]$ (**10**) in crystalline yields of 55 % after workup (Eq. 1). In the first step OH^- binds to one phosphorus atom of the *cyclo*-P_4 ligand in **1**, followed by a proposed tautomeric rearrangement with the formation of a P=O double and P-H single bond.



1 **9** (55 %)

The structure of **10** (Figure 6) reveals a folded *cyclo*-P_4 ligand in which one P atom bent out of the plane (P1). The hydrogen atom bonded to phosphorus (H1) was found on the electron density map and was freely refined. The P-P distances are in the range of single or slightly shortened single bonds (P1-P2 2.1659(7), P1-P4 2.1676(7), P2-P3 2.1984(8), P3-P4 2.1938(8) Å; WBIs 0.94-1.07). The P1-O1 bond (1.5200(15) Å) is in the range between a single and double bond (WBI of 1.08).

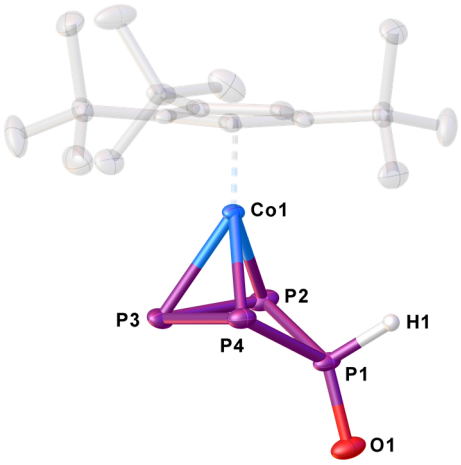


Figure 7: Molecular structure of the anion in **9** in the solid state. Thermal ellipsoids are shown at 50 % probability level. Hydrogen atoms, cations and solvent molecules are omitted for clarity.

The $^{31}P\{^{1}H\}$ NMR spectrum of **10** in thf-d_8 shows three multiplets centered at δ = 74.5, 29.0 and -21.8 ppm with an integral ratio of 2:1:1 indicating an A_2MX spin system. In the ^{31}P NMR

spectrum a coupling between H1 and all P atoms can be observed. In the ^{1}H NMR spectrum, a doublet of triplet of doublets at 7.78 ppm with the coupling constants of $^{1}J_{PH}$ = 356.8, $^{2}J_{PH}$ = 20.6 and $^{3}J_{PH}$ = 5.1 Hz could be detected among the characteristic signals for the Cp''' ligand.

9.3 Conclusion

In summary, we could show that **1** shows a unique tendency to release the ring strain of the *cyclo*-P_4 ligand in reactions with main group nucleophiles and upon reduction. Here, unprecedented aggregation and rearrangement processes occur. The reduction of **1** with K[CpFe(CO)$_2$] yields selecively the dinuclear dianionic complex [(Cp'''Co)$_2$(μ,η^3:η^3-P_8)]$^{2-}$ (**2**) comprising an open realgar-like P_8 cage which for the first time reveals a double η^3-coordinated P_8 ligand. Compound **1** was functionalized with the main group nucleophiles ^{t}BuLi and LiCH$_2$SiMe$_3$ and [Cp'''Co(η^3-P_4R)]$^{-}$ (R = ^{t}Bu (**4**), CH$_2$SiMe$_3$ (**7**)) could be isolated. Both compounds are metastable and show further rearrangement processes such as dimerization and/or fragmention. In comparision to other nucleophile substituted polyphosphorus complexes starting from a four membered ring in **1**, here is the first formed product highly reactive. Thus, compound **4** and **7** can act as a nucleophile and react with another equivalent of **1** under formation of the dinuclear complexes [(Cp'''Co)$_2$(μ,η^3:η^3-P_8R)]$^{-}$ (R = ^{t}Bu (**5**), CH$_2$SiMe$_3$ (**8**)) comprising organo substituted open realgar like P_8R ligands. For **4** also another reaction pathway was observed. The formal dimerization of **4** followed by a fragmentation gives [Cp'''Co(η^3-$P_5{}^{t}Bu_2$)]$^{-}$ (**6**) with an unprecendented diorgano-substituted *cyclo*-P_5 ligand and [Cp'''Co(η^3-P_3)]$^{-}$ (**3**).

9.4 Supporting Information

9.4.1 Synthetic procedures and experimental details

Synthetic Procedures: All manipulations were performed under an atmosphere of dry argon using standard glove-box and Schlenk techniques. All solvents were degassed and purified by standard procedures. The compounds [Cp'''Co(η^4-P_4)] (**1**)[35], $LiCH_2SiMe_3$[36] and K[CpFe$(CO)_2$][37] were prepared according to literature procedures. 2,2,2-cryptand, NaOH and ^{t}BuLi were purchased commercially.

The NMR spectra were recorded with a Bruker Avance 400 spectrometer (^{1}H: 400.13 MHz, ^{31}P: 161.976 MHz). The chemical shifts are given in ppm referenced to external $SiMe_4$ (^{1}H) and H_3PO_4 (^{31}P). Elemental analyses were determined with an Elementar Vario EL III apparatus. The ESI-MS spectra were acquired on a ThermoQuest Finnigan MAT TSQ 7000 mass spectrometer.

9.4.1.1 "Optimized" synthesis of [Cp'''Co(η^4-P_4)]

Two 1 L round bottom flasks were charged with P_4 (each 3.2 g, 25.83 mmol, 5.5 eq) and pentane was added (each ca. 600 mL). After stirring for 30 min it was cooled to 0 °C (ice bath, partial precipitation of P_4). Two 250 mL flasks were charged with [$(Cp'''Co)_2$tol] (each 3.2 g, 4.73 mmol, 1 eq) and dissolved in ca. 150 mL pentane and added to the P_4 solutions slowly (within ca. 15 min). The reaction mixtures were stirred for 30 min, combined in a 2 L round bottom flask and solvent was condensed off (still in ice bath). The brown residue was extracted with CH_2Cl_2 (grey solid should remain completely in 2 L flask to be disposed later (vide infra), (highly pyrophoric!!! (P_4)), silica was added and the solvent removed *in vacuo*. The preabsorbed reaction mixture was purified by column chromatography (SiO_2, pentane, 15x4 cm). With pentane a yellow fraction (P_4) was eluted which has to be neutralized and disposed immediately. In some cases, a weak brown band was eluted, which was disposed. The red fraction (**1**) was collected and the solvent removed *in vacuo* (the red fraction is directly followed by a brown one (dimerization product of **1**), which should not be eluted together with the red one, partially hard to recognize the transition of the bands). All work steps have to be conducted fast, otherwise a decrease of the yield is the result. After removing the solvent **1** can be obtained as a dark red powder (it is recommended to transfer the very concentrated solution of **1** in a small schlenk prior to complete evaporation of the solvent). When traces of P_4 are still present in the obtained solid, it can be sublimed out (vacuum and hot water). The highly pyrophoric residue of the extraction has to be neutralized and disposed very carefully according to the safety instructions.

Yield: 1.0-1.2 g (13-15 %).

9.4.1.2 Synthesis of $[K(dme)]_2[(Cp'''Co)_2(\mu,\eta^3:\eta^3\text{-}P_8)]$ (2a)

A solution of $K[CpFe(CO)_2]$ (260 mg, 1.201 mmol, 1 eq) in dme was added to a stirred solution of **1** (500 mg, 1.201 mmol, 1 eq) in dme at -50 °C while the color changed from dark red to purple. The reaction mixture was warmed to room temperature and after 2 h a color change from purple to brown to green was observed. The solvent was removed *in vacuo*. The residue was washed with hexane to remove $[CpFe(CO)_2]_2$ (brown solution). Hexane was added and dme was added slowly until complete dissolution. After storage at -30 °C overnight, **2a** could be obtained as dark green blocks. The supernatant was decanted off, washed with hexane and the crystals dried in vacuo.

Yield: 260 mg (40%)

^{1}H NMR (thf-d_8, 25 °C): δ [ppm] = 3.96 (s, 4H, $C_5H_2{}^t\text{Bu}_3$), 3.58 (s, 6H, dme), 3.28 (s, 8.5H, dme), 1.31 (s, 36H, $C_5H_2{}^t\textit{Bu}_3$), 1.22 (s, 18H, $C_5H_2{}^t\textit{Bu}_3$).

^{31}P{^{1}H} NMR (thf-d_8, 25 °C): δ [ppm] = 96.2 (m, 2P, P_A, $P_{A'}$), 83.1 (m, 4P, P_M, $P_{M'}$, $P_{M''}$, $P_{M'''}$), -124.2 (m, 2P, P_X, $P_{X'}$) (coupling constants given in table S1).

^{31}P NMR (thf-d_8, 25 °C): δ [ppm] = 96.2 (m, 2P, P_A, $P_{A'}$), 83.1 (m, 4P, P_M, $P_{M'}$, $P_{M''}$, $P_{M'''}$), -124.2 (m, 2P, P_X, $P_{X'}$) (coupling constants taken from simulation of ^{31}P{^{1}H} NMR spectrum).

ESI-MS (dme): *m/z* = 1279.14 (50 %, $[(Cp'''Co)_3P_{13}]^-$), 1217.20 (100 %, $[(Cp'''Co)_3P_{11}]^-$), 955.97 (23 %, $[(Cp'''Co)_2P_{12}]^-$), 895.07 (21 %, $[(Cp'''Co)_2P_{10}H]^-$), 833.12 (23%, $[(Cp'''Co)_2P_8H]$).

EA $C_{42}H_{78}O_4K_2P_8Co_2$: calc [%]: C 46.24; H 7.21; found [%]: C 46.11; H 7.04.

9.4.1.3 Synthesis of $[K(2,2,2\text{-crypt})]_2[(Cp'''Co)_2(\mu,\eta^3:\eta^3\text{-}P_8)]$ (2b)

A solution of $K[CpFe(CO)_2]$ (101.7 mg, 0.47 mmol, 1 eq) in dme was added to a stirred solution of **1** (196 mg, 0.47 mmol, 1 eq) in dme at -50 °C while the color changed from dark red to purple. The reaction mixture was warmed to room temperature and after 2 h a color change from purple to brown to green was observed. The solvent was removed *in vacuo*. The residue was washed with hexane to remove $[CpFe(CO)_2]_2$ (brown solution). The residue was dissolved in dme (dark green) and 2,2,2-cryptand (177.2 mg, 0.47 mmol, 1 eq) in dme was added. After stirring for 5 minutes some green precipitate was formed. Acetonitrile was added dropwise until complete dissolution. After storage at -30 °C, **2b** can be obtained as dark green plates. The supernatant was decanted off, washed with hexane and the crystals dried in vacuo.

Yield: 94 mg (24 %).

^{1}H NMR (CD_3CN, 25 °C): δ [ppm] = 3.94 (s, 4H, $C_5H_2{}^tBu_3$), 3.56 (s, 24H, 2,2,2-cryptand), 3.52 (t, 24H, 2,2,2-cryptand, $^1J_{HH}$ = 4.7 Hz), 2.53 (t, 24H, 2,2,2-cryptand, $^1J_{HH}$ = 4.7 Hz), 1.28 (s, 36H, $C_5H_2{}^tBu_3$), 1.21 (s, 18H, $C_5H_2{}^tBu_3$).

^{31}P{^{1}H} NMR (CD_3CN, 25 °C): δ [ppm] = 91.6 (m, 6P, P_8), -124.1 (m, 2P, P_8).

^{31}P NMR (CD_3CN, 25 °C): δ [ppm] = 91.6 (m, 6P, P_8), -124.1 (m, 2P, P_8).

ESI-MS (dme): *m/z* = 1279.14 (100 %, $[(Cp'''Co)_3P_{13}]^-$), 1217.20 (82 %, $[(Cp'''Co)_3P_{11}]^-$).

EA $C_{70}H_{130}O_{12}N_4K_2P_8Co_2$: calc [%]: C 50.54; H 7.88; N 3.37; found [%]: C 49.86; H 7.68; N 3.09.

9.4.1.4 Synthesis of [Li(2,2,2-crypt)][Cp'''Co(η^3-P$_4$^{t}Bu)] (4)

a) A solution of ^{t}BuLi in pentane (0.96 ml, 0.249 mol/L, 0.24 mmol, 1 eq) was added to a stirred solution of **I** (100 mg, 0.24 mmol, 1 eq) in thf at -80 °C while the color changed immediately from red to brown. After five minutes a solution of 2,2,2-cryptand (90.4 mg, 0.24 mmol, 1 eq) in thf was added and the reaction mixture warmed to room temperature. The solvent was reduced *in vacuo* and NMR spectra with a C_6D_6 capillary was recorded revealing the clean formation of **4**. The thf solution was layered with hexane at room temperature. After a few days, **4** can be obtained as brown flat rods. The supernatant was decanted off and the obtained crystals dried *in vacuo*.

Yield: 98 mg (48 %).

^{1}H NMR (thf-d_8, 25 °C): δ [ppm] = 4.90 (s, 2H, $C_5H_2{}^tBu_3$), 3.70 (s, 12H, 2,2,2-crypt), 3.64 (pt, $^3J_{HH}$ = 5.1 Hz, 12H, 2,2,2-crypt), 2.72 (pt, $^3J_{HH}$ = 5.1 Hz, 12H, 2,2,2-crypt), 1.47(s, 9H, $P_4{}^tBu$), 1.36, 1.35, 1.34 (three overlapping singlets, 27H, $C_5H_2{}^tBu_3$).

^{31}P{^{1}H} NMR (thf-d_8, 25 °C): δ [ppm] = 94.1 (t, $^1J_{PP}$ = 255.63 Hz, $^2J_{PP}$ = 2.48 Hz, 1P, P_A), 88.7 (t, $^1J_{PP}$ = 186.23 Hz, $^2J_{PP}$ = 3.97 Hz, 1P, P_M), -25.9 (dd, $^1J_{PP}$ = 255.63 Hz, $^1J_{PP}$ = 186.23 Hz, 2P, P_X, $P_{X'}$) (coupling constants obtained from the simulation, cf. Figure S4, Table S2).

^{31}P NMR (thf-d_8, 25 °C): δ [ppm] = 94.1 (t, $^1J_{PP}$ = 255.60 Hz, $^2J_{PP}$ = 1.49 Hz, $^5J_{PH}$ = 0.77 Hz, 1P, P_A), 88.7 (tdec, $^1J_{PP}$ = 186.26 Hz, $^2J_{PP}$ = -0.30 Hz, $^3J_{PH}$ = 9.12 Hz 1P, P_M), -26.0 (dd, $^1J_{PP}$ = 255.60 Hz, $^1J_{PP}$ = 186.26 Hz, $^4J_{PH}$ = -1.12 Hz, 2P, P_X, $P_{X'}$) (coupling constants obtained from the simulation, cf. Figure S4, Table S3).

EA $C_{39}H_{74}N_2O_6P_4CoLi$: calc [%]: C 54.67; H 8.71; N 3.27; found [%]: C 54.35; H 8.42; N 3.27.

b) A solution of ^{t}BuLi in pentane (0.96 ml, 0.249 mol/L, 0.24 mmol, 1 eq) was added to a stirred solution of **I** (100 mg, 0.24 mmol, 1 eq) in thf at -80 °C while the color changed immediately from red to brown. The reaction mixture was warmed to room temperature. The solvent was reduced *in vacuo* and NMR spectra in thf-d_8 were recorded showing a mixture of **3**, **4**, **5** and **6**.

Compound **5**:

^{31}P{^{1}H} NMR (thf-d_8, 25 °C): δ [ppm] = 231.9 (m, $^{1}J_{PP}$ = 470.35 Hz, $^{1}J_{PP}$ = 441.32 Hz, $^{2}J_{PP}$ = -1.21 Hz, $^{2}J_{PP}$ = 13.24 Hz, 1P, P_A), 130.9 (ddd, $^{1}J_{PP}$ = 346.33 Hz, $^{1}J_{PP}$ = 363.12 Hz, $^{2}J_{PP}$ = 14.02 Hz, $^{2}J_{PP}$ = -4.69 Hz, $^{2}J_{PP}$ = 69.86 Hz, $^{3}J_{PP}$ = -1.52 Hz, 2P, P_M), 74.7 (dddd, $^{1}J_{PP}$ = 470.35 Hz, $^{1}J_{PP}$ = 358.96 Hz, $^{2}J_{PP}$ = -4.69 Hz, $^{2}J_{PP}$ = 69.86 Hz, $^{2}J_{PP}$ = -16.59 Hz, $^{2}J_{PP}$ = -14.40, $^{3}J_{PP}$ = 1.02 Hz, 2P, P_N), 1.34 (dt, $^{1}J_{PP}$ = 441.32 Hz, $^{1}J_{PP}$ = 346.33 Hz, $^{2}J_{PP}$ = -14.40 Hz, $^{2}J_{PP}$ = 6.80 Hz, 1P, P_O), -123.9 (t, $^{1}J_{PP}$ = 363.12 Hz, $^{1}J_{PP}$ = 358.96 Hz, $^{2}J_{PP}$ = 6.80 Hz, $^{3}J_{PP}$ = -1.52 Hz, $^{3}J_{PP}$ = 1.02 Hz, $^{4}J_{PP}$ = 20.96 Hz, 2P, P_X) (coupling constants obtained from the simulation, cf. Figure S8, Table S5).

^{31}P NMR (thf-d_8, 25 °C): δ [ppm] = 231.9 (m, 1P, P_A), 130.9 (m, 2P, P_M), 74.7 (m, 2P, P_N), 1.34 (m, 1P, P_O), -123.9 (m, 2P, P_X) (signals 231.9 and 1.34 ppm show further broadening caused by proton coupling, too bad resolved for simulation).

Compound **6**:

^{31}P{^{1}H} NMR (thf-d_8, 25 °C): δ [ppm] = 106.8 (ddd, $^{1}J_{PP}$ = 400.71 Hz, $^{1}J_{PP}$ = 342.90 Hz, $^{2}J_{PP}$ = 65.46 Hz, $^{2}J_{PP}$ = 5.97 Hz, 1P, P_A), 98.9 (tdd, $^{1}J_{PP}$ = 352.77 Hz, $^{1}J_{PP}$ = 348.39, $^{2}J_{PP}$ = 65.46 Hz, $^{2}J_{PP}$ = 12.84 Hz, 1P, P_B), 77.7 (dddd, $^{1}J_{PP}$ = 352.77 Hz, $^{1}J_{PP}$ = 322.67 Hz, $^{2}J_{PP}$ = 5.97 Hz, $^{2}J_{PP}$ = 10.00 Hz, 1P, P_C), 31.3 (dddd, $^{1}J_{PP}$ = 400.71 Hz, $^{1}J_{PP}$ = 322.67 Hz, $^{2}J_{PP}$ = 12.84, $^{2}J_{PP}$ = 7.23 Hz, 1P, P_M), -146.9 (t, $^{1}J_{PP}$ = 342.90 Hz, $^{1}J_{PP}$ = 348.39 Hz, $^{2}J_{PP}$ = 10.00 Hz, $^{2}J_{PP}$ = 7.23 Hz, 1P, P_X) (coupling constants obtained from the simulation, cf. Figure S9, Table S6).

^{31}P{^{1}H} NMR (thf-d_8, 25 °C): δ [ppm] = 106.8 (m, 1P, P_A), 98.9 (m, 1P, P_B), 77.7 (m, 1P, P_C), 31.3 (m, 1P, P_M), -146.9 (m, 1P, P_X) (signals 77.7 and 31.3 ppm show further broadening caused by proton coupling, too bad resolved for simulation).

9.4.1.5 Synthesis of [Li(2,2,2-crypt)][Cp'''Co(η^3-P$_4$CH$_2$SiMe$_3$)] ([Li(2,2,2-crypt)]7) and [Li(12-c-4)$_2$][Cp'''Co(η^3-P$_4$CH$_2$SiMe$_3$)] ([Li(12-c-4)$_2$]7)

a) Reaction with 2,2,2-cryptand: A solution of $LiCH_2SiMe_3$ in thf (22.6 mg, 0.24 mmol, 1 eq) was added to a stirred solution of **1** (100 mg, 0.24 mmol, 1 eq) in thf at -80 °C while the color changed immediately from red to brown. After five minutes a solution of 2,2,2-cryptand (90.4 mg, 0.24 mmol, 1 eq) in thf was added and the reaction mixture warmed to room temperature.

The solvent was reduced *in vacuo* and NMR spectra in thf-d_8 were recorded revealing the formation two isomers **7a** and **7b** in a ratio of 1:0.25 beside other products. The residue was dissolved in a small amount thf and precipitated with pentane (brown oily solid). The NMR spectra in thf-d_8 of the obtained oil reveals a clean mixture of **7a** and **7b** in a ratio of 1:0.36.

Compound [Li(2,2,2-crypt)]**7a**:

^{1}H NMR (thf-d_8, 25 °C): δ [ppm] = 4.80 (s, 2H, $C_5H_2{}^t Bu_3$), 3.73 (s, 12H, 2,2,2-crypt), 3.67 (t, $^{3}J_{HH}$ = 4.9 Hz, 12H, 2,2,2-crypt), 2.75 (t, $^{3}J_{HH}$ = 4.9 Hz, 12H, 2,2,2-crypt), 2.20 (s, 2H, CH_2SiMe_3), 1.48 (s, 9H, $C_5H_2{}^t Bu_3$), 1.34 (s, 18H, $C_5H_2{}^t Bu_3$), 0.02 (s, 9H, CH_2SiMe_3).

^{31}P{^{1}H} NMR (thf-d_8, 25 °C): δ [ppm] = 52.3 (td, $^{1}J_{PP}$ = 260.89 Hz, $^{2}J_{PP}$ = 10.95 Hz, 1P, P_A), 45.9 (td, $^{1}J_{PP}$ = 152.24 Hz, $^{2}J_{PP}$ = 10.95 Hz, 1P, P_M), 18.8 (dd, $^{1}J_{PP}$ = 260.89 Hz, $^{1}J_{PP}$ = 152.24 Hz, $^{2}J_{PP}$ = -8.00 Hz, 2P, $P_{XX'}$), (coupling constants obtained from the simulation, cf. Figure S12, Table S7).

^{31}PNMR (thf-d_8, 25 °C): δ [ppm] = 52.3 (td, $^{1}J_{PP}$ = 260.89 Hz, $^{2}J_{PP}$ = 10.95 Hz, 1P, P_A), 45.9 (td, $^{1}J_{PP}$ = 152.24 Hz, $^{2}J_{PP}$ = 10.95 Hz, 1P, P_M), 18.8 (dd, $^{1}J_{PP}$ = 260.89 Hz, $^{1}J_{PP}$ = 152.24 Hz, $^{2}J_{PP}$ = -8.00 Hz, 2P, $P_{XX'}$), (coupling constants obtained from the simulation of the ^{31}P{^{1}H}, no further coupling observed).

Compound [Li(2,2,2-crypt)]**7b**:

^{1}H NMR (thf-d_8, 25 °C): δ [ppm] = 4.75 (s, 2H, $C_5H_2{}^t Bu_3$), 3.73 (s, 12H, 2,2,2-crypt), 3.67 (t, $^{3}J_{HH}$ = 4.9 Hz, 12H, 2,2,2-crypt), 2.75 (t, $^{3}J_{HH}$ = 4.9 Hz, 12H, 2,2,2-crypt), 1.36 (s, 18H, $C_5H_2{}^t Bu_3$), 1.31 (s, 2H, CH_2SiMe_3), 1.26 (s, 9H, $C_5H_2{}^t Bu_3$), -0.07 (s, 9H, CH_2SiMe_3).

^{31}P{^{1}H} NMR (thf-d_8, 25 °C): δ [ppm] = 39.4 (td, $^{1}J_{PP}$ = 135.82 Hz, $^{2}J_{PP}$ = 14.38 Hz, 1P, P_A), 3.8 (dd, $^{1}J_{PP}$ = 276.36 Hz, $^{1}J_{PP}$ = 135.82 Hz, $^{2}J_{PP}$ = -84.01 Hz, 2P, $P_{MM'}$), -78.2 (td, $^{1}J_{PP}$ = 276.36 Hz, $^{2}J_{PP}$ = 14.38 Hz, 1P, P_X), (coupling constants obtained from the simulation, cf. Figure S12, Table S7).

^{31}P NMR (thf-d_8, 25 °C): δ [ppm] = 39.4 (td, $^{1}J_{PP}$ = 135.82 Hz, $^{2}J_{PP}$ = 14.38 Hz, 1P, P_A), 3.8 (dd, $^{1}J_{PP}$ = 276.36 Hz, $^{1}J_{PP}$ = 135.82 Hz, $^{2}J_{PP}$ = -84.01 Hz, 2P, $P_{MM'}$), -78.2 (td, $^{1}J_{PP}$ = 276.36 Hz, $^{2}J_{PP}$ = 14.38 Hz, 1P, P_X), (coupling constants obtained from the simulation of the ^{31}P{^{1}H}, no further coupling observed).

b) Reaction with 12-c-4: A solution of $LiCH_2SiMe_3$ in thf (22.6 mg, 0.24 mmol, 1 eq) was added to a stirred solution of **1** (100 mg, 0.24 mmol, 1 eq) in thf at -80 °C while the color changed immediately from red to brown. After five minutes a solution of 12-c-4 in dme (0.60

mL, 0.48 mmol, 0.8102 mol/L, 2 eq) was added and the reaction mixture warmed to room temperature. The solvent was reduced *in vacuo* and NMR spectra in thf-d_8 were recorded revealing the formation two isomers **7a** and **7b** in a ratio of 1:1.33 beside other products. The residue was dissolved in a small amount thf and precipitated with pentane. The NMR spectra of the precipitated solid reveals a clean mixture of **7a** and **7b** in a ratio of 1:1.78. The supernatant was decanted off, the residue dissolved in thf and layered with hexane at room temperature. After a few days, very few single crystals of **7a** could be obtained.

Yield: 20 mg (precipitated solid, 10 %).

Compound [Li(12-c-4)$_2$]**7a**:

^{1}H NMR (thf-d_8, 25 °C): δ [ppm] = 4.83 (s, 2H, $C_5H_2{}^t Bu_3$), 3.77 (s, 32H, 12-c-4), 2.20 (s, 2H, CH_2SiMe_3), 1.48 (s, 9H, $C_5H_2{}^t Bu_3$), 1.34 (s, 18H, $C_5H_2{}^t Bu_3$), 0.02 (s, 9H, CH_2SiMe_3).

^{31}P{^{1}H} NMR (thf-d_8, 25 °C): δ [ppm] = 50.1 (td, $^1J_{PP}$ = 259.18 Hz, $^2J_{PP}$ = 10.53 Hz, 1P, P_A), 46.5 (td, $^1J_{PP}$ = 152.95 Hz, $^2J_{PP}$ = 10.53 Hz, 1P, P_M), 17.42 (dd, $^1J_{PP}$ = 259.18 Hz, $^1J_{PP}$ = 152.95 Hz, $^2J_{PP}$ = -8.00 Hz, 2P, $P_{XX'}$), (coupling constants obtained from the simulation, cf. Figure S12, Table S8).

^{31}PNMR (thf-d_8, 25 °C): δ [ppm] = 50.1 (td, $^1J_{PP}$ = 259.18 Hz, $^2J_{PP}$ = 10.53 Hz, 1P, P_A), 46.5 (td, $^1J_{PP}$ = 152.95 Hz, $^2J_{PP}$ = 10.53 Hz, 1P, P_M), 17.42 (dd, $^1J_{PP}$ = 259.18 Hz, $^1J_{PP}$ = 152.95 Hz, $^2J_{PP}$ = -8.00 Hz, 2P, $P_{XX'}$), (coupling constants obtained from the simulation of the ^{31}P{^{1}H}, no further coupling observed).

Compound [Li(12-c-4)$_2$]**7b**:

^{1}H NMR (thf-d_8, 25 °C): δ [ppm] = 4.79 (s, 2H, $C_5H_2{}^t Bu_3$), 3.77 (s, 32H, 12-c-4), 1.36 (s, 18H, $C_5H_2{}^t Bu_3$), 1.32 (s, 2H, CH_2SiMe_3), 1.26 (s, 9H, $C_5H_2{}^t Bu_3$), -0.07 (s, 9H, CH_2SiMe_3).

^{31}P{^{1}H} NMR (thf-d_8, 25 °C): δ [ppm] = 38.93 (td, $^1J_{PP}$ = 135.34 Hz, $^2J_{PP}$ = 13.76 Hz, 1P, P_A), 2.8 (dd, $^1J_{PP}$ = 273.40 Hz, $^1J_{PP}$ = 135.34 Hz, $^2J_{PP}$ = -84.00 Hz, 2P, $P_{MM'}$), -79.9 (td, $^1J_{PP}$ = 273.40 Hz, $^2J_{PP}$ = 13.76 Hz, 1P, P_X), (coupling constants obtained from the simulation, cf. Figure S12, Table S8).

^{31}P NMR (thf-d_8, 25 °C): δ [ppm] = 38.93 (td, $^1J_{PP}$ = 135.34 Hz, $^2J_{PP}$ = 13.76 Hz, 1P, P_A), 2.8 (dd, $^1J_{PP}$ = 273.40 Hz, $^1J_{PP}$ = 135.34 Hz, $^2J_{PP}$ = -84.00 Hz, 2P, $P_{MM'}$), -79.9 (td, $^1J_{PP}$ = 273.40 Hz, $^2J_{PP}$ = 13.76 Hz, 1P, P_X), (coupling constants obtained from the simulation of the ^{31}P{^{1}H}, no further coupling observed).

Precipitated solid **7a**/**7b**:

EA $C_{37}H_{72}O_8P_4CoLiSi$: calc [%]: C 51.51; H 8.41; found [%]: C 51.10; H 8.27.

9.4.1.6 Synthesis of $[Li(dme)_3][(Cp'''Co)_2(\mu,\eta^3{:}\eta^3\text{-}P_8CH_2SiMe_3$ (8)

A solution of $LiCH_2SiMe_3$ (11.3 mg, 0.12 mmol, 1 eq) in thf was added to a stirred solution of **1** (100 mg, 0.24 mmol, 1 eq) in thf at -80°C while the color changed from red to brown. The reaction mixture was warmed to room temperature, while the color changed to dark green. The solvent was removed *in vacuo*. Hexane was added to the residue (partial dissolution) and dme dropwise until complete dissolution. After storage at -30 °C **8** can be obtained as dark green blocks. The supernatant was decanted off and washed with cold (-50 °C) hexane. The crystals were dried *in vacuo*.

Yield: 47 mg (33%).

^{1}H NMR (thf-d_8, 300 K): δ [ppm] = 4.53 (s, 2H, $C_5H_2{}^t Bu_3$), 4.15 (s, 2H, $C_5H_2{}^t Bu_3$), 3.43 (s, 12H, Li(*dme*)$_3$), 3.27 (s, 12H, Li(*dme*)$_3$), 1.80 (br, 2H, $P_8CH_2SiMe_3$), 1.34 (s, 18H, $C_5H_2{}^t Bu_3$), 1.31 (s, 18H, $C_5H_2{}^t Bu_3$), 1.29 (s, 18H, $C_5H_2{}^t Bu_3$), 0.32 (s, 9H, $P_8CH_2SiMe_3$).

^{1}H{^{31}P} NMR (thf-d_8, 300 K, decoupled at -114 ppm): δ [ppm] = 4.53 (d, $^3J_{HH}$ = 2.2 Hz, 2H, $C_5H_2{}^t Bu_3$), 4.15 (d, d, $^3J_{HH}$ = 2.2 Hz, 2H, $C_5H_2{}^t Bu_3$), 3.43 (s, 12H, Li(*dme*)$_3$), 3.27 (s, 12H, Li(*dme*)$_3$), 1.80 (d, $^2J_{PH}$ = 8.5 Hz, 2H, $P_8CH_2SiMe_3$), 1.34 (s, 18H, $C_5H_2{}^t Bu_3$), 1.31 (s, 18H, $C_5H_2{}^t Bu_3$), 1.29 (s, 18H, $C_5H_2{}^t Bu_3$), 0.32 (s, 9H, $P_8CH_2SiMe_3$).

^{1}H{^{31}P} NMR (thf-d_8, 300 K, decoupled at +71 ppm): δ [ppm] = 4.53 (d, $^3J_{HH}$ = 2.2 Hz, 2H, $C_5H_2{}^t Bu_3$), 4.15 (d, d, $^3J_{HH}$ = 2.2 Hz, 2H, $C_5H_2{}^t Bu_3$), 3.43 (s, 12H, Li(*dme*)$_3$), 3.27 (s, 12H, Li(*dme*)$_3$), 1.80 (s, 2H, $P_8CH_2SiMe_3$), 1.34 (s, 18H, $C_5H_2{}^t Bu_3$), 1.31 (s, 18H, $C_5H_2{}^t Bu_3$), 1.29 (s, 18H, $C_5H_2{}^t Bu_3$), 0.32 (s, 9H, $P_8CH_2SiMe_3$).

^{31}P{^{1}H} NMR (thf-d_8, 193 K): δ [ppm] = 187.9 (q, $^1J_{PP}$ = 448.32 Hz, $^1J_{PP}$ = 424.01 Hz, $^2J_{PP}$ = -2.44 Hz, $^2J_{PP}$ = 12.49 Hz, 1P, P_A), 102.8 (td, $^1J_{PP}$ = 351.60 Hz, $^1J_{PP}$ = 366.96 Hz, $^2J_{PP}$ = -2.44 Hz, $^2J_{PP}$ = 6.65 Hz, $^2J_{PP}$ = 62.41 Hz, $^2J_{PP}$ = -12.85 Hz, $^3J_{PP}$ = 0.20 Hz, 2P, P_M), 72.5 (ddd, $^1J_{PP}$ = 448.32 Hz, $^1J_{PP}$ = 369.36 Hz, $^2J_{PP}$ = 62.41 Hz, $^2J_{PP}$ = -12.85 Hz, $^2J_{PP}$ = -3.66 Hz, $^2J_{PP}$ = -17.34 Hz, $^3J_{PP}$ = 0.87 Hz, 2P, P_N), 40.5 (dt, $^1J_{PP}$ = 424.01 Hz, $^1J_{PP}$ = 351.60 Hz, $^2J_{PP}$ = -17.34 Hz, $^2J_{PP}$ = 7.69 Hz, 1P, P_O), -118.8 (t, $^1J_{PP}$ = 366.96 Hz, $^1J_{PP}$ = 369.36 Hz, $^2J_{PP}$ = 12.49 Hz, $^2J_{PP}$ = 7.69 Hz, $^3J_{PP}$ = 0.20 Hz, $^3J_{PP}$ = 0.87 Hz, $^4J_{PP}$ = 19.47 Hz, 2P, P_X). (coupling constants obtained from the simulation, cf. Figure S13, Table S9).

^{31}P NMR (thf-d_8, 193 K): δ [ppm] = 187.9 (m, 1P, P_A), 102.8 (m, 2P, P_M), 72.5 (m, 2P, P_N), 40.5 (m, 1P, P_O), -118.8 (m, 2P, P_X). (no further broadening or splitting of the signals detected).

ESI-MS (anion, dme): *m/z* = 919.3 (100 %, $[M]^-$).

9.4.1.7 Synthesis of [Na(dme)$_2$][Cp'''Co(η^3-P$_4$(O)H)] (10)

NaOH (9.6 mg, 0.24 mmol, 1 eq) and **1** (100 mg, 0.24 mmol, 1 eq) were weighed in together, dme was added and stirred for three days. The solvent was reduced *in vacuo*, layered with hexane and stored at -30 °C. After a few days, **10** can be obtained as dark brown blocks. The supernatant was decanted off, washed with hexane and dried *in vacuo*.

Yield: 84 mg (55 %).

^{1}H NMR (thf-d$_8$, 300 K): δ [ppm] = 7.78 (dtd, $^1J_{PH}$ = 356.77 Hz, $^2J_{PH}$ = 20.56 Hz, $^3J_{PH}$ = 5.12 Hz, 1H, P$_4$(O)*H*), 4.95 (s, 2H, C$_5$*H*$_2$^{t}Bu$_3$), 3.43 (s, 8H, dme), 3.27 (s, 12H, dme), 1.36 (s, 18H, C$_5$H$_2$^{t}*Bu*$_3$), 1.34 (s, 9H, C$_5$H$_2$^{t}*Bu*$_3$).

^{1}H{^{31}P} NMR (thf-d$_8$, 300 K): δ [ppm] = 7.78 (s, 1H, P$_4$(O)*H*), 4.95 (s, 2H, C$_5$*H*$_2$^{t}Bu$_3$), 3.43 (s, 8H, dme), 3.27 (s, 12H, dme), 1.36 (s, 18H, C$_5$H$_2$^{t}*Bu*$_3$), 1.34 (s, 9H, C$_5$H$_2$^{t}*Bu*$_3$).

^{31}P{^{1}H} NMR (thf + C$_6$D$_6$ capillary, 25 °C): δ [ppm] = 74.8 (dd, $^1J_{PP}$ = 262.67 Hz, $^1J_{PP}$ = 246.57 Hz, $^2J_{PP}$ = -9.00 Hz, 2P, P_A), 29.0 (ddd, $^1J_{PP}$ = 262.67 Hz, $^2J_{PP}$ = 4.92Hz, 1P, P_M), -21.8 (t, $^1J_{PP}$ = 246.57 Hz, $^2J_{PP}$ = 4.92 Hz, 1P, P_X) (coupling constants obtained from the simulation, cf. Figure S17, Table S10).

^{31}P NMR (thf + C$_6$D$_6$ capillary, 25 °C): δ [ppm] = 74.8 (dd, $^1J_{PP}$ = 262.71 Hz, $^1J_{PP}$ = 246.64 Hz, $^2J_{PH}$ = 20.56 Hz, 2P, P_A), 29.0 (dddd, $^1J_{PP}$ = 262.67 Hz, $^2J_{PP}$ = 4.92Hz, $^1J_{PH}$ = 356.77 Hz, 1P, P_M), -21.8 (t, $^1J_{PP}$ = 246.57 Hz, $^2J_{PP}$ = 4.92 Hz, $^3J_{PH}$ = 5.12 Hz, 1P, P_X) (coupling constants obtained from the simulation, cf. Figure S17, Table S10).

ESI-MS (anion, dme): *m/z* = 867.2 (100 %. [2M+H]$^-$), 433.0 (12 %, [M]$^-$).

EA C$_{25}$H$_{50}$O$_5$P$_4$CoNa: calc [%]: C 47.18; H 7.92; found [%]: C 46.94; H 7.87.

9.4.2 NMR spectroscopic investigations

9.4.2.1 $[K(dme)]_2[(Cp'''Co)_2(\mu,\eta^3:\eta^3\text{-}P_8)]$ (2a)

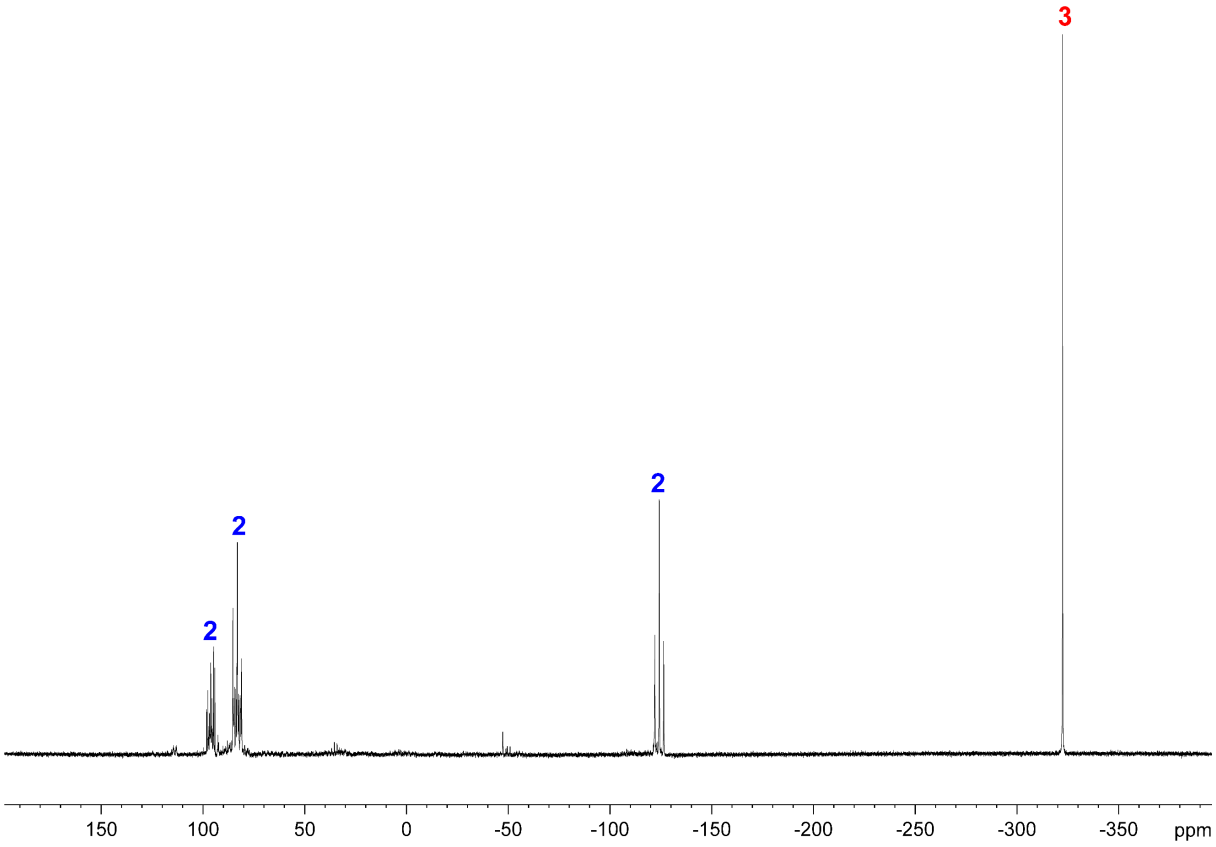


Figure S1: $^{31}P\{^1H\}$ NMR spectrum of the crude reaction mixture from the reaction of **1** with KC_8 in thf-d_8 at room temperature.

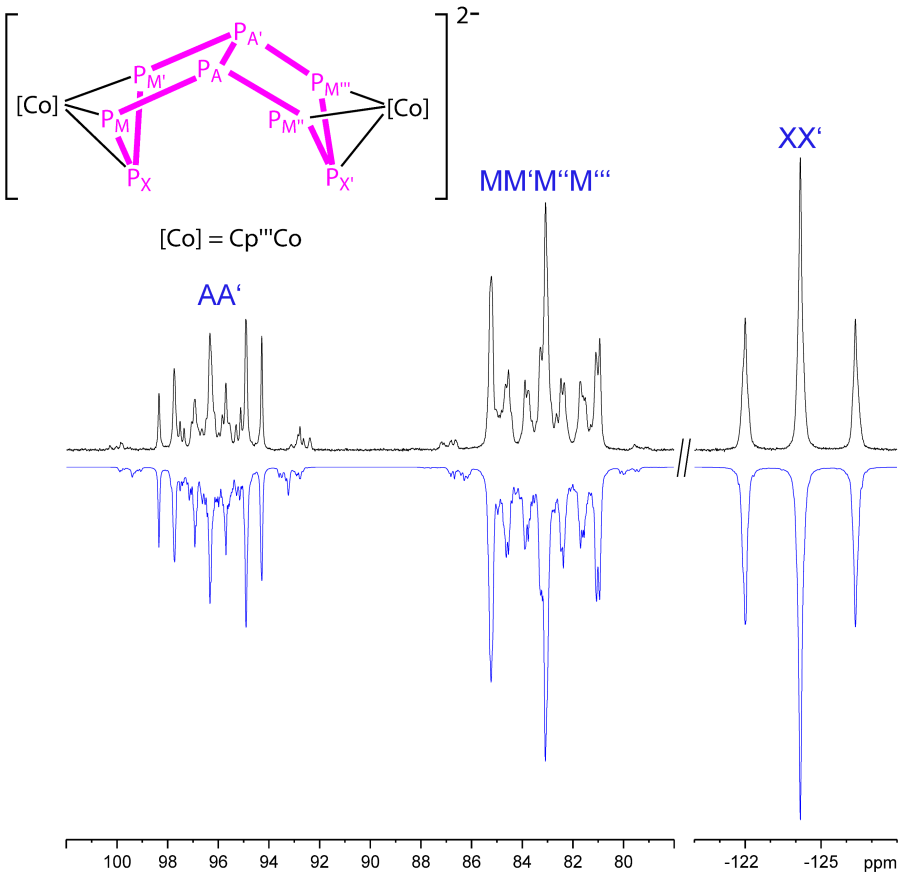


Figure S2: $^{31}P\{^{1}H\}$ NMR spectrum of **2a** in thf-d_8 at room temperature (experimental (black) and simulated (blue)).

Table S1: Coupling constants and chemical shifts obtained from the simulation.

coupling constants [Hz]

$^{1}J_{P_AP_{A'}}$	309.44	$^{2}J_{P_{A'}P_{M''}}$	23.96
$^{1}J_{P_AP_M}$	330.75	$^{2}J_{P_{A'}P_X}$	-4.96
$^{1}J_{P_AP_{M''}}$	301.97	$^{2}J_{P_{A'}P_{X'}}$	4.28
$^{1}J_{P_{A'}P_{M'}}$	292.35	$^{2}J_{P_MP_{M'}}$	-57.81
$^{1}J_{P_{A'}P_{M'''}}$	343.58	$^{2}J_{P_MP_{M''}}$	-20.81
$^{1}J_{P_MP_X}$	351.21	$^{2}J_{P_{M'}P_{M'''}}$	-11.67
$^{1}J_{P_{M'}P_X}$	359.89	$^{2}J_{P_{M''}P_{M'''}}$	44.81
$^{1}J_{P_{M''}P_{X'}}$	355.82	$^{3}J_{P_MP_{M'''}}$	-11.83
$^{1}J_{P_{M'''}P_{X'}}$	362.15	$^{3}J_{P_MP_{X'}}$	8.65
$^{2}J_{P_AP_{M'}}$	21.49	$^{3}J_{P_{M'}P_{M''}}$	19.83
$^{2}J_{P_AP_{M'''}}$	-10.88	$^{3}J_{P_{M'}P_{X'}}$	-5.40
$^{2}J_{P_AP_X}$	9.55	$^{3}J_{P_{M''}P_X}$	-1.67
$^{2}J_{P_AP_{X'}}$	-0.66	$^{3}J_{P_{M'''}P_X}$	-15.65
$^{2}J_{P_{A'}P_M}$	11.96	$^{4}J_{P_XP_{X'}}$	21.50

chemical shifts [ppm]

$P_{AA'}$	96.16		
$P_{MM'M''M'''}$	83.32	R value	1.56 %
$P_{XX'}$	-124.17		

9.4.2.2 $[K(2,2,2\text{-crypt})]_2[(Cp'''Co)_2(\mu,\eta^3{:}\eta^3\text{-}P_8)]$ (2b)

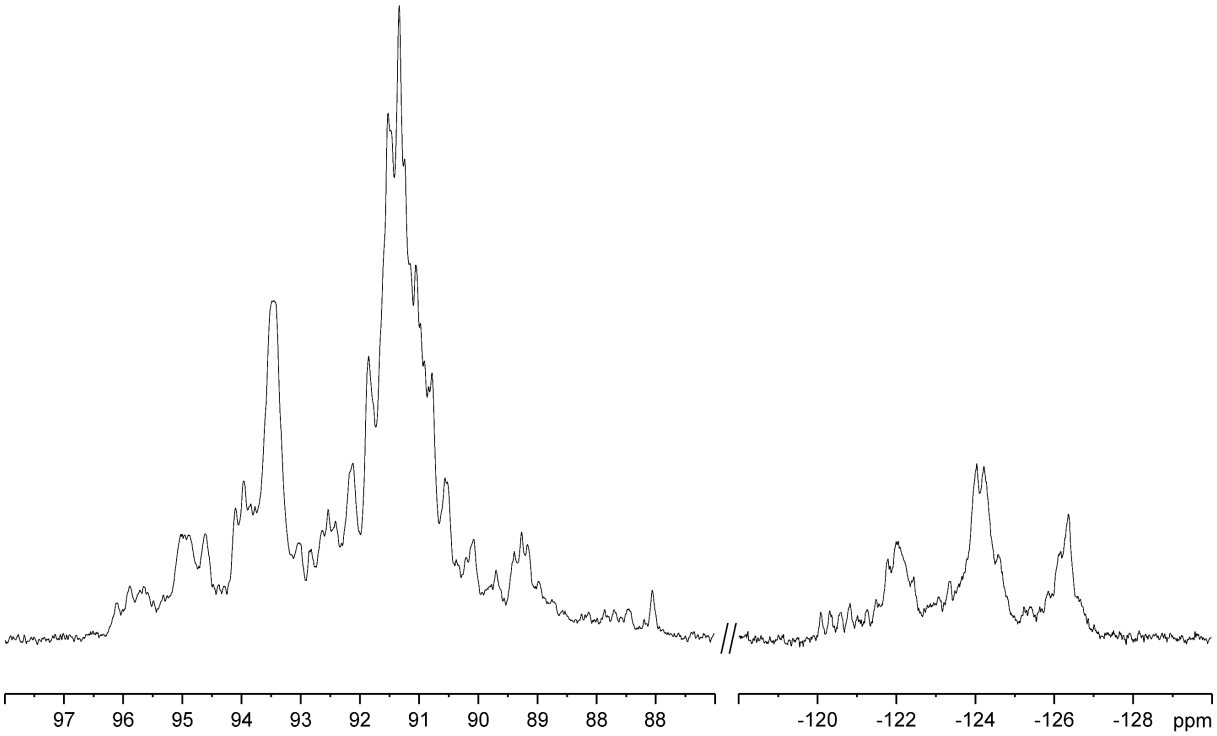


Figure S3: $^{31}P\{^1H\}$ NMR spectrum of **2b** in CD_3CN at room temperature.

9.4.2.3 [Li(2,2,2-crypt)][Cp'''Co(η^3-P$_4$^{t}Bu)] (4)

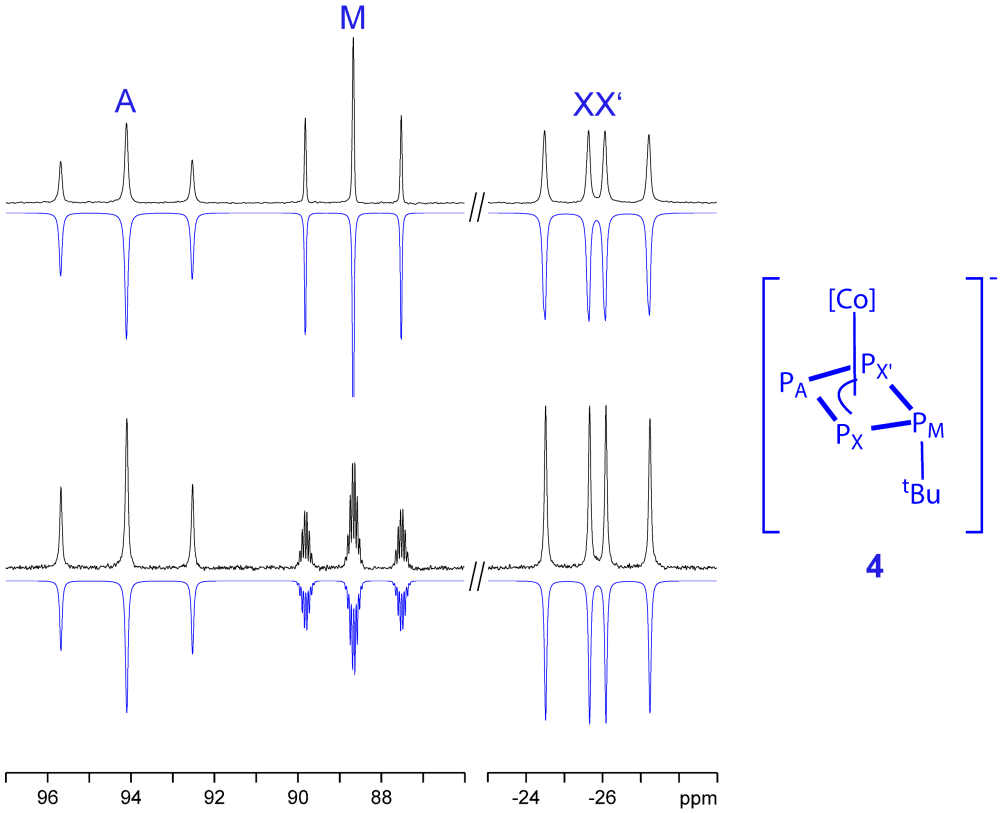


Figure S4: $^{31}P\{^1H\}$ (top) and ^{31}P (bottom) NMR spectrum of **4** thf with C_6D_6 capillary at room temperature (experimental (black) and simulated (blue)).

Table S2: Coupling constants and chemical shifts obtained from the simulation of the $^{31}P\{^1H\}$ NMR spectrum.

coupling constants [Hz]		chemical shifts [ppm]	
$^1J_{P_AP_X} = {}^1J_{P_AP_{X'}}$	255.63	P_A	94.13
$^1J_{P_MP_X} = {}^1J_{P_MP_{X'}}$	186.23	P_M	88.64
$^2J_{P_AP_M}$	2.48	P_X	-25.92
$^2J_{P_XP_{X'}}$	3.97	$P_{X'}$	-25.92
R value		0.84 %	

Table S3: Coupling constants and chemical shifts obtained from the simulation of the ^{31}P NMR spectrum.

coupling constants [Hz]		chemical shifts [ppm]	
$^1J_{P_AP_X} = {}^1J_{P_AP_{X'}}$	255.60	P_A	94.11
$^1J_{P_MP_X} = {}^1J_{P_MP_{X'}}$	186.26	P_M	88.62
$^2J_{P_AP_M}$	1.49	P_X	-25.95
$^2J_{P_XP_{X'}}$	-0.30	$P_{X'}$	-25.95
$^3J_{P_MH}$	9.12		
$^4J_{P_XH} = {}^4J_{P_{X'}H}$	-1.12		
$^5J_{P_AH}$	0.77		
R value		0.24%	

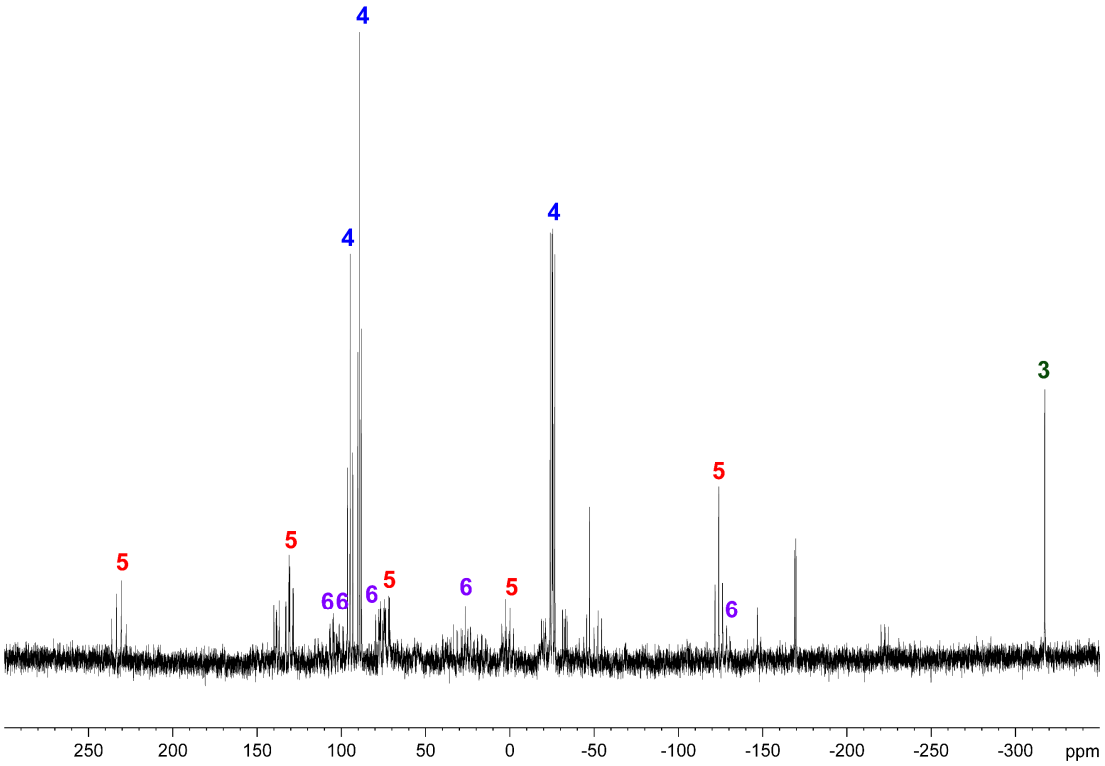


Figure S5: $^{31}P\{^{1}H\}$ NMR spectrum of the reaction of **1** with ^{t}BuLi at room temperature thf-d_8 at room temperature (large sweep).

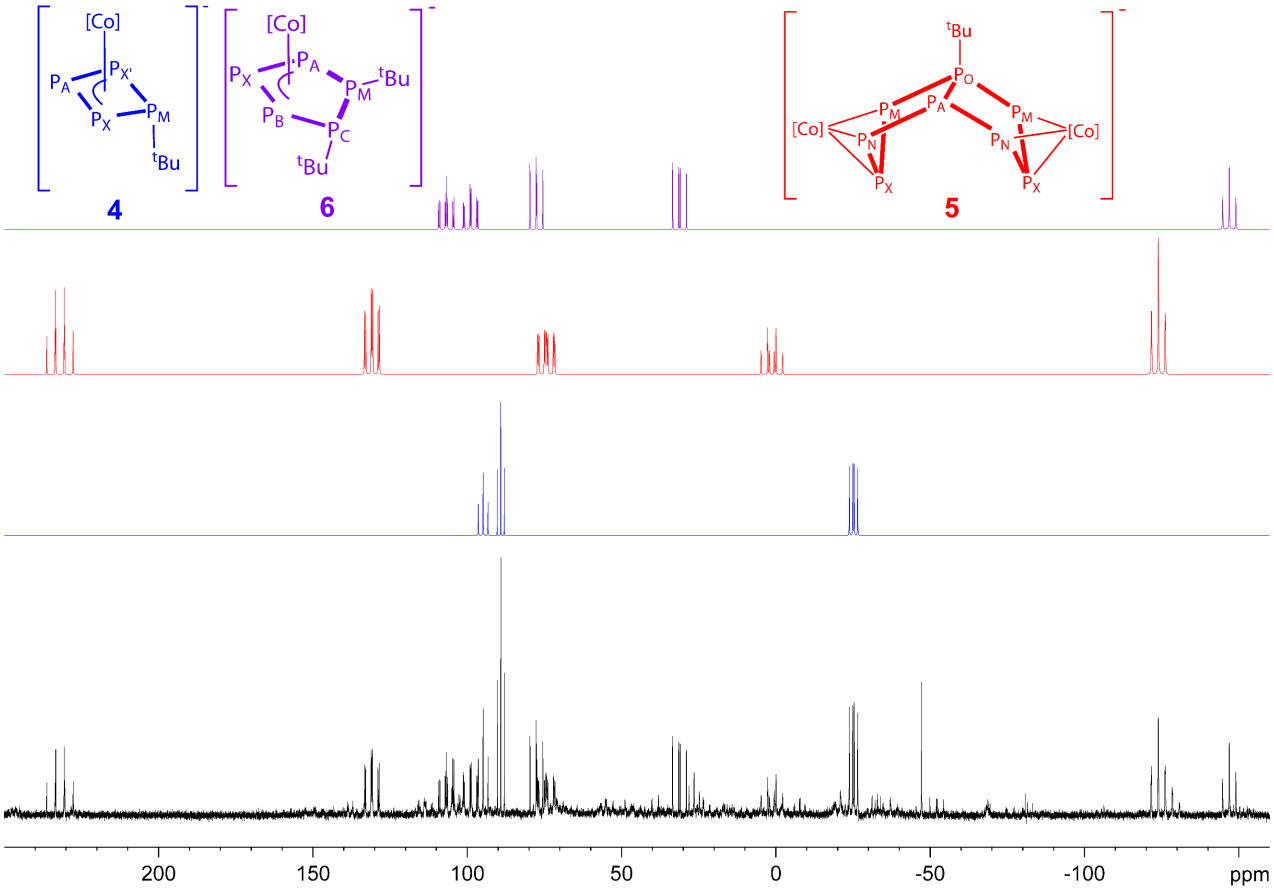


Figure S6: Part of the $^{31}P\{^{1}H\}$ NMR spectrum of the reaction of **1** with ^{t}BuLi at room temperature thf-d_8 at room temperature and the simulated spectra of **4** (blue), **5** (red) and **6** (purple).

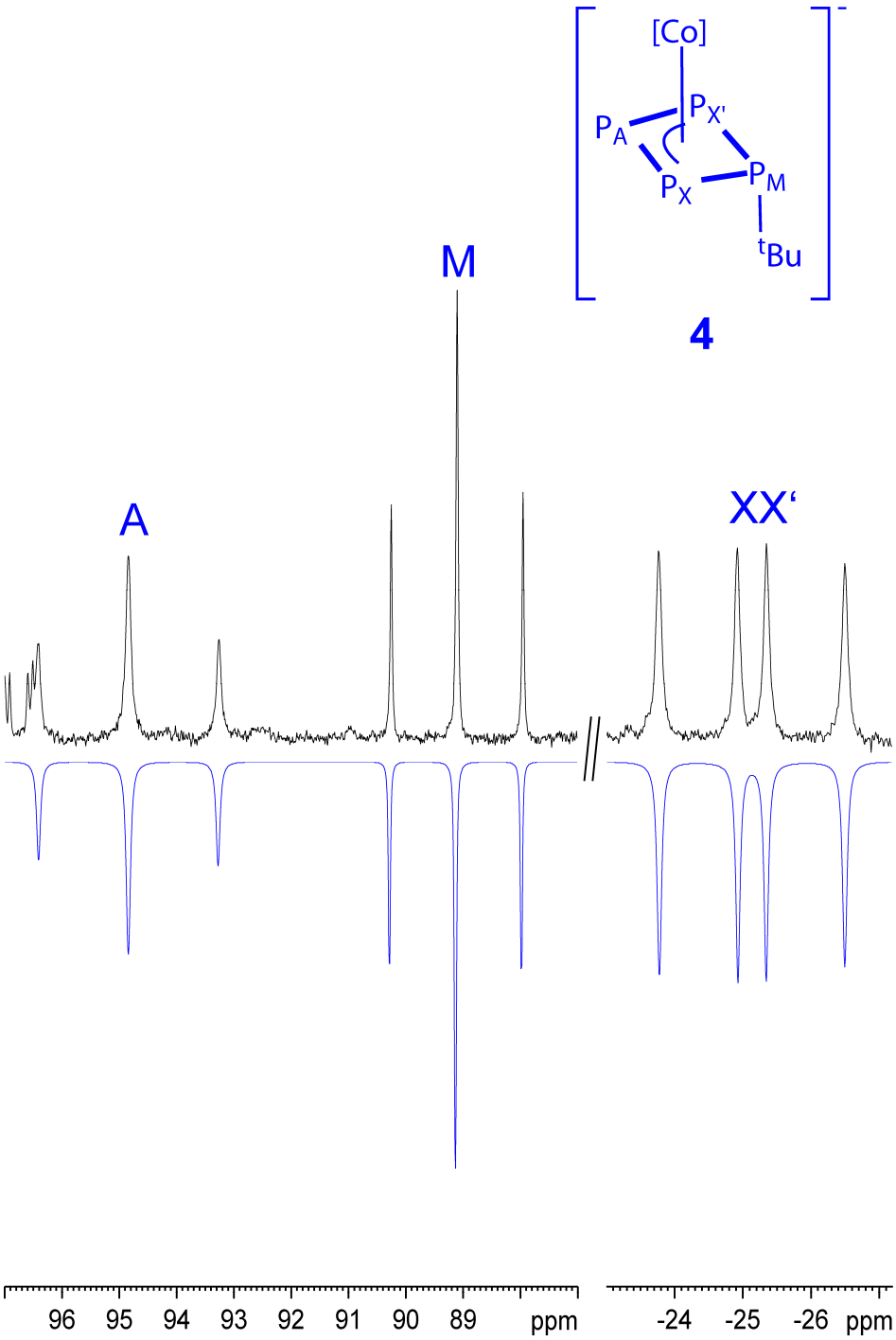


Figure S7: Part of the $^{31}P\{^{1}H\}$ NMR spectrum of the reaction of **1** with ^{t}BuLi at room temperature thf-d_8 at room temperature and the simulated spectrum of **4** (blue).

Table S4: Coupling constants and chemical shifts obtained from the simulation of **4** from the $^{31}P\{^{1}H\}$ NMR spectrum.

coupling constants [Hz]		chemical shifts [ppm]	
$^{1}J_{P_AP_X} = {}^{1}J_{P_AP_{X'}}$	253.71	P_A	94.83
$^{1}J_{P_MP_X} = {}^{1}J_{P_MP_{X'}}$	186.61	P_M	89.13
$^{2}J_{P_AP_M}$	2.99	P_X	-25.13
$^{2}J_{P_XP_{X'}}$	4.01	$P_{X'}$	-25.13

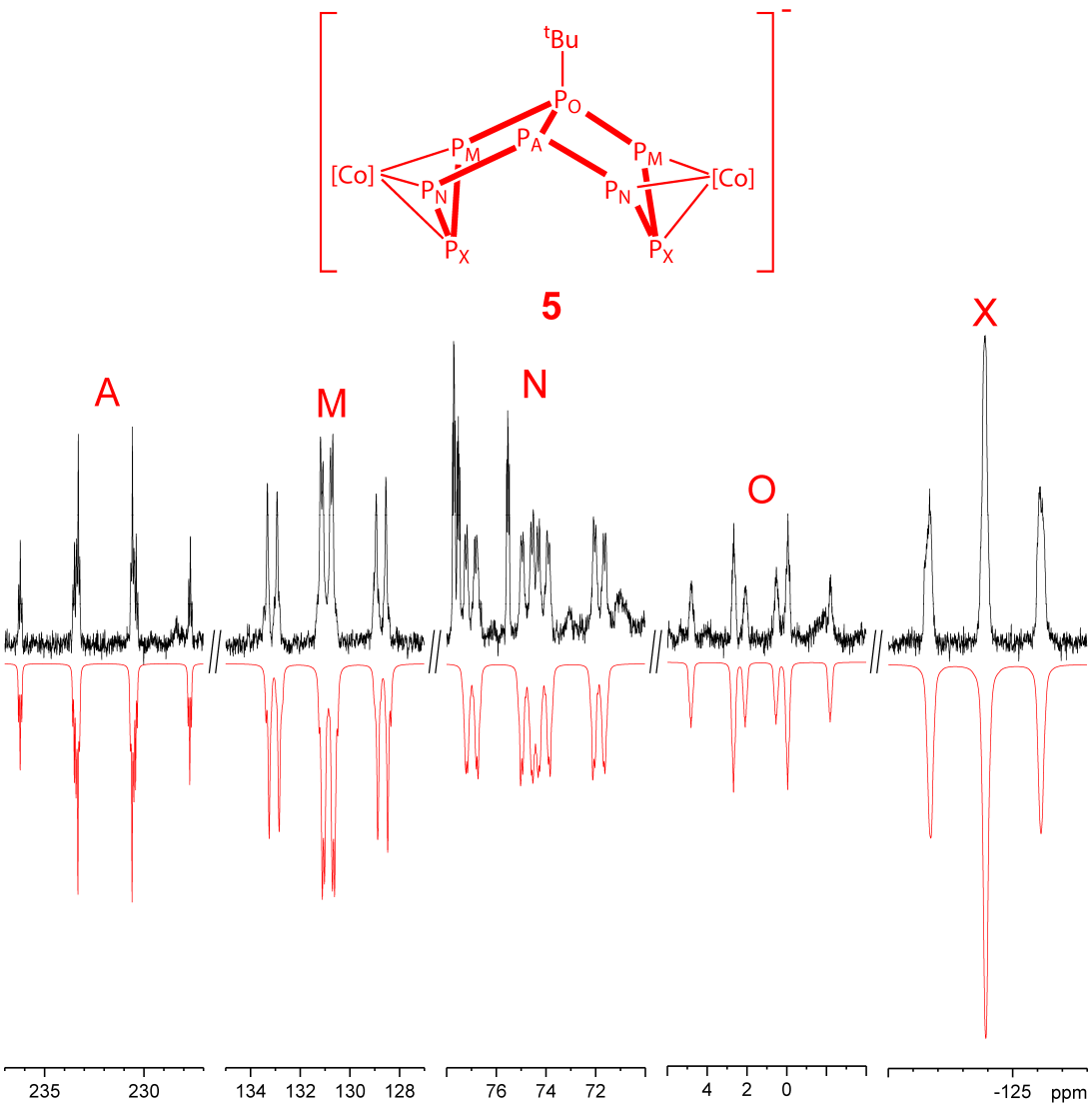


Figure S8: Part of the $^{31}P\{^{1}H\}$ NMR spectrum of the reaction of **1** with ^{t}BuLi at room temperature thf-d_8 at room temperature and the simulated spectrum of **5** (red).

Table S5: Coupling constants and chemical shifts obtained from the simulation of **5** from the $^{31}P\{^{1}H\}$ NMR spectrum.

coupling constants [Hz]			
$^{1}J_{P_AP_N}$	470.35	$^{2}J_{P_MP_N}$	-4.69
$^{1}J_{P_AP_O}$	441.32	$^{2}J_{P_MP_N}$	69.86
$^{1}J_{P_MP_O}$	346.33	$^{2}J_{P_NP_N}$	-16.59
$^{1}J_{P_MP_X}$	363.12	$^{2}J_{P_NP_O}$	-14.40
$^{1}J_{P_NP_X}$	358.96	$^{2}J_{P_OP_X}$	6.80
$^{2}J_{P_AP_M}$	-1.21	$^{3}J_{P_MP_X}$	-1.52
$^{2}J_{P_AP_X}$	13.24	$^{3}J_{P_NP_X}$	1.02
$^{2}J_{P_MP_M}$	14.02	$^{4}J_{P_XP_X}$	20.96

chemical shifts [ppm]	
P_A	231.93
P_M	130.85
P_N	74.73
P_O	1.34
P_X	-123.91

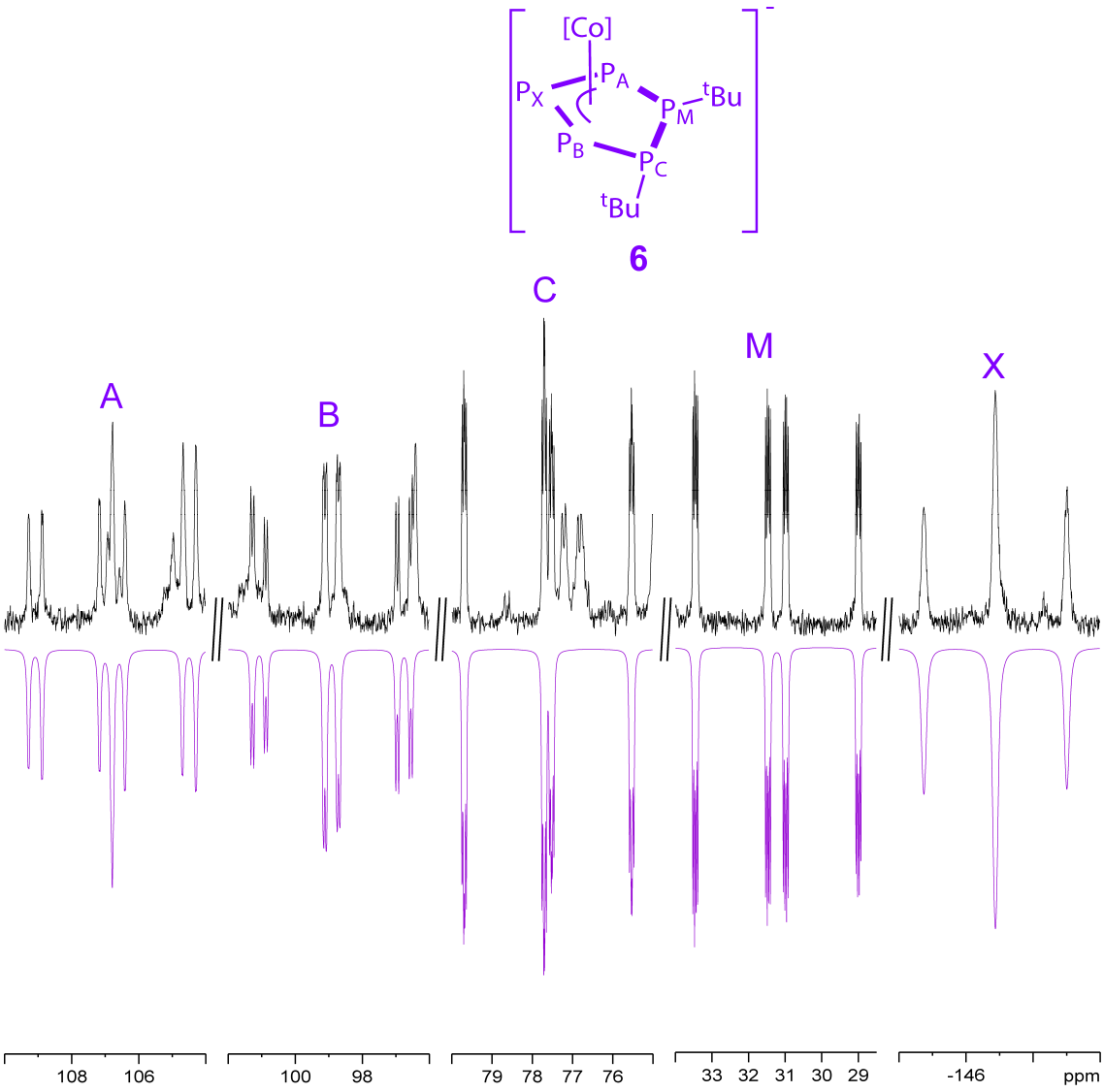


Figure S9: Part of the $^{31}P\{^{1}H\}$ NMR spectrum of the reaction of **1** with ^{t}BuLi at room temperature thf-d_8 at room temperature and the simulated spectrum of **6** (purple).

Table S6: Coupling constants and chemical shifts obtained from the simulation of **6** from the $^{31}P\{^{1}H\}$ NMR spectrum.

coupling constants [Hz]			
$^{1}J_{P_AP_M}$	400.71	$^{2}J_{P_AP_B}$	65.46
$^{1}J_{P_AP_X}$	342.90	$^{2}J_{P_AP_C}$	5.97
$^{1}J_{P_BP_C}$	352.77	$^{2}J_{P_BP_M}$	12.84
$^{1}J_{P_BP_X}$	348.39	$^{2}J_{P_CP_X}$	10.00
$^{1}J_{P_CP_M}$	322.67	$^{2}J_{P_MP_X}$	7.23

chemical shifts [ppm]	
P_A	106.76
P_B	98.86
P_C	77.65
P_M	31.27
P_X	-146.87

9.4.2.4 [Li(2,2,2-crypt)][Cp'''Co(η^3-$P_4CH_2SiMe_3$)] (7)

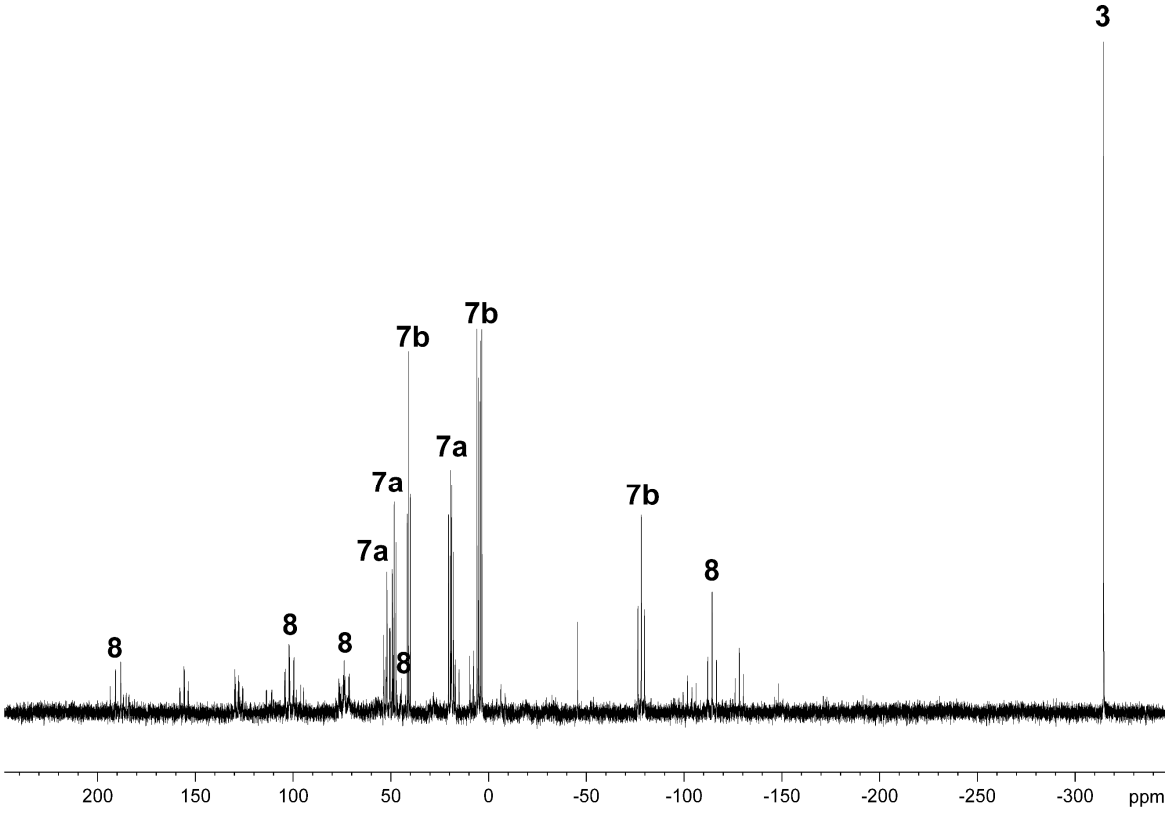


Figure S10: $^{31}P\{^1H\}$ NMR spectrum in thf-d_8 of the reaction of $LiCH_2SiMe_3$ with **1** after addition of 12-c-4.

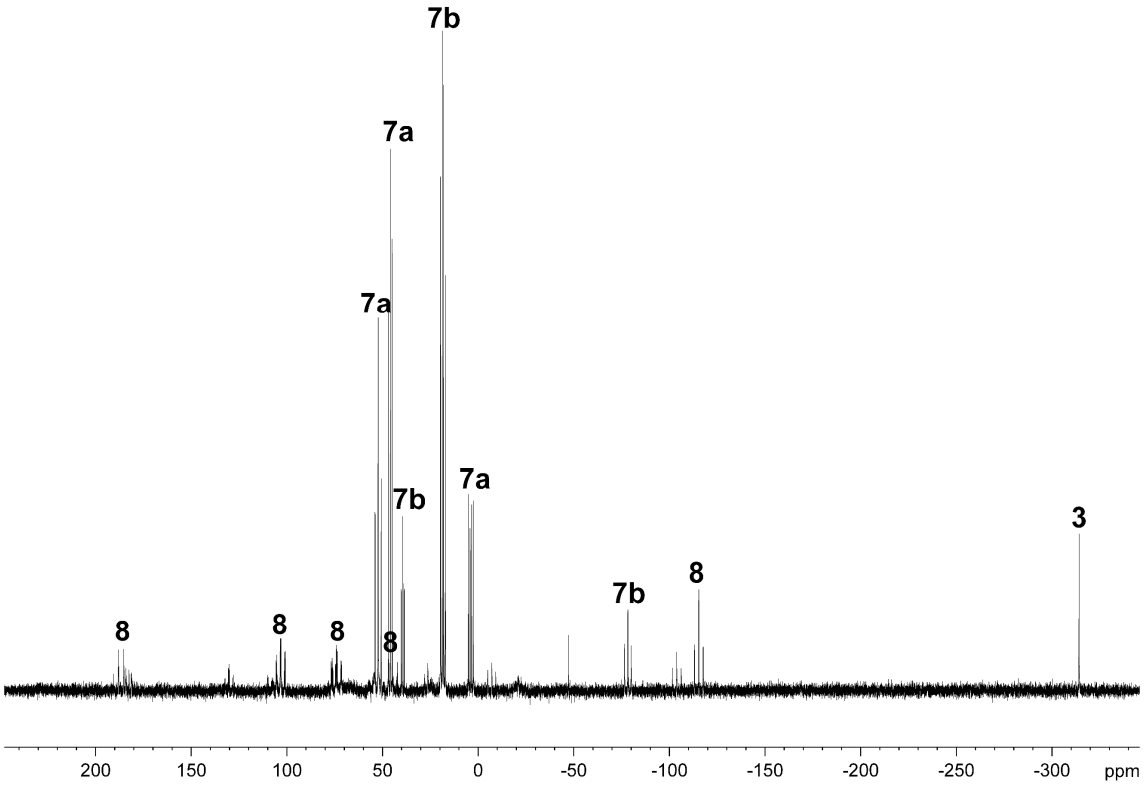


Figure S11: $^{31}P\{^1H\}$ NMR spectrum in thf-d_8 of the reaction of $LiCH_2SiMe_3$ with **1** after addition of 2,2,2-cryptand.

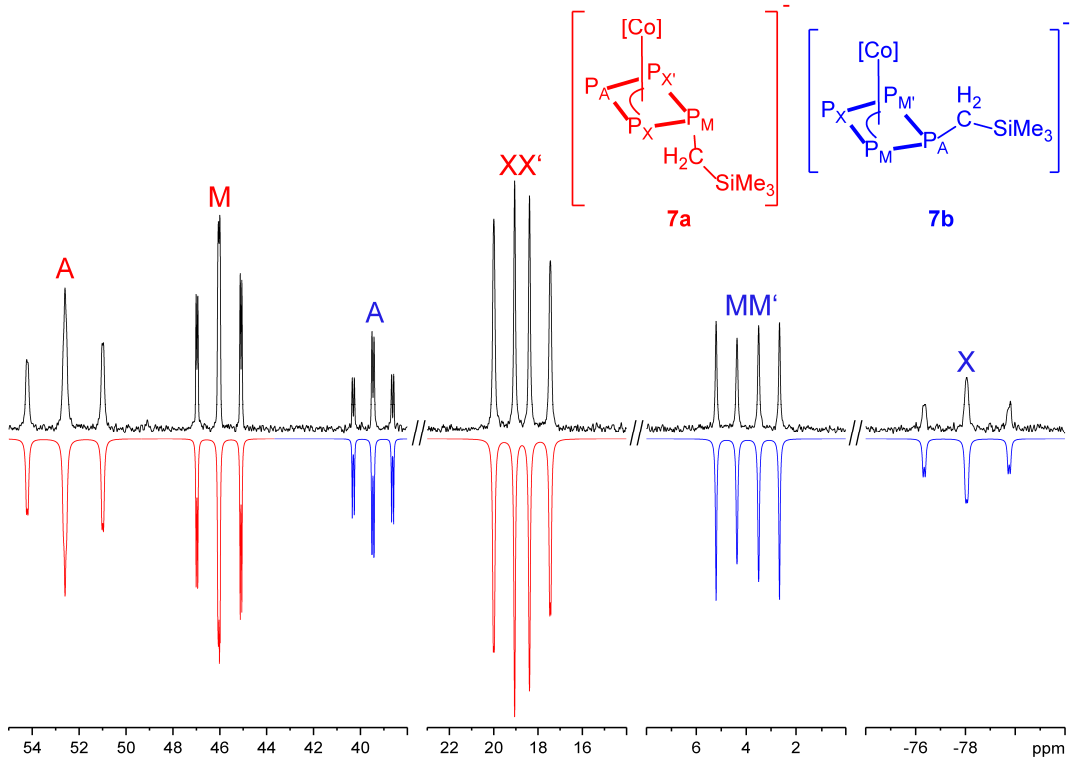


Figure S12: $^{31}P\{^{1}H\}$ NMR spectrum of the [Li(2,2,2-crypt)]**7a**/**7b** in thf-d_8 (experimental (black) and simulated (blue, red)).

Table S7: Coupling constants and chemical shifts obtained from the simulation ([Li(2,2,2-crypt)]**7a**/**7b**).

coupling constants [Hz]			
7a		**7b**	
$^1J_{P_AP_X} = {}^1J_{P_AP_{X'}}$	260.89	$^1J_{P_AP_M} = {}^1J_{P_AP_{M'}}$	135.82
$^1J_{P_MP_X} = {}^1J_{P_MP_{X'}}$	152.24	$^1J_{P_MP_X} = {}^1J_{P_{M'}P_X}$	276.36
$^2J_{P_AP_M}$	10.95	$^2J_{P_AP_X}$	14.38
$^2J_{P_XP_{X'}}$	-8.00	$^2J_{P_MP_{M'}}$	-84.01
chemical shifts [ppm]		chemical shifts [ppm]	
P_A	52.29	P_A	39.39
P_M	45.93	P_M	3.78
P_X	18.48	$P_{M'}$	3.78
$P_{X'}$	18.48	P_X	-78.24
R value	0.53 %		

Table S8: Coupling constants and chemical shifts obtained from the simulation ([Li(12-c-4)$_2$]**7a**/**7b**).

coupling constants [Hz]			
7a		**7b**	
$^1J_{P_AP_X} = {}^1J_{P_AP_{X'}}$	259.18	$^1J_{P_AP_M} = {}^1J_{P_AP_{M'}}$	135.34
$^1J_{P_MP_X} = {}^1J_{P_MP_{X'}}$	152.95	$^1J_{P_MP_X} = {}^1J_{P_{M'}P_X}$	273.40
$^2J_{P_AP_M}$	10.53	$^2J_{P_AP_X}$	13.76
$^2J_{P_XP_{X'}}$	-8.00	$^2J_{P_MP_{M'}}$	-84.00
chemical shifts [ppm]		chemical shifts [ppm]	
P_A	50.07	P_A	38.93
P_M	46.54	P_M	2.84
P_X	17.42	$P_{M'}$	2.84
$P_{X'}$	17.42	P_X	-79.93
R value	1.69 %		

9.4.2.5 $[Li(dme)_3][(Cp'''Co)_2(\mu,\eta^3{:}\eta^3\text{-}P_8CH_2SiMe_3)]$ (8)

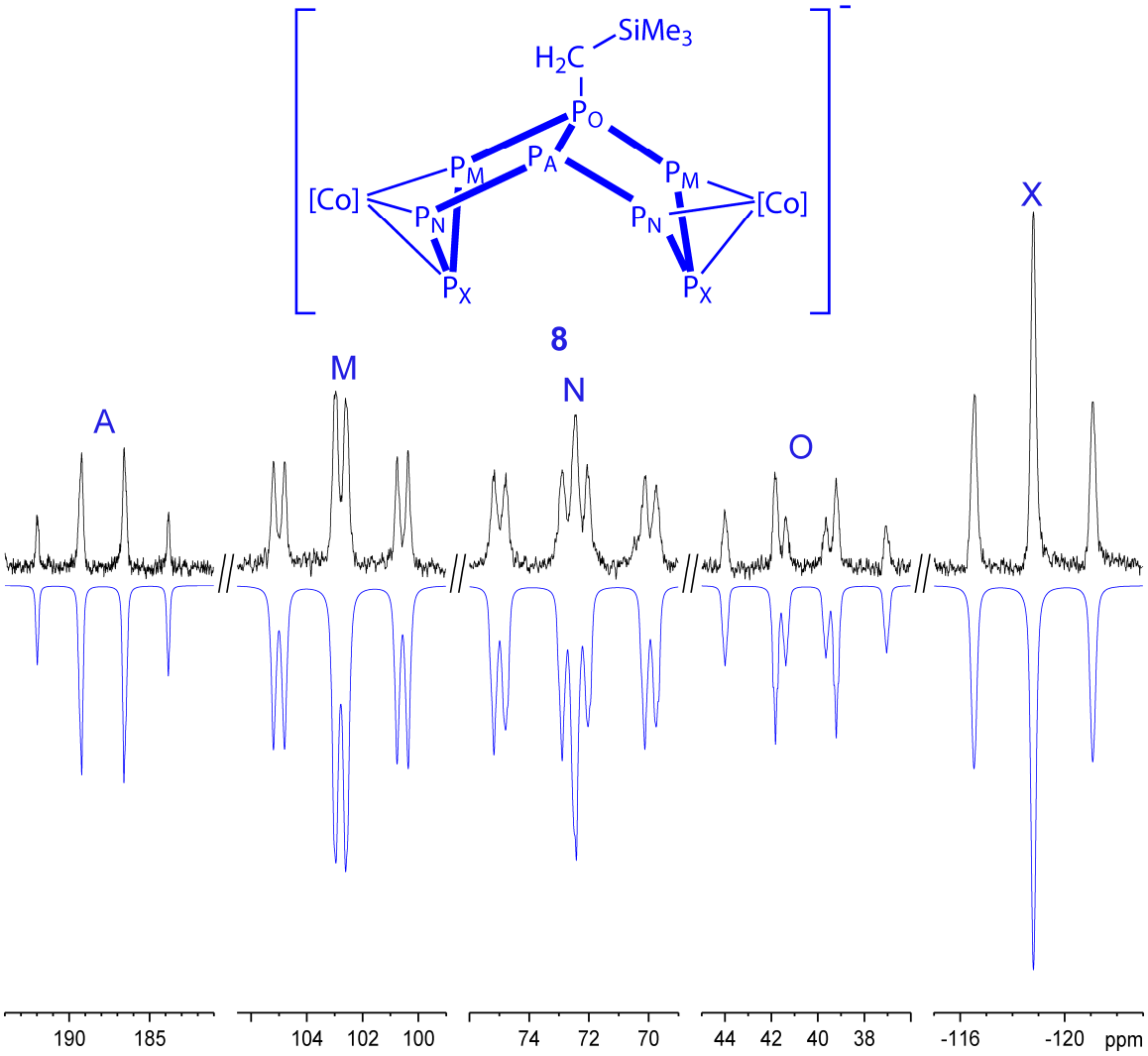


Figure S13: $^{31}P\{^1H\}$ NMR spectrum of **8** in thf-d_8 at 193 K (experimental (black) and simulated (blue)).

Table S9: Coupling constants and chemical shifts obtained from the simulation.

coupling constants [Hz]			
$^1J_{P_AP_N}$	448.32	$^2J_{P_MP_N}$	62.41
$^1J_{P_AP_O}$	424.01	$^2J_{P_MP_N}$	-12.85
$^1J_{P_MP_O}$	351.60	$^2J_{P_NP_N}$	-3.66
$^1J_{P_MP_X}$	366.96	$^2J_{P_NP_O}$	-17.34
$^1J_{P_NP_X}$	369.36	$^2J_{P_OP_X}$	7.69
$^2J_{P_AP_M}$	-2.44	$^3J_{P_MP_X}$	0.20
$^2J_{P_AP_X}$	12.49	$^3J_{P_NP_X}$	0.87
$^2J_{P_MP_M}$	6.65	$^4J_{P_XP_X}$	19.47
chemical shifts [ppm]			
P_A	187.87		
P_M	102.75	R value	1.53 %
P_N	74.48		
P_O	40.57		
P_X	-118.80		

9.4.2.6 VT-NMR study of the reaction of 1 with $LiCH_2SiMe_3$

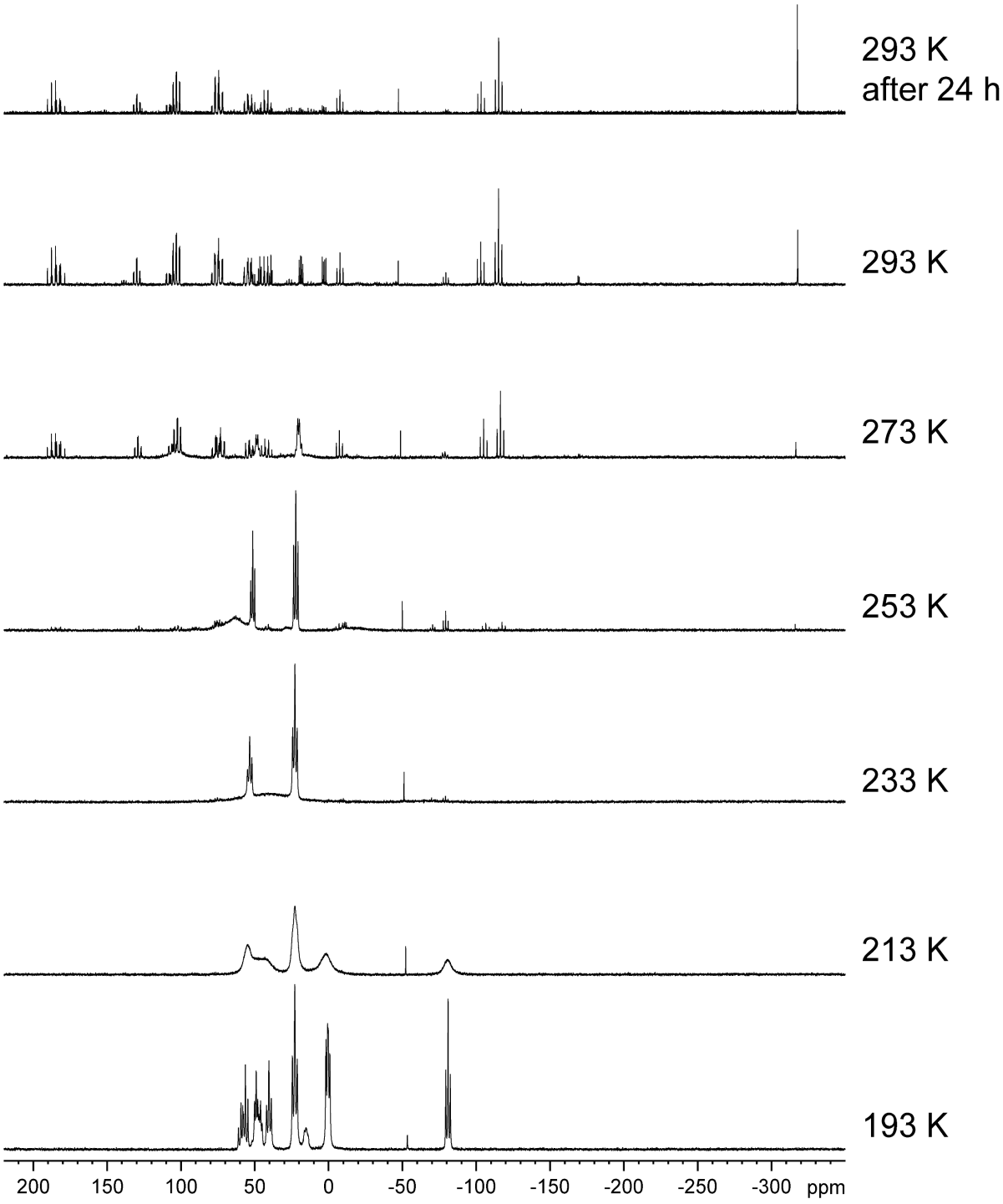


Figure S14: $^{31}P\{^1H\}$ VT NMR spectra of the reaction of **1** with LiCH2SiMe3 in thf-d_8 between 193 and 293 K and after 24 h at room temperature.

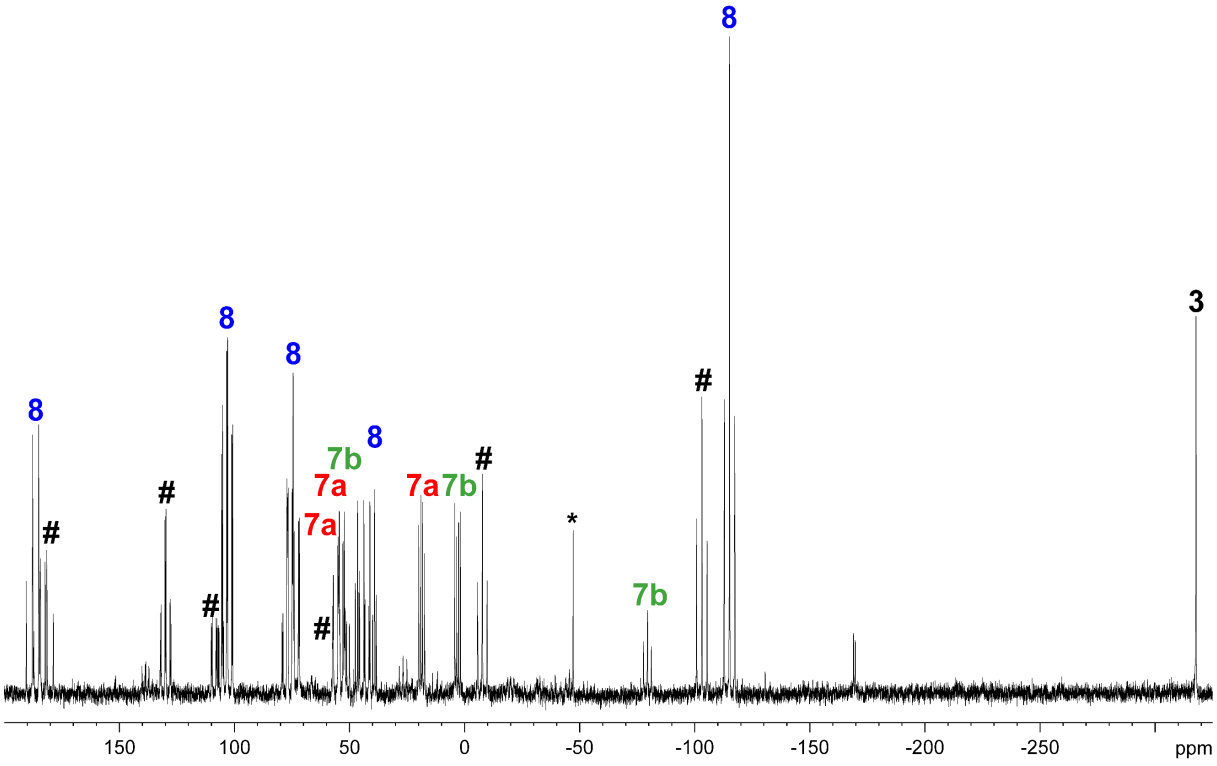


Figure S15: $^{31}P\{^{1}H\}$ NMR spectrum of the VT-NMR (S14) at 293 K (# unknown compound, * $[(Cp'''Co)_2(P_2)_2]$).

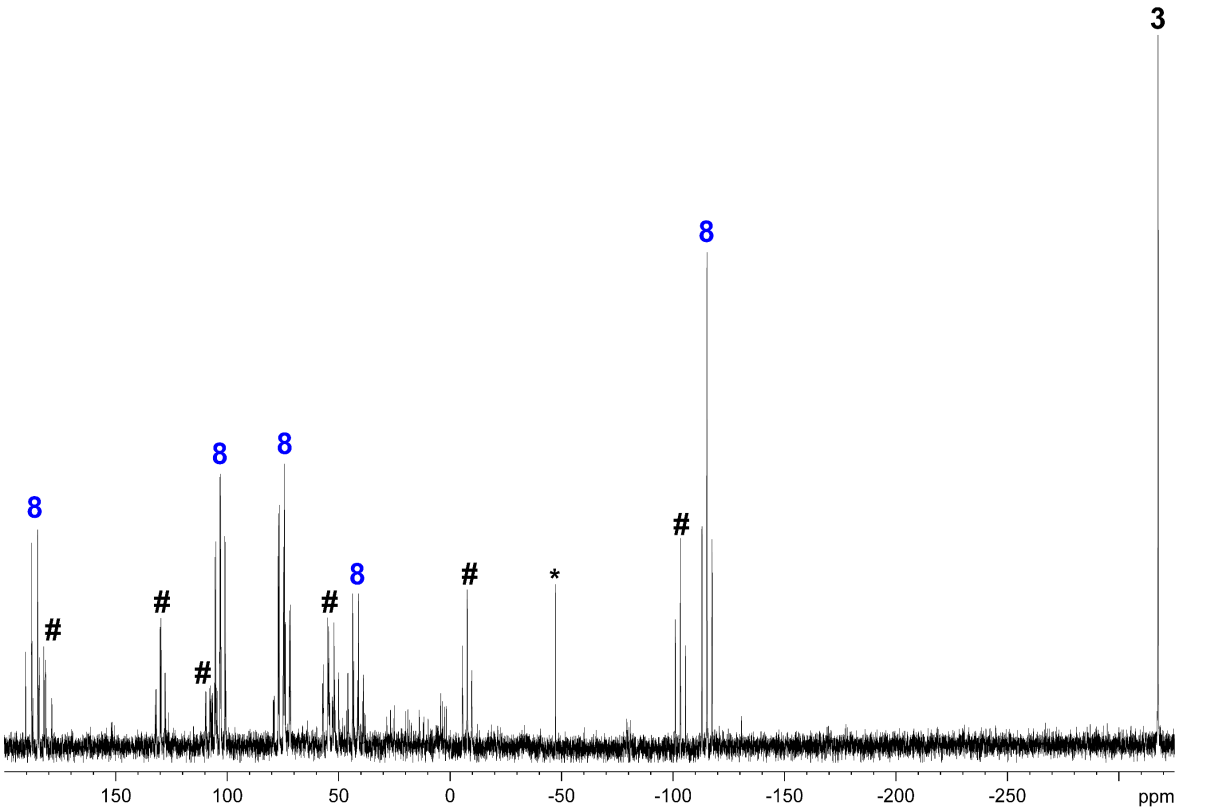


Figure S16: $^{31}P\{^{1}H\}$ NMR spectrum of the VT-NMR (S14) at 293 K after 24 h (# unknown compound, * $[(Cp'''Co)_2(P_2)_2]$).

9.4.2.7 [Na(dme)$_2$][Cp'''Co(η^3-P$_4$(O)H)] (10)

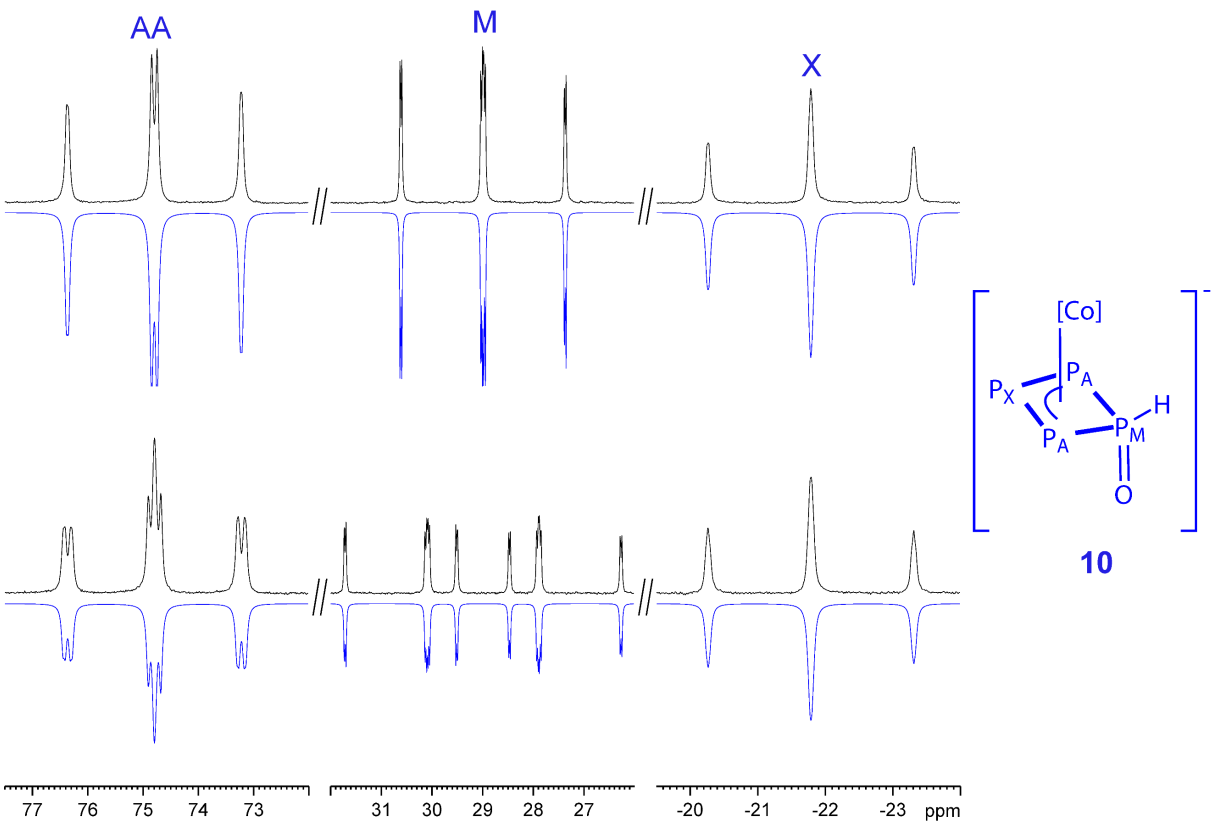


Figure S17: $^{31}P\{^1H\}$ (top) and ^{31}P (bottom) NMR spectrum of **10** thf-d$_8$ at room temperature (experimental (black) and simulated (blue)).

Table S10: Coupling constants and chemical shifts obtained from the simulation of the $^{31}P\{^1H\}$ NMR spectrum.

coupling constants [Hz]		chemical shifts [ppm]	
$^1J_{P_AP_M}$	262.67	P$_A$	74.78
$^1J_{P_AP_X}$	246.57	P$_M$	29.02
$^2J_{P_AP_A}$	-9.00	P$_X$	-21.77
$^2J_{P_MP_X}$	4.92		
R value		1.23 %	

Table S11: Coupling constants and chemical shifts obtained from the simulation of the ^{31}P NMR spectrum.

coupling constants [Hz]		chemical shifts [ppm]	
$^1J_{P_AP_M}$	262.71	P$_A$	74.77
$^1J_{P_AP_X}$	246.64	P$_M$	29.02
$^2J_{P_AP_A}$	0.00	P$_X$	-21.78
$^2J_{P_MP_X}$	4.98		
$^1J_{P_MH}$	356.77		
$^2J_{P_AH}$	20.56		
$^3J_{P_XH}$	5.12		
R value		0.41 %	

9.4.3 Cyclic voltammogram of 1

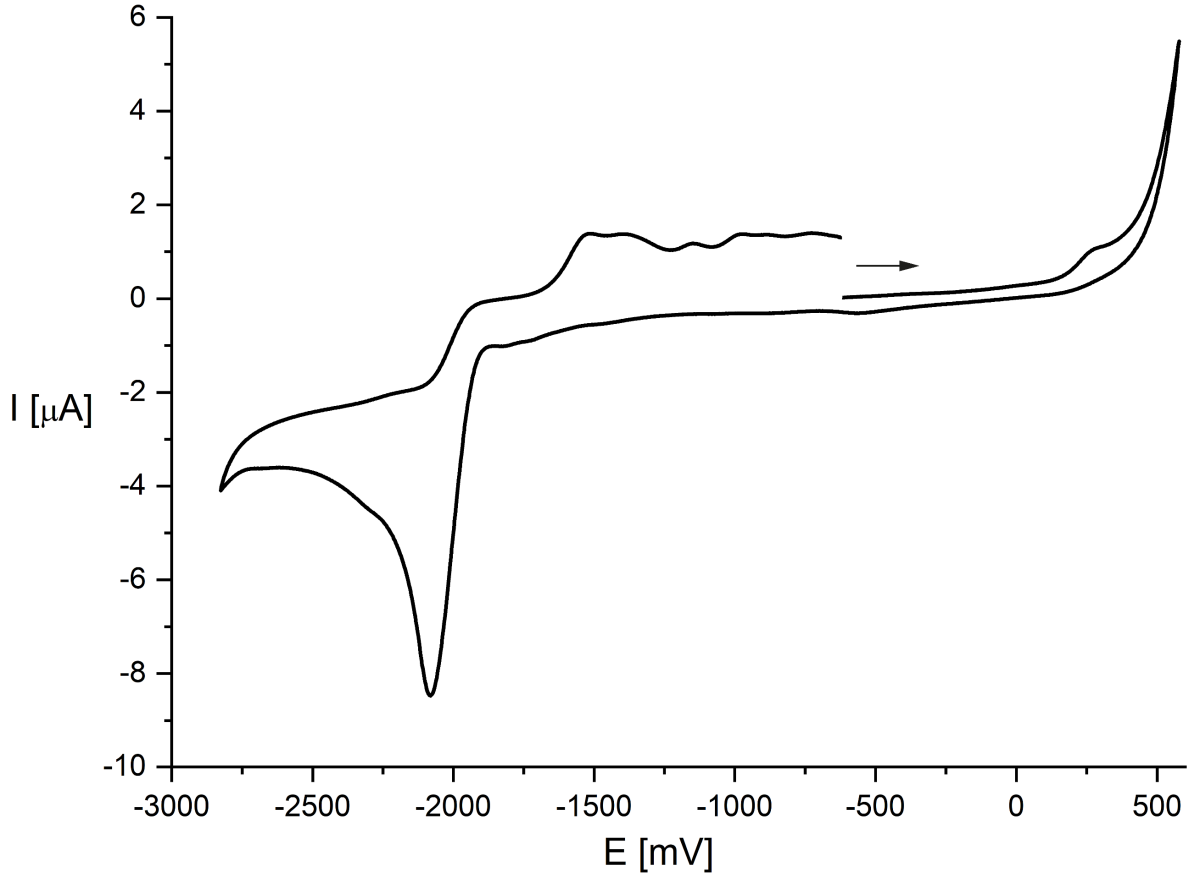


Figure S18. Cyclic voltammogram of **1** in thf against $[Cp_2Fe]/[Cp_2Fe]^+$ (electrolyte $^nBu_4NPF_6$, scan rate: 100 mV/s. temperature: r.t.).

9.4.4 Details on single crystal X-ray structure analysis

The X-ray diffraction experiments were performed on either an Gemini Ultra diffractometer (Oxford diffraction) with an AtlasS2 detector applying Mo radiation (λ = 0.71073 Å) (**2a**, **5**, **7a**) or Cu-K*α* radiation (λ = 1.54178 Å) (**2b**, **4**), a GV 50 diffractometer (Rigaku, formerly Agilent Technologies) with TitanS2 detector from applying Cu-K*α* radiation (λ = 1.54178 Å) (**6**, **10**) or SuperNova (Agilent Technologies) with an Atlas detector applying Cu-K*α* radiation (λ = 1.54178 Å) (**8**). All measurements were performed at 123 K. An analytical numeric absorption correction[38] using a multifaceted crystal model based on expressions derived by R.C. Clark & J.S. Reid using spherical harmonicsas implemented in SACLE3 ABSPACK was applied (**2a**, **2b**, **4**, **5**, **7**).[39] A numerical absorption correction based on gaussian integration over a multifaceted crystal model using *CrysAlisPro* using spherical harmonicsas implemented in SACLE3 ABSPACK was applied (**8**, **10**). All structures were solved by direct methods with ShelXT[40] and Olex2[41] and refined by full-matrix least-squares method against F^2 in

anisotropic approximation using ShelXL[42]. Hydrogen atoms were refined in calculated positions using riding on pivot atom model.

CCDC-1984450 (**2b**), CCDC-1984451 (**4**), CCDC-1984452 (**5**), CCDC-1984453 (**7a**), CCDC-1984454 (**8**) and CCDC-1984455 (**10**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: + 44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

9.4.4.1 $[K(dme)]_2[(Cp'''Co)_2(\mu,\eta^3:\eta^3\text{-}P_8)]$ (2a)

Crystals suitable for X-ray single crystal structure analysis can be obtained from a concentrated solution in a mixture of hexane and dme at -30 °C. Compound **2**a crystallizes in the orthorhombic space group *Cmce* as dark green blocks. Although a very good measurement was conducted (up to a resolution of 0.67 Å) a final refinement of the data was not possible. The anion can be modeled quite well, but the potassium counterions are located over several positions (partially side occupancies below 8 %) surrounded by dme molecules which cannot be modeled properly. The structure in solid state including the electron density map is depicted in Figure S19.

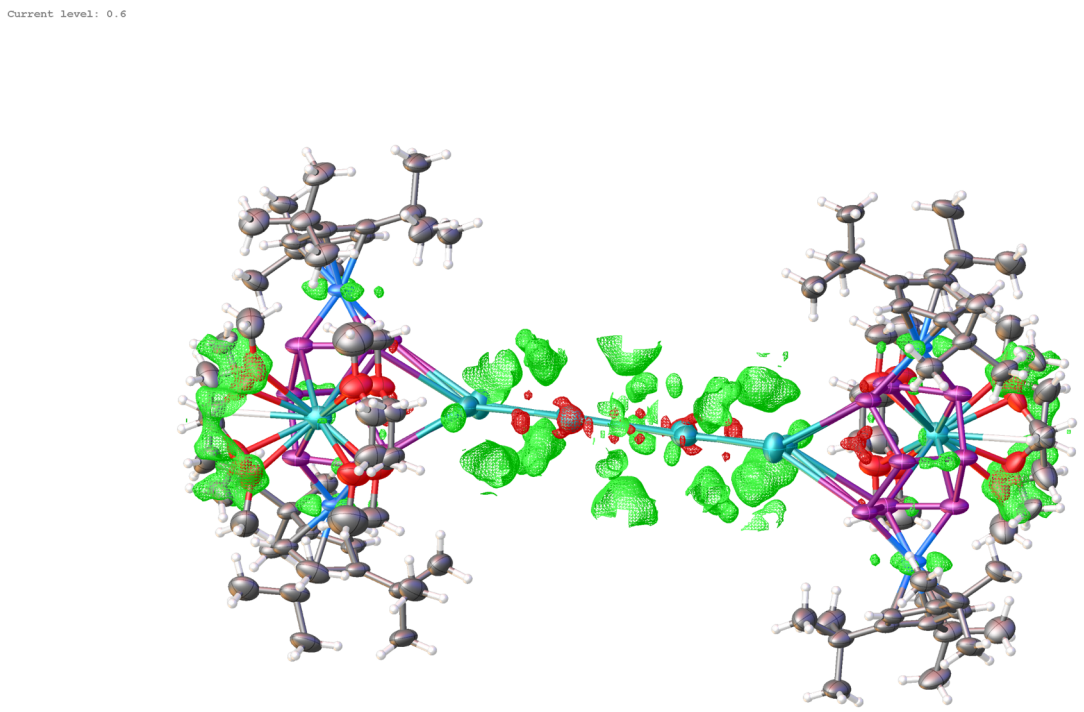


Figure S19. Part of the molecular structure of **2a** in solid state. Depicted is the unfished refinement with the electron density map.

9.4.4.2 $[K(2,2,2\text{-crypt})]_2[(Cp'''Co)_2(\mu,\eta^3{:}\eta^3\text{-}P_8)]$ (2b)

Crystals suitable for X-ray single crystal structure analysis can be obtained from a concentrated solution of **2b** in a mixture of dme and MeCN at -30 °C. Compound **2b** crystallizes in form of dark green plates in the triclinic space group $P\bar{1}$. The asymmetric unit contains one dianion of **2b**, two potassium counterions chelated by 2,2,2-cryptand and 1.5 molecules dme. The structure in solid state is depicted in Figure S20 and S21.

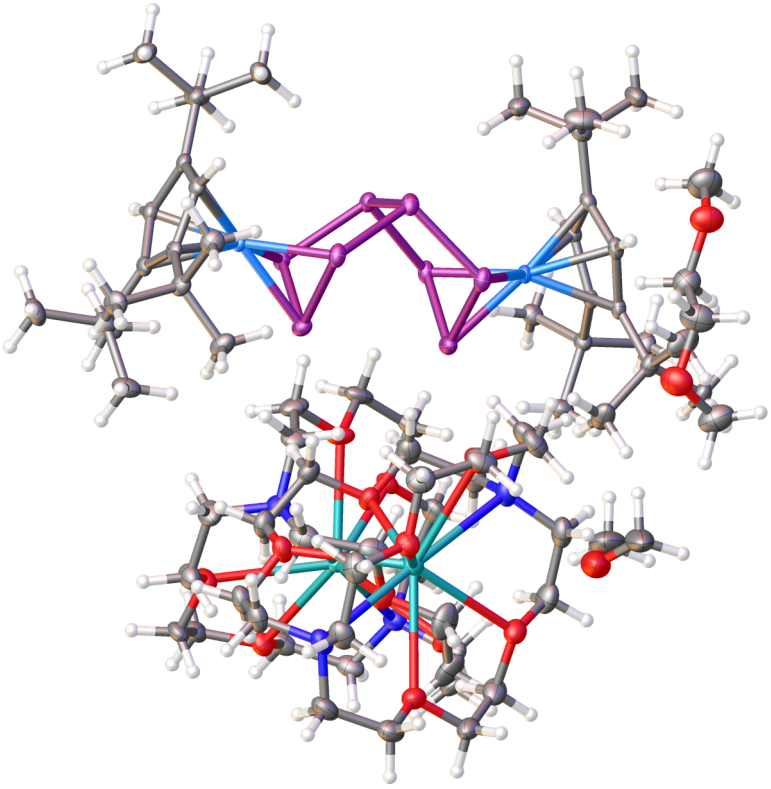


Figure S20: Molecular structure of **2b** in the solid state. Thermal ellipsoids are drawn with 50 % probability level.

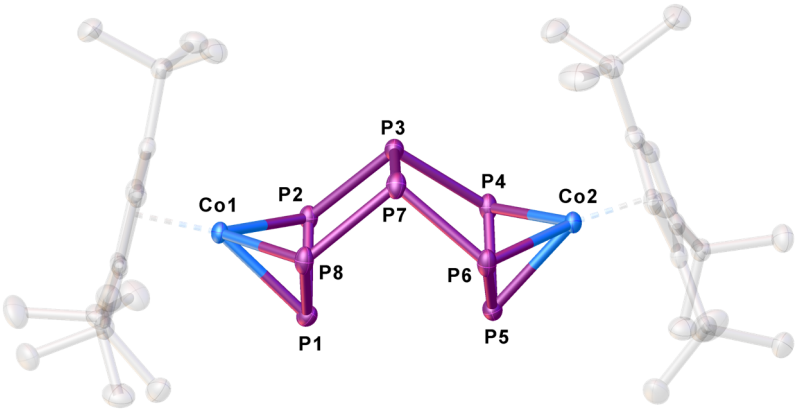


Figure S21: Molecular structure of the dianion in **2b** in the solid state. Thermal ellipsoids are drawn with 50 % probability level. Selected bond lengths [Å] and angles [°]: P1-P2 2.1554(6), P1-P5 3.4607(6), P1-P8 2.1577(6), P2-P3 2.2152(6), P3-P4 2.2151(6), P3-P7 2.1947(6), P4-P5 2.1519(6), P5-P6 2.1580(6), P6-P7 2.2247(6), P7-P8 2.2133(6).

9.4.4.3 [Li(2,2,2-crypt)][Cp'''Co(η^3-P$_4$^{t}Bu)] (4)

Crystals suitable for X-ray single crystal structure analysis can be obtained from a concentrated solution of **4** in a in thf layered with hexane at room temperature. Compound **4** crystallizes in form of brown flat rods in the orthorhombic space group *Pbca*. The asymmetric unit contains one anion of **4**, one lithium counterion chelated by 2,2,2-cryptand and one molecule thf. Since the crystals were only poorly diffracting, only a measurement until a resolution of 1.20 Å was conducted. The structure in solid state is depicted in Figure S22.

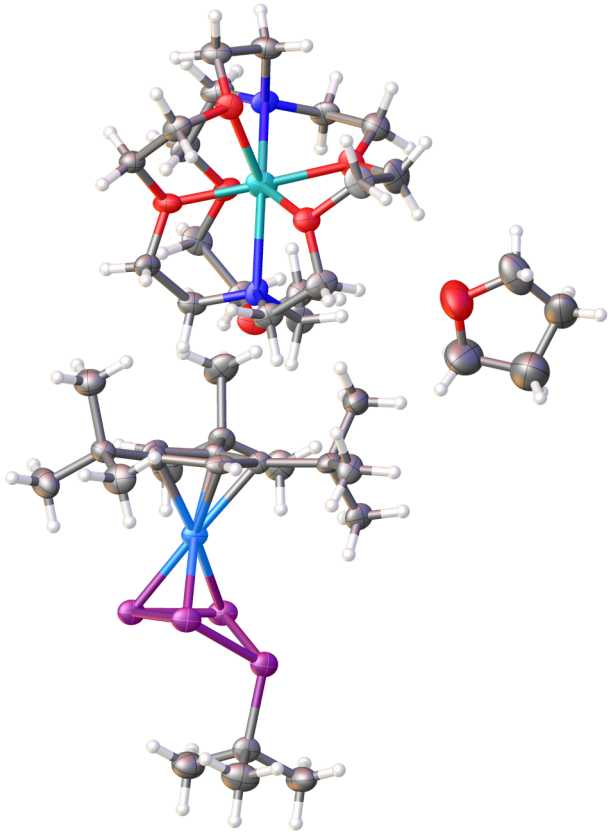


Figure S22: Molecular structure of **4** in the solid state. Thermal ellipsoids are drawn with 50 % probability level.

9.4.4.4 $[Li(thf)_3][(Cp'''Co)_2(\mu,\eta^3{:}\eta^3\text{-}P_8{}^tBu)]$ (5)

Crystals suitable for X-ray single crystal structure analysis can be obtained from a concentrated solution of **5** in pentane at -30 °C. Compound **5** crystallizes in form of dark brown blocks in the monoclinic space group *P2₁/c*. The asymmetric unit contains one anion of **5**, one lithium counterion chelated by three thf molecules, 0.25 free thf and 0.5 pentane molecules. One tBu group of one Cp''' ligand is disordered over two positions. Two of the coordinating thf molecules are disordered over two positions. The restraints DFIX, SIMU and SADI were applied to describe the disorder and the free solvent molecules properly. The measured crystal was a twin and therefore a HKLF5 refinement was applied. The structure in solid state is depicted in Figure S23 and S24.

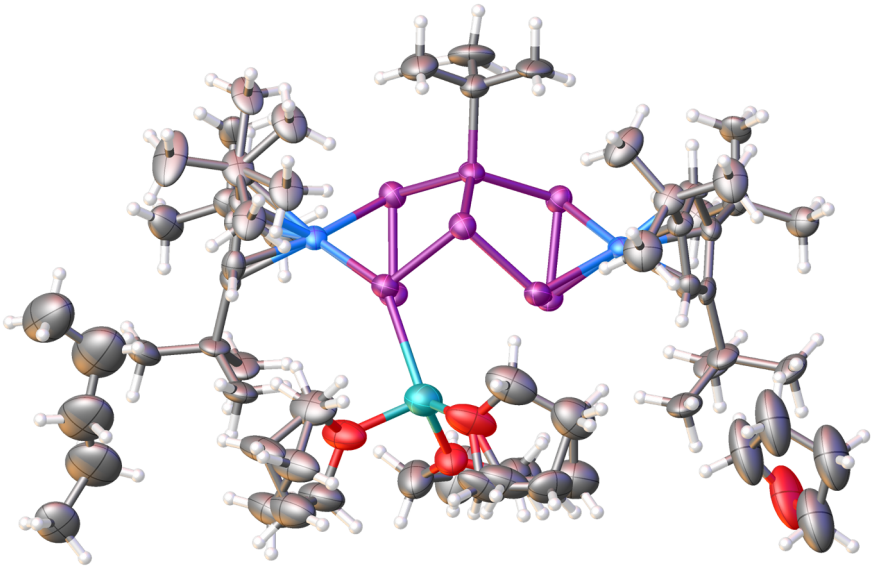


Figure S23: Molecular structure of **5** in the solid state. Thermal ellipsoids are drawn with 50 % probability level.

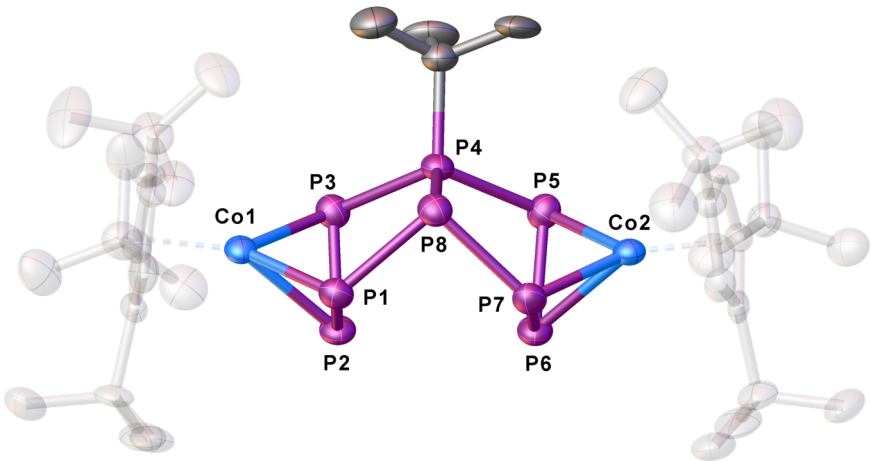


Figure S24: Molecular structure of the anion in **5** in the solid state. Thermal ellipsoids are drawn with 50 % probability level. Selected bond lengths [Å] and angles [°]: P1-P2 2.165(3), P1-P8 2.232(3), P2-P3 2.161(3), P2-P6 3.385(3), P3-P4 2.205(3), P4-P5 2.190(3), P4-P8 2.166(3), P5-P6 2.155(3), P6-P7 2.166(3), P7-P8 2.233(3).

9.4.4.5 [Li(12-c-4)$_2$][Cp’’’Co(η^3-P$_5$^{t}Bu$_2$)] (6)

Crystals of very poor quality were obtained from the reaction mixture of **1** and ^{t}BuLi in thf layered with hexane at -30 °C. A low resolution measurement gives a hint on the connectivity of **6**.

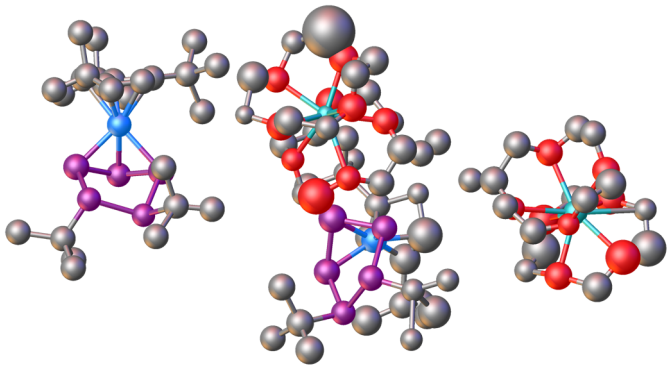


Figure S25: Molecular structure of **7** in solid state. Thermal ellipsoids are drawn with 50 % probability level.

9.4.4.6 [Li(2,2,2-crypt)][Cp’’’Co(η^3-P$_4$CH$_2$SiMe$_3$)] (7a)

Crystals suitable for X-ray single crystal structure analysis can be obtained from a concentrated solution of **7a** in thf layered with hexane -30 °C. Compound **7a** crystallizes in form of dark brown plates in the triclinic space group $P\bar{1}$. The asymmetric unit contains two anions of **7a**, two lithium atoms each chelated by two 12-c-4 molecules and 1.5 molecules thf. One thf molecule and all 12-c-4 are disordered over several positions. The restraints SIMU and SADI were applied to describe the disorder. The measured crystals was twinned and a HKLF5 refinement was applied. The structure in the solid state is depicted in Figure S26 and S27.

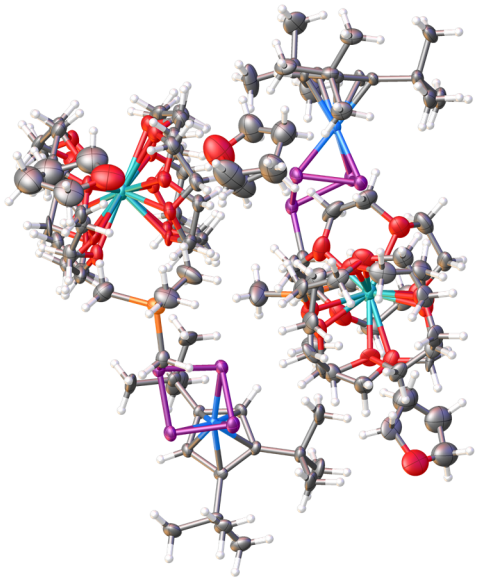


Figure S26: Molecular structure of **7a** in solid state. Thermal ellipsoids are drawn with 50 % probability level.

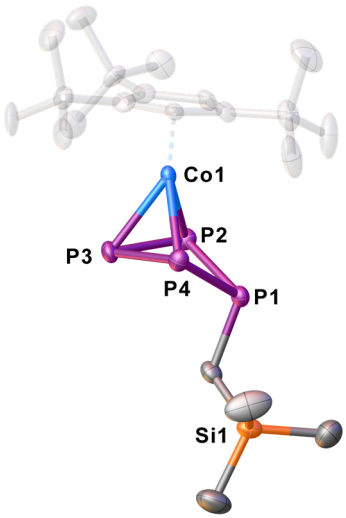


Figure S27: Molecular structure of one anion in **7a** in solid state. Thermal ellipsoids are drawn with 50 % probability level. Hydrogen atoms, cations and solvent molecules are omitted for clarity. Selected bond lengths [Å] and angles [°] of both anions: P1-P2 2.2283(16), P1-P4 2.2229(19), P2-P3 2.1877(17), P3-P4 2.1895(16), P5-P6 2.240(2), P5-P8 2.2286(16), P6-P7 2.1914(16), P7-P8 2.1898(17).

9.4.4.7 $[Li(dme)_3][(Cp'''Co)_2(\mu,\eta^3{:}\eta^3\text{-}P_8CH_2SiMe_3)]$ (8)

Crystals suitable for X-ray single crystal structure analysis can be obtained from a concentrated solution of **8** in a mixture of hexane and dme at -30 °C. Compound **8** crystallizes in form of dark green blocks in the triclinic space group $P\bar{1}$. The asymmetric unit contains one anion of **8**, one lithium counterion chelated by three molecules dme and 0.5 molecules hexane. The structure in solid state is depicted in Figure S28 and S29.

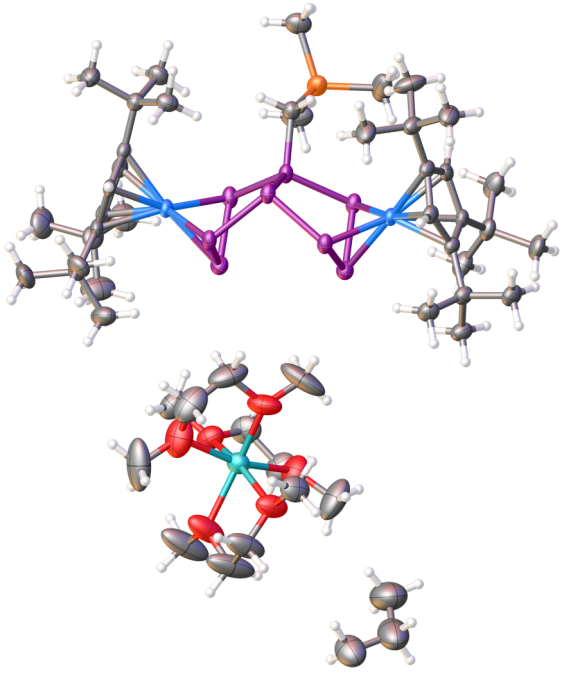


Figure S28: Molecular structure of **8** in the solid state. Thermal ellipsoids are drawn with 50 % probability level.

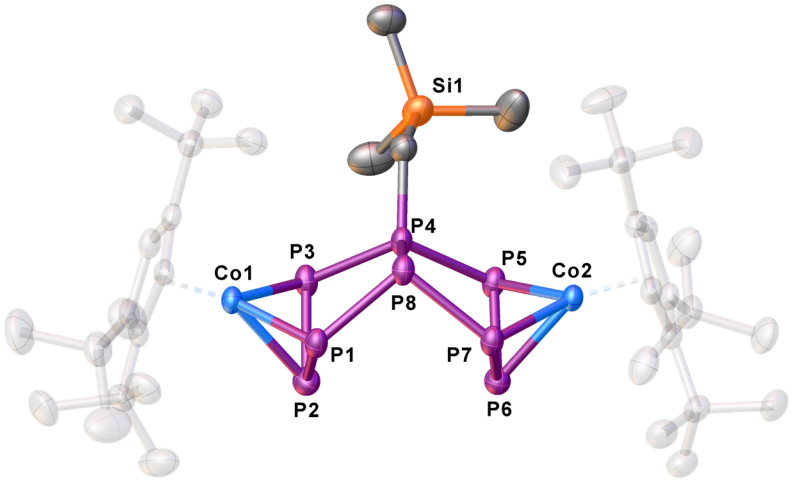


Figure S29: Molecular structure of the anion in **8** in the solid state. Thermal ellipsoids are drawn with 50 % probability level. Selected bond lengths [Å] and angles [°]: P1-P2 2.1643(11), P1-P8 2.2176(10), P2-P3 2.1574(11), P2-P6 3.7294(11), P3-P4 2.1948(10), P4-P5 2.1829(10), P4-P8 2.1738(10), P5-P6 2.1494(11), P6-P7 2.1575(11), P7-P8 2.2174(10).

9.4.4.8 [Na(dme)$_2$][Cp’’’Co(η^3-P$_4$(O)H)] (10)

Crystals suitable for X-ray single crystal structure analysis can be obtained from a concentrated solution of **10** in a in dme layered with hexane at -30 °C. Compound **10** crystallizes in form of dark brown blocks in the triclinic space group $P\bar{1}$. The asymmetric unit contains one anion of **10**, one sodium counterion chelated by two molecules dme. The structure in solid state is depicted in Figure S30 and S31.

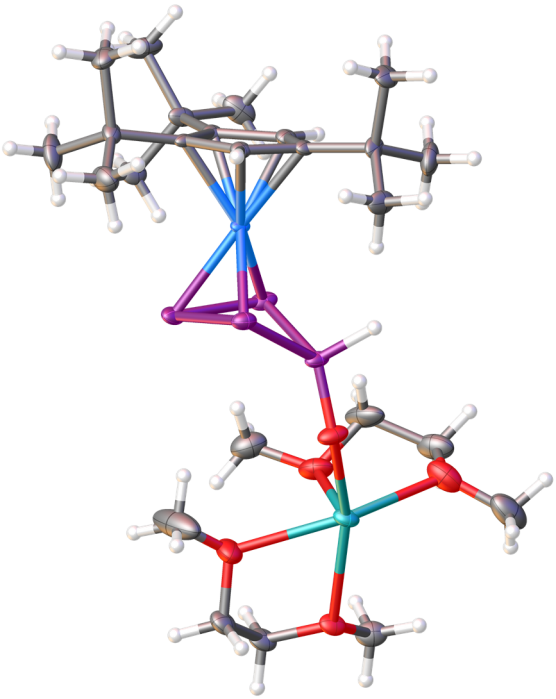


Figure S30: Molecular structure of **10** in the solid state. Thermal ellipsoids are drawn with 50 % probability level.

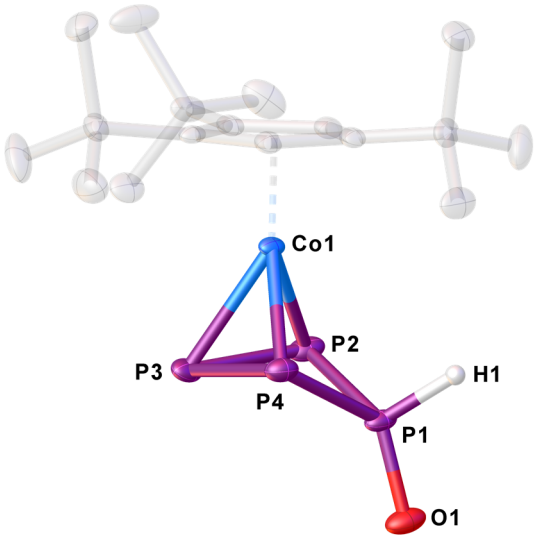


Figure S31: Molecular structure of the anion in **10** in the solid state. Thermal ellipsoids are drawn with 50 % probability level. Selected bond lengths [Å] and angles [°]: P1-P2 2.1659(7), P2-P3 2.1984(8), P3-P4 2.1938(8), P1-P4 2.1676(7), P1-H1 1.30(3), P1-O1 1.5200(15).

9.4.4.9 Crystallographic information

Table S12: Crystallographic data for all compounds

	2a	**2b**	**4**	**5**	**6**	**7a**	**8**	**10**
CCDC		1984450	1984451	1984452		1984453	1984454	1984455
Formula		$C_{76}H_{144}Co_2K_2N_4O_{15}P_8$	$C_{43}H_{82}CoLiN_2O_7P_4$	$C_{53.5}H_{99}Co_2LiO_{3.25}P_8$		$C_{80}H_{156}Co_2Li_2O_{17.5}P_8Si_2$	$C_{53}H_{106}Co_2LiO_6P_8Si$	$C_{25}H_{50}O_5NaP_4Co$
$D_{calc.}$/ g cm^{-3}		1.287	1.229	1.231		1.196	1.203	1.299
μ/mm^{-1}		5.379	4.248	0.768		0.531	6.043	6.376
Formula Weight		1797.76	928.85	1166.88		1833.72	1240.02	636.45
Colour	dark green	clear dark green	clear dark brown	dark brown		clear dark brown	clear dark green	clear dark brown
Shape	block	plate	needle	block		plate	plate	block
Size/mm^3	0.63×0.38×0.32	0.23×0.16×0.05	0.67×0.12×0.06	0.32×0.13×0.10		0.39×0.13×0.04	0.13×0.05×0.04	0.51×0.20×0.14
T/K	123	123	123(1)	123(1)		123(1)	123.01(10)	123.0(2)
Crystal System	orthorhombic	triclinic	orthorhombic	monoclinic	monoclinic	triclinic	triclinic	triclinic
Space Group	*Cmce*	*P*-1	*Pbca*	$P2_1/c$	*Pn*	*P*-1	*P*-1	*P*-1
a/Å	27.1353(5)	13.7131(2)	17.8715(3)	31.947(3)	13.520(3)	14.4740(7)	14.2675(3)	8.8103(3)
b/Å	26.3358(7)	15.2042(2)	22.5218(4)	15.5710(12)	26.875(4)	18.2968(4)	15.0423(4)	10.6602(3)
c/Å	21.7358(6)	25.3794(3)	24.9460(5)	12.6636(10)	15.467(5)	19.7326(6)	18.2337(5)	17.7138(5)
α/°	90	74.8590(10)	90	90	90	87.037(2)	102.047(2)	78.926(2)
β/°	90	78.8180(10)	90	91.670(8)	99.51(3)	77.660(4)	94.044(2)	89.741(2)
γ/°	90	65.9260(10)	90	90	90	86.306(3)	114.602(2)	85.158(2)
V/Å^3	15533.0(7)	4640.57(11)	10040.7(3)	6296.8(9)	5543(2)	5090.5(3)	3424.69(16)	1626.75(9)
Z		2	8	4		2	2	2
Z'		1	1	1		1	1	1
Wavelength/Å		1.54184	1.54184	0.71073		0.71073	1.54184	1.54184
Radiation type		CuK$_\alpha$	Cu K$_\alpha$	Mo K$_\alpha$		Mo K$_\alpha$	Cu K$_\alpha$	Cu K$_\alpha$
θ_{min}/°		3.386	3.544	3.242		3.307	3.462	2.542
θ_{max}/°		73.012	40.147	25.156		25.125	73.444	74.291
Measured Refl.		34504	13776	19403		26773	24262	10786
Independent Refl.		17809	3009	19403		26773	13133	6333
Reflections with I > 2(I)		16566	2723	9021		15803	10990	6143
R_{int}		0.0252	0.0414	.		.	0.0488	0.0425
Parameters		985	535	747		1430	668	342
Restraints		0	0	277		1102	0	0
Largest Peak		0.490	0.433	1.250		0.589	0.700	0.686
Deepest Hole		-0.360	-0.352	-0.620		-0.437	-0.486	-0.609
GooF		1.022	1.066	0.876		0.908	1.018	1.038
wR_2 (all data)		0.0794	0.1273	0.1886		0.1123	0.1321	0.1183
wR_2		0.0773	0.1223	0.1727		0.1051	0.1219	0.1169
R_1 (all data)		0.0344	0.0503	0.1377		0.0967	0.0608	0.0441
R_1		0.0311	0.0459	0.0745		0.0526	0.0494	0.0432

9.4.5 Computational Details

Gaussian 09 program package was used throughout.[43] Density functional theory (DFT) in form of Becke's three-parameter hybrid functioncal B3LYP[44] with def2-TZVP all electron basis set[45] was employed. For solvents effects has been accounted by using continuous polarizable continuum model (CPM).[46] The dielectric constant of thf (ε = 7.4257) has been used in the calculations. The Natural Bond Orbital (NBO) analysis has been performed with the NBO6 program.[47] The long range dispersion correction GD3BJ was applied.[48] The figures for the energy schemata were created using OLEX2.[41] The figures for the supporting information concerning the DFT calculations were created with Chemcraft.[49]

Table S13: Total energies for all optimized geometries (B3LYP/def2-TZVP level of theory).

	total energy [Ha]
1 [Cp'''Co(η^4-P_4)]	-3414.10100308
2 [(Cp'''Co)$_2$(μ,η^3:η^3-P_8)]$^{2-}$	-6328.46309287
3 [Cp'''Co(η^3-P_3)]$^-$	-3072.8032350
4a [Cp'''Co(η^3-$P_4{}^t$Bu)]$^-$ (endo isomer)	-3572.14117871
4b [Cp'''Co(η^3-$P_4{}^t$Bu)]$^-$ (exo isomer)	-3572.13664123
5 [(Cp'''Co)$_2$(μ,η^3:η^3-$P_8{}^t$Bu)]$^-$	-6986.30353930
6 [Cp'''Co(η^3-$P_5{}^t$Bu$_2$)]$^-$	-4071.49911149
7a [Cp'''Co(η^3-$P_4CH_2SiMe_3$)]$^-$ (endo isomer)	-3862.92310537
7b [Cp'''Co(η^3-$P_4CH_2SiMe_3$)]$^-$ (exo isomer)	-3862.92275672
8 [(Cp'''Co)$_2$(μ,η^3:η^3-$P_8CH_2SiMe_3$)]$^-$	-7277.08151112
9 [Cp'''Co(η^3-P_5(CH$_2$SiMe$_3$)$_2$)]$^-$	-4653.06490984
10 [Cp'''Co(η^3-P_4(O)H)]$^-$	-3490.11025036

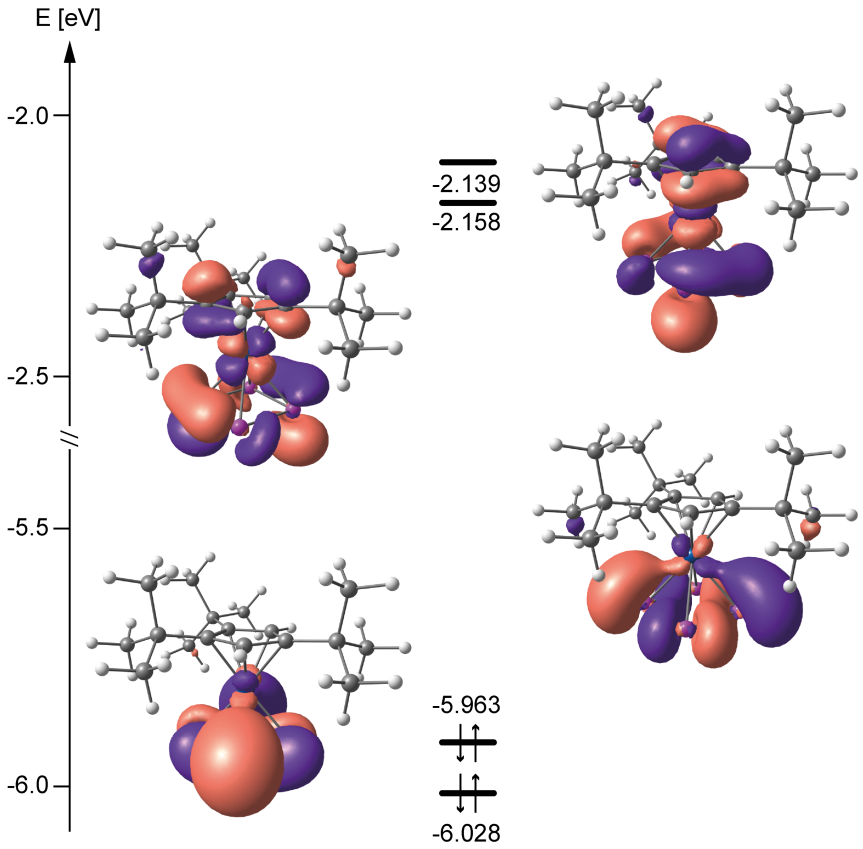
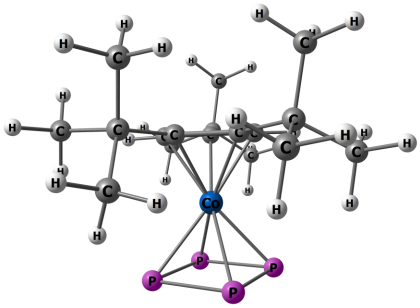
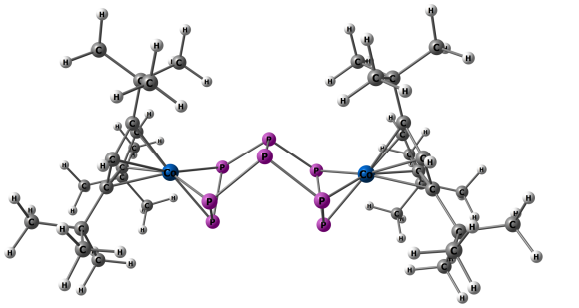


Figure S32: Molecular frontier orbitals of **1** (B3LYP/def2-TZVP level of theory.

Table S14: Optimized geometries of **1** (left), **2** (right). XYZ coordinated in angstroms. B3LYP/def2-TZVP level of theory.



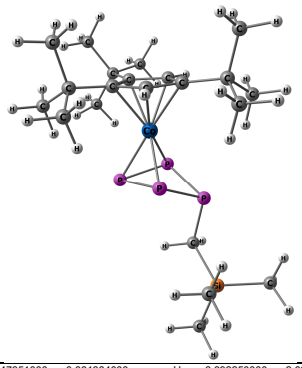
Co	-0.408168000	-0.538547000	-0.006352000	H	-1.830566000	3.780242000	-1.019022000
P	-2.337380000	-1.800346000	0.373219000	H	-2.866629000	1.660822000	-2.025728000
P	-0.515162000	-2.411411000	1.364220000	H	-4.308544000	1.998929000	-1.070804000
P	0.458579000	-2.616151000	-0.563909000	H	-3.524587000	0.420284000	-0.953829000
P	-1.365614000	-1.980853000	-1.552651000	H	-3.315378000	0.673198000	1.595764000
C	-1.101610000	1.425695000	0.083090000	H	-4.197911000	2.193416000	1.409185000
C	-0.283568000	1.113922000	1.197778000	H	-2.661424000	2.174354000	2.269712000
C	1.033190000	0.739624000	0.774553000	H	1.205984000	1.649673000	3.418163000
C	1.028263000	0.805612000	-0.680731000	H	2.388615000	0.453636000	3.941663000
C	-0.290187000	1.219186000	-1.058320000	H	0.790053000	-0.075582000	3.425335000
C	-2.490896000	2.020085000	0.098716000	H	2.041631000	-1.652965000	2.068764000
C	-2.310609000	3.544405000	-0.067907000	H	3.624139000	-0.953968000	2.410182000
C	-3.343566000	1.489436000	-1.060441000	H	3.098376000	-1.186951000	0.745906000
C	-3.203834000	1.744160000	1.426576000	H	3.756258000	1.496308000	0.689520000
C	2.142548000	0.494508000	1.802036000	H	3.951723000	1.502158000	2.437386000
C	1.585083000	0.644575000	3.229595000	H	2.773681000	2.576462000	1.675371000
C	2.765784000	-0.909096000	1.736642000	H	3.079865000	2.559767000	-1.072830000
C	3.221191000	1.581998000	1.630553000	H	1.811175000	2.826230000	-2.268772000
C	2.105389000	0.720236000	-1.766013000	H	3.374779000	2.169083000	-2.770359000
C	2.624373000	2.159882000	-1.977602000	H	3.951069000	-0.198254000	-2.351825000
C	3.289607000	-0.207270000	-1.484116000	H	2.953231000	-1.231732000	-1.330312000
C	1.493290000	0.234507000	-3.095074000	H	3.881021000	0.100562000	-0.628319000
H	-0.613699000	1.135785000	2.218566000	H	2.280255000	0.180624000	-3.848039000
H	-0.621333000	1.351209000	-2.070833000	H	0.726619000	0.904717000	-3.478843000
H	-1.696146000	3.954249000	0.735443000	H	1.058225000	-0.758704000	-2.986451000
H	-3.282948000	4.039853000	-0.042681000				



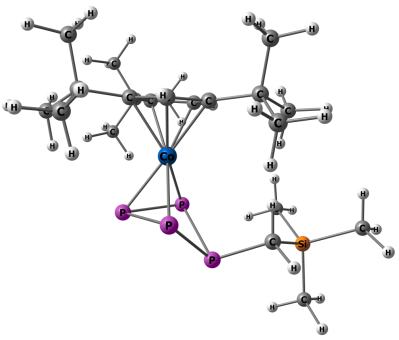
Co	-3.312766000	-0.098603000	-0.053425000	H	-3.913640000	-2.647455000	1.898689000
Co	3.312381000	-0.101957000	-0.041461000	C	-5.546422000	-1.008108000	3.185789000
P	-1.746035000	-0.106960000	-1.677834000	H	-4.493251000	-0.825748000	3.398501000
P	0.017755000	1.010734000	-0.940406000	H	-5.898903000	-1.780338000	3.872499000
P	1.727521000	-0.209689000	-1.641879000	H	-6.108237000	-0.094493000	3.388018000
P	-1.944336000	-1.883204000	-0.453992000	C	-5.129825000	4.016330000	0.473416000
P	-1.743203000	-0.795805000	1.414439000	H	-5.807183000	3.922292000	-0.378177000
P	1.756994000	-0.721101000	1.482858000	H	-4.834272000	5.065544000	0.560146000
P	-0.016459000	0.582211000	1.225777000	H	-5.681247000	3.741266000	1.374943000
P	1.945466000	-1.911916000	-0.321124000	C	5.780995000	-1.369573000	1.797055000
C	-4.370499000	1.684132000	0.178202000	C	7.278957000	-1.660930000	1.597439000
C	5.341243000	-0.310357000	-0.691722000	H	7.477728000	-2.205185000	0.678985000
C	-4.661684000	0.795642000	1.241166000	H	7.653412000	-2.266984000	2.426206000
H	-4.430712000	0.990529000	2.271161000	H	7.851962000	-0.731725000	1.569746000
C	5.955771000	-1.220365000	-1.759498000	C	-5.993624000	-1.101623000	-1.798157000
C	4.681824000	0.878773000	1.171211000	C	3.209669000	3.502178000	-1.241809000
H	4.468169000	1.144577000	2.189374000	H	3.891894000	3.400000000	-2.087711000
C	-5.262051000	-0.411910000	0.756946000	H	2.875854000	4.542156000	-1.208068000
C	-4.800836000	1.012176000	-0.996628000	H	2.342020000	2.867699000	-1.421632000
H	-4.696475000	1.405580000	-1.990593000	C	-5.368338000	-0.745951000	-3.161826000
C	4.783386000	0.945581000	-1.077894000	H	-5.582423000	0.281116000	-3.456887000
H	4.659809000	1.270881000	-2.093680000	H	-5.788412000	-1.398363000	-3.929939000
C	5.278874000	-0.356663000	0.758910000	H	-4.286405000	-0.876642000	-3.149072000
C	-5.352406000	-0.267288000	-0.685756000	C	-7.493676000	-0.747680000	-1.880318000
C	5.306533000	-0.945705000	-3.131171000	H	-8.019285000	-0.978940000	-0.955910000
H	4.223118000	-1.057299000	-3.087379000	H	-7.970930000	-1.303850000	-2.692082000
H	5.700822000	-1.653940000	-3.862592000	H	-7.619727000	0.318430000	-2.079084000
H	5.529883000	0.055950000	-3.497895000	C	-2.966509000	3.288115000	1.501129000
C	3.892197000	3.128355000	0.078950000	H	-3.475386000	3.033927000	2.432745000
C	4.372391000	1.694419000	0.055534000	H	-2.636313000	4.327271000	1.575322000
C	-3.892004000	3.114203000	0.291527000	H	-2.087363000	2.650365000	1.412264000
C	-7.247292000	-1.757329000	1.563800000	C	5.121413000	4.037779000	0.281009000
H	-7.811945000	-0.824741000	1.627294000	H	5.618905000	3.813949000	1.227032000
H	-7.600709000	-2.423638000	2.354769000	H	4.826438000	5.090706000	0.291114000
H	-7.480833000	-2.226289000	0.612218000	H	5.846078000	3.894038000	-0.523466000
C	7.456678000	-0.886633000	-1.893288000	C	4.980761000	-2.683798000	1.801529000
H	7.587523000	0.165965000	-2.151944000	H	3.947825000	-2.487533000	2.085016000
H	7.910728000	-1.490177000	-2.684297000	H	5.415189000	-3.377859000	2.527313000
H	8.001257000	-1.072874000	-0.969854000	H	4.963367000	-3.167605000	0.832557000
C	-3.144057000	3.549584000	-0.973862000	C	-5.830293000	-2.617363000	-1.638868000
H	-2.261649000	2.931289000	-1.135161000	H	-4.776995000	-2.878892000	-1.536478000
H	-2.826192000	4.590979000	-0.880584000	H	-6.226108000	-3.118825000	-2.525196000
H	-3.779086000	3.474619000	-1.858415000	H	-6.367714000	-3.008470000	-0.780716000

C	5.781655000	-2.721366000	-1.500852000	C	2.905631000	3.359373000	1.229376000
H	6.328500000	-3.062129000	-0.627258000	H	2.015625000	2.743350000	1.107028000
H	6.159068000	-3.282625000	-2.358984000	H	2.600895000	4.408596000	1.258671000
H	4.727852000	-2.965249000	-1.364799000	H	3.353325000	3.114908000	2.194064000
C	-5.741266000	-1.492810000	1.736760000	C	5.638898000	-0.782731000	3.214227000
C	-4.956302000	-2.812079000	1.631603000	H	6.217536000	0.135381000	3.331068000
H	-4.971812000	-3.233961000	0.634413000	H	6.007316000	-1.509104000	3.941404000
H	-5.379679000	-3.546589000	2.323127000	H	4.596889000	-0.571056000	3.452930000

Table S15: Optimized geometries of **7a** (left), **7b** (right). XYZ coordinated in angstroms. B3LYP/def2-TZVP level of theory.

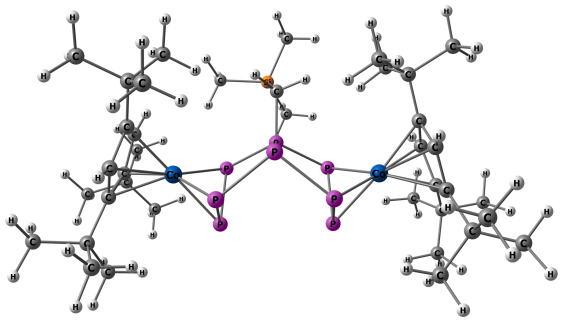


Co	-0.669106000	-0.047351000	-0.081384000	H	6.892250000	-2.089224000	-0.957118000
P	0.417185000	-1.994302000	-0.017222000	C	-2.055103000	4.258415000	0.234348000
P	0.721325000	-0.685682000	-1.765458000	H	-2.723350000	4.175456000	-0.625065000
P	2.446838000	0.324146000	-0.764081000	H	-1.655324000	5.275573000	0.259941000
P	1.287570000	-0.275137000	1.048524000	H	-2.646457000	4.100868000	1.138623000
Si	5.369635000	-0.436958000	0.126659000	C	-3.454595000	-0.198446000	-3.009866000
C	-2.074253000	1.172977000	-0.996390000	H	-3.941716000	0.776890000	-2.962800000
H	-1.989262000	1.519476000	-2.009140000	H	-3.999537000	-0.812841000	-3.729152000
C	-1.534829000	1.846498000	0.124253000	H	-2.440986000	-0.063444000	-3.387948000
C	3.842555000	-0.914448000	-0.858686000	C	0.014689000	3.399766000	1.348490000
H	3.473902000	-1.897687000	-0.551220000	H	-0.525582000	3.280379000	2.289128000
H	4.135078000	-0.989410000	-1.912639000	H	0.453865000	4.400069000	1.341897000
C	-2.557663000	-0.144604000	0.836095000	H	0.818838000	2.664534000	1.324277000
C	-1.844639000	1.025349000	1.241781000	C	-3.167600000	-2.578855000	1.466035000
H	-1.547539000	1.239341000	2.251419000	H	-3.900172000	-2.743782000	0.682596000
C	-2.711662000	-0.049674000	-0.607946000	H	-3.465879000	-3.189266000	2.321468000
C	-4.933561000	-1.066117000	-1.241209000	H	-2.197443000	-2.928428000	1.113987000
H	-5.059866000	-1.641362000	-0.329165000	C	6.158000000	1.090864000	-0.638305000
H	-5.482230000	-1.578363000	-2.035297000	H	6.437307000	0.906972000	-1.678883000
H	-5.394748000	-0.088537000	-1.086195000	H	7.060374000	1.382614000	-0.094807000
C	-0.913739000	3.225756000	0.141017000	H	5.464857000	1.934602000	-0.623615000
C	-2.802782000	-2.277686000	-1.879008000	C	-4.465054000	-0.626720000	2.366998000
H	-1.805819000	-2.142919000	-2.298564000	H	-4.402424000	0.392726000	2.751979000
H	-3.400573000	-2.852696000	-2.592114000	H	-4.847630000	-1.269969000	3.163889000
H	-2.697900000	-2.860318000	-0.972246000	H	-5.186583000	-0.632028000	1.551015000
C	-2.139805000	-1.100023000	3.127666000	C	4.936254000	-0.074772000	1.918299000
H	-1.120055000	-1.353765000	2.837333000	H	4.239186000	0.762257000	1.990598000
H	-2.486785000	-1.836166000	3.855309000	H	5.833990000	0.176149000	2.489644000
H	-2.123234000	-0.132802000	3.627913000	H	4.459602000	-0.936282000	2.390113000
C	-3.455821000	-0.905064000	-1.640703000	C	-0.110295000	3.485038000	-1.140175000
C	-3.076615000	-1.112985000	1.903104000	H	0.720705000	2.784746000	-1.224646000
C	6.609938000	-1.854560000	0.072223000	H	0.292334000	4.500981000	-1.129488000
H	6.187673000	-2.758930000	0.517086000	H	-0.733394000	3.384593000	-2.030260000
H	7.521231000	-1.603737000	0.621713000				

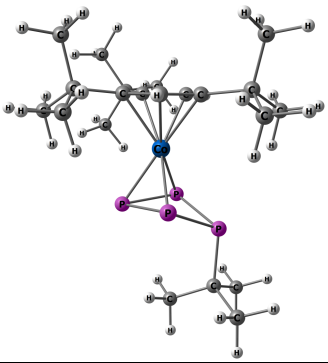


Co	0.588261000	-0.289588000	-0.319910000	H	-6.000836000	1.743961000	-0.531792000
P	0.568812000	-2.429698000	-0.925538000	C	0.478914000	4.263758000	-0.076754000
P	-0.903372000	-1.752966000	0.566166000	H	0.919095000	4.324837000	0.920439000
P	-2.360910000	-1.654171000	-1.140221000	H	-0.187318000	5.120204000	-0.210923000
P	-0.493262000	-0.984535000	-2.195092000	H	1.285747000	4.340668000	-0.807912000
Si	-4.640146000	-0.100799000	0.453867000	C	1.784847000	-0.152604000	3.523064000
C	0.935633000	1.118693000	1.177437000	H	1.807948000	0.912892000	3.757060000
H	0.330297000	1.201971000	2.060079000	H	2.187771000	-0.693925000	4.381184000
C	0.679896000	1.804020000	-0.032063000	H	0.746427000	-0.458020000	3.393669000
C	-3.323348000	-0.081196000	2.885275000	C	-0.880123000	2.902345000	-1.688852000
H	-2.629882000	0.734925000	-0.684247000	H	-0.092717000	2.965823000	-2.421361000
H	-3.821724000	0.143023000	-1.835893000	H	-1.557566000	3.746304000	-1.820293000
C	2.573902000	0.445460000	-0.302390000	H	-1.426174000	1.977508000	-1.843331000
C	1.691299000	1.373135000	-0.931284000	C	4.317267000	-1.435341000	-0.690466000
H	1.768931000	1.693949000	-1.953915000	H	4.673991000	-1.494916000	0.332618000
C	2.089314000	0.277784000	1.059289000	H	5.155333000	-1.697378000	-1.340525000
C	4.064648000	-0.029446000	2.596501000	H	3.531458000	-2.177233000	-0.828832000
H	4.769510000	-0.284753000	-0.638305000	C	-5.884511000	-1.469451000	0.118641000
H	4.410893000	-0.501724000	3.519251000	H	-6.343878000	-1.347657000	-0.865441000
H	4.098308000	1.053229000	2.735345000	H	-6.681804000	-1.467693000	0.866236000
C	-0.293645000	2.939672000	-0.251763000	H	-5.400359000	-2.447905000	0.140458000
C	2.564545000	-2.013035000	2.124418000	C	4.941154000	0.988049000	-0.850879000
H	1.527000000	-2.333376000	2.028320000	H	4.627472000	1.976506000	-1.191243000
H	2.989735000	-2.491022000	3.011701000	H	5.832158000	0.698973000	-1.414607000
H	3.099216000	-2.373555000	1.254874000	H	5.215551000	1.067324000	0.200427000
C	3.506783000	-0.095727000	-2.577386000	C	-3.872634000	-0.353332000	2.149443000
H	2.645733000	-0.734818000	-2.774724000	H	-3.373769000	-1.321366000	2.217585000
H	4.370809000	-0.502905000	-3.106146000	H	-4.637939000	-0.303158000	2.928639000
H	3.304817000	0.889095000	-2.996553000	H	-3.124262000	0.413795000	2.359846000
C	2.628426000	-0.483664000	2.277101000	C	-1.426107000	2.898536000	0.781274000
C	3.810330000	-0.039467000	-1.066686000	H	-1.927567000	1.932473000	0.776757000
C	-5.526824000	1.561601000	0.435774000	H	-2.166231000	3.671722000	0.564564000
H	-4.824425000	2.377489000	0.622978000	H	-1.047130000	3.073195000	1.789689000
H	-6.303227000	1.603437000	1.204236000				

Table S16: Optimized geometries of **8** (left), **4a** (right). XYZ coordinated in angstroms. B3LYP/def2-TZVP level of theory.



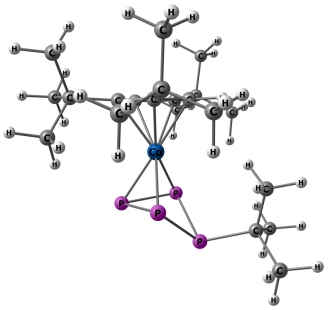
Co	-3.358929000	-0.512317000	0.140542000	H	3.124363000	3.134954000	0.093180000
Co	3.447489000	-0.356650000	0.027198000	C	5.717591000	-2.625471000	1.007728000
P	0.001954000	0.872673000	-0.249667000	C	6.020644000	-0.816833000	-2.099669000
P	0.061479000	-0.374700000	1.583816000	C	-7.287224000	-2.919154000	0.410801000
P	1.861258000	-1.626012000	1.051570000	H	-7.469509000	-2.541907000	1.429717000
P	1.872749000	0.466951000	-1.409020000	H	-7.645089000	-3.962505000	0.365774000
P	-1.895711000	-1.793449000	-1.101041000	H	-7.899801000	-2.322122000	-0.279120000
P	2.000419000	-1.708503000	-1.149531000	C	-4.967029000	-0.604417000	-3.166628000
P	-1.880148000	0.390656000	-1.340870000	H	-3.960022000	-0.162522000	-3.168769000
P	-1.677586000	-1.727370000	1.087201000	H	-5.419325000	-0.438514000	-4.154363000
Si	-0.335352000	4.038495000	-1.086255000	H	-4.846583000	-1.682290000	-3.017755000
C	4.713379000	1.057225000	0.942222000	C	-5.704650000	1.575806000	3.458463000
C	-4.610011000	0.463885000	1.527458000	H	-6.423550000	2.064413000	2.780925000
C	-5.333016000	-0.199090000	-0.625828000	H	-5.577899000	2.219169000	4.346631000
C	-4.891093000	0.895223000	0.201183000	H	-6.150520000	0.623852000	3.788200000
C	-4.779091000	1.916679000	-0.146083000	C	-5.828394000	1.572492000	-2.376675000
C	5.063498000	0.886165000	-0.431850000	H	-6.476218000	2.139367000	-1.689627000
H	5.023686000	1.673949000	-1.177167000	H	-6.200498000	1.738647000	-3.400741000
C	-4.855981000	-0.942768000	1.519668000	H	-4.813250000	1.991316000	-2.323739000
H	-4.713151000	-1.594788000	2.375865000	C	5.545642000	-2.771764000	2.539039000
C	5.452625000	-0.466753000	-0.704402000	H	6.187179000	-2.071196000	3.096785000
C	4.871280000	-0.226808000	1.530720000	H	5.827540000	-3.793678000	2.840833000
H	4.662590000	-0.452067000	2.571254000	H	4.501414000	-2.613164000	2.845552000
C	4.432662000	2.365658000	1.672159000	C	4.846772000	-3.737327000	0.378856000
C	5.331019000	-1.191422000	0.563411000	H	3.805948000	-3.651536000	0.723488000
C	-0.023905000	2.672615000	0.216314000	H	5.226536000	-4.727343000	0.687178000
H	0.942817000	2.875375000	0.705694000	H	4.833264000	-3.706253000	-0.714384000
H	-0.793349000	2.781844000	0.999370000	C	0.634402000	3.766813000	-2.681938000
C	-5.304275000	-1.386423000	0.230001000	H	1.718708000	3.710948000	-2.496560000
C	-5.545079000	-3.457605000	-1.332373000	H	0.445840000	4.595629000	-3.386191000
H	-6.133671000	-2.963966000	-2.114788000	H	0.340305000	2.823518000	-3.168038000
H	-5.845854000	-4.518568000	-1.324876000	C	-3.382101000	0.653598000	3.737715000
H	-4.482285000	-3.403510000	-1.611337000	H	-3.759825000	-0.328092000	4.063084000
C	5.740607000	2.822112000	2.363953000	H	-3.255370000	1.275528000	4.640422000



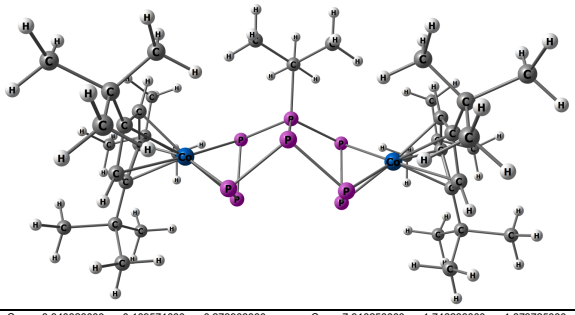
Co	0.183195000	-0.025855000	-0.063508000	H	2.905830000	0.357849000	3.415995000
P	-0.835209000	-1.921200000	-0.596456000	H	2.836201000	-1.321048000	3.957458000
P	-1.435415000	-0.941347000	1.283013000	H	1.357619000	-0.502533000	3.457986000
P	-2.914145000	0.355589000	0.243174000	C	-0.335889000	3.563416000	-1.102223000
P	-1.598568000	-0.065154000	-1.499012000	H	0.285089000	3.489663000	-1.996389000
C	1.401926000	1.049864000	1.221712000	H	-0.736708000	4.579045000	-1.058443000
H	1.143422000	1.263618000	2.241462000	H	-1.164895000	2.864338000	-1.207802000
C	1.062948000	1.871122000	0.123489000	C	2.934407000	-2.368391000	-1.494142000
C	2.202106000	-0.031280000	-0.656065000	H	3.507264000	-2.650400000	-0.616824000
C	1.555910000	1.189264000	-1.022293000	H	3.395594000	-2.860393000	-2.353628000
H	1.433502000	1.536663000	-2.031246000	H	1.919553000	-2.749305000	-1.382675000
C	2.102247000	-0.127028000	0.791099000	C	4.357363000	-0.334478000	-1.870882000
C	4.189412000	-1.253557000	1.657909000	H	4.358906000	0.728384000	-2.119575000
H	4.476982000	-1.712219000	0.716566000	H	4.882159000	-0.871690000	-2.665361000
H	4.595113000	-1.870028000	2.463810000	H	4.919099000	-0.462509000	-0.946602000
H	4.664836000	-0.271790000	1.709805000	C	-0.447514000	3.434924000	1.385224000
C	0.469093000	3.261830000	0.168323000	H	-1.293037000	2.749029000	1.332532000
C	1.990799000	-2.504427000	1.747963000	H	-0.833819000	4.456573000	1.418590000
H	0.939735000	-2.416739000	2.023407000	H	0.087271000	3.252526000	2.318718000
H	2.474333000	-3.186317000	2.453462000	C	-4.544842000	-0.614700000	0.015324000
H	2.032070000	-2.945670000	0.760070000	C	-5.351831000	0.152037000	-1.036783000
C	2.210611000	-0.658334000	-3.094035000	H	-5.514672000	1.189507000	-0.736132000
H	1.155746000	-0.925354000	-3.027157000	H	-4.834999000	0.156690000	-1.999165000
H	2.684086000	-1.288343000	-3.840929000	C	-6.331434000	-0.315908000	-1.183058000
H	2.283030000	-0.367185000	-3.453501000	C	-5.267280000	-0.570220000	1.365085000
C	2.663373000	-1.122288000	1.814170000	H	-6.246325000	-1.056705000	1.291793000
C	2.911279000	-0.855034000	-1.734836000	H	-4.692876000	-1.090152000	2.135309000
C	1.634809000	4.266472000	0.270782000	H	-5.425081000	0.457933000	1.698291000
H	2.218860000	4.089577000	1.176170000	C	-4.369711000	-2.063398000	-0.427025000
H	1.259514000	5.292820000	0.300098000	H	-5.349588000	-2.539066000	-0.550612000
H	2.304222000	4.171894000	-0.586729000	H	-3.836022000	-2.125268000	-1.375292000
C	2.421610000	-0.605112000	3.245100000	H	-3.801753000	-2.636188000	0.306183000

H	6.079204000	2.076448000	3.100807000	H	-2.393282000	0.494666000	3.283140000
H	5.594565000	3.781087000	2.891208000	C	7.213290000	-2.880637000	0.714255000
H	6.550218000	2.956509000	1.628410000	H	7.431852000	-2.938409000	-0.360263000
C	-4.347736000	1.336806000	2.750614000	H	7.520087000	-3.855005000	1.153721000
C	-5.777677000	-2.849415000	0.063608000	H	7.846532000	-2.102118000	1.152894000
C	3.340687000	2.176811000	2.742863000	C	-3.758741000	2.698263000	2.340656000
H	2.401416000	1.818784000	2.296722000	H	-2.821222000	2.563158000	1.782270000
H	3.145585000	3.126581000	3.269431000	H	-3.546537000	3.310371000	3.232811000
H	3.642032000	1.435054000	3.498976000	H	-4.453156000	3.269624000	1.704298000
C	-5.838697000	0.056558000	-2.068686000	C	5.402776000	0.105436000	-3.179507000
C	-7.309484000	-0.399762000	-2.213919000	H	4.304224000	0.045837000	-3.179886000
H	-7.423663000	-1.487955000	-2.134896000	H	5.765351000	-0.199207000	-4.174807000
H	-7.704068000	-0.099894000	-3.199760000	H	5.685629000	1.159979000	-3.045174000
H	-7.943225000	0.063137000	-1.440089000	C	7.548004000	-0.552487000	-2.085548000
C	0.230090000	5.663315000	-0.278682000	H	7.758937000	0.494958000	-1.817169000
H	-0.312230000	5.850123000	0.663534000	H	7.983369000	-0.743753000	-3.081908000
H	0.045337000	6.521914000	-0.946900000	H	8.069771000	-1.191950000	-1.359817000
H	1.308097000	5.643469000	-0.047267000	C	-2.180645000	4.175142000	-1.474447000
C	-5.036091000	-3.771555000	1.062620000	H	-2.552620000	3.240030000	-1.922580000
H	-3.944341000	-3.687171000	0.959704000	H	-2.368711000	4.999848000	-2.183142000
H	-5.322331000	-4.819632000	0.877410000	H	-2.768469000	4.370718000	-0.562312000
H	-5.294653000	-3.550104000	2.108639000	C	5.755999000	-2.258185000	-2.572878000
C	3.995830000	3.459891000	0.680429000	H	6.261495000	-3.008907000	-1.954003000
H	4.801627000	3.706848000	-0.029012000	H	6.134798000	-2.381142000	-3.601467000
H	3.732834000	4.386627000	1.217263000	H	4.678012000	-2.477813000	-2.575718000

Table S17: Optimized geometries of **4b** (left), **5** (right). XYZ coordinated in angstroms. B3LYP/def2-TZVP level of theory.

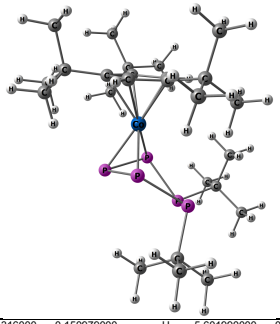


Co	-0.112579000	0.054051000	-0.506496000	H	-4.170450000	1.354418000	-1.745252000
P	0.418883000	-0.736931000	-2.513824000	H	-4.577232000	-0.063367000	-2.713443000
P	1.766942000	0.737444000	-1.597718000	H	-2.956459000	0.625029000	-2.809807000
P	3.037660000	-1.025433000	-1.080453000	C	1.210066000	3.169407000	1.226399000
P	0.999303000	-1.915377000	-0.742473000	H	1.190758000	2.689776000	2.206064000
C	-1.734022000	1.402031000	-0.493921000	H	1.586395000	4.186293000	1.361379000
H	-2.036403000	1.983046000	-1.344356000	H	1.907686000	2.623582000	0.593259000
C	-0.781294000	1.819974000	0.463722000	C	-2.114114000	-2.824007000	1.389097000
C	-1.535561000	-0.316555000	1.029510000	H	-3.085894000	-2.810363000	0.907508000
C	-0.656424000	0.759042000	1.391145000	H	-2.152508000	-3.581472000	2.175345000
H	-0.024079000	0.774343000	2.258688000	H	-1.365025000	-3.132859000	0.660406000
C	-2.226501000	0.095007000	-0.174418000	C	-2.820278000	-1.050709000	3.021807000
C	-4.603198000	-0.755932000	-0.126729000	H	-2.516806000	-0.142908000	3.546491000
H	-4.449294000	-1.495876000	0.652795000	H	-2.978484000	-1.837592000	3.764288000
H	-5.437338000	-1.095794000	-0.745551000	H	-3.771291000	-0.850082000	2.531484000
H	-4.896993000	0.179464000	0.354126000	C	-0.093369000	3.899713000	-0.774288000
C	-0.184226000	3.206217000	0.590007000	H	0.536941000	3.328814000	-1.455949000
C	-2.947649000	-1.854126000	-1.694685000	H	0.336927000	4.897216000	-0.658306000
H	-2.202925000	-1.647816000	-2.462313000	H	-1.078662000	4.014652000	-1.228701000
H	-3.822101000	-2.304188000	-2.173426000	C	3.887028000	-0.656601000	0.584270000
H	-2.520630000	-2.581213000	-1.016073000	C	4.727276000	-1.890175000	0.934041000
C	-0.443960000	-1.745809000	2.811806000	H	4.095420000	-2.771338000	1.070070000
H	0.362455000	-2.044183000	2.145164000	H	5.452635000	-2.114303000	0.149258000
H	-0.625048000	-2.557181000	3.519873000	H	5.276311000	-1.725552000	1.867793000
H	-0.116563000	-0.880256000	3.385045000	C	2.932181000	-0.347923000	1.731723000
C	-3.352977000	-0.541743000	-1.001076000	H	3.496603000	-0.055797000	2.625341000
C	-1.732619000	-1.477259000	2.012608000	H	2.245814000	0.454331000	1.474281000
C	-1.121842000	4.023641000	1.502448000	H	2.330955000	-1.219553000	1.985147000
H	-2.127423000	4.070275000	1.080272000	C	4.808086000	0.543558000	0.338548000
H	-0.749954000	5.045091000	1.618354000	H	5.418353000	0.740477000	1.226521000
H	-1.191560000	3.569450000	2.492715000	H	5.484009000	0.365065000	-0.501325000
C	-3.783592000	0.410745000	-2.132824000	H	4.231605000	1.444464000	0.120169000



Co	-3.340828000	-0.109571000	-0.273906000	C	7.310250000	-1.746266000	-1.873725000
Co	3.350333000	-0.115579000	-0.258184000	H	7.499301000	-0.793763000	-2.371588000
P	1.831262000	-0.873167000	1.242095000	H	7.682022000	-2.547596000	-2.517105000
P	-1.804194000	-0.916626000	1.186583000	H	7.883735000	-1.760552000	-0.947994000
P	0.001761000	0.328226000	1.106867000	C	-4.746663000	-2.568722000	2.153656000
P	1.703901000	0.215768000	-1.739673000	H	-4.709068000	-3.233128000	1.300667000
P	0.018586000	1.356313000	-0.820141000	H	-5.159066000	-3.125044000	2.999502000
P	1.815857000	-1.722906000	-0.754180000	H	-3.723059000	-2.289970000	2.397185000
P	-1.701877000	0.284339000	-1.753646000	C	-7.297252000	-1.797593000	-1.839402000
P	-1.802916000	-1.688842000	-0.839656000	H	-7.505501000	-0.847880000	-2.334858000
C	-4.700775000	1.478137000	-0.492884000	H	-7.858836000	-1.819352000	-0.906573000
C	-5.208561000	-0.499761000	0.663727000	H	-7.666089000	-2.604175000	-2.477897000
C	-4.982035000	0.444465000	-1.424643000	C	-5.781619000	-1.961985000	-1.597177000
H	-4.942899000	0.563406000	-2.490446000	C	4.803172000	-2.547635000	2.147957000
C	5.234695000	-0.478230000	0.656496000	H	5.220004000	-3.098785000	2.995028000
C	4.829024000	0.898512000	0.779503000	H	4.767295000	-3.215368000	1.297327000
H	4.661529000	1.405420000	1.711380000	H	3.778695000	-2.272472000	2.392885000
C	4.968199000	0.463672000	-1.428225000	C	-5.083974000	-1.951396000	-2.973019000
H	4.913057000	0.582406000	-2.493369000	H	-5.389543000	-2.834324000	-3.537306000
C	4.679394000	1.491955000	-0.492613000	H	-4.000596000	-1.971860000	-2.857677000
C	-4.824648000	0.884221000	0.781131000	H	-5.350271000	-1.079634000	-3.568692000
H	-4.660124000	1.396446000	1.710576000	C	5.085329000	-1.928952000	-2.979905000
C	-5.310777000	-0.771232000	-0.755471000	H	4.003816000	-1.965909000	-2.851678000
C	7.136826000	-1.658871000	1.789899000	H	5.396951000	-2.806467000	-3.549293000
H	7.473733000	-2.113362000	2.724593000	H	5.330930000	-1.052538000	-3.577601000
H	7.744546000	-0.771010000	1.603902000	C	-5.513357000	-3.345247000	-0.999548000
H	7.328552000	-2.368840000	0.989897000	H	-6.074387000	-3.525169000	-0.087747000
C	-5.866531000	3.644759000	-0.569734000	H	-4.451166000	-3.476508000	-0.794132000
H	-6.644556000	3.203911000	-1.196122000	H	-5.815552000	-4.108174000	-1.719974000
H	-5.794912000	4.708307000	-0.810201000	C	5.556792000	-3.318731000	-1.014284000
H	-6.176209000	3.548569000	0.472440000	H	6.126345000	-3.491469000	-0.106529000
C	-4.512176000	2.946180000	-0.805985000	H	5.865462000	-4.076253000	-1.737718000
C	-5.597257000	-1.310715000	1.908825000	H	4.497994000	-3.466023000	-0.802211000
C	4.457010000	2.955999000	-0.802790000	C	-4.094028000	3.153570000	-2.266030000
C	5.323304000	-0.747376000	-0.764000000	H	-3.165606000	2.624394000	-2.483161000
C	5.646253000	-1.286173000	1.895432000	H	-3.941575000	4.217246000	-2.460358000
C	-0.035699000	1.454309000	2.615047000	H	-4.859276000	2.796043000	-2.957047000
C	-7.087130000	-1.691453000	1.822168000	C	5.496112000	-0.423150000	3.162130000
H	-7.701856000	-0.808230000	1.637222000	H	4.462958000	-0.106210000	3.307112000
H	-7.411224000	-2.142010000	2.763283000	H	6.131665000	0.463109000	3.130399000
H	-7.283127000	-2.407878000	1.028811000	H	5.789074000	-1.013763000	4.031923000
C	-5.434299000	-0.446059000	3.172852000	C	-3.455794000	3.575890000	0.104070000
H	-4.402251000	-0.117061000	3.297985000	H	-3.707631000	3.451526000	1.157463000
H	-5.703733000	-1.040242000	4.047766000	H	-3.373597000	4.646595000	-0.097368000
H	-6.080684000	0.432669000	3.153743000	H	-2.485665000	3.113909000	-0.069275000
C	5.797500000	3.684309000	-0.578077000	C	-1.270423000	2.351659000	2.551054000
H	6.579559000	3.260727000	-1.211362000	H	-1.335560000	2.944514000	3.468029000
H	6.118389000	3.594706000	0.461325000	H	-2.185388000	1.769874000	2.448621000
H	5.700793000	4.746172000	-0.817243000	H	-1.210255000	3.035836000	1.707459000
C	5.800076000	-1.931088000	-1.612796000	C	4.021570000	3.155011000	-2.258938000
C	1.226855000	2.314238000	2.645403000	H	3.843215000	4.215089000	-2.450847000
H	1.224125000	2.926842000	3.551616000	H	3.103533000	2.605292000	-2.468857000
H	1.265832000	2.979277000	1.785869000	H	4.788843000	2.815657000	-2.956841000
H	2.130720000	1.705737000	2.644119000	C	3.394807000	3.561892000	0.116873000
C	-0.095144000	0.569170000	3.867987000	H	3.655269000	3.434978000	1.167929000
H	0.769741000	-0.090950000	3.934352000	H	2.431196000	3.084869000	-0.054598000
H	-0.994170000	-0.046613000	3.882642000	H	3.292870000	4.632269000	-0.077232000
H	-0.104820000	1.211428000	4.753188000				

Table S18: Optimized geometries of **6** (left), **3** (right). XYZ coordinated in angstroms. B3LYP/def2-TZVP level of theory.



Co	-0.753770000	-0.214316000	-0.150979000	H	-5.601990000	-0.683893000	-0.255186000
P	2.766237000	-0.744432000	0.231409000	H	-5.743229000	-2.179817000	-1.185224000
P	0.137632000	-0.576432000	-2.204139000	H	-4.990562000	-2.194700000	0.416671000
P	0.890937000	-1.697901000	-0.477341000	H	-4.490578000	-1.313567000	-3.159921000
P	0.516882000	1.321192000	-1.241063000	H	-4.473872000	0.267941000	-2.404821000
P	2.701079000	1.156898000	-0.894596000	H	-2.959039000	-0.454827000	-2.966943000
C	-4.749443000	2.022502000	-0.200595000	H	-3.074970000	-3.406335000	-0.623509000
C	-5.099767000	-1.617924000	-0.503284000	H	-3.715732000	-3.233729000	-2.249510000
C	-0.374224000	-2.443596000	3.005815000	H	-2.093546000	-2.630021000	-1.871362000
C	-3.721645000	-1.368967000	-1.152475000	H	-5.175921000	2.998004000	-0.447293000
C	-0.852409000	-0.989244000	3.081732000	H	-5.199365000	1.288753000	-0.864031000
C	3.034859000	2.517381000	0.399602000	H	-5.038450000	1.772371000	0.822281000
C	-2.153225000	-1.399945000	0.847558000	H	-3.061799000	1.632848000	-2.486268000
C	-1.501883000	-0.556610000	1.785171000	H	-3.345467000	3.325961000	-2.092332000
C	2.091102000	2.488377000	1.597667000	H	-1.750936000	2.598250000	-1.841994000
C	-3.216264000	2.070554000	-0.335550000	H	-3.170873000	4.178368000	0.130144000
C	-3.919709000	-0.660966000	-2.495558000	H	-3.046238000	3.158059000	1.564071000
C	-2.822661000	2.417499000	-1.780522000	H	-1.651850000	3.357049000	0.488079000
C	-1.918040000	-0.872328000	4.190610000	H	4.286262000	-3.107051000	1.010275000
C	0.338435000	-0.095422000	3.432581000	H	3.200964000	-3.658143000	-0.269899000
H	0.755439000	-0.385564000	4.400169000	H	4.953206000	-3.726269000	-0.507570000
H	1.115436000	-0.189812000	2.676471000	H	2.973863000	-2.299379000	-2.422473000
H	0.049018000	0.954310000	3.494123000	H	3.913538000	-0.824906000	-2.638699000
C	2.887769000	3.854124000	-0.339653000	H	4.729889000	-2.397263000	-2.644044000
C	4.138903000	-3.137926000	-0.071576000	H	5.507515000	-0.046278000	-0.813525000
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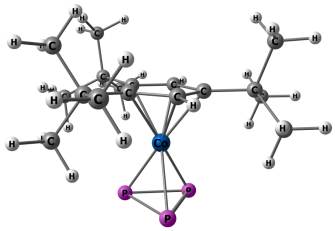
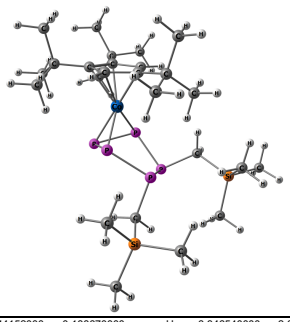
C	3.921620000	-1.816650000	-2.185296000	H	6.291352000	-1.631569000	-0.810968000
C	-2.847396000	-0.631924000	-0.131670000	H	1.048896000	2.562628000	1.287967000
C	-3.107032000	-2.743652000	-1.487117000	H	2.206160000	1.563336000	2.157748000
C	5.471403000	-1.046590000	-0.380493000	H	2.311119000	3.325016000	2.270400000
C	-2.613406000	0.761701000	0.194309000	H	4.615124000	1.427284000	1.426223000
C	-2.736863000	3.256714000	0.522470000	H	5.184899000	2.380363000	0.051811000
C	4.131969000	-1.728057000	-0.674716000	H	4.734868000	3.187666000	1.560865000
C	-1.777794000	0.762801000	1.366428000	H	-1.205491000	-3.128923000	2.831397000
H	-2.110457000	-2.472108000	0.867849000	H	0.346640000	-2.571985000	2.198403000
H	-1.415414000	1.645724000	1.857654000	H	0.100105000	-2.729423000	3.947352000
H	-2.785064000	-1.495569000	3.962368000	H	3.554099000	3.907983000	-1.203041000
H	-1.508847000	-1.193991000	5.151813000	H	1.866316000	3.999316000	-0.694295000
H	-2.260088000	0.159340000	4.291474000	H	3.136245000	4.680814000	0.334162000

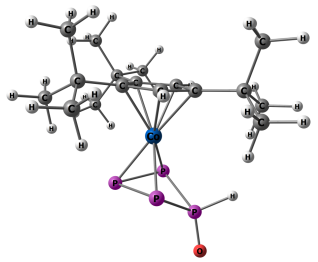


Co	10.613423000	3.991815000	9.769552000	H	10.923191000	-0.109333000	10.851724000
P	10.696768000	3.024863000	7.725082000	C	8.951259000	0.821485000	12.552582000
P	11.944618000	4.763784000	8.109731000	H	9.856266000	0.645345000	13.132270000
P	9.791237000	4.994193000	7.914428000	H	8.385435000	-0.113181000	12.512375000
C	10.125568000	4.975987000	11.538103000	H	8.350751000	1.560714000	13.085858000
C	9.733429000	6.420167000	11.764371000	C	8.325543000	6.699207000	11.226067000
C	10.016612000	2.652666000	11.239206000	H	8.274299000	6.488319000	10.157640000
C	11.432831000	4.440307000	11.610665000	H	8.063717000	7.747405000	11.387850000
H	12.320381000	5.029117000	11.749831000	H	7.576243000	6.087960000	11.732349000
C	9.263221000	3.866435000	11.324956000	C	13.127243000	1.532827000	10.230399000
H	8.196868000	3.935557000	11.216525000	H	12.376924000	0.854860000	9.841740000
C	11.416211000	3.017402000	11.431059000	H	14.054011000	0.970056000	10.376127000
C	9.274092000	1.317546000	11.127833000	H	13.298044000	2.297570000	9.473098000
C	12.706371000	2.196263000	11.553296000	C	13.879018000	3.110685000	11.956610000
C	9.751877000	6.696184000	13.280422000	H	14.070728000	3.872788000	11.200864000
H	9.054170000	6.037496000	13.801828000	H	14.783905000	2.508390000	12.057464000
H	9.466561000	7.730609000	13.489648000	H	13.696391000	3.606001000	12.911474000
H	10.748326000	6.526703000	13.692883000	C	12.580900000	1.144760000	12.670500000
C	7.936697000	1.512024000	10.385215000	H	12.304317000	1.621333000	13.613381000
H	7.255603000	2.172923000	10.919354000	H	13.537384000	0.636280000	12.815717000
H	7.437931000	0.546065000	10.282730000	H	11.835517000	0.386566000	12.450245000
H	8.106755000	1.921592000	9.389170000	C	10.723303000	7.365126000	11.069222000
C	10.013244000	0.217146000	10.358841000	H	11.739224000	7.221628000	11.440176000
H	10.266177000	0.560985000	9.356171000	H	10.444490000	8.406010000	11.251969000
H	9.362566000	-0.655844000	10.270076000	H	10.729661000	7.183516000	9.994522000

Table S19: Optimized geometries of **9** (left), **10** (right). XYZ coordinated in angstroms. B3LYP/def2-TZVP level of theory.



Co	-1.428363000	-0.144152000	-0.188670000	H	-6.346540000	2.009108000	-1.147389000
P	2.130523000	-0.539791000	-0.206261000	H	-6.099236000	0.341095000	-0.645377000
P	-0.810339000	-1.176093000	-2.119326000	H	-5.862535000	1.644136000	0.515036000
P	0.219154000	-1.653207000	-0.243352000	H	-4.239015000	0.048075000	-2.602822000
P	-0.432503000	0.944405000	-1.901906000	H	-4.753580000	1.677188000	-3.034269000
P	1.778450000	1.005871000	-1.752271000	H	-3.045753000	1.325254000	-2.734031000
C	-5.726920000	1.354805000	-0.529208000	H	-4.554001000	3.538695000	-1.547943000
C	-5.443841000	-1.933256000	1.082535000	H	-4.071649000	3.390972000	0.143422000
C	-0.133554000	-0.423564000	3.423852000	H	-2.875162000	3.178379000	-1.147565000
C	-4.221937000	-1.912321000	0.141022000	H	-0.843854000	-1.141681000	3.842526000
C	-0.848192000	0.825838000	2.896376000	H	0.422571000	-0.916206000	2.626388000
C	2.017042000	2.611014000	-0.825045000	H	0.566502000	-0.145378000	4.214798000
C	-2.415177000	-0.777779000	1.531350000	Si	3.732662000	2.913375000	-0.097483000
C	-1.793878000	0.476999000	1.769076000	Si	4.251373000	-2.824803000	0.035563000
C	-4.248607000	1.489677000	-0.938020000	C	4.092796000	4.760592000	-0.198126000
C	-4.696432000	-1.996993000	-1.312450000	H	3.327351000	5.337068000	0.327662000
C	-4.062267000	1.099140000	-2.414541000	H	5.060029000	4.998465000	0.252162000
C	-1.682476000	1.443900000	4.036333000	H	4.112305000	5.100531000	-1.236636000
C	0.205089000	1.838571000	2.437769000	C	5.059749000	1.990654000	-1.057859000
H	0.831342000	2.139312000	3.280860000	H	4.960786000	0.912586000	-0.924124000
H	0.847038000	1.401607000	1.675972000	H	4.998620000	2.200937000	-2.127580000
H	-0.254501000	2.737918000	2.025056000	H	6.053261000	2.283189000	-0.707864000
C	-3.374117000	-0.682616000	0.481433000	C	3.810706000	2.388863000	1.703681000
C	-3.411662000	-3.200018000	0.392687000	H	3.108972000	2.963003000	2.312051000
C	-3.364476000	0.700482000	0.037533000	H	3.559688000	1.332505000	1.805024000
C	-3.909338000	2.990447000	-0.858419000	H	4.815711000	2.548115000	2.103655000
C	3.273204000	-1.711542000	-1.119365000	C	5.390160000	-1.754373000	1.083380000
C	-2.385405000	1.370285000	0.845479000	H	4.812722000	-1.056263000	1.692203000
H	-2.169739000	-1.683407000	2.053231000	H	5.999515000	-2.367228000	1.752283000
H	-2.123512000	2.407181000	0.750525000	H	6.064832000	-1.168688000	0.453930000
H	-2.456730000	0.749776000	4.369767000	C	5.294676000	-4.011573000	-0.989278000
H	-1.046966000	1.684263000	4.892565000	H	5.897963000	-4.660861000	-0.349458000
H	-2.171724000	2.361793000	3.704898000	H	4.662484000	-4.647627000	-1.613616000
H	-6.072357000	-1.054433000	0.945553000	H	5.973535000	-3.464765000	-1.648283000
H	-6.052580000	-2.820950000	0.892288000	C	3.117164000	-3.814791000	1.157796000
H	-5.122084000	-1.957152000	2.125160000	H	2.435558000	-4.437598000	0.574992000
H	-5.206972000	-2.950147000	-1.466887000	H	3.698533000	-4.465021000	1.816783000
H	-5.397843000	-1.210691000	-1.573432000	H	2.506901000	-3.155312000	1.777343000
H	-3.845145000	-1.949352000	-1.991087000	H	1.264935000	2.728031000	-0.042507000
H	-3.154673000	-3.332953000	1.442662000	H	1.828899000	3.397162000	-1.563135000
H	-4.007511000	-4.064194000	0.092461000	H	3.993152000	-1.101863000	-1.672726000
H	-2.488710000	-3.194950000	-0.186875000	H	2.712326000	-2.289929000	-1.857890000



Co	-0.315892000	-0.232194000	-0.045065000	C	2.400116000	-0.458586000	1.808786000
P	-3.288776000	-0.999549000	0.089992000	C	2.032009000	0.008303000	3.230104000
H	-3.643393000	0.355208000	0.362992000	H	2.191043000	1.079928000	3.359187000
P	-1.595078000	-1.458850000	1.395359000	H	2.662867000	-0.514502000	3.951196000
P	-0.698515000	-2.392695000	-0.396654000	H	0.993714000	-0.221803000	3.469772000
P	-1.866177000	-0.930903000	-1.568138000	C	3.888550000	-0.115499000	1.615981000
O	-4.544823000	-1.834623000	0.057133000	H	4.287745000	-0.484849000	0.676277000
C	1.584522000	0.357807000	-0.680786000	H	4.478391000	-0.556970000	2.422556000
C	1.543962000	0.281728000	0.773154000	H	4.036960000	0.966056000	1.640518000
C	0.523246000	1.196396000	1.190513000	C	2.188050000	-1.981975000	1.798751000
H	0.222970000	1.346969000	2.209994000	H	1.166275000	-2.214219000	2.099051000
C	-0.072132000	1.840979000	0.080915000	H	2.869127000	-2.454218000	2.511998000
C	0.592001000	1.315035000	-1.059282000	H	2.351223000	-2.424219000	0.824143000
H	0.357562000	1.579257000	-2.073598000	C	-1.076838000	2.970762000	0.113567000
C	2.496974000	-0.241918000	-1.754024000	C	-1.993659000	2.933831000	-1.115269000
C	1.755183000	-0.308863000	-3.103676000	H	-1.423079000	3.004255000	-2.042383000
H	0.836707000	-0.889443000	-3.014937000	H	-2.690404000	3.774665000	-1.087749000
H	2.397246000	-0.789873000	-3.843662000	H	-2.566184000	2.007558000	-1.142903000
H	1.500582000	0.677979000	-3.487913000	C	-1.937097000	2.903881000	1.381179000
C	2.985303000	-1.667281000	-1.475056000	H	-2.478086000	1.959157000	1.432999000
H	3.625134000	-1.734084000	-0.601436000	H	-2.663639000	3.719196000	1.382856000
H	3.566505000	-2.019149000	-2.330143000	H	-1.329839000	2.999119000	2.282598000
H	2.138475000	-2.339308000	-1.335984000	C	-0.291605000	4.297796000	0.111794000
C	3.710030000	0.694913000	-1.932693000	H	0.368997000	4.356841000	0.979024000
H	3.379864000	1.698784000	-2.206170000	H	-0.974942000	5.150097000	0.142402000
H	4.362811000	0.322624000	-2.726354000	H	0.321759000	4.383300000	-0.787285000
H	4.297784000	0.773960000	-1.019498000				

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10. Phosphino-Stibine Ligands and their use in enforcing Metal-Metal Interactions

Martin Piesch, Francois Gabbai and Manfred Scheer

- Synthesis and characterization of all compounds was performed by Martin Piesch
- DFT calculations were performed by Martin Piesch
- X-ray measurements and calculations were done by Martin Piesch and finally checked by Michael Seidl
- Manuscript was written by Martin Piesch
- Figures were made by Martin Piesch

10.1 Introduction

***Abstract**: The phosphino-stibine ligands (o-$PPh_2C_6H_4)_2SbR$ (R = o-$PPh_2C_6H_4$ (**L1**), Ph (**L2**), Cl (**L3**)) were introduced into tungsten and molybdenum carbonyl complexes yielding $[W(CO)_4\{\eta^1:\eta^1$-(o-$PPh_2C_6H_4)_2SbR\}]$ (R = o-$PPh_2C_6H_4$ (**1**), Ph (**2**), Cl (**3**)), $[W(CO)_3\{\eta^1:\eta^1:\eta^1$-(o-$PPh_2C_6H_4)_3Sb\}]$ (**4**), $[W(CO)_3\{\eta^1:\eta^1:\eta^1$-(o-$PPh_2C_6H_4)_2SbCl\}]$ (**5**), $[(W(CO)_3\{\eta^1:\eta^1:\eta^1$-(o-$PPh_2C_6H_4)_2Sb\})_2]$ (**6**), $[Mo(CO)_3\{\eta^1:\eta^1:\eta^1$-(o-$PPh_2C_6H_4)_2SbR\}]$ (R = o-$PPh_2C_6H_4$ (**7**), Ph (**8**), Cl (**9**)). Compound **1** and **4** were reacted with coinage metal ions (Cu^+, Ag^+, Au^+) with coordinating counterion (Cl^-) and weakly coordinating counterion ($[PF_6]^-$) yielding $[W(CO)_4\{\eta^1:\eta^1:\eta^1:\eta^1:\eta^1$-(o-$PPh_2C_6H_4)_3Sb\}\{MCl\}]$ (M = Cu (**10**), Ag (**11**)), $[W(CO)_4\{\eta^1:\eta^1:\ \eta^1:\eta^1$-(o-$PPh_2C_6H_4)_2Sb\}\{\eta^1$-AuCl(o-$PPh_2C_6H_4)\}\{AuCl\}]$ (**12**) $[(W(CO)_4\{\eta^1:\eta^1:\eta^1:\eta^1$-(o-$PPh_2C_6H_4)_2Sb\})_2AuCl]$ (**13**), $[W(CO)_3(\mu$-$CO)\{\eta^1:\eta^1:\eta^1:\eta^1:\eta^1$-(o-$PPh_2C_6H_4)_3Sb\}\{Cu\}][PF_6]$ (**14**), $[W(CO)_4\{\eta^1:\eta^1:\eta^1:\eta^1:\eta^1$-(o-$PPh_2C_6H_4)_3Sb\}\{AgMeCN\}][PF_6]$ (**15**), $[W(CO)_4\{\eta^1:\eta^1:\eta^1:\eta^1:\eta^1$-(o-$PPh_2C_6H_4)_3Sb\}\{Au\}][PF_6]$ (**16**) $[W(CO)_2(\mu$-$CO)\{\eta^1:\eta^1:\eta^1:\eta^1:\eta^1:\eta^1$-(o-$PPh_2C_6H_4)_3Sb\}\{Cu_2(\mu$-$Cl)_2\}]$ (**17**), $[W(CO)_3\{\eta^1:\eta^1:\eta^1:\eta^1$-(o-$PPh_2C_6H_4)_3Sb\}\{AuCl\}]$ (**18**) $[W(CO)_2(\mu$-$CO)\{\eta^1:\eta^1:\eta^1:\eta^1:\ \eta^1$-(o-$PPh_2C_6H_4)_3Sb\}\{ML\}][PF_6]$ (M = Cu, L = MeCN (**19**), M = Ag, L = MeCN (**20**), M = Au (**21**). The complexes **10-21** show all metal-metal distances below the sum of the corresponding van der Waals radii, but only for **19-21** a significant interaction is present.*

Stibines are weaker donors than their lighter homologs (amines, phosphines) because of the higher s character and the poor availability of the lone pair of antimony.[1,2,3] To enhance the coordination properties the antimony atom is usually incorporated in a polydentate scaffold where the coordination to a metal is assisted by auxiliary ligands like phosphines. A well-known investigated example is the group of triphosphino-stibine ligands of the type (o-$PR_2C_6H_4)_3Sb$.[4] These ligands are soft σ-donors and can also undergo two electron oxidation while the ligand properties can be changed significantly. These ligands have been incorporated into several late transition metal complexes.[2,3] The phenyl substituted ligand can be coordinated to (tht)AuCl to yield [$\eta^1:\eta^1:\eta^1$-(o-$PPh_2C_6H_4)_3SbAuCl$] (**A**) in which the gold center is coordinated by the antimony and two phosphine arms (cf. Scheme 1). **A** can be oxidized using $PhICl_2$ to give [$\eta^1:\eta^1:\eta^1$-(o-$PPh_2C_6H_4)_3SbCl_2AuCl$] (**B**) (cf. Scheme 1). In this reaction an umpolung of the Au-Sb interaction takes place. In **A** a lone pair of Sb donates to Au, while in **B** Au donates to Sb.[5] The *iso*-propyl substituted ligand can be reacted with CuCl and AgCl to form the trinuclear cluster [$\eta^1:\eta^1:\eta^1:\eta^1:\eta^1:\eta^1$-(o-$P^iPr_2C_6H_4)_3SbM_3(\mu$-$Cl)_3$] (M = Cu, Ag) (**C**) where each metal atom is coordinated by the antimony and one phosphine arm of the ligand while three chlorine atoms are bridging all Cu and Ag atoms, respectively (cf. Scheme 1).[6]

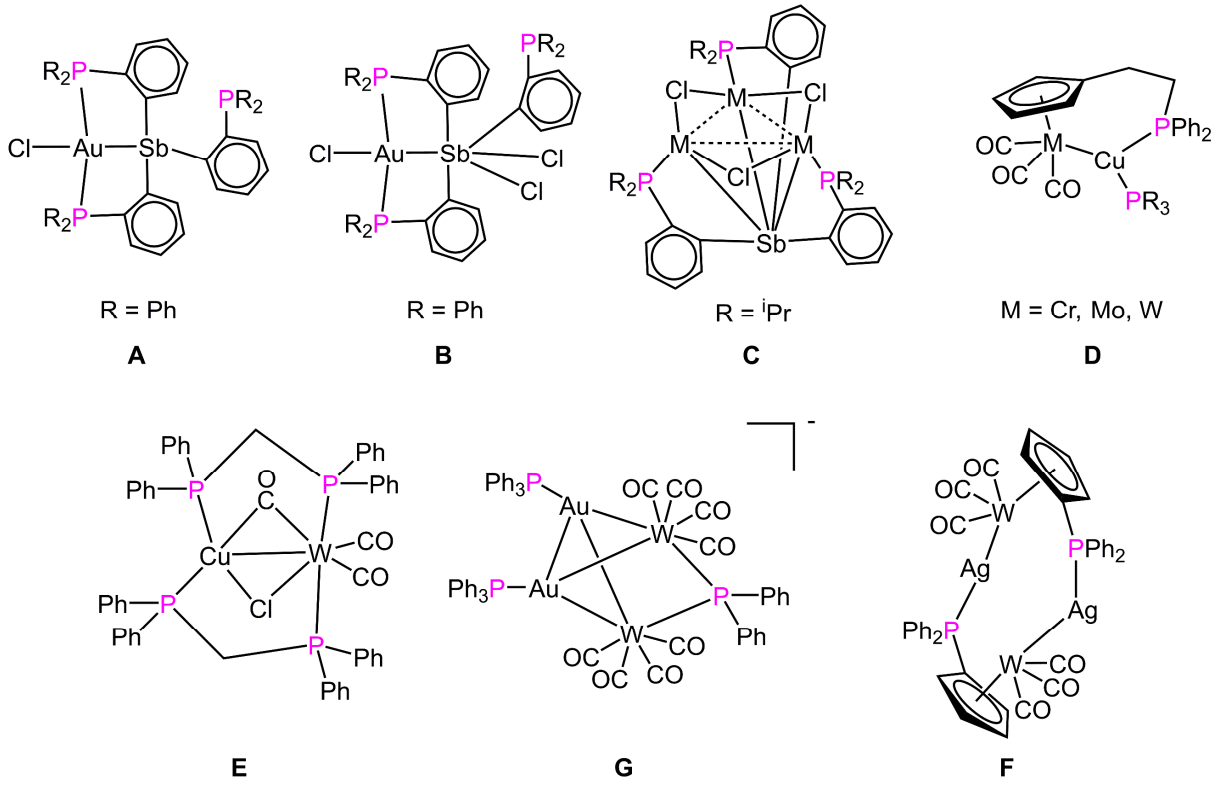
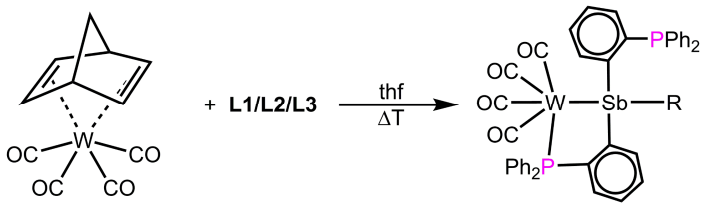


Figure 1. Selected complexes with polydentate phosphino stibine ligands and heterometallic complexes based on group six and coinage metals.

A widely investigated field of research targets cooperative effects in bi- or multimetallic systems. Several complexes based on group six and coinage metals have been synthesized. A suitable ligand framework is necessary in order to force an interaction of two such metals. In $[(\eta^5{:}\eta^1\text{-}C_5H_4(CH_2)_2PPh_2)M(CO)_3Cu(PR_3)]$ (M = Cr, Mo, W (**D**))[7] a diphenylphosphine side arm attached to Cp ligand over an ethylene bridge is used to force a copper atom into the coordination sphere of chromium, molybdenum and tungsten, respectively. Dppm (bis(diphenylphosphino)methane) was used to force Cu into proximity of a $\{W(CO)_3\}$ fragment in $[(CO)_2W(\mu\text{-}Ph_2CH_2PPh_2)_2(\mu\text{-}CO)(\mu\text{-}Cl)Cu]$ (**E**), while an additional coordination of one CO ligand is present at the Cu atom.[8] A Cp ligand with a directly attached PPh_2 unit can be used for the formation of dimeric tetrametallic complexes with Ag atoms in the coordination sphere of tungsten like in $[(CO)_3W(\mu\text{-}C_5H_4PPh_2)Ag]_2$ (**F**).[9] Examples for coordination compounds with gold and tungsten are also known. As an example $[NEt_4][(\mu\text{-}PPh_2)(\mu,\eta^2\text{-}(Ph_3PAu)_2)W_2(CO)_8]$ (**G**)[10] shows a tetrametallic core with two Au and two W atoms. **A-G** are depicted in Figure 1. The polyphosphino stibine ligands $(o\text{-}PPh_2C_6H_4)_2SbR$ (R = $o\text{-}PPh_2C_6H_4$ (**L1**), Ph (**L2**), Cl (**L3**) should be incorporated into molybdenum and tungsten carbonyl complexes (by reaction with $[W(CO)_4(nbd)]$ (nbd = 2,5-norbonadiene), $[W(CO)_3(cht)]$ (cht = 1,3,5-cycloheptatriene) and $[Mo(CO)_3(cht)]$). Afterwards, the free coordination sides should be used in the coordination chemistry with coinage metal salts to get access to complexes with metal-metal bonds (W-M, M = Cu, Ag, Au).

10.2 Results and Discussion

Reacting the ligands **L1-L3** with $[W(CO)_4(nbd)]$ in boiling thf overnight leads to the formation of $[W(CO)_4\{\eta^1{:}\eta^1\text{-}(o\text{-}PPh_2C_6H_4)_2SbR\}]$ (R = o-$PPh_2C_6H_4$ (**1**), Ph (**2**), Cl (**3**)) in crystalline yields of 72, 65 and 68 % (cf. Eq. 1). Compound **1**-**3** can be obtained as bright yellow solids.



(1)

R = o-$PPh_2C_6H_4$ (**1**, 72 %)
R = Ph (**2**, 65 %)
R = Cl (**3**, 68 %)

Crystals suitable for single crystal X-ray structure analysis can be obtained from concentrated solutions in thf (**1**), CH_2Cl_2 (**2**) or dimethoxyethane (**3**) layered with pentane (**1**) or hexane (**2**,**3**). The structures in the solid state (Figure 2) reveals that one phosphine group and the antimony atom are coordinated to the $\{W(CO)_4\}$ fragment, while the second phosphine substituent remains uncoordinated. In each of the $^{31}P\{^1H\}$ NMR spectra, two singlets at δ = 56.9 and -5.0 (thf-d_8, **1**), 54.8 and -4.7 (CD_2Cl_2, **2**), 56.7 and -12.2 ppm (thf-d_8, **3**) can be observed, while the low field shifted signals show additional tungsten satellites with $^1J_{PW}$ coupling constants in the range of 223 and 229 Hz.

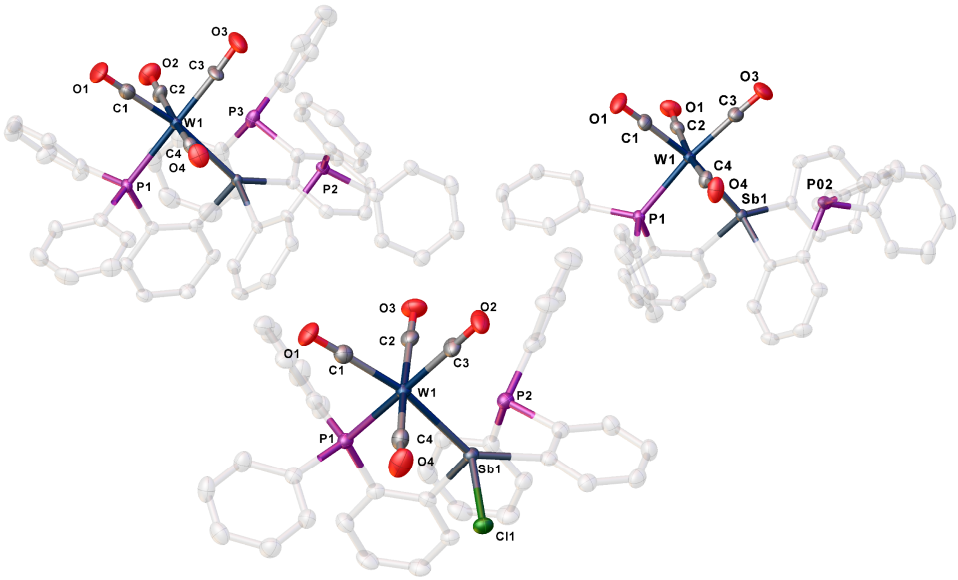
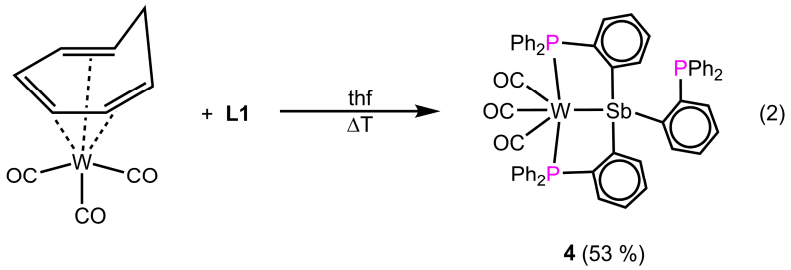


Figure 2. Molecular structures of **1** (top, left), **2** (top, right) and **3** (bottom) in the solid state. Thermal ellipsoids are shown at 50 % probability level. Hydrogen atoms and solvent molecules are omitted for clarity.

Reacting **L1** with $[W(CO)_3(cht)]$ (cht = 1,3,5-cycloheptatriene) in boiling thf overnight leads to the formation of $[W(CO)_3\{\eta^1{:}\eta^1{:}\eta^1\text{-}(o\text{-}PPh_2C_6H_4)_3Sb\}]$ (**4**) (cf. Eq. 2). Compound **4** can be isolated as a dark yellow solid in crystalline yield of 53 %. Alternatively, **4** can be obtained from irradiation of a solution of **1** in thf for several hours or when **1** is refluxed in decaline overnight.

But, in both cases a column chromatographic workup is necessary in order to isolate **4** and it can be obtained only in lower yield of 27 and 11 %, respectively.



(2)

4 (53 %)

Crystals suitable for single crystal X-ray structure analysis can be obtained from a concentrated solution in CH_2Cl_2 layered with hexane. The structure of **4** in solid state is shown in Figure 3. The structure in solid state reveals that now two phosphine arms and the antimony atoms are coordinated to a $\{W(CO)_3\}$ fragment, while one phosphine is still free. In the $^{31}P\{^1H\}$ NMR spectrum in thf-d_8 two singlets at δ = 57.8 and -4.7 can be observed, while the low field shifted signal show additional tungsten satellites with $^1J_{PW}$ coupling constants of 220 Hz. When $[W(CO)_4\{\eta^1:\eta^1\text{-}(o\text{-}PPh_2C_6H_4)_2SbCl\}]$ (**3**) is irradiated with UV light $[W(CO)_3\{\eta^1:\eta^1:\eta^1\text{-}(o\text{-}PPh_2C_6H_4)_2SbCl\}]$ (**5**) and $[(W(CO)_3\{\eta^1:\eta^1:\eta^1\text{-}(o\text{-}PPh_2C_6H_4)_2Sb\})_2]$ (**6**) can be isolated after column chromatographic workup as orange solids in low yields (cf. Eq. 3).

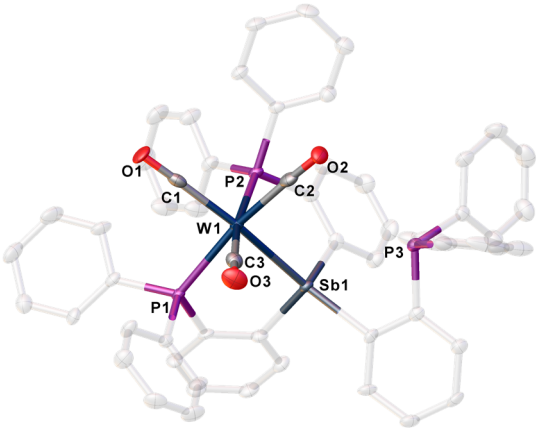
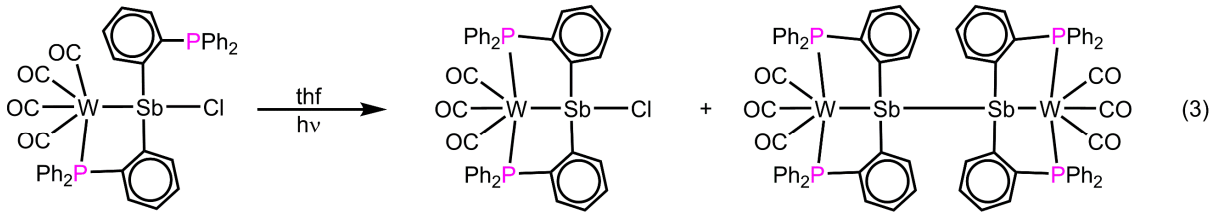


Figure 3. Molecular structure of **4** in the solid state. Thermal ellipsoids are shown at 50 % probability level. Hydrogen atoms are omitted for clarity.



(3)

3 **5** (7 %) **6**

Crystals suitable for single crystal X-ray structure analysis can be obtained from concentrated solutions in thf (**5**) or CH_2Cl_2 (**6**) layered with pentane (**5**) or hexane (**6**). The structures in solid state are depicted in Figure 4. The structure of **5** in the solid state reveals that the $\{W(CO)_3\}$ fragment is coordinated by two phosphine groups and the antimony atom. So, one CO ligand

is cleaved upon irradiation. The structure of **6** in solid state reveals a dimer consisting of two {W(CO)$_3${η^1:η^1-(o-PPh$_2$C$_6$H$_4$)$_2$Sb} fragments connected by an Sb-Sb bond. Compound **6** displays the formal reduction product of **5**.

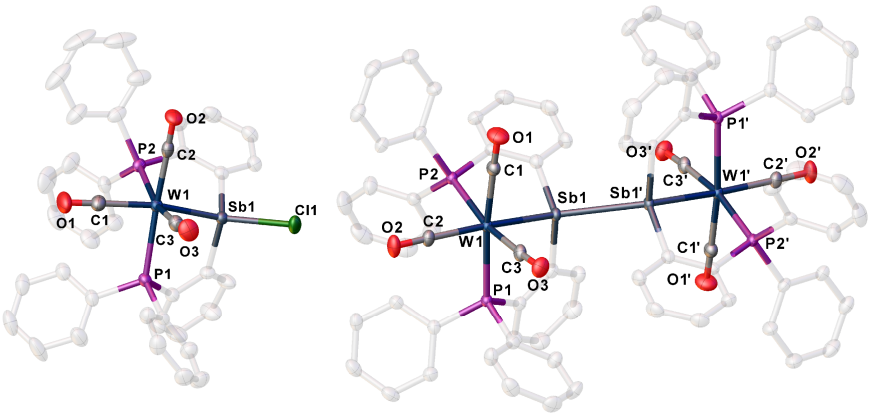
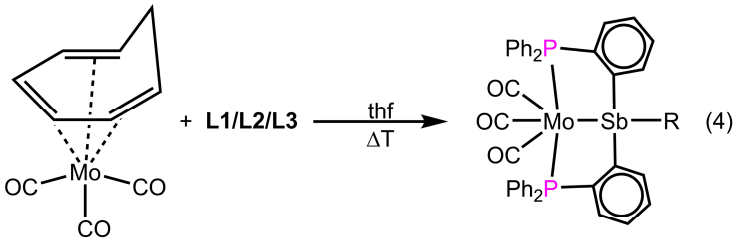


Figure 4. Molecular structures of **5** (left) and **6** (right) in solid state. Thermal ellipsoids are shown at 50 % probability level. Hydrogen atoms and solvent molecules are omitted for clarity.

The formation of **6** can be explained by a chlorine abstraction from **5** followed by a dimerization. The ^{31}P{^{1}H} NMR spectra reveal each a singlet at δ = 52.4 (CD_2Cl_2, **5**) and 52.4 ppm (thf-d_8, **6**) with tungsten satellites with $^1J_{PW}$ coupling constants of 212 Hz.

The ligands **L1**-**L3** can be reacted with [Mo(CO)$_3$(cht)] (cht = 1,3,5-cycloheptatriene) in boiling thf yielding [Mo(CO)$_3${η^1:η^1-(o-PPh$_2$C$_6$H$_4$)$_2$SbR}] (R = (o-PPh$_2$C$_6$H$_4$) (**7**), Ph (**8**), Cl (**9**)) in crystalline yields of 57, 47 and 25 % (Eq. 4). Compound **7** and **8** can be obtained as yellow, compound **9** as an orange solid.



(4)

R = o-PPh$_2$C$_6$H$_4$ (**7**, 57 %)
R = Ph (**8**, 47 %)
R = Cl (**9**, 25 %)

Crystals suitable for single crystal X-ray structure analysis can be obtained from concentrated solutions in CH_2Cl_2 (**7**,**9**) or dimethoxyethane (**8**) layered with hexane. The structures in solid state are shown in Figure 5. The structure reveals that two phosphine ligands and the antimony atom is coordinated to the {Mo(CO)$_3$} fragments, while the third substituent remains free. In the ^{31}P{^{1}H} NMR spectrum of **7** in CD_2Cl_2 two singlets at δ = 71.2 and -6.3 ppm can be observed. In the ^{31}P{^{1}H} spectra of **8** and **9** in thf-d_8 one singlet at δ = 73.4 (**8**) and 66.6 ppm (**9**) can be observed.

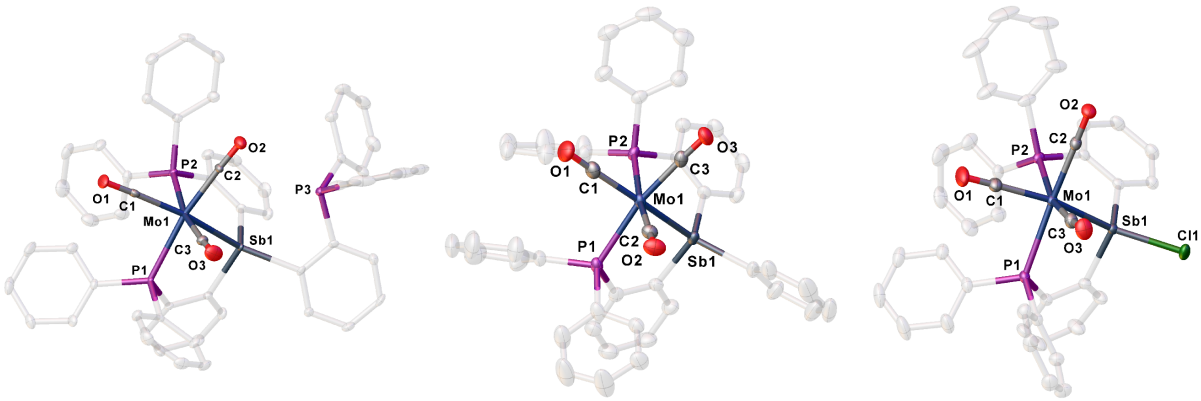
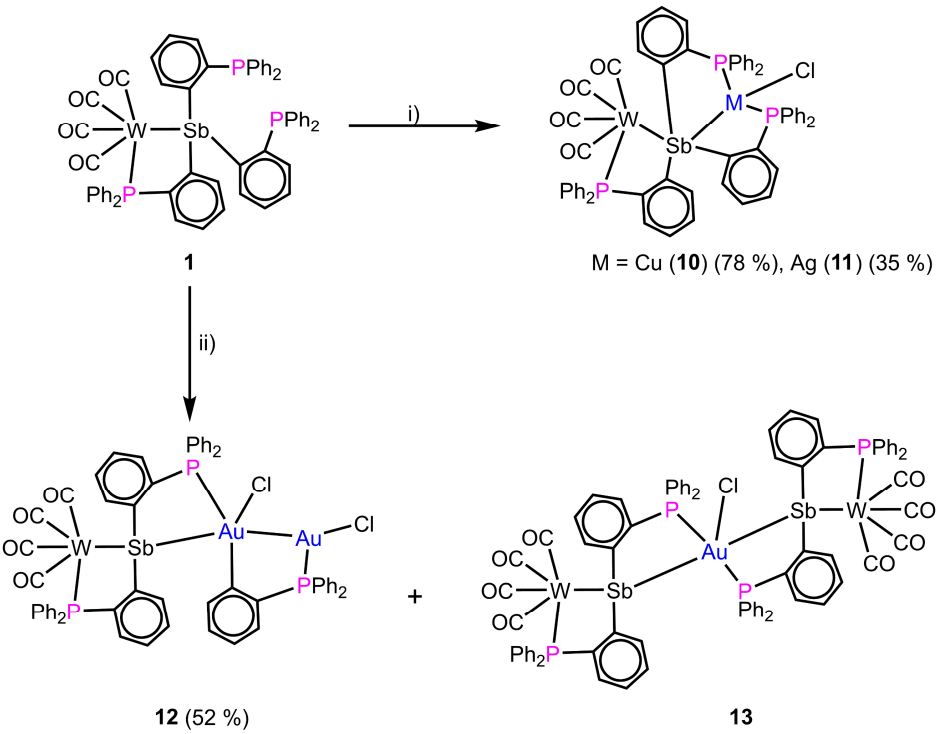


Figure 5. Molecular structures of **7** (left), **8** (middle) and **9** (right) in solid state. Thermal ellipsoids are shown at 50 % probability level. Hydrogen atoms and solvent molecules are omitted for clarity.

The reaction of $[W(CO)_4\{\eta^1{:}\eta^1\text{-}(o\text{-}PPh_2C_6H_4)_3Sb\}]$ (**1**) with one equivalent CuCl and AgCl leads to the formation of $[W(CO)_4\{\eta^1{:}\eta^1{:}\eta^1{:}\eta^1{:}\eta^1\text{-}(o\text{-}PPh_2C_6H_4)_3Sb\}\{MCl\}]$ (M = Cu (**1**), Ag (**2**)) in crystalline yields of 78 and 35 %, respectively (Scheme 1). Crystals suitable for single crystal X-ray structure analysis can be obtained after a few days from concentrated solutions in CH_2Cl_2 layered with hexane at room temperature. The structures of **10** and **11** in the solid state (Figure 2) show that the metal halides have been incorporated in the binding pocket of **1**. The Cu and Ag ions, respectively, are coordinated by the two phosphine side groups (P2 and P3) and the central Sb atom of the ligand framework. Due to the geometry of the ligand, the Cu and Ag atoms are brought into proximity of the $\{W(CO)_4\}$ fragment with W1-Cu1 and W1-Ag1 distances of 3.2383(5) Å and 3.1893(3)/3.3342(3) Å.



Scheme 1: Reaction of **1** with i) CuCl or AgCl and ii) (tht)AuCl in CH_2Cl_2 at room temperature.

The crystal structure of **11** shows two independent molecules with different W-Ag distances (3.1893(3) and 3.3342(3) Å) probably due to packing effects. Both W-M distances are far too long to be considered as a bond, but still below the sum of van der Waals radii (Σ_{vdW} (W-Cu) = 4.95 Å, Σ_{vdW} (W-Ag) = 5.10 Å).[11] However, a weak interaction was neglected by the calculated Wiberg Bond Indices (WBIs) of 0.03 each.

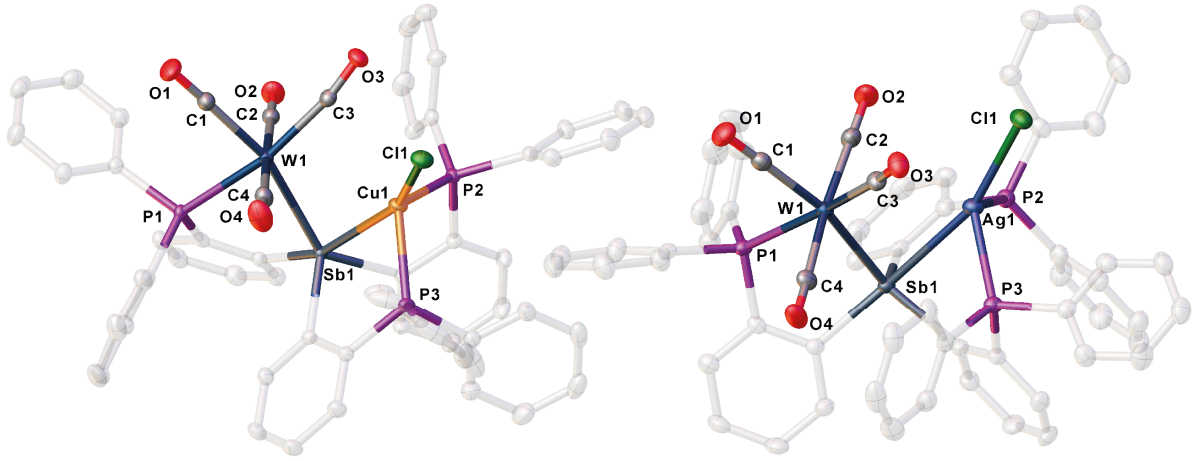


Figure 6: Molecular structures in solid state of **10** (left) and **11** (right). Thermal ellipsoids are drawn with 50 % probability level. Solvent molecules and hydrogen atoms are omitted for clarity.

Reacting **1** with two equivalents of (tht)AuCl yields $[W(CO)_4\{\eta^1{:}\eta^1{:}\eta^1\text{-}(o\text{-}PPh_2C_6H_4)_2Sb\}\{\eta^1\text{-}AuCl(o\text{-}PPh_2C_6H_4)\}\{AuCl\}]$ (**12**) in crystalline yields of 52 % beside traces of $[(W(CO)_4\{\eta^1{:}\eta^1{:}\eta^1\text{-}(o\text{-}PPh_2C_6H_4)_2Sb\})_2AuCl]$ (**13**) (Scheme 1). Using a 1:1 stoichiometry the reaction leads to a mixture of **1** and **12** (1:1) (according to $^{31}P\{^1H\}$ NMR spectrum). Crystals of **12** suitable for single crystal X-ray structure analysis can be obtained from a concentrated solution in *o*-$C_6H_4F_2$ layered with hexane at room temperature. Very few single crystals of **13** could be obtained from this crystallization setup after several weeks. The structure of **12** in the solid state (Figure 7, left) shows that one {AuCl} fragment has been inserted in an antimony-carbon bond of the ligand. This Au1 atom is coordinated by one phosphine group (P2) which is still connected to the central Sb of the ligand framework. The third phosphine group which is now connected with Au1 coordinates Au2 forcing it into proximity of Au1 (Au1-Au2 distance of 3.1302(2) Å). This distance is too long for aurophillic interactions underlined by a WBI of 0.01. Compound **13** is probably a decomposition product of **12**. The structure in the solid state (Figure 7, right) reveals a complex where a central {AuCl} is coordinated by two $(W(CO)_4\{\eta^1{:}\eta^1{:}\eta^1\text{-}(o\text{-}PPh_2C_6H_4)_2Sb\})$ fragments which have both lost one phosphine arm. In order to increase the strength of the interaction between the coinage metals and tungsten, the Cl ligand has been removed and replaced by the weakly coordinating anion $[PF_6]^-$. By this way the metal cations become electron poorer and therefore a stronger interaction with W can be expected. For copper and silver directly the $[PF_6]$ salts can be used ($[Cu(MeCN)_4][PF_6]$ and $Ag[PF_6]$), while for gold the corresponding salt has to be prepared *in situ* in the presence of **1**

due to the instability of "Au[PF_6]". The reaction of **1** with [$Cu(MeCN)_4$][PF_6], Ag[PF_6] and *in situ* generated "Au[PF_6]" gives [$W(CO)_3$(μ-CO){η^1:η^1:η^1:η^1:η^1-(o-$PPh_2C_6H_4$)$_3$Sb}{Cu}][PF_6] (**14**), [$W(CO)_4$\{η^1:η^1:η^1:η^1:η^1-(o-$PPh_2C_6H_4$)$_3$Sb\} {AgMeCN}][PF_6] (**15**) and [$W(CO)_4$\{η^1:η^1:η^1:η^1:η^1-(o-$PPh_2C_6H_4$)$_3$Sb}{Au}][PF_6] (**16**) in crystalline yields of 70, 69 and 69 %, respectively (Scheme 2).

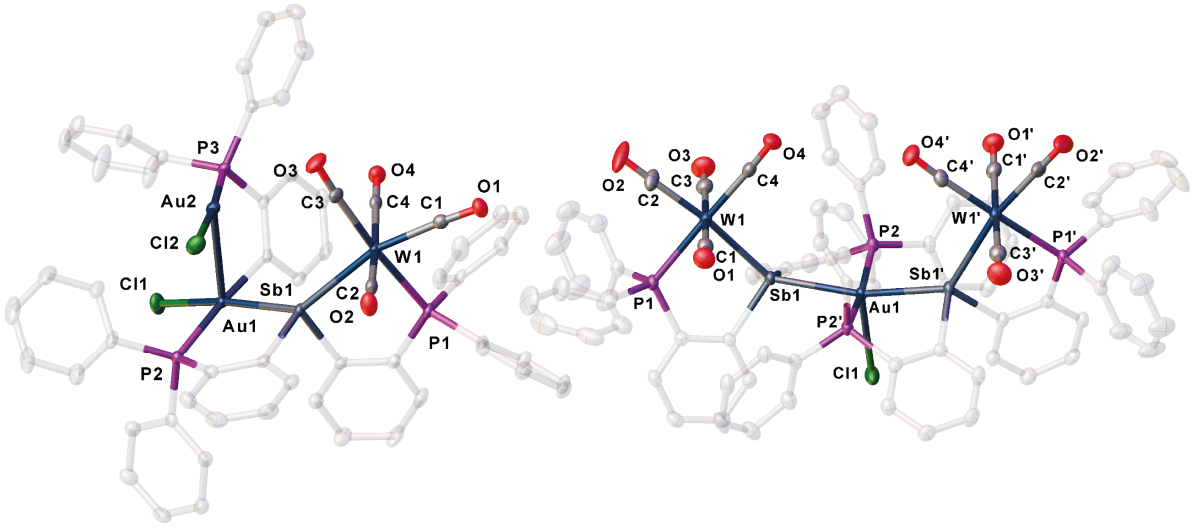
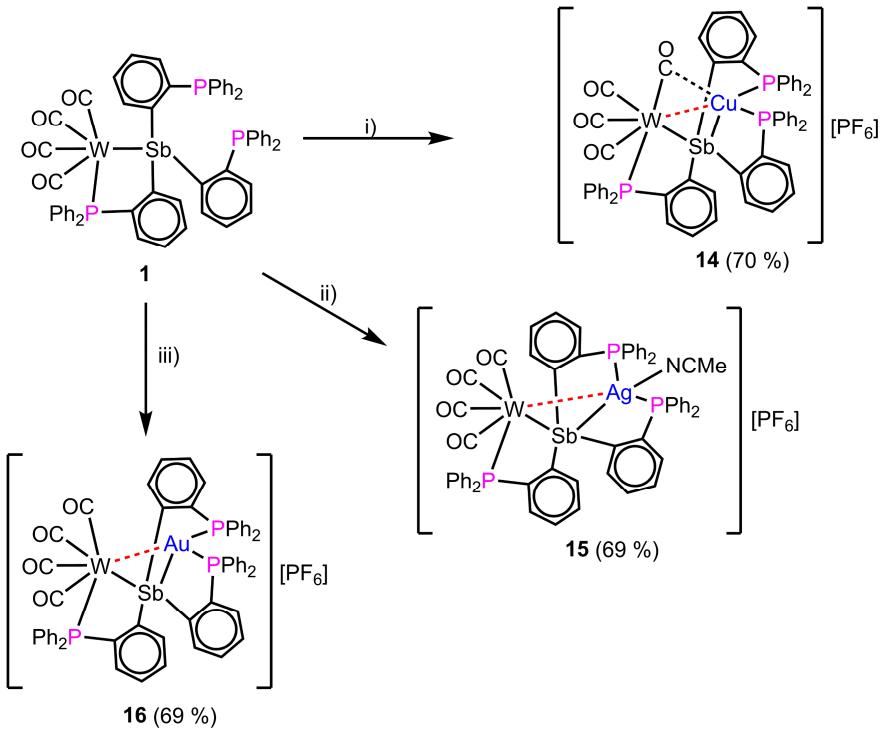


Figure 7: Molecular structure in the solid state of **12** (left) and **13** (right). Thermal ellipsoids are drawn with 50 % probability level. Solvent molecules and hydrogen atoms are omitted for clarity.

Crystals suitable for single crystals X-ray structure analysis can be obtained from concentrated solutions in *o*-$C_6H_4F_2$ (**14**) or CH_2Cl_2 (**15**, **16**) layered with pentane (**14**) or hexane (**15**, **16**) at room temperature.



Scheme 2: Reaction of **1** with i) [$Cu(MeCN)_4$][PF_6], ii)Ag[PF_6] and iii) Tl[PF_6] and (tht)AuCl (III) in CH_2Cl_2 at r.t.

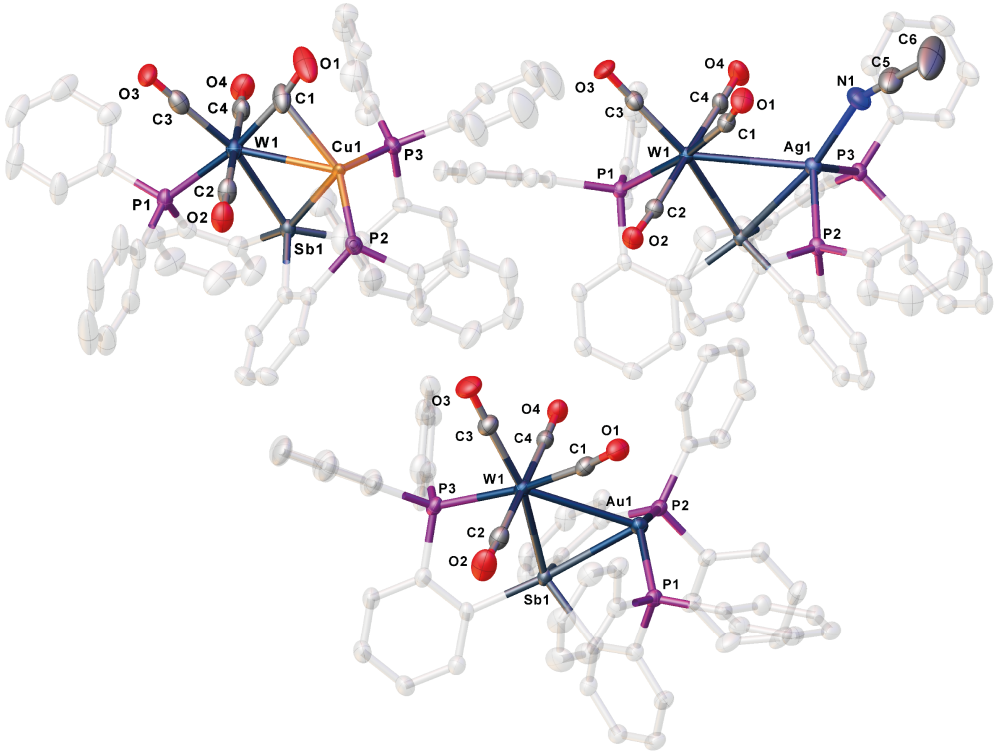
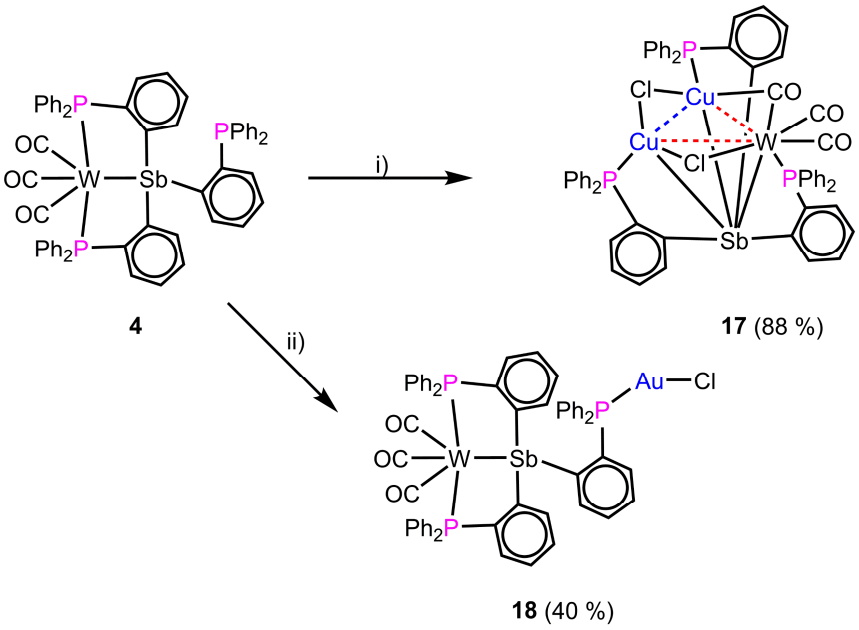


Figure 8: Molecular structures of the cations in **14** (top left), **15** (top right) and **16** (bottom) in the solid state. Thermal ellipsoids are drawn with 50 % probability level. Hydrogen atoms are omitted for clarity.

The structures in the solid state (Figure 8) reveal that the metals ions have been incorporated in the binding pocket of **1** and are coordinated by the two free phosphine side groups. For **14** an additional coordination of one carbonyl ligand (C1-Cu1 distance of 2.407(7) Å) is present, which is comparable with the values for $[CpW(CO)(\mu\text{-}CO)_2Cu(PPh_3)_2]$[12]. The bridging binding mode of the carbonyl ligand in **14** is also underlined by a band in the IR spectrum at 1826 cm^{-1} which is shifted to lower wavenumbers compared to the other bands of **14** at 2032, 1943 and 1928 cm^{-1}. The Ag atom of **15** is saturated by an acetonitrile molecule. The metal tungsten distances amount to 2.8645(11) (**14**), 3.2290(4) (**15**) and 3.14079(16) Å (**16**). Although all W-M distances are below the sum of van der Waals radii (Σ_{vdW} (W-Cu) 4.95, (W-Ag) = 5.10, (W-Au) 4.89 Å),[11] no significant interactions are present compared to the chlorine containing complexes **10**, **11**, **12**, underlined by WBIs of 0.06 (**14**), 0.04 (**15**) and 0.03 (**16**).

The size of the binding pocket of **1** can be changed when one carbonyl ligand is removed and $[W(CO)_3\{\eta^1{:}\eta^1{:}\eta^1\text{-}(o\text{-}PPh_2C_6H_4)_3Sb\}]$ (**4**) is used for similar reactions. The reaction of **4** with CuCl and (tht)AuCl yield $[W(CO)_2(\mu\text{-}CO)\{\eta^1{:}\eta^1{:}\eta^1{:}\eta^1{:}\eta^1\text{-}(o\text{-}PPh_2C_6H_4)_3Sb\}\{Cu_2(\mu\text{-}Cl)_2\}]$ (**17**) and $[W(CO)_3\{\eta^1{:}\eta^1{:}\eta^1{:}\eta^1\text{-}(o\text{-}PPh_2C_6H_4)_3Sb\}\{AuCl\}]$ (**18**) in crystalline yields of 88 and 40 %, respectively. (Scheme 3). Crystals of **8** and **9** suitable for single crystals X-ray structure analysis can be obtained from concentrated solutions in CH_2Cl_2 layered with hexane at room temperature.



Scheme 3: Reaction of **4** with i) CuCl and ii) (tht)AuCl in CH_2Cl_2 at r.t.

The structure of **8** in the solid state (Figure 9, left) reveals a trinuclear complex with a central three membered WCu_2 ring motif. The edges of the metalla-cycle are bridged by two chlorine atoms (W1-Cu1 and Cu1-Cu2) and one carbonyl ligand (W1-Cu2). Due to the asymmetry of the complex two different W-Cu distances are present (W1-Cu1 3.0849(11) and W1-Cu2 2.8359(11) Å). The Cu1-Cu2 distance amounts to 2.6826(14) Å. All M-M distance are below the sum of van der Waals radii (Σ_{vdW} (W-Cu) 4.95, (Cu-Cu) 4.76 Å) and only very weak interactions are present, confirmed by WBIs of 0.05 (W1-Cu1), 0.06 (W1-Cu2) and 0.03 (Cu1-Cu2).

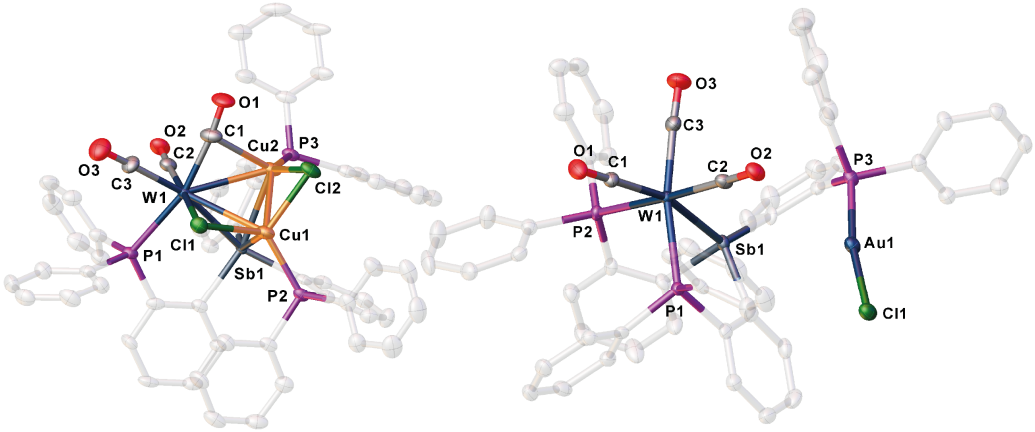
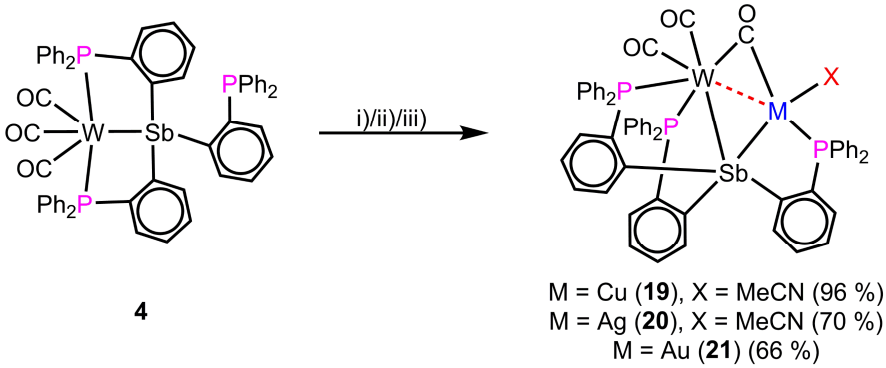


Figure 9: Molecular structures of **17** (left) and 18 (right) in the solid state. Thermal ellipsoids are drawn with 50 % probability level. Solvent molecules and hydrogen atoms are omitted for clarity.

The coordination of only one equivalent CuCl to **4** was not successful. The structure of the gold complex **18** in the solid state (Figure 5, right) shows that {AuCl} was coordinated by the last free phosphine group and directed away from the tungsten atom. The Au atom is coordinated almost linearly (171 °) by Cl1 and P3. In order to get a closer M-W contact the coinage metal

salts containing the weakly coordinating anion $[PF_6]^-$ were used. The reaction of **4** with $[Cu(MeCN)_4][PF_6]$, $Ag[PF_6]$ and *in situ* generated "$Au[PF_6]$" yields $[W(CO)_2(\mu\text{-}CO)\{\eta^1{:}\eta^1{:}\eta^1{:}\eta^1\text{-}(o\text{-}PPh_2C_6H_4)_3Sb\}\{ML\}][PF_6]$ (M = Cu, L = MeCN (**19**), M = Ag, L = MeCN (**20**), M = Au (**21**) in crystalline yields of 96, 70 and 66 %, respectively (Scheme 4).



4

M = Cu (**19**), X = MeCN (96 %)
M = Ag (**20**), X = MeCN (70 %)
M = Au (**21**) (66 %)

Scheme 4: Reaction of **4** with i) $[Cu(MeCN)_4][PF_6]$, ii) $Ag[PF_6]$ and iii) (tht)AuCl and $Tl[PF_6]$ in CH_2Cl_2 at room temperature.

Crystals suitable for X-ray single crystal structure analysis can be obtained from concentrated solutions in CH_2Cl_2 layered with hexane at room temperature. The structures in the solid state are shown in Figure 10. The metal ions have been incorporated in the binding pocket of **4**. They are coordinated by the last free phosphine arm (P3), the central Sb atom, one carbonyl ligand (C1 (**19**, **20**) or C3 (**21**)) and for **19** and **20** saturated by one acetonitrile molecule. The bridging CO ligand of all three complexes can also be underlined by bands in the corresponding IR spectra shifted to lower values (**19**: 1805, **20**: 1832, **21**:1801 cm^{-1}).

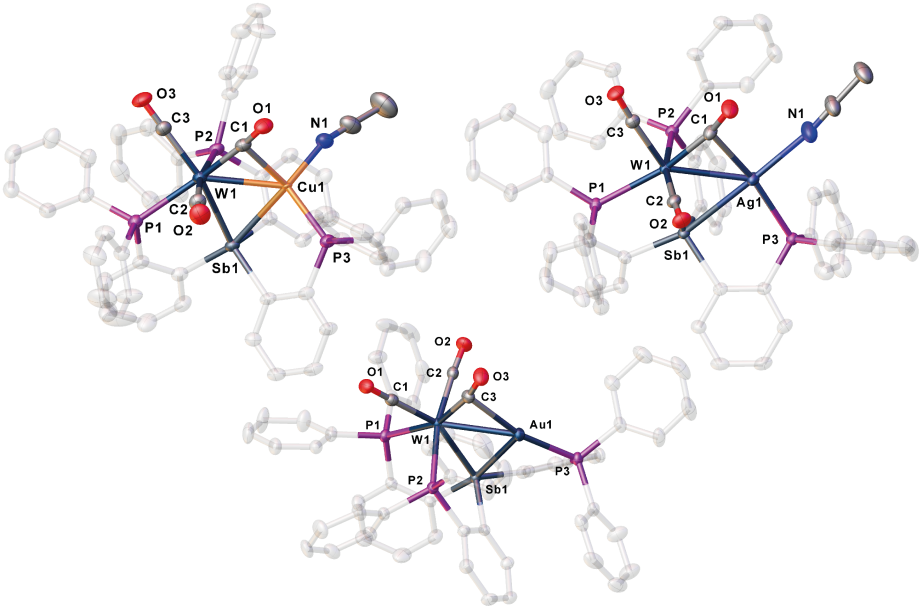


Figure 10: Structure in solid state of **19** (top left), **20** (top right) and **21** (bottom). Anions, solvent molecules and hydrogen atoms are omitted for clarity.

The tungsten metal distances are 2.7922(7) (**19**), 2.8891(3) (**20**) and 2.7551(2) Å (**21**). In all three cases a metal-metal interaction is present, confirmed by WBIs of 0.07 and 0.10, 0.17.

10.3 Conclusion

It could be shown that the ligands **L1**-**3** can be easily introduced into tungsten and molybdenum carbonyl complexes. The tungsten complexes with incorporated ligand **L1** ($[W(CO)_4\{\eta^1{:}\eta^1\text{-}(o\text{-}PPh_2C_6H_4)_3Sb\}]$ (**1**) and $[W(CO)_3\{\eta^1{:}\eta^1{:}\eta^1\text{-}(o\text{-}PPh_2C_6H_4)_3Sb\}]$ (**4**)) reveal suitable binding pockets with several free coordination sites for the incorporation of coinage metal ions. Copper, silver and gold salts including coordinating (Cl^-) or weakly coordinating counterions ($[PF_6]^-$) were used. In all reactions, the metals ions are coordinated by one or two phosphine groups, respectively, the antimony atom and are located in proximity of the tungsten atom (metal to tungsten distances below corresponding sum of van der Walls radii). The obtained products with Cl^- as a counterion show in general larger W-M (M = Cu, Ag, Au) distances compared to those with $[PF_6]^-$ as a counterion. The compounds derived from **4** show in general shorter M-W contacts than those derived from **1**. The shortest W-M distances are observed in $[W(CO)_2(\mu\text{-}CO)\{\eta^1{:}\eta^1{:}\eta^1{:}\eta^1\text{: }\eta^1\text{-}(o\text{-}PPh_2C_6H_4)_3Sb\}\{ML\}][PF_6]$ (M = Cu, L = MeCN (**19**), M = Ag, L = MeCN (**20**), M = Au (**21**). The strength of the interaction with the tungsten atom increases within the group (Cu<Ag<Au).

10.4 Supporting Information

10.4.1 Synthetic procedures and experimental details

Synthetic Procedures: All the manipulations were performed in an atmosphere of dry argon using standard glove-box and Schlenk techniques. All solvents were degassed and purified by standard procedures. The used silica had activation state 1. The compounds $[W(CO)_4(nbd)]$ (nbd = norbonadiene)[13], $[W(CO)_3(cht)]$ (cht = 1,3,5-cycloheptatriene)[14], $[Mo(CO)_3(cht)]$[15], $(o\text{-}PPh_2C_6H_4)_3Sb$ (**L1**)[4], $(o\text{-}PPh_2C_6H_4)_2SbPh$ (**L2**),[16] $(o\text{-}PPh_2C_6H_4)_2SbCl$ (**L3**)[17] and (tht)AuCl[18] (tht=tetrahydrothiophene) were prepared according to literature procedures. CuCl, $[Cu(MeCN)_4][PF_6]$, AgCl, $Ag[PF_6]$, $Tl[PF_6]$ were purchased commercially. The NMR spectra were recorded with a Bruker Avance 400 spectrometer (^1H: 400.13 MHz, ^{31}P: 161.976 MHz) with δ (in ppm) referenced to external $SiMe_4$ (^1H) and H_3PO_4 (^{31}P). IR spectra were measured with a varian FTS-800 spectrometer with diamond ATR-unit. All mass spectra were recorded with a Finnigan MAT 95 mass spectrometer (LIFDI-MS) or with a ThermoQuest Finnigan MAT TSQ 7000 mass spectrometer (ESI-MS). The C, H analyses were measured with an Elementar Vario EL III apparatus.

10.4.1.1 Synthesis of $[W(CO)_4\{\eta^1:\eta^1\text{-}(o\text{-}PPh_2C_6H_4)_3Sb\}]$ (1)

$[W(CO)_4(nbd)]$ (128 mg, 0.33 mmol) and $(o\text{-}PPh_2C_6H_4)_3Sb$ (300 mg, 0.33 mmol) were weighed in together and dissolved in 100 mL thf. After heating the reaction mixture under reflux for 18 h it was cooled to room temperature and the solvent removed *in vacuo*. The obtained yellow solid was dissolved in thf and layered with pentane at room temperature. After a few days **1** could be obtained as clear yellow plates. The supernatant was decanted off, the resulting crystals were washed tree times with pentane und dried *in vacuo*.

Yield 290 mg (72 %).

^1H NMR (thf-d_8, 25 °C): δ = 6.96-7.49 (several overlapping multipletts).

^{31}P NMR (thf-d_8, 25 °C): δ = -5.0 (s, 2P, *P*Ph_2)), 56.9 (s, 1P, *P*Ph_2-W).

$^{31}P\{^1H\}$ NMR (thf-d_8, 25 °C): δ = -5.0 (s, 2P, *P*Ph_2), 56.9 (s, $^1J_{PW}$ = 229 Hz, 1P, *P*Ph_2-W).

ATR-IR (diamond crystal): $\bar{\upsilon}$ = 2012 (vs, CO) 1898 (vs, CO), 1872 (s, CO) cm^{-1}.

LIFDI-MS (dme): *m/z* = 1174.1 (100 %, $[M\text{-}CO]^+$), 675.0 (9 %, $(o\text{-}PPh_2C_6H_4)_2Sb^+$).

EA $C_{58}H_{42}O_4P_3SbW$: calc: C 57.98; H 3.52 %; found: C 58.23; H 3.57 %.

10.4.1.2 Synthesis of [W(CO)$_4${η^1:η^1-(o-PPh$_2$C$_6$H$_4$)$_2$SbPh}] (2)

[W(CO)$_4$(nbd)] (268 mg, 0.69 mmol) and (o-PPh$_2$C$_6$H$_4$)$_2$SbPh (500 mg, 0.69 mmol) were weighed in together and dissolved in 100 mL thf. After heating the reaction mixture under reflux for 18 h it was cooled to room temperature and the solvent removed *in vacuo*. The obtained yellow solid was dissolved in dichloromethane and layered with hexane at room temperature. After a few days **3** could be obtained as clear yellow plates. The supernatant was decanted off, the resulting crystals were washed tree times with hexane und dried *in vacuo*.

Yield 456 mg (65 %).

^{1}H NMR (CD_2Cl_2, 25 °C): *δ* = 6.91 (m, 2H), 7.11 (m, 4H), 7.32 (m, 24H), 7.52 (m, 2H), 7.84 (m, 1H).

^{31}P NMR (CD_2Cl_2, 25 °C): *δ* = -4.7 (s, 1P, *P*Ph$_2$), 54.8 (s, $^1J_{PW}$ = 223 Hz, 1P, *P*Ph$_2$-W).

^{31}P{^{1}H} NMR (CD_2Cl_2, 25 °C): *δ* = -4.7 (s, 1P, *P*Ph$_2$), 54.8 (s, $^1J_{PW}$ = 225 Hz, $^1J_{PC}$ = 42 Hz, 1P, *P*Ph$_2$-W)**.**

ATR-IR (diamond crystal): $\bar{\nu}$ = 2008 (vs, CO) 1919 (m, CO), 1911 (m, CO), 1873 (s, CO) cm^{-1}.

LIFDI-MS (dme): *m/z* = 990.0 (100%, [M-CO]$^+$), 675.0 (2%, (o-PPh$_2$C$_6$H$_4$)$_2$Sb$^+$), 508.0 (5%, [M]$^{2+}$), 495.0 (1%, [M-CO]$^{2+}$), 480.0 (1 %,[M-2CO]$^{2+}$).

EA $C_{46}H_{33}O_4P_2SbW$: calc: C 54.31; H 3.27 %; found: C 54.19; H 3.30 %.

10.4.1.3 Synthesis of [W(CO)$_4${η^1:η^1-(o-PPh$_2$C$_6$H$_4$)$_2$SbCl}] (3)

[W(CO)$_4$(nbd)] (57 mg, 0.15 mmol) and (o-PPh$_2$C$_6$H$_4$)$_2$SbCl (100 mg, 0.15 mmol) were weighed in together and dissolved in 100 mL thf. After heating the reaction mixture under reflux for 17 h it was cooled to room temperature and the solvent removed *in vacuo*. The obtained yellow solid was dissolved in CH_2Cl_2 and layered with hexane at room temperature. After a few days **4** could be obtained as clear yellow plates. The supernatant was decanted off, the resulting crystals were washed tree times with hexane und dried *in vacuo*.

Yield: 99 mg (68 %).

^{1}H NMR (thf-d$_8$, 25 °C): *δ* = 6.77 (m, 2H), 7.02-7.49 (several overlapping multipletts, 23H), 7.53 (m, 3H), 7.66 (m, 1H), 7.83 (m, 1H).

^{31}P NMR (thf-d$_8$, 25 °C): *δ* = -12.2 (s, 2P, *P*Ph$_2$)), 56.7 (s, $^1J_{PW}$ = 225 Hz,1P, *P*Ph$_2$-W).

$^{31}P\{^{1}H\}$ NMR (thf-d_8, 25 °C): δ = -13.1 (s, 1P, *P*Ph_2), 55.7 (s, $^{1}J_{PW}$ = 225 Hz, $^{1}J_{PC}$ = 41 Hz , 1P, *P*Ph_2-W).

ATR-IR (diamond crystal): $\bar{\upsilon}$ = 2026 (vs, CO), 1939 (s,CO), 1916 (m, CO), 1889 (m, CO) cm^{-1}.

LIFDI-MS (dme): *m/z* = 976.0 (100 %, $[M]^+$), 948.0 (60 %, $[M\text{-}CO]^+$).

EA $C_{40}H_{28}O_4ClP_2SbW$: calc: C 49.28; H 2.90 %; found: C 49.33; H 3.32 %.

10.4.1.4 Synthesis of $[W(CO)_3\{\eta^1{:}\eta^1{:}\eta^1\text{-}(o\text{-}PPh_2C_6H_4)_3Sb\}]$ (4)

a) $[W(CO)_4(nbd)]$ (128 mg, 0.33 mmol) and $(o\text{-}PPh_2C_6H_4)_3Sb$ (300 mg, 0.33 mmol) were weighed in together and 100 mL decaline was added. The reaction mixture was stirred under reflux for 18 h, while the initial clear yellow solution turned to turbid brown. After cooling to room temperature the solvent was removed *in vacuo*. The brown residue was dissolved in thf and purified by column chromatography using silica (hexane, 15 x 2.5 cm). Using toluene a weak yellow fraction (compound **1**) followed by a brown intense fraction (compound **2**) could be obtained under high loss (column strong colored afterwards). The solvent was removed *in vacuo*. The residue was dissolved in dichloromethane and layered with hexane at room temperature. After a few days **2** could be obtained as dark yellow blocks. The supernatant was decanted off, the resulting crystals were washed three times with hexane und dried *in vacuo*.

Yield 42 mg (11 %).

b) A solution of **1** (2.0 g, 1.66 mmol) in thf was radiated for 63 h using a mercury TQ 150 lamp, while the color of the initial clear yellow solution turned into brown. The ^{31}P NMR spectrum of the crude solution shows the formation of **2** in 83 % yield. The solvent was removed in *in vacuo*. The residue was dissolved in dichloromethane and silca was added. The solvent was removed *in vacuo*. The preabsorbed product was purified by column chromatography (silica, hexane, 13 x 4.5 cm). Using toluene, a brown fraction could be eluted under high loss (column strong colored after procedure). The solvent was removed *in vacuo*. The residue was dissolved in dichloromethane, an excess of hexane added and cooled to -80 °C to precipitate **2** as a dark yellow powder. The supernatant was decanted off, the resulting powder was washed tree times with hexane und dried *in vacuo*.

Yield 530 mg (27 %).

c) A solution of **1** (1.2 g, 1.32 mmol) and $[W(CO)_3(cht)]$ (476 mg, 1.32 mmol) in thf was stirred under reflux for 24 h, while the color changed from red to dark yellow. The solvent was removed *in vacuo*, the residue dissolved in CH_2Cl_2 and layered with hexane. After a few days **2** could

be obtained as dark yellow blocks. The supernatant was decanted off, the resulting crystals were washed three times with hexane und dried *in vacuo*.

Yield: 826 mg (53 %)

^{1}H NMR (thf-d_8, 25 °C): δ = 6.85 (m, 8H), 7.08 (m, 6H), 7.19 (m, 14H), 7.29 (m, 4H), 7.40 (m, 4H), 7.51 (m, 1H), 7.57 (m, 2H), 7.72 (m, 2H), 7.95 (m, 1H).

^{31}P NMR (thf-d_8, 25 °C): δ = -4.7 (s, 2P, *P*Ph_2), 57.8 (s, $^{1}J_{PW}$ = 220 Hz, 1P, *P*Ph_2-W).

^{31}P{^{1}H} NMR (thf-d_8, 25 °C): δ = -4.7 (s, 1P, *P*Ph_2), 57.8 (s, $^{1}J_{PW}$ = 216 Hz, 2P, *P*Ph_2-W).

ATR-IR (diamond crystal): $\bar{\nu}$ = 1935 (vs, CO) 1859 (s, CO), 1838 (s, CO) cm^{-1}.

LIFDI-MS (dme): *m/z* = 1174.0 ([M]$^{+}$).

EA $C_{57}H_{42}O_3P_3SbW$: calc: C 58.34; H 3.61 %; found: C 58.33; H 3.77 %.

10.4.1.5 Synthesis of [W(CO)$_3${η^1:η^1:η^1-(o-$PPh_2C_6H_4$)$_2$SbCl}] (5)

[W(CO)$_4$(nbd)] (218 mg, 0.56 mmol) and (o-$PPh_2C_6H_4$)$_2$SbCl (383 mg, 0.56 mmol) were weighed in together and dissolved in 150 mL thf. After heating the reaction mixture under reflux for 18 h it was cooled to room temperature and radiated for 2 h with a mercury TQ 150 lamp. The initial yellow solution turned to orange. Silca was added and the solvent was removed *in vacuo*. The preabsorbed compound was purified by column chromatography using silica (hexane, 18 x 3.5 cm). Using toluene/hexane 1:3 a narrow weak yellow (**4**) and an orange fraction (**5**) could be eluted under high loss (column strong colored after procedure). The solvent was removed *in vacuo*, the residue dissolved in thf and layered with hexane. After a few days **5** could be obtained as orange plates. The supernatant was decanted off, the resulting crystals were washed tree times with hexane und dried *in vacuo*.

Yield 37 mg (7 %).

^{1}H NMR (CD_2Cl_2, 25 °C): δ = 6.81 (m, 4H), 6.90 (m, 4H), 7.14 (m, 3H), 7.35 (m, 12H), 7.66 (m, 3H), 8.45 (m, 2H).

^{31}P NMR (CD_2Cl_2, 25 °C): δ = *52.4* (s, *P*Ph_2-W).

^{31}P{^{1}H} NMR (CD_2Cl_2, 25 °C): δ = 52.4 (s, $^{1}J_{PW}$ = 212 Hz, *P*Ph_2-W)**.**

ATR-IR (diamond crystal): $\bar{\nu}$ = 1948 (vs, CO), 1860 (s, CO) cm^{-1}.

LIFDI-MS (dme): *m/z* = 948.0 (100 %, [M]$^{+}$).

EA $C_{39}H_{28}O_3ClP_2SbW$: calc: C 49.47; H 2.98 %; found: C 49.67; H 2.95 %.

10.4.1.6 Synthesis of $[(W(CO)_3\{\eta^1:\eta^1:\eta^1\text{-}(o\text{-}PPh_2C_6H_4)_2Sb\})_2]$ (6)

a) $[W(CO)_4(nbd)]$ (57 mg, 0.15 mmol) and $(o\text{-}PPh_2C_6H_4)_2SbCl$ (100 mg, 0.15 mmol) were weighed in together and dissolved in 30 mL toluene. After heating the reaction mixture under reflux for 21 h it was cooled to room tempature. The initial yellow solution turned to brown The solvent was removed *in vacuo* and the residue dissolved in CH_2Cl_2. After adding silica, the solvent was removed *in vacuo*. The preabsorbed compound was purified by column chromatography using silica (hexane, 15 x 2 cm). Using tolene a weak yellow (**4**) and a strong orange fraction (**6**) could be obtained under high loss (column strong colored afterewards). The solvent was removed *in vacuo*, the residue dissolved in thf and layered with pentane. After a few days **6** could be obtained as orange blocks. The supernatant was decanted off, the resulting crystals were washed tree times with pentane und dried *in vacuo*.

Yield: only a few crystals could be isolated.

b) $[W(CO)_4(nbd)]$ (114 mg, 0.29 mmol) and $(o\text{-}PPh_2C_6H_4)_2SbCl$ (200 mg, 0.29 mmol) were weighed in together and dissolved in 150 mL thf. After heating the reaction mixture under reflux for 18 h it was cooled to room temperature and radiated for 4 h with a mercury TQ 150 lamp. The initial yellow solution turned to orange. The ^{31}P NMR spectra of the reaction mixture shows the formation of **6** in 17 % and **5** in 54 % beside unidentified side products. Silca was added and the solvent was removed *in vacuo*. The preabsorbed compound was purified by column chromatography using silica (hexane, 18 x 3.5 cm). Using toluene/hexane 1:3 a narrow weak yellow (**5**) and an orange fraction (**5**) could be eluted under high loss (column strong colored after procedure). The solvent was removed *in vacuo*, the residue dissolved in thf and layered with hexane. After a few days **5** could be obtained as orange plates. The supernatant was decanted off, the resulting crystals were washed tree times with hexane und dried *in vacuo*.

Yield: only a few crystals could be isolated.

^{1}H NMR (thf-d_8, 25 °C): δ = 6.87 (m, 8H), 7.07-7.31 (several overlapping multipletts, 18H), 8.38 (m, 2H).

^{31}P NMR (thf-d_8, 25 °C): δ = 52.4 (s).

^{31}P{^{1}H} NMR (thf-d_8, 25 °C): δ = 52.4 (s, $^1J_{PW}$ = 212 Hz).

ATR-IR (diamond crystal): $\bar{\upsilon}$ = 1930 (vs, CO), 1844 (s, CO) cm^{-1}.

LIFDI-MS (dme): *m/z* = 1823.9 (100 %, $[M]^+$), 675.0 (57 %, $(o\text{-}PPh_2C_6H_4)_2Sb^+$).

EA $C_{78}H_{56}O_6P_4Sb_2W_2$: calc: C 51.35; H 3.09 %; found: C 50.89; H 3.32 %.

10.4.1.7 Synthesis of [Mo(CO)$_3${η^1:η^1:η^1-(o-PPh$_2$C$_6$H$_4$)$_3$Sb}] (7)

[Mo(CO)$_3$(cht)] (60 mg, 0.22 mmol) and (o-PPh$_2$C$_6$H$_4$)$_3$Sb (200 mg, 0.22 mmol) were weighed in together and dissolved in 100 mL thf. After stirring the reaction mixture under reflux for 18 h the solvent was removed *in vacuo*. The yellow residue was dissolved in dichloromethane and layered with hexane at room temperature. After a few days **7** could be obtained as yellow blocks. The supernatant was decanted off, the resulting crystals were washed three times with hexane und dried *in vacuo*.

Yield 137 mg (57 %).

^{1}H NMR (CD_2Cl_2, 25 °C): δ = 6.83 (m, 4H), 6.90 (m, 4H), 7.09-7.42 (several overlapping multipletts, 28H), 7.48-7.60 (several overlapping multipletts, 3H), 7.66 (m, 2H), 7.93 (m, 1H).

^{31}P NMR (CD_2Cl_2, 25 °C): δ = -6.3 (s, 1P, *P*Ph$_2$), 71.2 (s, 2P, *P*Ph$_2$-Mo)

^{31}P{^{1}H} NMR (CD_2Cl_2, 25 °C): δ = -6.3 (s, 1P, *P*Ph$_2$), 71.2 (s, 2P, *P*Ph$_2$-Mo)

ATR-IR (diamond crystal): $\bar{\upsilon}$ = 1941 (vs, CO) 1866 (s, CO), 1845 (s, CO) cm^{-1}.

LIFDI-MS (dme): *m/z* = 1086.0 (100%, [M]$^+$), 1058.0.0 (6%, [M-CO]$^+$).

EA $C_{57}H_{42}O_3P_3SbMo$: calc: C 63.06; H 3.90 %; found: C 62.92; H 4.10 %.

10.4.1.8 Synthesis of [Mo(CO)$_3${η^1:η^1:η^1-(o-PPh$_2$C$_6$H$_4$)$_2$SbPh}] (8)

[Mo(CO)$_3$(cht)] (75 mg, 0.28 mmol) and (o-PPh$_2$C$_6$H$_4$)$_2$SbPh (200 mg, 0.28 mmol) were weighed in together and dissolved in 100 mL thf. After stirring the reaction mixture under reflux for 16 h the solvent was removed *in vacuo*. The yellow residue was dissolved in dimethoxyethane and layered with hexane at room temperature. After a few days **8** could be obtained as yellow blocks. The supernatant was decanted off, the resulting crystals were washed three times with hexane und dried *in vacuo*.

Yield 116 mg (47 %).

^{1}H NMR (thf-d$_8$, 25 °C): δ = 6.88 (m, 7H), 7.08 (m, 3H), 7.23-7.48 (several overlapping multipletts, 15H), 7.56 (m, 3H), 7.83 (m, 2H), 7.99 (m, 3H).

^{31}P NMR (thf-d$_8$, 25 °C): δ = 73.4 (s).

^{31}P{^{1}H} NMR (thf-d$_8$, 25 °C): δ = 73.4 (s).

ATR-IR (diamond crystal): $\bar{\upsilon}$ = 1928 (vs, CO), 1854 (s, CO), 1818 (s, CO) cm^{-1}.

LIFDI-MS (dme): *m/z* = 902.0 (100 %, $[M]^+$).

EA $C_{45}H_{33}O_3P_2SbMo$: calc: C 59.96; H 3.69 %; found: C 59.82; H 3.79 %.

10.4.1.9 Synthesis of $[Mo(CO)_3\{\eta^1:\eta^1\text{-}(o\text{-}PPh_2C_6H_4)_2SbCl\}]$ (9)

$[Mo(CO)_3(cht)]$ (264 mg, 0.97 mmol) and $(o\text{-}PPh_2C_6H_4)_2SbCl$ (660 mg, 0.97 mmol) were weighed in together and dissolved in 200 mL thf. After stirring the reaction mixture under reflux for 18 h the solvent was removed *in vacuo*. The orange residue was dissolved in dichloromethane and layered with hexane at room temperature. After a few days **9** could be isolated as orange rods. The supernatant was decanted off, the resulting crystals were washed three times with hexane und dried *in vacuo*.

Yield 208 mg (25 %).

^{1}H NMR (thf-d_8, 25 °C): δ = 6.83 (m, 4H), 6.91 (m, 4H), 7.15 (m, 2H), 7.28-7.41 (several overlapping multipletts, 14H), 7.67 (m, 2H), 8.40 (m, 2H).

^{31}P NMR (thf-d_8, 25 °C): δ = 66.6 (s).

^{31}P{^{1}H} NMR (thf-d_8, 25 °C): δ = 66.6 (s).

ATR-IR (diamond crystal): $\bar{\upsilon}$ = 1955 (vs, CO), 1885 (m, CO), 1866 (s, CO), m 1856 (s, CO) $cm^{-1.}$

LIFDI-MS (dme): *m/z* = 859.8 (100 %, $[M]^+$).

EA $C_{39}H_{28}O_3P_2SbMo$ x 0.5 CH_2Cl_2: calc: C 52.58; H 3.24 %; found: C 52.38; H 3.40 %.

10.4.1.10 Synthesis of $[W(CO)_4\{\eta^1:\eta^1:\eta^1:\eta^1\text{-}(o\text{-}PPh_2C_6H_4)_3Sb\}\ \{CuCl\}]$ (10)

CuCl (8.2 mg, 0.083 mmol, 1 eq) and **1** (100 mg, 0.083 mmol, 1 eq) were weighed in together and 20 mL CH_2Cl_2 was added. After stirring overnight, the solvent of the yellow solution was removed *in vacuo*. The residue was dissolved in CH_2Cl_2 and layered with hexane. After a few days, **10** can be obtained as dark yellow blocks. The supernatant was decanted off, the residue washed with hexane and dried *in vacuo*.

Yield: 85 mg (79 %).

^{1}H NMR (CD_2Cl_2, 25 °C): δ [ppm] = 7.81 (m, 1H, *Ph*), 7.61-7.06 (m, 35 H, *Ph*), 7.04-6.88 (m, 6H, *Ph*).

^{31}P{^{1}H} NMR (CD_2Cl_2, 25 °C): δ [ppm] = 52.5 (s, 1P, $^{1}J_{PW}$ = 213 Hz, *P*W(CO)$_4$), -1.9 (s, 2P, *P*).

^{31}P NMR (CD_2Cl_2, 25 °C): δ [ppm] = 52.5 (s, 1P, $^{1}J_{PW}$ = 213 Hz, *P*W(CO)$_4$), -1.9 (s, 2P, *P*).

LIFDI-MS (dme): *m/z* = 1369.9 (4 %, $[M+2Cl]^+$), 1237.0 (9 %, $[M-Cu]^+$), 1174.0 (100 %, $[M-CuCl-CO]^+$), 1146.0 (16 %, $[M-CuCl-2CO]^+$).

EA $C_{58}H_{42}O_4P_3SbWCuCl$ x 0.2 CH_2Cl_2: calc [%]: C 53.06; H 3.24; found [%]: C 53.19; H 3.38.

ATR-IR (diamond crystal): $\bar{\upsilon}$ = 2011 (vs, CO),1931 (m, CO), 1919 (m, CO), 1899 (m, CO), 1881 (w, CO), 1869 (w, CO) cm^{-1}.

10.4.1.11 Synthesis of [W(CO)$_4${η^1:η^1:η^1:η^1-(o-PPh$_2$C$_6$H$_4$)$_3$Sb} {AgCl}] (11)

AgCl (11.9 mg, 0.083 mmol, 1 eq) and **1** (100 mg, 0.083 mmol, 1 eq) were sonicated in CH_2Cl_2/MeCN (5:1) for 14 h. The ^{31}P{^{1}H} spectrum of the reaction mixture reveals a mixture of **11** and **1** (4:1). It was filtered over diatomaceous earth and the solvent removed *in vacuo*. The residue was dissolved in CH_2Cl_2 and layered with hexane. After a few days, **11** could be obtained as yellow flat rods beside yellow blocks of **1**. The solvent was decanted off, the crystals washed with hexane and dried *in vacuo*. According to NMR spectra and elemental analysis a 4:1 mixture of **11** and **2** is obtained.

Yield: 49 mg (39.2 mg **11** (35 %), 9.9 mg **1**)

^{1}H NMR (CD_2Cl_2, 25 °C): δ [ppm] = 7.92 (m, 1H, *Ph*), 7.69 (m, 1H, *Ph*), 7.58-6.78 (m, 40 H, *Ph*).

^{31}P{^{1}H} NMR (CD_2Cl_2, 25 °C): δ [ppm] = 56.2 (s, 0.28P, $^{1}J_{PW}$ = 229 Hz, *P*W(CO)$_4$, **I**), 52.5 (s, 1P, $^{1}J_{PW}$ = 212 Hz, *P*W(CO)$_4$, **2**), 2.8 (d, 1P, $^{2}J_{PP}$ = 17 Hz, *P*, **2**), 1.1 (d, 1P, $^{2}J_{PP}$ = 17 Hz, *P*, **2**), -5.3 (s, 0.56P, *P*, **I**).

^{31}P NMR (CD_2Cl_2, 25 °C): δ [ppm] = 56.2 (s, 0.24P, *P*W(CO)$_4$, **I**), 52.5 (s, 1P, $^{1}J_{PW}$ = 212 Hz, *P*W(CO)$_4$, **2**), 2.8 (s, 1P, *P*, **2**), 1.1 (s, 1P, *P*, **2**), -5.3 (s, 0.56P, *P*, **I**).

LIFDI-MS (dme): *m/z* = 1309.1 (15 %, $[M-Cl]^+$), 1174.0 (100 %, $[M-AgCl-CO]^+$).

EA $(C_{58}H_{42}O_4P_3SbWAgCl)_{0.8}$ x $(C_{58}H_{42}O_4P_3SbW)_{0.2}$ x 1.3 CH_2Cl_2: calc [%]: C 50.66; H 3.16; found [%]: C 49.94; H 3.37.

ATR-IR (diamond crystal): $\bar{\upsilon}$ = 2025 (vs, CO), 1935 (s, CO), 1895 (vs, CO) cm^{-1}.

10.4.1.12 Synthesis of $[W(CO)_4\{\eta^1{:}\eta^1{:}\eta^1\text{-}(o\text{-}PPh_2C_6H_4)_2Sb\}\{\eta^1\text{-}AuCl(o\text{-}PPh_2C_6H_4)\}\{AuCl\}]$ (12) and $[(W(CO)_4\{\eta^1{:}\eta^1{:}\eta^1\text{-}(o\text{-}PPh_2C_6H_4)_2Sb\})_2AuCl]$ (13)

A solution of (tht)AuCl (53.4 mg, 0.166 mmol, 2 eq) in 10 mL CH_2Cl_2 was added to a stirred solution of **1** (100 mg, 0.083 mmol, 1 eq) in 10 mL CH_2Cl_2 while the color changed to orange. The solvent was removed *in vacuo* after stirring for 30 minutes. The residue was dissolved in CH_2Cl_2 and layered with hexane. After a few days **12** can be obtained as orange plates beside very few dark blocks of **13**. The solvent was decanted off, washed with hexane and dried *in vacuo*.

Compound **12**:

Yield: 72 mg (52 %).

^{1}H NMR (CD_2Cl_2, 25 °C): δ [ppm] = 8.04 (m, 2H, *Ph*), 7.70-7.22 (m, 34 H, *Ph*), 7.15 (m, 2H, *Ph*), 7.04 (m, 2H, *Ph*), 6.83 (m, 2H, *Ph*).

^{31}P{^{1}H} NMR (CD_2Cl_2, 25 °C): δ [ppm] = 61.2 (d, 1P, $^2J_{PP}$ = 8 Hz, *P*), 54.2 (s, 1P, $^1J_{PW}$ = 221 Hz, *P*W(CO)$_4$), 34.6 (d, 1P, $^2J_{PP}$ = 8 Hz, *P*).

^{31}P NMR (CD_2Cl_2, 25 °C): δ [ppm] = 61.2 (s, 1P, *P*), 54.2 (s, 1P, $^1J_{PW}$ = 221 Hz, *P*W(CO)$_4$), 34.6 (s, 1P, *P*).

LIFDI-MS (o-$C_6H_4F_2$): *m/z* = 1596.1 (20 %, $[M\text{-}2Cl]^+$).

EA $C_{58}H_{42}O_4P_3SbWAu_2Cl_2$: calc [%]: C 41.81; H 2.54; found [%]: C 42.08; H 2.87.

ATR-IR (diamond crystal): $\bar{\upsilon}$ = 2017 (vs, CO), 2005 (s, CO), 1922 (m, CO), 1904 (w, CO), 1868 (w, CO), 1845 (w, CO) cm^{-1}.

Compound **13**:

Yield: few crystals

^{1}H NMR (CD_2Cl_2, 25 °C): δ [ppm] = 9.34 (m, 1H, *Ph*) 8.59 (m, 1H, *Ph*), 7.74 (m, 3H, *Ph*), 7.64 (m, 5H, *Ph*), 7.42-7.28 (m, 17H, *Ph*), 7.18-6.75 (m, 14H, *Ph*), 6.36 (m, 1H, *Ph*).

^{31}P{^{1}H} NMR (CD_2Cl_2, 25 °C): δ [ppm] = 54.8 (s, 1P, $^1J_{PW}$ = 218 Hz, *P*W(CO)$_4$), 40.4 (s, 1P, *P*).

^{31}P NMR (CD_2Cl_2, 25 °C): δ [ppm] = 54.8 (s, 1P, $^1J_{PW}$ = 218 Hz, *P*W(CO)$_4$), 40.4 (s, 1P, *P*).

10.4.1.13 Synthesis of $[W(CO)_4\{\eta^1:\eta^1:\eta^1:\eta^1\text{-}(o\text{-}PPh_2C_6H_4)_3Sb\}\{Cu\}]\,[PF_6]$ (14)

$[Cu(MeCN)_4][PF_6]$ (31 mg, 0.083 mmol, 1 eq) and **1** (100 mg, 0.083 mmol, 1 eq) were weighed in together and 20 mL CH_2Cl_2 was added. After stirring overnight, the solvent of the yellow solution was removed *in vacuo*. The residue was dissolved in o-difluoro benzene and layered with hexane. After a few days, **14** can be obtained as dark yellow blocks. The supernatant was decanted off, the residue washed with hexane and dried *in vacuo*.

Yield: 82 mg (70 %).

^{1}H NMR (CD_2Cl_2, 25 °C): *δ* [ppm] = 8.51 (m, 1H, *Ph*), 7.87 (m, 1H, *Ph*), 7.71-6.99 (m, 36 H, *Ph*), 6.55 (m, 4H, *Ph*).

^{31}P{^{1}H} NMR (CD_2Cl_2, 25 °C): *δ* [ppm] = 49.4 (s, 1P, $^1J_{PW}$ = 199 Hz, *P*W(CO)$_4$), 5.8 (s, 2P, *P*), -143.9 (sept, 1P, $^1J_{PF}$ = 710 Hz, *P*F_6).

^{31}P NMR (CD_2Cl_2, 25 °C): *δ* [ppm] = 49.4 (s, 1P, $^1J_{PW}$ = 199 Hz, *P*W(CO)$_4$), 5.8 (s, 2P, *P*), -143.9 (sept, 1P, $^1J_{PF}$ = 710 Hz, *P*F_6).

^{19}F NMR (CD_2Cl_2, 25 °C): *δ* [ppm] = -73.4 (d, $^1J_{PF}$ = 710 Hz, P*F*$_6$).

ESI-MS (CH_2Cl_2): *m/z* = 1265.0 (100 %, $[M]^+$).

EA ($C_{58}H_{42}O_4P_4SbWCuF_6$ x 0.44 C_6H_{14}): calc [%]: C 50.30; H 3.35; found [%]: C 50.49; H 3.00.

ATR-IR (diamond crystal): $\bar{\upsilon}$ = 2032 (s, CO), 1943 (s, CO), 1928 (vs, CO), 1826 (m, CO) cm^{-1}.

10.4.1.14 Synthesis of $[W(CO)_4\{\eta^1:\eta^1:\eta^1:\eta^1\text{-}(o\text{-}PPh_2C_6H_4)_3Sb\}\{AgMeCN\}][PF_6]$ (15)

$Ag[PF_6]$ (21 mg, 0.083 mmol, 1 eq) and **1** (100 mg, 0.083 mmol, 1 eq) were weighed in together, 20 mL CH_2Cl_2 and 1 ml MeCN were added. After stirring overnight, the solvent of the yellow solution was removed *in vacuo*. The residue was dissolved in CH_2Cl_2 and layered with hexane. After a few days, **15** can be obtained as bright yellow blocks. The supernatant was decanted off, the residue washed with hexane and dried *in vacuo*.

Yield: 86 mg (69 %).

^{1}H NMR (CD_2Cl_2, 25 °C): *δ* [ppm] = 8.20 (m, 1H, *Ph*), 7.75 (m, 1H, *Ph*), 7.64 (m, 2H, *Ph*), 7.52-7.10 (m, 32 H, *Ph*), 7.00 (m, 2H, *Ph*), 6.86 (m, 2H, *Ph*), 1.98 (s, 3H, C*H*$_3$CN).

$^{31}P\{^{1}H\}$ NMR (CD_2Cl_2, 25 °C): δ [ppm] = 50.6 (s, 1P, $^{1}J_{PW}$ = 202 Hz, *P*W(CO)$_4$), 9.8 (d, 1P, $^{2}J_{PP}$ = 25 Hz, *P*), 7.6 (d, 1P, $^{2}J_{PP}$ = 25 Hz, *P*), -143.9 (sept, 1P, $^{1}J_{PF}$ = 710 Hz, *P*F_6).

^{31}P NMR (CD_2Cl_2, 25 °C): δ [ppm] = 50.6 (s, 1P, $^{1}J_{PW}$ = 202 Hz, *P*W(CO)$_4$), 9.8 (d, 1P, $^{2}J_{PP}$ = 25 Hz, *P*), 7.6 (d, 1P, $^{2}J_{PP}$ = 25 Hz, *P*), -143.9 (sept, 1P, $^{1}J_{PF}$ = 710 Hz, *P*F_6).

^{19}F NMR (CD_2Cl_2, 25 °C): δ [ppm] = -73.4 (d, $^{1}J_{PF}$ = 710 Hz, P*F*$_6$).

ESI-MS (CH_2Cl_2): *m/z* = 1309.0 (100 %, $[M\text{-}MeCN]^+$).

EA ($C_{60}H_{45}O_4NP_4SbWAgF_6$): calc [%]: C 48.19; H 3.03; N 0.94; found [%]: C 48.09; H 3.05; N 0.83.

ATR-IR (diamond crystal): $\bar{\upsilon}$ = 2021 (s, CO), 1924 (m, CO), 1902 (vs, CO) cm^{-1}.

10.4.1.15 Synthesis of $[W(CO)_4\{\eta^1{:}\eta^1{:}\eta^1{:}\eta^1\text{-}(o\text{-}PPh_2C_6H_4)_3Sb\}\ \{Au\}][PF_6]$ (16)

A solution of (tht)AuCl (26.7 mg, 0.083 mmol, 1 eq) was added to a stirred solution of **1** (100 mg, 0.083 mmol, 1 eq) and $TlPF_6$ (29.1 mg, 0.083 mmol, 1 eq) in CH_2Cl_2. After a few minutes the color changed to orange and a bright precipitate (TlCl) was obtained. After stirring for one hour, it was filtered over diatomaceous earth. The solvent was removed *in vacuo*, the residue dissolved in CH_2Cl_2 and layered with hexane. After a few days, **16** can be obtained as dark yellow blocks. The supernatant was decanted off, the crystals washed with hexane and dried *in vacuo*.

Yield: 88 mg (69 %).

^{1}H NMR (CD_2Cl_2, 25 °C): δ [ppm] = 8.45 (m, 1H, *Ph*), 7.80 (m, 5H, *Ph*), 7.62 (m, 11H, *Ph*), 7.45 (m, 3 H, *Ph*), 7.32 (m, 10H, *Ph*), 7,15 (m, 8H, *Ph*), 6.64 (m, 4H, *Ph*).

$^{31}P\{^{1}H\}$ NMR (CD_2Cl_2, 25 °C): δ [ppm] = 52.1 (s, 1P, $^{1}J_{PW}$ = 197 Hz, *P*W(CO)$_4$), 43.8 (s, 2P, *P*), -143.9 (sept, 1P, $^{1}J_{PF}$ = 710 Hz, *P*F_6).

^{31}P NMR (CD_2Cl_2, 25 °C): δ [ppm] = 52.1 (s, 1P, $^{1}J_{PW}$ = 197 Hz, *P*W(CO)$_4$), 43.8 (s, 2P, *P*), -143.9 (sept, 1P, $^{1}J_{PF}$ = 710 Hz, *P*F_6).

^{19}F NMR (CD_2Cl_2, 25 °C): δ [ppm] = -73.4 (d, $^{1}J_{PF}$ = 710 Hz, P*F*$_6$).

ESI-MS (CH_2Cl_2): *m/z* = 1399.1 (100 %, $[M]^+$).

EA ($C_{58}H_{42}O_4P_4SbWAuF_6$ x 0.9 CH_2Cl_2): calc [%]: C 43.67; H 2.73; found [%]: C 43.70; H 2.89.

ATR-IR (diamond crystal): $\bar{\upsilon}$ = 2025 (s, CO), 1914 (m, CO), 1882 (vs, CO) cm^{-1}.

10.4.1.16 Synthesis of $[W(CO)_2(\mu\text{-}CO)\{\eta^1{:}\eta^1{:}\eta^1{:}\eta^1{:}\eta^1\text{-}(o\text{-}PPh_2C_6H_4)_3Sb\}\{Cu_2(\mu\text{-}Cl)_2\}]$ (17)

CuCl (16.8 mg, 0.170 mmol, 2 eq) and **4** (100 mg, 0.085 mmol, 1 eq) were weighed in together, 20 mL CH_2Cl_2 and 1 ml MeCN were added. After stirring overnight, the solvent of the yellow solution was removed *in vacuo*. The residue was dissolved in CH_2Cl_2 and layered with hexane. After a few days, **17** can be obtained as orange plates. The supernatant was decanted off, the residue washed with hexane and dried *in vacuo*.

Yield: 102 mg (88 %).

^{1}H NMR (CD_2Cl_2, 25 °C): *δ* [ppm] = 7.61 (m, 2H, *Ph*), 7.53-7.21 (m, 23H, *Ph*), 7.14 (m, 7H, *Ph*), 7.02 (m, 2 H, *Ph*), 6.96 (m, 1H, *Ph*), 6.88 (m, 5H, *Ph*), 6.67 (m, 1H, *Ph*).

^{31}P{^{1}H} NMR (CD_2Cl_2, 25 °C): *δ* [ppm] = 59.9 (s, 1P, $^1J_{PW}$ = 212 Hz, *P*W(CO)$_4$), 14.0 (s, 1P, *P*), 5.5 (s, 1P, *P*).

^{31}P NMR (CD_2Cl_2, 25 °C): *δ* [ppm] = 59.9 (s, 1P, $^1J_{PW}$ = 212 Hz, *P*W(CO)$_4$), 14.0 (s, 1P, *P*), 5.5 (s, 1P, *P*).

LIFDI-MS (o-$C_6H_4F_2$): *m/z* = 1372.0 (21 %, $[M]^+$), 1237.1 (20 %, $[M\text{-}Cu\text{-}2Cl]^+$), 1174.2 (100 %, $[M\text{-}2Cu\text{-}2Cl]^+$), 1149.2 (21 %, $[M\text{-}2Cu\text{-}2Cl\text{-}CO]^+$).

EA ($C_{57}H_{42}O_3P_3SbWCu_2Cl_2$): calc [%]: C 49.92; H 3.09; found [%]: C 49.98; H 3.18.

ATR-IR (diamond crystal): $\bar{\upsilon}$ = 1934 (vs, CO), 1846 (m, CO), 1801 (w, CO) cm^{-1}.

10.4.1.17 Synthesis of $[W(CO)_3\{\eta^1{:}\eta^1{:}\eta^1\text{-}(o\text{-}PPh_2C_6H_4)_3Sb\}\{AuCl\}]$ (18)

(tht)AuCl (27.3 mg, 0.085 mmol, 1 eq) in CH_2Cl_2 was added to a stirred solution of **4** (100 mg, 0.085 mmol, 1 eq) in CH_2Cl_2. After stirring for 5 hours, the solvent of the yellow solution was removed *in vacuo*. The residue was dissolved in CH_2Cl_2 and layered with hexane. After a few days, **18** can be obtained as bright yellow needles. The supernatant was decanted off, the residue washed with hexane and dried *in vacuo*.

Yield: 37 mg (40 %).

^{1}H NMR (CD_2Cl_2, 25 °C): *δ* [ppm] = 8.20 (m, 1H, *Ph*), 7.82-6.50 (m, 41H, *Ph*).

^{31}P{^{1}H} NMR (CD_2Cl_2, 25 °C): *δ* [ppm] = 59.3 (br, $\omega_{1/2}$ = 142 Hz, 1P, *P*W(CO)$_4$), 50.2 (br, $\omega_{1/2}$ = 202 Hz,1P, *P*W(CO)$_4$), 30.6 (s, 1P, *P*).

^{31}P NMR (CD_2Cl_2, 25 °C): *δ* [ppm] = 59.2 (br, $\omega_{1/2}$ = 220 Hz, 1P, *P*W(CO)$_4$), 50.2 (br, $\omega_{1/2}$ = 213 Hz,1P, *P*W(CO)$_4$), 30.6 (s, 1P, *P*).

LIFDI-MS (o-$C_6H_4F_2$): *m/z* = 1371.2 (26 %, [M-Cl]$^+$), 1174.2 (100 %, [M-Au-Cl]$^+$).

EA ($C_{57}H_{42}O_3P_3SbWAuCl$): calc [%]: C 48.70; H 3.01; found [%]: C 48.63; H 3.01.

ATR-IR (diamond crystal): $\bar{\upsilon}$ = 1931 (vs, CO), 1859 (s, CO), 1828 (m, CO) cm^{-1}.

10.4.1.18 Synthesis of [W(CO)$_2$(μ-CO){η^1:η^1:η^1:η^1-(o-PPh$_2$C$_6$H$_4$)$_3$Sb}{CuMeCN}][PF$_6$] (19)

[Cu(MeCN)$_4$][PF$_6$] (31.7 mg, 0.085 mmol, 1 eq) and **4** (100 mg, 0.085 mmol, 1 eq) were weighed in together and 20 mL CH_2Cl_2 was added. After stirring for 1 hour, the solvent of the yellow solution was removed *in vacuo*. The residue was dissolved in CH_2Cl_2 and layered with hexane. After a few days, **19** can be obtained as yellow blocks. The supernatant was decanted off, the residue washed with hexane and dried *in vacuo*.

Yield: 80 mg (66 %).

^{1}H NMR (CD_2Cl_2, 25 °C): *δ* [ppm] = 8.24 (m, 1H, *Ph*), 7.83 (m, 2H, *Ph*), 7.61 (m, 1H, *Ph*), 7.39 (m, 18H, *Ph*), 7.20 (m, 12H, *Ph*), 6.93 (m, 4H, *Ph*), 6.61 (m, 4H, *Ph*), 1.98 (s, 3H, C*H*$_3$CN).

^{31}P{^{1}H} NMR (CD_2Cl_2, 25 °C): *δ* [ppm] = 59.9 (s, 2P, $^1J_{PW}$ = 212 Hz, *P*W(CO)$_4$), -4.1 (s, 1P, *P*), -143.9 (sept, 1P, $^1J_{PF}$ = 710 Hz, *P*F$_6$).

^{31}P NMR (CD_2Cl_2, 25 °C): *δ* [ppm] = 59.9 (s, 2P, $^1J_{PW}$ = 212 Hz, *P*W(CO)$_4$), -4.1 (s, 1P, *P*), -143.9 (sept, 1P, $^1J_{PF}$ = 710 Hz, *P*F$_6$).

^{19}F NMR (CD_2Cl_2, 25 °C): *δ* [ppm] = -73.4 (d, $^1J_{PF}$ = 710 Hz, P*F*$_6$).

ESI-MS (CH_2Cl_2): *m/z* = 1273.0 (100 %, [M-MeCN]$^+$).

ATR-IR (diamond crystal): $\bar{\upsilon}$ = 1945 (s, CO), 1870 (s, CO), 1840 (vs, CO), 1805 (w, CO) cm^{-1}.

10.4.1.19 Synthesis of [W(CO)$_2$(μ-CO){η^1:η^1:η^1:η^1-(o-PPh$_2$C$_6$H$_4$)$_3$Sb}{AgMeCN}][PF$_6$] (20)

Ag[PF$_6$] (21.5 mg, 0.085 mmol, 1 eq) and **4** (100 mg, 0.085 mmol, 1 eq) were weighed in together, 20 mL CH_2Cl_2 and 1 mL MeCN were added. After stirring for 3 hours, the solvent of the yellow solution was removed *in vacuo*. The residue was dissolved in CH_2Cl_2 and layered

with hexane. After a few days, **20** can be obtained as yellow needles. The supernatant was decanted off, the residue washed with hexane and dried *in vacuo*.

Yield: 86 mg (70 %).

^{1}H NMR (CD_2Cl_2, 25 °C): *δ* [ppm] = 7.83 (m, 2H, *Ph*), 7.59 (m, 1H, *Ph*), 7.54-7.11 (m, 30H, *Ph*), 6.98 (m, 4H, *Ph*), 6.62 (m, 4H, *Ph*), 1.96 (s, 3H, C*H*$_3$CN).

^{31}P{^{1}H} NMR (CD_2Cl_2, 25 °C): *δ* [ppm] = 53.8 (br, 2P, , *P*W(CO)$_4$), 1.4 (dd, $^{2}J_{PP}$ = 33 Hz, $^{2}J_{PP}$ = 468 Hz, 1P, *P*), -143.9 (sept, 1P, $^{1}J_{PF}$ = 710 Hz, *P*F$_6$).

^{31}P NMR (CD_2Cl_2, 25 °C): *δ* [ppm] = 53.8 (br, 2P, , *P*W(CO)$_4$), 1.4 (d, $^{2}J_{PP}$ = 468 Hz, 1P, *P*), -143.9 (sept, 1P, $^{1}J_{PF}$ = 710 Hz, *P*F$_6$).

^{19}F NMR (CD_2Cl_2, 25 °C): *δ* [ppm] = -73.4 (d, $^{1}J_{PF}$ = 710 Hz, P*F*$_6$).

ESI-MS (CH_2Cl_2): *m/z* = 1281.0 (100 %, [M-MeCN]$^{+}$).

EA ($C_{59}H_{45}NO_3F_6P_4SbWAg$ x 0.5 CH_2Cl_2): calc [%]: C 47.89; H 3.11; N 0.94; found [%]: C 47.79; H 3.09; N 0.93.

ATR-IR (diamond crystal): $\bar{\upsilon}$ = 1954 (vs, CO), 1890 (s, CO), 1886 (s, CO), 1846 (s, CO), 1839 (s, CO), 1832 (s, CO) cm^{-1}.

10.4.1.20 Synthesis of [W(CO)$_2$(μ-CO){η^1:η^1:η^1:η^1-(o-PPh$_2$C$_6$H$_4$)$_3$Sb}{Au}][PF$_6$] (21)

Tl[PF$_6$] (29.8 mg, 0.085 mmol, 1 eq) and **4** (100 mg, 0.085 mmol, 1 eq) were weighed in together and 20 mL CH_2Cl_2 was added. A solution of (tht)AuCl (27.3 mg, 0.085 mmol, 1 eq) in 10 mL CH_2Cl_2 was added. After stirring for 2 hours, the turbid (TlCl) yellow solution was filtered over diatomaceous earth and the solvent removed *in vacuo*. The residue was dissolved in CH_2Cl_2 and layered with hexane. After a few days, **21** can be obtained as yellow plates. The supernatant was decanted off, the residue washed with hexane and dried *in vacuo*.

Yield: 85 mg (66 %).

^{1}H NMR (CD_2Cl_2, 25 °C): *δ* [ppm] = 8.35 (m, 1H, *Ph*), 7.91 (m, 2H, *Ph*), 7.62 (m, 2H, *Ph*), 7.48 (m, 13H, *Ph*), 7.30 (m, 16H, *Ph*), 6.99 (m, 4H, *Ph*), 6.67 (m, 4H, *Ph*).

^{31}P{^{1}H} NMR (CD_2Cl_2, 25 °C): *δ* [ppm] = 51.5 (s, 2P, $^{1}J_{PW}$ = 192 Hz , *P*W(CO)$_4$), 35.9 (s, 1P, *P*), -143.9 (sept, 1P, $^{1}J_{PF}$ = 710 Hz, *P*F$_6$).

^{31}P NMR (CD_2Cl_2, 25 °C): *δ* [ppm] = 51.5 (s, 2P, $^{1}J_{PW}$ = 192 Hz , *P*W(CO)$_4$), 35.9 (s, 1P, *P*), -143.9 (sept, 1P, $^{1}J_{PF}$ = 710 Hz, *P*F$_6$).

^{19}F NMR (CD_2Cl_2, 25 °C): δ [ppm] = -73.4 (d, $^1J_{PF}$ = 710 Hz, PF_6).

ESI-MS (CH_2Cl_2): *m/z* = 1371.1 (100 %, $[M]^+$).

EA ($C_{57}H_{42}O_3F_6P_4SbWAu$): calc [%]: C 45.18; H 2.79; found [%]: C 45.35; H 2.88.

ATR-IR (diamond crystal): $\bar{\upsilon}$ = 1966 (vs, CO), 1905 (s, CO), 1809 (s, CO), 1801 (s, CO) cm^{-1}.

10.4.2 Details on single crystal X-ray structure analysis

The X-ray diffraction experiments were performed on either an Gemini Ultra diffractometer (Oxford diffraction) with an AtlasS2 detector with Mo radiation (λ = 0.71073 Å) (**6**, **9, 10, 12, 21**) or Cu-K*α* radiation (λ = 1.54178 Å) (**3, 11, 13, 15, 17, 18, 20**), a GV 50 diffractometer (Rigaku, formerly Agilent Technologies) with TitanS2 detector applying Cu-K*α* radiation (λ = 1.54178 Å) (**1**, **4**, **5**) or Cu-K*β* radiation (λ = 1.39222 Å) (**14**, **16**, **19**) or SuperNova (Agilent Technologies) with an Atlas detector applying Cu-K*α* radiation (λ = 1.54178 Å) (**7**, **8**) or Mo radiation (λ = 0.71073 Å) (**2**). All measurements were performed at 123 K. Data collection and reduction were performed with CrysAlispro[19] (Version V1.171.41.21a, 2019 (**11**), V1.171.40.14a, 2018 (**1, 2, 4, 5, 10**, **12**, **14**, **15**, **16**, **17**, **18**, **19**, **20**, **21**), V1.171.37.34, 2014 (**3,8**), V1.171.38.43, 2015 (**6, 7, 9, 13**). A gaussian absorption correction was performed using CrysAlisPro for **1**, **2**, **3**, **4**, **5**, **6**, **10**, **11**, **12**, **15**, **16**, **17**, **19**, **20**, **21**.[19] For **7**, **8**, **9**,**13**, 1**4**, **18** an analytical absorption correction was performed using CrysAlisPro using a multifaceted crystal model based on expressions derived by R.C. Clark & J.S. Reid.[20] Using Olex2,[21] all structures were solved by ShelXT.[22] A least-square refinement on F^2 was carried out with ShelXL.[23] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were located in idealized positions and refined isotropically according to riding model.

10.4.2.1 $[W(CO)_4\{\eta^1:\eta^1\text{-}(o\text{-}PPh_2C_6H_4)_3Sb\}]$ (1)

Compound **1** crystallizes from a concentrated solution in thf layered with pentane at room temperature in the monoclinic space group $P2_1/c$ as clear yellow plates. The asymmetric unit contains two molecules of **1**. The structure in solid state is depicted in Figure S1 and S2.

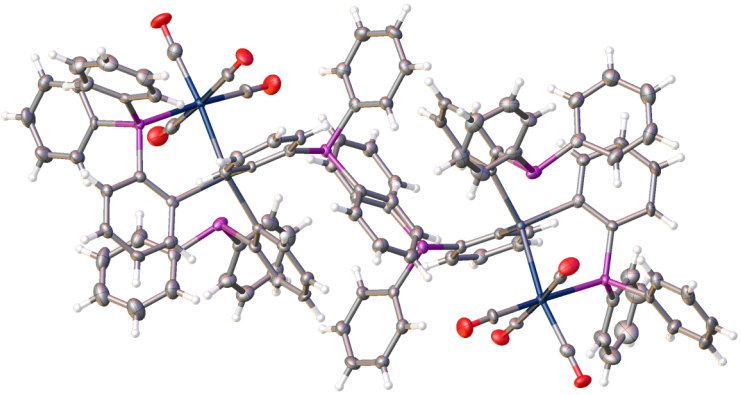


Figure S1: Molecular structure of **1** in solid state. Thermal ellipsoids are drawn with 50 % probability level.

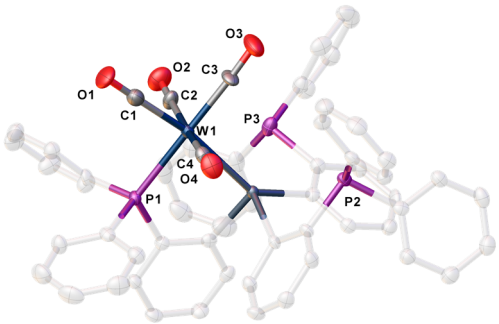


Figure S2: Molecular structure of **1** in solid state. Thermal ellipsoids are drawn with 50 % probability level. Selected bond lengths [Å]: W1-P1 2.5140(11), W1-P2 4.85348(5), W1-P3 4.56940(5), W1-Sb1 2.7506(3), W1-C1 2.040(6), W1-C2 1.981(5), W1-C3 2.026(5), W1-C4 1.959(6), C1-O1 1.151(7), C2-O2 1.154(7), C3-O3 1.140(7), C4-O4 1.161(7).

10.4.2.2 $[W(CO)_4\{\eta^1:\eta^1\text{-}(o\text{-}PPh_2C_6H_4)_2SbPh\}]$ (2)

Compound **2** crystallizes from a concentrated solution in CH_2Cl_2 layered with hexane at room temperature in the monoclinic space group $P2_1/n$ as clear yellow plates. The asymmetric unit contains two molecules of **2** and 0.4 molecules CH_2Cl_2. The CH_2Cl_2 molecule is disordered over two positions The structure in solid state is depicted in Figure S3 and S4.

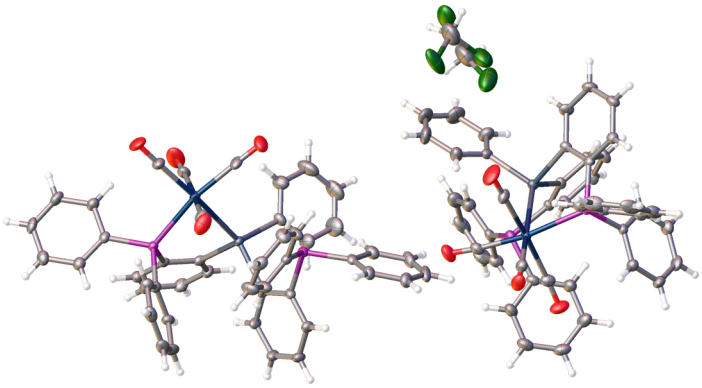


Figure S3: Molecular structure of **2** in solid state. Thermal ellipsoids are drawn with 50 % probability level.

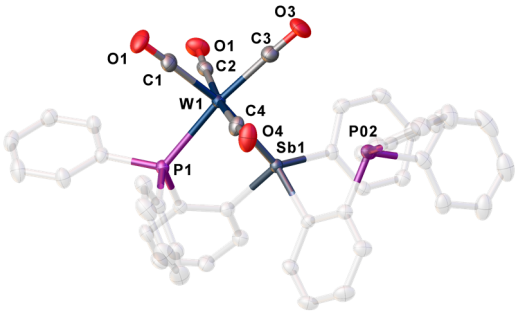


Figure S4: Molecular structure of **2** in solid state. Thermal ellipsoids are drawn with 50 % probability level. Selected bond lengths [Å]: W1-P1 2.5024(8), W1-P2 4.5795(10), W1-Sb1 2.7055(2), W1-C1 2.024(3), W1-C2 1.983(3), W1-C3 1.976(3), W1-C4 2.046(3), C1-O1 1.152(4), C2-O2 1.149(4), C3-O3 1.147(4), C4-O4 1.133(4).

10.4.2.3 $[W(CO)_4\{\eta^1:\eta^1\text{-}(o\text{-}PPh_2C_6H_4)_2SbCl\}]$ (3)

Compound **3** crystallizes from a concentrated solution in CH_2Cl_2 layered with hexane at room temperature in the triclinic space group $P\bar{1}$ as clear yellow plates. The asymmetric unit contains one molecule of **3**. A solvent mask was calculated and 53.0 electrons were found in a volume of 166.0 Å^3 in 1 void. This is consistent with the presence of 0.6 [CH_2Cl_2] per formula unit which account for 50.4 electrons. The structure in solid state is depicted in Figure S5.

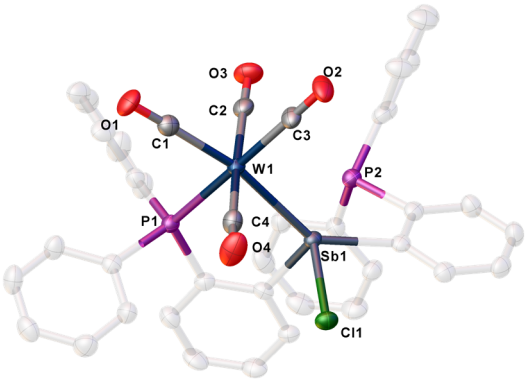


Figure S5: Molecular structure of **3** in solid state. Thermal ellipsoids are drawn with 50 % probability level. Selected bond lengths [Å]: W1-P1 2.5140(7), W1-P2 4.64062(19), W1-Sb1 2.6938(2), W1-C1 2.052(4), W1-C2 1.995(3), W1-C3 2.042(3), W1-C4 1.987(3), C1-O1 1.136(4), C2-O2 1.145(4), C3-O3 1.135(4), C4-O4 1.149(4), Sb1-Cl1 2.4293(7).

10.4.2.4 $[W(CO)_3\{\eta^1:\eta^1:\eta^1\text{-}(o\text{-}PPh_2C_6H_4)_3Sb\}]$ (4)

Compound **4** crystallizes from a concentrated solution in CH_2Cl_2 layered with hexane at room temperature in the monoclinic space group $P2_1/n$ as dark yellow blocks. The asymmetric unit contains one molecule of **4**. The structure in solid state is depicted in Figure S6.

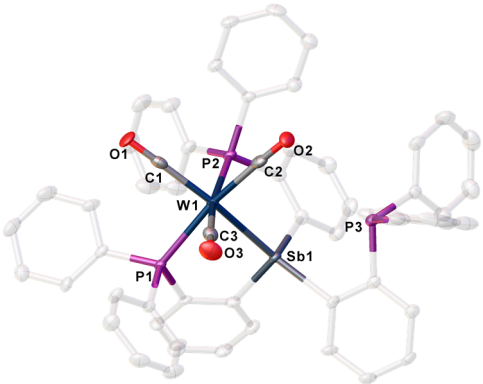


Figure S6: Molecular structure of **4** in solid state. Thermal ellipsoids are drawn with 50 % probability level. Selected bond lengths [Å]: W1-P1 2.5091(12), W1-P2 2.5048(11), W1-P3 4.62455(8), W1-Sb1 2.6777(3), W1-C1 1.968(6), W1-C2 1.997(5), W1-C3 1.989(6), C1-O1 1.156(7), C2-O2 1.146(7), C3-O3 1.157(7).

10.4.2.5 $[W(CO)_3\{\eta^1:\eta^1:\eta^1\text{-}(o\text{-}PPh_2C_6H_4)_2SbCl\}]$ (5)

Compound **5** crystallizes from a concentrated solution in CH_2Cl_2 layered with hexane at room temperature in the monoclinic space group $P2_1/n$ as orange plates. The asymmetric unit contains one molecule of **5**. A solvent mask was calculated and 138.0 electrons were found in a volume of 512.0 Å^3 in 1 void. This is consistent with the presence of 0.8 [CH_2Cl_2] per formula unit which account for 134.4 electrons. The structure in solid state is depicted in Figure S7.

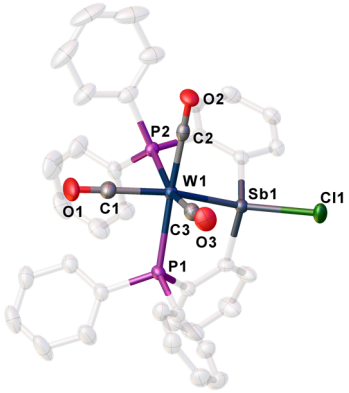


Figure S7: Molecular structure of **5** in solid state. Thermal ellipsoids are drawn with 50 % probability level. Selected bond lengths [Å]: W1-P1 2.5490(8), W1-P2 2.5308(8), W1-Sb1 2.6440(2)), W1-C1 1.983(4), W1-C2 1.998(4), W1-C3 1.971(4), C1-O1 1.157(4), C2-O2 1.145(5), C3-O3 1.156(5), Sb1-Cl1 2.3687(8).

10.4.2.6 $[(W(CO)_3\{\eta^1:\eta^1:\eta^1\text{-}(o\text{-}PPh_2C_6H_4)_2Sb\})_2]$ (6)

Compound **6** crystallizes from a concentrated solution in CH_2Cl_2 layered with acetonitrile at room temperature in the monoclinic space group $P2_1/n$ as orange plates. The asymmetric unit contains one half molecule of **6**, 1.25 molecules CH_2Cl_2 and half a molecule of CH_3CN. The structure in solid state is depicted in Figure S8 and S9.

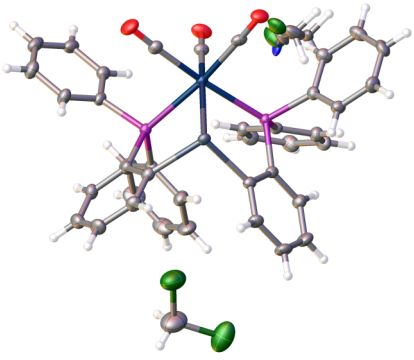


Figure S8: Molecular structure of **6** in solid state (asymmetric unit). Thermal ellipsoids are drawn with 50 % probability level.

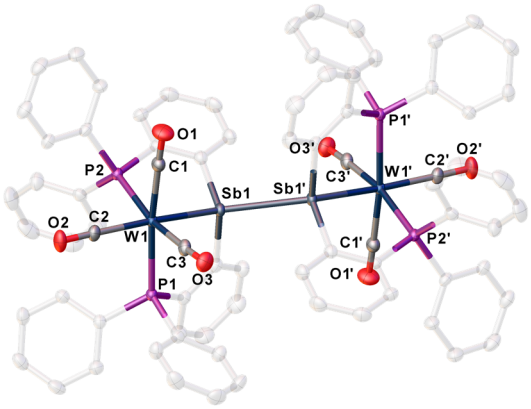


Figure S9: Molecular structure of **6** in solid state. Thermal ellipsoids are drawn with 50 % probability level. Selected bond lengths [Å]: W1-P1 2.5049(9), W1-P2 2.5323(9), W1-Sb1 2.6716(2), W1-C1 1.995(4), W1-C2 1.969(3), W1-C3 1.978(4), C1-O1 1.152(4), C2-O2 1.163(4), C3-O3 1.156(4), Sb1-Sb1' 2.8091(4).

10.4.2.7 $[Mo(CO)_3\{\eta^1{:}\eta^1{:}\eta^1\text{-}(o\text{-}PPh_2C_6H_4)_3Sb\}]$ (7)

Compound **7** crystallizes from a concentrated solution in CH_2Cl_2 layered with hexane at room temperature in the monoclinic space group $P2_1/n$ as yellow blocks. The asymmetric unit contains one molecule of **7**. The structure in solid state is depicted in Figure S10.

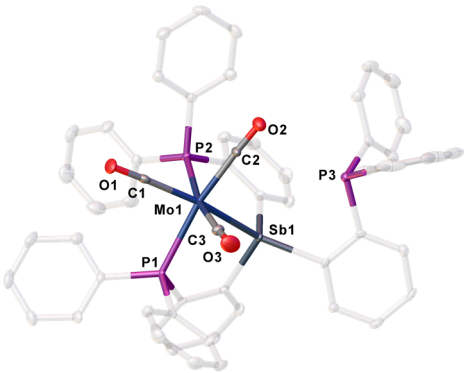


Figure S10: Molecular structure of **7** in solid state. Thermal ellipsoids are drawn with 50 % probability level. Selected bond lengths [Å]: Mo1-P1 2.5150(8), Mo1-P2 2.5163(9), Mo1-P3 4.6325(10), Mo1-Sb1 2.6770(3), Mo1-C1 1.990(3), Mo1-C2 1.966(4), Mo1-C3 2.005(4), C1-O1 1.151(4), C2-O2 1.164(5), C3-O3 1.138(4).

10.4.2.8 $[Mo(CO)_3\{\eta^1:\eta^1:\eta^1\text{-}(o\text{-}PPh_2C_6H_4)_2SbPh\}]$ (8)

Compound **8** crystallizes from a concentrated solution in dimethoxyethane layered with hexane at room temperature in the monoclinic space group $P2_1/n$ as yellow blocks. The asymmetric unit contains one molecule of **8**. The structure in solid state is depicted in Figure S11.

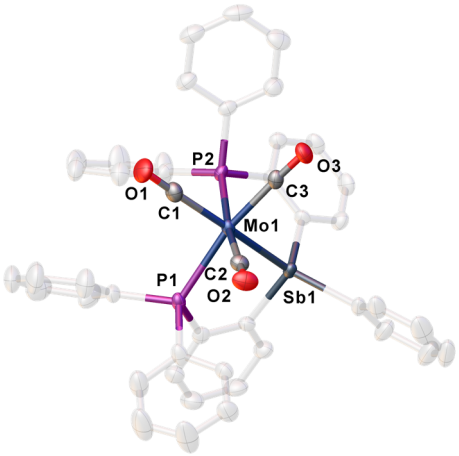


Figure S11: Molecular structure of **8** in solid state. Thermal ellipsoids are drawn with 50 % probability level. Selected bond lengths [Å]: Mo1-P1 2.5275(10), Mo1-P2 2.5383(10), Mo1-Sb1 2.6746(4), Mo1-C1 1.971 (4), Mo1-C2 1.987(4), Mo1-C3 1.979(4), C1-O1 1.155(5), C2-O2 1.150(5), C3-O3 1.157(5).

10.4.2.9 $[Mo(CO)_3\{\eta^1:\eta^1:\eta^1\text{-}(o\text{-}PPh_2C_6H_4)_2SbCl\}]$ (9)

Compound **9** crystallizes from a concentrated solution in CH_2Cl_2 layered with hexane at room temperature in the monoclinic space group $P2_1/n$ as orange rods. The asymmetric unit contains one molecule of **9**. The structure in solid state is depicted in Figure S12 and S13.

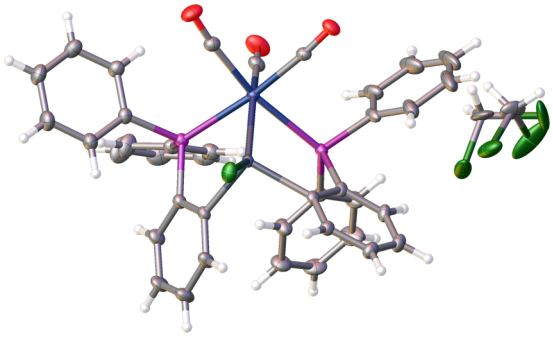


Figure S12: Molecular structure of **9** in solid state. Thermal ellipsoids are drawn with 50 % probability level.

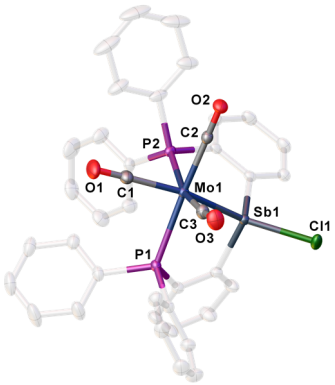


Figure S13: Molecular structure of **9** in solid state. Thermal ellipsoids are drawn with 50 % probability level. Selected bond lengths [Å]: Mo1-P1 2.5661(7), Mo1-P2 2.5444(7), Mo1-Sb1 2.6439(3), Mo1-C1 1.981(3), Mo1-C2 1.981(3), Mo1-C3 1.996(3), C1-O1 1.146(4), C2-O2 1.155(3), C3-O3 1.151(3).

10.4.2.10 $[W(CO)_4\{\eta^1{:}\eta^1{:}\eta^1{:}\eta^1\text{-}(o\text{-}PPh_2C_6H_4)_3Sb\}\{CuCl\}]$ (10)

Compound **10** crystallizes from a concentrated solution in CH_2Cl_2 layered with hexane at room temperature in the monoclinic space group $P2_1/n$ as clear dark yellow blocks. The asymmetric unit contains molecule of **10** and two CH_2Cl_2 molecules. The structure in solid state is depicted in Figure S14 and S15.

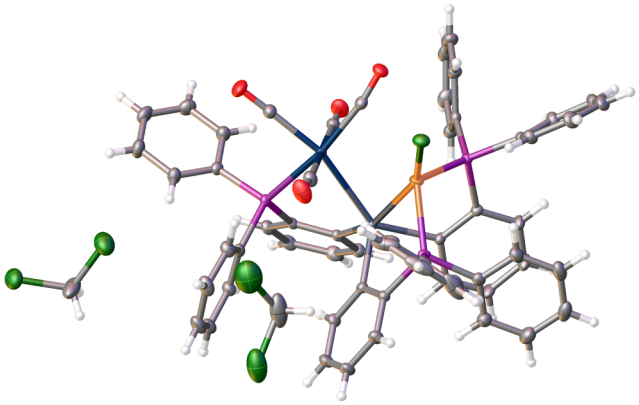


Figure S14: Molecular structure of **10** in solid state. Thermal ellipsoids are drawn with 50 % probability level.

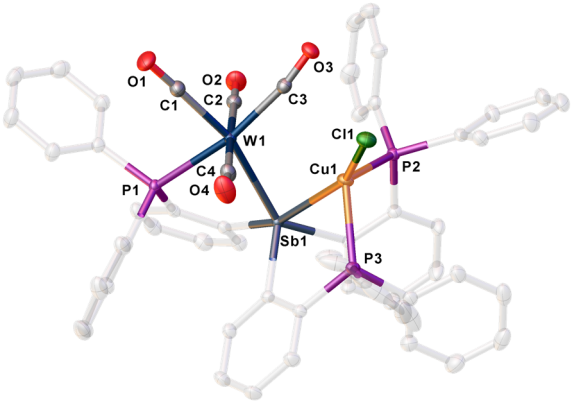


Figure S15: Molecular structure of **10** in solid state. Thermal ellipsoids are drawn with 50 % probability level. Solvent molecules and hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: C1-O1 1.1563(18), C2-O2 1.1482(19), C3-O3 1.1507(18), C4-O4 1.145(2), C1-W1 1.9752(14), C2-W1 2.0307(16), C3-W1 2.0096(15), C4-W1 2.0307(16), P1-W1 2.5156(3), P2-Cu1 2.3107(4), P3-Cu1 2.3240(4), Sb1-W1 2.76386(10), Sb1-Cu1 2.83938(19), Cu1-Cl1 2.2571(4),W1-Cu1 3.2383(5).

10.4.2.11 $[W(CO)_4\{\eta^1{:}\eta^1{:}\eta^1{:}\eta^1\text{-}(o\text{-}PPh_2C_6H_4)_3Sb\}\{AgCl\}]$ (11)

Compound **11** crystallizes from a concentrated solution in CH_2Cl_2 layered with hexane at room temperature in the monoclinic space group $P2_1/n$ as clear light yellow needles. The asymmetric unit contains two molecules of **11** and three CH_2Cl_2 molecules. A solvent mask was calculated and 168 electrons were found in a volume of 660 Å^3 in 4 voids per unit cell. This is consistent with the presence of 1[CH2Cl2] per Asymmetric Unit which account for 168 electrons per unit cell. The structure in solid state is depicted in Figure S16 and S17.

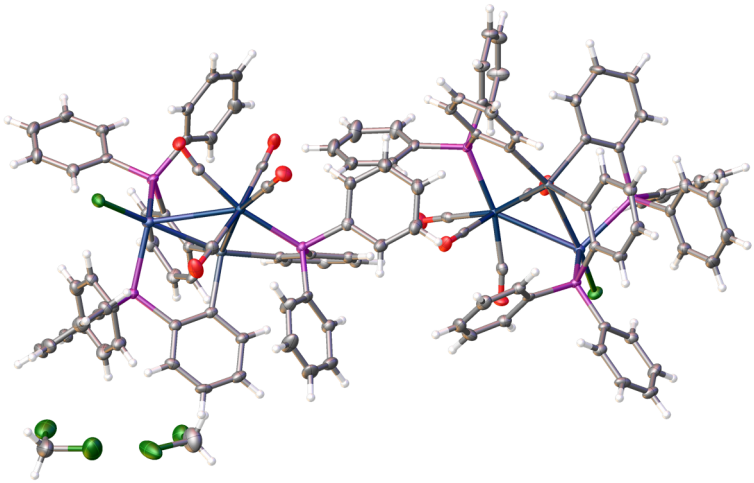


Figure S16: Molecular structure of **11** in the solid state. Thermal ellipsoids are drawn with 50 % probability level.

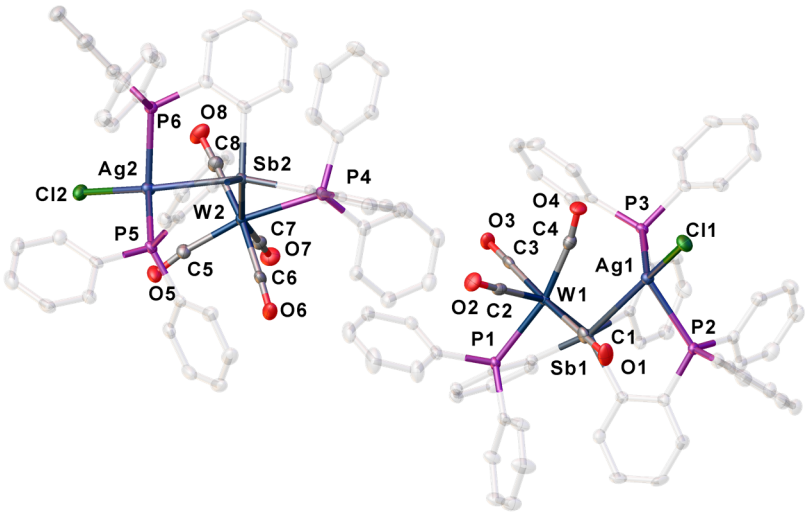


Figure S17: Molecular structure of **11** in the solid state. Thermal ellipsoids are drawn with 50 % probability level. Solvent molecules and hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: C1-O1 1.156(5), C2-O2 1.142(5), C3-O3 1.149(5), C4-O4 1.149(5), C1-W1 2.031(4), C2-W1 1.983(4), C3-W1 2.034(4), C4-W1 2.012(4), P1-W1 2.5123(9), P2-Ag1 2.5414(9), P3-Ag1 2.5419(9), Sb1-W1 2.7774(3), Sb1-Ag1 2.9997(3), Ag1-Cl1 2.5062(9),W1-Ag1 3.1893(3). C5-O5 1.145(5), C6-O6 1.138(5), C7-O7 1.158(5), C8-O8 1.153(5), C5-W2 2.016(4), C6-W2 2.37(4), C7-W2 1.980(4), C8-W2 2.022(4), P4-W2 2.5429(9), P5-Ag2 2.5469(10), P6-Ag2 2.5247(9), Sb2-W2 2.7670(3), Sb2-Ag2 2.9717(3), Ag2-Cl2 2.4927(9), W2-Ag2 3.3342(3).

10.4.2.12 $[W(CO)_4\{\eta^1{:}\eta^1{:}\eta^1\text{-}(o\text{-}PPh_2C_6H_4)_2Sb\}\{\eta^1\text{-}AuCl(o\text{-}PPh_2C_6H_4)\}\{AuCl\}]$ (12)

Compound **12** crystallizes from a concentrated solution in *o*-$C_6H_4F_2$ layered with hexane at room temperature in the triclinic space group $P\bar{1}$ as clear intense orange needles. The asymmetric unit contains molecule of **12** and one *o*-$C_6H_4F_2$ molecule. One F atom of the solvent molecule is disordered over two positions with occupancies of 67.44 and 32.56 %. The structure in solid state is depicted in Figure S18 and S19.

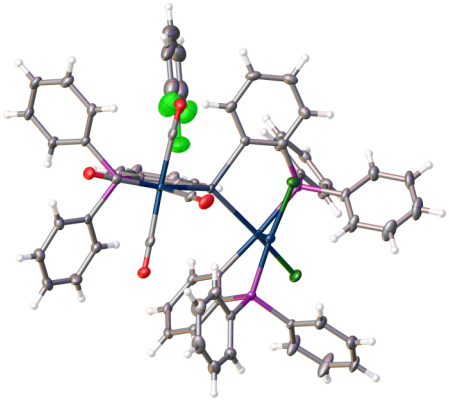


Figure S18: Molecular structure of **12** in solid state. Thermal ellipsoids are drawn with 50 % probability level.

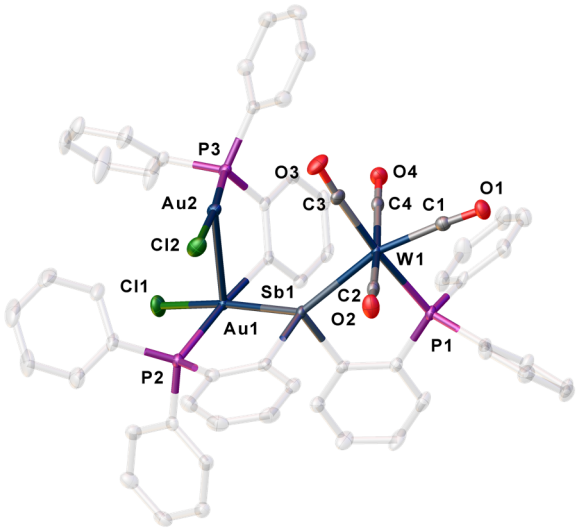


Figure S19: Molecular structure of **12** in solid state. Thermal ellipsoids are drawn with 50 % probability level. Solvent molecules and hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: C1-O1 1.155(4), C2-O2 1.139(4), C3-O3 1.154(5), C4-O4 1.149(4), C1-W1 1.978(4), C2-W1 2.034(4), C3-W1 2.003(4), C4-W1 2.042(4), P1-W1 2.5095(10), P2-Au1 2.3531(9), P3-Au2 2.2396(9), Au1-Au2 3.1302(2), Au1-Cl1 2.4003(9), Au2-Cl2 2.2859(9), Sb1-W1 2.7263(2), Sb1-Au1 2.5929(3), W1-Au1 4.9639(4), W1-Au2 4.4404(4).

10.4.2.13 $[(W(CO)_4\{\eta^1{:}\eta^1{:}\eta^1\text{-}(o\text{-}PPh_2C_6H_4)_2Sb\})_2AuCl]$ (13)

Compound **13** crystallizes from a concentrated solution in CH_2Cl_2 layered with hexane at room temperature in the monoclinic space group *I2/a* as a clear dark red needle. The asymmetric unit contains half a molecule of **13** and 0.7 hexane molecule. A solvent mask was calculated and 264 electrons were found in a volume of 1276 Å in 2 voids per unit cell. This is consistent with the presence of 1.4 hexane which account for 280 electrons per unit cell. The structure in solid state is depicted in Figure S20 and S21.

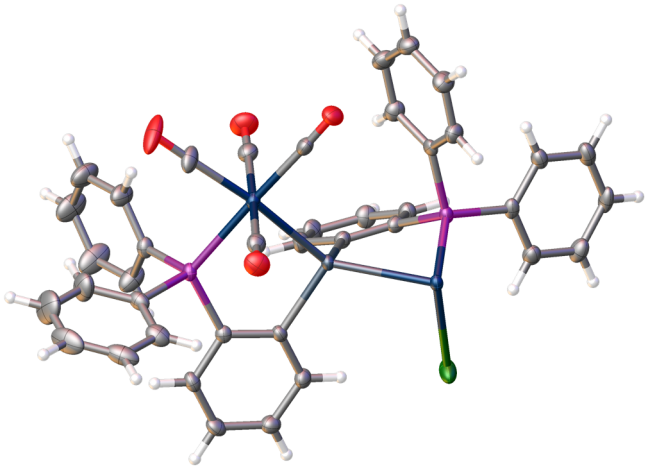


Figure S20: Molecular structure of **13** in solid state. Thermal ellipsoids are drawn with 50 % probability level.

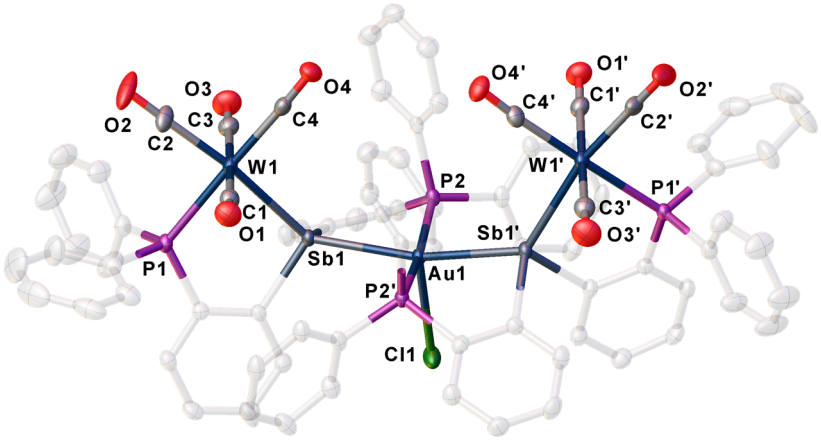


Figure S21: Molecular structure of **13** in solid state. Thermal ellipsoids are drawn with 50 % probability level. Solvent molecules and hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: C1-O1 1.140(4), C2-O2 1.145(4), C3-O3 1.142(4), C4-O4 1.142(4), C1-W1 2.049(3), C2-W1 1.974(3), C3-W1 2.035(3), C4-W1 2.003(3), P1-W1 2.4969(7), P2-Au1 2.3313(7), Au1-Cl1 2.7415(10), Sb1-W1 2.74231(19), Sb1-Au1 2.71684(16).

10.4.2.14 $[W(CO)_4\{\eta^1{:}\eta^1{:}\eta^1{:}\eta^1\text{-}(o\text{-}PPh_2C_6H_4)_3Sb\}\{Cu\}][PF_6]$ (14)

Compound **14** crystallizes from a concentrated solution in *o*-$C_6H_4F_2$ layered with hexane at room temperature in the monoclinic space group $P2_1/n$ as a clear light yellow block. The asymmetric unit contains one cation of **14**, one $[PF_6]^-$ counterion and 1.75 hexane molecule. A solvent mask was calculated and 346 electrons were found in a volume of 1148 Å in 1 void per unit cell. This is consistent with the presence of 1.75 hexane which account for 350 electrons per unit cell. Two phenyl groups of the ligand are disordered over two positions (45:55 and 62.4:37.6). The structure in solid state is depicted in Figure S22 and S23.

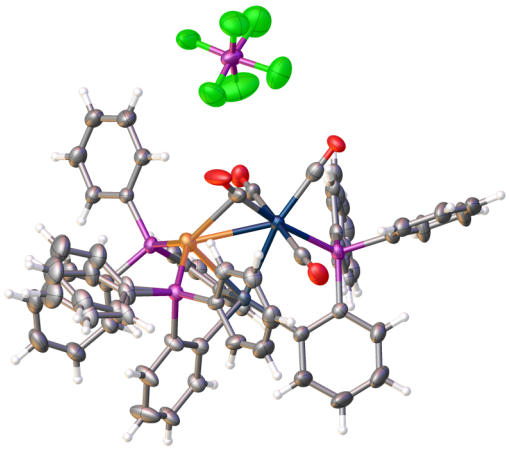


Figure S22: Molecular structure of **14** in solid state. Thermal ellipsoids are drawn with 50 % probability level.

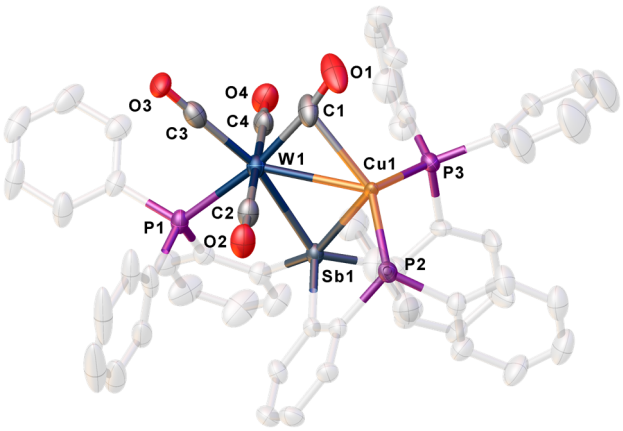


Figure S23: Molecular structure of the cation in **14** in the solid state. Thermal ellipsoids are drawn with 50 % probability level. Solvent molecules and hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: C1-O1 1.167(8), C2-O2 1.142(7), C3-O3 1.131(7), C4-O4 1.144(7), C1-W1 1.982(6), C2-W1 2.042(5), C3-W1 2.013(6), C4-W1 2.037(5), C1-Cu1 2.406(7), P1-W1 2.5186(13), P2-Cu1 2.2931(16), P3-Cu1 2.2893(16), Sb1-W1 2.7576(4), Sb1-Cu1 2.7231(11).

10.4.2.15 $[W(CO)_4\{\eta^1{:}\eta^1{:}\eta^1{:}\eta^1\text{-}(o\text{-}PPh_2C_6H_4)_3Sb\}\{AgMeCN\}][PF_6]$ (15)

Compound **15** crystallizes from a concentrated solution in CH_2Cl_2 layered with hexane at room temperature in the triclinic space group $P\bar{1}$ as a clear light yellow block. The asymmetric unit contains one cation of **15**, two half $[PF_6]^-$ counterions (located on symmetry positions) and 1.35 CH_2Cl_2 molecules. The CCH_3 fragment of the coordinating acetonitrile is disordered over two positions (55:45). One F atom of one $[PF_6]^-$ is disordered over two positions (89:11). The restraints SIMU and SADI were applied to describe one CH_2Cl_2 molecule. The restraints SIMU and SADI were applied to describe the disorder of the MeCN molecule and $[PF_6]^-$ counterion. The structure in solid state is depicted in Figure S24 and S25.

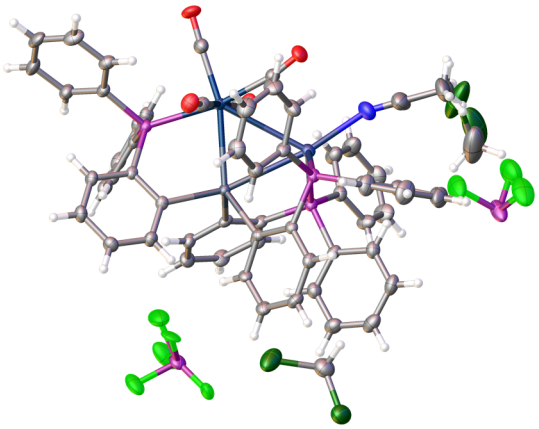


Figure S24: Molecular structure of **15** in solid state. Thermal ellipsoids are drawn with 50 % probability level.

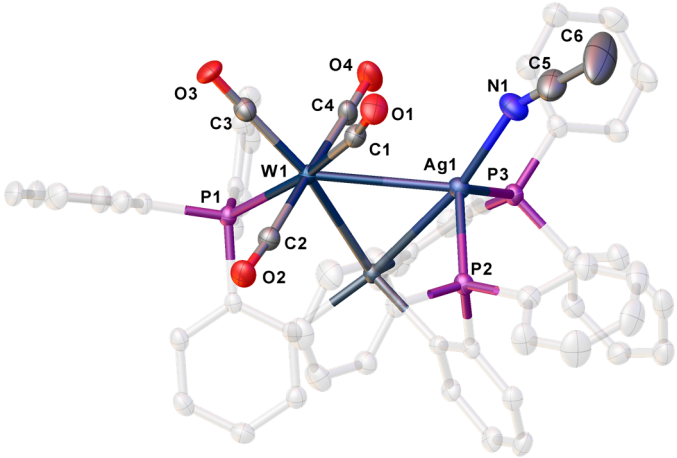


Figure S25: Molecular structure of the cation in **15** in the solid state. Depicted is only the MeCN with higher occupation. Solvent molecules and hydrogen atoms are omitted for clarity.Thermal ellipsoids are drawn with 50 % probability level. Selected bond lengths [Å] and angles [°]: C1-O1 1.159(6), C2-O2 1.148(6), C3-O3 1.148(6), C4-O4 1.141(6), C1-W1 2.000(5), C2-W1 2.033(5), C3-W1 1.983(5), C4-W1 2.032(5), P1-W1 2.5250(10), P2-Ag1 2.5381(12), P3-Ag1 2.5112(11), Ag1-C1 2.754(5), Ag1-N1 2.338(5), Sb1-W1 2.7769(3), Sb1-Ag1 2.9873(4), W1-Ag1 3.2290(4).

10.4.2.16 $[W(CO)_4\{\eta^1{:}\eta^1{:}\eta^1{:}\eta^1\text{-}(o\text{-}PPh_2C_6H_4)_3Sb\}\{Au\}][PF_6]$ (16)

Compound **16** crystallizes from a concentrated solution in CH_2Cl_2 layered with hexane at room temperature in the triclinic space group $P\bar{1}$ as a clear dark yellow block. The asymmetric unit contains two cations of **16**, two $[PF_6]^-$ counterions and two CH_2Cl_2 molecules. One cation of **16** is partially disordered over two positions, one $[PF_6]^-$ is disordered over two positions (78:22) and both CH_2Cl_2 molecules are disordered over two positions (55:45 and 56:44). The restraints SIMU and SADI were applied to describe the disorder. The structure in solid state is depicted in Figure S26 and S27.

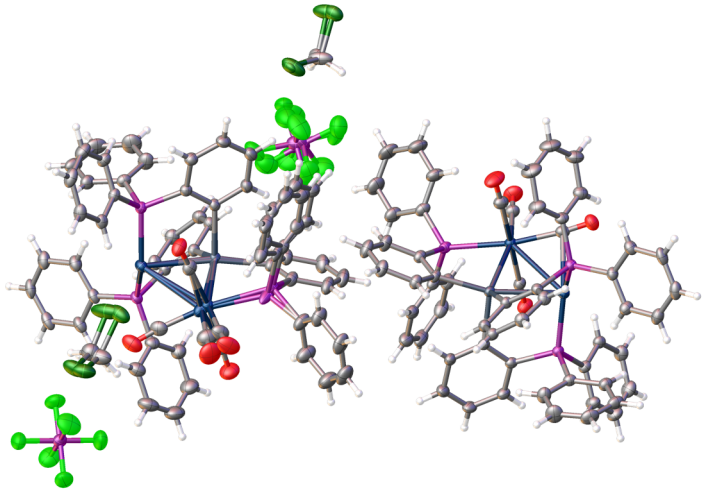


Figure S26: Molecular structure of **16** in solid state. Thermal ellipsoids are drawn with 50 % probability level.

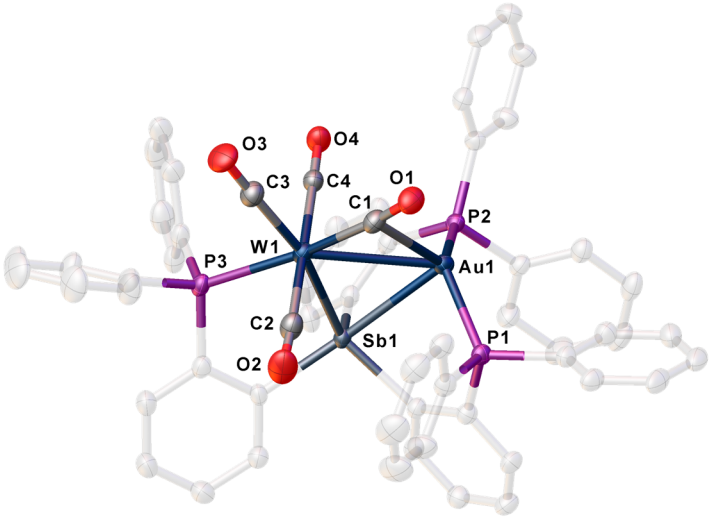


Figure S27: Molecular structure of the non-disordered cation in **16** in the solid state. Thermal ellipsoids are drawn with 50 % probability level. Solvent molecules and hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: C1-O1 1.157(4), C2-O2 1.142(4), C3-O3 1.151(4), C4-O4 1.140(4), C1-W1 2.007(3), C2-W1 2.043(3), C3-W1 1.979(3), C4-W1 2.030(3), C1-Au1 2.710(3), P3-W1 2.5128(7), P1-Au1 2.3530(6), P2-Au1 2.3151(6), Sb1-W1 2.7776(2), Sb1-Au1 2.82781(19), W1-Au1 3.14079(16).

10.4.2.17 $[W(CO)_2(\mu\text{-}CO)\{\eta^1{:}\eta^1{:}\eta^1{:}\eta^1{:}\eta^1\text{-}(o\text{-}PPh_2C_6H_4)_3Sb\}\{Cu_2(\mu\text{-}Cl)_2\}]$ (17)

Compound **17** crystallizes from a concentrated solution in CH_2Cl_2 layered with hexane at room temperature in the monoclinic space group *P2₁/n* as a clear light red block. The asymmetric unit contains molecule **17** and 2.75 CH_2Cl_2 molecules. One CH_2Cl_2 molecules are disordered over two positions (80:20). The restraints SIMU and SADI were applied to describe the CH_2Cl_2 molecules partially. The structure in solid state is depicted in Figure S28 and S29.

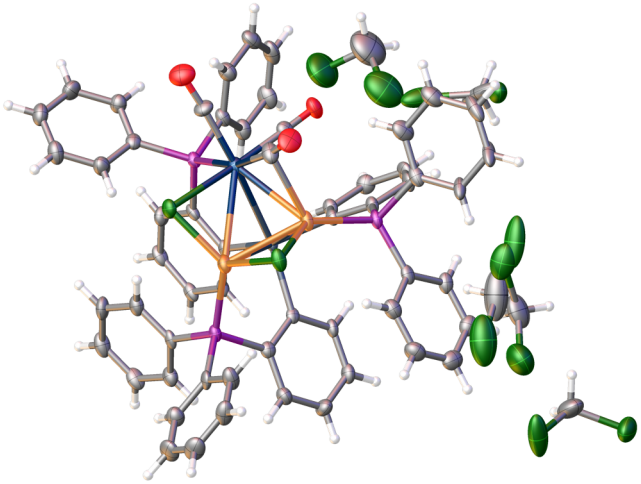


Figure S28: Molecular structure of **17** in solid state. Thermal ellipsoids are drawn with 50 % probability level.

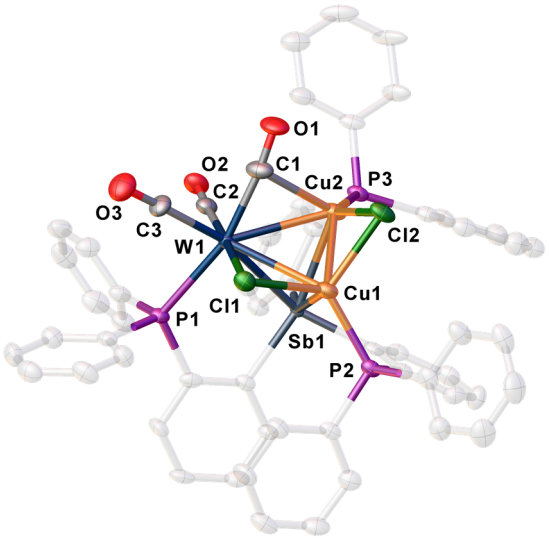


Figure S29: Molecular structure of **17** in solid state. Thermal ellipsoids are drawn with 50 % probability level. Solvent molecules and hydrogen atoms are omitted for clarity.Selected bond lengths [Å] and angles [°]: C1-O1 1.158(9), C2-O2 1.149(9), C3-O3 1.181(9), C1-W1 1.975(8), C2-W1 1.955(8), C3-W1 1.947(7), C1-Cu2 2.291(8), P1-W1 2.5270(16), P2-Cu1 2.206(2), P3-Cu2 2.2289(19), Sb1-W1 2.8312(5), Sb1-Cu1 2.9298(11), Sb1-Cu2 2.7576(10), W1-Cl1 2.5843(16), Cu1-Cl1 2.2610(19), Cu1-Cl2 2.3432(18), Cu2-Cl2 2.2628(19), W1-Cu1 3.0849(11), W1-Cu2 2.8359(11), Cu1-Cu2 2.6826(14).

10.4.2.18 $[W(CO)_3\{\eta^1{:}\eta^1{:}\eta^1\text{-}(o\text{-}PPh_2C_6H_4)_3Sb\}\{AuCl\}]$ (18)

Compound **18** crystallizes from a concentrated solution in CH_2Cl_2 layered with hexane at room temperature in the monoclinic space group $P2_1$ as a clear light yellow plate. The asymmetric unit contains one molecule **18**. The structure in solid state is depicted in Figure S30 and S31.

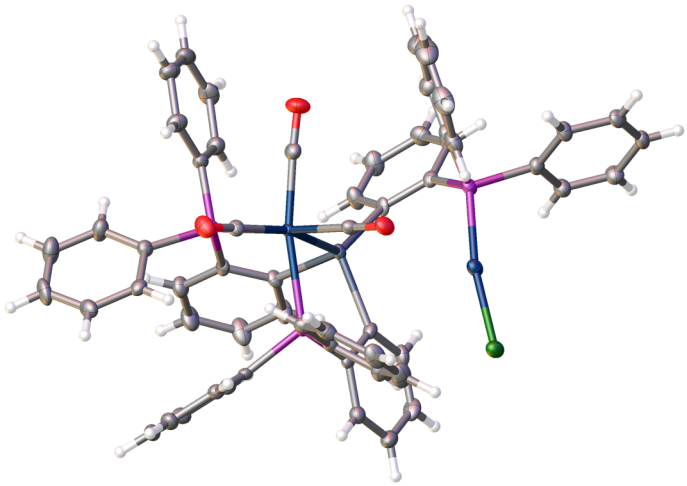


Figure S30: Molecular structure of **18** in solid state. Thermal ellipsoids are drawn with 50 % probability level.

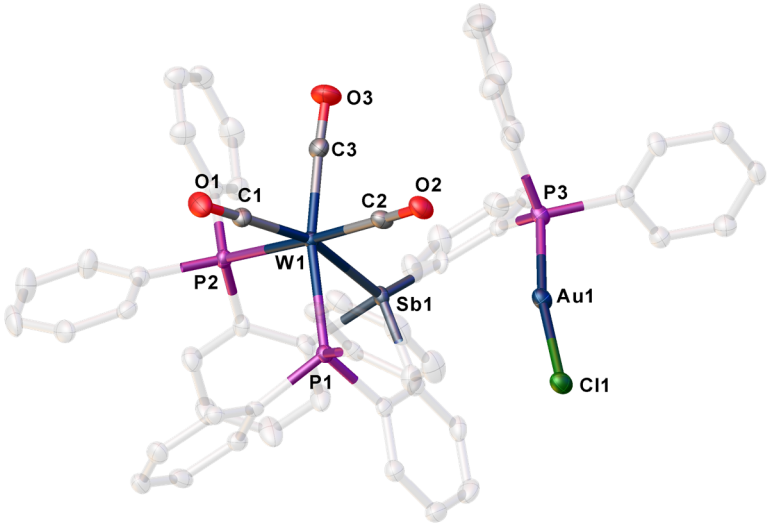


Figure S31: Molecular structure of **18** in solid state. Thermal ellipsoids are drawn with 50 % probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: C1-O1 1.154(7), C2-O2 1.149(7), C3-O3 1.152(8), C1-W1 1.977(5), C2-W1 1.991(5), C3-W1 1.990(6), P1-W1 2.5169(14), P2-W1 2.5102(12), P3-Au1 2.2280(15), Sb1-W1 2.6790(4), Sb1-Au1 3.6195(3), Au1-Cl1 2.2940(14), W1-Au1 4.9181(3).

10.4.2.19 $[W(CO)_2(\mu\text{-}CO)\{\eta^1{:}\eta^1{:}\eta^1{:}\eta^1\text{-}(o\text{-}PPh_2C_6H_4)_3Sb\}\{CuMeCN\}]\ [PF_6]$ (19)

Compound **19** crystallizes from a concentrated solution in CH_2Cl_2 layered with hexane at room temperature in the triclinic space group $P\bar{1}$ as a clear light yellow block. The asymmetric unit contains one cation of **19** and two half counterions $[PF_6]^-$ (located on symmetry positions). The structure in solid state is depicted in Figure S32 and S33.

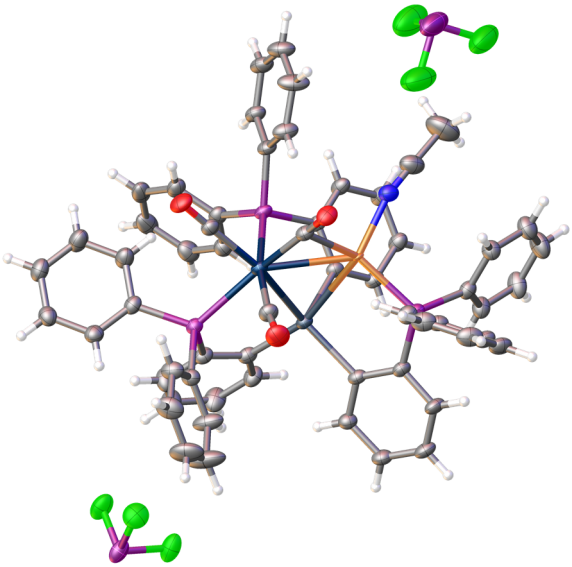


Figure S32: Molecular structure of **19** in solid state. Thermal ellipsoids are drawn with 50 % probability level.

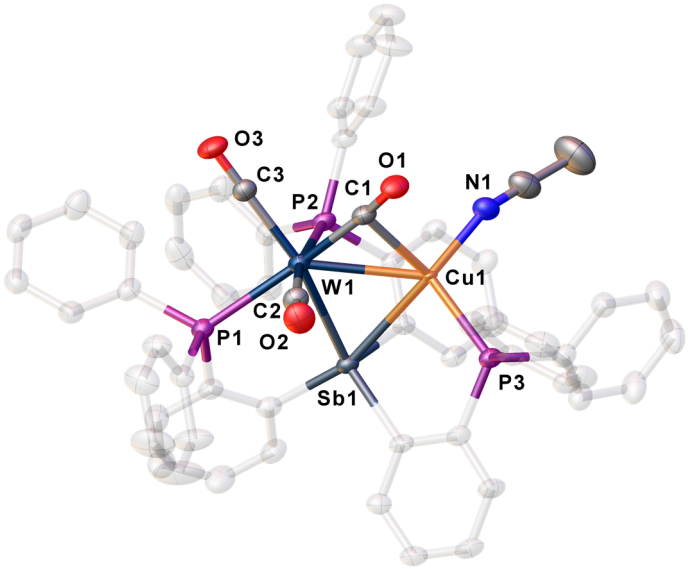


Figure S33: Molecular structure of the cation in **19** in the solid state. Thermal ellipsoids are drawn with 50 % probability level. Solvent molecules and hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: C1-O1 1.175(5), C2-O2 1.152(5), C3-O3 1.156(5), C1-W1 1.970(4), C2-W1 1.996(4), C3-W1 1.985(4), C1-Cu1 2.202(4), P1-W1 2.5336(9), P2-W1 2.5701(8), P3-Cu1 2.2424(11), Cu1-N1 1.997(4), Sb1-W1 2.6892(3), Sb1-Cu1 2.7994(7), W1-Cu1 2.7922(7).

10.4.2.20 $[W(CO)_2(\mu\text{-}CO)\{\eta^1{:}\eta^1{:}\eta^1{:}\eta^1\text{-}(o\text{-}PPh_2C_6H_4)_3Sb\}\{AgMeCN\}]\ [PF_6]$ (20)

Compound **20** crystallizes from a concentrated solution in CH_2Cl_2 layered with hexane at room temperature in the monoclinic space group *P2₁/n* as a clear light yellow needle. The asymmetric unit contains one cation of **20**, one counterion $[PF_6]^-$, 0.69 molecules CH_2Cl_2 and 0.48 molecules MeCN. The $[PF_6]^-$ counterion is disordered over three positions (50:30:20). The coordinated MeCN is disordered over two positions (64:36). The restraints SIMU, SADI, RIGU were applied to describe the disorder. The structure in solid state is depicted in Figure S34 and S35.

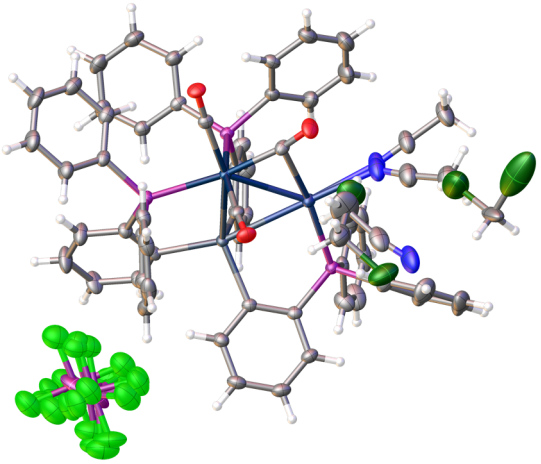


Figure S34: Molecular structure of **20** in solid state. Thermal ellipsoids are drawn with 50 % probability level.

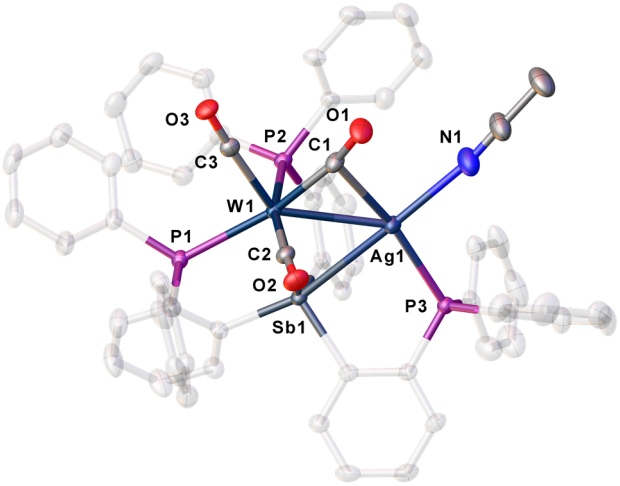


Figure S35: Molecular structure of the cation in **20** in the solid state. Thermal ellipsoids are drawn with 50 % probability level. Solvent molecules and hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: C1-O1 1.156(5), C2-O2 1.156(4), C3-O3 1.145(4), C1-W1 2.003(4), C2-W1 1.990(4), C3-W1 1.989(3), C1-Ag1 2.446(3), P1-W1 2.5300(8), P2-W1 2.5202(8), P3-Ag1 2.4508(8), Ag1-N1 2.342(4), Sb1-W1 2.6986(2), Sb1-Ag1 2.9968(3), W1-Ag1 2.8891(3).

10.4.2.21 $[W(CO)_2(\mu\text{-}CO)\{\eta^1{:}\eta^1{:}\eta^1{:}\eta^1\text{-}(o\text{-}PPh_2C_6H_4)_3Sb\}\{Au\}][PF_6]$ (21)

Compound **21** crystallizes from a concentrated solution in CH_2Cl_2 layered with hexane at room temperature in the monoclinic space group $P2_1/n$ as a clear light yellow block. The asymmetric unit contains one cation of **21**, one counterion $[PF_6]^-$ and 1.7 molecules. The $[PF_6]^-$ counterion is disordered over two positions (59:41). The restrains SIMU and RIGU were applied to describe the disorder. The structure in solid state is depicted in Figure S36 and S37.

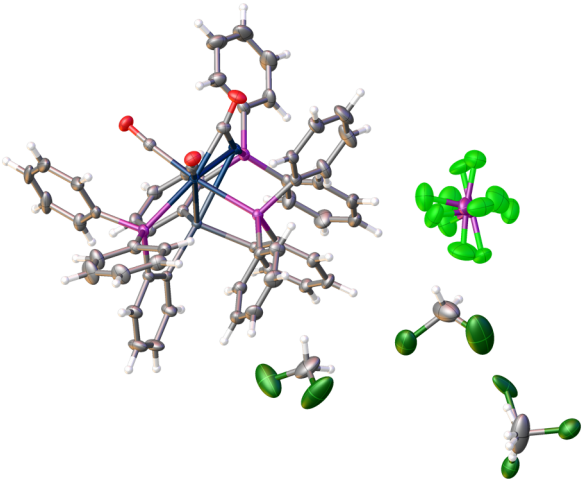


Figure S36: Molecular structure of **21** in solid state. Thermal ellipsoids are drawn with 50 % probability level.

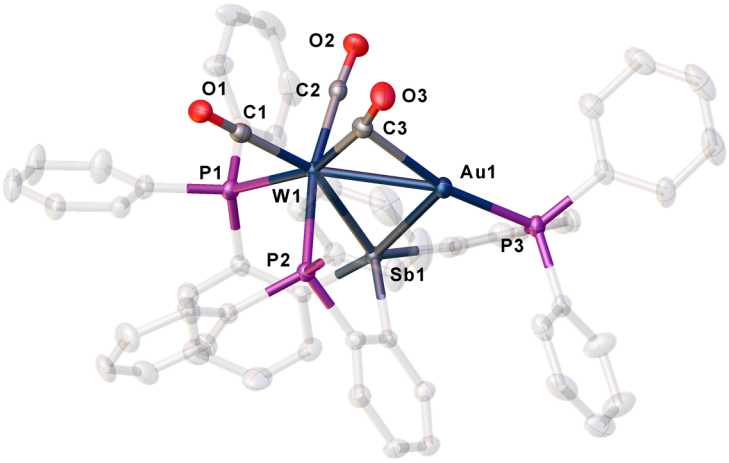


Figure S37: Molecular structure of the cation in **21** in the solid state. Thermal ellipsoids are drawn with 50 % probability level. Solvent molecules and hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: C1-O1 1.157(5), C2-O2 1.148(5), C3-O3 1.170(5), C1-W1 1.989(4), C2-W1 2.003(4), C3-W1 1.998(4), C3-Au1 2.338(4), P1-W1 2.5437(10), P2-W1 2.5214(10), P3-Au1 2.2851(10), Sb1-W1 2.7116(3), Sb1-Au1 2.8697(3), W1-Au1 2.7551(2).

10.4.2.22 Crystallographic Data

Table S1: Crystallographic data for **1**-**9**.

	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**
Formula	$C_{116}H_{84}O_8P_6Sb_2W_2$	$C_{46}H_{33}O_4P_2SbW$	$C_{43}H_{35}ClO_4P_2SbW$	$C_{57}H_{42}O_3P_3SbW$	$C_{39.8}H_{29.6}Cl_{2.6}O_3P_2SbW$	$C_{41.25}H_{32}Cl_{2.5}N_{0.5}O_3P_2SbW$	$C_{57}H_{42}MoO_3P_3Sb$	$C_{45}H_{33}MoO_3P_2Sb$	$C_{39.8}H_{29.6}Cl_{2.6}MoO_3P_2Sb$
$D_{calc.}$/ g cm^{-3}	1.623	1.716	1.782	1.631	1.797	1.755	1.506	1.613	1.647
μ/mm^{-1}	9.914	3.730	12.950	10.172	14.094	3.901	7.920	9.682	1.366
Formula Weight	2402.85	1017.26	1018.70	1173.41	1015.54	1038.84	1085.50	901.34	927.63
Colour	clear light yellow	clear light yellow	clear light yellow	clear dark yellow	clear dark yellow	clear light orange	clear light yellow	clear dark yellow	clear light orange
Shape	block	plate	trapezoid	block	block	block	block	block	block
Size/mm^3	0.25×0.23×0.19	0.27×0.22×0.12	0.25×0.15×0.09	0.19×0.12×0.07	0.32×0.20×0.05	0.33×0.22×0.14	0.43×0.28×0.22	0.38×0.28×0.20	0.53×0.33×0.24
T/K	122.98(10)	123.00(10)	123	122.96(15)	122.99(17)	123	123.01(10)	123.00(10)	123
Crystal System	monoclinic	monoclinic	triclinic	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
Space Group	$P2_1/c$	$P2_1/n$	P-1	$P2_1/n$	$P2_1/n$	$P2_1/c$	$P2_1/n$	$P2_1/n$	$P2_1/n$
a/Å	18.3796(2)	18.8878(3)	10.3754(3)	12.8041(3)	10.6955(2)	14.4324(3)	12.8125(2)	14.7738(2)	10.6890(2)
b/Å	13.7807(2)	16.48880(10)	11.2282(4)	19.1831(4)	25.2806(3)	18.4715(4)	19.1860(2)	14.9907(2)	25.2311(5)
c/Å	39.0326(4)	26.4002(3)	17.2897(5)	19.5342(3)	13.8876(2)	15.6431(4)	19.5578(2)	16.8603(2)	13.8729(2)
α/°	90	90	83.577(2)	90	90	90	90	90	90
β/°	95.7430(10)	106.6930(10)	81.021(3)	95.213(2)	90.906(2)	109.512(3)	95.1950(10)	96.3120(10)	90.615(2)
γ/°	90	90	73.019(3)	90	90	90	90	90	90
V/Å^3	9836.7(2)	7875.50(17)	1898.09(11)	4778.19(17)	3754.58(10)	3930.77(17)	4787.96(10)	3711.41(8)	3741.24(12)
Z	4	8	2	4	4	4	4	4	4
Z'	1	2	1	1	1	1	1	1	1
Wavelength/Å	1.54184	0.71073	1.54184	1.54184	1.54184	0.71073	1.54184	1.54184	0.71073
Radiation type	CuK$_\alpha$	MoK$_\alpha$	CuK$_\alpha$	CuK$_\alpha$	CuK$_\alpha$	MoK$_\alpha$	CuK$_\alpha$	CuK$_\alpha$	MoK$_\alpha$
θ_{min}/°	2.416	3.319	4.127	3.236	3.497	3.328	3.966	3.778	3.352
θ_{max}/°	74.243	32.100	66.314	74.130	74.930	30.034	67.079	67.065	30.033
Measured Refl.	54761	58372	23610	26389	40593	34305	25339	38147	55003
Independent Refl.	19320	24951	6652	9301	7542	11473	8502	6625	10930
Reflections with I > 2(I)	17424	20253	6310	8216	7407	9667	8269	6602	9957
R_{int}	0.0634	0.0353	0.0384	0.0823	0.0601	0.0292	0.0441	0.0492	0.0245
Parameters	1207	973	442	586	424	501	586	469	478
Restraints	0	0	0	0	0	26	0	0	69
Largest Peak	3.133	1.735	1.944	2.230	1.281	1.298	2.790	1.752	1.051
Deepest Hole	-1.953	-1.372	-0.695	-3.806	-1.196	-1.225	-1.586	-1.158	-0.775
GooF	1.054	1.040	1.049	1.028	1.050	1.072	1.087	1.075	1.078
wR_2 (all data)	0.1419	0.0721	0.0547	0.1311	0.0845	0.0731	0.1196	0.1046	0.0573
wR_2	0.1372	0.0654	0.0538	0.1254	0.0841	0.0692	0.1187	0.1046	0.0558
R_1 (all data)	0.0569	0.0479	0.0250	0.0565	0.0314	0.0410	0.0447	0.0394	0.0278
R_1	0.0527	0.0327	0.0232	0.0507	0.0310	0.0301	0.0439	0.0394	0.0237

Table S2: Crystallographic data for **10**-**21**.

	10	**11**	**12**	**13**	**14**	**15**	**16**	**17**	**18**	**19**	**20**	**21**
Formula	$C_{60}H_{46}Cl_5CuO_4P_3SbW$	$Ag_2C_{119}Cl_8H_{90}O_8P_6Sb_2W_2$	$C_{64}H_{46}Au_2Cl_2F_2O_4P_3SbW$	$AuC_{88.4}ClH_{75.6}O_8P_4Sb_2W_2$	$C_{68.5}CuF_6H_{66.5}O_4P_4SbW$	$C_{61.35}H_{47.7}AgCl_{2.7}F_6NO_4P_4SbW$	$Au_2C_{132}Cl_8F_{12}H_{120}O_8P_8Sb_2W_2$	$C_{59.77}H_{47.54}ClCu_2O_3P_3SbW$	$C_{57}H_{42}AuClO_3P_3SbW$	$C_{59}H_{45}CuF_6NO_3P_4SbW$	$C_{60.65}H_{47.82}AgCl_{1.38}F_6N_{1.48}O_3P_4SbW$	$C_{58.7}H_{45.4}AuCl_{3.4}F_6O_3P_4SbW$
$D_{calc.}$/ g cm^{-3}	1.740	1.774	2.043	1.860	1.717	1.773	1.936	1.796	1.878	1.757	1.746	1.872
μ/mm^{-1}	3.269	13.437	7.727	15.379	6.711	12.221	10.762	12.099	15.661	7.476	11.957	5.215
Formula Weight	1470.27	2944.26	1780.35	2233.38	1560.73	1609.97	3598.77	1606.748	1405.83	1422.98	1545.61	1659.72
Colour	clear dark yellow	clear light yellow	clear orange	clear dark red	clear light yellow	clear light yellow	clear dark yellow	clear light red	clear light yellow	clear light yellow	clear light yellow	clear light yellow
Shape	block	needle	needle	needle	block	block	block	block	plate	block	needle	block
Size/mm^3	0.65×0.40×0.29	0.50×0.12×0.05	0.38×0.07×0.05	0.38×0.09×0.07	0.42×0.16×0.10	0.59×0.27×0.11	0.45×0.29×0.24	0.27×0.17×0.12	0.26×0.11×0.04	0.16×0.09×0.07	0.41×0.08×0.05	0.68×0.33×0.29
T/K	123	123	123	123	123.00(10)	123(1)	123.00(10)	123(1)	123(1)	123.01(11)	123	123
Crystal System	monoclinic	monoclinic	triclinic	monoclinic	monoclinic	triclinic	triclinic	monoclinic	monoclinic	triclinic	monoclinic	monoclinic
Space Group	$P2_1/n$	$P2_1/n$	P-1	$I2/a$	$P2_1/n$	P-1	P-1	$P2_1/n$	$P2_1$	P-1	$P2_1/n$	$P2_1/n$
a/Å	13.35920(10)	10.59820(10)	13.6227(2)	28.1784(3)	13.3553(2)	10.5734(4)	11.00250(10)	15.3444(3)	10.41326(5)	9.2830(3)	14.7149(3)	14.7854(3)
b/Å	22.84920(10)	23.01660(10)	14.1314(2)	13.84420(10)	23.2911(3)	13.0750(4)	23.9970(3)	18.8371(4)	21.09731(12)	13.3463(5)	19.7407(4)	19.7226(3)
c/Å	18.60380(10)	45.4915(3)	15.5884(3)	22.3139(2)	19.5328(2)	22.9061(9)	25.0343(3)	20.9101(4)	11.32988(5)	22.0387(9)	20.7094(4)	20.6640(5)
α/°	90	90	98.8900(10)	90	90	77.347(3)	105.5160(10)	90	90	88.054(3)	90	90
β/°	98.7670(10)	96.4710(10)	95.1060(10)	113.6000(10)	96.5640(10)	88.149(3)	97.3420(10)	100.521(2)	93.0015(4)	81.984(3)	102.179(2)	102.232(2)
γ/°	90	90	100.5170(10)	90	90	77.493(3)	99.6290(10)	90	90	84.411(3)	90	90
V/Å^3	5612.41(6)	11026.25(14)	2893.73(8)	7976.77(14)	6036.04(13)	3016.10(19)	6174.68(13)	5942.3(2)	2485.67(2)	2690.35(17)	5880.3(2)	5889.0(2)
Z	4	4	2	4	4	2	2	4	2	2	4	4
Z'	1	1	1	0.5	1	1	1	1	1	1	1	1
Wavelength/Å	0.71073	1.54184	0.71073	1.54184	1.39222	1.54184	1.39222	1.54184	1.54184	1.39222	1.54184	0.71073
Radiation type	Mo K_α	Cu K_α	Mo K_α	Cu K_α	Cu K_β	Cu K_α	Cu K_β	Cu K_α	Cu K_α	Cu K_β	Cu K_α	Mo K_α
θ_{min}/°	3.359	3.841	3.191	3.423	2.676	3.547	2.775	3.75	3.907	3.005	3.802	3.353
θ_{max}/°	37.725	66.796	28.282	67.079	74.495	72.967	74.047	72.77	74.602	74.796	72.877	32.246
Measured Refl.	166559	114070	26189	32543	49535	21886	132102	32964	65955	30452	23452	35548
Independent Refl.	28895	19436	14330	7130	16358	11634	33606	11556	9760	14594	11378	18696
Reflections with I > 2(I)	25790	17750	12534	6999	15894	10723	32877	10726	9647	12918	10474	15484
R_{int}	0.0297	0.0477	0.0219	0.0314	0.0282	0.0392	0.0400	0.0458	0.0593	0.0367	0.0289	0.0236
Parameters	676	1297	721	443	786	800	1621	757	604	689	913	793
Restraints	0	0	3	0	384	75	313	42	1	0	550	144
Largest Peak	2.529	1.177	1.399	0.647	1.396	2.925	1.115	4.0909	1.268	1.991	1.474	2.821
Deepest Hole	-1.117	-0.924	-0.981	-0.907	-2.112	-1.883	-1.140	-3.2619	-0.641	-1.613	-0.673	-1.127
GooF	1.077	1.016	1.025	1.083	1.196	1.069	1.150	1.0518	1.028	1.031	1.058	1.087
wR_2 (all data)	0.0537	0.0699	0.0561	0.0466	0.1219	0.1066	0.0675	0.1279	0.0524	0.1185	0.0722	0.0821
wR_2	0.0519	0.0677	0.0534	0.0463	0.1215	0.1038	0.0671	0.1254	0.0522	0.1129	0.0702	0.0766
R_1 (all data)	0.0297	0.0314	0.0354	0.0196	0.0549	0.0434	0.0292	0.0603	0.0221	0.0476	0.0311	0.0511
R_1	0.0237	0.0278	0.0276	0.0191	0.0540	0.0400	0.0284	0.0561	0.0217	0.0420	0.0276	0.0365
Flack Parameter									-0.015(3)			
Hooft Parameter									-0.030(3)			

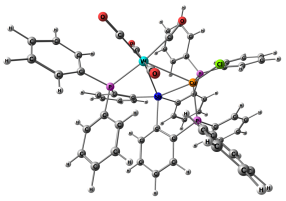
10.4.3 Computational Details

Gaussian 09 program[24] was used throughout. Density functional theory (DFT) in form of or BP86[25] (Becke's exchange and Perdew 86 correlation functional) with def2-TZVP all electron basis set was employed. For solvents effects has been accounted by using continuous polarizable continuum model (CPM).[26] The dielectric constant of dichloromethane (ε = 8.93) has been used in the calculations of the cations (**14**, **15**, **16**, **19**, **20**, **21**). The Natural Bond Orbital (NBO) analysis has been performed with the NBO6 program.[27] The long range dispersion correction GD3BJ was applied.[28] The figures for the supporting information concerning the DFT calculations were created with Chemcraft.[29]

Table S3: Total energies for all optimized geometries (BP86/def2-TZVP level of theory).

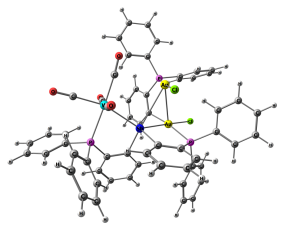
	total energy [Ha]
10 $[W(CO)_4\{\eta^1{:}\eta^1{:}\eta^1{:}\eta^1\text{-}(o\text{-}PPh_2C_6H_4)_3Sb\}\{CuCl\}]$	-5970.84136015
11 $[W(CO)_4\{\eta^1{:}\eta^1{:}\eta^1{:}\eta^1\text{-}(o\text{-}PPh_2C_6H_4)_3Sb\}\{AgCl\}]$	-4477.13521401
12 $[W(CO)_4\{\eta^1{:}\eta^1{:}\eta^1{:}\eta^1\text{-}(o\text{-}PPh_2C_6H_4)_2Sb\}$ $\{\eta^1\text{-}AuCl(o\text{-}PPh_2C_6H_4)\}\{AuCl\}]$	-5062.20187374
13 $[(W(CO)_4\{\eta^1{:}\eta^1{:}\eta^1{:}\eta^1\text{-}(o\text{-}PPh_2C_6H_4)_2Sb\})_2AuCl]$	
14 $[W(CO)_3(\mu\text{-}CO)\{\eta^1{:}\eta^1{:}\eta^1{:}\eta^1{:}\eta^1\text{-}(o\text{-}PPh_2C_6H_4)_3Sb\}\{Cu\}]^+$	-5510.36824102
15 $[W(CO)_4\{\eta^1{:}\eta^1{:}\eta^1{:}\eta^1{:}\eta^1\text{-}(o\text{-}PPh_2C_6H_4)_3Sb\}\{AgMeCN\}]^+$	-4149.50506370
16 $[W(CO)_4\{\eta^1{:}\eta^1{:}\eta^1{:}\eta^1{:}\eta^1\text{-}(o\text{-}PPh_2C_6H_4)_3Sb\}\{Au\}]^+$	-4005.45820135
17 $[W(CO)_2(\mu\text{-}CO)\{\eta^1{:}\eta^1{:}\eta^1{:}\eta^1{:}\eta^1{:}\eta^1\text{-}(o\text{-}PPh_2C_6H_4)_3Sb\}\{Cu_2(\mu\text{-}Cl)_2\}]$	-7958.63084809
18 $[W(CO)_3\{\eta^1{:}\eta^1{:}\eta^1{:}\eta^1\text{-}(o\text{-}PPh_2C_6H_4)_3Sb\}\{AuCl\}]$	-4352.52475218
19 $[W(CO)_2(\mu\text{-}CO)\{\eta^1{:}\eta^1{:}\eta^1{:}\eta^1{:}\eta^1\text{-}(o\text{-}PPh_2C_6H_4)_3Sb\}\{CuMeCN\}]^+$	-5529.81041966
20 $[W(CO)_2(\mu\text{-}CO)\{\eta^1{:}\eta^1{:}\eta^1{:}\eta^1{:}\eta^1\text{-}(o\text{-}PPh_2C_6H_4)_3Sb\}\{AgMeCN\}]^+$	-4036.10784837
21 $[W(CO)_2(\mu\text{-}CO)\{\eta^1{:}\eta^1{:}\eta^1{:}\eta^1{:}\eta^1\text{-}(o\text{-}PPh_2C_6H_4)_3Sb\}\{Au\}]^+$	-3892.06475106

Table S4: Optimized geometry of **10** (left) and **11** (right). XYZ coordinates in angstroms. BP86/def2-TZVP level of theory.



W	-1.577172000	-0.919276000	-1.297513000	C	-2.786531000	-1.405305000	4.524945000	W	1.668956000	-0.801622000	-1.345775000	C	-6.158634000	-2.168066000	-1.620282000
Sb	-0.240223000	-0.082577000	1.060602000	H	-2.643115000	-1.817150000	5.525616000	Sb	0.310687000	-0.093520000	1.047418000	H	-6.711725000	-1.633574000	-2.394386000
Cu	1.459806000	0.002975000	-1.132811000	C	4.825029000	-3.290927000	0.149532000	Ag	-1.590621000	-0.018761000	-1.260459000	C	-5.742860000	1.524758000	2.339985000
P	-3.328732000	0.163154000	0.181456000	H	4.330538000	-3.832923000	0.957742000	Cl	-2.445892000	0.151440000	-3.585247000	H	-6.645137000	1.344985000	2.926921000
Cl	2.160033000	0.197881000	-3.289220000	C	-0.989195000	3.903313000	2.856467000	P	3.427150000	0.189045000	0.201124000	C	1.104125000	3.875462000	2.831237000
P	2.497535000	-1.695644000	0.017258000	H	-1.667181000	4.318299000	3.603904000	P	-2.469214000	-1.864447000	0.097490000	H	1.800198000	4.262588000	3.576641000
P	1.892339000	2.076536000	-0.271029000	C	3.789416000	-0.807472000	3.859883000	P	-1.938062000	2.162947000	-0.210115000	C	-0.076740000	-4.949280000	1.472166000
O	0.269499000	-2.664409000	-3.198104000	H	4.695626000	-0.907978000	4.459119000	O	4.002775000	-1.305877000	-3.393508000	H	0.436511000	-5.229540000	2.393553000
O	-2.349756000	-3.635151000	0.211625000	C	2.182221000	3.420198000	-1.469457000	O	-0.099444000	-2.559929000	-3.310668000	C	-3.452141000	2.308574000	2.200818000
O	-3.907290000	-1.676541000	-3.269474000	C	-7.526643000	-1.194282000	-1.210708000	O	2.446758000	-3.589933000	0.027168000	H	-2.572718000	2.740725000	2.678923000
O	-1.233584000	1.468550000	-3.400748000	H	-8.500414000	-1.530128000	-1.570971000	O	1.076411000	1.745705000	-3.202377000	C	2.801793000	2.888893000	-0.280102000
C	-0.327660000	-1.984698000	-2.463633000	C	6.107113000	-3.662406000	-0.256073000	C	-1.395352000	-0.570669000	2.302991000	H	2.103139000	2.504756000	-1.019816000
C	-1.849271000	-0.612570000	2.433343000	H	6.619199000	-4.483550000	0.248730000	C	3.223957000	-0.467646000	1.913748000	C	0.019670000	-5.760086000	0.339382000
C	-2.012098000	-2.639811000	-0.286246000	C	-4.386130000	3.955039000	1.389845000	C	0.234126000	2.006035000	1.553016000	H	0.611295000	-6.676413000	0.370601000
C	-3.033703000	-1.399330000	-2.544671000	H	-5.099669000	4.403344000	2.083352000	C	-4.142260000	-2.452784000	-0.303453000	C	0.233806000	4.741093000	2.162666000
C	-1.293864000	0.658631000	-2.565586000	C	-6.681667000	-2.085476000	-0.538887000	C	1.917034000	-0.649043000	2.410455000	H	0.243951000	5.809575000	2.383983000
C	-0.194179000	2.010711000	1.575198000	H	-6.992820000	-3.118415000	-0.374092000	C	3.575223000	1.995984000	0.470109000	C	5.497323000	-1.658510000	-0.177935000
C	-3.149250000	-0.407993000	1.929153000	C	6.062082000	-1.954833000	-1.975394000	C	-2.525436000	-1.255335000	1.819177000	H	4.820315000	-2.385966000	0.271044000
C	1.626404000	-3.297054000	0.211009000	H	6.534593000	-1.445591000	-2.817180000	C	2.127112000	-2.570502000	-0.430851000	C	-2.388610000	3.520161000	-1.336839000
C	1.489790000	-0.516283000	2.299654000	C	0.268304000	-4.878232000	1.457668000	C	-4.717579000	-3.566648000	0.332400000	C	4.125597000	-1.355443000	3.986779000
C	-3.428298000	1.985488000	0.348133000	H	-0.262502000	-5.143384000	2.373488000	H	-4.146452000	-4.124022000	1.077274000	H	4.987738000	-1.628321000	4.597544000
C	0.734531000	2.836040000	0.923107000	C	4.569401000	1.430950000	-0.052964000	C	0.464944000	-1.869152000	-2.559453000	C	-2.014583000	4.640120000	-3.454006000
C	-1.043155000	2.541512000	2.552130000	H	4.469775000	1.181356000	-1.110592000	C	3.126703000	-1.124779000	-2.641584000	H	-1.499673000	4.692532000	-4.414767000
H	-1.766435000	1.901236000	3.059364000	C	4.806808000	2.063637000	2.656235000	C	1.105614000	2.513380000	2.524049000	C	-6.014236000	-3.963647000	0.003342000
C	-5.025828000	-0.329939000	-0.279948000	H	4.894196000	2.301167000	3.717611000	H	1.808832000	1.849800000	3.029600000	H	-6.460346000	-4.826545000	0.500934000
C	0.940698000	-3.655819000	1.381533000	C	-2.589071000	4.191707000	-0.217154000	C	-4.860199000	-1.767026000	-1.294461000	C	-2.494064000	-0.248700000	4.441100000
H	0.944128000	-2.991382000	2.245798000	H	-1.888241000	4.816166000	-0.772537000	H	-4.382718000	-0.943326000	-1.831679000	H	-2.482904000	0.157264000	5.453909000
C	-4.257488000	-0.667185000	2.748898000	C	6.730508000	-2.989098000	-1.314421000	C	-0.828160000	-3.771573000	1.432897000	C	4.551380000	3.867566000	1.664810000
H	-5.267517000	-0.507051000	2.368763000	H	7.732197000	-3.284112000	-1.632339000	H	-0.910348000	-3.153787000	2.327378000	H	5.231025000	4.247781000	2.429389000
C	-4.347491000	2.569076000	1.235605000	C	3.586266000	2.259902000	2.004320000	C	4.451026000	2.493171000	1.449295000	C	7.235153000	0.184679000	-1.358660000
H	-5.031217000	1.940385000	1.808410000	H	2.728234000	2.645731000	2.554824000	H	5.052685000	1.806080000	2.046356000	H	7.907455000	0.906814000	-1.825121000
C	-1.675014000	-1.120601000	3.722839000	C	-3.507213000	4.767786000	0.663422000	C	1.250618000	0.862690000	-2.462313000	C	-5.708048000	1.179666000	0.983512000
H	-0.672491000	-1.311428000	4.108893000	H	-3.533062000	5.850844000	0.794622000	C	5.118581000	-0.309004000	-0.279558000	H	-6.579906000	0.729181000	0.506280000
C	2.629218000	-1.136893000	1.754615000	C	3.272903000	4.296766000	-1.375486000	C	-3.415415000	1.968310000	0.843364000	C	-3.619168000	-0.921646000	3.961780000
C	-2.549944000	2.804793000	-0.370476000	H	4.016507000	4.159874000	-0.589201000	C	5.992501000	0.609130000	-0.878221000	H	-4.496720000	-1.045803000	4.597968000
H	-1.816073000	2.350984000	-1.033656000	C	-0.085243000	4.736681000	2.188423000	H	5.702381000	1.656093000	-0.973648000	C	7.613967000	-1.155148000	-1.242724000
C	4.163727000	-2.228660000	-0.492028000	H	-0.053063000	5.803439000	2.416142000	C	-4.550485000	1.397752000	0.239499000	H	8.584630000	-1.484396000	-1.617147000
C	3.779777000	-1.270070000	2.541635000	C	5.783833000	1.234492000	0.602355000	H	-4.520301000	1.126334000	-0.817418000	C	6.741513000	-2.075527000	-0.650117000
H	4.679582000	-1.717016000	2.118982000	H	6.632785000	0.822855000	0.053985000	C	-0.677359000	2.865996000	0.912793000	H	7.028439000	-3.124582000	-0.560161000
C	1.626948000	-4.180143000	-0.881898000	C	1.234521000	3.596042000	-2.489037000	C	-1.389991000	-0.059443000	3.604753000	C	-6.738509000	-3.259599000	-0.967324000
H	2.157609000	-3.911730000	-1.796009000	H	0.403907000	2.898467000	-2.583376000	H	-0.537961000	0.518773000	3.966866000	H	-7.751676000	-3.574159000	-1.224025000
C	0.776244000	4.206837000	1.227502000	C	5.905172000	1.552229000	1.960172000	C	-1.490138000	-3.397847000	0.253607000	C	-0.655738000	4.238960000	1.212265000
H	1.484809000	4.855489000	0.709315000	H	6.852860000	1.390838000	2.476737000	C	1.728436000	-1.209242000	3.676569000	H	-1.346068000	4.913139000	0.702610000
C	-4.075356000	-1.162558000	4.043115000	C	1.365953000	4.649646000	-3.393935000	H	0.720756000	-1.382855000	4.056768000	C	-2.973442000	5.601161000	-3.116234000
H	-4.944503000	-1.373329000	4.668421000	H	0.625212000	4.778094000	-4.185048000	C	-1.726679000	3.596654000	-2.571805000	H	-3.204062000	6.410445000	-3.811382000
C	4.779567000	-1.575227000	-1.568722000	C	-7.116130000	0.123988000	-1.425158000	H	-1.006242000	2.826762000	-2.846770000	C	-0.633489000	-5.387166000	-0.841280000
H	4.231810000	-0.796689000	-2.105815000	H	-7.766303000	0.821912000	-1.955494000	C	-3.639095000	-1.414953000	2.655323000	H	-0.554497000	-6.011654000	-1.732729000
C	-5.433991000	-1.660096000	-0.083387000	C	2.453221000	5.525837000	-3.297445000	H	-4.532436000	-1.913522000	2.278561000	C	-3.648412000	5.516747000	-1.893189000
H	-4.775569000	-2.365411000	0.425289000	H	2.561002000	6.344387000	-4.011351000	C	2.829623000	-1.569541000	4.462093000	H	-4.404364000	6.259337000	-1.631436000
C	-5.870269000	0.557474000	-0.961592000	C	0.952909000	-5.398286000	-0.802075000	H	2.671829000	-2.020910000	5.443316000	C	-4.615538000	2.086297000	2.943919000
H	-5.554467000	1.587114000	-1.134212000	H	0.958664000	-6.074295000	-1.658907000	C	4.322956000	-0.807502000	2.716302000	H	-4.634603000	2.345441000	4.003726000
C	1.512789000	-0.031906000	3.610990000	C	0.271067000	-5.751432000	0.368081000	H	5.337147000	-0.668874000	2.339075000	C	3.778484000	4.755343000	0.907132000
H	0.652299000	0.501016000	4.019016000	H	-0.259598000	-6.703121000	0.426488000	C	-3.360023000	4.478727000	-1.004154000	H	3.851850000	5.829634000	1.084270000
C	3.463104000	1.947389000	0.644939000	C	3.406733000	5.345459000	-2.290646000	H	-3.894604000	4.408014000	-0.055275000	C	2.903267000	4.264817000	-0.064711000
C	2.657968000	-0.191403000	4.397777000	H	4.258904000	6.023338000	-2.214433000	C	-1.380144000	-4.210818000	-0.887665000	H	2.285691000	4.949643000	-0.647077000
H	2.671594000	0.191845000	5.419472000					H	-1.880984000	-3.918284000	-1.811753000					

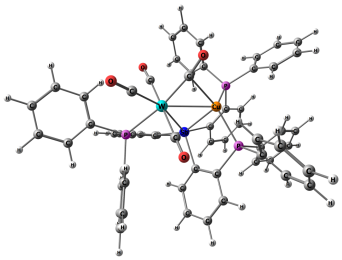
Table S5: Optimized geometry of **12** (left) and **13** (right). XYZ coordinates in angstroms. BP86/def2-TZVP level of theory.

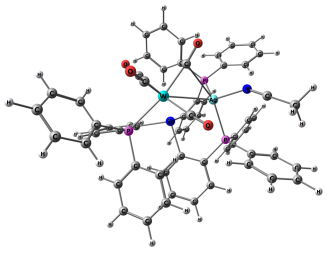


Au	1.673947000	0.738065000	1.042108000	H	-1.389844000	3.634160000	4.297458000	W	4.189485000	0.238766000	-1.777793000	C	2.611509000	-3.796865000	0.780310000
Au	1.615860000	-1.233903000	-1.446080000	C	-3.232020000	2.652988000	3.721976000	Sb	2.627116000	0.553052000	0.465067000	H	2.494674000	-3.943586000	-0.292214000
W	-2.437172000	-1.357969000	-0.809841000	H	-3.804698000	3.058077000	4.557861000	P	-0.219451000	2.327303000	0.675035000	C	-4.308694000	0.678331000	4.382899000
Sb	-0.692845000	0.625169000	-0.025313000	C	0.684892000	5.951303000	1.861221000	P	5.882244000	-0.099131000	0.066983000	H	-3.949320000	0.761218000	5.409870000
P	2.219504000	-2.527700000	0.308797000	H	-0.200100000	6.589498000	1.853054000	O	1.994380000	0.685606000	-4.016553000	C	-6.932105000	-1.379162000	0.334669000
Cl	1.163038000	-0.013536000	-3.377618000	C	0.432788000	-0.614938000	3.449213000	O	3.764260000	-2.918372000	-2.089931000	C	-6.080916000	0.921418000	2.752779000
P	2.067981000	2.693060000	-0.215485000	H	0.171422000	0.406308000	3.730178000	O	4.556057000	3.424096000	-1.749244000	H	-7.113150000	1.180110000	2.509242000
P	-3.927485000	0.304162000	0.393542000	C	0.417981000	-6.133902000	-0.367186000	O	6.503224000	-0.000280000	-3.909514000	C	-2.785586000	-0.517653000	-3.171148000
Cl	3.850749000	0.869532000	2.130396000	H	-0.604881000	-6.512747000	-0.392933000	C	3.894286000	-0.133136000	2.062284000	C	-5.633556000	-0.083917000	-3.129253000
O	-2.024609000	-3.067051000	1.868802000	C	0.453934000	-2.977965000	3.988337000	C	5.221650000	-0.447658000	1.744766000	C	1.818230000	-2.829201000	2.883960000
O	-2.669651000	-0.101480000	-3.746847000	H	0.220158000	-3.797447000	4.669519000	C	6.540159000	-2.780997000	-0.114135000	H	1.108361000	-2.174762000	3.416270000

O	-5.102067000	-2.963414000	-1.312591000	C	0.125873000	-1.662219000	4.324551000	H	5.487571000	-2.936650000	0.126772000	C	-1.126328000	-4.476458000	1.889880000
O	-0.819822000	-3.472518000	-2.541452000	H	-0.372520000	-1.445562000	5.271580000	C	1.230446000	3.183902000	1.356037000	H	-0.149522000	-4.950834000	1.998092000
C	1.360043000	-2.197530000	1.876387000	C	4.384656000	3.969421000	-1.178161000	C	-1.666664000	3.047667000	1.491544000	C	0.267979000	-2.799112000	-1.071344000
C	1.062515000	-0.867293000	2.224422000	H	3.992958000	4.891255000	-0.745663000	C	7.056984000	-1.477554000	-0.178901000	C	-3.534668000	-4.536869000	2.150415000
C	-3.122798000	1.284835000	1.722836000	C	2.802171000	-6.494753000	-0.605597000	C	8.410818000	-1.282861000	-0.477291000	H	-4.439285000	-5.061230000	2.462663000
C	1.068124000	-3.246592000	2.765833000	H	3.643267000	-7.157593000	-0.815552000	H	8.824220000	-0.274552000	-0.523207000	C	-2.477226000	-2.561428000	1.230619000
H	1.312081000	-4.274328000	2.494228000	C	-5.433409000	3.552805000	-2.550658000	C	-2.611114000	3.798075000	0.780909000	C	-4.440733000	-2.267704000	-1.741338000
C	-2.150560000	-2.403802000	0.920948000	H	-5.748316000	4.307001000	-3.273617000	H	-2.494484000	3.944799000	-0.291636000	C	-3.442887000	0.226299000	3.382522000
C	0.774524000	2.989036000	-1.456738000	C	4.189004000	1.577549000	-1.579044000	C	4.308139000	-0.678197000	4.382785000	H	-2.407622000	-0.028806000	3.625466000
C	2.948875000	4.301215000	1.883646000	H	3.633995000	0.644348000	-1.460687000	H	3.948677000	-0.760957000	5.409735000	C	2.916625000	-3.401490000	3.451701000
H	3.813815000	3.636767000	1.906204000	C	6.226696000	-1.782589000	-0.078005000	C	6.932533000	1.378148000	0.334454000	C	0.569225000	-1.838657000	-2.046922000
C	-1.760704000	1.594189000	1.589874000	H	6.898331000	-1.433874000	-0.863839000	C	6.080397000	-0.921780000	2.752784000	H	0.785883000	-0.810320000	-1.754917000
C	-0.445066000	2.302143000	-1.368117000	C	3.992904000	-2.352870000	0.669723000	H	7.112575000	-1.180756000	2.509314000	C	-3.631815000	-3.246008000	1.619578000
C	-4.097395000	-2.389776000	-1.141046000	C	-3.857487000	1.815005000	2.795667000	C	2.785724000	0.517718000	-3.171497000	H	-4.612977000	-2.774529000	1.524663000
C	0.960039000	3.974692000	-2.439016000	H	-4.917404000	1.576809000	2.900431000	C	5.633707000	0.083688000	-3.129486000	C	-3.891250000	1.774647000	-1.912468000
H	1.917523000	4.492734000	-2.519234000	C	5.402479000	1.593713000	-2.264526000	C	-1.817559000	2.830222000	2.884367000	C	-0.017311000	-4.121752000	-1.448264000
C	0.813434000	4.937944000	0.908283000	H	5.798586000	0.668690000	-2.685886000	H	-1.107709000	2.175625000	3.416509000	H	-0.273240000	-4.867851000	-0.694591000
H	0.028721000	4.783927000	0.167547000	C	4.495267000	-2.654792000	1.943231000	C	1.126939000	4.476951000	1.889679000	C	0.013784000	-4.476991000	-2.795964000
C	0.649463000	-4.792495000	-0.068080000	H	3.816965000	-2.970341000	2.737069000	H	0.150215000	4.951466000	1.998025000	H	-0.210822000	-5.503907000	-3.087624000
H	-0.187568000	-4.126479000	0.140280000	C	6.725858000	-2.082776000	1.193191000	C	-0.268121000	2.799954000	-1.071253000	C	-7.372199000	3.875940000	-0.345143000
C	-1.313372000	3.636993000	-3.195427000	H	7.790708000	-1.966866000	1.402146000	C	5.535313000	4.537019000	2.149904000	H	-6.962973000	4.886280000	-0.290336000
H	-2.134749000	3.886884000	-3.868847000	C	1.683634000	6.144297000	2.819740000	H	4.440048000	5.061248000	2.462034000	C	-5.622771000	1.040443000	4.064873000
C	-1.353107000	-2.691453000	-1.858030000	H	1.581267000	6.936659000	3.563116000	C	2.477473000	2.561712000	1.230247000	H	-6.296297000	1.407440000	4.840914000
C	3.040217000	-5.151605000	-0.300262000	C	2.814884000	5.319250000	2.827668000	C	4.441008000	2.267517000	-1.741546000	C	-2.283924000	-5.148192000	2.291295000
H	4.061560000	-4.770059000	-0.269446000	H	3.594395000	5.464958000	3.577222000	C	3.442504000	-0.226010000	3.382331000	H	-2.206102000	-6.149838000	2.715969000
C	1.962843000	-4.296442000	-0.029496000	C	-6.704156000	-0.071437000	0.843607000	H	2.407280000	0.029334000	3.625194000	C	3.713618000	-4.348766000	1.437752000
C	-1.491645000	2.641961000	-2.230858000	H	-6.877790000	0.654108000	0.048548000	C	-2.915667000	3.402793000	3.452374000	H	4.444941000	-4.939123000	0.881368000
H	-2.449678000	2.126930000	-2.169035000	C	-4.870802000	3.940383000	-1.332269000	C	-0.569446000	1.839579000	-2.046885000	C	-7.510055000	-1.988383000	-0.792262000
C	1.948046000	4.111682000	0.914375000	H	-4.744745000	4.998702000	-1.098019000	H	-0.786049000	0.811214000	-1.754947000	H	-7.342443000	-1.567726000	-1.784443000
C	-2.605190000	-0.489766000	-2.653724000	C	1.494225000	-6.987228000	-0.638615000	C	3.632199000	3.246137000	1.619069000	C	0.594442000	-2.201117000	-3.393553000
C	-5.396198000	-0.400293000	1.221837000	H	1.311693000	-8.036502000	-0.876550000	H	4.613282000	2.774514000	1.524048000	H	0.824821000	-1.447712000	-4.144644000
C	-4.587323000	1.611860000	-0.707807000	C	6.110651000	2.792644000	-2.405881000	C	3.891038000	-1.774740000	-1.913182000	C	3.886886000	-4.144768000	2.821302000
C	-1.143561000	2.447085000	2.511225000	H	7.063648000	2.803115000	-2.937506000	C	0.017156000	4.122619000	-1.448092000	H	4.752751000	-4.564764000	3.337580000
H	-0.083695000	2.691227000	2.411379000	C	-5.185628000	-1.332234000	2.252291000	H	0.273158000	4.868653000	-0.694379000	C	-8.725203000	3.679873000	-0.648863000
C	4.862374000	-1.917657000	-0.340262000	H	-4.170410000	-1.590163000	2.556085000	C	-0.014051000	4.477975000	-2.795758000	H	-9.374310000	4.537259000	-0.833408000
H	4.461397000	-1.679504000	-1.327870000	C	-7.578451000	-1.595427000	2.514032000	H	0.210540000	5.504914000	-3.087350000	C	0.319812000	-3.517837000	-3.768432000
C	-5.162512000	1.227666000	-1.931800000	H	-8.427976000	-2.062352000	3.015149000	C	7.369904000	-3.877488000	-0.343239000	H	0.334984000	-3.798121000	-4.822655000
H	-5.260084000	0.168794000	-2.177148000	C	5.603411000	3.976897000	-1.861149000	H	6.960138000	-4.887571000	-0.287732000	C	-8.475846000	-3.707893000	0.612761000
C	3.673848000	2.767378000	-1.041238000	H	6.158331000	4.910486000	-1.966304000	C	5.622149000	-1.040635000	4.064857000	H	-9.071572000	-4.615637000	0.720636000
C	-4.454641000	2.975997000	-0.409867000	C	-6.271864000	-1.921250000	2.898392000	H	6.295541000	-1.407762000	4.840954000	C	-9.240857000	2.382732000	-0.713327000
H	-4.005596000	3.290238000	0.532004000	H	-6.098537000	-2.639441000	3.701555000	C	2.284681000	5.148527000	2.290936000	H	-10.295104000	2.222311000	-0.945299000
C	-0.081652000	4.289882000	-3.312390000	C	5.859783000	-2.521207000	2.200999000	H	2.207058000	6.150187000	2.715613000	C	-8.287119000	-3.138321000	-0.651500000
H	0.067365000	5.048607000	-4.082085000	H	6.246800000	-2.746221000	3.196140000	C	-3.712917000	4.350262000	1.438622000	H	-8.733927000	-3.597968000	-1.534429000
C	-5.587624000	2.192871000	-2.844588000	C	-7.791152000	-0.672330000	1.487373000	H	-4.444216000	4.940822000	0.882425000	C	-7.127054000	-1.951405000	1.599658000
H	-6.027263000	1.882088000	-3.793537000	H	-8.807153000	-0.413288000	1.184414000	C	7.510845000	1.986938000	-0.792525000	H	-6.674272000	-1.500100000	2.482628000
C	-1.878139000	2.977045000	3.575677000					H	7.343131000	1.566199000	-1.784653000	C	-7.890448000	-3.115237000	1.734486000
								C	-0.594755000	2.202151000	-3.393487000	H	-8.024907000	-3.557537000	2.723029000
								H	-0.825171000	1.448806000	-4.144625000	H	8.026084000	3.556431000	2.722556000
								C	-3.885899000	4.146306000	2.822212000	Au	0.000019000	0.000372000	0.879016000
								H	-4.751528000	4.566525000	3.338703000	W	-4.189411000	-0.238920000	-1.777471000
								C	8.722966000	-3.682345000	-0.647304000	Sb	-2.627129000	-0.552853000	0.465351000
								H	9.371572000	-4.540201000	-0.831428000	P	0.219515000	-2.326578000	0.674982000
								C	-0.320158000	3.518902000	-3.768280000	P	-5.882441000	0.098534000	0.067054000
								H	-0.335406000	3.799271000	-4.822479000	Cl	0.000115000	0.000382000	3.759697000
								C	8.477273000	3.706248000	0.612303000	O	-1.994161000	-0.685444000	-4.016146000
								H	9.073388000	4.613749000	0.720084000	O	-3.765426000	2.918472000	-2.088653000
								C	9.239336000	-2.385530000	-0.712626000	O	-4.555384000	-3.424316000	-1.749842000
								H	10.293640000	-2.225839000	-0.944844000	O	-6.503035000	0.000016000	-3.909326000
								C	8.288404000	3.136556000	-0.651882000	C	-3.894559000	0.133257000	2.062451000
								H	8.735489000	3.595865000	-1.534847000	C	-5.221997000	0.447462000	1.744832000
								C	7.127625000	1.950511000	1.599367000	C	-6.541817000	2.780044000	-0.115511000
								H	6.674567000	1.499550000	2.482371000	H	-5.489272000	2.936428000	0.125090000
								C	7.891518000	3.114029000	1.734073000	C	-1.230104000	-3.183425000	1.356246000
								C	-7.057918000	1.476272000	-0.179349000	C	1.667039000	-3.046700000	1.491175000
								C	-8.411688000	1.280668000	-0.477453000	H	-8.824539000	0.272104000	-0.522723000

Table S6: Optimized geometry of **14** (left) and **15** (right). XYZ coordinates in angstroms. BP86/def2-TZVP level of theory.

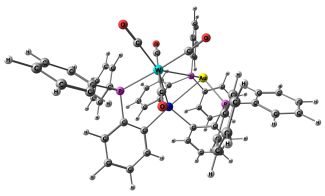


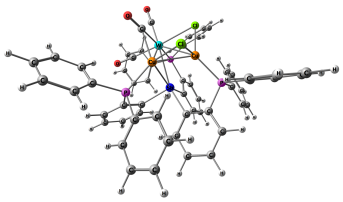


W	-1.354306000	-0.399768000	-1.412645000	C	-4.234416000	-1.424932000	2.380081000	W	-1.561482000	-0.622878000	-1.397779000	H	0.164723000	3.763027000	-1.396470000
Sb	-0.268758000	-0.043295000	1.129693000	H	-5.219249000	-1.438414000	1.911328000	Sb	-0.358880000	-0.276224000	1.129461000	C	-2.919814000	4.171050000	0.531144000
Cu	1.357581000	-0.047430000	-1.029049000	C	0.333438000	-5.125900000	1.051402000	Ag	1.437019000	0.062686000	-1.150229000	H	-2.311063000	4.938247000	0.051124000
P	2.052716000	1.978120000	-0.299754000	H	-0.111008000	-5.528681000	1.962978000	P	-3.412714000	0.096570000	0.202630000	C	-7.513240000	-1.018361000	-1.618277000
P	2.470218000	-1.786675000	-0.107613000	C	0.236457000	-5.833002000	-0.149258000	P	2.442298000	-1.919203000	-0.080827000	H	-8.463921000	-1.287299000	-2.081395000
P	-3.385152000	-0.003649000	0.081088000	H	-0.286168000	-6.790265000	-0.179358000	P	1.905844000	2.109566000	0.174935000	C	-1.836497000	-1.737124000	3.531297000
O	-1.870297000	-3.487546000	-0.707057000	C	4.805460000	-3.373143000	-0.149434000	O	-1.005715000	2.147290000	-2.904965000	H	-0.841409000	-1.939124000	3.930228000
O	-0.931194000	2.710495000	-2.060373000	H	4.311117000	-4.018376000	0.578971000	O	-2.336095000	-3.595578000	-0.486785000	C	1.354470000	5.336331000	-2.262136000
O	-3.344500000	-0.497430000	-3.864573000	C	-1.083744000	1.587285000	-1.807398000	O	-3.812805000	-0.879359000	-3.582419000	H	0.506223000	5.787666000	-2.779146000
C	0.800772000	2.823794000	0.747687000	C	-2.608840000	-0.472516000	-2.963731000	C	1.365088000	-0.907393000	2.278554000	C	-2.815178000	2.842638000	0.114936000
C	-1.637010000	-2.379744000	-0.956941000	C	-6.265332000	-2.410348000	-1.587050000	C	-0.278162000	1.734960000	1.898761000	H	-2.126450000	2.575372000	-0.682806000
C	1.580261000	-3.377341000	-0.072563000	H	-6.298151000	-3.396367000	-2.052967000	C	-2.962672000	-2.219691000	4.208178000	C	3.416595000	1.796993000	1.142049000
C	-0.105925000	2.060621000	1.514206000	C	3.347912000	4.870102000	-3.656932000	H	-2.838325000	-2.792071000	5.128977000	C	-4.399263000	-1.268783000	2.504638000
C	0.776072000	4.221432000	0.858417000	H	3.650367000	5.546070000	-4.458369000	C	-1.174608000	1.181998000	-2.273505000	H	-5.399599000	-1.101852000	2.103190000
H	1.455336000	4.826784000	0.257043000	C	-4.135851000	2.069589000	1.855605000	O	0.292050000	-1.993142000	-3.580291000	C	1.369970000	-0.563728000	3.634434000
C	-3.158928000	-0.813859000	1.721200000	H	-4.175917000	1.307339000	2.633935000	C	2.242590000	3.611006000	-0.801555000	H	0.513057000	-0.053671000	4.078008000
C	2.573515000	3.138173000	-1.598876000	C	2.525101000	3.775422000	-3.939647000	C	2.499095000	-1.508175000	1.698783000	C	0.815255000	-3.966518000	1.046349000

C	1.472850000	-0.658764000	2.245268000	H	2.186387000	3.591120000	-4.960154000	C	-1.158129000	2.124012000	2.914734000	H	0.920138000	-3.462242000	2.006896000
C	-0.985462000	4.082775000	2.515158000	C	5.791423000	1.512525000	2.379574000	H	-1.887509000	1.414667000	3.308766000	C	4.512251000	1.236886000	0.461811000
H	-1.681027000	4.568729000	3.200277000	H	6.676059000	1.369543000	3.002004000	N	2.056201000	0.892160000	-3.161339000	H	4.438614000	1.041295000	-0.608725000
C	-1.891910000	-0.796667000	2.336285000	C	0.099003000	-0.965628000	-2.691074000	C	1.438369000	-3.446230000	-0.097887000	C	0.672977000	3.969570000	1.888567000
O	0.824948000	-1.357223000	-3.529306000	C	3.718404000	-1.544917000	2.433889000	C	3.627459000	-1.747777000	2.494801000	H	1.391796000	4.688459000	1.491825000
C	3.511906000	1.864720000	0.789380000	H	4.591684000	-2.014253000	1.981145000	H	4.521251000	-2.183207000	2.047765000	C	0.070735000	-5.146184000	0.963432000
C	-4.989985000	-0.638178000	-0.526072000	C	-7.434185000	-1.652276000	-1.458444000	C	-4.448668000	2.185928000	1.777460000	H	-0.412637000	-5.540923000	1.858536000
C	2.574132000	-1.315401000	1.658095000	H	-8.383825000	-2.045205000	-1.825075000	H	-5.040122000	1.416106000	2.275260000	C	-4.553567000	3.513474000	2.192643000
C	-5.048379000	-1.905386000	-1.128970000	C	-6.164628000	0.119295000	-0.398921000	C	-3.576837000	1.843145000	0.730580000	H	-5.229517000	3.772445000	3.009181000
H	-4.145011000	-2.501579000	-1.245497000	H	-6.133100000	1.107053000	0.060906000	C	-2.009203000	-2.518805000	-0.768412000	C	5.900003000	-4.131749000	-0.392716000
C	-0.976252000	2.689100000	2.407872000	C	-3.737123000	2.714423000	-0.446476000	C	-2.972910000	-0.788922000	-2.779443000	H	6.293850000	-5.073660000	-0.007394000
H	-1.667019000	2.093985000	3.006272000	H	-3.484924000	2.448791000	-1.472736000	C	0.659855000	2.653226000	1.394318000	C	5.768780000	1.156260000	2.524492000
C	-0.120650000	4.846932000	1.728069000	C	-4.045776000	-2.023455000	3.629452000	C	2.634080000	5.891805000	-2.387962000	H	6.678993000	0.897322000	3.067582000
H	-0.137679000	5.935770000	1.793111000	H	-4.886636000	-2.507524000	4.128207000	H	2.786802000	6.780482000	-3.002190000	C	-0.311439000	-1.461021000	-2.732974000
C	2.660222000	-0.517801000	4.354351000	C	-2.785193000	-2.011876000	4.229995000	C	3.523337000	4.166217000	-0.932335000	C	4.678113000	1.701292000	3.206874000
H	2.694346000	-0.197529000	5.396540000	H	-2.633128000	-2.492151000	5.197848000	H	4.368579000	3.723265000	-0.404787000	H	4.734136000	1.866216000	4.283923000
C	2.141300000	2.909223000	-2.914102000	C	5.845086000	1.231960000	1.009421000	C	4.105607000	-2.505972000	-0.527798000	C	6.678416000	-3.342556000	-1.248390000
H	1.509177000	2.047656000	-3.135953000	H	6.769652000	0.871203000	0.556085000	C	-1.989480000	-1.023944000	2.340388000	H	7.681111000	-3.669922000	-1.528117000
C	1.462509000	-4.080713000	-1.284425000	C	-7.380321000	-0.387972000	-0.866103000	C	-1.129731000	3.429871000	3.408077000	C	3.715368000	5.301564000	-1.726857000
H	1.898084000	-3.670186000	-2.197588000	H	-8.286833000	0.211177000	-0.766580000	H	-1.830884000	3.727683000	4.188691000	H	4.714476000	5.730689000	-1.819333000
C	3.461511000	2.147413000	2.160070000	C	-1.706089000	-1.397628000	3.583553000	C	-3.275210000	-0.800892000	1.808597000	C	-6.658426000	-2.018898000	-1.141458000
H	2.534666000	2.498790000	2.613324000	H	-0.720697000	-1.417792000	4.050458000	C	4.616211000	-3.719003000	-0.034434000	H	-6.939506000	-3.069467000	-1.230444000
C	1.527294000	-0.249049000	3.582027000	C	3.756242000	-1.159748000	3.775535000	H	4.004350000	-4.340495000	0.621765000	C	-7.144402000	0.324360000	-1.503957000
H	0.701223000	0.312661000	4.022704000	H	4.656181000	-1.344693000	4.363295000	C	3.504068000	2.025384000	2.521529000	H	-7.804387000	1.108736000	-1.878072000
C	-3.765670000	1.723992000	0.546820000	C	4.759698000	-1.450563000	-1.632658000	H	2.653271000	2.440184000	3.062544000	C	6.166814000	-2.145100000	-1.756995000
C	3.796920000	5.092287000	-2.349917000	H	4.219819000	-0.601864000	-2.056381000	C	-4.241005000	-1.975395000	3.700196000	H	6.764433000	-1.537953000	-2.438689000
H	4.450051000	5.938645000	-2.131446000	C	6.092591000	-3.678807000	-0.592653000	H	-5.120923000	-2.347520000	4.227172000	C	5.684947000	0.924982000	1.147069000
C	0.800472000	-5.306859000	-1.317496000	H	6.608718000	-4.554502000	-0.196074000	C	-5.927648000	0.671508000	-0.909358000	H	6.525225000	0.484729000	0.608030000
H	0.717665000	-5.851163000	-2.259583000	C	-4.451416000	3.393626000	2.167931000	H	-5.643804000	1.721110000	-0.824933000	C	0.561515000	-5.296059000	-1.401138000
C	1.004737000	-3.900840000	1.094010000	H	-4.732696000	3.653951000	3.189588000	C	4.880595000	-1.730844000	-1.402266000	H	0.461097000	-5.809912000	-2.358522000
H	1.086981000	-3.360552000	2.037792000	C	-4.045813000	4.037513000	-0.129399000	H	4.464740000	-0.812012000	-1.818837000	C	-5.439464000	-1.678729000	-0.555325000
C	4.601767000	1.972055000	2.949281000	H	-4.011396000	4.801372000	-0.907414000	C	1.300015000	-4.116234000	-1.325872000	H	-4.776267000	-2.466405000	-0.195616000
H	4.554225000	2.188928000	4.017384000	C	-4.397357000	4.380548000	1.180293000	H	1.777699000	-3.714683000	-2.220825000	C	-3.788702000	4.507710000	1.571286000
C	4.141265000	-2.241382000	-0.653566000	H	-4.631653000	5.416691000	1.429198000	C	2.489708000	-0.834070000	4.426194000	H	-3.864730000	5.543099000	1.906981000
C	3.417391000	4.227673000	-1.322247000	C	6.047317000	-1.760692000	-2.076272000	H	2.485184000	-0.560945000	5.482452000	C	-0.054313000	-5.814563000	-0.256081000
H	3.790728000	4.387215000	-0.309379000	H	6.523190000	-1.141859000	-2.838382000	C	-5.071747000	-0.328413000	-0.427428000	H	-0.638595000	-6.733799000	-0.319205000
C	4.712066000	1.408907000	0.217888000	C	6.717010000	-2.868768000	-1.549284000	C	3.619468000	-1.418662000	3.851843000	C	2.313338000	1.817102000	-3.814708000
H	4.759584000	1.201716000	-0.851299000	H	7.722840000	-3.112567000	-1.895101000	H	4.508267000	-1.604845000	4.456169000	C	2.634834000	2.967038000	-4.630132000
								C	-0.220416000	4.355878000	2.887269000	H	1.714638000	3.381567000	-5.063798000
								H	-0.204099000	5.380224000	3.262297000	H	3.318439000	2.676336000	-5.439587000
								C	1.160644000	4.197086000	-1.482489000	H	3.111939000	3.737518000	-4.006959000

Table S7: Optimized geometry of **16** (left) and **17** (right). XYZ coordinates in angstroms. BP86/def2-TZVP level of theory.

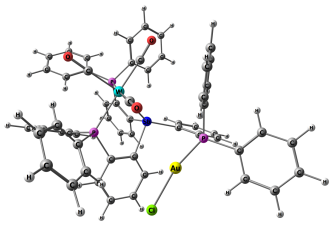


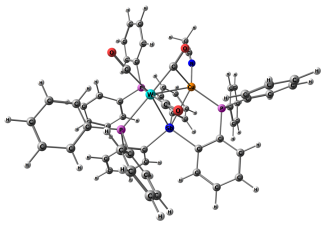


Au	-1.690825000	0.052144000	-0.933258000	C	1.736905000	-1.432376000	3.647029000	W	1.194524000	-1.071052000	-1.414673000	H	-3.945011000	0.548563000	-0.679066000
W	1.581803000	-0.470560000	-1.384284000	H	0.731818000	-1.506790000	4.063014000	Sb	-0.151503000	0.034239000	0.845624000	C	3.649092000	-2.156714000	0.962884000
Sb	0.351200000	-0.138916000	1.108894000	C	3.247129000	-0.774843000	1.861025000	Cu	-1.590190000	-0.792389000	-1.350685000	C	-5.940430000	-0.653397000	2.437232000
P	-1.947334000	2.263460000	-0.273917000	C	-1.176713000	-4.014346000	-1.553782000	Cu	-0.362014000	1.443070000	-1.551551000	H	-6.491022000	-0.986831000	3.318605000
P	-2.415984000	-2.015581000	-0.096962000	H	-1.548080000	-3.473401000	-2.425577000	Cl	-2.348437000	0.831195000	-2.769690000	C	3.408388000	-2.416688000	2.317905000
P	3.500835000	0.034446000	0.227460000	C	-5.865041000	-4.175744000	-0.681580000	Cl	1.468921000	1.134065000	-2.844749000	H	2.979770000	-1.642699000	2.953353000
O	0.996046000	2.563927000	-2.225869000	H	-6.178437000	-5.220844000	-0.675427000	P	-2.789005000	-1.948723000	0.110632000	C	4.673628000	0.127114000	-0.471477000
O	-0.420043000	-1.428807000	-3.660256000	C	2.983029000	-0.538604000	-2.789590000	P	3.116140000	-0.589355000	0.174884000	C	-1.203961000	5.832268000	-1.091637000
O	3.826706000	-0.569389000	-3.594307000	C	1.898330000	-2.430101000	-0.876634000	P	-0.818904000	3.155383000	-0.255552000	H	-0.238159000	6.057792000	-0.637699000
O	2.131621000	-3.531381000	-0.594539000	C	-0.916162000	-4.195458000	0.858375000	O	-0.728540000	-2.423105000	-3.543274000	C	-2.574628000	-4.483477000	-0.982491000
C	-4.122163000	-2.510566000	-0.460685000	H	-1.093670000	-3.803564000	1.860684000	O	0.830616000	-3.820149000	0.029396000	H	-1.502623000	-4.349685000	-0.822641000
C	-1.412476000	-3.513219000	-0.262103000	C	-4.310901000	1.962463000	3.085265000	O	3.361097000	-2.468143000	-3.210226000	C	-2.959773000	4.243126000	-1.633492000
C	-2.375846000	3.546270000	-1.478141000	H	-4.175345000	1.951714000	4.167431000	C	-1.676010000	1.354247000	1.673298000	H	-3.345783000	3.221984000	-1.617280000
C	0.234944000	1.974138000	1.532298000	C	-0.401643000	4.243642000	0.941493000	C	-4.188158000	-1.006408000	0.801823000	C	6.987260000	1.410095000	-1.405412000
C	-4.525505000	-3.854193000	-0.447165000	H	-1.002386000	4.935354000	0.350040000	C	0.617680000	3.888229000	0.591636000	H	7.887787000	1.907839000	-1.769431000
H	-3.797250000	-4.642928000	-0.254197000	C	-3.556095000	-1.544280000	3.833254000	C	-1.823394000	-2.484786000	1.571186000	C	4.214469000	-3.163759000	0.161877000
C	-1.983413000	3.380625000	-2.814836000	H	-4.413093000	-1.825211000	4.446735000	C	-4.900790000	-1.436073000	1.932201000	H	4.401312000	-2.980321000	-0.896312000
H	-1.429856000	2.489427000	-3.110774000	C	-0.472894000	-5.206305000	-1.716609000	H	-4.637672000	-2.373705000	2.424826000	C	-3.051868000	-5.648698000	-1.581312000
C	-2.532518000	-0.762623000	4.369806000	H	-0.293309000	-5.595397000	-2.719820000	C	-2.417968000	0.940256000	2.783664000	H	-2.348394000	-6.423048000	-1.891812000
H	-2.583056000	-0.419505000	5.404104000	C	-6.397552000	-1.822814000	-0.930912000	H	-2.255341000	-0.048045000	3.216170000	C	-4.426109000	-5.820678000	-1.791096000
C	-2.408776000	-1.597483000	1.689758000	H	-7.124685000	-1.031566000	-1.119536000	C	1.896693000	3.515538000	0.153721000	H	-4.796115000	-6.731171000	-2.265460000
C	1.140055000	2.491676000	2.466488000	C	2.812127000	-1.981766000	4.354641000	H	1.989499000	2.828218000	-0.690269000	C	0.970736000	-2.765596000	-0.479283000
H	1.759273000	1.813811000	3.056275000	H	2.635642000	-2.466801000	5.316134000	C	1.490821000	0.773954000	2.041489000	C	-3.629375000	3.037007000	2.767766000
C	-1.364263000	-0.824837000	2.240342000	C	3.665809000	2.791168000	-0.235088000	C	-0.761175000	-1.677090000	2.018015000	H	-4.402095000	3.686791000	3.181761000
C	-4.647367000	1.983662000	0.311142000	H	3.281526000	2.553621000	-1.224717000	C	2.327001000	2.074861000	3.902580000	C	1.614477000	5.240322000	2.335995000
H	-4.778594000	1.989934000	-0.773150000	C	0.527068000	4.746767000	1.854469000	H	2.140251000	2.710047000	4.769951000	H	1.506431000	5.905024000	3.194836000
C	-0.569844000	2.859381000	0.779737000	H	0.651775000	5.825472000	1.957592000	C	2.800790000	0.484106000	1.641703000	C	3.030911000	4.002430000	0.805632000
C	1.212477000	1.471908000	-1.885970000	C	6.154376000	0.275149000	-0.696506000	C	-2.137097000	-3.660878000	2.269503000	H	4.021622000	3.689931000	0.471920000
C	-3.369470000	2.180682000	0.864975000	H	6.031948000	1.350557000	-0.565359000	H	-2.946051000	-4.302312000	1.915402000	C	5.724242000	1.880917000	-1.781135000
C	4.402534000	2.078140000	1.959754000	C	-6.800694000	-3.163462000	-0.918791000	C	-1.895911000	2.626271000	1.121562000	H	5.634025000	2.745123000	-2.441665000
H	4.567627000	1.290448000	2.695391000	H	-7.845695000	-3.419717000	-1.100265000	C	-0.045401000	-2.034632000	3.162748000	C	5.941793000	-0.345277000	-0.099838000
C	-3.499395000	-1.950596000	2.498052000	C	4.320622000	-1.318956000	2.581801000	H	0.769285000	-1.400686000	3.517212000	H	6.031500000	-1.211721000	0.556408000
H	-4.317678000	-2.533175000	2.073448000	H	5.328066000	-1.280542000	2.165567000	C	-1.404368000	-4.024026000	3.402043000	C	2.889420000	4.864827000	1.895914000
C	-2.304634000	4.355448000	-3.760979000	C	-5.577510000	1.758128000	2.534274000	H	-1.648072000	-4.946711000	3.931150000	H	3.774441000	5.235072000	2.416065000
H	-1.997807000	4.223572000	-4.799506000	H	-6.435820000	1.584905000	3.185107000	C	1.252520000	1.571024000	3.166259000	C	7.092937000	0.294022000	-0.569675000
C	-1.444706000	-0.398508000	3.570036000	C	5.287570000	-1.983243000	-0.526608000	H	0.229535000	1.816479000	3.456996000	H	8.075568000	-0.081829000	-0.278750000
H	-0.669580000	0.246058000	3.989640000	H	4.489016000	-2.675157000	-0.260607000	C	-1.720332000	4.530240000	-1.032999000	C	-5.556374000	0.992091000	0.699414000
C	-3.113891000	4.681104000	-1.098089000	C	-5.745343000	1.777992000	1.143983000	C	3.875459000	0.990422000	2.390876000	H	-5.800025000	1.944930000	0.227251000
H	-3.449160000	4.796837000	-0.066121000	H	-6.733314000	1.624304000	0.707279000	H	4.900716000	0.776373000	2.084885000	C	3.715094000	-3.667154000	2.863511000
C	3.873058000	1.765775000	0.697112000	C	4.705420000	3.401246000	2.283799000	C	3.638057000	1.779288000	3.516127000	H	3.511748000	-3.858909000	3.918536000
C	-5.059555000	-1.496475000	-0.712417000	H	5.110348000	3.635877000	3.269626000	H	4.479716000	2.178742000	4.084242000	C	-6.267981000	0.560651000	1.822318000
H	-4.731946000	-0.455244000	-0.724304000	C	4.478963000	4.422786000	1.355673000	C	-0.105677000	-1.825999000	-2.738847000	H	-7.072706000	1.176073000	2.228275000
C	0.255568000	-1.063965000	-2.776970000	H	4.703152000	5.458167000	1.617101000	C	-0.361938000	-3.209181000	3.852876000	C	4.572837000	1.239760000	-1.321589000
C	-3.025647000	5.491078000	-3.378593000	C	6.487620000	-2.481428000	-1.032559000	H	0.213551000	-3.492748000	4.735819000	H	3.588437000	1.584634000	-1.640354000
H	-3.280485000	6.249744000	-4.120277000	H	6.614051000	-3.557973000	-1.158214000	C	-5.322445000	-4.823749000	-1.395604000	C	2.560743000	-1.942198000	-2.536579000

C	5.115490000	-0.599708000	-0.350493000	C	4.102392000	-1.920941000	3.823795000	H	-6.393814000	-4.953622000	-1.558536000	C	4.533958000	-4.404500000	0.711352000
C	-3.206287000	2.177285000	2.255659000	H	4.942794000	-2.350356000	4.371176000	C	-3.394309000	1.779132000	3.329053000	H	4.975491000	-5.176433000	0.078673000
H	-2.220380000	2.335267000	2.692022000	C	7.522115000	-1.605084000	-1.381040000	H	-3.984616000	1.438261000	4.180671000	C	-1.929448000	6.843042000	-1.730170000
C	-3.432954000	5.650976000	-2.049154000	H	8.457985000	-1.996464000	-1.783061000	C	-2.879410000	3.462903000	1.670096000	H	-1.522751000	7.855029000	-1.771608000
H	-4.005993000	6.530871000	-1.752896000	C	-0.203802000	-5.384598000	0.685469000	H	-3.060644000	4.445227000	1.230896000	C	4.278497000	-4.663339000	2.063591000
C	1.949529000	-0.823998000	2.406792000	H	0.183485000	-5.913574000	1.557540000	C	-4.852315000	-3.655379000	-0.787848000	H	4.517308000	-5.639595000	2.488796000
C	1.281695000	3.871285000	2.635629000	C	7.352101000	-0.228902000	-1.213318000	H	-5.552995000	-2.878469000	-0.479023000	C	-3.682194000	5.257548000	-2.260782000
H	1.998826000	4.257183000	3.360329000	H	8.154051000	0.460411000	-1.482584000	C	-3.477384000	-3.484304000	-0.574795000	H	-4.644980000	5.029827000	-2.721544000
C	3.963090000	4.115038000	0.093942000	C	0.010095000	-5.894423000	-0.597602000	C	0.478922000	4.750455000	1.690556000	C	-3.169247000	6.560039000	-2.309937000
H	3.788201000	4.905495000	-0.637224000	H	0.566884000	-6.823461000	-0.728720000	H	-0.514651000	5.024106000	2.050172000	H	-3.734490000	7.351229000	-2.805430000
								C	-4.517832000	0.212018000	0.188702000				

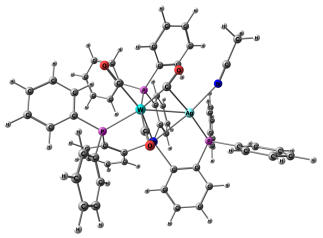
Table S8: Optimized geometry of **18** (left) and **19** (right). XYZ coordinates in angstroms. BP86/def2-TZVP level of theory.





Au	-3.086121000	-1.493219000	0.173163000	C	3.418737000	-1.815989000	1.985549000	W	-0.844932000	-0.039746000	1.332201000	C	-3.448952000	2.065391000	-3.415710000
W	1.284327000	0.107850000	-1.329394000	H	2.667597000	-1.192943000	2.469309000	Sb	0.250631000	-0.765966000	-1.040709000	H	-3.345874000	1.922871000	-4.492129000
Sb	-0.171388000	0.626172000	0.915410000	C	4.671972000	-1.969424000	2.576893000	Cu	1.826643000	0.594141000	0.864426000	C	3.498572000	-4.350699000	-1.922965000
Cl	-3.105407000	-3.813373000	0.369742000	H	4.889646000	-1.453577000	3.513470000	P	-2.744218000	-1.258842000	0.131760000	H	4.196401000	-5.178212000	-2.058402000
P	1.510089000	-2.056675000	-0.027360000	C	5.642143000	-2.774460000	1.970659000	P	3.447817000	-0.744224000	0.066372000	C	-2.467443000	-1.215522000	-4.526596000
P	2.890060000	1.512181000	0.016518000	H	6.625593000	-2.888791000	2.429553000	P	-0.989155000	2.079014000	-0.088023000	H	-2.388937000	-1.230928000	-5.614864000
P	-3.573030000	0.687731000	-0.011983000	C	5.342171000	-3.436383000	0.777140000	O	1.188043000	0.823340000	3.605032000	C	6.494421000	-1.958770000	2.568523000
O	3.593134000	-0.718844000	-3.297915000	H	6.086937000	-4.078807000	0.303762000	O	-2.714961000	1.153770000	3.578300000	H	7.584381000	-1.918028000	2.603760000
O	0.793459000	2.577629000	-3.240821000	C	4.087453000	-3.280595000	0.179189000	O	-0.124840000	-2.752233000	2.786519000	C	-3.695744000	2.427096000	-0.660662000
O	-0.869643000	-1.464765000	-3.038229000	H	3.867419000	-3.806957000	-0.749023000	N	2.404969000	2.447499000	1.150863000	H	-3.790795000	2.601134000	0.411459000
C	2.721919000	-0.427231000	-2.561346000	C	4.699820000	1.319605000	-0.177816000	C	0.982041000	1.084898000	-1.852723000	C	-2.988538000	-3.608171000	1.621602000
C	0.950026000	1.690624000	-2.492481000	C	5.207283000	0.040705000	-0.444308000	C	0.537790000	0.575016000	2.647580000	H	-3.513514000	-2.974737000	2.339161000
C	-0.089530000	-0.881670000	-2.386821000	H	4.520584000	-0.793859000	-0.575032000	C	2.005743000	1.167143000	-2.801549000	C	5.781156000	-2.572813000	3.602326000
C	-0.475028000	-1.285517000	1.856448000	C	6.584459000	-0.167576000	-0.534290000	H	2.430637000	0.259305000	-3.231957000	H	6.314434000	-3.009527000	4.448244000
C	0.377600000	-2.308802000	1.417731000	H	6.964143000	-1.170304000	-0.735859000	C	-1.418591000	-1.124377000	-2.349706000	C	4.382560000	-2.624237000	3.555597000
C	0.403485000	-3.521867000	2.127719000	C	7.467507000	0.903986000	-0.370017000	C	1.703048000	-2.239855000	-1.553225000	H	3.822911000	-3.099502000	4.362634000
H	1.081945000	-4.318892000	1.817233000	H	8.544408000	0.743329000	-0.447049000	C	5.815768000	-1.396362000	1.483215000	C	-6.806903000	-1.825488000	0.475156000
C	-0.430245000	-3.713337000	3.229477000	C	6.967731000	2.185044000	-0.109893000	H	6.372691000	-0.918728000	0.675794000	H	-7.532330000	-2.587300000	0.185186000
H	-0.408230000	-4.663987000	3.764592000	H	7.652532000	3.025432000	0.017709000	C	0.414795000	2.249085000	-1.297753000	C	-6.290982000	0.289268000	1.533750000
C	-1.290227000	-2.691538000	3.649118000	C	5.590241000	2.393564000	-0.009820000	C	-2.542568000	-3.067200000	0.404361000	H	-6.608088000	1.182067000	2.074798000
H	-1.944477000	-2.844467000	4.509190000	H	5.205607000	3.393000000	0.197775000	C	4.415689000	-1.446089000	1.436929000	C	-1.494995000	6.077835000	0.797097000
C	-1.305403000	-1.472906000	2.969311000	C	2.618237000	3.301230000	-0.289446000	C	-0.460827000	-1.771893000	2.245905000	H	-1.871069000	6.968200000	0.290590000
H	-1.965732000	-0.668658000	3.302186000	C	3.071135000	3.861234000	-1.495500000	C	-2.055347000	0.693391000	2.729295000	C	-0.552847000	3.787148000	2.093052000
C	1.391937000	1.097420000	2.351458000	H	3.649583000	3.253021000	-2.193443000	C	0.902159000	3.496518000	-1.709110000	H	-0.195302000	2.893109000	2.601070000
C	2.666807000	1.400568000	1.847148000	C	2.773985000	5.186833000	-1.812177000	H	0.471584000	4.412417000	-1.304134000	C	-4.939250000	0.106550000	1.232283000
C	3.743152000	1.555098000	2.734163000	H	3.133770000	5.610961000	-2.751276000	C	-4.510995000	-1.032710000	0.543371000	H	-4.211263000	0.849140000	1.544449000
H	4.738177000	1.780602000	2.349679000	C	2.004672000	5.964413000	-0.938848000	C	2.962744000	-2.201543000	-0.928033000	C	-0.541368000	5.017862000	2.754033000
C	3.555103000	1.380537000	4.106496000	H	1.764804000	6.998289000	-1.193062000	C	-2.427271000	2.214006000	-1.220892000	H	-0.171710000	5.076467000	3.778904000
H	4.403352000	1.481272000	4.785728000	C	1.544492000	5.410363000	0.258981000	C	-2.310046000	2.041668000	-2.607384000	C	-1.862197000	-3.889224000	-0.502882000
C	2.289621000	1.056907000	4.606287000	H	0.946425000	6.009763000	0.947892000	H	-1.332448000	1.883585000	-3.061252000	H	-1.533767000	-3.491812000	-1.462958000
H	2.144694000	0.897472000	5.676263000	C	1.856343000	4.087411000	0.586315000	C	-2.677236000	-1.164806000	-1.721131000	C	-3.721349000	-1.224609000	-3.910538000
C	1.210075000	0.921988000	3.728754000	H	1.508729000	3.669489000	1.532011000	C	-1.311114000	-1.155236000	-3.742619000	H	-4.627930000	-1.240655000	-4.517401000
H	0.229334000	0.649721000	4.124086000	C	-5.383293000	0.872951000	-0.135954000	H	-0.331236000	-1.110482000	-4.222574000	C	-3.829009000	-1.200962000	-2.517396000
C	-1.743051000	1.830340000	1.797701000	C	-5.956273000	1.903651000	-0.896272000	C	-5.456443000	-2.009145000	0.177246000	H	-4.815983000	-1.196912000	-2.056441000
C	-3.092432000	1.744876000	1.398519000	H	-5.318936000	2.589852000	-1.455591000	H	-5.133792000	-2.918979000	-0.330566000	C	-2.754263000	-4.949740000	1.921820000
C	-4.056229000	2.544585000	2.031723000	C	-7.345233000	2.046844000	-0.939052000	C	-7.227656000	-0.673290000	1.150123000	H	-3.106583000	-5.359532000	2.869890000
H	-5.101266000	2.472719000	1.730222000	H	-7.787204000	2.846083000	-1.536167000	H	-8.283864000	-0.534568000	1.386911000	C	5.809423000	0.505601000	-3.082344000
C	-3.684868000	3.444436000	3.033603000	C	-8.164915000	1.168207000	-0.223647000	C	2.509732000	2.416252000	-3.172934000	H	6.084764000	0.153942000	-4.077978000
H	-4.445471000	4.059085000	3.517236000	H	-9.249679000	1.280585000	-0.262361000	H	3.336695000	2.480324000	-3.881232000	C	-4.832381000	2.442997000	-1.468423000
C	-2.343110000	3.565136000	3.395319000	C	-7.595225000	0.138729000	0.533807000	C	3.698376000	-2.057401000	2.480732000	H	-5.813144000	2.600011000	-1.016973000
H	-2.039493000	4.279508000	4.162347000	H	-8.232170000	-0.553906000	1.086100000	H	2.606857000	-2.092247000	2.449219000	C	-1.007625000	6.166072000	2.106005000
C	-1.379470000	2.760592000	2.777903000	C	-6.208468000	-0.013527000	0.574629000	C	-1.510158000	4.848054000	0.136160000	H	-1.001712000	7.126866000	2.623233000
H	-0.335528000	2.858753000	3.075402000	H	-5.759117000	-0.825505000	1.150735000	H	-1.910176000	4.782339000	-0.876738000	C	5.915556000	2.183462000	-1.341533000
C	1.157486000	-3.479871000	-1.129147000	C	-2.931050000	1.564653000	-1.464821000	C	-1.027088000	3.693662000	0.777400000	H	6.275525000	3.145737000	-0.973980000
C	0.046699000	-4.309939000	-0.934020000	C	-2.965605000	0.897257000	-2.697856000	C	4.990095000	-0.286622000	-2.273186000	C	-4.711692000	2.256511000	-2.849494000
H	-0.614485000	-4.162537000	-0.081950000	H	-3.261444000	-0.152173000	-2.737239000	H	4.628903000	-1.245837000	-2.644992000	H	-5.600714000	2.262466000	-3.482084000
C	-0.266489000	-5.303768000	-1.866942000	C	-2.614382000	1.577005000	-3.863665000	C	5.091929000	1.400261000	-0.534108000	C	6.269860000	1.741776000	-2.621609000
H	-1.151123000	-5.923022000	-1.707073000	H	-2.633785000	1.054250000	-4.820875000	H	4.804761000	1.755778000	0.455831000	H	6.904114000	2.361107000	-3.257797000
C	0.531543000	-5.489278000	-2.997085000	C	-2.224136000	2.918057000	-3.801264000	C	2.254033000	-4.370668000	-2.561293000	C	2.563202000	3.595967000	1.120842000
H	0.285290000	-6.264818000	-3.724618000	H	-1.937873000	3.444320000	-4.712831000	H	1.977713000	-5.212558000	-3.197908000	C	-2.060161000	-5.763440000	1.018725000
C	1.637906000	-4.656730000	-3.203732000	C	-2.169374000	3.577699000	-2.570340000	C	1.958008000	3.576746000	-2.622351000	H	-1.869890000	-6.810474000	1.259824000
H	2.258633000	-4.777455000	-4.093412000	H	-1.840095000	4.616309000	-2.519090000	H	2.348298000	4.555162000	-2.907138000	C	2.738110000	5.028520000	1.072066000
C	1.940535000	-3.650700000	-2.286548000	C	-2.522759000	2.906015000	-1.399462000	C	3.853233000	-3.271336000	-1.111549000	H	1.758799000	5.517766000	1.180738000
H	2.770582000	-2.976656000	-2.494283000	H	-2.484003000	3.422839000	-0.440050000	H	4.825750000	-3.257332000	-0.615671000	H	3.187885000	5.314773000	0.111303000
C	3.118516000	-2.458121000	0.772149000					C	1.352669000	-3.319103000	-2.372281000	H	3.394003000	5.355369000	1.890844000
								H	0.376772000	-3.349014000	-2.860661000	C	-1.614583000	-5.229753000	-0.192840000
								C	4.621021000	0.158745000	-0.995834000	H	-1.077654000	-5.856600000	-0.906765000

Table S9: Optimized geometry of **20** (left) and **21** (right). XYZ coordinates in angstroms. BP86/def2-TZVP level of theory.



W	1.050284000	0.246606000	-1.267583000	H	4.036566000	-1.604857000	-2.984665000	W	-1.024579000	-0.072180000	-1.274201000	C	-2.490671000	-4.028420000	0.212069000
Sb	-0.113310000	-1.219109000	0.725139000	C	-3.986492000	1.323790000	1.643185000	Au	1.754754000	0.165196000	-1.213914000	H	-2.068759000	-3.833197000	1.198581000
Ag	-1.816049000	0.432789000	-1.098509000	H	-3.550994000	1.877194000	0.808401000	Sb	0.218891000	-0.866671000	1.032331000	C	6.369946000	-0.514509000	-0.616192000
P	-3.473378000	-0.890659000	0.067845000	C	4.037900000	1.867195000	3.053726000	P	-0.993326000	2.080366000	0.081625000	H	6.521715000	0.134294000	0.247313000
P	0.785969000	1.966920000	0.584413000	H	4.448075000	1.143891000	3.760246000	P	3.616654000	-0.453130000	-0.006740000	C	-1.168621000	3.820520000	-2.096158000
P	3.005749000	-1.065764000	-0.330314000	C	-4.713355000	-1.581350000	-2.302629000	P	-2.904560000	-1.233734000	-0.008026000	H	-2.142881000	3.362610000	-2.272219000
O	0.657958000	-1.965119000	-3.494893000	H	-3.691620000	-1.695937000	-2.673214000	C	-2.459839000	0.515651000	-2.527965000	C	-5.709583000	-1.523076000	-0.022474000
O	-0.481505000	1.986664000	-3.429468000	C	5.821083000	-1.177081000	-0.496278000	O	-3.266739000	0.851463000	-3.298439000	H	-5.531274000	-2.582231000	0.167177000
O	3.227849000	1.906825000	-2.826743000	H	5.700999000	-2.253170000	-0.626278000	O	0.527952000	1.373443000	-3.652544000	C	-4.170827000	2.263133000	2.634816000
C	-1.573602000	-2.776555000	0.921499000	C	6.142672000	1.582554000	-0.185250000	O	-0.482413000	-2.770393000	-2.838974000	H	-4.506193000	1.673502000	3.489393000
C	-1.400590000	-0.176285000	3.375945000	H	6.258283000	2.660431000	-0.065392000	C	0.098077000	0.835741000	-2.692697000	C	4.272299000	3.159177000	1.758822000
H	-1.771040000	-1.196547000	3.490915000	C	4.180402000	3.977586000	1.880300000	C	-0.717559000	-1.785125000	-2.259176000	H	4.071064000	4.203815000	1.518041000
C	0.858906000	-1.164106000	-2.668035000	H	4.700951000	4.914671000	1.675282000	C	1.874593000	-2.151050000	1.489845000	C	-3.288519000	3.764380000	0.442314000
C	-0.707118000	0.196594000	2.219888000	C	4.717126000	3.061865000	2.788655000	C	0.714117000	0.950534000	2.048772000	H	-2.947819000	4.363906000	-0.401382000
C	2.438873000	1.285336000	-2.229624000	H	5.663280000	3.276441000	3.287695000	C	0.121459000	2.118399000	1.554706000	C	-0.676437000	4.755900000	-3.006549000
C	2.296728000	2.503727000	1.483003000	C	2.860038000	-5.015298000	-1.539215000	C	-1.364939000	-1.459235000	2.366926000	H	-1.287212000	5.047173000	-3.862432000
C	2.834658000	1.591438000	2.408305000	H	2.521552000	-5.969737000	-1.132255000	C	3.178910000	-1.931148000	0.990136000	C	-3.573200000	-1.737569000	4.049628000
H	2.313544000	0.656961000	2.619360000	C	-7.103754000	-1.655403000	-2.678265000	C	-4.873539000	0.709529000	-0.455265000	H	-4.440455000	-1.832497000	4.704715000
C	2.825553000	-1.685646000	1.403819000	H	-7.949399000	-1.836865000	-3.343574000	H	-4.043984000	1.399148000	-0.591546000	C	4.901531000	2.822215000	2.961908000
C	1.544168000	-1.962269000	1.906469000	C	-6.245647000	-1.015146000	-0.503532000	C	-2.660266000	-1.422518000	1.821672000	H	5.192905000	3.607121000	3.661424000
C	-3.401847000	-4.894457000	1.050712000	H	-6.420890000	-0.699765000	0.525964000	C	5.079011000	-0.938667000	-0.960993000	C	0.601899000	5.298622000	-2.836845000
H	-4.115609000	-5.718361000	1.095279000	C	-4.622561000	-0.791334000	2.654012000	C	-2.524396000	2.681930000	0.897196000	H	0.990454000	6.018924000	-3.558389000
C	0.011067000	3.500004000	-0.049341000	H	-4.681933000	-1.880249000	2.615155000	C	-0.397075000	3.439255000	-0.985119000	C	-2.509084000	-5.334625000	-0.287945000
C	3.208493000	-2.630309000	-1.264194000	C	2.509191000	-2.693594000	4.004528000	C	1.607578000	-3.292774000	2.254144000	H	-2.092581000	-6.146634000	0.310491000
C	-1.632607000	0.766266000	4.377362000	H	2.384836000	-3.073700000	5.019890000	H	0.598010000	-3.480159000	2.624382000	C	-3.602477000	-4.552833000	-2.300829000
H	-2.186484000	0.483687000	5.273304000	C	3.947535000	-1.911030000	2.216261000	C	1.494847000	0.977490000	3.209001000	H	-4.037830000	-4.753446000	-3.281084000
C	-2.926449000	-2.555386000	0.589131000	H	4.947389000	-1.687050000	1.843605000	H	1.961106000	0.064371000	3.582958000	C	1.086774000	3.355119000	3.407114000
C	-0.234748000	1.502810000	2.055458000	C	7.101371000	-0.621125000	-0.469557000	C	-2.968706000	1.943705000	2.008319000	H	1.231060000	4.297447000	3.937497000
C	-0.090105000	1.336677000	-2.527505000	H	7.973181000	-1.268996000	-0.574778000	H	-2.371742000	1.114748000	2.388738000	C	1.384759000	4.901192000	-1.749800000
C	-2.061985000	-5.106100000	1.386873000	C	-4.432990000	2.000316000	2.777861000	C	4.185527000	-2.867801000	1.275839000	H	2.389383000	5.306594000	-1.617928000
H	-1.721455000	-6.096746000	1.692118000	H	-4.344697000	3.086373000	2.831320000	H	5.190078000	-2.714147000	0.878717000	C	7.267708000	-1.762747000	-2.489439000
C	-1.148382000	-4.049328000	1.318029000	C	3.809860000	-3.718406000	-3.348009000	C	4.130927000	0.810205000	1.186307000	H	8.122401000	-2.083751000	-3.086888000
H	-0.100206000	-4.226518000	1.565832000	H	4.211961000	-3.657831000	-4.360660000	C	0.886594000	3.979641000	-0.825254000	C	-7.257901000	0.304909000	-0.384196000
C	-4.935051000	-1.186201000	-0.971523000	C	7.264857000	0.759754000	-0.312925000	H	1.502733000	3.672087000	0.018729000	H	-8.282344000	0.672436000	-0.464089000
C	-3.831271000	-3.627368000	0.650157000	H	8.266559000	1.192640000	-0.296446000	C	-4.624653000	-0.641377000	-0.181764000	C	7.461743000	-0.927994000	-1.385361000
H	-4.874936000	-3.467873000	0.373551000	C	-5.795380000	-1.822122000	-3.148896000	C	-6.183234000	1.181347000	-0.554442000	H	8.466265000	-0.596296000	-1.118342000
C	1.387571000	-2.471814000	3.200490000	H	-5.618573000	-2.131975000	-4.180078000	H	-6.358600000	2.236603000	-0.767010000	C	-3.066106000	-5.599727000	-1.541195000
H	0.391552000	-2.672810000	3.599597000	C	3.376651000	-4.947285000	-2.835123000	C	0.298949000	3.323375000	2.257422000	H	-3.083914000	-6.619928000	-1.927792000
C	2.973432000	3.702976000	1.226976000	H	3.441764000	-5.848363000	-3.447095000	H	-0.185542000	4.235873000	1.905046000	C	4.758146000	0.472288000	2.394767000
H	2.564154000	4.428046000	0.523415000	C	-1.176434000	5.772951000	-1.195503000	C	4.881807000	-1.765952000	-2.080398000	H	4.931191000	-0.574200000	2.649915000
C	4.689231000	-0.352443000	-0.364435000	H	-1.634635000	6.659635000	-1.636610000	H	3.872169000	-2.079573000	-2.355737000	C	5.977063000	-2.181765000	-2.836078000
C	4.861508000	1.029078000	-0.211252000	C	-4.974126000	1.284604000	3.851358000	C	-3.021841000	-2.979281000	-0.548987000	H	5.823708000	-2.826561000	-3.702623000
H	3.993674000	1.677553000	-0.111637000	H	-5.311639000	1.813528000	4.744009000	C	3.887839000	2.155450000	0.870690000	C	-3.574225000	-3.247625000	-1.812560000
C	2.782031000	-3.861987000	-0.751111000	C	3.786266000	-2.405488000	3.512213000	H	3.387611000	2.403185000	-0.067754000	H	-3.979672000	-2.432452000	-2.415129000
H	2.395343000	-3.927669000	0.266463000	H	4.663556000	-2.563333000	4.141510000	C	1.689515000	2.184050000	3.882357000	C	-2.281951000	-1.786243000	4.583892000
C	-1.236216000	3.952798000	0.402441000	C	-1.826106000	5.083427000	-0.168973000	H	2.309449000	2.212244000	4.779124000	H	-2.135256000	-1.917376000	5.657112000
H	-1.755232000	3.417471000	1.196092000	H	-2.799069000	5.422327000	0.191053000	C	-3.763723000	-1.560583000	2.677852000	C	-4.942621000	3.331653000	2.164997000
C	-4.082096000	-0.075959000	1.575454000	C	-7.326190000	-1.249120000	-1.359307000	H	-4.775811000	-1.515187000	2.276357000	H	-5.888624000	3.579027000	2.648876000
C	0.644034000	4.178614000	-1.105652000	H	-8.344884000	-1.114763000	-0.991736000	C	2.623037000	-4.210274000	2.541689000	C	5.145131000	1.481910000	3.277757000
H	1.587980000	3.806957000	-1.506463000	C	-5.069070000	-0.108928000	3.787826000	H	2.399814000	-5.094946000	3.139827000	H	5.628879000	1.220059000	4.219895000
C	-1.150814000	2.073115000	4.230608000	H	-5.484105000	-0.668498000	4.627629000	C	-1.176234000	-1.643392000	3.741286000	C	-7.018446000	-1.048548000	-0.120964000
H	-1.321701000	2.809379000	5.017389000	N	-3.168187000	2.145195000	-1.888601000	H	-0.170864000	-1.653046000	4.166427000	H	-7.853547000	-1.739816000	0.003214000
C	-0.446397000	2.438767000	3.084583000	C	-3.373674000	3.106159000	-2.505024000	C	3.912500000	-3.995993000	2.052134000	C	-4.494314000	4.084322000	1.076721000
H	-0.047941000	3.450689000	2.991769000	C	-3.625992000	4.298190000	-3.284507000	H	4.709050000	-4.709895000	2.265741000	H	-5.084045000	4.927853000	0.713883000
C	0.058607000	5.313279000	-1.666799000	H	-4.271982000	4.055614000	-4.139539000								
H	0.564510000	5.834295000	-2.481050000	H	-2.671812000	4.700340000	-3.651605000								
C	3.717948000	-2.564137000	-2.571911000	H	-4.119232000	5.056448000	-2.661449000								

10.5 References

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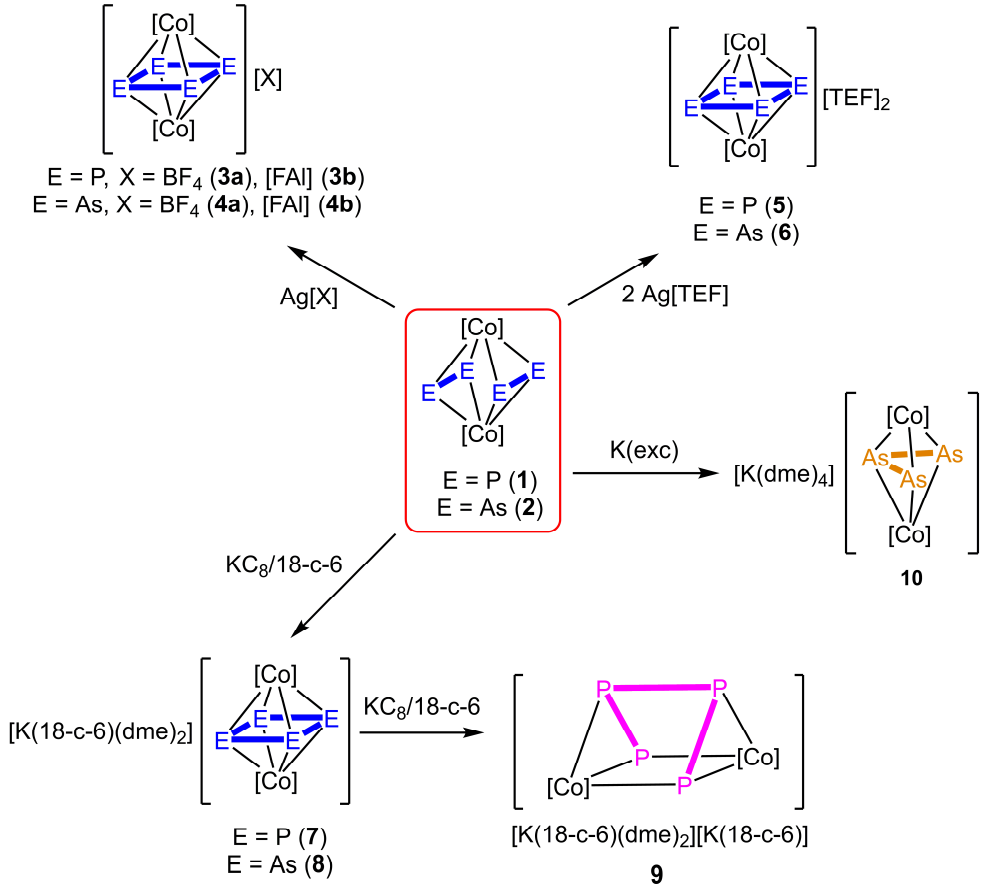
11. Summary

11.1 Element-Element Bond Formation upon Oxidation and Reduction

The redox chemistry of polypnictogen (E_n) ligand complexes was studied in our group in the past. Depending on the nature of the E_n ligand anionic and cationic radical species, respectively, are formed which dimerize subsequently under the formation of a new E-E bond. This behavior was observed for the oxidation and reduction of [Cp*Fe(η^5-P_5)] and for the oxidation of [{CpMo(CO)$_2$}(μ,η^2:η^2-E_2)] (E = P, As, Sb, Bi). When instead the E_n ligand is incorporated in a triple-decker scaffold like in [(CpMo)$_2$(μ,η^6:η^6-P_6)] the oxidation leads only to slight change in the geometry of the *cyclo*-P_6 ligand (bis-allylic distortion). Therefore, the question arose, how compounds including a high steric protection of two separated E_n ligands in a triple-decker moiety will respond to the withdrawal or additions of electrons, respectively. Therefore, the cobalt complexes [(Cp'''Co)$_2$(μ,η^2:η^2-E_2)$_2$] (E = P (**1**), As (**2**)) were selected as a suitable platform for such investigations.

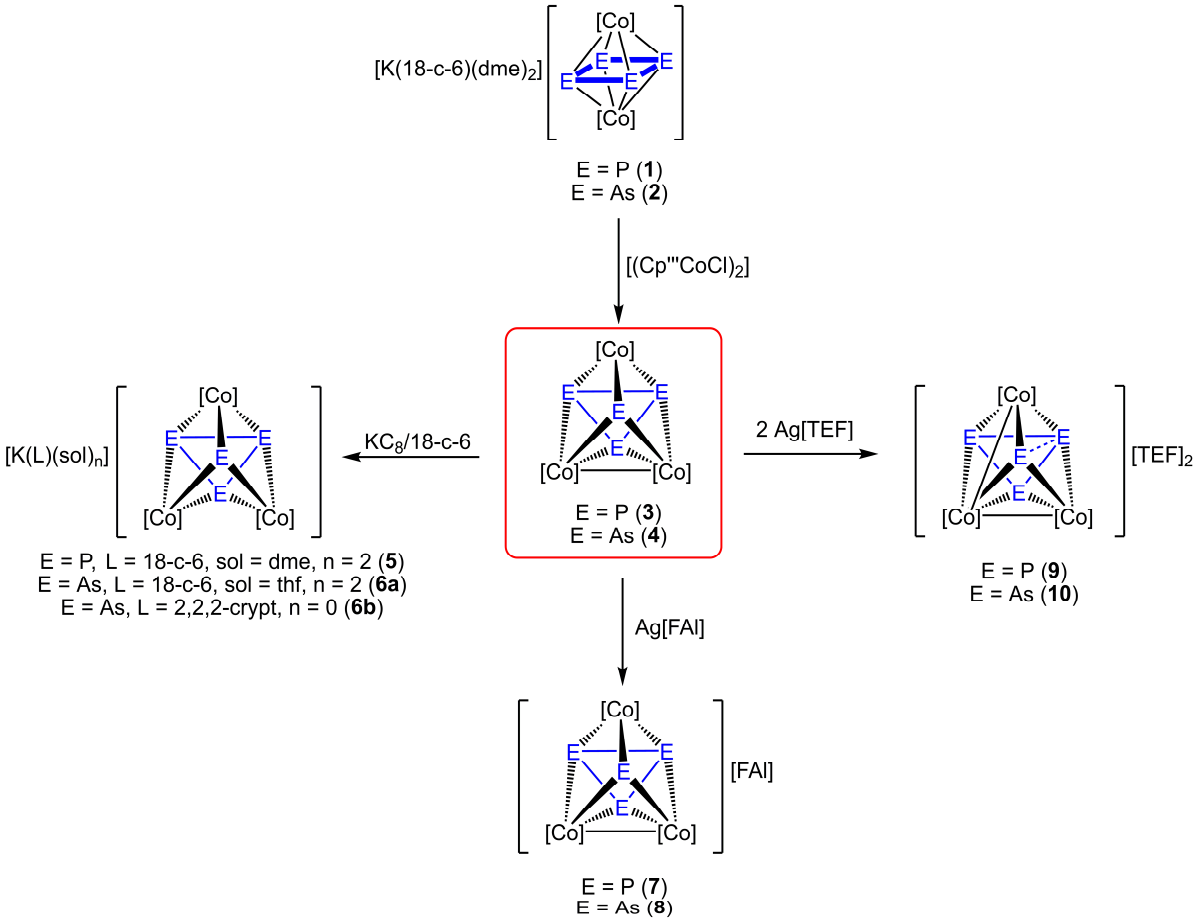


Scheme 1: Summary of the redox chemistry of **1** and **2** ([Co] = Cp'''Co).

First studies by cyclic voltammetry reveal several electrochemically reversible redox processes (**1**: two oxidation and one reduction, **2**: two oxidation and two reduction processes). During this work it was possible to synthesize two oxidized and two reduced species of both phosphorus (**1**) and arsenic derivative (**2**), while all obtained products are all highly sensitive towards air and moisture (cf. Scheme 1). Compound **1** and **2** can be oxidized with $AgBF_4$ or Ag[FAl] to the corresponding paramagnetic monocations $[(Cp'''Co)_2(\mu,\eta^4:\eta^4\text{-}E_4)]^+$ (**3a**, **3b**, **4a**, **4b**). The oxidation induces a cyclization of the two separated E_2 units (E_2^{2-}) in **1** and **2** to form a rectangular *cyclo*-E_4 (cyclo-butadiene like) ligand as middle deck (E_4^{3-}). The paramagnetism was studied by EPR spectroscopy and Evans NMR. Using two equivalents of Ag[TEF] gives the diamagnetic dications $[(Cp'''Co)_2(\mu,\eta^4:\eta^4\text{-}E_4)]^{2+}$ (**5**, **6**), which reveal a completely symmetric aromatic *cyclo*-E_4 ligand as middle deck (E_4^{2-}). On the other hand, the reduction of **1** and **2** with potassium graphite in presence of 18-c-6 yields the paramagnetic monoanions $[(Cp'''Co)_2(\mu,\eta^4:\eta^4\text{-}E_4)]^-$ (**7**, **8**) in which the former separated E_2 ligands have also been transformed into a *cyclo*-butadiene like *cyclo*-E_4 ligand (formally E_4^{5-}). The paramagnetism was studied by EPR spectroscopy and Evans-NMR measurements. The further reduction is different for the phosphorus and the arsenic complex, respectively. Reacting **1** with two equivalents KC_8 in the presence of 18-c-6 gives $[(Cp'''Co)_2(\mu,\eta^3:\eta^3\text{-}P_4)]^{2-}$ (**9**) where one P-P bond of the *cyclo*-butadiene ligand in **7** is cleaved and the ligand rearranges to a butadiene-like P_4 chain building up a Co_2P_4 prism as a central structural motif. Instead, the reaction of **2** with two equivalents KC_8 yields only the monoanion **8**. But by using an excess of potassium (four fold or higher) the abstraction of one As atom and the formation of $[(Cp'''Co)_2(\mu,\eta^3:\eta^3\text{-}As_3)]^-$ (**10**) is observed. Compound **10** shows an unprecedented allylic As_3 ligand as middle deck. All mentioned redox processes (except the formation of **10**) are fully reversible and can completely be reversed by the addition of stoichiometric amounts of KC_8 and $AgBF_4$, respectively. In conclusion, complexes **1** and **2** display unique platforms for versatile redox chemistry in over five and four redox stages, respectively, where all stages can be fully characterized. For this system the formation of new E-E bonds is observed for both oxidation and reduction processes, what is in the contrast to the common behavior, that oxidation leads to bond formation (e.g. S_8) and reduction leads to bond cleavages (e.g. cyclic phosphanes). Especially, the reversibility of the redox processes is remarkable.

11.2 Synthesis and Redox Chemistry of $[(Cp'''Co)_3E_4]$ (E = P, As) Cluster Complexes

The distinct redox chemistry $[(Cp'''Co)_2(\mu,\eta^2:\eta^2\text{-}E_2)_2]$ over several redox stages yielded a set of cationic and anion products, but all of them are extremely sensitive towards air and moisture. Therefore, the question arose, how the stability of such oxidized and reduces species can be increased while the distinct redox properties remain unchanged. Therefore, the introduction of a third {Cp'''Co} fragment was targeted and the redox behavior of the corresponding compounds $[(Cp'''Co)_3(\mu_3,\eta^2:\eta^2:\eta^2\text{-}E_3)(\mu_3\text{-}E)]$ (E = P (**3**), As (**4**) was investigated.



Scheme 2: Summary of the synthesis and the redox chemistry of $[(Cp'''Co)_3(\mu_3,\eta^2:\eta^2:\eta^2\text{-}E_3)(\mu_3\text{-}E)]$ (E = P (**3**), As (**4**), [Co] = Cp'''Co).

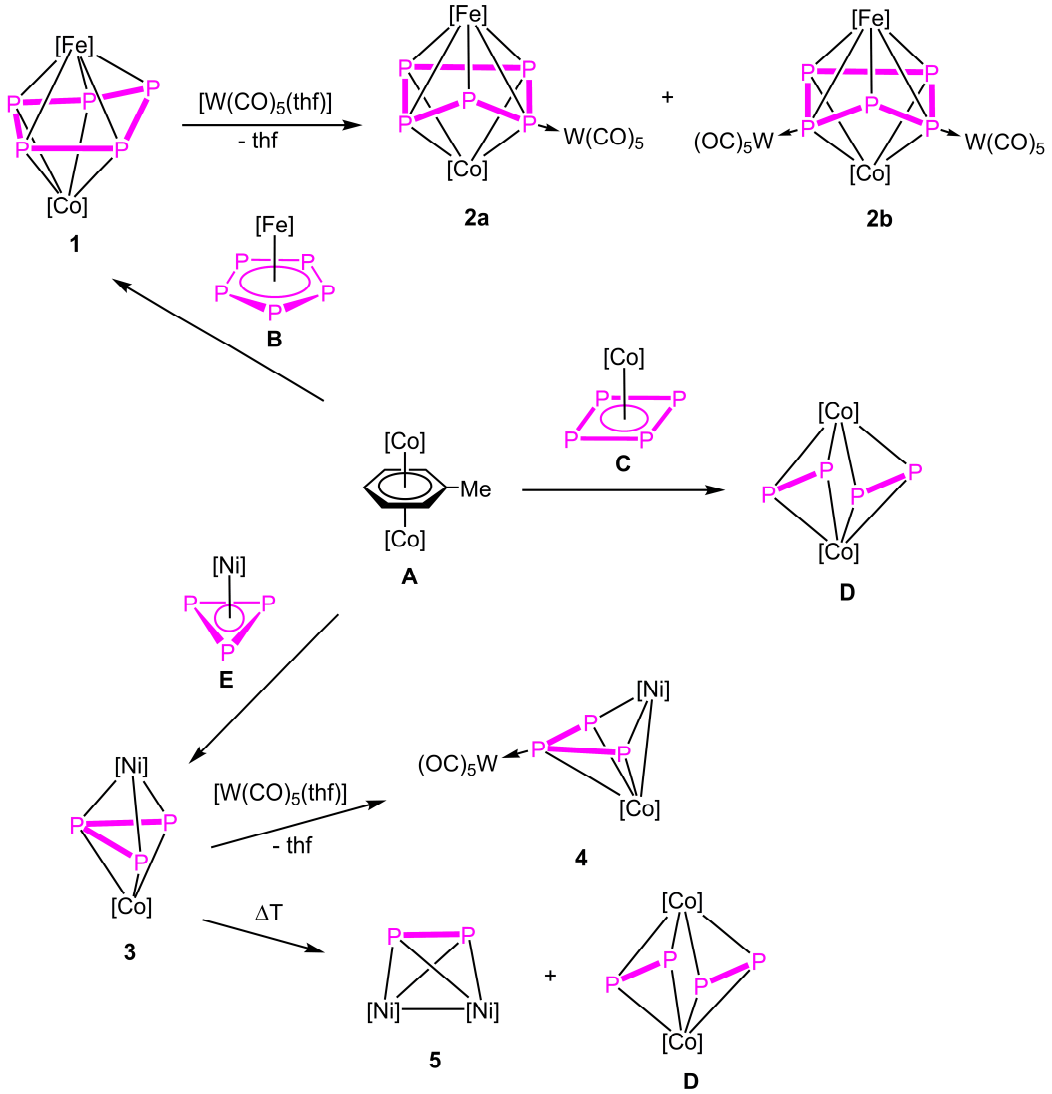
The reduced compounds $[(Cp'''Co)_2(\mu,\eta^4:\eta^4\text{-}E_4)]^-$ (E = P (**1**), As (**2**)) can be quenched with $[(Cp'''CoCl)_2]$ to yield the trinuclear cluster $[(Cp'''Co)_3(\mu_3,\eta^2:\eta^2:\eta^2\text{-}E_3)(\mu_3\text{-}E)]$ (E = P (**3**), As (**4**) (Scheme 2). First investigations of the redox behavior by cyclic voltammetry show a broad variety of electrochemically reversible reduction processes (**3**: two; **4**: one) and oxidation processes (**3**: three; **4**: two). While the structures in the solid state show a Co-Co bond and therefore a certain asymmetry in **3** and **4**, in solution these bonds are cleaved and all Cp''' ligands become equivalent in the related NMR spectra. Interestingly, an even electron number

and the behavior in the NMR suggest diamagnetic compounds, but both are EPR active (solid state and in solution) suggesting partial biradical character to be present. During this work the monoanions $[(Cp'''Co)_3(\mu_3,\eta^2{:}\eta^2{:}\eta^2\text{-}E_3)(\mu_3\text{-}E)]^-$ (**5**, **6a,b**), the cations $[(Cp'''Co)_3(\mu_3,\eta^2{:}\eta^2{:}\eta^2\text{-}E_3)(\mu_3\text{-}E)]^+$ (**7**, **8**) and the dications $[(Cp'''Co)_3(\mu_3,\eta^2{:}\eta^2{:}\eta^2\text{-}E_3)(\mu_3\text{-}E)]^{2+}$ (**9**, **10**) were synthesized by the reduction of **3** and **4**, respectively, with KC_8 and by the oxidation with Ag[FAl] and Ag[TEF], respectively. The Co_3E_4 core of the cluster **3** and **4** responds to the addition and withdrawal of electrons only with slight changes in the geometry. The former Co-Co bond in **3** and **4** is cleaved by reduction (**5**, **6a,b**) or remains unchanged upon the oxidation to **7** and **8**, respectively. The oxidation leads to a distortion with the third {Cp'''Co} being shifted into the direction of one of the other {Cp'''Co} fragments, which is stronger for the arsenic derivative compared to the phosphorus one. The second oxidation to **9** and **10** finally leads to the formation of a second Co-Co bond. All mentioned redox processes are fully reversible and can be reversed by addition of stoichiometric amounts of KC_8 and $AgBF_4$, respectively. In conclusion, the cluster complexes **3** and **4** show both a distinct redox chemistry of four redox stages, while the obtained products are much more stable compared to the species obtained from the reactions of $[(Cp'''Co)_2(\mu,\eta^2{:}\eta^2\text{-}E_2)_2]$ (cf. 11.1), especially for the cationic compounds.

11.3 A General Pathway to Heterobimetallic Triple-Decker Complexes

A new synthetic route to heterobimetallic triple-decker complexes was developed. The reactive cobalt-toluene triple-decker complex **A** can be reacted under very mild conditions with complexes containing aromatic polyphosphorus ligands like $[Cp^*Fe(\eta^5\text{-}P_5)]$ (**B**), $[Cp'''Co(\eta^4\text{-}P_4)]$ (**C**) and $[Cp'''Ni(\eta^3\text{-}P_3)]$ (**E**) to yield the new heterobimetallic triple-decker complexes $[(Cp^*Fe)(Cp'''Co)(\mu,\eta^5{:}\eta^4\text{-}P_5)]$ (**1**) and $[(Cp'''Co)(Cp'''Ni)(\mu,\eta^3{:}\eta^3\text{-}P_3)]$ (**3**) (cf. Scheme 3). The bent *cyclo*-P_5 ligand in **1** shows a tumbling process in solution indicated by an extremely broad signal in the $^{31}P\{^1H\}$ NMR spectrum. Depending on the temperature, this process becomes faster and all P atoms become equivalent on the NMR time scale (sharp singlet in the $^{31}P\{^1H\}$ NMR spectra at high temperatures) or can be slowed down and at low temperatures the *cyclo*-P_5 ligand is present analog to what is observed in the solid state (three sharp multiplets in the $^{31}P\{^1H\}$ NMR spectra at low temperatures). This dynamic process can be blocked by the coordination to $\{W(CO)_5\}$ units partially in $[(Cp^*Fe)(Cp'''Co)(\mu_3,\eta^5{:}\eta^4{:}\eta^1\text{-}P_5)\{W(CO)_5\}]$ (**2a**) or completely in $[(Cp^*Fe)(Cp'''Co)(\mu_4,\eta^5{:}\eta^4{:}\eta^1{:}\eta^1\text{-}P_5)\{W(CO)_5\}_2]$ (**2b**). The $^{31}P\{^1H\}$ NMR spectrum of **2a** at room temperature shows several broad signals which sharpen at low temperatures to five multiplets indicating that the P_5 ligand is still quite flexible. In contrast, the $^{31}P\{^1H\}$ NMR spectrum of **2b** shows already at room temperature three sharp

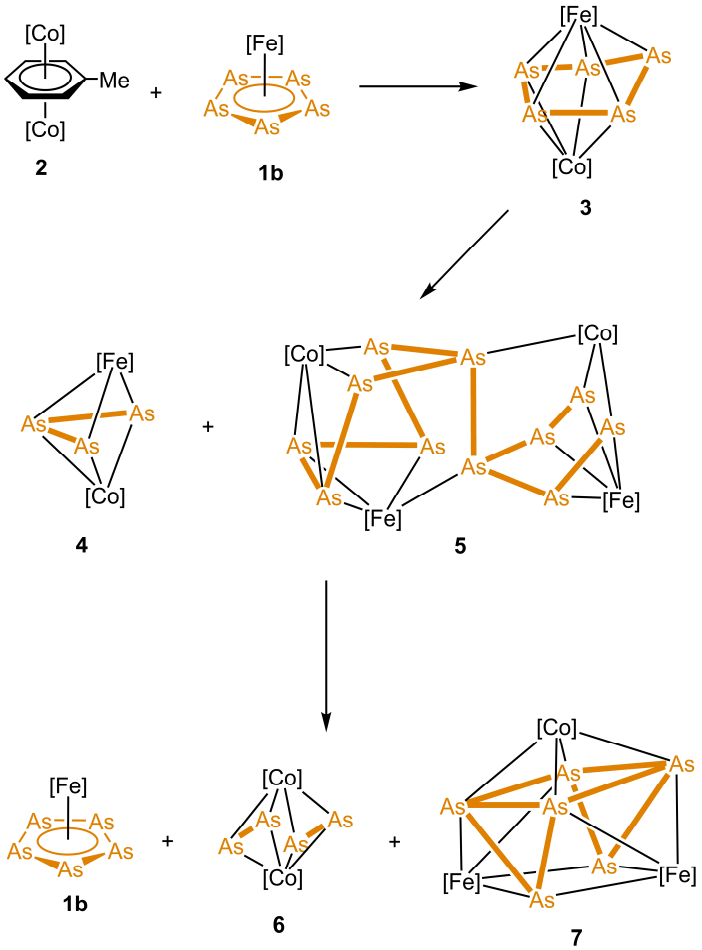
multiplets revealing a rigid structure. Complex **3** shows also a dynamic behavior in solution what is different to that of **1**. In solution an equilibrium between a *cyclo*-P_3 ligand and an open allylic P_3 chain ligand is present, which is dependent on the polarity of the solvent and on the temperature. The allylic form is predominant at low temperatures, especially in polar solvents. The equilibrium can be shifted completely to the allylic form when **3** is coordinated to a $\{W(CO)_5\}$ unit. Although the coordination of the outer P atoms would be energetically favored (only detected in traces in the $^{31}P\{^1H\}$ spectrum of the crude reaction mixture), the coordination of the central P atom of the P_3 ligand followed by a rearrangement to form $[(Cp'''Co)(Cp'''Ni)(\mu_3,\eta^3{:}\eta^2{:}\eta^1\text{-}P_3)\{W(CO)_5\}]$ (**4**) is observed. Compound **3** is thermally unstable. By thermolysis **3** can be converted selectively into the tetrahedrane complex $[(Cp'''Ni)_2(\mu,\eta^2{:}\eta^2\text{-}P_2)]$ (**5**) and $[(Cp'''Co)_2(\mu,\eta^2{:}\eta^2\text{-}P_2)_2]$ (**D**).



Scheme 3: Summary of the reactions of $[(Cp'''Co)_2(\mu,\eta^4{:}\eta^4\text{-}C_7H_8)]$ (**A**) with $[Cp^*Fe(\eta^5\text{-}P_5)]$ (B), $[Cp'''Co(\eta^4\text{-}P_4)]$ (**C**), $[Cp'''Ni(\eta^3\text{-}P_3)]$ (**E**) and subsequent reactions.

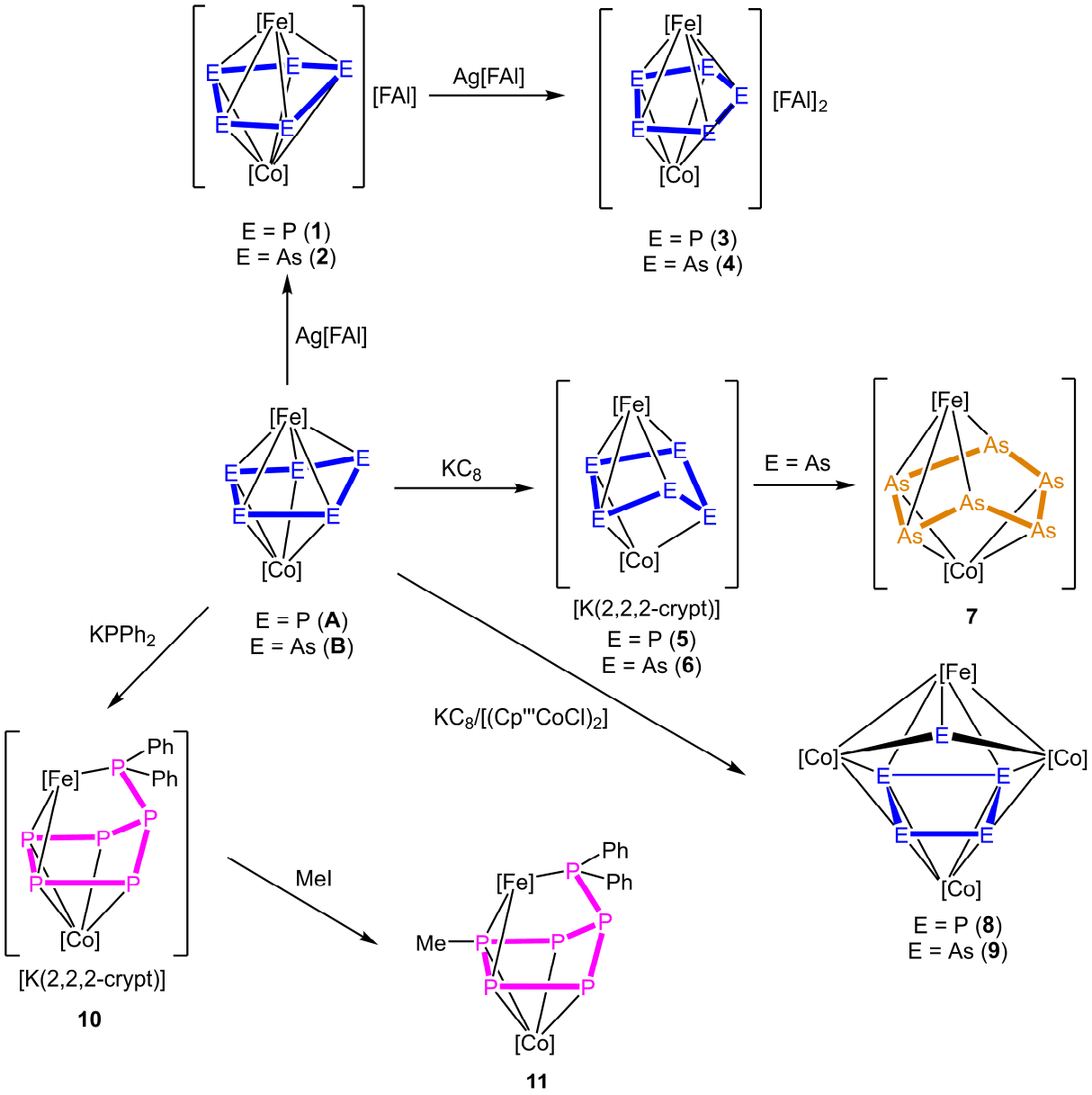
11.4 Synthesis of novel Heterobimetallic Arsenic Triple-Decker Complex and its versatile Fragmentation Chemistry

The reaction of the reactive cobalt-toluene triple-decker complex **2** with [Cp*Fe(η^5-As_5)] (**1b**) yields the metastable heterobimetallic triple-decker complex [(Cp*Fe)(Cp'''Co)(μ,η^5:η^4-As_5)] (**3**) (cf. Scheme 4). Compound **3** fragmentizes in the presence of acetonitrile or by thermal activation. Addition of MeCN to a solution of **3** in CH_2Cl_2 leads to a partial conversion into [(Cp*Fe)(Cp'''Co)(μ,η^3:η^3-As_3)] (**4**) and [(Cp*Fe)$_2$(Cp'''Co)$_2$(μ_4,η^4:η^4:η^3-As_{11})] (**5**). Compound **4** represents the second triple-decker complex with an open allylic As_3 ligand as a middle deck and **5** shows the largest reported polyarsenic ligand in a neutral heterometallic complex so far. Thermolysis of **3** leads to the formation of **1b**, **4**, **5**, [(Cp'''Co)$_2$(μ,η^2:η^2-As_2)$_2$] (**6**) and [(Cp*Fe)$_2$(Cp'''Co)(μ_3,η^2:η^2:η^2-As_3)$_2$] (**7**). Depending on the temperature and reaction time either a mixture of **1b**, **3**, **4**, **5**, **6** and **7** or a mixture of **1b**, **6** and **7** is obtained. The thermolysis of **3** in boiling decalin for three hours leads to a complete conversion of **3** into **1b**, **6** and **7**, what can be used to get access to **7** in a preparative scale. The conversion of three equivalents of **3** into each one equivalent **1b**, **6** and **7** proceeds stoichiometrically and is strongly exothermic.



Scheme 4: Synthesis of [(Cp*Fe)(Cp'''Co)(μ,η^5:η^4-As_5)] (**3**) and its fragmentation chemistry ([Co] = Cp'''Co, [Fe] = Cp*).

11.5 Functionalization of Heterobimetallic E_n Triple-Decker Complexes (E = P, As)



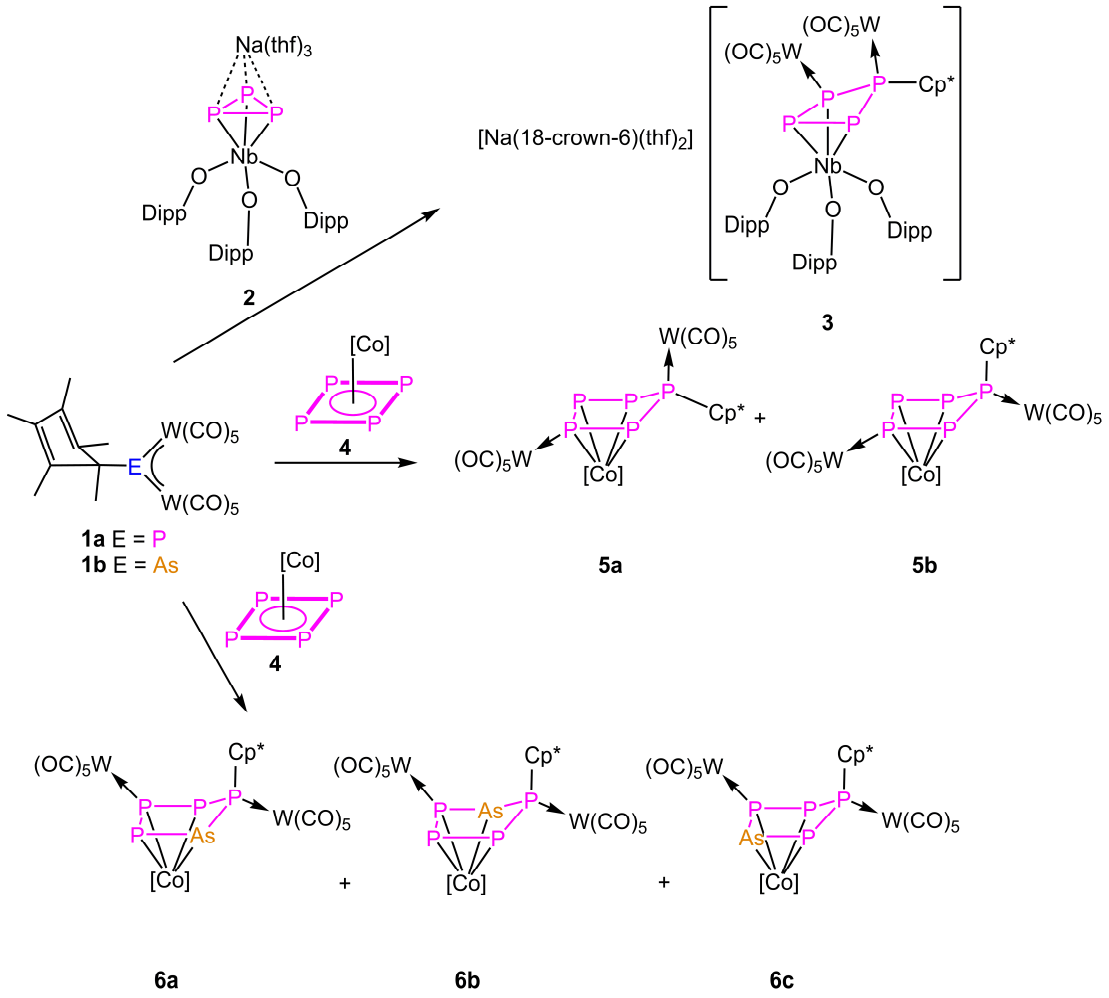
Scheme 5: Summarized redox chemistry, reactivity towards nucleophiles and electrophiles of [(Cp*Fe)(Cp'''Co)(μ,η^5:η^4-E_5)] (E = P (**A**), As (**B**)).

The redox chemistry of the heterobimetallic triple-decker complexes [(Cp*Fe)(Cp'''Co)(μ,η^5:η^4-E_5)] (E = P (**A**), As (**B**)) was first investigated by cyclic voltammetry and then realized in a preparative scale (cf. Scheme 5). The CVs show both two electrochemically reversible oxidation and one reversible reduction process. Using Ag[FAl] the monocations [(Cp*Fe)(Cp'''Co)(μ,η^5:η^5-E_5)][FAl] (**1**, **2**) and the dications [(Cp*Fe)(Cp'''Co)(μ,η^5:η^5-E_5)][FAl]$_2$ (**3**, **4**) can be obtained. The strongly bent *cyclo*-E_5 middle deck (**A**, **B**) responds to the withdrawal of electrons by the planarization of the ligand with all

E atoms coming into the coordination sphere of both metal fragments. In the monocations (**1**, **2**) the *cyclo*-E_5 ligand is still folded, while in the dications (**3**, **4**) the middle deck is completely planar. The reduction of **1** with KC_8 leads to [K(2,2,2-crypt)][(Cp*Fe)(Cp'''Co)(μ,η^4:η^3-P_5)] and the geometry of the middle deck changes in the opposite direction. The P atom which was initially bent into the direction of the Fe fragment is turned to the other side, now coordinated to Co. For **B** a similar structure to **5** is predicted (**6**) but could only be proofed by paramagnetic signals in the ^{1}H NMR spectrum and a strong resonance in the EPR spectrum of the precipitated solid from the crude reaction mixture. After a few weeks, [K(2,2,2-crypt)][(Cp*Fe)(Cp'''Co)(μ,η^4:η^4-As_6)] (**7**) can be obtained from the reaction mixture in high yields, which shows an As_6 ligand and additionally [(Cp*Fe)(Cp'''Co)(μ,η^3:η^3-As_3)] (cf. 11.4) could be identified as a side product. All redox processes except the formation of **7** are fully reversible and can be completely reversed by addition of stoichiometric amounts of KC_8 or $AgBF_4$, respectively. Both **A** and **B** can be *in situ* reduced twice (attempts to isolate the dianionic species yielded always only **5** and **7**) and quenched with [(Cp'''CoCl)$_2$] to yield the novel cluster complexes [(Cp*Fe)(Cp'''Co)$_3$(μ$_4$,η^4:η^2:η^2:η^2-E_4)(μ$_3$-E)] (E = P (**8**), As (**9**)). The cyclic voltammograms of **8** and **9** reveal both a set of electrochemically reversible redox processes, which might be of interest for subsequent transformations. **A** can be reacted with the nucleophile $KPPh_2$ to yield [K(2,2,2-crypt)][(Cp*Fe)(Cp'''Co)(μ,η^4:η^3-P_6Ph_2)] (**10**). The nucleophile was added to the P atom bent out of the plane (**A**) and is now coordinating to the {Cp*Fe} fragment. Compound **10** can be quenched with the electrophile MeI and [(Cp*Fe)(Cp'''Co)(μ,η^4:η^3-P_6Ph_2Me)] (**11**) can be isolated. The methyl substituent was attached to the backbone of P_6Ph_2 ligand and not to same P atom, where the nucleophile PPh_2^- was bond.

11.6 Ring Expansions of non-polar Polyphosphorus Rings

The pnictinidines Cp*E{W(CO)$_5$}$_2$ (E = P (**1a**), As (**1b**)) were reacted with the P_n ligand complexes [Na(thf)$_3$][(DippO)$_3$Nb(η^3-P_3)] (**2**) and [Cp'''Co(η^4-P_4)] (**4**) to expand the *cyclo*-P_3 and the *cyclo*-P_4 ligand, respectively (Scheme 6). The reaction of **1a** with **2** leads to the formation of [Na(18-c-6)(thf)$_2$][(ODipp)$_3$Nb{μ$_3$,η^3:η^1:η^1-P_4Cp*{W(CO)$_5$}$_2$}] (**3**) where the *cyclo*-P_3 ligand was expanded to a *cyclo*-P_4 ligand substituted by one Cp* and two {W(CO)$_5$} fragments. When **4** is reacted with **1a** two isomeric compounds [Cp'''Co(μ$_3$,η^4:η^1;η^1-P_5Cp*{W(CO)$_5$}$_2$)] (**5a**, **5b**) are formed. They differ only in the orientation of the Cp* and {W(CO)$_5$} substituent attached to the same P atom, while **5a** displays the kinetic and **5b** the thermodynamic product according to DFT calculations. The ratio of **5a** and **5b** can be controlled by the reaction temperature, with conducting the reaction at higher temperature the content of the thermodynamic product **5b** can be increased.

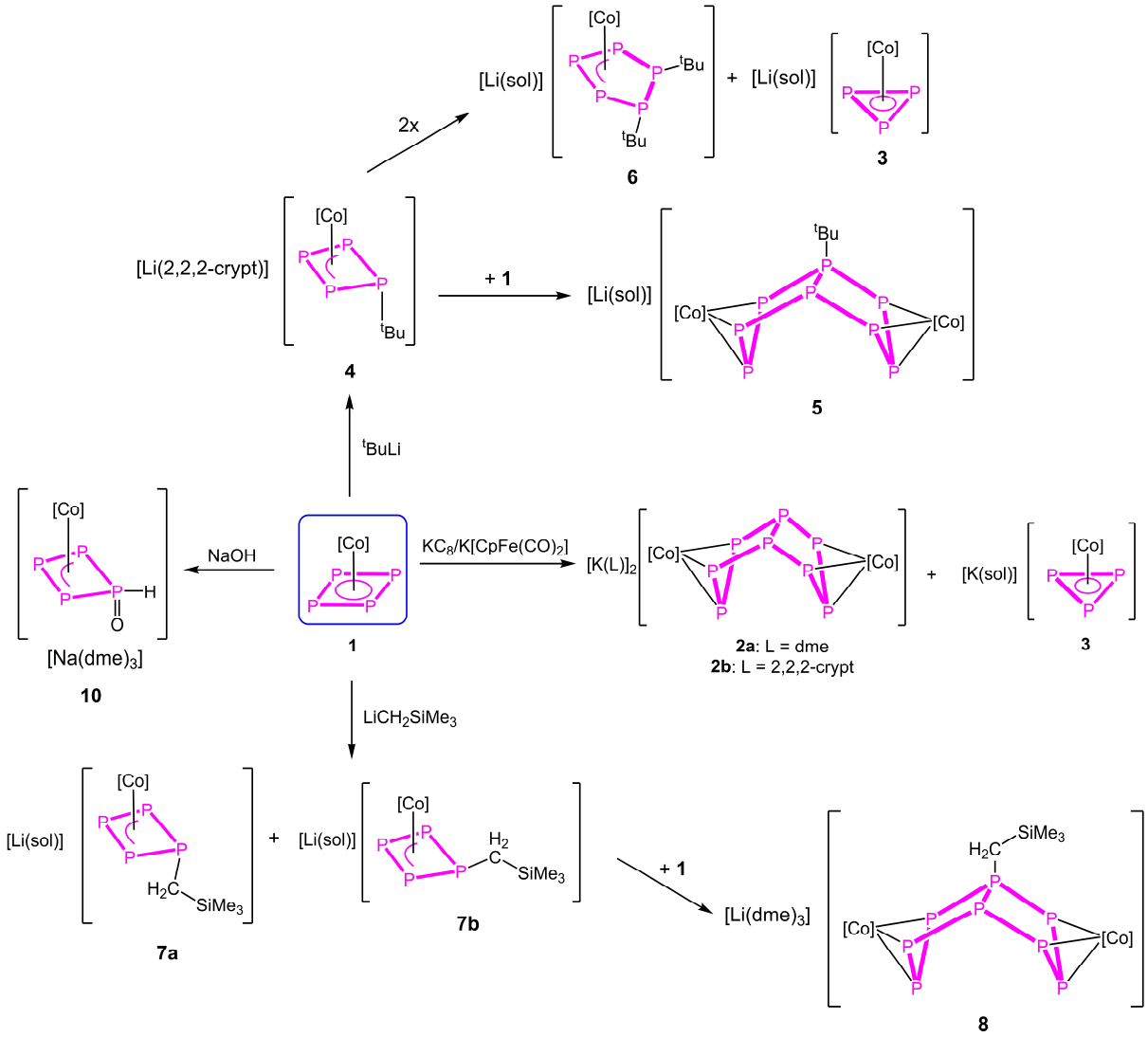


Scheme 6: Summarized reactivity of Cp*E{W(CO)$_5$}$_2$ (E = P (**1a**), As (**1b**)) with [Na(thf)$_3$][(DippO)$_3$Nb(η^3-P$_3$)] (**2**) and [Cp'''Co(η^4-P$_4$)] (**4**) ([Co] = Cp'''Co).

When the analog arsenic compound **1b** is used instead three isomers of [Cp'''Co(μ$_3$,η^4:η^1;η^1-P$_4$AsCp*{W(CO)$_5$}$_2$)] (**6a-c**) can be isolated, which crystallize together. These isomers differ only in the position of the As atoms. A possible reaction mechanism was suggest based on DFT calculations and time and temperature dependent ^{31}P{^{1}H} NMR spectroscopy. The first steps would be the adduct formation of **1b** and **4**, followed by the insertion into a P-P bond accompanied by a shift of one {W(CO)$_5$} fragment. These processes could not be tracked within the VT NMR studies. Several further 1,2 and 1,3 shifts of Cp* and {W(CO)$_5$} fragments can take place leading finally to the isomers **6a-c**. Three intermediates prior to the final formation of **6a-c** can be detected in the VT NMR spectra.

11.7 Transformation of the *cyclo*-P_4 Ligand in [Cp'''Co(η^4-P_4)]

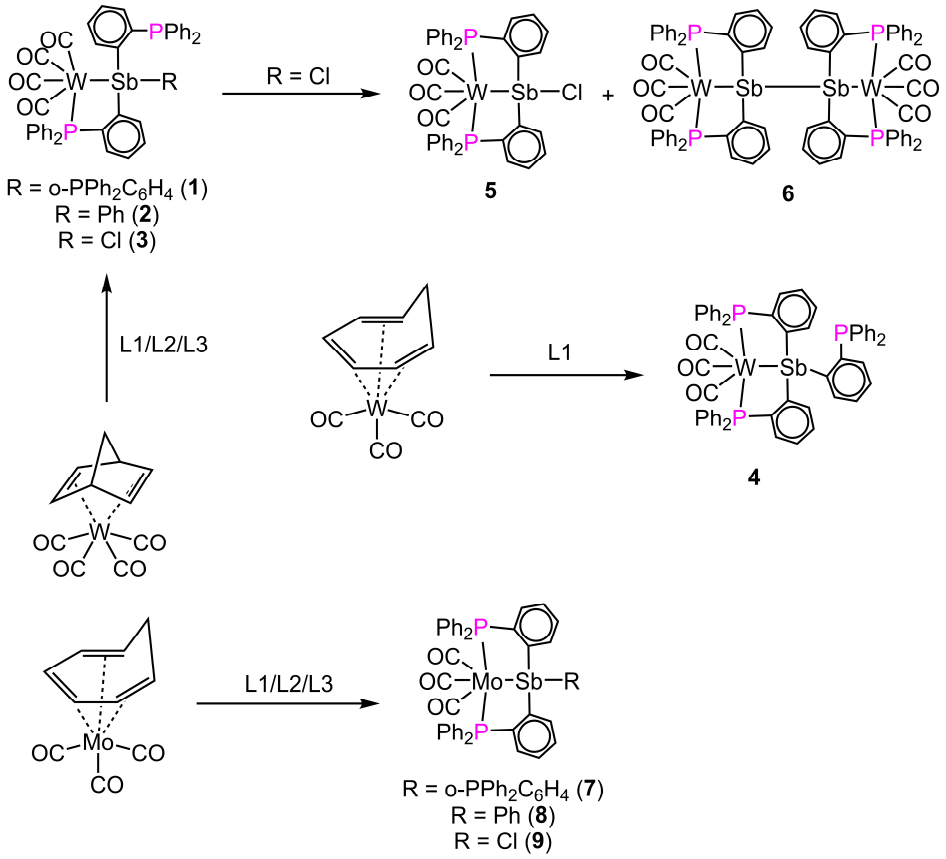
The reduction and reactivity towards main group nucleophiles of [Cp*Fe(η^5-P_5)] and [Cp'''Ni(η^3-P_3)] was studied by our group in the past. The reactions with main group nucleophiles like $LiNMe_2$, $LiCH_2SiMe_3$, $LiPH_2$, $LiPPh_2$, etc. yielded a set of mono and dinuclear complexes showing functionalized polyphosphorus ligands where the initial cycles are retained (three and five membered *cyclo*-P_n ligands). The reduction on the other hand leads either to a folding of the P_n ligand (e.g. in [Cp*Fe(η^4-P_5)]$^{2-}$) or an additional dimerization and formation of a new P-P bond (e.g. [(Cp*Fe)$_2$(μ,η^4:η^4-P_{10})]$^{2-}$) or an aggregation accompanied by fragmentation (e.g. [(Cp'''Ni)$_2$(μ,η^2:η^2-P_8)]$^{2-}$). This kind of chemistry should be extended to the *cyclo*-P_4 complex [Cp'''Co(η^4-P_4)] (**1**) which shows an high intrinsic tendency to dimerize irreversibly to give a linked 5- and 3-membered P_8 ligand in [(Cp'''Co)$_2$(μ,η^4:η^3-P_8)].



Scheme 7: Summarized reactivity of [Cp'''Co(η^4-P_4)] (**1**) with reducing agents and main group-based nucleophiles.

The reduction of [Cp'''Co(η^4-P_4)] (**1**) with usual reducing agents like K, KC_8 and KH proceeds unselectively yielding always a mixture of [(Cp'''Co)$_2$(μ,η^3:η^3-P_8)]$^{2-}$ (**2**) and [Cp'''Co(η^3-P_3)]$^-$ (**3**) (Scheme 7). With K[CpFe(CO)$_2$] a selective reduction of **1** to **2** can be achieved. Compound **2** shows a P_8 ligand consisting of two condensed five-membered rings (*cis*-bicyclo[3.3.0]octane) and is similar to realgar analog P_8 ligands, but with one cleaved P-P bond. In contrast to all reported P_8 ligand complexes with a realgar analog structural motif, **2** is coordinating in η^3:η^3 fashion to two {Cp'''Co} fragments, while in all other cases the P_8 ligand is coordinating in η^1:η^1 or η^2 to two or four metal fragments. **2** represents the first compound with such an open realgar-like P_8 ligand. Compound **1** can be functionalized with ^{t}BuLi and LiCH$_2$SiMe$_3$ yielding [Cp'''Co(η^3-P_4R)]$^-$ (R = ^{t}Bu (**4**), CH$_2$SiMe$_3$ (**7**), Scheme 7). The nucleophiles are attached to one P atom, which is now bent out of the plane of the former *cyclo*-P_4 ligand. The nucleophile can be located either in endo or in exo position. For R = ^{t}Bu only the endo isomer was detected in the ^{31}P{^{1}H} NMR spectrum and investigated by X-ray diffractions. The exo-isomer is energetically disfavored by 11.91 kJ·mol^{-1}. For R = CH$_2$SiMe$_3$ both isomers are very close in energy (0.92 kJ·mol^{-1}, endo-isomer being favored) and both isomers can be observed in the ^{31}P{^{1}H} NMR spectrum (ratio depending on reaction conditions). Only the endo isomer could be characterized by X-ray diffractions. **4** and **7** are still highly reactive and show further reactivity. They can act as a nucleophile on their own and react with another equivalent **1** to form [(Cp'''Co)$_2$(μ,η^3:η^3-P_8R)]$^-$ (R = ^{t}Bu (**5**), CH$_2$SiMe$_3$ (**9**)), which comprise an unprecedented substituted open realgar-like P_8R ligand. For R = ^{t}Bu a second subsequent pathway was observed. Formally two molecules of **4** dimerize and fragmentize into [Cp'''Co(η^3-P_3)]$^-$ (**3**) and [Cp'''Co(η^3-$P_5{}^t$Bu$_2$)]$^-$ (**6**), the latter comprising an unprecedented di-organo substituted *cyclo*-$P_5{}^t$Bu$_2$ ligand. For R = CH$_2$SiMe$_3$ no to **6** analog species [Cp'''Co(η^3-P_5(CH$_2$SiMe$_3$)$_2$)]$^-$ (**9**) was observed. Both subsequent pathways are strongly exothermic and probably driven by the release of the ring strain of the four membered ring. For R = ^{t}Bu the formation of **3** and **6** is more favored than the formation of **5**, while for R = CH$_2$SiMe$_3$ the situation is vice versa, the formation of **8** being more favored. Compound **1** can also be functionalized with NaOH as an oxygen-based nucleophile. The OH$^-$ unit is attached to one P atom of the *cyclo*-P_4 ligand followed by a suggested tautomerism and finally a P=O double bond and a P-H single bond are formed.

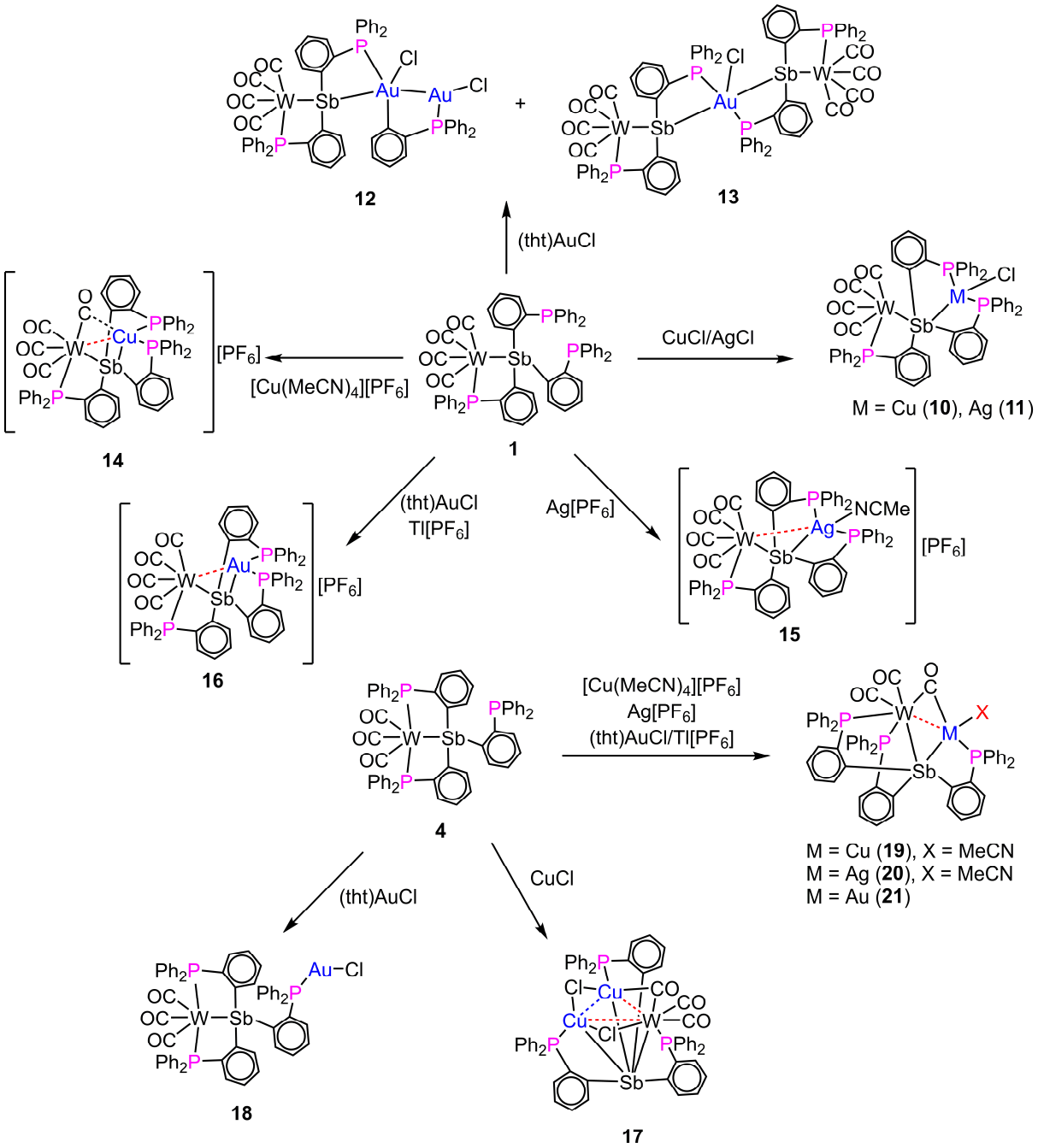
11.8 Phosphino-Stibine Ligands and their use in enforcing Metal-Metal Interactions



Scheme 8: Summarized reactions of **L1-3** with $[W(CO)_4(nbd)]$, $[W(CO)_3(cht)]$ and $[Mo(CO)_3(cht)]$.

The polydentate phosphino antimony ligands $(o\text{-}PPh_2C_6H_4)_2SbR$ (R = $o\text{-}PPh_2C_6H_4$ (**L1**), Ph (**L2**), Cl (**L3**)) can easily be introduced to tungsten and molybdenum carbonyl complexes by thermolysis with $[W(CO)_4(nbd)]$, $[W(CO)_3(cht)]$ and $[Mo(CO)_3(cht)]$ yielding **1**, **2**, **3**, **4**, **7**, **8** and **9** (Scheme 8). Compound **1** can also be transformed into **4** by irradiation or thermolysis. In both cases a column chromatographic workup is necessary what results in low yields. **3** is unstable toward irradiation and thermal stress. In the first step one CO ligand is removed and one of the free phosphine arms coordinates to the W atom, whereby **5** is formed. The chlorine atom of **5** can be removed, followed by a dimerization under formation of the distibane **6**. The complexes $[W(CO)_4\{\eta^1{:}\eta^1\text{-}(o\text{-}PPh_2C_6H_4)_3Sb\}]$ (**1**) and $[W(CO)_3\{\eta^1{:}\eta^1{:}\eta^1\text{-}(o\text{-}PPh_2C_6H_4)_3Sb\}]$ (**4**) were reacted with coinage metal salts with a coordinating anion (CuCl, AgCl, (tht)AuCl) and weakly coordinating anion ($[Cu(MeCN)_4][PF_6]$, $Ag[PF_6]$ and in situ generated $Au[PF_6]$), respectively, yielding $[W(CO)_4\{\eta^1{:}\eta^1{:}\eta^1{:}\eta^1{:}\eta^1\text{-}(o\text{-}PPh_2C_6H_4)_3Sb\}\{MCl\}]$ (M = Cu (**10**), Ag (**11**)), $[W(CO)_4\{\eta^1{:}\eta^1{:}\ \eta^1{:}\eta^1\text{-}(o\text{-}PPh_2C_6H_4)_2Sb\}\{\eta^1\text{-}AuCl(o\text{-}PPh_2C_6H_4)\}\{AuCl\}]$ (**12**) $[(W(CO)_4\{\eta^1{:}\eta^1{:}\eta^1{:}\eta^1\text{-}(o\text{-}PPh_2C_6H_4)_2Sb\})_2AuCl]$ (**13**), $[W(CO)_3(\mu\text{-}CO)\{\eta^1{:}\eta^1{:}\eta^1{:}\eta^1{:}\eta^1\text{-}(o\text{-}PPh_2C_6H_4)_3Sb\}\{Cu\}][PF_6]$ (**14**), $[W(CO)_4\{\eta^1{:}\eta^1{:}\eta^1{:}\eta^1{:}\eta^1\text{-}(o\text{-}PPh_2C_6H_4)_3Sb\}\{AgMeCN\}][PF_6]$ (**15**), $[W(CO)_4\{\eta^1{:}\eta^1{:}\eta^1{:}\eta^1{:}\eta^1\text{-}(o\text{-}PPh_2C_6H_4)_3Sb\}\{Au\}][PF_6]$ (**16**) $[W(CO)_2(\mu\text{-}$

CO){η^1:η^1:η^1:η^1:η^1-(o-$PPh_2C_6H_4)_3$Sb}{$Cu_2(\mu$-Cl)$_2$}] (**17**), [$W(CO)_3${η^1:η^1:η^1:η^1-(o-$PPh_2C_6H_4)_3$Sb}{AuCl}] (**18**) [$W(CO)_2(\mu$-CO){η^1:η^1:η^1:η^1-(o-$PPh_2C_6H_4)_3$Sb}{ML}][PF_6] (M = Cu, L = MeCN (**19**), M = Ag, L = MeCN (**20**), M = Au (**21**) (Scheme 9). All obtained products (**10-21**) reveal M-W (M = Cu, Ag, Au) bond distances below the sums of van der Waals radii, while only **19-21** show a significant metal-metal interaction according to DFT calculations.



Scheme 9: Summarized reactions of **1** and **4** with coinage metal salts with coordinating anions (Cl^-) and weakly coordinating anions ($[PF_6]^-$).

12. Appendices

12.1 Thematic List of Abbreviations

NMR spectroscopy	
NMR	nuclear magnetic resonance
δ	chemical shift
ppm	parts per million
s(NMR)	singlet
d(NMR)	doublet
t(NMR)	triplet
q(NMR)	quartet
sept(NMR)	septet
br(NMR)	broad
m(NMR)	multiplet
J(NMR)	coupling constant
Hz	Hertz [s^{-1}]
COSY	correlation spectroscopy
$\omega_{1/2}$	full width at half maximum
VT	various temperature
μ_{eff}	effective magnetic moment
μ_B	Bohr magneton

Mass spectrometry	
MS	mass spectrometry
ESI	electro spray ionization
LIFDI	liquid injection field desorption ionization
EI	electron impact
m/z	mass to charge ratio

Infrared spectroscopy	
IR	infrared spectroscopy
ATR	attenuated total reflection
w(IR)	weak
m(IR)	medium
s(IR)	strong
vs(IR)	very strong
$\bar{\upsilon}$	wavenumber [cm^{-1}]

Theoretical computations	
DFT	density functional theory
HOMO	highest occupied molecular orbital
LUMO	lowest unoccupied molecular orbital
SOMO	single occupied molecular orbital
vdW	van der Waals
WBI	Wiberg Bond Indices
NBO	Natural Bond Orbital

Weakly coordinating anions	
[TEF]	$[Al\{OC(CF_3)_3\}_4]$
[FAl]	$[FAl\{OC_6F_{10}(C_6F_5)\}_3]$

EPR spectroscopy	
EPR	electron paramagnetic resonance
g	gyromagnetic factor
iso	isotropic

Solvents		Other	
thf	tetrahydrofuran, C_4H_8O	Å	Angstroem, 1 Å = 10^{-10} m
dme	1,2-dimethoxyethane, $C_4H_{10}O_2$	T	temperature [°C] or [K]
Et_2O	diethyl ether, $C_4H_{10}O$	d	distance
DCM	dichloromethane, CH_2Cl_2	c	concentration [mol·L^{-1}]
tol	toluene, C_7H_8	M	metal (specified in text)
MeCN	acetonitrile, CH_3CN	L	ligand (specified in text)
		sol	solvent (specified in text)
		E	pnictogen atom (group 15)
		r.t.	room temperature
		EA	elemental analysis
		exc	excess
		CV	cyclic voltammetry
		R	organic residue
		X	halogen
		E_n	polypnictogen
		P_n	polyphosphorus
		As_n	polyarsenic

Ligands and Substituents

Cp	cyclopentadienyl, $C_5H_5^-$
Cp*	1,2,3,4,5-pentamethylcyclopentadienyl, $C_5Me_5^-$
Cp''	1,3-di-tertbutyl-cyclopentadienyl, $C_5H_3{}^tBu_2$
Cp'''	1,2,4-tri-tertbutyl-cyclopentadienyl, $C_5H_2{}^tBu_3$
Cp^R	cyclopentadienyl with variable residues
Cp^{tBu}	1-tertbutyl-2,3,4,5-tetramethyl-cyclopentadienyl, $C_5{}^tBuMe_4$
Cp^{iPr}	1,2,3,4-tetra-isopropyl-cyclopentadienyl
Cp^+	1-Ethyl-2,3,4,5-tetramethyl-cyclopentadienyl, C_5EtMe_4
Cp^{Me}	Methylcyclopentadienyl, C_5MeH_4
Cy	cyclohexyl
NN^{fc}	1,10-fc(NSitBuMe2)2, fc = ferrocenylene
TMEDA	tetramethylendiamine
N_3N	$N(CH_2CH_2NSiMe_3)_3{}^{3-}$
nacnac	1,3-diketiminato
12-c-4	12-crown-4, 1,4,7,10-tetraoxacyclododecane
18-c-6	18-crown-6, 1,4,7,10,13,16-hexaoxacyclooctadecane
2,2,2-crypt	[2,2,2-cryptand],4,7,13,16,21,24-Hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane
TPB	tris[2-(diisopropylphosphino)-phenylborane]
Me	methyl

^{t}Bu	tert-butyl
^{Ph}PP^{Cy}	PhP($CH_2CH_2PCy_2$)$_2$)
Ar^{Dipp}	2,6-diisopropyl
PHDI	bis(2,6-diisopropylphenyl)phenanthrene-9,10-diimin
nbd	2,5-norbonadiene
cht	1,3,5-cyloheptatriene

12.2 List of numbered compounds

12.2.1 Introduction

I $[Rh(PPh_3)Cl(\eta^2\text{-}P_4)]$
II $[Co(CO)_3(\eta^3\text{-}As_3)]$
IIIa $[(N_3N)W{\equiv}P]$
IIIb $[(N_3N)W{\equiv}As]$
IVa $[\{CpW(CO)_2\}\{Cr(CO)_5\}_2(\mu_3\text{-}P)]$
IVb $[\{CpW(CO)_2\}\{Cr(CO)_5\}_2(\mu_3\text{-}As)]$
Va $[(CpCr(CO)_2)_2(\mu,\eta^2\text{:}\eta^2\text{-}P_2)]$
Vb $[(CpCr(CO)_2)_2(\mu,\eta^2\text{:}\eta^2\text{-}As_2)]$
VIa $[(CpMo(CO)_2)_2(\mu,\eta^2\text{:}\eta^2\text{-}P_2)]$
VIb $[(CpMo(CO)_2)_2(\mu,\eta^2\text{:}\eta^2\text{-}As_2)]$
VIIa $[(CpW(CO)_2)_2(\mu,\eta^2\text{:}\eta^2\text{-}P_2)]$
VIIb $[(CpW(CO)_2)_2(\mu,\eta^2\text{:}\eta^2\text{-}As_2)]$
VIIIa $[(Cp'''Co)_2(\mu,\eta^2\text{:}\eta^2\text{-}P_2)_2]$
VIIIb $[(Cp'''Co)_2(\mu,\eta^2\text{:}\eta^2\text{-}As_2)_2]$
IXa $[Cp^RNi(\eta^3\text{-}P_3)]$
IXb $[Cp^RNi(\eta^3\text{-}As_3)]$
Xa $[Cp^RCr(CO)_2(\eta^3\text{-}P_3)]$
Xb $[Cp^RCr(CO)_2(\eta^3\text{-}As_3)]$
XIa $[Cp^RMo(CO)_2(\eta^3\text{-}P_3)]$
XIb $[Cp^RMo(CO)_2(\eta^3\text{-}As_3)]$
XIIa $[Cp^RW(CO)_2(\eta^3\text{-}P_3)]$
XIIb $[Cp^RW(CO)_2(\eta^3\text{-}As_3)]$
XIII $[(Cp'''Ni)_2(\mu,\eta^3\text{:}\eta^3\text{-}P_3)]$
XIV $[Cp^RV(CO)_2(\eta^4\text{-}P_4)]$
XVa $[Cp^RNb(CO)_2(\eta^4\text{-}P_4)]$
XVb $[Cp^RNb(CO)_2(\eta^4\text{-}As_4)]$
XVI $[Cp^RTa(CO)_2(\eta^4\text{-}P_4)]$
XVII $[Cp'''Co(\eta^4\text{-}P_4)]$
XVIII $[Cp^RCo(\mu_4,\eta^4\text{:}\eta^1\text{:}\eta^1\text{:}\eta^1\text{-}P_4)\{Cr(CO)_5\}_3]$
XIXa $[Cp^RCo(\mu_5,\eta^4\text{:}\eta^1\text{:}\eta^1\text{:}\eta^1\text{:}\eta^1\text{-}P_4)\{Cr(CO)_5\}_4]$
XIXb $[Cp^RRh(\mu_5,\eta^4\text{:}\eta^1\text{:}\eta^1\text{:}\eta^1\text{:}\eta^1\text{-}P_4)\{Cr(CO)_5\}_4]$
XX $[(Cp''Fe)\}(\mu,\eta^4\text{:}\eta^1\text{-}P_4)\ \{Cp''Fe(CO)_2\}]$
XXIa $[Cp^RFe(\eta^5\text{-}P_5)]$
XXIb $[Cp^RFe(\eta^5\text{-}As_5)]$
XXIIa $[Cp^RRu(\eta^5\text{-}P_5)]$
XXIIb $[Cp^RRu(\eta^5\text{-}As_5)]$
XXIIIa $[(Cp^RCr)_2(\mu,\eta^5\text{:}\eta^5\text{-}P_5)]$
XIIIb $[(Cp^RCr)_2(\mu,\eta^5\text{:}\eta^5\text{-}As_5)]$
XIV $[(Cp^RMo)_2(\mu,\eta^5\text{:}\eta^5\text{-}As_5)]$
XV $[(Cp^RMn)_2(\mu,\eta^5\text{:}\eta^5\text{-}P_5)]$
XVI $[(Cp^RTi)_2(\mu,\eta^6\text{:}\eta^6\text{-}P_6)]$
XVII $[(Cp^RV)_2(\mu,\eta^6\text{:}\eta^6\text{-}P_6)]$
XVIII $[(Cp^RNb)_2(\mu,\eta^6\text{:}\eta^6\text{-}P_6)]$
XXIXa $[(Cp^RMo)_2(\mu,\eta^6\text{:}\eta^6\text{-}P_6)]$
XXIXb $[(Cp^RMo)_2(\mu,\eta^6\text{:}\eta^6\text{-}As_6)]$
XXX $[(Cp^RW)_2(\mu,\eta^6\text{:}\eta^6\text{-}P_6)]$
XXXIa $[(Cp^RFe)(CpFe)(\mu,\eta^5\text{:}\eta^5\text{-}P_5)][PF_6]$
XXXIb $[(Cp^RFe)(CpFe)(\mu,\eta^5\text{:}\eta^5\text{-}As_5)][PF_6]$
XXXIIa $[(Cp^*Fe)(Cr(CO)_3)(\mu,\eta^5\text{:}\eta^5\text{-}P_5)]$
XXXIIb $[(Cp^*Fe)(Cr(CO)_3)(\mu,\eta^5\text{:}\eta^5\text{-}As_5)]$
XXXIIIa $[(Cp^*Fe)(Mo(CO)_3)(\mu,\eta^5\text{:}\eta^5\text{-}P_5)]$
XXXIIIb $[(Cp^*Fe)(Mo(CO)_3)(\mu,\eta^5\text{:}\eta^5\text{-}As_5)]$
XXXIV $[(Cp^*Fe)(W(CO)_3)(\mu,\eta^5\text{:}\eta^5\text{-}As_5)]$
XXXVa $[(Cp^*Fe)(Cp''Ta)(\mu,\eta^4\text{:}\eta^3\text{-}P_5)]$
XXXVb $[(Cp^*Fe)(Cp''Ta)(\mu,\eta^4\text{:}\eta^3\text{-}As_5)]$
XXXVI $[(Cp^*Fe)(Cp^*Rh(CO))(\mu,\eta^5\text{:}\eta^2\text{-}As_5)]$
XXXVII $[(Cp^*Fe)(Cp^*Ir(CO))(\mu,\eta^5\text{:}\eta^2\text{-}P_5)]$
XXXVIII $[(Cp^*Fe)(Cp^*Ir(CO))_2(\mu,\eta^4\text{:}\eta^1\text{:}\eta^1\text{-}P_5)]$
XXXIX $[(Cp^*Fe)(Cp^*Ir(CO))_4(\mu,\eta^4\text{:}\eta^2\text{:}\eta^1\text{:}\eta^1\text{:}\eta^1\text{-}P_5)]$
XL $[Cp^*Fe(\mu_3,\eta^5\text{:}\eta^1\text{:}\eta^1\text{-}P_5)CuCl]_n$
XLI $[Cp^*Fe(\mu_4,\eta^5\text{:}\eta^2\text{:}\eta^2\text{:}\eta^1\text{-}As_5)(CuCl)_3(MeCN)]_n$
XLII $[Cp^*Fe(\mu_3,\eta^5\text{:}\eta^2\text{:}\eta^1\text{-}P_5)Ag]_n[TEF]_n$
XLIII $[(Cp^*Fe)_2(\mu,\eta^4\text{:}\eta^4\text{-}P_{10})]^{2+}$
XLIV $[(Cp^*Fe)_2(\mu,\eta^4\text{:}\eta^4\text{-}P_{10})]^{2-}$
XLV $[Cp^*Fe(\eta^4\text{-}P_5)]^{2-}$
XLVI $[(Cp^*Fe)_2(\mu,\eta^2\text{:}\eta^2\text{-}As_2)_2]^{-}$
XLVII $[(Cp^*Fe)_2(\mu,\eta^4\text{:}\eta^4\text{-}As_{10})]^{2-}$
XLVIII $[(Cp^*Fe)_2\ (\mu,\eta^2\text{:}\eta^2\text{:}\eta^2\text{:}\eta^2\text{-}As_{14})]^{2-}$
XLIX $[(Cp^*Fe)_4(\mu_4,\eta^4\text{:}\eta^3\text{:}\eta^3\text{:}\eta^2\text{:}\eta^2\text{:}\eta^1\text{:}\eta^1\text{-}As_{18})]^{2-}$
L $[Cp^*Fe(\eta^4\text{-}P_5CH_2SiMe_3)]^{-}$
LI $[Cp^*Fe(\eta^4\text{-}P_5NMe_2)]^{-}$
LII $[(Cp^*Fe)_2(\mu,\eta^4\text{:}\eta^4\text{-}P_5NP_5)]^{3-}$
LIII $[Cp^*Fe(\eta^4\text{-}P_5PH_2)]^{-}$
LIV $[(Cp^*Fe)_2(\mu,\eta^4\text{:}\eta^4\text{-}P_5PHP_5)]^{2-}$
LV $[(Cp^*Fe)(Cp'''Cr)(\mu,\eta^5\text{:}\eta^4\text{-}P_5CH_2SiMe_3)]$
LVI $[(Cp^*Fe)(Cp'''Fe)(\mu,\eta^5\text{:}\eta^4\text{-}P_5NMe_2)]$
LVII $[(Cp^*Fe)(Cp'''Co)(\mu,\eta^5\text{:}\eta^4\text{-}P_5CH_2SiMe_3)]$
LVIII $[(Cp^*Fe)(Cp'''Co)(\mu,\eta^5\text{:}\eta^4\text{-}P_5NMe_2)]$
LIX $[(Cp^*Fe)(Cp'''Ni)(\mu,\eta^5\text{:}\eta^4\text{-}P_5NMe_2)]$

12.2.2 Element-Element Bond Formation upon Oxidation and Reduction

A	$[Cp^*Fe(\eta^4\text{-}P_5)]^{2-}$	**4a**	$[(Cp'''Co)_2(\mu,\eta^4\text{:}\eta^4\text{-}As_4)][BF_4]$
B	$[(Cp^*Fe)_2(\mu,\eta^4\text{:}\eta^4\text{-}P_{10})]^{2+}$	**4b**	$[(Cp'''Co)_2(\mu,\eta^4\text{:}\eta^4\text{-}As_4)][FAl]$
C	$[\{CpMo(CO)_2\}_4(\mu,\eta^2\text{:}\eta^2\text{:}\eta^2\text{:}\eta^2\text{-}P_4)]^{2+}$	**5**	$[(Cp'''Co)_2(\mu,\eta^4\text{:}\eta^4\text{-}P_4)][TEF]_2$
D	$[\{CpMo(CO)_2\}_4(\mu,\eta^2\text{:}\eta^2\text{:}\eta^2\text{:}\eta^2\text{-}P_4)]^{2+}$	**6**	$[(Cp'''Co)_2(\mu,\eta^4\text{:}\eta^4\text{-}As_4)][TEF]_2$
E	$[(Cp^RMo)_2(\mu,\eta^6\text{:}\eta^6\text{-}P_6)]^{+}$	**7**	$[K(18\text{-}c\text{-}6)(dme)_2][(Cp'''Co)_2(\mu,\eta^4\text{:}\eta^4\text{-}P_4)]$
1	$[(Cp'''Co)_2(\mu,\eta^2\text{:}\eta^2\text{-}P_2)_2]$	**8**	$[K(18\text{-}c\text{-}6)(dme)_2][(Cp'''Co)_2(\mu,\eta^4\text{:}\eta^4\text{-}As_4)]$
2	$[(Cp'''Co)_2(\mu,\eta^2\text{:}\eta^2\text{-}As_2)_2]$	**9**	$[K(18\text{-}c\text{-}6)(dme)_2][K(18\text{-}c\text{-}6)][(Cp'''Co)_2(\mu,\eta^3\text{:}\eta^3\text{-}P_4)]$
3a	$[(Cp'''Co)_2(\mu,\eta^4\text{:}\eta^4\text{-}P_4)][BF_4]$	**I9-a**	$[(Cp'''Co)_2(\mu,\eta^4\text{:}\eta^4\text{-}P_4)]^{2-}$
3b	$[(Cp'''Co)_2(\mu,\eta^4\text{:}\eta^4\text{-}P_4)][FAl]$	**10**	$[K(dme)_4][(Cp'''Co)_2(\mu,\eta^3\text{:}\eta^3\text{-}As_3)]$

12.2.3 Synthesis and Redox Chemistry $[(Cp'''Co)_3E_4]$ (E = P, As) Cluster Complexes

A	$[(Cp^RMo)_2(\mu,\eta^6\text{:}\eta^6\text{-}P_6)]$	**5**	$[K(18\text{-}c\text{-}6)(dme)_2][(Cp'''Co)_3(\mu_3,\eta^2\text{:}\eta^2\text{:}\eta^2\text{-}P_3)(\mu_3\text{-}P)]$
B	$[(Cp'''Co)_2(\mu,\eta^2\text{:}\eta^2\text{-}P_2)_2]$	**6a**	$[K(18\text{-}c\text{-}6)(thf)_2][(Cp'''Co)_3(\mu_3,\eta^2\text{:}\eta^2\text{:}\eta^2\text{-}As_3)(\mu_3\text{-}As)]$
C	$[(Cp'''Co)_2(\mu,\eta^2\text{:}\eta^2\text{-}As_2)_2]$	**6b**	$[K(2,2,2\text{-crypt})][(Cp'''Co)_3(\mu_3,\eta^2\text{:}\eta^2\text{:}\eta^2\text{-}As_3)(\mu_3\text{-}As)]$
D	$[(Cp^*Fe)(Cp'''Co)(\mu,\eta^5\text{:}\eta^4\text{-}P_5)]$	**7**	$[(Cp'''Co)_3(\mu_3,\eta^2\text{:}\eta^2\text{:}\eta^2\text{-}P_3)(\mu_3\text{-}P)][FAl]$
1	$[K(18\text{-}c\text{-}6)(dme)_2][(Cp'''Co)_2(\mu,\eta^4\text{:}\eta^4\text{-}P_4)]$	**8**	$[(Cp'''Co)_3(\mu_3,\eta^2\text{:}\eta^2\text{:}\eta^2\text{-}As_3)(\mu_3\text{-}As)][FAl]$
2	$[K(18\text{-}c\text{-}6)(dme)_2][(Cp'''Co)_2(\mu,\eta^4\text{:}\eta^4\text{-}As_4)]$	**9**	$[(Cp'''Co)_3(\mu_3,\eta^2\text{:}\eta^2\text{:}\eta^2\text{-}P_3)(\mu_3\text{-}P)][TEF]_2$
3	$[(Cp'''Co)_3(\mu_3,\eta^2\text{:}\eta^2\text{:}\eta^2\text{-}P_3)(\mu_3\text{-}P)]$	**10**	$[(Cp'''Co)_3(\mu_3,\eta^2\text{:}\eta^2\text{:}\eta^2\text{-}As_3)(\mu_3\text{-}As)][TEF]_2$
4	$[(Cp'''Co)_3(\mu_3,\eta^2\text{:}\eta^2\text{:}\eta^2\text{-}As_3)(\mu_3\text{-}As)]$		

12.2.4 A General Pathway to Heterobimetallic Triple-Decker Complexes

A	$[(Cp'''Co)_2(\mu,\eta^4\text{:}\eta^4\text{-}C_7H_8)]$	**2a**	$[(Cp^*Fe)(Cp'''Co)(\mu_3,\eta^5\text{:}\eta^4\text{:}\eta^1\text{-}P_5)\{W(CO)_5\}]$
B	$[Cp^*Fe(\eta^5\text{-}P_5)]$	**2b**	$[(Cp^*Fe)(Cp'''Co)(\mu_4,\eta^5\text{:}\eta^4\text{:}\eta^1\text{:}\eta^1\text{-}P_5)\{W(CO)_5\}_2]$
C	$[Cp'''Co(\eta^4\text{-}P_4)]$	**3**	$[(Cp'''Co)(Cp'''Ni)(\mu,\eta^3\text{:}\eta^3\text{-}P_3)]$
D	$[(Cp'''Co)_2(\mu,\eta^2\text{:}\eta^2\text{-}P_2)_2]$	**4**	$[(Cp'''Co)(Cp'''Ni)(\mu_3,\eta^3\text{:}\eta^2\text{:}\eta^1\text{-}P_3)\{W(CO)_5\}]$
E	$[Cp'''Ni(\eta^3\text{-}P_3)]$	**5**	$[(Cp'''Ni)_2(\mu,\eta^2\text{:}\eta^2\text{-}P_2)]$
1	$[(Cp^*Fe)(Cp'''Co)(\mu,\eta^5\text{:}\eta^4\text{-}P_5)]$		

12.2.5 Synthesis of a novel Heterobimetallic Arsenic Triple-Decker Complex and its versatile Fragmentation Chemistry

A	$[(Cp^*Fe)(Cp^*Rh(CO))(\mu,\eta^5{:}\eta^2\text{-}As_5)]$
B	$[(Cp^*Fe)(Cp^*Ir(CO))(\mu,\eta^5{:}\eta^2\text{-}P_5)]$
C	$[(Cp^*Fe)(Cp^*Ir(CO))_2(\mu,\eta^4{:}\eta^1{:}\eta^1\text{-}P_5)]$
D	$[(Cp^*Fe)(Cp'''Ta)(\mu,\eta^4{:}\eta^3\text{-}P_5)]$
E	$[(Cp^*Fe)(Cp'''Ta)(\mu,\eta^4{:}\eta^3\text{-}As_5)]$
1a	$[Cp^*Fe(\eta^5\text{-}P_5)]$
1b	$[Cp^*Fe(\eta^5\text{-}As_5)]$
2	$[(Cp'''Co)_2(\mu,\eta^4{:}\eta^4\text{-}C_7H_8)]$
3	$[(Cp^*Fe)(Cp'''Co)(\mu,\eta^5{:}\eta^4\text{-}As_5)]$
4	$[(Cp^*Fe)(Cp'''Co)(\mu,\eta^3{:}\eta^3\text{-}As_3)]$
5	$[(Cp^*Fe)_2(Cp'''Co)_2(\mu_4,\eta^4{:}\eta^4{:}\eta^4{:}\eta^3\text{-}As_{11})]$
6	$[(Cp'''Co)_2(\mu,\eta^2{:}\eta^2\text{-}As_2)_2]$
7	$[(Cp^*Fe)_2(Cp'''Co)(\mu_3,\eta^2{:}\eta^2{:}\eta^2\text{-}As_3)_2]$

12.2.6 Functionalization of Heterobimetallic E_n Triple-Decker Complexes (E = P, As)

I	$[(Cp^*Fe)_2(\mu,\eta^4{:}\eta^4\text{-}P_{10})]^{2-}$
II	$[Cp^*Fe(\eta^4\text{-}P_5)]^{2-}$
III	$[(Cp^*Fe)_2(\mu,\eta^4{:}\eta^4\text{-}P_{10})]^{2+}$
IV	$[\{CpMo(CO)_2\}_2(\mu,\eta^2{:}\eta^2\text{-}E_2)]$
V	$[(Cp^RMo)_2(\mu,\eta^6{:}\eta^6\text{-}P_6)]^+$
VI	$[(Cp'''Co)_2(\mu,\eta^4{:}\eta^4\text{-}E_4)]^{+/2+/-}$
A	$[(Cp^*Fe)(Cp'''Co)(\mu,\eta^5{:}\eta^4\text{-}P_5)]$
B	$[(Cp^*Fe)(Cp'''Co)(\mu,\eta^5{:}\eta^4\text{-}As_5)]$
1	$[(Cp^*Fe)(Cp'''Co)(\mu,\eta^5{:}\eta^5\text{-}P_5)][FAl]$
2	$[(Cp^*Fe)(Cp'''Co)(\mu,\eta^5{:}\eta^5\text{-}As_5)][FAl]$
3	$[(Cp^*Fe)(Cp'''Co)(\mu,\eta^5{:}\eta^5\text{-}P_5)][FAl]_2$
4	$[(Cp^*Fe)(Cp'''Co)(\mu,\eta^5{:}\eta^5\text{-}As_5)][FAl]_2$
5	[K(2,2,2-crypt][$(Cp^*Fe)(Cp'''Co)(\mu,\eta^4{:}\eta^3\text{-}P_5)$]
6	$[(Cp^*Fe)(Cp'''Co)(\mu,\eta^4{:}\eta^3\text{-}As_5)]^-$
7	[K(2,2,2-crypt)][$(Cp^*Fe)(Cp'''Co)(\mu,\eta^4{:}\eta^4\text{-}As_6)$]
8	$[(Cp^*Fe)(Cp'''Co)_3(\mu_4,\eta^4{:}\eta^2{:}\eta^2{:}\eta^2\text{-}P_4)(\mu_3\text{-}P)]$
9	$[(Cp^*Fe)(Cp'''Co)_3(\mu_4,\eta^4{:}\eta^2{:}\eta^2{:}\eta^2\text{-}As_4)(\mu_3\text{-}As)]$
10	[K(2,2,2-crypt)][$(Cp^*Fe)(Cp'''Co)(\mu,\eta^4{:}\eta^3\text{-}P_6Ph_2)$]
11	$[(Cp^*Fe)(Cp'''Co)(\mu,\eta^4{:}\eta^3\text{-}P_6Ph_2Me)]$

12.2.7 Ring Expansions of non-polar Polyphosphorus Rings

A	$[^tBu_3P_3MeCNR]^+$
B	$[^tBu_3P_3CN^iPr]^+$
C	$[^tBu_3P_3Ga\{C(SiMe_3)_3\}]$
D	$[^tBu_3P_3PR_2]^+$
1a	$[Cp^*P\{W(CO)_5\}_2]$
1b	$[Cp^*As\{W(CO)_5\}_2]$
2	$[Na(thf)_3][(\eta^3\text{-}P_3)Nb(ODipp)_3]$
3	$[Na(18\text{-}c\text{-}6)(thf)_2][\{W(CO)_5\}_2\{\mu_3,\eta^3{:}\eta^1{:}\eta^1\text{-}P_4Cp^*\}Nb(ODipp)_3]$
4	$[Cp'''Co(\eta^4\text{-}P_4)]$
5a,b	$[\{W(CO)_5\}_2(\mu_3,\eta^4{:}\eta^1{:}\eta^1\text{-}P_5Cp^*)CoCp''']$
6a-c	$[Cp'''Co(\mu_3,\eta^4{:}\eta^1{:}\eta^1\text{-}P_4AsCp^*)\{W(CO)_5\}_2]$

12.2.8 Transformation of the *cyclo*-P_4 Ligand in [Cp'''Co(η^4-P_4)]

A	[$Cp^R M(CO)_2(\eta^4\text{-}P_4)$] (M = V, Nb, Ta)
B	[$^{Ph}PP^{Cy}{}_2Fe(\eta^4\text{-}P_4)$]
C	[$(Ar^{Dipp}CN)_2Mo(CO)_2(\eta^4\text{-}P_4)$]
D	[$(PHDI)Co(\eta^4\text{-}P_4)$]$^-$
E	[$(Cp'''Co)_2(\mu,\eta^4\text{:}\eta^3\text{-}P_8)$]
1	[$Cp'''Co(\eta^4\text{-}P_4)$]
2a	[$K(dme)]_2[(Cp'''Co)_2(\mu,\eta^3\text{:}\eta^3\text{-}P_8)$]
2b	[$K(2,2,2\text{-cryptand})]_2[(Cp'''Co)_2(\mu,\eta^3\text{:}\eta^3\text{-}P_8)$]
3	[$Cp'''Co(\eta^3\text{-}P_3)$]$^-$
4	[$Li(2,2,2\text{-crypt})][Cp'''Co(\eta^3\text{-}P_4{}^tBu)$]
5	[$Li(thf)_3][(Cp'''Co)_2(\mu,\eta^3\text{:}\eta^3\text{-}P_8{}^tBu)$]
6	[$Cp'''Co(\eta^3\text{-}P_5{}^tBu_2)$]$^-$
7	[$Li(12\text{-c-}4)_2][Cp'''Co(\eta^3\text{-}P_3CH_2SiMe_3)$]
8	[$Li(dme)_3][(Cp'''Co)_2(\mu,\eta^3\text{:}\eta^3\text{-}P_8CH_2SiMe_3)$]
9	[$Cp'''Co(\eta^3\text{-}P_5(CH_2SiMe_3)_2)$]$^-$
10	[$Na(dme)_3][Cp'''Co(\eta^3\text{-}P_4(O)H$]

12.2.9 Phosphino-Stibine Ligands and their use in enforcing Metal-Metal Interactions

L1	$(o\text{-}PPh_2C_6H_4)_3Sb$
L2	$(o\text{-}PPh_2C_6H_4)_2SbPh$
L3	$(o\text{-}PPh_2C_6H_4)_2SbCl$
A	[$\eta^1\text{:}\eta^1\text{:}\eta^1\text{-}(o\text{-}PPh_2C_6H_4)_3SbAuCl$]
B	[$\eta^1\text{:}\eta^1\text{:}\eta^1\text{-}(o\text{-}PPh_2C_6H_4)_3SbCl_2AuCl$]
C	[$\eta^1\text{:}\eta^1\text{:}\eta^1\text{:}\eta^1\text{:}\eta^1\text{-}(o\text{-}P^iPr_2C_6H_4)_3SbM_3(\mu\text{-}Cl)_3$] (M = Cu, Ag)
D	[$(\eta^5\text{:}\eta^1\text{-}C_5H_4(CH_2)_2PPh_2)M(CO)_3Cu(PR_3)$] (M = Cr, Mo, W)
E	[$(CO)_2W(\mu\text{-}Ph_2CH_2PPh_2)_2(\mu\text{-}CO)(\mu\text{-}Cl)Cu$]
F	[$(CO)_3W(\mu\text{-}C_5H_4PPh_2)Ag]_2$
G	[$NEt_4][(\mu\text{-}PPh_2)(\mu,\eta^2\text{-}(Ph_3PAu)_2)W_2(CO)_8$]
1	[$W(CO)_4\{\eta^1\text{:}\eta^1\text{-}(o\text{-}PPh_2C_6H_4)_3Sb\}$]
2	[$W(CO)_4\{\eta^1\text{:}\eta^1\text{-}(o\text{-}PPh_2C_6H_4)_2SbPh\}$]
3	[$W(CO)_4\{\eta^1\text{:}\eta^1\text{-}(o\text{-}PPh_2C_6H_4)_2SbCl\}$]
4	[$W(CO)_3\{\eta^1\text{:}\eta^1\text{:}\eta^1\text{-}(o\text{-}PPh_2C_6H_4)_3Sb\}$]
5	[$W(CO)_3\{\eta^1\text{:}\eta^1\text{:}\eta^1\text{-}(o\text{-}PPh_2C_6H_4)_2SbCl\}$]
6	[$(W(CO)_3\{\eta^1\text{:}\eta^1\text{:}\eta^1\text{-}(o\text{-}PPh_2C_6H_4)_2Sb\})_2$]
7	[$Mo(CO)_3\{\eta^1\text{:}\eta^1\text{:}\eta^1\text{-}(o\text{-}PPh_2C_6H_4)_3Sb\}$]
8	[$Mo(CO)_3\{\eta^1\text{:}\eta^1\text{:}\eta^1\text{-}(o\text{-}PPh_2C_6H_4)_2SbPh\}$]
9	[$Mo(CO)_3\{\eta^1\text{:}\eta^1\text{:}\eta^1\text{-}(o\text{-}PPh_2C_6H_4)_2SbCl\}$]
10	[$W(CO)_4\{\eta^1\text{:}\eta^1\text{:}\eta^1\text{:}\eta^1\text{:}\eta^1\text{-}(o\text{-}PPh_2C_6H_4)_3Sb\}\{CuCl\}$]
11	[$W(CO)_4\{\eta^1\text{:}\eta^1\text{:}\eta^1\text{:}\eta^1\text{:}\eta^1\text{-}(o\text{-}PPh_2C_6H_4)_3Sb\}\{AgCl\}$]
12	[$W(CO)_4\{\eta^1\text{:}\eta^1\text{:}\ \eta^1\text{:}\eta^1\text{-}(o\text{-}PPh_2C_6H_4)_2Sb\}\{\eta^1\text{-}AuCl(o\text{-}PPh_2C_6H_4)\}\{AuCl\}$]
13	[$(W(CO)_4\{\eta^1\text{:}\eta^1\text{:}\ \eta^1\text{:}\eta^1\text{-}(o\text{-}PPh_2C_6H_4)_2Sb\})_2AuCl$]
14	[$W(CO)_3(\mu\text{-}CO)\{\eta^1\text{:}\eta^1\text{:}\eta^1\text{:}\eta^1\text{:}\eta^1\text{-}(o\text{-}PPh_2C_6H_4)_3Sb\}\{Cu\}][PF_6$]
15	[$W(CO)_4\{\eta^1\text{:}\eta^1\text{:}\eta^1\text{:}\eta^1\text{:}\eta^1\text{-}(o\text{-}PPh_2C_6H_4)_3Sb\}\{AgMeCN\}][PF_6$]
16	[$W(CO)_4\{\eta^1\text{:}\eta^1\text{:}\eta^1\text{:}\eta^1\text{:}\eta^1\text{-}(o\text{-}PPh_2C_6H_4)_3Sb\}\{Au\}][PF_6$]
17	[$W(CO)_2(\mu\text{-}CO)\{\eta^1\text{:}\eta^1\text{:}\eta^1\text{:}\eta^1\text{:}\eta^1\text{:}\eta^1\text{-}(o\text{-}PPh_2C_6H_4)_3Sb\}\{Cu_2(\mu\text{-}Cl)_2\}$]
18	[$W(CO)_3\{\eta^1\text{:}\eta^1\text{:}\eta^1\text{:}\eta^1\text{-}(o\text{-}PPh_2C_6H_4)_3Sb\}\{AuCl\}$]
19	[$W(CO)_2(\mu\text{-}CO)\{\eta^1\text{:}\eta^1\text{:}\eta^1\text{:}\eta^1\text{:}\ \eta^1\text{-}(o\text{-}PPh_2C_6H_4)_3Sb\}\{CuMeCN\}][PF_6$]
20	[$W(CO)_2(\mu\text{-}CO)\{\eta^1\text{:}\eta^1\text{:}\eta^1\text{:}\eta^1\text{:}\ \eta^1\text{-}(o\text{-}PPh_2C_6H_4)_3Sb\}\{AgMeCN\}][PF_6$]
21	[$W(CO)_2(\mu\text{-}CO)\{\eta^1\text{:}\eta^1\text{:}\eta^1\text{:}\eta^1\text{:}\ \eta^1\text{-}(o\text{-}PPh_2C_6H_4)_3Sb\}\{Au\}][PF_6$]

12.3 Acknowledgements

Finally, I want to thank…

- Prof. Dr. M. Scheer for giving me the opportunity to work on such interesting research topics under excellence conditions, supervision and the complete freedom to pursue my own ideas, for giving me the chance for research stays in the United States (College Station, Texas, Prof. Dr. F. Gabbai and Berkeley, California, Prof. Dr. D. Tilley), the possibility to join national (Göttingen, Berlin, München) and international conferences (Kyoto, Japan; Uppsala, Schweden; Bristol, Great Britain).
- Dr. Gábor Balázs for helping me and giving me advice in uncountable situations, training me to perform DFT calculations on my own and sparing him much time with my stuff ;), for proofreading of every single paper and chapter of this thesis, for giving me chances for “super save disposal” of chemicals.
- Dr. Michael Seidl for checking and finishing hundreds of crystal structures especially some awful [TEF] structures (sorry for that ;)) and transforming supposed crap into publishable structures.
- Prof. Dr. F. Gabbai and Prof. Dr. D. Tilley for giving me the opportunity to spend time and work in their groups during my research stays.
- the staff of the central analytics of the University of Regensburg: X-ray, MS, EA and NMR, especially Georgine Stühler for measurement of uncountable NMR spectra, Wolfgang Söllner (LIFDI) and Josef Kiermaier (ESI) for MS measurements.
- the staff of the glass blowing, electronics and mechanics facility of the University Regensburg.
- my former lab colleges Dr. Eva-Maria Rummel and Dr. Andreas Seitz for their supervision during my master thesis, answering numerous questions and helping me with everything to get started.
- all present and former members of the research group: Andi, Andrea, Anna, Babsi, Barbara B., Claudia G., Christoph, Dominik, Eva, Fabi, Felix L., Felix R., Helena, Julian L. Julian M., Karin, Kevin, Lena, Luis, Maria, Martin W., Martina, Matthias A., Matthias H., Mehdi, Michael S., Nase, Petra, Stephan, Schotti, Thach, Tobi, Reini, Rudi, Veronika.
- my present lab colleges Veronika Heinl and Stephan Reichl for standing me, useful discussions, many politically incorrect conservations (…) and a wonderful time.
- The Fonds der chemischen Industrie for a Ph. D. fellowship and the DFG for financial support within the projects sche 384/38-1, sche 384/33-2 and sche 384/36-1.
- especially my parents for their enduring support.
- Lisa for her enduring support and patience with me spending too much time on the weekends at the university with measuring crystals…, standing sometimes my bad moods after exhausting days in the lab and everything else.