Abstract: A systematic study on the reactivity of the triple-decker complex \([\text{Cp}'''\text{Co})_2\mu_1\eta^1\text{-C}_5\text{H}_5\]) (A) (\text{Cp}'''' = 1,2,4-tri(tert-butyl)cyclopentadienyl) towards sandwich complexes containing cyclo-\text{P}_5, cyclo-\text{P}_6, and cyclo-\text{P}_7 ligands under mild conditions is presented. The heterobimetallic triple-decker sandwich complexes \([\text{Cp}^*\text{Fe}(\text{Cp}'''\text{Co})\mu_1\eta^1\text{-P}_5]\) (1) and \([\text{Cp}'''\text{Co}(\text{Cp}'''\text{Ni})\mu_1\eta^1\text{-P}_5]\) (3) (\text{Cp}''' = 1,2,3,4,5-pentamethylcyclopentadienyl) 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 \((\text{W}^\text{III})(\text{CO})_3\) fragments, leading to the complexes \([\text{Cp}^*\text{Fe}(\text{Cp}'''\text{Co})\mu_1\eta^1\text{-P}_5](\text{W}(\text{CO})_3)\) (2a), \([\text{Cp}^*\text{Fe}(\text{Cp}'''\text{Co})\mu_1\eta^1\text{-P}_5](\text{W}(\text{CO})_3)\) (2b), and \([\text{Cp}'''\text{Co}(\text{Cp}'''\text{Ni})\mu_1\eta^1\text{-P}_5](\text{W}(\text{CO})_3)\) (4), respectively. The thermolysis of 3 leads to the tetrahedron complex \([\text{Cp}'''\text{Ni}_2\mu_1\eta^1\text{-P}_5]\) (5). All compounds were fully characterized using single-crystal X-ray structure analysis, NMR spectroscopy, mass spectrometry, and elemental analysis.

The transformation of the \(\text{P}_5\) 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 \([\text{Cp}'''\text{Co})_2\mu_1\eta^1\text{-C}_5\text{H}_5\]) (A) to \([\text{Cp}'''\text{Co})_2\mu_1\eta^1\text{-C}_5\text{H}_5\]) (A) to yield phosphorus cages with, for example, a \(\text{C}_4\text{H}_4\text{P}_3\) or, at low temperatures, the metal-controlled aggregation of \(\text{P}_5\) molecules occur to form large neutral polyporphosphorus cages with, for example, a \(\text{P}_{18}\) or \(\text{P}_{30}\) ligand, respectively. All reactions of the mentioned carbonyl or nacnac complexes with \(\text{P}_5\) lead to either sandwich complexes with a \(\text{P}_5\) ligand as an end deck (e.g. \([\text{Cp}^*\text{Fe}(\text{Cp}'''\text{Co})\mu_1\eta^1\text{-P}_5]\)) or a middle deck in homometallic triple-decker complexes (e.g. \([\text{Cp}'''\text{Co})_2\mu_1\eta^1\text{-P}_5]\)). But no heterobimetallic compounds can be obtained that way. Moreover, there are only very few examples known that are accessible from reactions of \([\text{Cp}'''\text{Co})_2\mu_1\eta^1\text{-P}_5]\) (M = Fe, Ru) with cationic fragments or carbonyl compounds. 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. On the other hand, substituted derivatives of heterobimetallic triple-decker complexes can be obtained from the electrophilic quenching of pentaphosphaferrocene \((\text{Cp}^*\text{Fe}(\eta^1\text{-P}_5\text{R}))\) functionalized by main-group nucleophiles, resulting in e.g. \([\text{Cp}^*\text{Fe}(\text{Cp}'''\text{Co})\mu_1\eta^1\text{-P}_5\text{Me}_3]\) (Figure 1).

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

A plethora of kinetic products. Another type of complex used in the activation of \(\text{P}_5\) is the reactive cobalt toluene triple-decker complex \([\text{Cp}'''\text{Co})_2\mu_1\eta^1\text{-C}_5\text{H}_5\]) (A) which dissociates in solution into a \(\text{C}_4\text{H}_4\text{P}_3\text{Co}\text{C}_5\text{H}_5\)) and \((\text{Cp}'''\text{Co})\text{Co}\text{C}_5\text{H}_5\)) fragment. Its reactivity towards white phosphorus strongly depends on the reaction conditions. Thus, at room temperature, the cleavage of the \(\text{P}_5\) tetrahedron into two \(\text{P}_5\) units or forming \([\text{Cp}'''\text{Co})_2\mu_1\eta^1\text{-P}_5\text{Co}\text{C}_5\text{H}_5\]) or, at low temperatures, the metal-controlled aggregation of \(\text{P}_5\) molecules occur to form large neutral polyporphosphorus cages with, for example, a \(\text{P}_{18}\) or \(\text{P}_{30}\) ligand, respectively. All reactions of the mentioned carbonyl or nacnac complexes with \(\text{P}_5\) lead to either sandwich complexes with a \(\text{P}_5\) ligand as an end deck (e.g. \([\text{Cp}^*\text{Fe}(\text{Cp}'''\text{Co})\mu_1\eta^1\text{-P}_5]\)) or a middle deck in homometallic triple-decker complexes (e.g. \([\text{Cp}'''\text{Co})_2\mu_1\eta^1\text{-P}_5\text{Co}\text{C}_5\text{H}_5\)) But no heterobimetallic compounds can be obtained that way. Moreover, there are only very few examples known that are accessible from reactions of \([\text{Cp}'''\text{Co})_2\mu_1\eta^1\text{-P}_5\text{Co}\text{C}_5\text{H}_5\)) (M = Fe, Ru) with cationic fragments or carbonyl compounds. 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. On the other hand, substituted derivatives of heterobimetallic triple-decker complexes can be obtained from the electrophilic quenching of pentaphosphaferrocene \((\text{Cp}^*\text{Fe}(\eta^1\text{-P}_5\text{R}))\) functionalized by main-group nucleophiles, resulting in e.g. \([\text{Cp}^*\text{Fe}(\text{Cp}'''\text{Co})\mu_1\eta^1\text{-P}_5\text{Me}_3]\) (Figure 1).

A General Pathway to Heterobimetallic Triple-Decker Complexes

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Dedicated to Professor H. Brunner on the occasion of his 85th birthday


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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)(μ1η4-η15-C5H5)] (A) with compounds containing cyclo-P₅ ligands as end-decks, such as [Cp'''Fe(μ1η4-η15-P)] (B), [Cp'''Co(μ1η4-η15-P)] (C) and [Cp'''Ni(μ1η4-η15-P)] (E) at room temperature. Herein, we report the synthesis and properties of two new mixed metal triple-decker sandwich complexes comprising cyclo-P₅ (n = 3 and 5) middle decks, respectively, as well as their reaction behavior towards white phosphorus and their thermal stability.

The reaction of [(Cp'''Co)(μ1η4-η15-C5H5)] (A) with pentaphosphephaferrocene ([Cp'''Fe(μ1η4-η15-P)] (B)) in pentane at room temperature leads to the quantitative formation of [(Cp'''Fe)-(Cp'''Co)(μ1η4-η15-P)] (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-P₅ ligand (the thermolysis leads to the formation of P₅, P₆ and P₁, ligand-containing complexes). Alternatively, 1 can be also obtained by the reaction of K₂[dime],[[Cp'''Fe(μ1η4-η15-P)] with [(Cp'''CoCl)] in lower yield (cf. Supporting Information).

The crystal structure of 1 reveals a dinuclear complex bearing a cyclo-P₅ ligand in an envelope conformation, coordinating in η⁴ fashion to the Cp'''Co fragment and η⁶ fashion to the Cp'''Fe fragment (Figure 2). Both Cp'''M fragments are twisted by approximately 16° to each other and P₁ is bent out of the plane by approx. 34°. 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, whereas 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 H NMR spectrum reveals four sharp singlets corresponding to one Cp* and one freely rotating Cp''' ligand, whereas the ³¹P(H) NMR spectrum shows one very broad signal at δ = –160 ppm (ω₁,₂ = 16000 Hz). Upon cooling to –80 °C, the signals in the H NMR spectra remain unchanged, while the broad signal observed in the ³¹P(H) 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 ³¹P(H) NMR spectrum at 213 K (cf. Supporting Information). The magnitude of the ¹Jₚₖ 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 H NMR spectra do not change, while the broad signal in the ³¹P(H) NMR spectrum sharpens to a singlet at δ = –115.3 ppm (ω₁/₂ = 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 ΔG° of this process at the coalescence temperature (Tc = 293 K) amounts to 48.2 kJ mol⁻¹ (cf. Supporting Information).[21] All these findings indicate that the dynamic process proceeds at the cyclo-P₅ ligand. Compound 1 is thermally stable. Refluxing 1 in toluene for one day leads to only minor decomposion. As a decomposition product, [Cp'''Fe(η⁴-P₅)] has been identified by ³¹P(H) NMR spectroscopy.

To block the dynamic process in solution at room temperature, 1 was reacted with an excess of [W(CO)₅(thf)] (2.2 equiv) and the mono- and dicoordinated compounds [(Cp'''Fe)-(Cp'''Co)(μ1η4-η15-P₅)]W(CO)₅ (2a) and [(Cp'''Fe)-(Cp'''Co)(μ1η4-η15-P₅)]W(CO)₅ (2b) are formed [Eq. 2]. The stoichiometric reaction (1:1) leads to a selective formation of 2a (according to ³¹P(H) NMR).
According to the $^{31}$P{$^1$H} NMR spectrum of the reaction mixture, 2a and 2b are formed in an approximately 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 $-30^\circ$C. For 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, whereas 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{$^1$H} 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{$^1$H} 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. Supporting Information).

The reaction of [(Cp'''Co)$_2$($m$,h$_4$:h$_4$-C$_7$H$_8$)] (A) with [Cp'''Co($\eta^5$-P$_4$)] (C) in toluene at room temperature leads to the quantitative formation of [(Cp'''Co)$_2$($\mu_1\eta^1:\eta^1$-P$_2$)$_2$] (D) [Eq. 3].

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. The cyclo-P$_4$ ligand in A with [Cp'''Ni($\eta^3$-P$_3$)] (E) at room temperature for few minutes results in the quantitative formation of the dinuclear complex [(Cp'''Co)(Cp'''Ni)($\mu_1\eta^1:\eta^1$-P$_2$)] (3) [Eq. 4].

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$_1$ 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$_1$ 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 P(κ) ligands are tilted by 18° to each other. Compared to the P–P bond lengths in E[9] (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.

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 (2r\text{vdW} = 3.80 Å).

The Wiberg Bond Index of 0.22 indicates a weak interaction between the two phosphorus atoms P1 and P3. In the 1H and 31P[1H] NMR spectra of 3, a dynamic process can be observed that is dependent on the temperature and the solvent used (CD2Cl2 or [D8]toluene) (Figure 6). The 31P[1H] NMR in CD2Cl2 spectrum shows three broad signals centered at \(\delta = 377.3, 249.7\) 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 \(\delta = 366.8\) and 126.2 ppm increases in comparison to the singlet at \(\delta = 237.8\) ppm. This clearly confirms the presence of a fixed allylic P3 ligand (3b) at low temperature (Figure 6). The singlet at \(\delta = 237.8\) ppm can be assigned to the compound 3a bearing a cyclo-P3 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 31P[1H] NMR spectra, Figure 6). The situation can also be monitored in the VT 31P[1H] NMR spectra (cf. Supporting Information). Warming up a solution of 3 in [D8]toluene to 363 K, in the 31P[1H] 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 \(\delta = 285.8\) and \(\delta = 43.7\) ppm arise, which can be assigned to a new Ni complex (5, vide infra) and D7.

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, Supporting Information), which raises the question as to whether the equilibrium between 3a and 3b can be shifted by coordination to a (W(CO)5) fragment [Eq. 5].

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

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

Figure 6. VT 31P[1H] NMR spectra of 3 in CD2Cl2 at different temperatures between 183 and 300 K and the proposed temperature-dependent equilibrium. Integral ratio given for measurement in CD2Cl2 (black) and [D8]toluene (red).
Reacting 3 with an excess of [W(CO)](thf) (2.2 equiv) yields [[Cp'''Co][Cp'''Ni]µ,η¹-η¹-η¹-P₃]W(CO)]₃ (4) as a major product (coordination of [W(CO)]₃ at the central P atom (P2)) beside small amounts of I₄-B/I₄-C (coordination of [W(CO)]₃ at the outer P atom (P1 or P3)). According to the ³¹P(¹H) NMR spectrum of the reaction mixture 4 and I₄-B/I₄-C are present in a ratio of 1.04:0.1. 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 CH₂Cl₂ layered with MeCN at room temperature. In 4, the [W(CO)]₃ fragment is coordinated to the central P atom of the three-membered chain (Figure 7). Upon the coordination of Co and Ni to W and in 4 and (coordination of {W(CO)}₃ to a{ W(CO)}₃ to 4 layered with MeCN at room temperature. In T Energetic profile of the reaction of...
Crystals suitable for X-ray single-crystal structure analysis can be obtained by storing a concentrated solution of 5 in hexane at \(-30^\circ C\).

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 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'''Ni]_2[Cp'''Co]) (Cp''' = CH_2P(C_6H_4F_3)). The 31P([H] NMR spectrum of 5 contains a sharp singlet at \(\delta = 282.7\) ppm.

![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 Supporting Information.](image)

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_2 at room temperature. After column chromatographic workup, ([Cp*Fe(η^3-P_3)] (B) could be isolated as a byproduct and separated from the additionally formed ([Cp'''Co]_2[Cp'''Ni](η^3-P_3)) (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, 3 was reacted with P_2. According to the 31P([H] NMR spectrum, ([Cp'''Ni](η^3-P_3)) (E) is quantitatively formed, next to the cobalt complexes ([Cp'''Co](η^3-P_3)) (C, 40%) and ([Cp'''Co](η^3-P_3)) (D, 42%), beside traces (<1%) of other P-rich compounds.

The results show a novel synthetic route to two new heterobimetallic triple-decker complexes was developed. Both can be obtained in gram scale under mild reaction conditions. ([Cp'''Co]_2[Cp'''Ni](η^3-C_6H_4)) (A) serves as a source of unsaturated (Cp'''Co) fragments, reacting with ([Cp*Fe(η^3-P_3)] (B) and ([Cp'''Ni](η^3-P_3)) (E) to yield ([Cp*Fe(Cp'''Co](η^3-P_3)] (1) and ([Cp'''Co]([Cp'''Ni](η^3-P_3)) (3), respectively. Both compounds exhibit unique flexibilities in solution, which can be inhibited by coordination to (WCO)_2 fragments resulting in ([Cp*Fe(Cp'''Co](η^3-P_3)](WCO)_2) (2a) or ([Cp*Fe(Cp'''Co](η^3-P_3)](WCO)_2) (2b) and ([Cp'''Co]([Cp'''Ni](η^3-P_3)](WCO)_2) (4), respectively. Additionally, 3 is thermally unstable and fragmentizes upon warming into ([Cp'''Co](η^3-P_3)) (D) and ([Cp'''Ni](η^3-P_3)) (5). The (Cp'''Co) fragment in 1 and 3 is still labile bound and can be released to undergo further reactions for instance with P_2.

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### Conflict of Interest

The authors declare no conflict of interest.

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