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Polyphosphorus Compounds Derived from P_4 Conversion with Sterically Demanding Cobalt Complexes

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The conversion of P_4 with $[Cp^{Bn}Co(CO)_2]$ ($Cp^{Bn}=C_5(CH_2C_6H_5)_5$) under thermal conditions gives almost exclusively the P_{10} complex $[(Cp^{Bn}Co)_4(\mu^4\text{-}\eta^4{:}\eta^4{:}\eta^2{:}\eta^2{:}\eta^1{:}\eta^1\text{-}P_{10})]$. However, its reaction with $[Cp^{Bn}Co]_n$, under mild conditions afforded a mixture of products including the P_8 species $[(Cp^{Bn}Co)_3(\mu_3\text{-}\eta^4{:}\eta^2{:}\eta^2{:}\eta^1{:}\eta^1\text{-}P_8)]$ and a rare Co_3 cluster $[(Cp^{Bn}Co)_2Co(\mu_3\text{-}\eta^5{:}\eta^2{:}\eta^1{:}\eta^1\text{-}C_{40}H_{33})(\mu\text{-}H)(\mu_3\text{-}H)]$. The products were studied in solution by multinuclear NMR spectroscopy and mass spectrometry and, for some compounds in the solid state, by single crystal X-ray diffraction.

Introduction

White phosphorus (P_4) is known as the most important allotrope of its element and is widely used as a starting material for the synthesis of organophosphorus compounds.[1] Common industrial methods for these syntheses include steps in which hazardous and toxic chemicals are involved. Thus, tremendous efforts have been made to find alternative pathways which are in accordance with the global pursuit of environmentally friendly processes.[2] In this field, remarkable success was achieved in converting P_4 by main group elements[3d,2c] and transition metal complexes,[3a–c] which prompted the synthesis of a large number of compounds with versatile bonding patterns. Experimentally, transition metal complexes containing cyclopentadienyl and carbonyl ligands $[(Cp^RM(CO)_n)_2]$ were found to be useful starting materials in the reaction with P_4. Common approaches proceed by thermolysis or photolysis conditions to give the thermodynamically most stable products which are predominantly cluster compounds with low P-nuclearity (number of P atoms less than or equal to 4).[3,4] In contrast, the conversion of P_4 leading to the aggregation of P units to form high P-nuclearity compounds (number of P atoms greater than four) has been less investigated, as such P-derivatives are more challenging to synthesise.[3,5] This is not surprising, because such processes require, besides transition metal-CO bond cleavage, both cleavage and coupling reactions of P–P bonds. Moreover, the larger these polyphosphorus compounds are, the more conformational and structural diversity they can adopt, which can also explain why selective syntheses of such species are very limited.[6] To this field, our group contributed by actively studying the reactivity of P_4 in the coordination sphere of transition metals. Accordingly, fixation and release, aggregation and functionalisation of P_4 were realised.[7] Furthermore, the stability and easy accessibility of a number of those compounds allowed to further study their reactivities especially as building blocks in supramolecular chemistry affording fascinating inorganic nanospheres,[8] as well as coordination polymers.[8a,9] Thus, further investigations to enrich the library of such compounds with new candidates as well as to understand the reaction conditions which allow to obtain them selectively are still of interest. In one approach,[6d] the formation of large P_n species was attainable from the reaction of P_4 with the triple-decker complex $[(Cp'''Co)_2(\eta^4{:}\eta^4\text{-}C_7H_8)]$ ($Cp'''=1,2,4\text{-}C_5H_2(t\text{Bu})_3$) which dissociates in solution to give 14 VE (valence electrons) $Cp'''Co$ moieties.[10] In that respect, a controlled synthesis of P_4-, P_8-, P_{12}-, P_{16}- and even P_{24}-containing cobalt complexes was reported depending on the type of reaction procedure and the temperature used. Interestingly, in a former study of the Scherer group, the great impact on the reaction outcomes not only of the reaction conditions but also the ligand-stabilizing cobalt became apparent.[5a,b] Therein, the thermolysis of $[(Cp''Co(CO)_2]$ ($Cp''=1,3\text{-}C_5H_3(SiMe_3)_2$) with P_4 afforded exclusively the P_{10} compound $[(Cp''Co)_2(P_5\text{-}P_5)(Cp''Co)_2]$. Using $[(Cp'''Co(CO)_2]$ instead allowed for the formation of a mixture of the compounds $[(Cp'''Co)_2(P_2)_2]$, $([(Cp'''Co)_3(P_5\text{-}P_3)])$ and $[(Cp'''Co)_3(P_5\text{-}P_7)]$, with no traces of the P_{10} species. Herein, we compare the reaction behaviour of the cobalt complex $[Cp^{Bn}Co(CO)_2]$ (**1**)[11] stabilised by the bulky pentabenzylcyclopentadienyl ligand (Cp^{Bn}) with the newly synthesised 14 VE precursor complex $[Cp^{Bn}Co]_n$ in their reaction with P_4 under thermal and mild reaction

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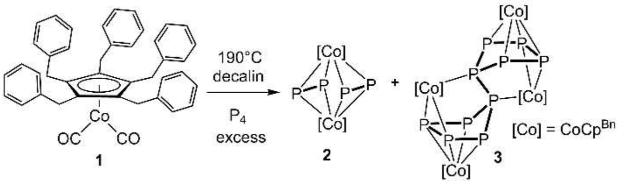
conditions, respectively. The products obtained were studied in solution and by X-ray crystallography if feasible.

Results and Discussion

In a first step, [Cp$^{\mathrm{Bn}}$Co(CO)$_2$] (**1**) was reacted with an excess of P$_4$ in boiling decalin [Eq. (1)] and the reaction progress was monitored by IR and ^{31}P{^{1}H} NMR spectroscopy. After refluxing for 50 minutes, the carbonyl bands of **1** (2013 cm^{-1}, 1955 cm^{-1}) disappeared. Additionally, in the ^{31}P{^{1}H} NMR spectrum of the crude reaction mixture, two sets of signals (a singlet at −1.8 ppm and three multiplets at 252.8, 126.6 and −123.9 ppm) with a 1:19 ratio appeared. Column chromatographic workup and subsequent recrystallisation from cyclohexane allowed the isolation of the complexes [(Cp$^{\mathrm{Bn}}$Co)$_2$(μ-η^2:η^2-P$_2$)$_2$] (**2**, blue crystals) and [(Cp$^{\mathrm{Bn}}$Co)$_4$(μ$_4$-η^4:η^4:η^2:η^2:η^1:η^1-P$_{10}$)] (**3**, green crystals) in 4% and 75% yield, respectively, which reflects the 1:19 ratio observed in the crude ^{31}P{^{1}H} NMR.



(1)

Complex **2** is isolated as an air-sensitive solid. It is well soluble in CH$_2$Cl$_2$, toluene and hot cyclohexane, but nearly insoluble in hexane and cold cyclohexane. Its FD mass spectrum reveals only the molecular ion peak without fragmentation. In its EI mass spectrum, however, in addition to the molecular ion peak, the dicationic species [(Cp$^{\mathrm{Bn}}$Co)$_2$(μ-η^2:η^2-P$_2$)$_2$]$^{2+}$ is also detected. In the ^{1}H NMR spectrum in C$_6$D$_6$, two multiplets at 6.80 and 6.60 ppm in a ratio of 3:2 for the phenyl protons and a sharp singlet for the methylene H atoms at 4.27 ppm are found. In the ^{31}P{^{1}H} NMR spectrum, a sharp singlet at −1.8 ppm is observed, which is downfield shifted as compared to that reported for the similar compound containing Cp‴ ligands (−46.9 ppm).[12]

Complex **2** crystallises in the tetragonal space group I4$_1$/a. The asymmetric unit contains one molecule of **2** and 1.3 cyclohexane molecules. Its molecular structure reveals a dinuclear cobalt complex in which the two CoCp$^{\mathrm{Bn}}$ fragments are bridged by two P$_2$ units (Figure 1a). Complex **2** is isostructural to the previously reported complexes [(Cp$^{\mathrm{R}}$Co)$_2$(μ-η^2:η^2-P$_2$)$_2$] (Cp$^{\mathrm{R}}$ = (C(CH$_3$))$_5$,[13] C$_5$H$_3$(*t*Bu)$_2$,[14] C$_5$H$_2$(*t*Bu)$_3$,[12,5b] and C$_5$H$_3$(SiMe$_3$)$_2$,[5a] but also to some extent remarkable. All of the aforementioned complexes comprise each two equal P–P bond lengths of about 2.05 Å and the P$_2$ units are separated by two similar P···P distances ranging between 2.663(2) and 2.720(4) Å. In **2**, however, the Co$_2$P$_4$ unit is significantly distorted. The P2–P3 (2.065(1) Å) and P1–P4 (2.058(1) Å) bond lengths differ by 0.007 Å and the two P$_2$ units are located nonparallel with a long P1···P3 (2.754 Å) and a short P2···P4 (2.588(1) Å) distance between the Co atoms. The distortion is also reflected in the Co–P bond lengths, as two of them (involving the P1 and P3 atoms) are shorter (ranging between 2.281(8) and 2.305(7) Å) than those involving the P2 and P4 atoms (ranging between 2.321(8) and 2.335(8) Å). The two Cp$^{\mathrm{Bn}}$ ligands are tilted by 8.49(1)° against each other. This distortion of **2** seems to be present only in the solid state, since the spectroscopic observations indicate a symmetrical complex on the NMR timescale. Interestingly, compound **2** shows a remarkable packing in the crystal lattice (Figure 1b). Molecules of **2** arrange to give infinite columns in which every second molecule is turned by 90°. Thereby, phenyl rings from two neighbouring molecules lie in close vicinity with observable short phenyl-phenyl distances (ca. 3.478(3) Å) and a twist angle of ca. 40°, revealing possible intermolecular π···π interactions.[15] Seemingly, the columns of the molecules of **2** arrange next to one another in such a way as to maximise these intermolecular interactions.

Complex **3** can be crystallised from hot cyclohexane or CH$_2$Cl$_2$ as slightly air-sensitive green crystals. Its FD mass

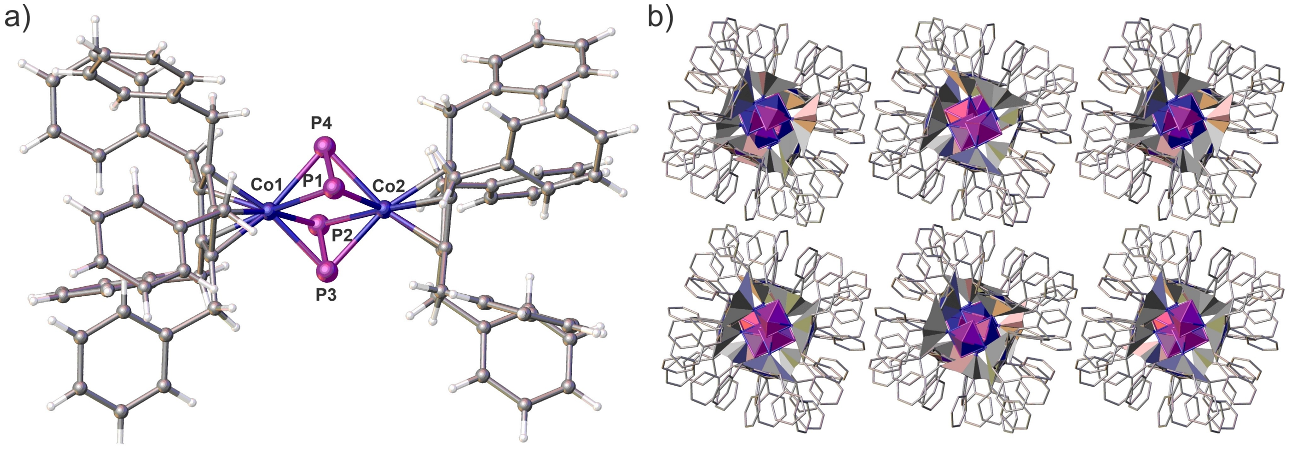


Figure 1. a) Molecular structure of complex **2** in the solid state; b) Arrangement of **2** in the crystal structure. The vacancies between columns of molecules **2** are occupied by cyclohexane molecules.

spectrum shows the molecular ion as the base peak next to traces of the cations $[(Cp^{Bn}Co)_2P_6]^+$ and $[(Cp^{Bn}Co)_2P_4]^+$. However, severe fragmentation of **3** is observed under EI conditions. The molecular ion peak appears in only 4% and the cation $[(Cp^{Bn}Co)_2P_4]^+$ forms the largest complex fragment while the base peak is attributed to the $[Cp^{Bn}]^+$ cation. The ^1H NMR spectrum of **3** in C_6D_6 reveals signals for the two magnetically inequivalent Cp^{Bn} ligands. Thus, two sharp singlets at 4.59 and 4.23 ppm (for the methylene H atoms) and two sets of multiplets each in a ratio of 3:2 in between 7.20 and 6.48 ppm (for the phenyl protons) are detectable. In the $^{31}P\{^1H\}$ NMR spectrum, three multiplets at 252.8, 126.6 and −123.9 ppm are observed in a ratio of 1:2:2. The simulation[16] of the spectrum reveals an $A_2M_2M'_2X_2X'_2$ spin system (Figure 2).

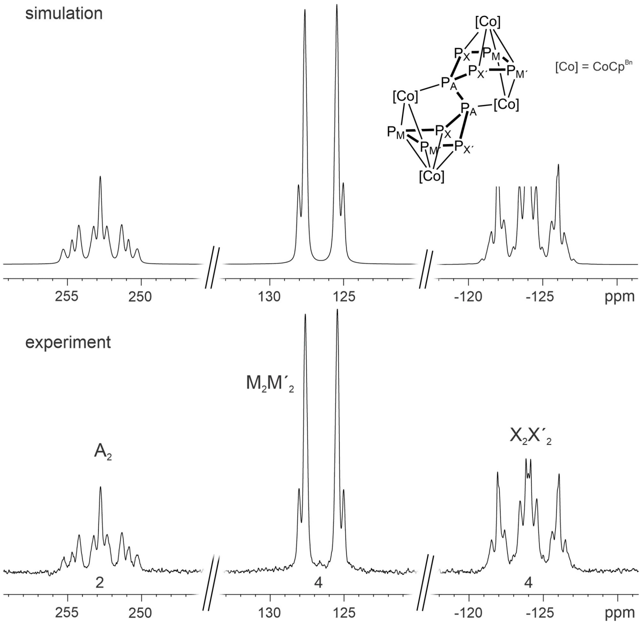


Figure 2. Experimental (C_6D_6, 162.0 MHz, 300 K; bottom) and simulated (top) $^{31}P\{^1H\}$ NMR spectrum of **3**.

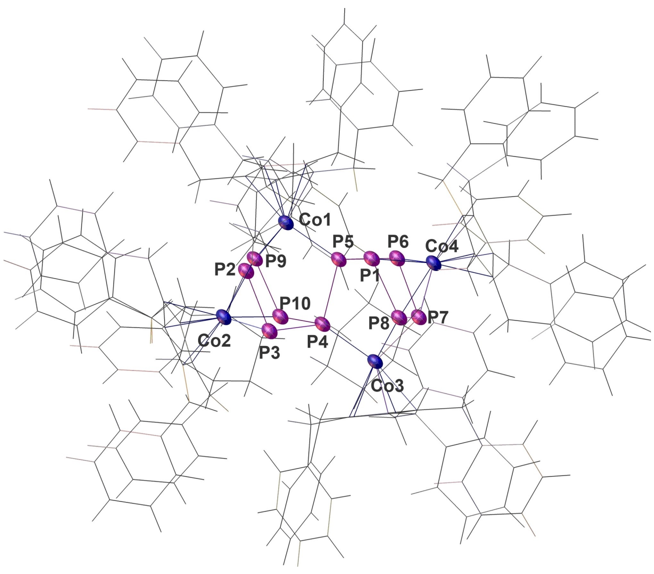
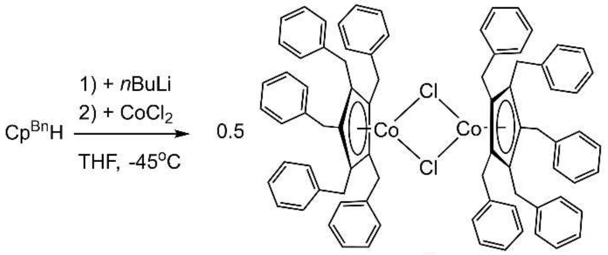


Figure 3. Molecular structure of complex **3** in the solid state. The Cp^{Bn} ligands are depicted as wireframes for clarity.

Complex **3** crystallises in the monoclinic space group *C*2/*c*. The asymmetric unit contains one molecule of **3** and five cyclohexane molecules. Its crystal structure analysis reveals a P_{10} ligand stabilised by four $CoCp^{Bn}$ metal fragments (Figure 3) and is isostructural to the $[(Cp''Co)_4(\mu_4\text{-}\eta^4{:}\eta^4{:}\eta^2{:}\eta^2{:}\eta^1{:}\eta^1\text{-}P_{10})]$ derivative.[5a] The structure of the P_{10} ligand in **3** is distorted by torsion around the P4–P5 bond, which is reflected in the tilt angle of 28.6(5)° between the Cp^{Bn} ligands at the Co2 and Co4 atoms. It is stabilised in the coordination sphere of four 14 VE $CoCp^{Bn}$ fragments and serves as a 16-electron donor. The P2P3P9P10 and P1P6P7P8 moieties bind to Co2 and Co4 with relatively long Co–P bonds (2.301(1)-2.345(9) Å), while the P4/P5 atoms engage in short Co–P bonds with Co1 and Co3 (2.147(1)–2.143(1) Å), respectively. All P–P bonds are in the range of single bonds, except for the P2–P9/P7–P8 bonds (2.491(1)/2.471(1) Å) which are significantly elongated and reasonably close to the longest known P–P bonds.[17] The benzyl groups at the Cp^{Bn} ligands are all pointing away from the Co_4P_{10} unit, except for two of them. Complex **3** is arranged in two-dimensional (2D) layers in the crystal structure with each molecule of **3** being surrounded by the six nearest neighbouring molecules.

As a result of the harsh reaction conditions, the thermolysis of $[Cp^{Bn}Co(CO)_2]$ (**1**) with P_4 yields almost exclusively the P_{10} complex **3**. Thus, in an alternative approach, we aimed at the conversion of P_4 under mild conditions to gain insight into the reactivity difference as compared to the harsh conditions. In this context, the release of the unsaturated 14 VE Cp^RCo species under mild conditions, as successfully utilised in the case of the triple-decker complex $[(Cp'''Co)_2(\eta^4{:}\eta^4\text{-}C_7H_8)]$[10] for P_4 conversion, crossed our minds.[6b] Thus, the synthesis of a similar compound stabilised by the Cp^{Bn} ligand was targeted. Accordingly, $[\{Cp^{Bn}CoCl\}_2]$ (**4**) was synthesised first to be subsequently reduced with potassium metal referring to the synthesis of the Cp‴ derivative.[10] An *in situ* prepared solution of $LiCp^{Bn}$ in THF was added to a suspension of $CoCl_2$ in THF at −45 °C. The resulting dark brown crude product was recrystallised in hot toluene to give $[\{Cp^{Bn}CoCl\}_2]$ (**4**) as air-sensitive black crystals in 61% yield [Eq. (2)].

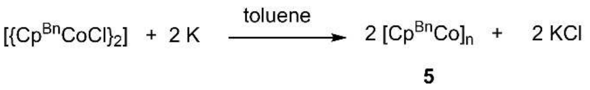


(2)

4

In the FD mass spectrum of **4**, solely the molecular ion peak is observed without fragmentation. Due to its paramagnetic nature, the ^1H NMR spectrum shows three broad signals at 7.01 ($\omega_{1/2}=28$ Hz), 6.52 ($\omega_{1/2}=16$ Hz) and 4.88 ($\omega_{1/2}=165$ Hz) ppm, with the latter being assigned to the methylene H atoms, which are the ones closest to the Co atoms. Complex **4** crystallises in the triclinic space group $P\bar{1}$.The asymmetric unit contains half a molecule of **4** (Figure 4). In the crystal structure, the Co_2Cl_2 unit forms a planar square with Co–Cl bond lengths between 2.257(3) and 2.267(3) Å, which are longer than those reported for $[\{(C_5H\mathit{i}Pr_4)CoCl\}_2]$ (average: 2.229(2) Å).[18]

The reduction of **4** was conducted by stirring a toluene solution of **4** over potassium for one week. This reaction resulted in a red-brown solid, which was dissolved in Et_2O and filtrated. Yet, all attempts to purify the crude product by recrystallisation from Et_2O, Et_2O/hexane or toluene/hexane mixtures failed. Apparently, the $CoCp^{Bn}$ fragments do not combine to form a defined triple-decker complex as was observed for the Cp‴ and the Cp* derivatives. This is attributed to the fact that each $CoCp^{Bn}$ fragment possesses five phenyl rings which themselves can potentially coordinate to other $CoCp^{Bn}$ fragments. Hence, upon removal of the toluene solvent from the initial reaction mixture, the reaction product seems to form an oligomeric species with the approximate composition $[Cp^{Bn}Co]_n$ (**5**) [Eq. (3)]. Unfortunately, further attempts to purify **5** by column chromatography resulted in its decomposition. By eluting the column with toluene, removing the solvent and subsequently dissolving the brown solid in hexane/toluene mixtures, a few crystals of the cobaltocene complex $[Cp^{Bn}{}_2Co]$ were found (for further information see ESI). Therefore, compound **5** was reacted with P_4 without further purification.



$$[\{Cp^{Bn}CoCl\}_2] + 2\,K \xrightarrow{\text{toluene}} 2\,\underset{\mathbf{5}}{[Cp^{Bn}Co]_n} + 2\,KCl \qquad (3)$$

A solution of the crude **5** in toluene was slowly added to a solution of P_4 in toluene at −60 °C. This mixture was warmed to room temperature and stirred overnight yielding a mixture of several products [Eq. (4)]. A column chromatographic workup of the reaction mixture allowed the isolation of four different fractions. A red fraction of $[Cp^{Bn}Co(\eta^4\text{-}C_7H_{10})]$ (**6**), a blue fraction of **2**, a red-brown fraction containing a mixture of the P_8 species $[(Cp^{Bn}Co)_3(\mu_3\text{-}\eta^4{:}\eta^2{:}\eta^2{:}\eta^1{:}\eta^1\text{-}P_8)]$ (**7**) and the Co cluster $[(Cp^{Bn}Co)_2Co(\mu_3\text{-}\eta^5{:}\eta^2{:}\eta^1{:}\eta^1\text{-}C_{40}H_{33})(\mu\text{-}H)(\mu_3\text{-}H)]$ (**8**) and a final brown fraction containing **3** in addition to other partially unidentified P_n species [Eq. (4)].

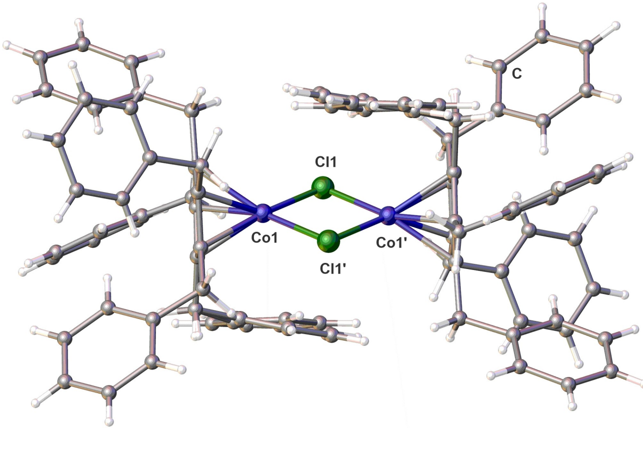
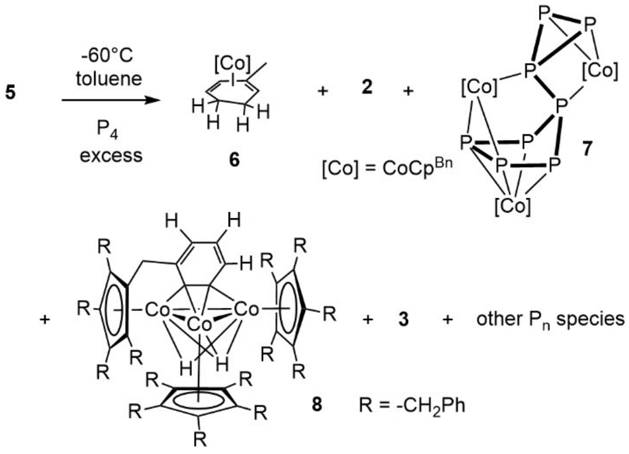


Figure 4. Molecular structure of complex **4** in the solid state.



(4)

Complex **6** is obtained as a minor product in 4% yield. It is probably an impurity of the starting material **5**, which is formed due to hydrogenation of a toluene solvent molecule. In this reaction, the hydrogenation agent could be complex **8**. Compound **6** is an orange solid that has good solubility in hexane, toluene and CH_2Cl_2. In the FD mass spectrum, only the molecular ion peak is observed without fragmentation. In its ^1H and $^{13}C\{^1H\}$ NMR spectra, the expected signals attributable to the phenyl groups of the Cp^{Bn} ligand, the methylene H and C atoms as well as the dihydrotoluene ligand are detected. Complex **6** crystallises as orange prisms from hexane solutions in the triclinic space group $P\bar{1}$. The crystal structure analysis of **6** reveals a sandwich complex containing a Cp^{Bn} ligand and a dihydrotoluene ligand (Figure 5). The dihydrotoluene ligand is disordered over two positions and binds with its π-system in η^4 fashion to the Co centre and acts as a four-electron donor ligand. Thus, the cobalt atom attains the 18-VE configuration, which is reflected in the stability of **6**.

Complexes **7** and **8** elute together due to their very similar retention times in a total yield of 2%. Complex **7** could be detected in the FD mass spectrum of this mixed fraction in the form of its molecular ion peak. Furthermore, it was identified by its $^{31}P\{^1H\}$ NMR spectrum (Figure 6). The shape of the signals is very similar to the shapes observed for the Cp‴ derivative previously reported by our group, which indicates that **7** is isostructural. However, the chemical shifts seem to be influenced by the substituent on the cyclopentadienyl ligand and are shifted to lower fields compared to the Cp‴ compound (for further information see ESI). The simulation[16] of the $^{31}P\{^1H\}$ NMR spectrum reveals an $AA'BCXX'Y_2$ spin system.

All attempts to obtain single crystals of **7** failed. However, from toluene/hexane mixtures of the crude product, few crystals of compound **8** were obtained.

Complex **8** crystallises as brown blocks from toluene/hexane mixtures in the triclinic space group $P\bar{1}$. The asymmetric unit contains two molecules of **8** and three toluene solvent molecules. Its crystal structure analysis reveals a trinuclear cobalt complex with the composition $(Cp^{Bn}Co)_3$ (Figure 7). The

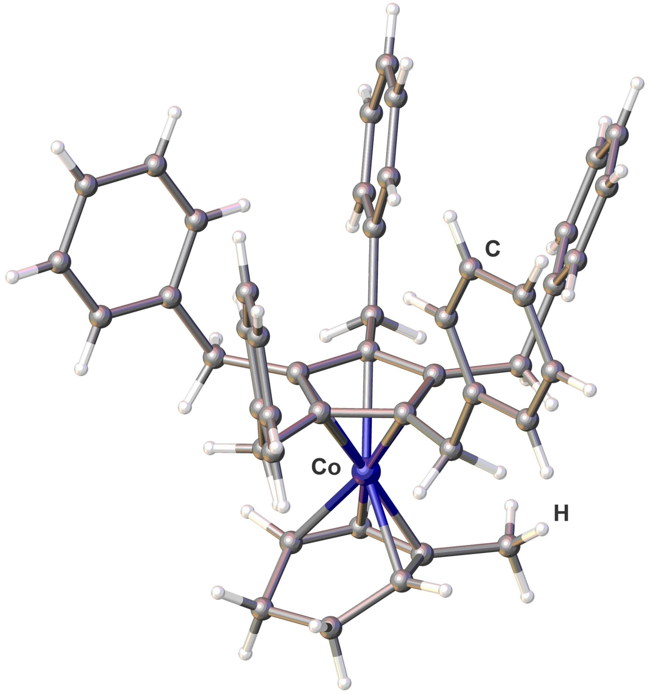


Figure 5. Molecular structure of **6** in the solid state. The disorder in the dihydrotoluene ligand is removed for clarity (see SI for details).

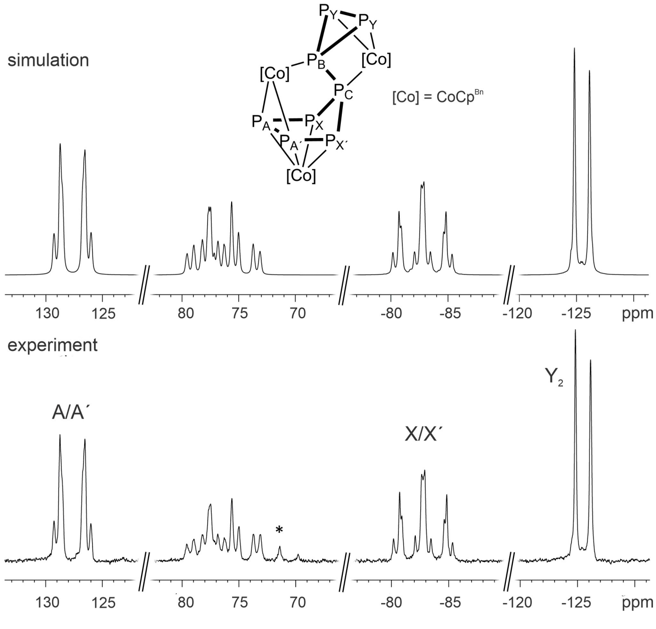


Figure 6. Experimental (C_6D_6, 162.0 MHz, 300 K; bottom) and simulated (top) $^{31}P\{^1H\}$ NMR spectrum of **7**. *Unidentified impurity.

Co atoms are bridged by two hydrido ligands in addition to one benzyl group of the Cp^{Bn} ligand at the Co3 atom. This results from a two-fold C–H activation of the $-CH_2Ph$ group of one of the Cp^{Bn} ligands. Accordingly, each cobalt atom attains the 18-VE configuration. The Co–Co bond lengths of 2.505(8) to 2.593(8) Å represent Co–Co single bonds. The C–C bond lengths of the dehydrobenzyl ligand reflect its benzyne nature. The C147–C37 (1.429(6) Å) and C149–C75 (1.428(6) Å) bonds represent single bonds, the C75–C151 (1.379(6) Å), C151–C19 (1.415(6) Å) and C19–C147 (1.375(6) Å) bond lengths show a diene system and the C37–C149 bond (1.389(6) Å) is in the range of a long double bond, due to the coordination to the Co1 unit. Triangular $(CpCo)_3$ fragments are known to be capable of activating C–H bonds of alkenes, with the formation of a central unit isostructural to **8** being observed.[19] However, to the best of our knowledge, no other Co trimer triggering a C–H arene activation has been reported to date.

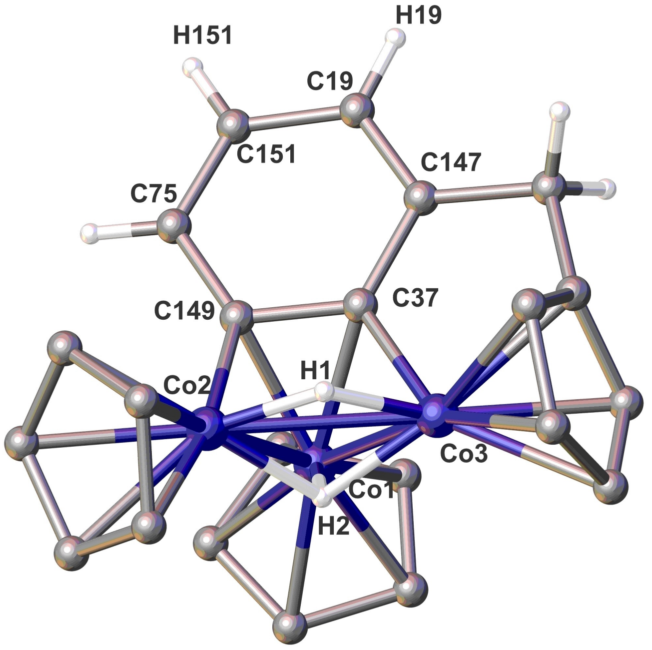


Figure 7. Molecular structure of **8** in the solid state. All benzyl groups have been omitted for clarity except for the group bridging the Co atoms.

The $^{31}P\{^1H\}$ NMR spectrum of the final fraction of the column chromatography shows signals of several P_n species. The major component is the P_{10} ligand complex **3**, which was obtained as the main product from the thermolysis reaction. An FD mass spectrometric analysis of this fraction showed the cation **3**$^+$ in addition to traces of the cations $[(Cp^{Bn}Co)_3P_6]^+$, $[(Cp^{Bn}Co)_4P_{13}]^+$ and **2**$^+$. However, due to the size of the Cp^{Bn} ligand, the molecular weight of larger P_n ligand complexes increases very strongly, which makes their detection under mass spectrometric conditions very challenging. A thin-layer chromatogram of this fraction showed several spots with very similar retention times and also a decomposition pattern. Therefore, no further attempts to separate the complexes were carried out. The structural characterisation of complexes **6** and **8** suggest a partial disproportionation of the starting material **5**, which is consistent with the rather low yield of the obtained P_n species.

Conclusions

The conversion of P_4 by $[Cp^{Bn}Co(CO)_2]$ ($Cp^{Bn}=C_5(CH_2C_6H_5)_5$) under thermal conditions gives almost exclusively the P_{10} complex $[(Cp^{Bn}Co)_4(\mu_4\text{-}\eta^4{:}\eta^4{:}\eta^2{:}\eta^2{:}\eta^1{:}\eta^1\text{-}P_{10})]$. However, its reaction with $[Cp^{Bn}Co]_n$, under mild conditions afforded a mixture of several products including the P_8 species $[(Cp^{Bn}Co)_3(\mu_3\text{-}\eta^4{:}\eta^2{:}\eta^2{:}\eta^1{:}\eta^1\text{-}P_8)]$ and the unique Co_3 cluster $[(Cp^{Bn}Co)_2Co(\mu_3\text{-}\eta^5{:}\eta^2{:}\eta^1{:}\eta^1\text{-}C_{40}H_{33})(\mu\text{-}H)(\mu_3\text{-}H)]$. The reactions were studied in solution, by multinuclear NMR spectroscopy, and mass spectrometry. Compounds **2**, **3**, **4**, **6** and **7** were additionally characterised in the solid state by single crystal X-ray diffraction. Current studies of our group in this field involve the extension of the conversion of P_4 with other unsaturated transition metal fragments bearing bulky substituents and their comparison with literature-reported examples.

Supplementary Data

CCDC-2333714 (**2**), CCDC-2333715 (**3**), CCDC-2333716 (**4**), CCDC-2333717 (**6**), and CCDC-2333718 (**8**) contain the supplementary crystallographic data for this paper. These data are provided free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: +4412233366033.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

Keywords: ^{31}P NMR · white phosphorus · polyphosphorus compounds · cobalt · sterically demanding

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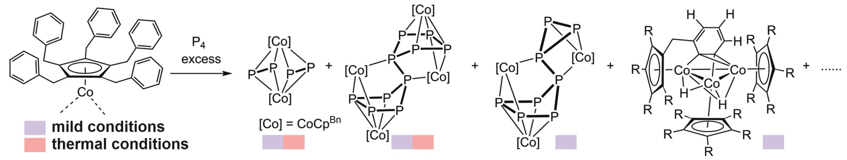

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Polyphosphorus Compounds Derived from P_4 Conversion with Sterically Demanding Cobalt Complexes