Phosphorus Cages

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Access to Extended Polyphosphorus Frameworks**

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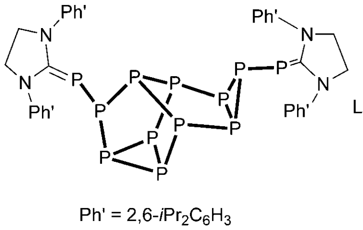
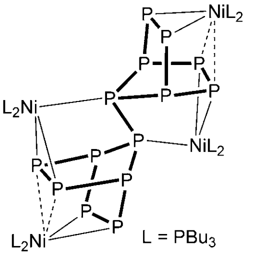
Dedicated to Professor Malcolm H. Chisholm on the occasion of his 65th birthday

The activation of P_4 is an current topic in chemistry. Recently, a big impact was made by main-group elements that are able to open one,[1] two,[2]or three P–P bonds[3] and can degrade the P_4 moiety to a P_2 or P_1 unit.[4] Aggregation of P_4 by N-heterocyclic carbenes (NHCs) has also shown that the large P_{12} unit in **A** can be achieved.[5] Moreover, larger cationic P_n^+ ($n \leq 89$)[6] and anionic P_n^- ($n \leq 49$)[6,7] polyphosphorus species have been generated in the gas phase using laser ablation techniques. Earlier investigations in organic solvents by Baudler and co-workers led to a large number of organo-substituted polyphosphorus compounds.[8] They have also achieved the synthesis of mixtures of the larger polyphosphides, such as P_{16}^{2-}, P_{19}^{3-}, and P_{21}^{3-}.[9] Some of these structures were partially isolated and structurally characterized[10] as was the polyphosphide P_{26}^{4-}.[11]

In contrast to this activation of P_4 with main-group compounds and elements,[12] the activation of P_4 by transition-metal compounds is an established field[13] and of high interest regarding the development of processes for the synthesis of organophosphorus compounds that circumvent PCl_3 as a key precursor. To date, the largest neutral P_n species found is $[\{(Bu_3P)_2Ni\}_4P_{14}]$ (**B**), which was synthesized by the condensation of two P_7 units starting from $Li_3P_7{\cdot}3\,DME$.[14] Using P_4 as starting material, the largest structurally characterized neutral P_n ligand complexes are $[\{CpCr(CO)_2\}_5(P_{10})]$[15] and $[(Cp^RM)_4P_{10}]$ (M = Rh, $Cp^R = Cp'' = \eta^5$-1,3-tBu$_2$C$_5$H$_3$;[16] M = Co, $Cp^R = Cp^{Si} = \eta^5$-1,3-(SiMe$_3$)$_2$C$_5$H$_3$)[17] (**C**). The structure of **C** is reminicent of the condensation of two *cyclo*-P_5 units. The largest P_n complex obtained from P_4 to date is $[(Cp'''Co)_3P_{12}]$ (**D**; $Cp''' = \eta^5$-1,2,4-tBu$_3$C$_5$H$_2$), which was identified by ^{31}P NMR spectroscopy and obtained by Scherer and co-workers as a minor product (3%) after the co-thermolysis of $[Cp'''Co(CO)_2]$ with P_4 at 190° or in moderate yields (23%) by photolysis at room temperature followed by $[(Cp'''Co)_3P_8]$ (10%).[18] Furthermore, in both reactions, $[(Cp'''Co)_2(P_2)_2]$ was formed in the thermolysis as major (22%) and in the photolysis as the minor product (4%).



A



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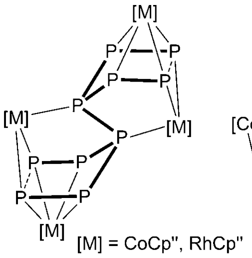
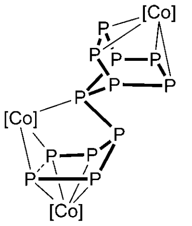


C



D

The current level of knowledge raised the question as to whether there are rational ways to synthesize larger neutral P_n aggregates to mimic the transformation of P_4 to Hittorf's phosphorus,[19] or other polyphosphorus structures, which are calculated to be more stable than P_4 phosphorus.[20] For this reason, the use of an unsaturated complex fragment that is able to consume P_4 tetrahedra and combine these to larger species seemed to be advantageous. As it is obvious that Cp^RCo moieties play an important role in the stabilization of large P_n units, the use of $[(Cp'''Co)_2(\eta^4{:}\eta^4\text{-}C_7H_8)]$ (**1**)[21] came to mind. Complex **1** partly dissociates in solution to liberate electronically unsaturated 14-valence-electron [Cp'''Co] fragments.[21] These highly reactive metal/ligand fragments could then react with P_4 under very mild conditions, in contrast to the rather low reactivity of $[Cp'''Co(CO)_2]$ with P_4.[22] Herein we present the use of this unsaturated complex to form products selectively, depending on the type of reaction procedure and the temperature. These controlled reactions can be used to achieve the largest structurally characterized polyphosphorus complexes containing P_{16} and P_{24} units.

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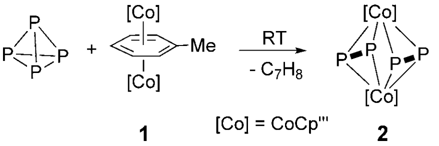
Supporting information for this article, including full synthetic and spectroscopic details for **3**, **5**, **6**, and **7**, crystallographic details and full details and references for the DFT calculations, is available on the WWW under http://dx.doi.org/10.1002/anie.201001000.

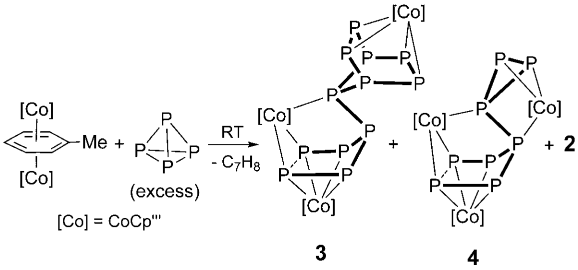
Moreover, there is evidence from mass spectrometry of even higher P_n species. Finally, for the first time, the P_{12} complex **D** was also synthesized for the first time in high yields and structurally characterized.

By adding a solution of P_4 in toluene to a solution of the cobalt complex **1** at room temperature, a quantitative formation of the violet dinuclear cobalt complex **2** was observed [Eq. (1)].



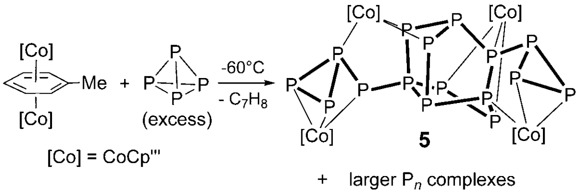
(1)

In contrast, when a solution of **1** was slowly added to a solution of an excess of P_4 at room temperature, the ^{31}P NMR spectrum of the crude reaction mixture revealed the P_{12} complex **3** as the main product, which can be isolated after chromatographic workup in 41 % yield followed by **2** (14 %) and the P_8 complex **4** (5 %) [Eq. (2)]. Obviously, the existence of an excess of P_4 during the slow addition of the cobalt complex leads to an aggregation of P_4 units and thus to larger P_n units.



(2)

By carrying out the same procedure at −60 °C, the ^{31}P NMR spectrum of the crude reaction mixture revealed a novel P_{16} ligand complex $[(Cp'''Co)_4P_{16}]$ (**5**) as the main product and signals of even larger phosphorus ligand complexes are observed [Eq. (3)].



(3)

Due to the partial decomposition of the larger P_n ligand complexes during the chromatographic workup, the separation of the reaction products is achieved first by column chromatography to obtain a combined fraction of the larger P_n ligand complexes. Furthermore, the FDI mass spectrometric analysis of this fraction reveals the presence of $[(Cp'''Co)_5P_{24}]$, $[(Cp'''Co)_5P_{26}]$, $[(Cp'''Co)_6P_{26}]$, and complexes up to $[(Cp'''Co)_6P_{29}]$.[23] Subsequent fast thin-layer chromatographic separation in a glove box yields $[(Cp'''Co)_5P_{24}]$ (**6**) in addition to **5**.

The crystal structure analysis of **3**[23] (Figure 1) confirms the P_7-P_5 composition of the P_{12} ligand that was deduced from ^{31}P NMR investigations by the Scherer group.[18] The P_{12} framework can be formally derived from a P_5 "cyclopentadiene" bound to a P_7 "norbornadiene" fragment by a P–P bond (Figure 2). This framework is stabilized by the coordination sphere of three 14-valence-electron {Cp'''Co} fragments to serve as an overall 12-electron donor ligand. The Co2–P7 bond (2.1489(2) Å) is significantly shorter than the Co–P bonds at Co1 (average value: 2.3280(2) Å) and Co3 (average value: 2.3356(2) Å), which represents the formal dative bond from the P7 atom. Co2 receives the remaining two electrons from the P8–P9 unit. The P8–P9 distance (2.4121(2) Å) is close to the longest-known P–P bonds. Compared to the ionic compound $[Ag(\eta^2\text{-}P_4)_2]^+[Al\{OC(CF_3)_3\}_4]^-$[24] (2.329(2) Å), the P8–P9 distance in **3** is elongated by 0.083 Å, but is still 0.05 Å shorter than in the "side-on" coordinated P–P edge of the P_4 molecule in $[ClRh(PPh_3)_2(\eta^2\text{-}P_4)]$[25] (2.462(2) Å).[26] Moreover, the compounds $[(Cp''Rh)_4P_{10}]$[16] ($Cp'' = \eta^5\text{-}1,3\text{-}tBu_2C_5H_3$) and $[(Cp^{Si}Co)_4P_{10}]$[17] ($Cp^{Si} = \eta^5\text{-}1,3\text{-}(SiMe_3)_2C_5H_3$), which have an analogous coordination mode in this region, have distinctly longer P–P distances (2.624(2) Å and 2.4743(15) Å).

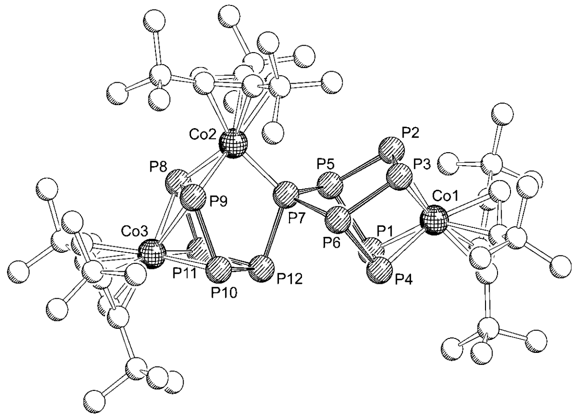


Figure 1. Molecular structure of **3** (hydrogen atoms omitted for clarity).

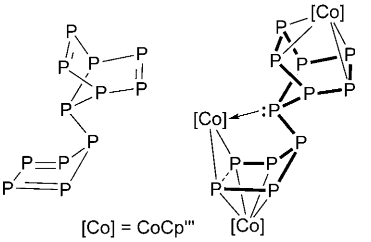


Figure 2. P_{12} skeleton and coordination mode of complex **3**.

Compound **5** is ruby-colored and readily soluble in organic solvents. It is very air-sensitive, but stable in the solid state under argon for months. Solutions of **5** can be handled at room temperature without decomposition. In the FDI mass spectrometric analysis, the molecular ion is found along with the complex fragments $[(\mathrm{CoCp'''})_3\mathrm{P}_{12}]^+$ and $[(\mathrm{CoCp'''})_2\mathrm{P}_4]^+$, thus revealing the decomposition process of **5**.

The ^{1}H NMR spectrum of complex **5** in C_6D_6 at 27 °C reveals a hindered rotation of all four Cp''' ligands; for example, 12 singlets of the 12 *t*Bu groups are observed. Attempts to measure ^{1}H NMR spectra at higher temperatures to obtain free rotation of the Cp''' groups failed owing to the decomposition of **5**. At 27 °C, the $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR spectrum of the P_{16} ligand complex **5** consists of 13 signal groups in the ratio of 1:1:2:1:1:1:1:2:1:2:1:1:1 between $\delta = 210$ and -95 ppm.[23]

The X-ray structure analysis of **5** (Figure 3) reveals a polyphosphorus cage consisting of 16 phosphorus atoms stabilized by four {Cp'''Co} fragments. The central P_9 cage of the polycyclic P_{16} skeleton is connected to a P_3 ring and a P_4 unit. The unprecedented architecture of the P_{16} core of **5** is very different from that found in compound **3**.

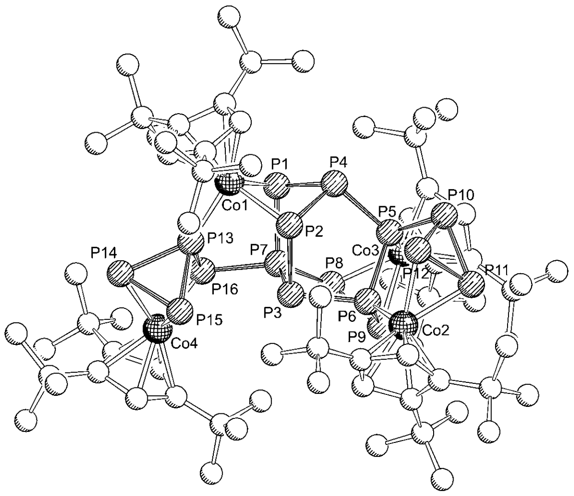


Figure 3. Molecular structure of **5** (hydrogen atoms omitted for clarity).

The P_{16} ligand acts as a 16-electron donor ligand towards four {Cp'''Co} fragments. Each cobalt center is coordinated by three phosphorus atoms of the P_{16} ligand (Figure 4). Each cobalt atom is thereby coordinated to one phosphorus atom with a shorter dative bond (2.1651(16)–2.2218(16) Å) and by two longer Co–P bonds (2.2703(16)–2.3192(17) Å). The P7–P16 bond (2.2334(19) Å) is in the range of a single bond, but is to a certain extent remarkable. From an electronic viewpoint, it can be seen to be zwitterionic, or in a more systematic way as a phosphanylidene-σ^4-phosphorane, which is incorporated into a push–pull system towards the {Cp'''Co} fragment. The latter class of compounds is meanwhile established in phosphorus chemistry[27] and is found for example in $[(2,6\text{-}\mathrm{Mes}_2\mathrm{C}_6\mathrm{H}_3)\mathrm{P}(\mathrm{AuCl})_2\mathrm{PMe}_3]$,[27a] in which, upon coordination of the phosphanylidene phosphorus to AuCl fragments, significant lengthening of the P–P bond from 2.084(2) Å to 2.205(1) Å is observed.

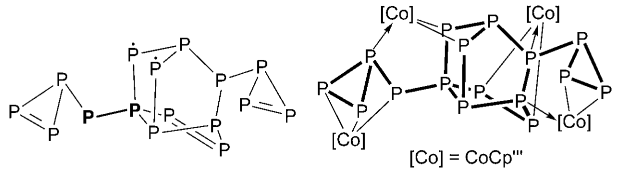


Figure 4. P_{16} skeleton and coordination mode of complex **5**.

To gain a deeper understanding of the nature of the P–P bonds in **5**, we performed a topological analysis[28] of the electron density ρ and the electron localization function (ELF)[29,30] obtained from density functional (DFT) calculations, and compared the results with several model phosphorous compounds containing P–P bonds with different characteristics (Supporting Information, Table S1, Figure S9, and discussion[23]). Based on these comparisons, we found that all of the P–P bonds in **5** are typical single P–P bonds. Specifically the topological parameters of the P7–P16 bond are similar to a usual single P–P bond. However, the results of the NBO charge analysis (Supporting Information, Table S2[23]) shows a slightly increased positive charge on P7 and negative charge on P16, thus indicating a certain degree of polar character for this bond.

Along with the P_{16} ligand complex **5**, a brown compound **6** was isolated by thin-layer chromatographic separation; compound **6** is very air sensitive and readily soluble in hexane and dichloromethane. In the FDI mass spectrometric analysis, the molecular ion of **6** is observed next to traces of the fragments $[(\mathrm{CoCp'''})_4\mathrm{P}_{19}]^+$, $[(\mathrm{CoCp'''})_4\mathrm{P}_{12}]^+$, and $[(\mathrm{CoCp'''})_3\mathrm{P}_{17}]^+$.

In the ^{1}H NMR spectrum of complex **6** in C_6D_6 at 27 °C, signals for five Cp''' ligands are observed. Only two show free rotation on the NMR timescale, which can be assigned to the Co4 and Co5 atoms by steric considerations (see Figure 5). The $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR spectrum of the P_{24} ligand complex at 27 °C consists of 12 signal groups in the ratio of 1:1:1:2:2:5:2:2:2:2:2:2 between $\delta = 350$ and -140 ppm. Upon cooling to -60 °C, the signals sharpen significantly.[23]

Numerous attempts to obtain single crystals of **6** failed, which may be due to the high flexibility of the phosphorus framework that results in the broad signals in the ^{31}P NMR

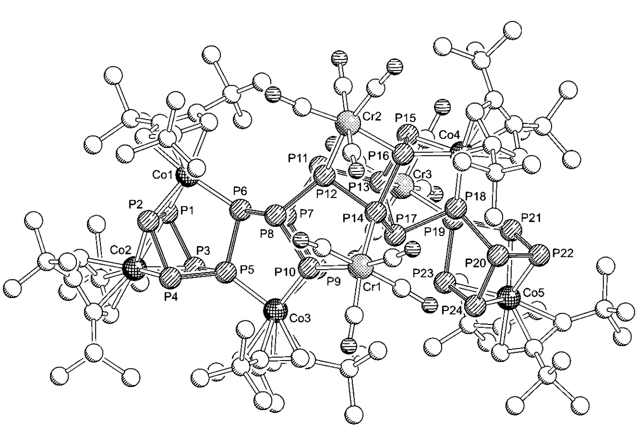
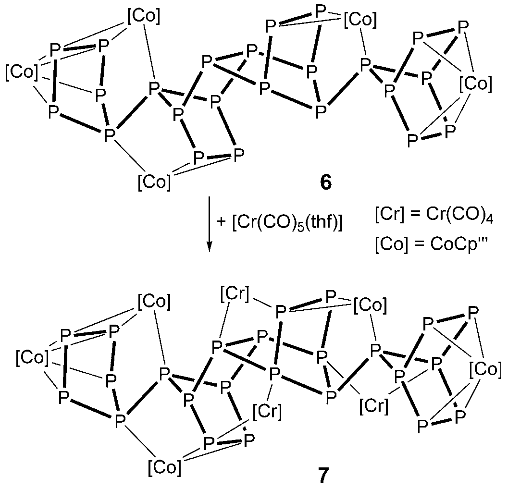


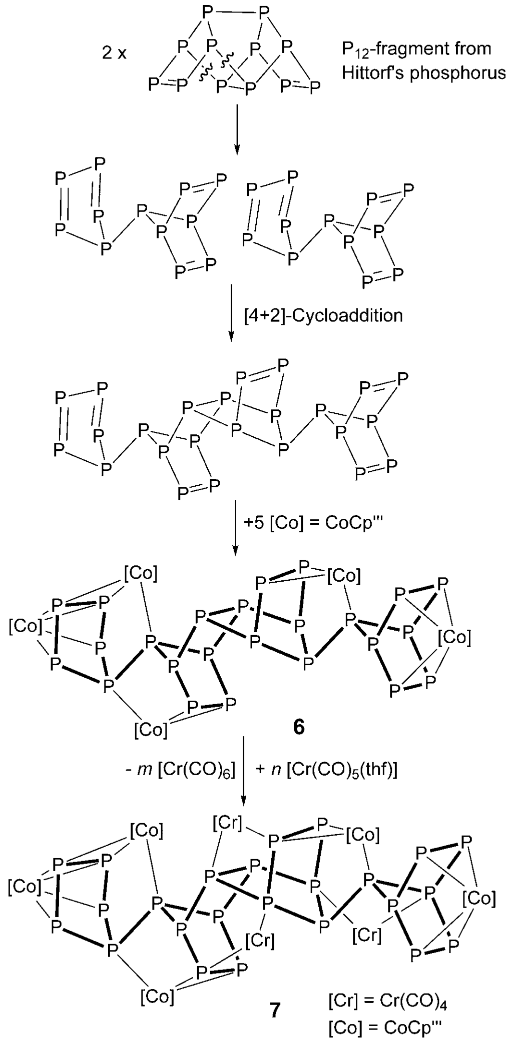
Figure 5. Molecular structure of **7** (hydrogen atoms omitted for clarity).

spectrum at room temperature. To stabilize the P_{24} ligand, we added [Cr(CO)$_5$(thf)] to **6**. After months of storage in a cold hexane solution (−35 °C), brown rods of [(Cp‴Co)$_5$P$_{24}${Cr(CO)$_4$}$_3$] (**7**) formed (Scheme 1). The ^{31}P{^{1}H} NMR spectrum of **7**[23] shows 16 groups of signals. Compared to **6**, the signals are clearly sharper, thus revealing a more rigid structure.



Scheme 1.

The X-ray structure analysis of **7** (Figure 5) shows a P_{24} core that is stabilized by five {CoCp‴} and three {Cr(CO)$_4$} fragments. The polycyclic phosphorus framework of **7** consists of seven five-membered rings and three six-membered rings. The central P_{12} fragment is reminiscent of a section of Hittorf's phosphorus in which the P_8 cuneane (here P_6Co units, with Co instead of a P_2 moiety) are linked by a P_2 unit. The P_{24} ligand acts as a 32-electron donor ligand towards five {Cp‴Co} fragments and three {Cr(CO)$_4$} fragments. Each {Cr(CO)$_4$} fragment is coordinated by two lone pairs of the P_{24} framework, whereby the complex becomes rigid. The coordination modes of the phosphorus ligand to the CoCp‴ fragments is similar to those in the P_{12} ligand complex **3**. As in the crystal structures of **3** and **7**, the dative bonds are much shorter than the other Co−P bonds. The P−P bonds are in the order of P−P single bonds, whereas the formal P−P double bonds (average: 2.151 Å) of the P_{24} skeleton (Scheme 2) are typically shorter than the formal single bonds (average: 2.228 Å). The only exception is the P1−P2 bond (2.482(4) Å), which is even 0.070 Å longer than the analogous P−P bond in **3**. The similar architecture of the phosphorus ligands of **3** and **5** suggests a formation of the P_{24} ligand by a [4+2] cycloaddition of two P_{12} units (Scheme 2), which are stabilized by {Cp‴Co} moieties in **6** and finally by additional {Cr(CO)$_4$} units in **7**. Interestingly, the starting P_{12} units can be rationalized as sections of Hittorf's phosphorus; a subsequent cycloaddition, aggregation, and stabilization by {Cp‴Co} and {Cr(CO)$_4$} fragments is thus rationalized.



Scheme 2. Proposed cycloaddition of two P_{12} moieties formed formally from a section of Hittorf's phosphorus, ultimately resulting in the P_{24} cage of **6** and **7**.

In summary, it has been shown that by using the right reaction procedure with P_4, the use of unsaturated complex fragments opens up the way to the aggregation of P_4 units to P_8, P_{12}, P_{16}, and P_{24} ligand complexes that could be characterized by X-ray diffraction. These are the largest polyphosphorus compounds that have been characterized by X-ray diffraction. As a result of the thin-layer separation, even larger P_n ligand complexes, such as [(Cp‴Co)$_6$P$_{29}$], are detected and identified by mass spectrometry. The new synthetic concept of the metal-controlled self-aggregation of P_4 molecules to form large neutral polyphosphorus cages gives insight into the formation of larger allotropes of phosphorus arising from elemental P_4.

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