A *cyclo*-P₆ Ligand Complex for the Formation of Planar 2D Layers

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Abstract: The all-phosphorus analogue of benzene, stabilized as middle deck in triple-decker complexes, is a promising building block for the formation of graphene-like sheet structures. The reaction of [(CpMo)₂(μ,η¹⁻,η⁶-P₆)] (1) with CuX (X = Br, I) leads to self-assembly into unprecedented 2D networks of [[(CpMo)₃P₆(CuI)]₃] (2) and [[(CpMo)₃P₆(CuBr)]₃] (3). X-ray structural analyses show a unique deformation of the previously planar cyclo-P₆ ligand. This includes bending of one P atom in an envelope conformation as well as a bisallylic distortion. Despite this, 2 and 3 form planar layers. Both polymers were furthermore analyzed by ³¹P({¹H} magic angle spinning (MAS) NMR spectroscopy, revealing signals corresponding to six non-equivalent phosphorus sites. A peak assignment is achieved by 2D correlation spectra as well as by DFT chemical shift computations.

Tailored syntheses of the inorganic analogues of organic molecules, is a fascinating area of fundamental research. Following the so-called isosbestic principle,[5] substitution of methine moieties by phosphorus atoms appears quite promising. In fact, 2016 marks the 50th anniversary of the first successful synthesis of a phosphabenzene in which one CH unit is replaced by a P atom,[2] which set the stage for the ultimate goal, namely the preparation of carbon-free hexaphosphabenzene. Since then, many theoretical studies with respect to its aromaticity were reported that outlined the instability of a free cyclo-P₆ unit.[5] Nevertheless, its detection in an inert stabilizing matrix at low temperature might be feasible such that the challenge remains. A synthetic approach demonstrated by the Scherer group is the stabilization of the P₆ ring by coordination to transition metals, thus affording a triple-decker complex [(Cp⁺Mo⁺)(μ,η¹⁻,η⁶-P₆)] (Cp⁺ = η⁵-C₅Me₅) bearing a planar P₆ middle deck for the first time (Figure 1).[10] Triple-decker complexes containing the cyclo-P₆ unit could also be obtained for vanadium,[8] tungsten,[5] or niobium.[10] Quite recently, the sandwich complex [(CpMo)₃(μ,η¹⁻,η⁶-P₆)] (1) with the parent Cp ligands was synthesized and characterized.[5] In the case of the Mo and W complexes, the cyclo-P₆ ring has a perfect D₃h symmetry, whereas V and Nb derivatives exhibit a slight bisallylic distortion.[8a] It should be noted that the middle deck in [(Cp⁺T₈⁺)(μ,η¹⁻,η⁶-P₆)] has a chair conformation (Figure 1).[8]

In contrast to benzene, the presence of lone pairs at the phosphorus atoms converts these triple-decker complexes into excellent building blocks for supramolecular chemistry. Particularly intriguing is the possibility of graphene-like honeycomb networks resulting from reaction with Lewis acidic metal salts, an unmet challenge to date.

We have applied Lewis acidic coinage metal salts for linkage of unsubstituted P₆ complexes[9] and also for [(Cp⁺Mo⁺)(μ,η¹⁻,η⁶-P₆)] (Cp⁺ = Cp⁺, Cp⁺Br = η⁵-C₅(CH₂)₄H₅) [10] for example, the coordination of the bare cations Cu⁺, Ag⁺, and TI⁺ was studied revealing discrete [M(Cp⁺Mo⁺)(μ,η¹⁻,η⁶-P₆)]⁺ (M = Cu, Ag) units as well as a two-dimensional coordination network for M = Ti[10b] In this structure, the positively charged layers are separated by the weakly coordinating anions [Al(O(CF₃)₂)₄]⁻, forming an alternating network of catonic and anionic sheets.

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[1] Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.201504644.
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Figure 1. Triple-decker complexes containing a cyclo-P₆ middle deck.
Except for rather weak interactions of the $P_6$ unit with a mercury trimer $[\text{o-C}_6\text{H}_3\text{Hg}_3]$ yielding a super-sandwich structure,[27] the corresponding supramolecular chemistry of 1 utilizing its coordination properties is hitherto unknown.

The $P_6$ unit offers competitive coordination sites (Figure 2), which also presents potential problems. A considerable variety of connectivity renders the growth of single crystals suitable for X-ray analysis challenging. Indeed, twinned or layered crystals may be also encountered but occur in particular in the case of Cp rings. The obtained polymeric products are often insoluble and are sometimes even microcrystalline powders so that X-ray diffraction analysis is crucial for a determination of the exact coordination pattern. Since modern solid-state NMR techniques provide complementary information including the number of independent molecules in the unit cell, intermolecular distances or connectivity, the spatial proximity of constituent moieties, and even orientation relations, it is a very powerful tool for structure determination, particularly in case of powdered compounds (“NMR crystallography”).[11]

Herein, we report the coordination properties of the parent triple-decker complex 1 towards CuX ($X = \text{Br}, I$) revealing unprecedented 2D networks with similarities to graphene-like monolayers and distortion of the $P_6$ middle deck. All polymers were characterized by X-ray diffraction analysis as well as 1D $^{31}P({}^1H)$ magic-angle spinning (MAS) NMR spectroscopy where the peak assignment is based on the analysis of 2D $^{31}P$/$^{13}P$ MAS NMR correlation spectra and (split basis set) density functional theory (DFT) $^{31}P$ chemical shift computations.

When a colorless solution of CuX ($X = \text{Br}, I$) in CH$_2$CN is layered above an orange-brown solution of 1 in CH$_3$Cl$_2$ or toluene, an immediate color change to gray-black at the phase boundary occurs. During the diffusion process, a black powder precipitates and small black crystals are formed. The products are insoluble in hexane, toluene, CH$_2$Cl$_2$, CH$_3$CN, or THF, but possess a good solubility in pyridine, though at the cost of some fragmentation of the compounds, as seen by the recorded singlet peak at $\delta = -351.5$ ppm in the corresponding $^{31}P({}^1H)$ solution NMR spectra (in [D$_6$]pyridine) of the black microcrystalline solid and precipitate attributed to the starting compound 1.

Therefore, an effort was made to derive suitable crystallization conditions for the coordination products, applying a range of solvent mixtures and dilution conditions (see the Experimental Section).

In the presence of CuBr, the polymer $[([\text{CpMo}]_2(\mu_3-P_6)^{3,3,3,1,1,1,1,1,1,1,1,1},P_3)(\mu_3-P_3)^{3,3,1,1,1,1,1,1,1,1,1,1})\text{Cu}_2(\mu_3-P_3)_4]_n$ (2) crystallizes as black plates in the centrosymmetric triclinic space group $P\overline{1}$ (no. 2). Its X-ray structural analysis reveals a two-dimensional network with a cyclo-$P_6$ middle deck in a 1,2,4,5-coordination mode (Figure 2, type C; Figure 3). Each of the four $P$ atoms coordinates two Cu atoms in a $\eta^1:\eta^1$ fashion (Figure 3a). These in turn link the triple-decker complexes by forming (Cu$_2P_3$) four-membered rings. Taking into account the $\mu$-Br ligands, contorted five-membered (P$_2$Cu$_2$Br) rings become also visible (Figure 3a; for bond lengths, see the Supporting Information). A distinctive feature in 2 is the distortion of the cyclo-$P_6$ middle deck which is no longer planar.

The side view illustrates that one $P$ atom is bent out of the plane by 1.141(3) Å and therefore solely coordinated to one molybdenum atom with a bond length of 2.652(3) Å (Figure 4b). In comparison to the other Mo–P distances (2.400(2) Å–2.657(3) Å), this bond appears significantly elongated. Furthermore, the $P_6$ ring shows a significant bisallylic distortion where the $P_6$ units are separated by 2.652(3) Å and 2.444(3) Å, respectively. The remaining $P$–$P$ bond lengths are 2.168(4) Å and 2.162(4) Å for one $P_6$ ligand and 2.138(3) Å and 2.136(5) Å for the other (containing the envelope $P$ atom), thus
in between as single and double bond, and even shorter than in complex 1 (P–P{}_{\text{average}} 2.177(2) \AA). The distortion of the whole unit leads the Cp ligands to be inclined by 9.26° compared to a parallel arrangement in 1.

Notably, the geometry found is unique for P₆ middle decks, which most likely results from the coordination to Cu. Though the vanadium[5] and niobium[6] derivatives as well as the one-electron oxidation product of 1[10a] also show bis-allylic distortion, the P₆-ring remains planar in all examples (Figure 1). Furthermore, no chair-like conformation is present in 2, hampering comparison to the titanium complex (Figure 4). Despite the distorted P₆-ring, compound 2 forms planar layers (Figure 5).

In the presence of CuI, the compound \(\{\left(\text{CpMo}\right)\left(\mu\eta^3:3:1:1, P\eta\right)\left(\mu\eta^3:2:1:1, P\eta\right)\}_{0.84}\{\left(\text{CpMo}\right)\left(\mu\eta^6:6:1:1:1, P\eta\right)\}_{0.16}\text{Cu}_2(\mu\eta^3)\}\) is obtained, crystallizing as black plates in the monoclinic space group C2/m (no. 12). Its structure is comprised of a two-dimensional polymer with a 1,2,4,5-coordination mode of the middle deck (Figure 2, type C; Figure 6, Figure 7), comparable to 2. In this structure, unlike that of the Br derivative, each P atom is bound to one copper atom, which in turn forms \{Cu(P₆)₆\} six-membered and \{Cu(μ-I)₄\} four-membered rings, resulting in a characteristic tetrahedral environment for Cu (for bond lengths, see the Supporting Information). Hence, the Cu halide framework is much less extended than in 2. The cyclo-P₆-rings, however, prove to be disordered exhibiting two distinct coordination modes: \(\{\left(\text{CpMo}\right)\left(\mu\eta^3:3:1:1, P\eta\right)\left(\mu\eta^3:2:1:1, P\eta\right)\}_{0.84}\{\left(\text{CpMo}\right)\left(\mu\eta^6:6:1:1:1, P\eta\right)\}_{0.16}\text{Cu}_2(\mu\eta^3)\} (\text{3a}; Figure 6) and \(\{\left(\text{CpMo}\right)\left(\mu\eta^3:3:1:1, P\eta\right)\left(\mu\eta^3:2:1:1, P\eta\right)\}_{0.84}\{\left(\text{CpMo}\right)\left(\mu\eta^6:6:1:1:1, P\eta\right)\}_{0.16}\text{Cu}_2(\mu\eta^3)\} (\text{3b}; Figure 7) with corresponding occupancy factors of 0.84 and 0.16, respectively.

The middle deck in 3a shows the same bisallylic distortion as in 2 but with more uniform distances of 2.563(8) Å and 2.544(8) Å between the P₆ fragments (Figure 4). The bending of one P atom out of the plane by 1.113(9) Å is somewhat less distinctive but in a comparable range as of 2, though the Cp ligands retain their parallel arrangement in 3a. The bent phosphorus atom is additionally disordered over the mirror plane with an occupancy factor of 0.42 each. The distance between molybdenum and this out-of-plane phosphorus atom (2.683(8) Å) is the longest among all of the Mo–P bond lengths (2.434(4) Å–2.598(4) Å), but possible uncertainties caused by the disorder cannot be discounted. Again, the remaining P–P bond lengths (\(\eta^3:3:1:1\)-P; 2.127(7) Å, 2.132(7) Å; \(\eta^3:2:1:1\)-P 2.151(9), 2.147(10) Å) are shortened compared to those of 1.

Surprisingly, with an occupancy factor of 0.16, the intact cyclo-P₆ middle deck is present (substructure 3b, Figure 7, Figure 4d). It is located on a mirror plane and is therefore perfectly planar. The coordination to Cu leads to a shortening of the
P–P bond lengths with respect to those of 1, which is consistent with 2 and 3a and most significant for $P_{\text{coord}}-P_{\text{coord}}$ with values of 2.00(3) Å and 2.01(4) Å, respectively ($P-P_{\text{coord}}$ 2.03(3)–2.132(7) Å).

The question whether the bent (3a) and planar (3b) cyclo-P$_6$ middle decks occur within the same layer or the layers comprising the same middle decks form with different probability cannot be answered solely from structural data. As with 2 absolutely planar sheet-like structures are also formed in 3 (Figure 5b).

Compared to the coordination polymer built from ([Cp*Mo]$_2$)$_2$(-η$_4$-P$_4$)$_2$) and Tl[Al(O(CF$_3$)$_3$)$_3$] that maintains planarity of the middle decks, the coordination mode as well as the distortion of the cyclo-P$_6$ ligand in 2 and 3 are unique.

Because the polymer networks are insoluble in common solvents and fragmentation is observed in pyridine, $^{31}$P($^1$H) MAS NMR spectra of both compounds (2 and 3) were recorded. Even though the $^{31}$P chemical shifts (with respect to H$_3$PO$_4$) occur over a rather large range of values, the magnitude of the range of observed signals (ca. 700 ppm) is remarkable. To achieve a sufficient spectral resolution while allowing for quantitative interpretation of the acquired spectra, the conflicting demands of the significant $^{31}$P chemical shift anisotropy and line-broadening contributions from $^{31}$P–63Cu dipolar couplings have to be considered. Thus, the $^{31}$P($^1$H) MAS NMR spectra of 2 and 3 were recorded at fast MAS and a magnetic field of 4.7 T rather than at 11.7 T.

The $^{31}$P($^1$H) MAS NMR spectrum of 2 (Figure 8) at first glance exhibits four rather broad peaks and a sharp peak at $-347.4$ ppm with spinning sidebands (marked with asterisks). The latter signal can readily be attributed to the presence of residual 1, whereas assignment of the signals for the P$_6$ unit is not straightforward. The corresponding isotropic chemical shifts however could be unambiguously identified from the diagonal peaks in a 2D $^{31}$P–$^{31}$P correlation spectrum of 2 (Figure 9).

In contrast, the $^{31}$P MAS NMR spectrum of 3 (Figure 11) demonstrates the presence of the different coordination modes of the cyclo-P$_6$ unit as documented by the larger range of signals compared to 2, which yield Gaussian-type peaks at 283.4, 270.3, 114.4, 35.9, −22.3, −37.6 ppm as well as −345 and...
—653 ppm. Though unambiguous spectral fitting could not yet be achieved, in part owing to the presence of residual 1 and further impurities, $^{31}$P DFT chemical shift computations at PBE1PBE/cc-pVQZ level of theory based on representative structure cutouts of 3a and 3b (for labeling, see Figure 10) indicated that the constituents of the P$_2$ unit in 3b resonate between —350 ppm and —520 ppm. Hence, they are significantly shifted towards more negative values (DFT: P2/P7 = 353, P1/P8 = 394, P5 = 455, P6 = 519 ppm). In the case of 3a, phosphorus sites are computed as: P3 234, P2 234, P8 227, P5 11, P1 = 30, and P4 = 368 ppm, which is more comparable to those of 2, reflecting a similar distortion of the P$_2$ unit in 3a (see Figure 4).

Nevertheless, further impact of local coordination, including bond lengths, torsion angles, or even the orientation of [CpMo] units on the local density distribution at the distinct phosphorus sites in 2 and 3 is evident, rendering $^{31}$P MAS NMR a sensitive probe for structure elucidation of such compounds.

In summary, the first coordination polymers 2 and 3 containing the parent triple-decker complex 1 are obtained by the self-assembly with CuX (Br, I). Their structures reveal two-dimensional polymers with the cyclo-P$_6$ middle deck in a 1,2,4,5-coordination mode to copper. Resembling graphene-like sheets, the layers hereby formed are planar. Surprisingly, the coordination profoundly affects the geometry of the P$_2$ unit of 1 as evidenced by a significant bisylilic distortion and unprecedented envelope conformation of one phosphorus atom in both polymers. Owing to insolubility of 2 and 3, they were comprehensively characterized by 1D and 2D $^{31}$P(H) MAS NMR spectroscopy. The obtained signals are spread over a remarkable range of more than 900 ppm and correspond to six independent phosphorus atoms, consistent with the distorted P$_6$ moiety. Furthermore, DFT chemical shift computations allow a reliable assignment of the signals.

**Experimental Section**

All of the reactions were performed under an inert atmosphere of dry nitrogen or argon with standard vacuum, Schlenk, and glove-box techniques. Solvents were purified, dried, and degassed prior to use by standard procedures. Complex 1 was synthesized following the reported procedure. Commercially available chemicals were used without further purification. Solution NMR spectra were recorded on a Bruker Avance 300 spectrometer. The corresponding ESI-MS spectra were acquired on a ThermoQuest Finnigan MAT TSQ 7000 mass spectrometer, whereas elemental analyses were performed on a Vario EL III apparatus.

Synthesis of 2: In a large Schlenk tube, a bright orange-brown solution of 1 (100 mg, 0.20 mmol) in CH$_2$Cl$_2$ (100 mL) is carefully layered first with a solvent mixture CH$_2$Cl$_2$/CH$_3$CN (2:1, 20 mL), then with a colorless solution of CuBr (186 mg, 1.30 mmol) in CH$_3$CN (50 mL). Already after one day, the formation of small black crystals of 2 at the phase boundary, sometimes in addition to red plates of 1, can be observed. After complete diffusion the mother liquor is decanted, the crystals are washed with CH$_2$Cl$_2$ to remove residues of the starting material 1. Afterwards the crystals are washed with hexane (3 × 15 mL) and dried in vacuo to yield 105 mg of 2 (0.05 mmol, 53%). The synthesis of 2 can also be down-scaled to a few mg of the starting materials and accordingly a few mL of solvents. Crystals suitable for X-ray structural analysis can be obtained, when a solution of 2 (4 mg, 0.008 mmol) in CH$_2$Cl$_2$ (5 mL) is layered first with a solvent mixture CH$_2$Cl$_2$/CH$_3$CN (2:1, 2 mL), afterwards with a solution of CuBr (7 mg, 0.05 mmol) in the same solvent mixture of CH$_2$Cl$_2$/CH$_3$CN (2:1, 5 mL) in a thin Schlenk tube.

Analytical data of 2: $^1$H NMR ([D$_2$]pyridine): $\delta$ ppm = 2.55 (s, (CpMo),P$_2$); $^3$P([H]) NMR ([D$_2$]pyridine): $\delta$ ppm = —351.60 (s, (CpMo),P$_2$); Positive-ion ESI-MS (pyridine): m/z (%) = 711.9 ([CpMo],P$_2$CuBr$_2$([H$_2$]N))$_3^+$, 899.5 ([CpMo],P$_2$CuBr$_2$([C$_6$H$_5$CN])$_3^+$, 885.85 ([CpMo],P$_2$CuBr$_2$([H$_2$]N))$_3^+$, 795.6 ([CpMo],P$_2$CuBr$_2$([C$_6$H$_5$CN])$_3^+$, 729.9 ([CpMo],P$_2$CuBr$_2$([H$_2$]N))$_3^+$, 711.9 ([CpMo],P$_2$CuBr$_2$([C$_6$H$_5$CN])$_3^+$, 649.7 ([CpMo],P$_2$CuBr$_2$([C$_6$H$_5$CN])$_3^+$, 508.6 ([CuBr$_2$([H$_2$]N))$_3^+$, 364.7 ([CuBr$_2$([C$_6$H$_5$CN])$_3^+$, 220.9 (100% [CuBr$_2$([H$_2$]N))$_3^+$, 182.9 (60%) [CuBr$_2$([C$_6$H$_5$CN])$_3^+$; Negative-ion ESI-MS (pyridine): m/z (%) = 796.2 (4) [CuBr$_2$], 654.3 (3) [CuBr$_2$], 510.4 (4) [CuBr$_2$], 366.4 (27) [CuBr$_2$], 222.5 (100%) [CuBr$_2$]; Elemental analysis: Calculated (%) for [(CpMo),P$_2$]CuBr$_2$): C 11.10, H 0.93; found: C 11.19, H 0.98.

Synthesis of 3: In a large Schlenk tube, a bright orange-brown solution of 1 (90 mg, 0.18 mmol) in CH$_2$Cl$_2$ (120 mL) is carefully layered first with a solvent mixture CH$_2$Cl$_2$/CH$_3$CN (2:1, 20 mL), then with a colorless solution of Cul (203 mg, 1.07 mmol) in CH$_2$CN (60 mL). Already after one day, formation of small black crystals of 3 at the phase boundary in addition to red plates of 1 can be observed. After complete diffusion the mother liquor is decanted, the crystals are washed with several times with CH$_2$Cl$_2$ to remove 1. When the CH$_2$Cl$_2$ solution is absolutely colorless, the crystals are washed with a toluene/hexane mixture and dried in vacuo to yield 75 mg of 3 (0.084 mmol, 47%). The synthesis of 3 can also be down-scaled to a few mg of the starting materials and accordingly a few mL of solvents. Crystals suitable for X-ray structural analysis can be obtained when a solution of 1 (4 mg, 0.008 mmol) in toluene (5 mL) is layered with a solution of Cul (8 mg, 0.04 mmol) in a solvent mixture of CH$_2$Cl$_2$ (5 mL) and CH$_3$CN (1 mL) in a thin Schlenk tube. Analytical data of 3: $^1$H NMR ([D$_2$]pyridine): $\delta$ ppm = 2.53 (s,
Crystal data for [(CpMo)₃Cu]⁺: M = 888.76, monoclinic, space group C2/m, a = 10.3181(5), b = 18.5529(12), c = 13.5161(6), α = 77.09(4), β = 86.78(4), γ = 73.20(4). V = 1023.80(9) Å³, Z = 2, Dcalcd = 2.590 g cm⁻³, black plate 0.13 x 0.06 x 0.10 mm; Cu Kα radiation, θ = 123.0(2) K, 13687 measured, 8496 independent, 6645 observed reflections Rint = 0.060, μ = 13.5 mm⁻¹, refinement (on F²) with SHELXL2014. 254 parameters, 92 restraints, R1 = 0.060 (I > 2σ(I)), wR2 = 0.165 (all data), Goof = 1.00, max/min residual electron density 1.92 and −2.60 e Å⁻³.

The ³¹P/(H) MAS NMR spectra of 2 and 3 were recorded at 4.7 T (¹H) resonance at 81.02 MHz and 25 kHz MAS using a Bruker Avance III 200 spectrometer and a Bruker 2.5 mm MAS NMR probe accumulating 2048 scans at a relaxation delay of 90 s and SPINALE64 high power proton decoupling. All pulse lengths were adjusted with respect to a radio-frequency field strength of 100 kHz (that is, π/2 pulses of 2.5 μs). To avoid severe baseline distortions, the rotor-synchronized Hahn spin echo sequence was applied (with echo delays of a rotor period (τR = 40 μs), corrected for finite pulse durations). The signal (FID of 32k points) was sampled with a dwell time of 0.5 μs and zero-filled to 128k points prior to processing. Spectral fitting was performed with DMFit.[16] All DFT PBE1PBE computations (with 6–311G(d,p) (for H, C, O), cc-pVQZ (for P), LANL2DZ (for Mo, Cu, Br, I) were done as implemented in the Gaussian09 software package.[15] The obtained ¹P chemical shielding tensor was “translated” into chemical shifts δ with respect to H₃PO₄ (δstandard = 0 ppm; δstandard[cc-pVQZ] = 349.5899 ppm) using the expression δsample = δstandard + δstandard[cc-pVQZ] − δstandard[cc-pVQZ].

Acknowledgements

C.H. is grateful for a PhD fellowship of the Fonds der Chemischen Industrie. The Deutsche Forschungsgemeinschaft supported this work. The European Research Council (ERC) is acknowledged for the support in the SELFPHOS AdG-2013-339072 project. G.B. appreciates access to WWU-PALMA, the High Performance Computing facilities, kindly provided by Prof. A. Heuer (University of Münster).

Keywords: coordination polymers, copper, hexaphosphabenzenes, molybdenum, triple-decker complexes.