

The Potential of Molybdenum Complexes Bearing Unsubstituted Heterodiatomic Group 15 Elements as Linkers in Supramolecular Chemistry

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Dedicated to Professor E. Niecke on the occasion of his 80th birthday

Abstract: The reactions of tetrahedral molybdenum complexes bearing unsubstituted heterodiatomic Group 15 elements, $[\text{Cp}_2\text{Mo}_2(\text{CO})_4(\mu, \eta^2: \eta^2\text{-PE})]$ ($\text{Cp} = \text{C}_5\text{H}_5$; $\text{E} = \text{As}$ (**1**), Sb (**2**)), with Cu^{I} halides afforded seven unprecedented neutral supramolecular assemblies. Depending on the Mo_2PE units and the Cu^{I} halide, the oligomers $[\{\text{Cp}_2\text{Mo}_2(\text{CO})_4\{\mu, \eta^2: \eta^2: \eta^2\text{-PE}\}\}_n\{\text{Cu}(\mu\text{-X})\}_n]$ ($\text{E} = \text{As}$ ($\text{X} = \text{Cl}$ (**3**), Br (**4**)); $\text{E} = \text{Sb}$ ($\text{X} = \text{Cl}$ (**6**), Br (**7**))) or the 1D coordination polymers $[\{\text{Cp}_2\text{Mo}_2(\text{CO})_4\{\mu, \eta^2: \eta^2: \eta^2\text{-PE}\}\}_n\{\text{Cu}(\mu\text{-I})\}_n]$ (**5**) and $[\{\text{Cp}_2\text{Mo}_2(\text{CO})_4\{\mu, \eta^2: \eta^2: \eta^2\text{-PE}\}\}_n\{\text{Cu}(\mu\text{-X})\}_n]$ ($\text{X} = \text{I}$ (**8**), Br (**9**)) are accessible. These solid-state aggregates are the first and only examples featuring the organometallic heterodiatomic Mo_2PE complexes **1** and **2** as linking moieties. DFT calculations demonstrate that complexes **1** and **2** present a unique class of mixed-donor ligands coordinating to Cu^{I} centers via the P lone pair and the P–E σ -bond, revealing an unprecedented coordination mode.

For the last two decades, metal-directed self-assembly has proved to be a simple yet effective strategy for the facile construction of well-defined solid-state structures.^[1] Using this method, a large variety of discrete assemblies and multidimensional arrays have been designed by skillful selection of multitopic organic linkers to connect coordinatively unsaturated metal centers. The ligands employed are most commonly N- or O-donor-containing organic molecules^[1b] whereas S-, Se-, and P-donor-containing compounds are less common.^[2] Moreover, few examples of (P,N), (N,O), (P,S), and other mixed-donor ligands are known to also link different metal centers.^[3] Compared to organic molecules, organometallic building blocks have only very rarely been involved as connectors in supramolecular chemistry.^[4] For that reason, our group developed the concept of using organometallic complexes bearing “naked” polyphosphorus (P_n) donor atoms as connectors between metal ions.^[5] These compounds possess very flexible coordination modes, which

allow the synthesis of a large library of discrete (monomers,^[6b,c] dimers,^[6a,b,d] spherical aggregates,^[7] nanobowls,^[8] and nanosized capsules^[9]) and polymeric (1D, 2D, and 3D coordination polymers (CPs))^[6a,10] supramolecular assemblies in moderate to excellent yields. Interestingly, few of these P_n compounds could be further involved in three-component reactions together with Ag^{I} or Cu^{I} salts and ditopic N-donor organic molecules to afford unprecedented organometallic–organic hybrid polymers.^[11] In contrast to the rather large number of assemblies based on P_n -ligand complexes, few aggregates have been reported by ourselves and others featuring As_n -^[12] and Sb_n -ligand complexes,^[13] respectively, as building blocks. These E_n -ligand complexes show coordination behaviors towards metal ions that differ from that of their P_n -ligand analogues, paving the way for new advances in the supramolecular chemistry of softer Lewis bases.

In view of these initial results concerning homoatomic linkers, the question arose as to which coordination mode would establish mixed P_nE_m -donor complexes ($\text{E} = \text{As}$, Sb) to potentially reach a new level of insight into their coordination behavior. In fact, because of the hindered accessibility of the lone pair of the heavier congeners of phosphorus, such P_nE_m complexes were expected to have very different coordination behaviors compared to homoatomic P_n or E_n compounds. Additionally, we were also facing the fact that, in general, very rarely (P,As) mixed-donor compounds^[14] and no examples of (P,Sb) compounds have been used as linking moieties between metal ions. We report herein the first examples of supramolecular aggregates featuring the tetrahedral heterodiatomic Group 15 complexes $[\text{Cp}_2\text{Mo}_2(\text{CO})_4(\mu, \eta^2: \eta^2\text{-PE})]$ ($\text{E} = \text{As}$ (**1**), Sb (**2**)) as linkers in supramolecular chemistry. Moreover, their X-ray structures and DFT calculations show that these compounds represent a unique type of donor ligand as they coordinate to unsaturated Cu^{I} ions via the P lone pair and the P–E σ -bond.

In order to evaluate the bonding situation in complexes **1** and **2** towards the unsaturated Cu^{I} centers, we performed DFT calculations at the B3LYP/def2TZVP level of theory. The results show that the lone pairs of the As and Sb atoms are lower in energy than that of the P atom (Figure 1a). More pronounced is, however, the increase in energy of the P–E σ -bond for the heavier congeners, which allows for a more effective overlap of these orbitals with the unoccupied orbitals of Cu, instead of the lone pair. This indicates that for heavier congeners, the P–E σ -bond should be involved in the bonding with unsaturated transition-metal fragments.

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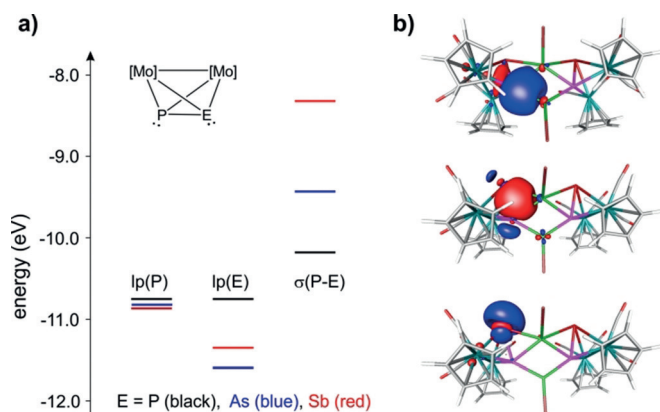


Figure 1. a) Frontier orbital energy diagram of $[\text{Cp}_2\text{Mo}_2(\text{CO})_4(\mu, \eta^2\text{-PE})]$ ($\text{E} = \text{P}$, As , and Sb), calculated at the B3LYP/def2-TZVP level of theory. b) One set of the localized molecular orbitals in **7** representing the coordination of the P lone pair (top), the P–Sb σ -bond (middle), and the lone pair of Sb (bottom).

Inspired by these calculations, the ligand complex **1**^[15] was initially reacted with the Cu^{I} salts CuCl , CuBr , and CuI in a 1:1 stoichiometric ratio in a mixture of CH_2Cl_2 and CH_3CN at room temperature (Figure 2a). These reactions afforded the neutral oligomeric complexes $[\{\text{Cp}_2\text{Mo}_2(\text{CO})_4\{\mu_4, \eta^2: \eta^2: \eta^2: \eta^2\text{-PAs}\}_4\{\text{CuX}\}\{\text{Cu}(\mu\text{-X})\}_2]$ ($\text{X} = \text{Cl}$ (**3**), $\text{X} = \text{Br}$ (**4**)) as well as the neutral 1D CP $[\{\text{Cp}_2\text{Mo}_2(\text{CO})_4\{\mu_4, \eta^2: \eta^2: \eta^2: \eta^2\text{-PAs}\}\{\text{Cu}(\mu\text{-I})\}]_n$ (**5**) in excellent yields (86–92%). Interestingly, these compounds are air- and light-stable in the solid state for several days while they show decomposition within hours in solutions of CH_3CN under air. Compounds **3–5** are insoluble in most common organic solvents, and are only soluble in trace amounts of donor solvents such as CH_3CN without complete dissociation into their building blocks, as evidenced by ^{31}P NMR spectroscopy.

Single crystals of products **3** (orange plates), **4** (red blocks), and **5** (orange rods) were characterized by X-ray crystallography (Figure 2b,c; Table S1 in the Supporting Information). Their structures display similar tetrameric cores for **3** and **4** and a polymeric core for **5**. Each of the molecules **3** and **4** consists of four Mo_2PAs units **1** and four CuX ($\text{X} = \text{Cl}$ (**3**), Br (**4**)) moieties. Within these compounds, all ligands **1** are similar, each adopting a $\eta^2: \eta^1$ -coordination mode, which is the most favored coordination mode according to the DFT calculations. Within these compounds, there are two types of Cu (central Cu(in) and peripheral Cu(out)) and halide (terminal X(ter) and bridging X(br)) ions. The Cu(in) ions are each pentacoordinated to two P atoms, two X^- ions, and one Cu^{I} ion, while the Cu(out) ions are each hexacoordinated to two P atoms, two As atoms, one Cu^{I} ion, and one X^- ion. The Cu(in)⋯Cu(out) distances between two neighboring Cu(in) and Cu(out) ions in **3** and **4** are in the range of about 2.64 to 2.69 Å, and thus shorter than the sum of their van der Waals radii (2.80 Å), revealing possible Cu⋯Cu interactions.^[16] However, the Cu(in)⋯Cu(in) distances within the Cu(in)₂X-(br)₂ four-membered rings are in the range of about 3.20 to 3.28 Å, revealing no cuprophilic interaction. The structure of **5** reveals a linear 1D chain consisting of planar four-membered Cu_2I_2 and six-membered $\text{Cu}_2\text{P}_2\text{As}_2$ ring motifs, alternately arranged in an orthogonal manner. This structure is similar to that of 1D CPs obtained from the reaction of its homodiatom analogue $[\text{Cp}_2\text{Mo}_2(\text{CO})_4(\mu, \eta^2: \eta^2\text{-P}_2)]$.^[18] All of the Cu^{I} ions in **5** adopt a distorted tetrahedral coordination geometry with one P atom, one As atom, and two I^- ions. In contrast to what was observed in the tetramers **3** and **4**, all of the Mo_2PAs (**1**) ligands in **5** adopt an $\eta^1: \eta^1$ -coordination mode. The P–As bond lengths in **3** to **5** (2.240(4)–2.298(4) Å) are comparable to that of the non-coordinated ligand complex **1** (2.232(4) Å).^[15b] The Cu–P bond lengths are in the range of (2.210(6)–2.293(1) Å), and the Cu–As bond lengths range

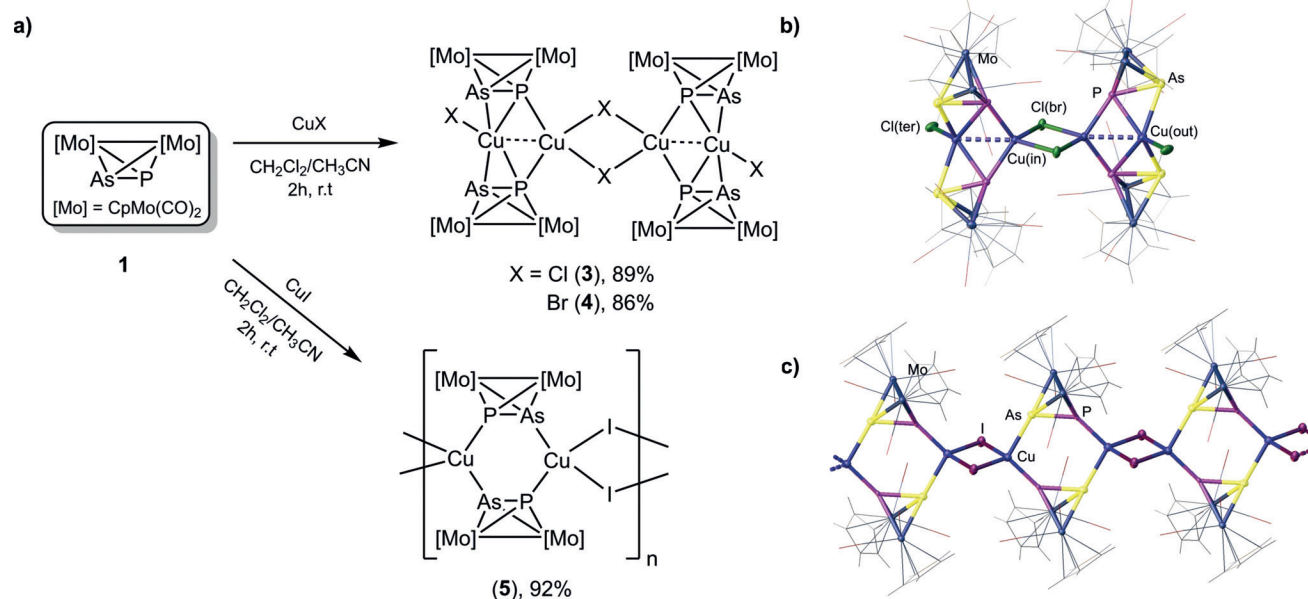


Figure 2. a) Synthesis of compounds **3–5**. b) Molecular structure of **3** (**4** has a similar structure; see the Supporting Information) in the solid state. c) Section of the 1D polymer **5**.^[17]

from 2.461(9) to 2.584(2) Å. The room-temperature ^{31}P NMR spectra of **3–5** in CD_3CN display single signals for **3** (22.1 ppm), **4** (22.9 ppm), and **5** (24.1 ppm), respectively, which are 4 to 6 ppm upfield-shifted compared to that of the free complex (28.5 ppm), thus revealing an incomplete dissociation of these aggregates in solutions of CH_3CN .

Further, the ligand complex $[\text{Cp}_2\text{Mo}_2(\text{CO})_4(\mu, \eta^2: \eta^1\text{-PSb})]$ (**2**) was reacted with the Cu^{I} salts CuCl , CuBr , and CuI under experimental conditions similar to those used for **1** (Figure 3a). These reactions afforded the neutral oligomeric complexes $[\{\text{Cp}_2\text{Mo}_2(\text{CO})_4\}(\mu_4, \eta^2: \eta^2: \eta^1\text{-PSb})_4\{\text{CuX}\}\{\text{Cu}(\mu\text{-X})\}_2]$ ($\text{X} = \text{Cl}$ (**6**), $\text{X} = \text{Br}$ (**7**)) and the neutral 1D CPs $[\{\text{Cp}_2\text{Mo}_2(\text{CO})_4\}(\mu_4, \eta^2: \eta^2: \eta^1\text{-PSb})_2\{\text{Cu}(\mu\text{-X})\}_3]_n$ ($\text{X} = \text{Br}$ (**9**), $\text{X} = \text{I}$ (**8**)) in moderate to good yields (52–72 %). Unlike **3–5**, the adducts **6–9** are air-sensitive and could only be isolated and stored at ambient conditions under an inert atmosphere. Moreover, these compounds are insoluble in common solvents and could only be characterized in the solid state. Their X-ray structures showed that **6** and **7** are isomorphous and have structures similar to those of **3** and **4**, while **8** represents an unprecedented 1D polymer (Figure 3b,c).

The coordination environments of all Cu and halide ions in **6** and **7** are similar to those found for the tetramers **3** and **4**. The $[\text{Cp}_2\text{Mo}_2(\text{CO})_4(\mu, \eta^2: \eta^2: \eta^1\text{-PSb})]$ units within these compounds possess each a $\eta^2: \eta^1$ -coordination mode, which was predicted by DFT calculations. The $\text{Cu}(\text{in})\cdots\text{Cu}(\text{out})$ distances in **6** and **7** are in the range of about 2.53 to 2.54 Å, suggesting possible $\text{Cu}\cdots\text{Cu}$ interactions.^[16] In contrast to what was observed for all coordination compounds **3–7**, the crystal structure of **8** indicates that it contains a stoichiometry of the building blocks differing from the one used during the synthesis for the starting materials. Two types of Cu ions exist in **8**, the central $\text{Cu}(\text{in})$ and the peripheral $\text{Cu}(\text{out})$ ions, with the $\text{Cu}(\text{in})$ being hexacoordinated to two P and two Sb

atoms, and two Cu^{I} ions and the $\text{Cu}(\text{out})$ being each pentacoordinated to one P atom, one Cu ion, and three I^- ions. The $\text{Cu}(\text{in})\cdots\text{Cu}(\text{out})$ distances are in the range of 2.65 to 2.66 Å, thereby revealing possible $\text{Cu}\cdots\text{Cu}$ interactions.^[16] Interestingly, the $\text{Cu}(\text{out})\cdots\text{Cu}(\text{out})$ distances within two consecutive $\text{Cu}(\text{out})_2(\mu\text{-I})_2$ four-membered rings are different from each other (ca. 2.86 and 3.31 Å); however, both are longer than the sum of their van der Waals radii, revealing no cuprophilic interactions. As a consequence of the short $\text{Cu}\cdots\text{Cu}$ distance between the $\text{Cu}(\text{in})$ and $\text{Cu}(\text{out})$ ions in **8**, this compound can also be described as an infinite chain of Cu_3 repeating units stabilized by two organometallic ligands of **2** and one I^- ion, and connected to each other via two $\mu\text{-I}$ ligands. To the best of our knowledge, no such polynuclear Cu^{I} chains stabilized by organometallic ligands had previously been reported.^[16] The P–Sb bond lengths in **6–8** (2.445(8)–2.508(3) Å) are comparable to that of the non-coordinated complex **2** (2.469(9) Å).^[15b] The Cu–P bond lengths are in the range of 2.280(2) to 2.508(3) Å, and the Cu–Sb bond lengths are in between 2.667(4) and 2.771(7) Å.

As the differences in the electronic structures of $[\text{Cp}_2\text{Mo}_2(\text{CO})_4(\mu, \eta^2: \eta^2: \eta^1\text{-P}_2)]$, **1**, and **2** are most accentuated for **2**, we investigated the electronic structure of complex **7** by DFT calculations (Figure 1b and the Supporting Information). Geometry optimization in the gas phase led to a geometry that is very close to the experimentally found geometry, indicating that this geometry is not a result of the packing effects in the solid state. The $\text{Cu}\cdots\text{Cu}$ distance of 2.593 Å in the optimized geometry is only slightly longer than the experimental value of 2.534(4) Å. The bonding between the two units of **2** and CuBr in **7** can best be described as being built up from a coordination of the P lone pair to $\text{Cu}(\text{in})$ and a coordination of the P–Sb σ -bond in **2** to the $\text{Cu}(\text{out})$ atom. This is confirmed by the localized molecular orbitals depicted

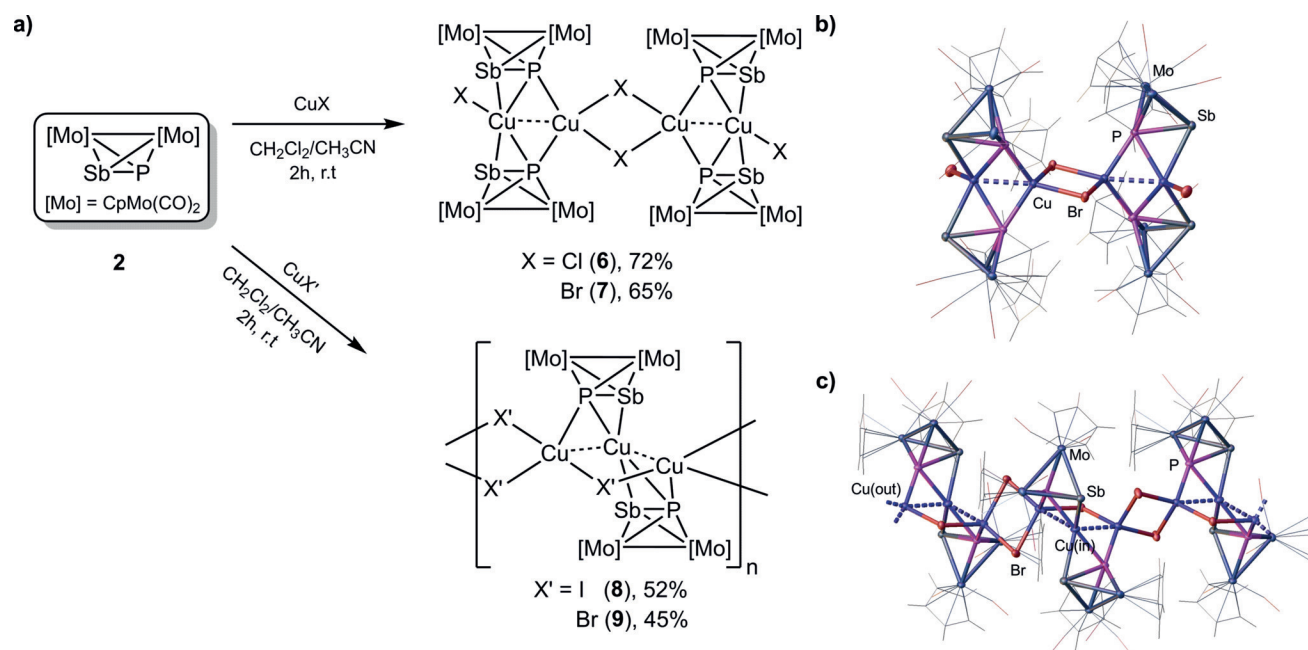


Figure 3. a) Synthesis of compounds **6–9**. b) Molecular structure of **7** (**6** has a similar structure; see the Supporting Information). c) Section of the 1D polymer **9** (**8** has a similar structure).^[17]

in Figure 1b. The removal of electron density from the P–Sb σ -bond upon coordination of **2** to copper is also reflected in the Wiberg bond indices (WBIs). The WBI of the P–Sb bond (0.81) is substantially lower in **7** than in **2** (1.11). The WBI of the Cu(out)–P bond (0.57) is considerably higher than for the Cu(in)–P bond (0.39), while the WBI of the Cu(in)–Sb bond is only 0.29. For the Cu(in)–Cu(out) unit, a WBI of 0.29 was found; however, no pronounced orbital overlap between the two Cu centers was detected, but quite a few molecular orbitals show low contributions from the two copper centers in a bonding combination.

To study the effect of varying the ratio of the reactants on the reaction outcomes, we used the reaction of complex **2** with CuBr as an example. Two additional ratios of stoichiometry were used (1:2 and 2:3). From the first reaction, two types of crystals were obtained; red blocks (**7**) and dark red needles (**9**), with the second reaction affording exclusively **9** in good isolated yield (45%). The X-ray structure of **9** shows a 1D polymer, which is similar in structure to **8**. The coordination environments of all Cu^I and Br[−] ions as well as the Mo₂PSb moieties in **9** are similar to those described for **8**, which renders **9** another example of an infinite chain of Cu₃ units supported by the organometallic complex **2**.

The obtained supramolecular aggregates **3–9** demonstrate the high potential of the tetrahedral complexes Mo₂PAs (**1**) and Mo₂PSb (**2**) as heterodiatom donor ligands in the coordination chemistry of Cu^I and open the door to their use in supramolecular chemistry. Interestingly, the reactions of these complexes with Cu^I afforded products different from those obtained under similar reaction conditions with their homodiatom analogues [Cp₂Mo₂(CO)₄(μ , η^2 : η^2 -E₂)] (E = P, As).^[12,18] This is due to the unique donor nature of **1** and **2**, involving coordination via the lone pair of the P atom and the P–E σ -bond. In addition, the two 1D CPs **8** and **9** represent the first examples of infinite connected Cu^I chains stabilized by organometallic ligands. Current investigations in this field focus on the synthesis of the new, so far non-existing heavier complexes [Cp₂Mo₂(CO)₄(μ , η^2 : η^2 -AsE')] (E' = Sb, Bi) and [Cp₂Mo₂(CO)₄(μ , η^2 : η^2 -SbBi)] and their potential use as linkers in supramolecular chemistry.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: antimony · arsenic · copper · heterodiatom units · phosphorus

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