

Discrete and polymeric organometallic-organic hybrid materials based on the diphosphorus complex $[\text{Cp}_2\text{Mo}_2(\text{CO})_4(\eta^2\text{-P}_2)]$, Cu(I) salts and 2,2'-bipyrimidine

Mehdi Elsayed Moussa,^[a] Bianca Attenberger,^[a] Michael Seidl,^[a] Anderea Schreiner,^[a] and Manfred Scheer*^[a]

Dedicated to Professor D. Stalke on the occasion of his 60th birthday

Abstract: The reaction of the diphosphorus complex $[\text{Cp}_2\text{Mo}_2(\text{CO})_4(\eta^2\text{-P}_2)]$ (**1**), with the Cu^I salts $[\text{Cu}(\text{CH}_3\text{CN})_4][\text{BF}_4]$ or $[\text{Cu}(\text{CH}_3\text{CN})_4][\text{PF}_6]$ and a mixture of $[\text{Cu}(\text{CH}_3\text{CN})_4][\text{BF}_4]$ and CuCl in the presence of 2,2'-bipyrimidine (**2**) is studied. Depending on the Cu^I salts used and the layering solvent involved in the crystallisation, a variety of novel coordination compounds are accessible in moderate to excellent yields (26-80%): the novel dicationic molecular organometallic-organic hybrid complexes $[\{\text{Cp}_2\text{Mo}_2(\text{CO})_4(\mu_3, \eta^{1:2:2}\text{-P}_2)\}_4(\mu_2, \eta^{1:1:1:1}\text{-C}_8\text{H}_6\text{N}_4)\text{Cu}_2][\text{BF}_4]_2$ (**3**) and $[\{\text{Cp}_2\text{Mo}_2(\text{CO})_4(\mu_3, \eta^{1:2:2}\text{-P}_2)\}_2\{\text{Cp}_2\text{Mo}_2(\text{CO})_4(\mu_3, \eta^{2:2:2}\text{-P}_2)\}_2(\mu_2, \eta^{1:1:1:1}\text{-C}_8\text{H}_6\text{N}_4)\text{Cu}_2][\text{PF}_6]_2$ (**4**), the unique neutral 1D organometallic-organic hybrid polymer $[\{\text{Cp}_2\text{Mo}_2(\text{CO})_4(\mu_4, \eta^{1:1:2:2}\text{-P}_2)\}_2(\mu_2, \eta^{1:1:1:1}\text{-C}_8\text{N}_6\text{N}_4)(\text{CuCl})_2]_n$ (**5**) and the unprecedented 2D organometallic-organic hybrid polymer $[\{\text{Cp}_2\text{Mo}_2(\text{CO})_4(\mu_4, \eta^{1:1:2:2}\text{-P}_2)\}_2(\mu_2, \eta^{1:1:1:1}\text{-C}_8\text{H}_6\text{N}_4)\{\text{Cu}_2(\mu\text{-Cl})\}_2][\text{BF}_4]_{2n}$ (**6**).

Introduction

The synthesis of supramolecular aggregates and networks through metal-directed self-assembly has been a rapidly growing area in recent years.^[1] One of the most efficient strategies to design and construct such coordination assemblies is to select suitable multidentate ligands that enable to control and predict the final outcome of the aggregation reactions.^[2] In contrast to typical approaches in this area, in which nitrogen-, oxygen-, or sulfur-donor-containing organic ligands are employed to connect different metal centers,^[3] our group established an alternative approach by utilizing organometallic polyphosphorus (P_n) ligand complexes with flexible coordination modes as connectors between metal ions. This novel method allows the synthesis of 1D and 2D coordination polymers,^[4] nano-sized fullerene-like supramolecular spherical aggregates,^[5] and a huge molecular organometallic capsule.^[6] An alternative approach by using three-component reactions was also developed in our group. In those reactions, bipyridyl ligands, silver or copper metal ions and e.g., the tetrahedral complex $[\text{Cp}_2\text{Mo}_2(\text{CO})_4(\eta^2\text{-P}_2)]$ ($\text{Cp} = \text{C}_5\text{H}_5$) (**1**) are all involved in a one-pot synthesis to form unique organometallic-organic hybrid polymers.^[7b-d] More recently, a

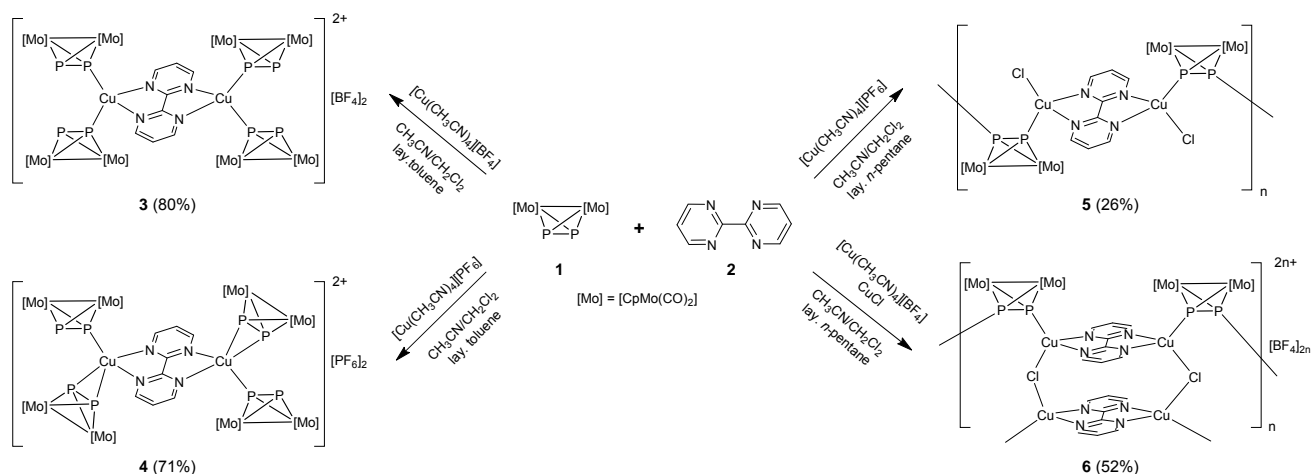
similar reaction was performed using 2,2'-bipyrimidine "bpym" (**2**) as a connector in the presence of AgBF_4 . This reaction afforded an unprecedented "mixed" hybrid polymer in which organometallic and inorganic nodes are linked by organic spacers.^[7a] These results motivated us to expand our research by performing similar reactions using copper(I) salts instead of AgBF_4 . Herein, we show that the three-component reaction of the P_2 ligand complex **1** with the copper(I) salts $[\text{Cu}(\text{CH}_3\text{CN})_4][\text{BF}_4]$ or $[\text{Cu}(\text{CH}_3\text{CN})_4][\text{PF}_6]$ in the presence of 2,2'-bipyrimidine "bpym" (**2**) allows the access to the two novel dicationic organometallic-organic coordination complexes $[\{\text{Cp}_2\text{Mo}_2(\text{CO})_4(\mu_3, \eta^{1:2:2}\text{-P}_2)\}_4(\mu_2, \eta^{1:1:1:1}\text{-C}_8\text{H}_6\text{N}_4)\text{Cu}_2][\text{BF}_4]_2$ (**3**) and $[\{\text{Cp}_2\text{Mo}_2(\text{CO})_4(\mu_3, \eta^{1:2:2}\text{-P}_2)\}_2\{\text{Cp}_2\text{Mo}_2(\text{CO})_4(\mu_3, \eta^{2:2:2}\text{-P}_2)\}_2(\mu_2, \eta^{1:1:1:1}\text{-C}_8\text{H}_6\text{N}_4)\text{Cu}_2][\text{PF}_6]_2$ (**4**) and one unique neutral 1D organometallic-organic hybrid polymer $[\{\text{Cp}_2\text{Mo}_2(\text{CO})_4(\mu_4, \eta^{1:1:2:2}\text{-P}_2)\}_2(\mu_2, \eta^{1:1:1:1}\text{-C}_8\text{N}_6\text{N}_4)(\text{CuCl})_2]_n$ (**5**). In addition, we show for the first time the possibility to conduct a four-component reaction using a mixture of $[\text{Cu}(\text{CH}_3\text{CN})_4][\text{BF}_4]$ and CuCl. This new approach results in an unprecedented cationic 2D organometallic-organic hybrid polymer $[\{\text{Cp}_2\text{Mo}_2(\text{CO})_4(\mu_4, \eta^{1:1:2:2}\text{-P}_2)\}_2(\mu_2, \eta^{1:1:1:1}\text{-C}_8\text{H}_6\text{N}_4)\{\text{Cu}_2(\mu\text{-Cl})\}_2][\text{BF}_4]_{2n}$ (**6**). To the best of our knowledge, no other four-component reaction has been conducted in a metal-directed self-assembly approach especially leading to the isolation of only one product in the solid state out of many possible combinations of the starting material.

Results and Discussion

The reaction of the P_2 ligand complex **1** with 0.5 equivalents of $[\text{Cu}(\text{CH}_3\text{CN})_4][\text{BF}_4]$ and bpym **2** in a mixture of CH_2Cl_2 and CH_3CN at room temperature followed by a slow diffusion of toluene leads to the selective formation of compound **3** as dark red crystals in excellent yield (80%) suitable for X-ray diffraction studies (Scheme 1). Using $[\text{Cu}(\text{CH}_3\text{CN})_4][\text{PF}_6]$ instead, another product **4** is accessible as red crystals in 71% yield (Scheme 1). X-ray structure analysis performed on single crystals of **3** and **4** show that they have similar molecular structures. The compounds **3** (Figure 1a) and **4** (Figure 1b) crystallize in the triclinic space group P-1 (Table S1, see SI). They contain two molecules of CH_3CN and four molecules of CH_2Cl_2 per formula unit in their crystal lattices. Both compounds consist of two $[(\text{Cu})(1)_2]^+$ fragments that are connected to each other by one bpym (**2**) spacer (Figure 1). To each copper atom in **3**, two P_2 ligand complexes **1** are coordinated via an *end-on* η^1 -coordination mode (Figure 1a). This coordination

[a] Dr. M. Elsayed Moussa, Dr. B. Attenberger, Dr. M. Seidl, A. Schreiner, Prof. Dr. M. Scheer
Institut für Anorganische Chemie der Universität Regensburg,
93040 Regensburg (Germany)
E-mail: manfred.scheer@chemie.uni-regensburg.de
<http://www.uni-regensburg.de/chemie-pharmazie/anorganische-chemie-scheer/>

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Scheme 1. Different pathways of the reaction of the P₂ ligand complex **1** with 2,2'-bipyrimidine (**2**) and Cu(I) salts. Synthesis of the coordination compounds **3-6**.

mode of the P₂ ligand was previously observed only for organometallic-organic complexes based on Ag[Al{OC(CF₃)₃}₄].^[7] The coordination sphere of each of the two copper atoms in **3** is completed by one bridging ligand **2** adopting a bis(bidentate) binding mode. Consequently, each Cu atom possesses a distorted tetrahedral coordination environment consisting of two P atoms and two N atoms. Selected bond lengths and angles for the derivatives **3** and **4** are given in the tables S2 and S3 (See SI). The Cu(bpym)Cu unit in **3** is almost planar (maximum deviation from the mean plane ≈0.10 Å). The P-P bond lengths (2.083(1)-2.086(1) Å) are well comparable to those of the non-coordinated ligand **1** (2.079(6) Å).^[8] The Cu-P bond lengths (2.207(8)-2.228(8) Å) are slightly shortened (2.273(1)-2.279(1) Å) compared to those of a 2D hybrid polymer based on the P₂ ligand **1**, [Cu(CH₃CN)₄][BF₄] and dipyriddyethene.^[7d] Unlike to what was observed in **3**, two P₂ ligand complexes of **1** coordinate to each copper atom in **4** in different coordination modes (Figure 1b). The atoms P1 and P2 in **4** are located in the vicinity of Cu1 with the distances of 2.380(2) Å (Cu1-P1) and of 2.379(2) Å (Cu1-P2). Consequently, the P₂ ligand consisting of P1 and P2 is coordinated to Cu1 by a *side-on* η²-coordination mode. On the other hand, the atom P3 in **4** is located far from the Cu1 ion (Cu-P3 = 3.658(3) Å), which results in an *end-on* η¹-coordination mode of the corresponding

P₂ ligand **1** consisting of P3 and P4 (Figure 1b). In this compound, the Cu(bpym)Cu unit is almost exactly planar (maximum deviation from the mean plane ≈0.03 Å). In both the derivatives **3** and **4**, the counteranions and solvent molecules are located outside the self-assembled units. In the crystal packing, these anions are located between the dicationic units and interact to numerous different Cp substituents of the P₂ ligand complexes **1** and to the protons at the “bpym” linker **2**. These weak interactions, in addition to the different sizes of the two counteranions, could be the reason for the difference in the coordination modes of the two P₂ ligand complexes **1** in both the derivatives **3** and **4**. A similar phosphine-donor based structural motif to **3** and **4** possessing four PPh₃ ligands was reported by C. Vogler *et. al.* in 1989.^[9] Other related compounds with various phosphorus- and arsenic-based ligands, but not containing chelating ligands as in the present case of complex **1**, were more recently published.^[10]

A similar reaction of the P₂ ligand complex **1** with [Cu(CH₃CN)₄][PF₆] and “bpym” **2**, however, by using the diffusion of *n*-pentane instead of toluene leads to the formation of the CuCl containing compound **5** in a moderate isolated yield (26%, Scheme 1). Obviously, the solvent serves as a chloride ion provider. This kind of Cl⁻ abstraction of dichloromethane caused

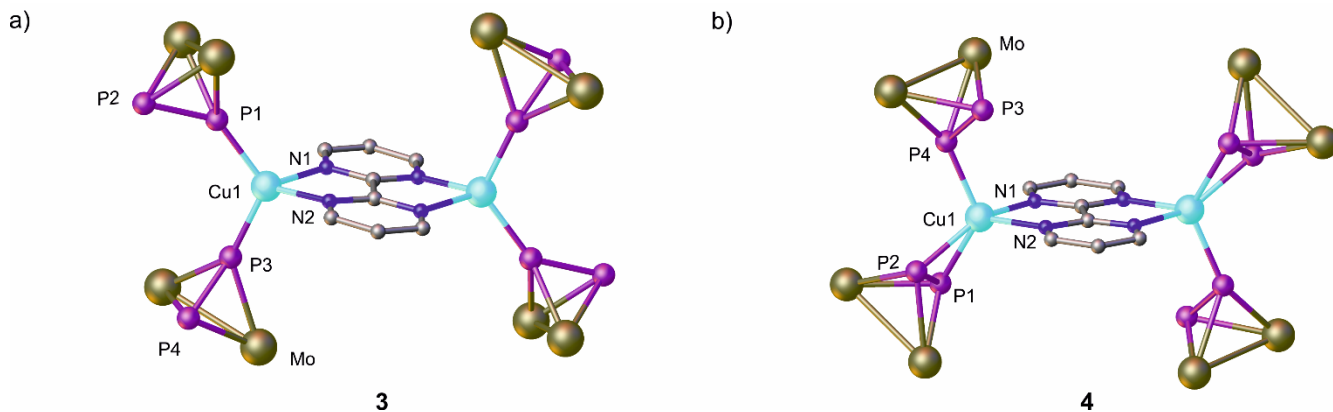


Figure 1. Structure of the molecular unit of: a) **3** and b) **4** in the solid state. Cp and CO ligands, hydrogen atoms and counterions are omitted for clarity.

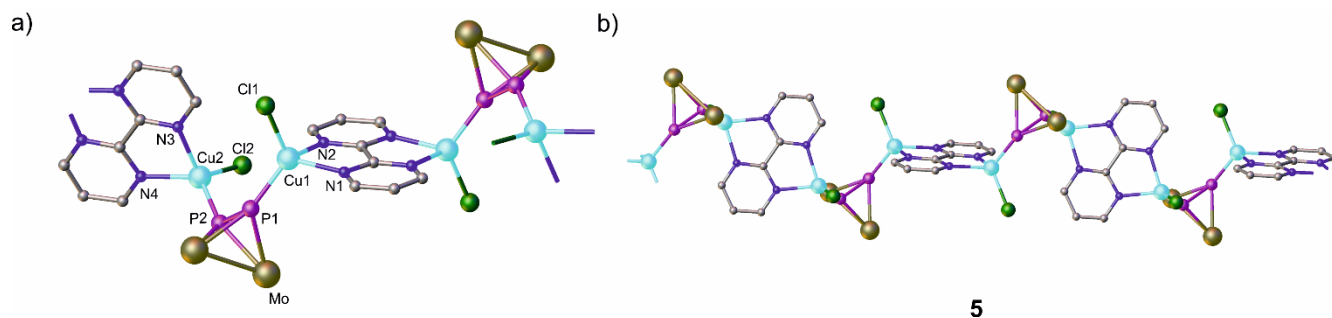


Figure 2. a) Structure of the repeating unit of **5** in the solid state, b) Section of the 1D polymer **5** in the solid state. Cp and CO ligands, hydrogen atoms and counterions are omitted for clarity.

photocatalytic or thermolytic decomposition has already been reported in literature.^[11] X-ray structure analysis performed on single crystals of **5** shows that this compound is a unique neutral 1D organometallic-organic hybrid polymer. The compound crystallizes in the triclinic space group P-1 (Table S1, see SI), a section of the polymeric structure is depicted in Figure 2. The infinite 1D chain structure of **5** consists of ClCu(1)CuCl neutral organometallic nodes that are linked together by “bpym” spacers (Figure 2). Within the organometallic nodes to each Cu(I) atom, one P₂ ligand complex **1** is coordinated via a bridging $\eta^1:\eta^1$ -coordination mode.^[7] In addition, one Cl⁻ ion is also coordinated to each Cu(I) atom, resulting in a distorted tetrahedral coordination environment by one P atom, one Cl atom and two N atoms. The planes of the two neighboring “bpym” linkers **2** form an angle of 75.6° to each other, providing the repeating units for the polymer **5** shown in Figure 2a. Selected bond lengths and angles for **5** are given in Table S4 (See SI). One of the Cu(bpym)Cu units in **5** is planar while the other one deviates only slightly from the planarity (maximum deviation from the mean plane ≈ 0.06 Å). The coordination of the P₂ units **1** in **5** to the

copper atoms results in a small elongation of the P-P bond lengths (2.090(3) Å) compared to those of the non-coordinated P₂ ligand in **1** and also in the compounds **3** and **4**. The Cu-P bond lengths (2.187(3), 2.219(2) Å) compare to those observed for **3** and **4**. Even though [Cu(CH₃CN)₄][PF₆]⁻ was involved in the reaction leading to **5**, no PF₆⁻ anions are present in the crystal structure of **5**, which renders **5** the first neutral organometallic-organic hybrid polymer reported to date.

This result motivated us to target a selective synthesis of neutral hybrid polymers. For that purpose, a unique (for the first time in our approach) four-component stoichiometric reaction of the P₂ ligand complex **1**, CuCl, [Cu(CH₃CN)₄][BF₄]⁻ and “bpym” **2** was performed. This reaction, however, leads to the formation of compound **6** as red single crystals suitable for X-ray structure analysis in moderate yield (52%, Scheme 1). Compound **6** turned out to be a novel cationic 2D organometallic-organic hybrid polymer. A section of the two-dimensional polymeric structure is depicted in Figure 3. This derivative crystallizes in the monoclinic space group P2₁/c

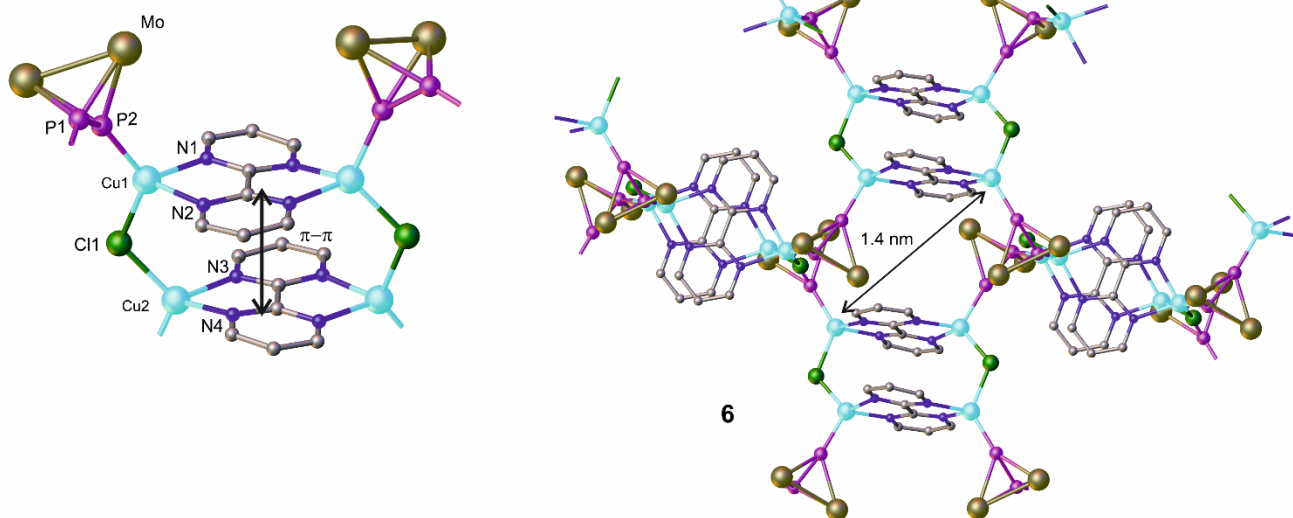


Figure 3. a) Structure of the repeating unit of **6** in the solid state (the arrow indicates the short π - π contact between the bpym ligands), b) Section of the 2D network **6** in the solid state (the arrow indicates the maximum diameter of the meshes). Cp and CO ligands, hydrogen atoms and counterions are omitted for clarity.

(Table S1, see SI). The 2D network **6** can be described as follows: two Cu atoms are bridged via one Cl atom forming a $[\text{Cu}_2\text{Cl}]^+$ unit. Two of these $[\text{Cu}_2\text{Cl}]^+$ units are bridged by two bpym linkers **2** forming a dicationic $(\text{Cu}_2\text{Cl})_2(\mathbf{2})_2$ metallacycle (Figure 3a). Within each metallacycle of **6**, the two bpym molecules **3** are located parallel displaced to each other with short contacts along their π -systems (ca. 3.488–3.747 Å) revealing π - π interactions (Figure 3a). The coordination sphere of each Cu(I) atom is completed by one additional P atom of a bridging $\eta^1:\eta^1$ coordinated P_2 ligand **1**, connecting two neighboring metallacycles (Figure 2b). Consequently, within **6**, each Cu atom possesses a distorted tetrahedral coordination geometry consisting of one P atom, one Cl atom and two N atoms. Similar to what was observed for the derivatives **3–5**, the Cu(bpym)Cu units in **6** are almost planar to each other (maximum deviation from the mean plane 0.13 Å). Selected bond lengths and angles for **6** are given in Table S5 (See SI). The P-P bond lengths in **6** (2.0943(11) Å) are slightly elongated compared to those of the non-coordinated ligand **1** and compounds **3–5**. The Cu-P bond lengths (2.1823(8), 2.2192(8) Å) are comparable to those found in **3–5**. The tetrafluoroborate anions and solvent molecules in **6** are located outside the assembled structure and lie near the $[\text{Cu}_2\text{Cl}]^+$ units with no interactions to the copper cations. The 2D network of **6** is virtually porous with two types of cavities of the meshes. Small cavities generated inside and large cavities generated outside the formed metallacycles with a maximum dimensions of ca. 1.4 nm outside and 0.7 nm inside.^[12]

The derivatives **3–6** are well soluble (**3,4**) or slightly soluble (**5,6**) in donor solvents such as CH_3CN , but completely insoluble in other common organic solvents as for instance CH_2Cl_2 , THF and *n*-pentane. The room temperature $^{31}\text{P}\{^1\text{H}\}$ NMR spectra in CD_3CN of **3** (-55.6 ppm), **4** (-71.7 ppm) and **6** (-47.6 ppm) show single signals, upfield shifted compared to that of the free P_2 ligand complex **1** (-43.2 ppm). Only the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **5** (-42.5 ppm) is comparable to that of the free ligand. This probably indicates a degradation of the polymeric structure in solution. The room temperature ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of **3–6** show signals corresponding to the proton and carbon nuclei of the Cp and CO ligands of **1** and the linker **2**. In the ESI mass spectra of **3–6**, peaks for various cationic fragments e.g. $[\text{Cu}(\mathbf{1})\mathbf{2}]^+$, $[\text{Cu}(\mathbf{1})_2(\mathbf{2})_2]^+$ and $[\text{Cu}(\mathbf{1})(\text{CH}_3\text{CN})]^+$ were detected (further details see SI).

Conclusions

In conclusion, we succeeded in the synthesis of the four novel organometallic-organic hybrid compounds **3–6** by the three-component reaction of the diphosphorus ligand complex $[\text{Cp}_2\text{Mo}_2(\text{CO})_4(\eta^2\text{-P}_2)]$ (**1**) and the monovalent copper(I) salts $[\text{Cu}(\text{CH}_3\text{CN})_4][\text{BF}_4]$ and $[\text{Cu}(\text{CH}_3\text{CN})_4][\text{PF}_6]$ or

the four-component reaction using a mixture of $[\text{Cu}(\text{CH}_3\text{CN})_4][\text{PF}_6]$ and CuCl in the presence of the organic ligand “bpym” **2**. The compounds **3** and **4** are novel organometallic-organic coordination complexes. The derivative **6** is a new 2D organometallic-organic hybrid polymer, while the compound **5** presents the first neutral 1D organometallic-organic hybrid polymer reported to date. The flexible coordination modes of the P_2 ligand complex **1** (η^1 -, $\eta^1:\eta^1$ - and η^2 -coordination modes) observed in these compounds, in addition to the Cl^- abstraction from the solution dichloromethane, leads to a large variety of organometallic nodes within the formed complexes. Current investigations in this field focus on the use of other P_n ligand complexes e.g., pentaphosphaferrocene with coinage metal salts in the presence of a variety of rigid tri- and tetra-topic organic molecules targeting the synthesis of a new class of 3D hybrid polymers.

CCDC 1530455 (for **3**), 1530456 (for **4**), 1530457 (for **5**) and 1530458 (for **6**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center.

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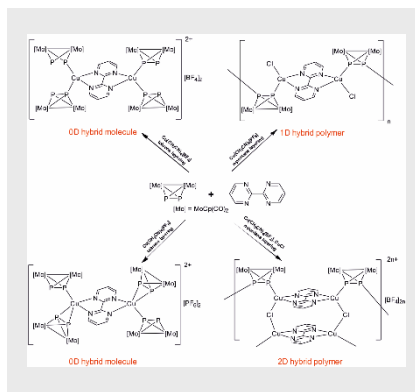
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- [12] Calculated from the largest distance between the Cu⁺ ions minus the doubled ionic radius of Cu⁺ for the coordination number 4 (0.74 Å).
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SHORT COMMUNICATION

The reaction of the diphosphorus complex $[\text{Cp}_2\text{Mo}_2(\text{CO})_4(\eta^2\text{-P}_2)]$ ($\text{Cp} = \text{C}_5\text{H}_5$) with different copper(I) salts and 2,2'-bipyrimidine afforded four new coordination compounds: two novel cationic organometallic-organic complexes, one cationic 2D hybrid polymer and the first neutral 1D organometallic-organic hybrid polymer.



Polyphosphorus Coordination Compounds

Mehdi Elsayed Moussa, Bianca Attenberger, Michael Seidl, Andrea Schreiner and Manfred Scheer

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Novel discrete and polymeric organometallic-organic hybrid materials based on the diphosphorus complex $[\text{Cp}_2\text{Mo}_2(\text{CO})_4(\eta^2\text{-P}_2)]$, Cu(I) salts and 2,2'-bipyrimidine.