

Coordination Polymers

Preorganized Ag^I Bimetallic Precursor with Labile Diphosphorus Ligands for a Programmed Synthesis of Organometallic–Organic Hybrid PolymersMehdi Elsayed Moussa,^[a] Michael Seidl,^[a] Gábor Balázs,^[a] Manfred Zabel,^[a]
Alexander V. Virovets,^[b, c] Bianca Attenberger,^[a] Andrea Schreiner,^[a] and Manfred Scheer*^[a]*Dedicated to Professor Joachim Heinicke on the occasion of his 70th birthday.*

Abstract: An Ag^I dimer capped with labile organometallic diphosphorus ligands [Cp₂Mo₂(CO)₄(η²-P₂)] (Cp = C₅H₅) acts as a highly pre-organized molecular precursor to direct the construction of 1D or 2D, and 3D organometallic–organic hybrid coordination polymers upon reaction with ditopic pyridine-based linkers. The formation of the supramolecular aggregates can be controlled by the stoichiometry of the organic molecules, and the mechanism is supported by DFT calculations.

The syntheses and design of coordination polymers (CPs) are currently receiving great interest due to their fascinating self-assemblies and potential applications.^[1] These compounds are generally built up by tailor-made organic molecules with appropriate functional groups (bearing N, O or S donor atoms) to coordinate on metal ions with specific directionalities.^[2] Due to the lack of ligands with other donor atoms in this field, our group started to use organometallic polyphosphorus (P_n) and polyarsenic (As_n) ligand complexes as connecting moieties between metal ions.^[3] The assembly reactions of these uncommon ligands with metal salts afforded a variety of 1D and 2D

CPs as well as a large library of finite supramolecular assemblies including fascinating inorganic nanospheres.^[4] Moreover, one of those P_n ligand complexes, the tetrahedrane complex [Cp₂Mo₂(CO)₄(η²-P₂)] (**1**; Cp = C₅H₅), was reacted with Ag^I and Cu^I salts in the presence of pyridine-based linkers to give unprecedented organometallic–organic hybrid polymers.^[5] Generally, a major problem associated with the synthesis of CPs is their low selectivity. In fact, a predictable and controlled synthesis of targeted architectures is extremely challenging because such supramolecular aggregation reactions are usually sensitive to the experimental conditions.^[6] To avoid low selectivity, one important approach in this field lies in the development of the pre-organized bimetallic building blocks. These precursors possess coordination sites occupied by labile ligands arranged at the desired angles so that the final arrangement and orientation of the coordinated molecules may be predicted with reasonable accuracy leading usually to one single thermodynamic product. Actually, such pre-organized precursors are widely involved in constructing supramolecular coordination networks and complexes.^[7] However, their use in building CPs is much less developed.^[8] Therefore, the question arises whether it is possible to design a bimetallic precursor to control infinite regular arrangements in the solid state. Evidently, an Ag^I ion is not a suitable building block for designing molecular precursors due to its flexible coordination sphere, which affords usually very versatile structures upon reaction with different organic linkers.^[2d,9] Similarly, flexible organic molecules are not attractive linkers either, because their use often leads to unpredictable frameworks due to their conformational freedom.^[10] However, we took on both challenges by designing a bimetallic Ag complex by the use of the diphosphorus ligand complex [Cp₂Mo₂(CO)₄(η²-P₂)] (**1**) with AgBF₄ (**2**) in combination with different flexible organic linkers. Due to the various possible coordination modes of the P₂ ligand complex **1**^[11] and the flexible coordination sphere of the Ag^I cation in the presence of the organic linkers **6–8** (Scheme 1) with various degrees of flexibility, a number of combinations is, in principle, possible resulting in a variety of accessible products. However, experimentally only predictable combinations were observed leading, in each case, selectively to one product evolving from the coordination of the corresponding organic linker to a pre-designed Ag^I precursor intermediate (Scheme 1, Figures 2–4). Although few examples of bimetallic precursors were used to

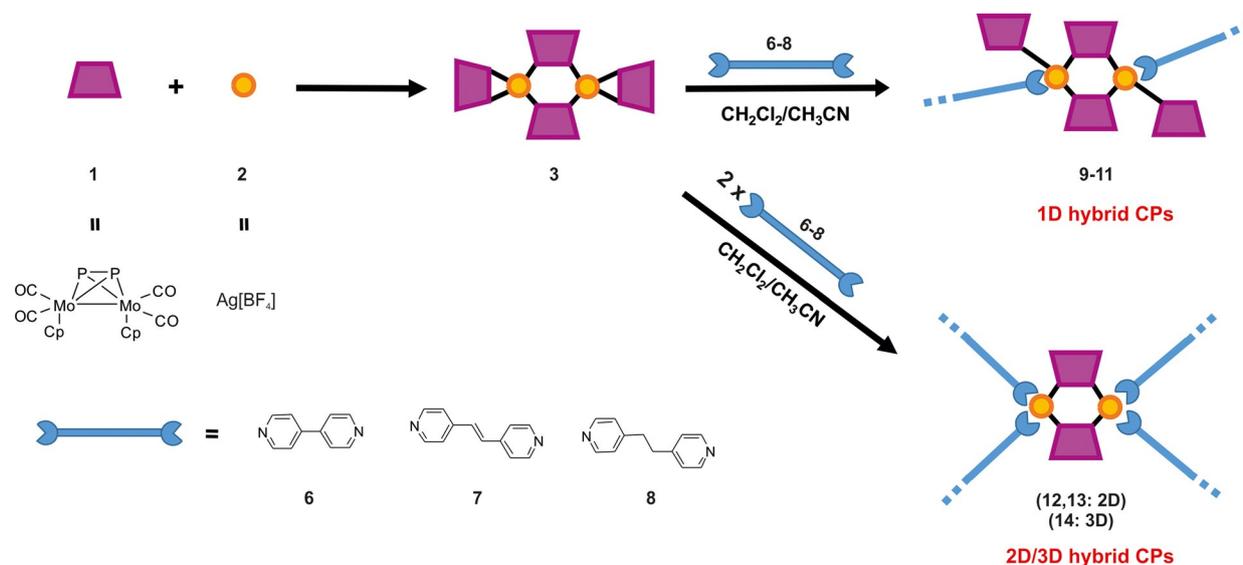
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Scheme 1. The reaction of the dimeric complex **3** with the ditopic organic linkers **6–8**. Synthesis of the 1D organometallic-organic hybrid CPs **9–11**, the 2D organometallic-organic hybrid CPs **12–13** and the 3D organometallic-organic hybrid CP **14**.

build CPs,^[12] to the best of our knowledge, no dimeric-based precursor was used so far as a building block for a general controlled synthesis of CPs of different dimensionality.

Previously, we showed that the reaction of the P₂ ligand complex **1** with Ag[BF₄] (**2**) affords compound **3**, which possesses a dimeric [Ag₂(**1**)₄][BF₄]₂ structure in the solid state with two μ-η¹:η¹ bridging ligands **1** and two ligands of **1** in a η² side-on coordination mode (Figure 1, Scheme 1).^[13] In order to study the dimer **3** as a suitable precursor for a predictable synthesis of organometallic-organic hybrid CPs, DFT calculations were performed at the B3LYP/def2-TZVP level of theory. Accordingly, the η²→η¹ transition of the terminal P₂ ligands **1** in the preformed dimeric complex **3** with the subsequent coordination of pyridine as a model ligand leading to **4** is exothermic (−32.7 kJ mol^{−1}) in solution (Figure 1). Moreover, the full substitution of the terminal ligands **1** in **4** with pyridine ligands leading to **5** is also exothermic in solution (−22.3 kJ mol^{−1}, Figure 1), however, slightly less than in the first step. It means that these two processes (change of the coordination mode of the ligand complex **1** and its substitution) might be accessed

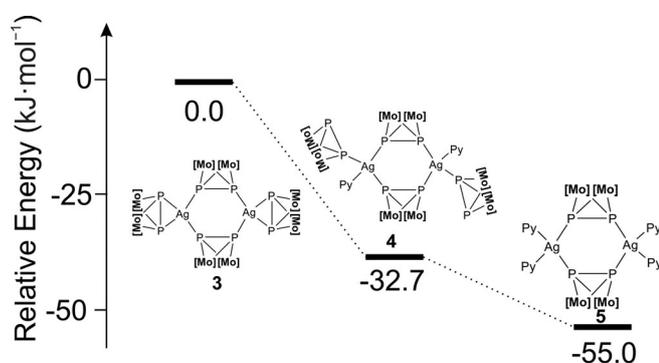


Figure 1. Energy diagram of the reaction of **3** with pyridine. The positive charges, ligands added or cleaved are not depicted. [Mo] = CpMo(CO)₂.

stepwise.^[14] Importantly, it is also revealed that such reactions allow to retain a stable Ag₂P₄ six-membered ring motif present in the dimer **3**. This indicates that, starting from the silver dimer **3**, it should be possible to control a targeted synthesis of organometallic-organic hybrid CPs using the appropriate stoichiometry of the organic linkers involved. In addition, the final outcome of the reactions should be attainable regardless of the nature (length, flexibility) of the organic linker.

Based on these DFT calculations, **3** was first prepared from the reaction of the P₂ ligand complex **1** and Ag[BF₄] (**2**) and reacted in situ with each of the organic linkers **4,4'**-bipyridine (**6**), 1,2-bis(4-pyridyl)ethylene (**7**) and 1,2-bis(4-pyridyl)ethane (**8**) in a 1:1 stoichiometry in a mixture of CH₂Cl₂ and CH₃CN at room temperature. These reactions afforded selectively the 1D polymers **9–11** as orange crystalline solids in good (56–77%) yields (Scheme 1, Figure 2). The compounds **9–11** were crystallized at room temperature from pentane diffusion into CH₂Cl₂/CH₃CN solutions of the crude reaction mixtures and were examined by X-ray structure analysis (further details in the Supporting Information). Their crystal structures show that the assemblies **9–11** are 1D organometallic-organic CPs with Ag₂(**1**)₄ repeating units (nodes) linked up via the organic spacers (Scheme 1, Figure 2). In these compounds, each η²-coordinating ligand complex **1** present in the parent dimer **3** changed its coordination mode to a η¹-coordination. Due to this η²→η¹ transition, the vacant site left on each Ag atom is filled by a pyridine function of the corresponding ditopic pyridine-based linker. The Ag₂P₄ six-membered ring motif of **3** as well as the coordination sphere of the Ag^I centers are conserved in the structures of the CPs **9–11**. As a result, each silver ion comprises a distorted tetrahedral environment with three P and one N atoms. In the polymeric chains of **9–11**, all the Ag₂P₄ ring motifs are parallel to each other. These Ag₂P₄ rings themselves are almost planar showing only a slight distortion towards a chair conformation (fold angles 3.41(8)–10.68(9), 4.81(1)° and

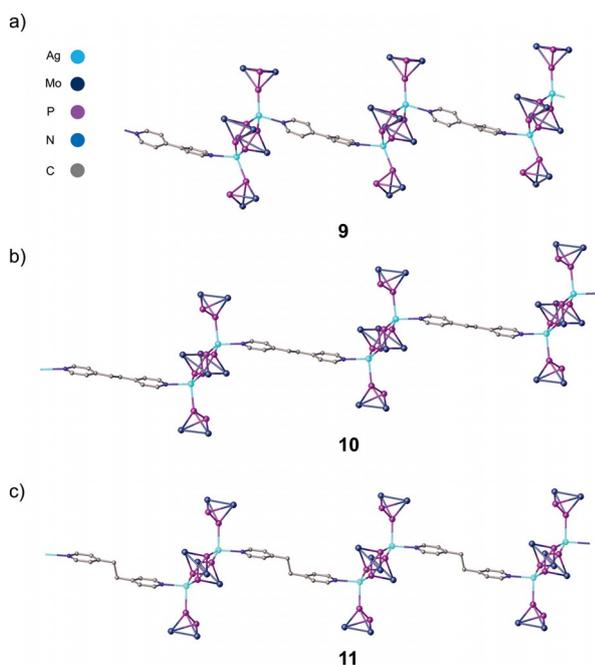


Figure 2. Sections of the cationic CPs of **9–11** in the solid state. Cp and CO ligands as well as hydrogen atoms are omitted for clarity.

5.29(4)°, respectively). The P–P bond lengths in **9** (2.088(3)–2.113(3) Å), **10** (2.084(3)–2.094(3) Å) and **11** (2.085(4)–2.089(9) Å) are slightly elongated compared to those of the non-coordinated ligand **1** (2.079(6) Å)^[15] and slightly shortened compared to those of the complex **3** (2.096(3)–2.136(3) Å).^[13] The Ag–P bond lengths in **9–11** (2.4644(12)–2.5468(8) Å) are slightly shortened compared to those of **3** (2.487(3)–2.699(2) Å). The Ag...Ag distances in **9** ($d(\text{Ag}\cdots\text{Ag}) > 4.39$ Å), **10** ($d(\text{Ag}\cdots\text{Ag}) > 4.49$ Å) and **11** ($d(\text{Ag}\cdots\text{Ag}) > 4.51$ Å) are large suggesting no argentophilic interaction.^[16]

The obtained results are in full agreement with the DFT calculations and show the possibility to control (using one equivalent of organic linkers) a $\eta^2 \rightarrow \eta^1$ transition of the coordination mode of the P_2 ligand complex **1** in **3**. This in turn allows the coordination of only one pyridine function on each Ag^I ion

leading to the selective synthesis of 1D organometallic-organic hybrid CPs.

These results motivated us to perform the reaction of the complex **3** with the ligands **6–8** in a 1:2 stoichiometry under similar conditions as used to synthesize the CPs **9–11**. According to the DFT calculations, under these stoichiometric ratios, the full substitution of the η^2 -coordinated P_2 ligand **1** in the Ag^I dimer **3** should have been attainable. Actually, these reactions afforded completely different results as only the compounds **12–14** were isolated from the reaction mixtures in good yields (51–66%) with no traces of the polymers **9–11** crystallized from the corresponding reactions. The compounds **12** and **13** are 2D organometallic-organic hybrid CPs, while the derivative **14** represents a 3D organometallic-organic hybrid CP (Figures 3 and 4). All CPs **12–14** consist of $\text{Ag}_2(\text{P})_2$ repeating units (nodes), which are linked to polycationic chains via the linkers **6–8**, respectively (Scheme 1, Figures 3 and 4). In these derivatives, the η^2 side-on coordinating ligands **1** present in the starting dimer **3** are each fully substituted by two pyridine functions of the ditopic pyridine-based linkers **6–8**. Nevertheless, the Ag_2P_4 six-membered ring motif of **3** as well as the coordination sphere of the Ag^I centers are retained in the structures of **12–14**. In these CPs, each Ag^I ion comprises a distorted tetrahedral environment with two P and two N atoms. In the polymeric chains of **12**, the $\text{Ag}_2(\text{P})_2$ ring motifs are noticeably oriented to each other (fold angle 48.60(5)°), while they are parallel to each other in **13**. The Ag_2P_4 rings themselves in **12** show also a higher distortion towards a chair conformation than in **13** and **14** (fold angles 18.78(13), 8.46(10)° and 7.29(9)°, respectively). Organometallic $\text{Ag}_2(\text{P})_2$ units form the edges of the 2D polymeric networks in **12** and **13** and the 3D network of **14** with cavities of the meshes having rhombic (**12**, **13**) and elliptical (**14**) shapes with sizes of 16.2×17.6 Å, 17.5×21.9 Å and 49.6×50.0 Å, respectively.^[20] The P–P bond lengths in **12** (2.090(2) Å), **13** (2.083(2) Å) and **14** (2.089(2) Å) are slightly elongated compared to those of CPs **9–11**. The Ag–P bond lengths in **12** (2.436(3) Å), **13** (2.426(2) Å) and **14** (2.464(8) Å) are in the expected range and comparable to those of the 1D CPs **9–11**. The Ag...Ag distances in **12** ($d(\text{Ag}\cdots\text{Ag}) > 4.14$ Å), **13** ($d(\text{Ag}\cdots\text{Ag}) > 4.63$ Å) and **14** ($d(\text{Ag}\cdots\text{Ag}) > 4.75$ Å) are large with-

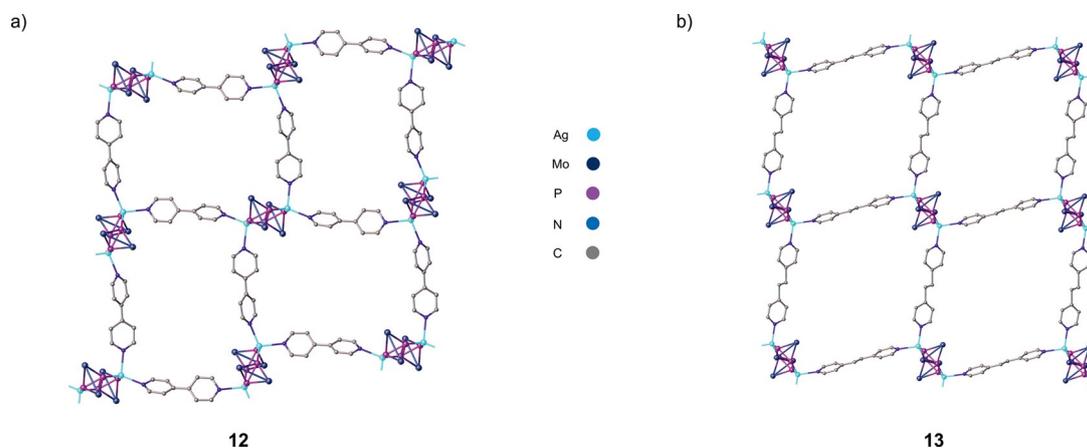


Figure 3. Section of the 2D polymeric networks of a) **12** and b) **13** in the solid state. Cp and CO ligands and H atoms are omitted for clarity.

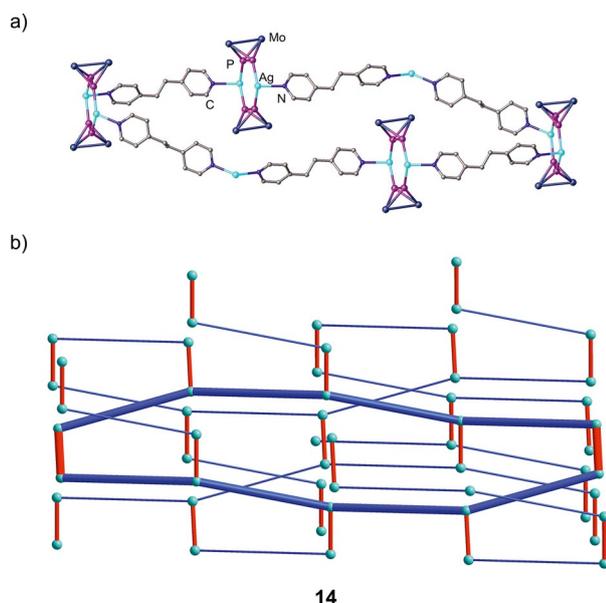


Figure 4. (a) The shortest $\text{Ag}_{10}(\mathbf{8})_6[\mathbf{1}]_8$ ring and (b) the topology of the ths net in **14** with the shortest 10-membered ring highlighted as thick cylinders. Cp and CO ligands as well as hydrogen atoms are omitted for clarity.

out argentophilic interactions.^[16] The uninodal self-dual 3D net in **14** belongs to the ths topological type (ThSi₂-type, Figure 4, see also the Supporting Information),^[17–19] whereas the 2D underlying nets in **12** and **13** belong to the hcb topology (honeycomb net).^[17a]

Even though the networks **12–14** have not got the same dimensionality, all of them are composed of the same ratio of the initial building blocks ([P₂ ligand complex **1**]:[Ag^I ion]:[organic linker]=1:1:1). One explanation for the difference in their topologies is the high degree of flexibility of the linker **8** compared to the linkers **6** and **7**. This flexibility probably allows a freer orientation in space leading to an extension of the network **14** in three dimensions.

The derivatives **9–14** are slightly soluble (**9–11**) or almost insoluble (**12–14**) in donor solvents such as CH₃CN but completely insoluble in other common organic solvents such as CH₂Cl₂, THF and *n*-pentane. Their room temperature ³¹P NMR spectra in CD₃CN show single signals ranging between –91.2 and –64.2 ppm, which are all upfield shifted compared to the free P₂ ligand complex **1** (–43.2 ppm). Their room temperature ¹H NMR spectra present signals corresponding to the hydrogen nuclei of the ligand **1** and the linkers **6–8** (further details in the Supporting Information).

In conclusion, we have shown the possibility to use the Ag^I dimer **3**, capped by four organometallic diphosphorus ligands **1**, in a controlled synthesis of 1D and 2D, or even 3D organometallic–organic hybrid CPs. This is possible due to the lability of each of the two terminal (η²-coordinated) ligands of **1**, which can change their coordination mode from η² to η¹ creating a vacant site on each Ag^I center of the dimer **3**. These vacant sites can accept each a pyridine function of one pyridine-based linker leading to an extension of the formed aggregate in one dimension, exclusively resulting in 1D hybrid CPs.

In a subsequent reaction, complex **1** acts as a leaving group where a complete substitution on each Ag^I center of the dimer **3** by two pyridine functions of two pyridyl-based organic linkers occurs, leading to an extension of the system in two or three dimensions, exclusively giving multi-dimensional organometallic–organic hybrid CPs.

These results show the importance of designing preorganized molecular precursors as a powerful tool for the predictable construction of multi-dimensional CPs in addition to the well-developed area of bimetallic precursors used for the synthesis of squares, triangles, rectangles and higher finite dimensional superstructures.^[2c,7] Current investigations involve the use of multitopic (tri- and tetra-) pyridine-based linkers for a controlled synthesis of 3D organometallic–organic hybrid networks with their potential applications.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: controlled synthesis · diphosphorus complex · hybrid coordination polymers · organometallic node · preorganized precursor

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