Hybrid Materials

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Diphosphorus Complexes as Building Blocks for the Design of Phosphorus-Containing Organometallic–Organic Hybrid Materials**

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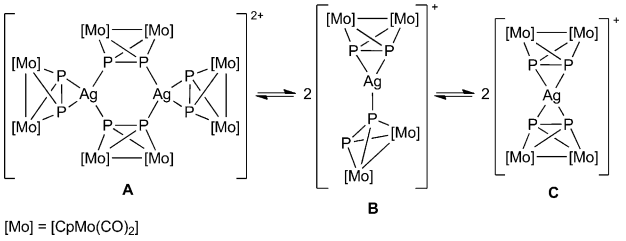
Metal-directed self-assembly is a versatile and well-established method for the construction of discrete and polymeric supramolecular architectures.[1] Most of such assemblies are interconnected by di- or oligotopic organic linker molecules featuring N, O, or S donor atoms. One large research area is dedicated to the construction of metal–organic frameworks (MOFs)[2] in which Lewis acidic metal cations are linked usually by carboxylates to form rigid 3D porous materials with unique properties for energy or gas storage purposes.[2g,h] In addition to this development, research into covalent organic frameworks (COFs) has been developed to control the porosity and composition of such materials by using covalent bonds.[3] To the best of our knowledge there are no materials known that contain both organometallic and organic linkers to form 2D or 3D networks by coordination to Lewis acidic metal centers. With their multiple functionalities, the organometallic units could decisively influence the properties of the formed networks.

The potential of organometallic complexes with bare phosphorus ligands[4] as bridging units between the metal centers has been extensively explored by our group.[5] These complexes posses a versatile coordination behavior and allow the formation of one- and two-dimensional coordination polymers[6] as well as fullerene-like spherical giant molecules with copper(I) halides.[7] If coinage or earth metal salts of weakly coordinating anions (WCAs) are reacted with the P_n ligand complexes, supramolecular assemblies are formed that exhibit dynamic behavior in solution.[8] Herein we show how the latter unique property of P_n ligand complexes can be utilized for the syntheses of unprecedented organometallic–organic hybrid polymers when combined with ditopic organic linker molecules.

In the reaction of the tetrahedrane complex $[Cp_2Mo_2(CO)_4(\eta^2\text{-}P_2)]$ (**1**)[9] with the Ag^I WCA salt $Ag[Al\{OC(CF_3)_3\}_4]$ (**2**),[10] a compound is formed that possesses a dimeric $[Ag_2(\mathbf{1})_4][Al\{OC(CF_3)_3\}_4]_2$ structure(**3**)[8c] in the solid state with two $\mu\text{-}\eta^1\text{:}\eta^1$ bridging ligands **1** and two ligands in η^2 side-on coordination (**A**, Scheme 1). In CH_2Cl_2 solution, however, a dynamic monomer–dimer equilibrium occurs (Scheme 1).[8c] According to DFT calculations, the



Scheme 1. Proposed equilibria for the cations of **3** in CH_2Cl_2 solution.

energy barrier for a change of the coordination mode of one unit of **1** from η^2 side-on (**C**) to η^1 end-on (**B**) is only 9 kJ mol^{-1}. Such a $\eta^2 \rightarrow \eta^1$ transition potentially generates a coordinatively unsaturated metal center. This leads to the question as to whether the silver ions in **3** are accessible by additional ditopic organic ligands, which would make the compound a suitable precursor for expanded coordination networks.

The reaction of **3** with the ditopic ligand *trans*-1,2-di(pyridine-4-yl)ethene (**4**) in a 1:2 stoichiometry in CH_2Cl_2 leads to the formation of **5a** in the form of a red–orange crystalline solid suitable for single crystal X-ray structure analysis (Scheme 2).[11] The same product can also be obtained in a one-pot reaction of the starting materials **1**, **2**, and **4**. Indeed, the compound turned out to be a one-dimensional organometallic–organic hybrid polymer consisting of $[Ag_2(\mathbf{1})_4]$ units, which are linked to polycationic chains by the connectors **4** (Figure 1).

The coordination mode of the formerly side-on coordinating complexes **1** turned into an end-on coordination, which enabled the integration of the organic linker molecules. Nevertheless, the Ag_2P_4 six-membered ring motif of **3** is conserved in the structure of **5a**. Interestingly, the six-membered ring in **5a** is virtually planar (folding angles: 2.23(7)°, 1.99(7)°), while in **3** a pronounced chair conformation is present (folding angle: 20.69(2)°). The silver ions comprise a distorted tetrahedral environment with three P atoms and one N atom. Compared to the free complex **1** (2.079(6) Å),[7] the P–P bond lengths in **5a** are slightly elongated (2.083(4)–2.095(4) Å). The Ag–P distances are in a typical range (2.464(3)–2.537(2) Å). The pyridine linkers are *trans* to each other, with the pyridine ring planes being almost perpendicular to the average plane of the Ag_2P_4 ring (folding angles: 87.97(20)°, 87.59(17)°).

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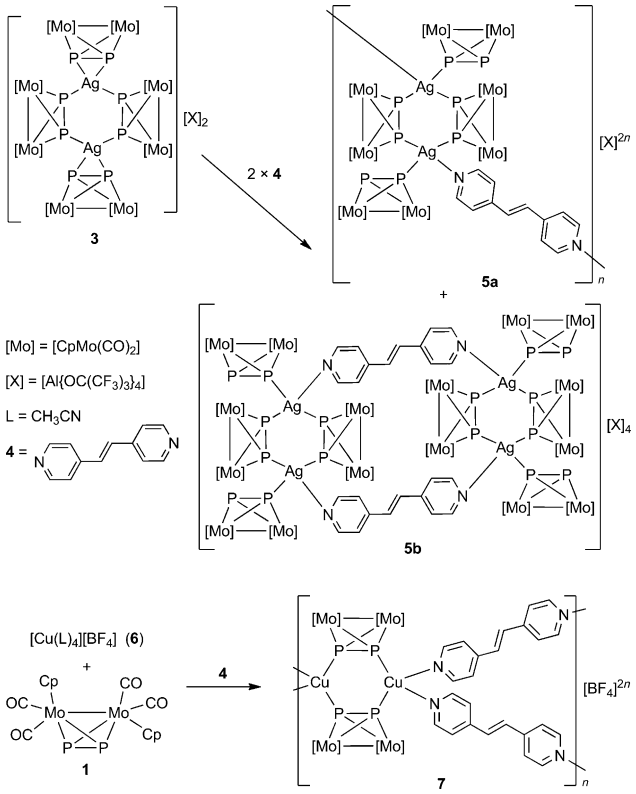

Scheme 2. Syntheses of compounds **5a**,**b** and **7**.

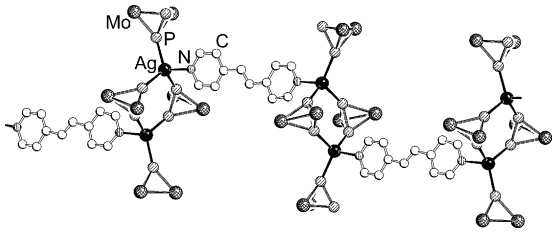

Figure 1. Section of the cationic coordination polymer of **5a** in the solid state (SCHAKAL99).[15] Cp and CO ligands as well as hydrogen atoms are omitted for clarity.

From the same reaction mixture, crystals of another compound, **5b**, could be obtained that were suitable for a single crystal X-ray structure analysis[11] (Scheme 2). Compound **5b** is a structural isomer of **5a**. In **5b** the organic linker molecules show a *cis* arrangement relative to the Ag,Ag axis, thus leading to the formation of a discrete metallaparacyclophane aggregate (Figure 2). The P–P (2.087(3)–2.102(4) Å) and the Ag–P bond lengths (2.480(2)–2.566(2) Å) in **5b** are in a similar range to those of **5a**. However, the Ag_2P_4 six-membered rings deviate significantly from planarity. They exhibit a distorted boat conformation with folding angles of 21.34(5)° and 23.70(7)°. A π–π interaction between the heteroaromatic rings of the connectors can be excluded because of a large distance between the ring centroids (5.372(1) Å). Compound **5b** is the first example of a metallaparacyclophane assembled solely from metal salt cations, P_n ligand complexes, and organic linkers. In contrast, a number

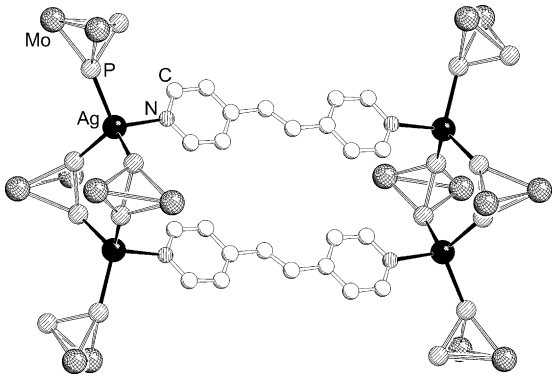

Figure 2. Molecular structure of the tetracation of **5b** in the solid state (SCHAKAL99).[12] Cp and CO ligands as well as hydrogen atoms are omitted for clarity.

of metallaparacyclophane compounds are known that are assembled by dimetallic building blocks of different types.[12]

In the $^{31}P\{^1H\}$ NMR spectrum of **5a** in CD_2Cl_2 at room temperature, a broad singlet at −87.5 ppm is detected, which is shifted upfield compared to uncoordinated **1** ($\delta = -43.2$ ppm). For comparison, the ^{31}P NMR chemical shift of compound **3** in CD_2Cl_2 is −96.1 ppm.[13] The ^1H, $^{13}C\{^1H\}$, and $^{19}F\{^1H\}$ NMR spectra of **5** exhibit characteristic signals for the organic ligands and the counteranion. The ESI mass spectrum of **5** in CH_2Cl_2 shows a base peak in the cation mode for the monocation $[Ag\{Cp_2Mo_2(CO)_4P_2\}_2]^+$ as well as peaks for smaller fragments. In the anionic mode, the peak with 100% intensity corresponds to the intact $[Al\{OC(CF_3)_3\}_4]^-$ anion. Presumably, dissociation takes place in solution accompanied by equilibria between different mono- and dicationic species, rendering all phosphorus nuclei equivalent on the NMR timescale. This equilibrium might be responsible for the simultaneous and reversible formation of 1D polymeric (**5a**) as well as discrete molecular assemblies (**5b**). To increase the rigidity of these materials and decrease the solubility of the products, a different counterion was needed.

Upon changing the metal salt source from $Ag[Al\{OC(CF_3)_3\}_4]$ to $[Cu(CH_3CN)_4][BF_4]$ (**6**), completely different results were obtained in reactions with linker **4**. Independent of the reaction stoichiometry, the two-dimensional coordination network **7** (Scheme 2) is formed as orange single crystals suitable for single crystal X-ray crystallography.[11]

In **7**, each side-on coordinating complex **1** present in the parent compound **3** is substituted by the pyridine functions of two linker molecules (Figure 3a). As a consequence, a 2D network is formed with every Cu^I ion in a distorted tetrahedral coordination sphere and P_2N_2 environment. Organometallic $Cu_2P_2Mo_2$ units form the vertices of the 2D assembly, revealing the novel design of this network. Owing to the relatively large N-Cu-N angles (110.32(16)°), the cavities of the meshes have a rhombic shape. The maximum diameter of the cavities is 2.20 nm.[14] In the crystal packing these voids are occupied with disordered solvent molecules and anions. The P–P bond lengths in **7** (2.083(2) Å) compare to those of the free ligand **1** (2.079(6) Å) and of the compounds **5a,b** (2.083(4)–2.102(4) Å). The metal–phosphorus bonds (2.273(1), 2.279(1) Å) are shorter than in **5a,b** as

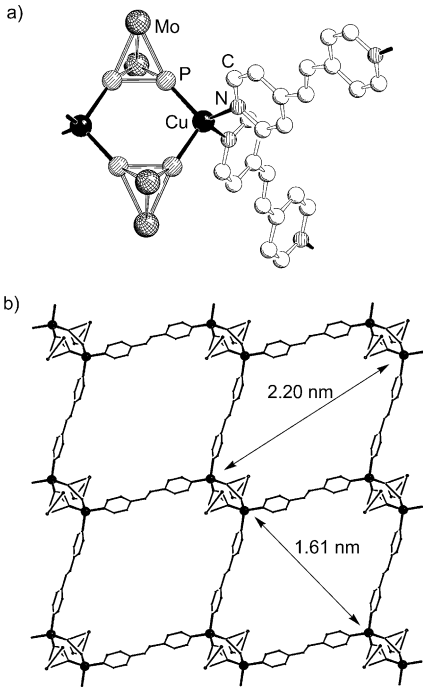

Figure 3. a) Structure of the dicationic repeating unit of **7** in the solid state (SCHAKAL99).[12] b) Section of the 2D polymeric network of **7**. Cp and CO ligands and H atoms are omitted for clarity.

expected owing to the smaller ionic radius of Cu^I compared to Ag^I. The Cu_2P_4 six-membered rings that are connected by the organic linkers are nearly planar, with a folding angle of only 3.61(5)°.

Compound **7** dissolves moderately only in donor solvents such as CH_3CN, whereby a degradation of the polymeric structure takes place. In the ^1H and $^{13}C\{^1H\}$ NMR spectra in CD_3CN at room temperature, typical signals for the Cp and CO ligands as well as for the bridging ligand **4** are observed. The $^{19}F\{^1H\}$ NMR spectrum shows a signal for the tetrafluoroborate anion, and the $^{31}P\{^1H\}$ NMR spectrum exhibits a singlet at a chemical shift ($\delta = -43.5$ ppm) that is very similar to the free ligand **1** ($\delta = -43.2$ ppm). In the ESI mass spectrum, peaks for the cations $[Cu(\mathbf{1})_2]^+$, $[Cu(\mathbf{1})(\mathbf{4})]^+$, $[Cu(\mathbf{1})(CH_3CN)]^+$, and $[Cu(\mathbf{4})(CH_3CN)]^+$ were detected in the cation mode and a peak for $[BF_4]^-$ in the anion mode.

In conclusion, a novel strategy was discovered for the synthesis of unprecedented organometallic–organic hybrid polymers featuring units with bare organometallic phosphorus ligands as well as organic pyridine linker molecules. The dynamic behavior of the precursor compounds in solution was utilized. These do not only show monomer–dimer equilibria, but also a flexible coordination mode of the ligands generating temporary available coordination sites. The resulting compounds exhibit interesting rectangular or 1D polymeric structures. By changing the counterion, more rigid and insoluble polymers can be obtained revealing unprecedented organometallic–organic hybrid materials with cavities in the nanometer range. With the organic linker molecules the novel synthetic route opens up new opportunities to incorporate defined functionalities in solid-state architectures of phosphorus ligand complexes.

Experimental Section

5a and **5b**: A solution of $Ag[Al\{OC(CF_3)_3\}_4]$ (**2**; 41 mg, 0.035 mmol), $[Cp_2Mo_2(CO)_4P_2]$ (**1**; 35 mg, 0.07 mmol), and *trans*-1,2-di(pyridine-4-yl)ethene (**4**; 13 mg, 0.07 mmol) in CH_2Cl_2 (10 mL) was stirred for 3 h at room temperature in the dark. Afterwards, the mixture was filtered and the red–orange solution was stored at −28 °C. Within 5 days single crystals of **5a**·$2CH_2Cl_2$ and **5b**·$2CH_2Cl_2$ are formed. These crystals were isolated by filtration, washed with pentane (2 × 2 mL), and dried in the vacuum. According to the elemental analysis one of the CH_2Cl_2 solvent molecules per asymmetric unit is lost. Concentration of the mother liquor to half of the original volume and storage at −28 °C led to further crystallization of **5a** and **5b**, which were isolated and dried in the same way. Overall yield: 46 mg (59 %). Owing to the different color and shape, the crystals of **5a** and **5b** can be manually separated. The ratio of both compounds was about 1:1. Note that the reaction of the precursor **3** with the organic linker **4** leads to the same result. ^1H NMR (CD_2Cl_2, 400 MHz): $\delta = 5.33$ (s, C_5H_5), 7.29 (s, H_5), 7.49 (m, H_3), 8.59 ppm (m, H_2); $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 101 MHz): $\delta = 87.7$ (s, C_5H_5), 121.6 (q, $^1J_{FC} = 290$ Hz; CF_3), 122.0 (s, C_3), 131.2 (s, C_5), 144.6 (s, C_4), 150.6 (s, C_2), 223.0 ppm (CO); $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 162 MHz): $\delta = -87.5$ ppm (br s); $^{19}F\{^1H\}$ NMR (CD_2Cl_2, 282 MHz): $\delta = -75.6$ ppm (s, CF_3); C,H,N analysis calcd (%) for $Ag_2Al_2C_{101}Cl_2F_{72}H_{53}Mo_8N_2O_{24}P_8$ (4402.32 g mol^{-1}): C 27.56, H 1.19, N 0.64; found: C 27.86, H 1.21, N 0.76; for more details, see the Supporting Information.

7: A solution of $[Cu(CH_3CN)_4][BF_4]$ (**6**; 19 mg, 0.06 mmol) and one equivalent of $[Cp_2Mo_2(CO)_4P_2]$ (**1**; 30 mg, 0.06 mmol) in a mixture of CH_2Cl_2 (5 mL) and CH_3CN (2 mL) was stirred for 10 min at room temperature. Afterwards, the solution was layered with a solution of one equivalent of *trans*-1,2-di(pyridine-4-yl)ethene (**4**; 11 mg, 0.06 mmol) in toluene (5 mL) using a teflon capillary. Within two weeks red crystals of the compound **7**·CH_2Cl_2·CH_3CN formed, which were suitable for single-crystal X-ray diffraction analysis. These crystals were isolated by filtration, washed with *n*-pentane (3 × 2 mL), and dried in the vacuum. According to the elemental analysis, all of the solvent molecules were removed during the drying process: Yield: 38 mg (76 %). ^1H NMR (CD_3CN, 400 MHz): $\delta = 5.31$ (s, C_5H_5), 7.41 (s, H_5), 7.52 (m, H_3), 8.58 ppm (m, H_2); $^{13}C\{^1H\}$ NMR (CD_3CN, 101 MHz): $\delta = 87.4$ (s, C_5H_5), 122.3 (s; C_3), 131.5 (s, C_5), 144.7 (s, C_4), 151.3 ppm (s, C_2); $^{31}P\{^1H\}$ NMR (CH_2Cl_2/CD_3CN, 162 MHz): $\delta = -43.5$ ppm (s); $^{19}F\{^1H\}$ NMR (CD_3CN, 282 MHz): $\delta = -150.6$ ppm (s, BF_4); C,H,N analysis calcd (%) for $C_{26}H_{20}BCuF_4Mo_2N_2O_4P_2$ (1657.27 g mol^{-1}): C 37.69, H 2.43, N 3.38; found: C 38.29, H 2.60, N 3.17; for more details, see the Supporting Information.

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[11] The crystal structure analyses were performed on an Oxford Diffraction Gemini R Ultra CCD diffractometer using $Cu_{K\alpha}$ radiation ($\lambda = 1.54178$ Å). The structures were solved with the programs SIR-97[16] (**5b**) and SHELXS-97[17] (**5a**, **7**); full-matrix-least-squares refinement on F^2 in SHELXL-97[17] was performed with anisotropic displacements for the nonhydrogen atoms. Hydrogen atoms were located in idealized positions and refined isotropically according to a riding model. **5a** was refined as a racemic twin with a ratio of the twin components of 51.2/48.8 (Flack parameter: 0.488(8)). **5a**·2 CH_2Cl_2: $C_{102}H_{54}Ag_2Al_2Cl_4F_{72}Mo_8N_2O_{24}P_8$, $M_r = 4486.25$, crystal dimensions $0.13 \times 0.08 \times 0.03$ mm^3, orthorhombic, space group $P2_12_12_1$, $a = 20.9863(5)$, $b = 21.8253(4)$, $c = 30.9669(7)$ Å, $V = 14183.8(5)$ Å^3, $Z = 4$, $T = 100(1)$ K, $\rho_{calc} = 2.101$ Mg m^{-3}, $\mu = 10.895$ mm^{-1}, 49104 reflections collected, 22912 unique reflections ($R_{int} = 0.0398$), 2018 parameters, $R_1 = 0.0456$, $wR_2 = 0.1220$. **5b**·6 CH_2Cl_2: $C_{206}H_{112}Ag_4Al_4Cl_{12}F_{144}Mo_{16}N_4O_{48}P_{16}$, $M_r = 9142.36$, crystal dimensions $0.23 \times 0.14 \times 0.03$ mm^3, monoclinic, space group $P2_1/n$, $a = 24.2411(4)$, $b = 21.8544(4)$, $c = 27.7987(5)$ Å, $\beta = 93.330(2)°$, $V = 14702.2(4)$ Å^3, $Z = 2$, $T = 123(1)$ K, $\rho_{calc} = 2.065$ Mg m^{-3}, $\mu = 10.853$ mm^{-1}, 49104 reflections collected, 22912 unique reflections ($R_{int} = 0.0856$), 2154 parameters, $R_1 = 0.0541$, $wR_2 = 0.1147$. **7**·CH_2Cl_2: $C_{29}H_{25}BCl_2CuF_4Mo_2N_3O_4P_2$, $M_r = 954.60$, crystal dimensions $0.30 \times 0.22 \times 0.13$ mm^3, triclinic, space group $P\bar{1}$, $a = 11.3084(4)$, $b = 12.5205(3)$, $c = 14.6913(5)$ Å, $\alpha = 65.995(3)$, $\beta = 71.303(3)$, $\gamma = 87.705(2)°$, $V = 1790.07(11)$ Å^3, $Z = 2$, $T = 123(1)$ K, $\rho_{calc} = 1.771$ Mg m^{-3}, $\mu = 9.084$ mm^{-1}, 24621 reflections collected, 6711 unique reflections ($R_{int} = 0.0473$), 434 parameters, $R_1 = 0.0451$, $wR_2 = 0.1247$. CCDC 823817 (**5a**), CCDC 823818 (**5b**), and CCDC 823819 (**7**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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