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Coordination Polymers

An Unusual Building Block for Supramolecular Aggregates: The Mixed Group 15/16 Element Ligand Complex $[(Cp^*Mo)_2(\mu,\eta^3\text{-}P_3)(\mu,\eta^2\text{-}PS)]$**

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Dedicated to Professor Dieter Fenske on the occasion of his 65th birthday

The construction of supramolecular aggregates and networks by the self-organization of discrete units has become one of the most exciting and rewarding areas of chemical research.[1] The most common approach in this field involves the use of organic compounds containing nitrogen-, oxygen-, and/or sulfur-donor atoms as linkers for different metal centers. In contrast, we employ organometallic E_n-ligand complexes (E = P, As) as connecting moieties, and we have already succeeded in isolating several oligomers,[2,3] one-dimensional (1D)[2,4] and two-dimensional (2D)[4a] polymers, and even fullerene-like aggregates.[5] The versatility of E_n-ligand complexes in supramolecular chemistry thus provided us with the incentive to explore the potential of organometallic E_mS_n-ligand complexes[6] to act as such, since the question arises whether coordinatively unsaturated metal centers will coordinate to both the pnicogen and sulfur atoms of the ligand or whether a preference for one element type will be demonstrated.

The coordination properties of the cationic complexes $[(\text{triphos})Co(\eta^3\text{-}E_2S)]^+$ (triphos = 1,1,1-tris(diphenylphosphanylmethyl)ethane; E = P (**1a**), As (**1b**)) have been studied by Stoppioni and co-workers.[6c] For example, although Lewis acidic transition-metal carbonyl fragments do not coordinate to the E_2S rings in these cations, the 14-electron carbene-like moiety $\{Pt(PPh_3)\}$ readily inserts into an E−E or E−S bond.[7] Much more recently, we reported on the synthesis and characterization of the first supramolecular compounds incorporating organometallic E_mS_n-ligand complexes as linking units, based on the As_2S_3-ligand complex $[(Cp^*Mo)_2(\mu,\eta^2\text{-}AsS)_2(\mu\text{-}S)]$ (**2**; $Cp^* = C_5Me_5$), in which only one sulfur atom per unit of **2** is engaged in coordination.[8]

We were particularly interested in employing P_mS_n-ligand complexes as building blocks for supramolecular aggregates because we intended to exploit the favorable NMR features of the ^{31}P nucleus in the elucidation of the resulting structures, both in solution and in the solid state. Phosphorus and sulfur are practically indistinguishable by X-ray crystallography, and, if both elements are present in a compound, their assignment can be a challenge unless there is no doubt as to which position each element occupies in the compound's structure. For example, Krossing and co-workers synthesized and structurally characterized two 1D polymers comprising chains of silver cations bridged either singly or doubly by the inorganic cage molecule P_4S_3.[9] The positions of the phosphorus and sulfur atoms in the structures could be easily assigned since it is clear which corners of the P_4S_3 cage these elements occupy, and thus the first examples of P_4S_3 complexes exhibiting sulfur coordination could be unambiguously confirmed.

We anticipated that the assignment of the positions of the phosphorus and sulfur atoms in supramolecular structures containing organometallic P_mS_n-ligand complexes might not be as straightforward as in the case of the polymers reported by Krossing and co-workers and that solid-state ^{31}P magic angle spinning (MAS) NMR spectroscopy would be necessary for a reliable assignment. We report herein on the synthesis and characterization of two novel 1D polymers based on the P_4S-ligand complex $[(Cp^*Mo)_2(\mu,\eta^3\text{-}P_3)(\mu,\eta^2\text{-}PS)]$ (**3**).[10] The elucidation of the solid-state structures of the polymers could only be achieved by a combination of X-ray crystallography and ^{31}P MAS NMR spectroscopy.

Reaction of **3** with CuI and $Ag[Al\{OC(CF_3)_3\}_4]$,[11] respectively, leads to the formation of the novel 1D polymers **4** and **5**. Crystals of **4** can be obtained as dark red rods by slow diffusion of a CH_3CN solution of CuI into a CH_2Cl_2 solution of **3** at room temperature. Polymer **5** can be crystallized in the form of red-brown needles by slow diffusion of a toluene solution of **3** into a CH_2Cl_2 solution of $Ag[Al\{OC(CF_3)_3\}_4]$ at room temperature in the absence of light. Both polymers are air-sensitive, but can be stored indefinitely under an inert atmosphere at ambient conditions. Polymers **4** and **5** are only sparingly soluble in polar solvents such as CH_3CN, the solubility of **5** being slightly better than that of **4**. The

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electrospray ionization (ESI) mass spectra of **4** and **5** in CH_3CN indicate that they dissolve under essentially complete depolymerization.[12]

$$[\{Cu(\mu\text{-}I)\}_3\{(Cp^*Mo)_2(\mu_3,\eta^3:\eta^3:\eta^1\text{-}P_3)(\mu,\eta^2\text{-}PS)\}\text{-}\{(Cp^*Mo)_2(\mu_3,\eta^3:\eta^3:\eta^1\text{-}P_3)(\mu_3,\eta^2:\eta^2:\eta^1\text{-}PS)\}]_n \quad \mathbf{4}$$

$$[Ag\{(Cp^*Mo)_2(\mu_3,\eta^3:\eta^3:\eta^1\text{-}P_3)(\mu,\eta^2\text{-}PS)\}\{(Cp^*Mo)_2\text{-}(\mu_3,\eta^3:\eta^3:\eta^1\text{-}P_3)(\mu_3,\eta^2:\eta^2:\eta^1\text{-}PS)\}]_n[Al\{OC(CF_3)_3\}_4]_n \quad \mathbf{5}$$

The 1D polymeric structures of **4** and **5** were revealed by X-ray crystallographic characterization.[13] Complex **4** consists of a stack of distorted $\{Cu_3I_3\}$ rings bridged by units of **3**, with a further unit of **3** being coordinated to each $\{Cu_3I_3\}$ ring as a terminal ligand (Figure 1). Although discrete $\{Cu_3X_3\}$ rings (X = Cl, Br, I) are apparently the predominant species in CuX vapor,[14] such rings represent a structural rarity in the solid state[15] and, to the best of our knowledge, had not been observed previously for X = I. The lengths of the Cu–P (2.211(1)–2.220(1) Å) and Cu–I (2.556(1)–2.689(1) Å) bonds are comparable to the corresponding bond lengths found in the complex $[Cu_2I_2(PPh_3)_3]$ (2.219(3)–2.267(3) Å and 2.500(2)–2.819(1) Å, respectively).[16] Considering the interatomic distances Cu1···Cu2 (2.554(7) Å) and Cu1···Cu3 (2.79(2) Å), the existence of weak interactions between the atom Cu1 and the atoms Cu2 and Cu3, respectively, is likely, since these contacts are shorter than or equal to twice the van der Waals radius of copper (1.40 Å).[17,18]

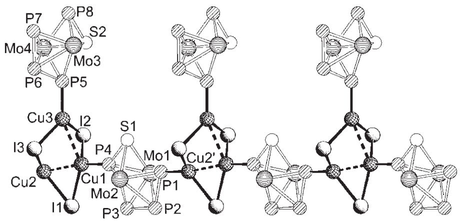


Figure 1. Section of the 1D polymeric structure of **4** (Cp* ligands are omitted for clarity). Selected bond lengths [Å], interatomic separations [Å], and angles [°]: P1-P2 2.187(1), P2-P3 2.155(2), P5-P6 2.191(1), P6-P7 2.149(1), S1-P4 2.088(1), S2-P8 2.081(1), Cu1-P4 2.220(1), Cu2'-P1 2.218(1), Cu3-P5 2.211(1), Cu1-I1 2.616(1), Cu2-I1 2.583(1), Cu1-I2 2.671(1), Cu3-I2 2.557(1), Cu2-I3 2.689(1), Cu3-I3 2.556(1), Cu1···Cu2 2.554(7), Cu1···Cu3 2.79(2); I1-Cu1-I2 109.40(3), I1-Cu1-P4 111.96(4), I2-Cu1-P4 121.45(4), I1-Cu2-I2 96.78(2), I1-Cu2-P1 124.28(4), I3-Cu2-P1 116.80(4), I2-Cu3-I3 111.78(2), I2-Cu3-P5 121.00(4), I3-Cu3-P5 125.04(4), Cu1-I1-Cu2 58.85(2), Cu1-I2-Cu3 64.58(2), Cu2-I3-Cu3 81.81(2).

The undulated 1D polymeric structure of **5** (Figure 2) consists of a chain of Ag^I centers singly bridged by units of **3**. Each silver atom is coordinated to a further unit of **3** in a terminal fashion and is thus in a trigonal coordination mode (separation of Ag1 from the P1-P5-P12 plane: 0.004(1) Å; separation of Ag2 from the P4'-P11-P13 plane: 0.037(1) Å). The lengths of the Ag–P bonds in **5** (2.464(5)–2.489(6) Å) are within the range defined by those found in the tricoordinate silver complex $[Ag\{(PPh_2)_2C_2B_9H_{10}\}(PPh_3)]$ (2.397(1)–2.494(1) Å).[19]

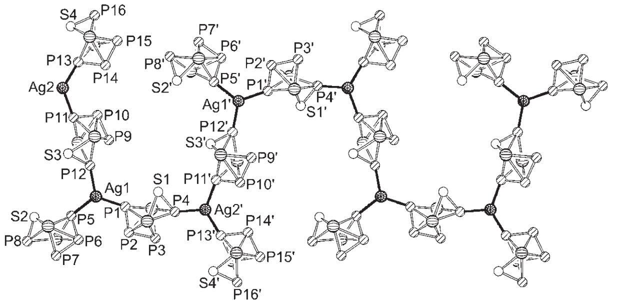
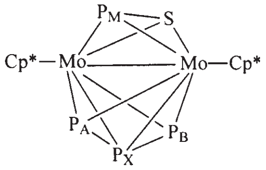


Figure 2. View of a section of the undulated polycationic chain in **5** along the crystallographic *b* axis (Cp* ligands are omitted for clarity). Selected bond lengths [Å] and angles [°]: P1-P2 2.173(9), P2-P3 2.15(1), P5-P6 2.163(8), P6-P7 2.162(9), P9-P10 2.141(8), P10-P11 2.189(8), P13-P14 2.182(6), P14-P15 2.160(8), S1-P4 2.100(8), S2-P8 2.09(1), S3-P12 2.097(7), S4-P16 2.069(9), Ag1-P1 2.477(5), Ag1-P5 2.477(5), Ag1-P12 2.489(6), Ag2'-P4 2.481(5), Ag2-P11 2.489(6), Ag2-P13 2.464(5); P1-Ag1-P5 123.5(2), P1-Ag1-P12 119.6(2), P5-Ag1-P12 117.0(2), P4-Ag2'-P11' 113.7(2), P4-Ag2'-P13' 119.7(2), P11-Ag2-P13 126.6(2).

The elements phosphorus and sulfur are essentially indistinguishable by X-ray crystallography. The assignment of these elements in the PS ligands of both the bridging and pendant units of **3** as shown in Figure 1 and Figure 2 was facilitated by solid-state ^{31}P MAS NMR measurements on the polymers and ^{31}P NMR measurements on **5** in solution.[20] It is helpful to consider the ^{31}P NMR spectral properties of the starting complex **3** (Table 1) before discussing the spectra of **4** and **5**. For **3**, P_A resonates at $\delta = 345.3$ ppm, P_B at $\delta = 325.0$ ppm, P_M at $\delta = -130.1$ ppm, and P_X at $\delta = -365.8$ ppm in the solid state.

Table 1: Structure and ^{31}P NMR chemical shifts of **3**.



P atom	δ [ppm] (CHCl$_3$ solution)[a]	δ [ppm] (solid state)
P_A	343.3	345.3
P_B	320.8	325.0
P_M	−132.0	−130.1
P_X	−366.5	−365.8

[a] Simulated J_{PP} coupling constants: $J_{AX} = 375$, $J_{BX} = 392$, $J_{AM} = 64$, $J_{MX} = 19$, $J_{AB} = 15$, $J_{BM} < 10$ Hz.[10]

The experimental and simulated solid-state ^{31}P MAS NMR spectra of **4** at room temperature are depicted in Figure 3. As demonstrated by X-ray crystallography, **4** contains both bridging and pendant units of **3**, which are therefore chemically distinct. Furthermore, the bridging units coordinate through the P_3 as well as the PS ligand, while the pendant units are bound only through the P_3 ligand. The spectrum of **4** displays two signals in the region where the P_M resonances would be expected, one at lower field with

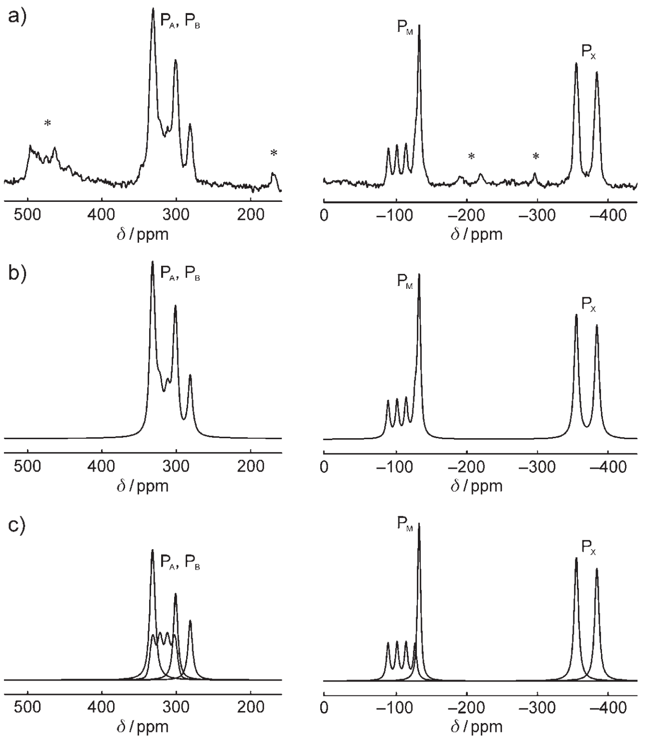


Figure 3. Experimental and simulated solid-state ^{31}P MAS NMR spectra of the polymer **4**, with P-atom assignments. Spinning side bands are marked with asterisks. a) Experimental spectrum; b) simulated spectrum; c) simulated spectrum showing individual components.

coupling to $^{63/65}$Cu ($\delta = -107.5$ ppm; $^1J_{\mathrm{CuP}} = 1500$ Hz) and one at higher field ($\delta = -132.8$ ppm) without such coupling. This observation does not only demonstrate that the P_M atoms of the bridging and pendant units of **3** are electronically distinct, but also that the phosphorus atoms, and not the sulfur atoms, of the PS ligands in the bridging units of **3** are coordinated. In view of the geometrical arrangement of the phosphorus atoms in **3** (Table 1), this result in turn confirms that the P_B atoms of the P_3 ligands of the bridging units of **3** are coordinated. Two signals are observed in the region where the P_X resonances would be expected, the higher-field signal ($\delta = -384.2$ ppm) probably attributable to the pendant units of **3** and the lower-field signal ($\delta = -354.8$ ppm) resulting from the bridging units, as is the case with the P_M resonances. The region of the NMR spectrum encompassing the P_A and P_B resonances displays a group of at least partly superimposed signals.

Several simulations were performed on the basis of the assumption that one would expect two signals for the bridging unit of **3** and two signals for the pendant unit of **3**, as deduced from the structure of **4** given in Figure 1. Three signals ($\delta =$ 281.7, 301.3, 331.1 ppm) could be easily and unambiguously identified while the remaining signal had to be simulated. The simulation yielding the best agreement with experimental spectra is displayed in Figure 3. The simulated spectrum exhibits a characteristic splitting for the remaining signal, indicating coupling to $^{63/65}$Cu ($\delta = 317$ ppm; $^1J_{\mathrm{CuP}} = 1200$ Hz). Owing to structural considerations, this component is most likely attributable to the P_B atoms of the bridging units of **3**, because a characteristic splitting of the signal resulting from the coupling to $^{63/65}$Cu was also shown for P_M (see above). The other three resonances in this region of the simulated spectrum do not reveal any coupling to neighboring $^{63/65}$Cu nuclei. It is evident from the X-ray crystal structure of **4** that the pendant units of **3** are coordinated by the P_3 ligands (P_A-P_X-P_B). Therefore, we assume the existence of a dynamic process which may average the coupling and, hence, the splitting of the corresponding signal in the NMR spectrum.[21] Although coordination through the P_B atoms was chosen for the structural representation in Figure 1, a statistical distribution is not unlikely.

The solid-state ^{31}P MAS NMR spectrum of **5**[20] displays four broad resonances ($\delta = -367.2$ (P_X), -128.2 (P_M), 295.51 (P_B), 340.3 ppm (P_A)) with no resolvable coupling to $^{107/109}$Ag. As is the case with polymer **4**, polymer **5** contains both bridging and pendant units of **3**. The bridging units of **3** coordinate through the P_3 as well as the PS ligand, while the pendant units are bound only through the P_3 ligand. The chemical shifts of the phosphorus atoms in **5** are all essentially identical to those of the starting material **3** in the solid state (Table 1), with the exception that the signal of the P_B atoms appears about 30 ppm further upfield. This result suggests that the P_3 ligands of both the bridging and pendant units of **3** coordinate to the silver atoms through the P_B atoms, which in turn implies that the PS ligands of the bridging units of **3** coordinate through the phosphorus (P_M) and not the sulfur atoms.

The ^{31}P NMR spectrum of **5** in CD_3CN[20] is characteristic of an ABMX spin system, as is that of the starting complex **3** in $CHCl_3$.[10] All resonances are shifted 10–15 ppm upfield with respect to those of uncoordinated **3** (Table 1), with the exception of the signal attributable to P_M, whose chemical shift is essentially identical to that of the P_M atom in uncoordinated **3**. None of the signals demonstrate coupling to the $^{107/109}$Ag nuclei. In the room-temperature positive-ion ESI mass spectrum of **5** in CH_3CN, the most abundant fragment, which also happens to be the largest fragment observed, is attributable to the cation $[\mathrm{Ag}\{(\mathrm{Cp^*Mo})_2\mathrm{P_4S}\}_2]^+$ (**I**). Thus, assuming that only the cation **I** is present in solution, the NMR data imply that coordination of the two units of **3** to the $\mathrm{Ag^I}$ center is exclusively through the P_3 ligands. Moreover, the resulting complex in solution appears to be fluxional[22] and consequently, one could envisage two possible structural variations of the cation **I**, depicted schematically as $\mathbf{I_A}$ and $\mathbf{I_B}$ in Figure 4.

Both forms consist of a $\mathrm{Ag^+}$ ion, "sandwiched" between the two P_3 edges of the two units of **3**, but differ in the way the P_3 edges are arranged with respect to each other. As illustrated, one P_3 ligand in $\mathbf{I_A}$ is the reflection of the other, whereas in $\mathbf{I_B}$, the $\mathrm{Ag^+}$ ion can be regarded as an inversion center. In both variations, the P_3 ligands can essentially "slip" back and forth with respect to the $\mathrm{Ag^+}$ ion, as indicated by the double-headed arrows, and at any one time, the ligands may both be η^1-coordinated or η^2-coordinated, or one ligand may be η^1-coordinated while the other is η^2-coordinated. Interconversion between $\mathbf{I_A}$ and $\mathbf{I_B}$ could occur following appropriate rotation of one of the P_3 ligands about the axis of its bond to $\mathrm{Ag^+}$. It is obvious that several structures are possible

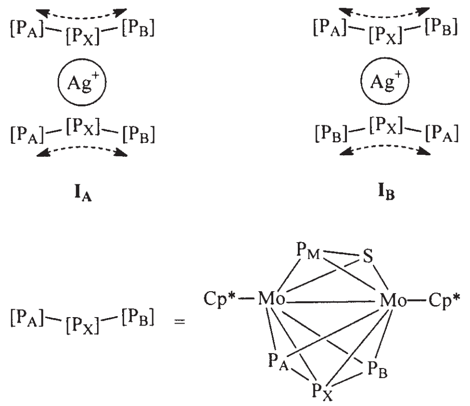


Figure 4. Schematic representation of the two structural variations proposed for the cation **I** in CD_3CN solution.

for **I**, which, from the standpoint of energetics, are most probably indistinguishable, and thus interconversion between these structures is likely to be facile. This would in turn lead to all three P resonances of the P_3 ligand being shifted upfield, albeit without any detectable coupling to the $^{107/109}$Ag nuclei. Density functional theory (DFT) calculations on various linkage isomers of the cation **I**[20] suggest that coordination of the Ag^+ ion to the P_3 ligands rather than the PS ligands is preferred and that the energy difference between the relevant isomers is marginal. The theoretical calculations thus support the conclusions drawn from the experimental evidence.

In conclusion, reaction of **3** with CuI yields the polymer **4**, whose core structure consists of a stack of $\{Cu_3I_3\}$ rings bridged by units of **3**, while $Ag[Al\{OC(CF_3)_3\}_4]$ reacts with **3** to yield the undulated 1D polymer **5**, in which the polycationic chain comprises a backbone of Ag^+ ions singly bridged by units of **3**. The ^{31}P MAS NMR spectra of **4** and **5** were crucial in determining the coordination mode of the PS ligands in the polymers and demonstrated that the S atoms are not involved in coordination at all. The solution NMR and ESI mass spectra of **5** suggest that the polymer dissolves under depolymerization to a monomeric species consisting of the cation **I**, in which the PS ligands are not involved in coordination with Ag^+, as corroborated by DFT calculations on selected linkage isomers of **I**. The results demonstrate that complex **3** can function as an efficient building block for the construction of 1D coordination polymers and thus reveal its potential as a ligand in supramolecular chemistry. Furthermore, it is clear that solid-state MAS NMR spectroscopy can be an excellent complement to X-ray crystallography.

Experimental Section

All manipulations were performed under nitrogen using standard glove-box and Schlenk techniques. All solvents were freshly distilled from appropriate drying agents immediately prior to use. Complex **3**[10] and $Ag[Al\{OC(CF_3)_3\}_4]$[11] were synthesized according to literature procedures. CuI (Aldrich) was purified before use. Solution NMR spectra were acquired on a Bruker Avance400 spectrometer. Solid-state NMR spectra were recorded on a Bruker Avance300 solid-state spectrometer using 2.5-mm probes with MAS rates of 20 kHz. 90° single-pulse experiments were performed, and all chemical shifts are reported relative to H_3PO_4, with NaH_2PO_4 as a secondary standard. Solid-state NMR spectral simulations were performed by using the DMFIT program.[23] ESI mass spectra were measured on a Finnigan Thermoquest TSQ 7000 mass spectrometer. IR spectra were recorded on a Varian FTS 800 spectrometer.

4:[20] A solution of CuI (20 mg, 0.10 mmol) in CH_3CN (10 mL) was carefully layered over a solution of **3** (33 mg, 0.05 mmol) in CH_2Cl_2 (10 mL) at room temperature. The vessel was left at room temperature in the dark and **4** deposited as dark red prisms within a month. These crystals were filtered, washed with CH_2Cl_2 (2×3 mL), and dried under vacuum at room temperature. Yield: 40 mg (83 %); m.p.: 168 °C (decomp); ^{31}P MAS NMR (121.50 MHz, 25 °C): $\delta = -384.2$ (br), -354.8 (br), -132.8 (br), -107.5 (m; $^1J_{CuP} = 1500$ Hz), 281.7 (br), 301.3 (br), 331.1 ppm (br). Elemental analysis (%) calcd for $C_{40}H_{60}Cu_3I_3Mo_4P_8S_2$ (1807.95): C 26.57, H 3.34, S 3.55; found: C 26.45, H 3.49, S 3.56.

5:[20] A solution of **3** (25 mg, 0.04 mmol) in toluene (5 mL) was carefully layered over a solution of $Ag[Al\{OC(CF_3)_3\}_4]\cdot CH_2Cl_2$ (24 mg, 0.02 mmol) in CH_2Cl_2 (3 mL) at room temperature. The vessel was left at room temperature in the dark and brown needles of **5**$\cdot 0.25n\,C_7H_8$ appeared within a month. These crystals were filtered, washed with pentane (2×3 mL), and dried under vacuum at room temperature. The solvent of crystallization was completely removed during the drying process. Yield: 30 mg (64 %); m.p. > 220 °C; ^{1}H NMR (CD_3CN, 400.13 MHz, 27 °C): $\delta = 1.93$ ppm (s; CH_3); $^{13}C\{^1H\}$ NMR (CD_3CN, 100.63 MHz, 27 °C): $\delta = 14.00$ (s; CH_3), 107.00 ppm (s; Cp*); ^{27}Al NMR (CD_3CN, 104.26 MHz, 27 °C): $\delta = 34.38$ ppm (s; $[Al\{OC(CF_3)_3\}_4]^-$); ^{19}F NMR (CD_3CN, 376.47 MHz, 27 °C): $\delta = -74.74$ ppm (s; CF_3); $^{31}P\{^1H\}$ NMR (CD_3CN, 161.93 MHz, 27 °C): ABMX spin system, $\delta = -373.8$ (m; $^1J_{AX} = 375$ Hz, $^1J_{BX} = 386$ Hz, $^2J_{MX} = 22$ Hz; P_X), -132.1 (dd; $^2J_{AM} = 57$ Hz, $^2J_{XM} = 18$ Hz; P_M), 304.9 (d; $^1J_{XB} = 384$ Hz; P_B), 327.3 ppm (dd; $^1J_{XA} = 380$ Hz, $^2J_{MA} = 57$ Hz; P_A); ^{31}P MAS NMR (121.50 MHz, 25 °C): $\delta = -367.2$ (br), -128.2 (br), 295.51 (br), 340.3 ppm (br). Elemental analysis (%) calcd for $C_{56}H_{60}AgAlF_{36}Mo_4O_4P_8S_2$ (2311.56): C 29.10, H 2.62, S 2.77; found: C 29.30, H 2.49, S 3.06.

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[1] Reviews: a) W. Huang, H.-B. Zhu, S.-H. Gou, *Coord. Chem. Rev.* **2006**, *250*, 414–423; b) N. C. Gianneschi, M. S. Masar III, C. A. Mirkin, *Acc. Chem. Res.* **2005**, *38*, 825–837; c) M. Ruben, J. Rojo, F. J. Romero-Salguero, L. H. Uppadine, J.-M. Lehn, *Angew. Chem.* **2004**, *116*, 3728–3747; *Angew. Chem. Int. Ed.* **2004**, *43*, 3644–3662; d) L. Carlucci, G. Ciani, D. M. Proserpio, *Coord. Chem. Rev.* **2003**, *246*, 247–289; e) G. F. Swiegers, T. J. Malefetse, *Coord. Chem. Rev.* **2002**, *225*, 91–121.

[2] J. Bai, E. Leiner, M. Scheer, *Angew. Chem.* **2002**, *114*, 820–823; *Angew. Chem. Int. Ed.* **2002**, *41*, 783–786.

[3] L. J. Gregoriades, H. Krauss, J. Wachter, A. V. Virovets, M. Sierka, M. Scheer, *Angew. Chem.* **2006**, *118*, 4295–4298; *Angew. Chem. Int. Ed.* **2006**, *45*, 4189–4192.

[4] a) J. Bai, A. V. Virovets, M. Scheer, *Angew. Chem.* **2002**, *114*, 1808–1811; *Angew. Chem. Int. Ed.* **2002**, *41*, 1737–1740; b) M. Scheer, L. Gregoriades, J. Bai, M. Sierka, G. Brunklaus, H. Eckert, *Chem. Eur. J.* **2005**, *11*, 2163–2169; c) M. Scheer, L. J. Gregoriades, A. V. Virovets, W. Kunz, R. Neueder, I. Krossing, *Angew. Chem.* **2006**, *118*, 5818–5822; *Angew. Chem. Int. Ed.* **2006**, *45*, 5689–5693.

[5] a) J. Bai, A. V. Virovets, M. Scheer, *Science* **2003**, *300*, 781–783; b) M. Scheer, J. Bai, B. P. Johnson, R. Merkle, A. V. Virovets, C. E. Anson, *Eur. J. Inorg. Chem.* **2005**, 4023–4026; c) B. P. Johnson, F. Dielmann, G. Balázs, M. Sierka, M. Scheer, *Angew.*

Chem. **2006**, *118*, 2533–2536; *Angew. Chem. Int. Ed.* **2006**, *45*, 2473–2475.

[6] Reviews: a) J. Wachter, *Angew. Chem.* **1998**, *110*, 782–800; *Angew. Chem. Int. Ed.* **1998**, *37*, 750–768; b) K. H. Whitmire, *Adv. Organomet. Chem.* **1998**, *42*, 1–145; c) M. Di Vaira, P. Stoppioni, *Coord. Chem. Rev.* **1992**, *120*, 259–279.

[7] a) M. Di Vaira, S. Moneti, M. Peruzzini, P. Stoppioni, *J. Organomet. Chem.* **1984**, *266*, c8–c10; b) M. Di Vaira, P. Stoppioni, M. Peruzzini, *Acta Crystallogr. Sect. C* **1987**, *43*, 1284–1287.

[8] M. Pronold, M. Scheer, J. Wachter, M. Zabel, *Inorg. Chem.* **2007**, *46*, 1396–1400.

[9] A. Adolf, M. Gonsior, I. Krossing, *J. Am. Chem. Soc.* **2002**, *124*, 7111–7116.

[10] H. Brunner, U. Klement, W. Meier, J. Wachter, O. Serhadle, M. L. Ziegler, *J. Organomet. Chem.* **1987**, *335*, 339–352.

[11] I. Krossing, *Chem. Eur. J.* **2001**, *7*, 490–502.

[12] Owing to the poor solubility of the polymers **4** and **5**, the molecular mass of the species in solution could not be determined.

[13] The crystal structure analyses of **4** and **5**$\cdot 0.25n\,C_7H_8$ were performed on a STOE IPDS diffractometer with $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å). The structures were solved by direct methods with the program SIR-97[24], and full-matrix least-squares refinement on F^2 in SHELXL-97[25] was performed with anisotropic displacements for non-H atoms in **4**. In the case of **5**$\cdot 0.25n\,C_7H_8$, only the heavier atoms (P, S, Mo, Ag) were refined anisotropically owing to poor crystal quality. Despite repeated attempts, higher-quality crystals of polymer **5** could not be grown. The hydrogen atoms in both structures were located in idealized positions and refined isotropically according to the riding model. The $[Al(OC(CF_3)_3)_4]^-$ ion generally has a strong tendency to be rotationally disordered in two different ways: 1) rotation of the CCF_3 moiety about the C–C bond and 2) rotation of the whole $OC(CF_3)_3$ group about the O–C bond. In the structure of **5**$\cdot 0.25n\,C_7H_8$, we observed both types of disorder, which, in combination with the isotropic refinement performed for the lighter atoms in this polymer, led to a somewhat elevated wR_2 value. **4**: $C_{40}H_{60}Cu_3I_3Mo_4P_8S_2$, $M_r = 1807.89$, crystal dimensions $0.52 \times 0.20 \times 0.16$ mm³, triclinic, space group $P\bar{1}$ (No. 2), $a = 10.836(1)$, $b = 15.791(2)$, $c = 18.157(2)$ Å, $\alpha = 76.31(1)$, $\beta = 76.56(1)$, $\gamma = 70.87(1)$°, $T = 173(1)$ K, $Z = 2$, $V = 2811.1(5)$ Å³, $\rho_{calcd} = 2.136$ Mg m^{-3}, $\mu = 3.954$ mm^{-1}, 32095 reflections collected, 10172 unique reflections ($R_{int} = 0.0277$, $2\theta_{max} = 51.78°$), 541 parameters, $R_1 = 0.0266$, $wR_2 = 0.0678$. **5**$\cdot 0.25n\,C_7H_8$: $C_{115.5}H_{124}Ag_2Al_2F_{72}Mo_8O_8P_{16}S_4$, $M_r = 4669.13$, crystal dimensions $0.22 \times 0.12 \times 0.08$ mm³, orthorhombic, space group *Pnma* (No. 62), $a = 45.899(2)$, $b = 33.486(1)$, $c = 22.478(1)$ Å, $T = 110(1)$ K, $Z = 8$, $V = 34548(2)$ Å³, $\rho_{calcd} = 1.795$ Mg m^{-3}, $\mu = 1.112$ mm^{-1}, 80287 reflections collected, 24594 unique reflections ($R_{int} = 0.1459$, $2\theta_{max} = 48.24°$), 929 parameters, $R_1 = 0.1091$, $wR_2 = 0.2666$. CCDC-634458 (**5**$\cdot 0.25n\,C_7H_8$) and CCDC-634459 (**4**) 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.

[14] a) G. Krabbes, H. Oppermann, *Z. Anorg. Allg. Chem.* **1977**, *435*, 33–44; b) T. P. Martin, H. Schaber, *J. Chem. Phys.* **1980**, *73*, 3541–3546.

[15] For examples of crystallographically characterized compounds containing discrete $\{Cu_3X_3\}$ rings, see: a) P. C. Healy, B. W. Skelton, A. H. White, *J. Chem. Soc. Dalton Trans.* **1989**, 971–976; b) L. Chen, L. K. Thompson, S. S. Tandon, J. N. Bridson, *Inorg. Chem.* **1993**, *32*, 4063–4068; c) C. Näther, I. Jeß, *Z. Naturforsch. B* **2002**, *57*, 1133–1140; d) C. Näther, I. Jeß, *J. Solid State Chem.* **2002**, *169*, 103–112; e) G. Kickelbick, D. Rutzinger, T. Gallauner, *Monatsh. Chem.* **2002**, *133*, 1157–1164.

[16] P. G. Eller, G. J. Kubas, R. R. Ryan, *Inorg. Chem.* **1977**, *16*, 2454–2462.

[17] N. Wiberg, *Holleman–Wiberg Lehrbuch der Anorganischen Chemie*, 34th ed., de Gruyter, Berlin, **1995**.

[18] a) A. Vega, J.-Y. Saillard, *Inorg. Chem.* **2004**, *43*, 4012–4018; b) J. Zhou, G.-Q. Bian, J. Dai, Y. Zhang, Q.-Y. Zhu, W. Lu, *Inorg. Chem.* **2006**, *45*, 8486–8488.

[19] O. Crespo, M. C. Gimeno, P. G. Jones, A. Laguna, *J. Chem. Soc. Dalton Trans.* **1996**, 4583–4588.

[20] See the Supporting Information.

[21] Measurement of the solid-state ^{31}P MAS NMR spectrum of polymer **4** at 190 K yields nevertheless a spectrum comparable to that of the polymer at room temperature.

[22] Owing to the poor solubility of polymer **5**, low-temperature NMR measurements could not be undertaken.

[23] D. Massiot, F. Fayon, M. Capron, I. King, S. Le Calvé, B. Alonso, J.-O. Durand, B. Bujoli, Z. Gan, G. Hoatson, *Magn. Reson. Chem.* **2002**, *40*, 70–76.

[24] A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, *J. Appl. Crystallogr.* **1993**, *26*, 343–350.

[25] G. M. Sheldrick, SHELXL-97, University of Göttingen, **1997**.