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# A New Building Block for Organometallic–Inorganic Hybrid Polymers: The Mixed Group 15/16 Element Ligand Complex $[Cp^*{}_2Mo_2(\mu,\eta^{2:2}\text{-}PSe)_2(\mu\text{-}Se)]$ $(Cp^* = C_5Me_5)$

Michael Bodensteiner,[a] Michal Dušek,[b] Marek M. Kubicki,[c] Michael Pronold,[a]
Manfred Scheer,[a] Joachim Wachter,*[a] and Manfred Zabel[a]

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The synthesis and spectroscopic characterization of $[Cp^*{}_2Mo_2P_2Se_3]$ (**1**; $Cp^* = C_5Me_5$) and its use as a molecular building block in the formation of copper(I) halide polymers is described. The reaction of **1** in $CH_2Cl_2$ with 2 equiv. of CuBr and CuI in $CH_3CN$ under diffusion conditions gave $[(Cp^*{}_2Mo_2P_2Se_3)_2(CuBr)_2]$ (**2**) and $[(Cp^*{}_2Mo_2P_2Se_3)(CuX)_3(CH_3CN)]_n$ (X = I; **3**/**4**), respectively. The structure of **2** is distinguished by a central $Cu_2Br_2$ ring coordinated on each side by a tripledecker complex through one of its P atoms. A 2D network is formed by weak interactions between Se atoms of neighboring molecules. Compound $[(Cp^*{}_2Mo_2P_2Se_3)(CuI)_3(CH_3CN)]_n$ exists in two isomeric forms **3** and **4**. The crystal structure of **3** can be described as a two-dimensional polymer that is formed by ribbons containing looped chains of three $Cu_2I_2$ rings and attached $[Cp^*{}_2Mo_2P_2Se_3]$ molecules. The structure of **4** contains a ribbon in which tripledecker molecules are linked through their P atoms to $(CuI)_6$ clusters. The ribbons are connected by weak Se···Se interactions. The reaction of a mixture of **1** and $P_4Se_3$ with CuI gave $[(Cp^*{}_2Mo_2P_2Se_3)(P_4Se_3)(CuI)_2]_n$. The crystal structure analysis of **5** reveals a new type of organometallic–inorganic framework in which **1** and $P_4Se_3$ are linked by $Cu_2I_2$ rings.

## Introduction

Organic molecules with N,[1] P,[2] S, or Se[3] atoms are useful building blocks for the synthesis of supramolecular organic–inorganic hybrid materials. Copper(I) halides form aggregates of variable size.[4] The introduction of bifunctional P,N[5] or S,N[6] organic linkers gives rise to the formation of polymers with interesting physical properties. As little was known about the coordination properties of bifunctional organic P,S(Se) ligands we performed self-assembly reactions between copper(I) halides and organometallic complexes with mixed group 15/16 element ligands. This led to the construction of polymers with very diverse dimensionalities, the nature of which depends strongly on the competing coordination properties of both the pnicogen and chalcogen atoms. Thus, the simultaneous connection of P and S atoms by metal centers has been achieved with the tripledecker complex $[Cp^*{}_2Mo_2(\mu,\eta^{2:2}\text{-}PS)_2S]$ ($Cp^* = \eta^5\text{-}C_5Me_5$).[7] By contrast, the isostructural arsenic homologue provides only sulfur lone-pairs for coordination.[8] Interestingly, $[Cp^*{}_2Mo_2P_4S]$, which may formally be derived from elusive $[Cp^*{}_2Mo_2P_5]$,[9] forms a one-dimensional polymer with CuI using exclusively lone-pairs of phosphorus.[10]

In this paper we report on the synthesis and characterization of a new building block in organometallic–inorganic polymer chemistry and its reactions with copper(I) halides. The characterization of $[Cp^*{}_2Mo_2(\mu,\eta^{2:2}\text{-}PSe)_2Se]$ (**1**) and its products by X-ray crystallography and $^{31}P$ MAS NMR spectroscopy allowed the unequivocal assignment of the positions of the main group elements and their unexpected versatile coordination behavior. An extension of this work dealt with the simultaneous and competitive coordination of **1** and $P_4Se_3$ at $Cu^I$ centers leading to a new type of organometallic–inorganic hybrid polymers.

## Results and Discussion

### Synthesis of $[Cp^*{}_2Mo_2P_2Se_3]$

$[Cp^*{}_2Mo_2P_2Se_3]$ was synthesized in analogy to the reaction of $[Cp^*Mo(CO)_2]_2$ and $P_4S_3$[11] using $P_4Se_3$ in boiling toluene. The intense red compound $[Cp^*{}_2Mo_2P_2Se_3]$ (**1**) along with the already known $[Cp^*Mo(CO)_2P_3]$[12] and $[Cp^*{}_2Mo_2(CO)_4P_2]$[12] were isolated by chromatography. Each product was identified by IR and $^{31}P$ NMR spectroscopy with the composition of **1** being additionally verified by mass spectroscopy and elemental analysis. NMR and mass spectroscopic data also showed evidence of

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[a] Institut für Anorganische Chemie der Universität Regensburg,
93040 Regensburg, Germany
Fax: +49-941-943-4439
E-mail: Joachim.Wachter@chemie.uni-regensburg.de
[b] Institute of Physics ASCR,
18221 Prague, Czech Republic
[c] Institut de Chimie Moléculaire de l'Université de Bourgogne,
UMR 5260,
21078 Dijon, France

$[Cp^*_2Mo_2P_4Se]$, which is a structural analogue of the known $[Cp^*_2Mo_2P_4S]$.[11] Separation of an analytically pure compound was not possible.

The $^{31}P$ NMR spectrum of **1** in $C_6D_6$ solution shows a singlet at $\delta = 83.8$ ppm, but in accord with the natural abundance of $^{77}Se$, satellites are observed, which are characteristic of a statistical distribution of $^{77}Se$ (Figure 1) throughout the *cyclo*-$P_2Se_3$ middle deck. Thus, P–Se coupling constants of 50, 100, and 225 Hz were found by simulation. Note that a $J_{P,P} = 56$ Hz coupling is only observed for an assumed asymmetric distribution of the NMR-active $^{77}Se$ nuclei. The $^{77}Se$ NMR spectrum reveals two groups of broad signals at $\delta = 68.7$ and $-259.0$ ppm, which is in agreement with the presence of two chemically different Se sites. $^{77}Se$–$^{77}Se$ coupling was not observed.

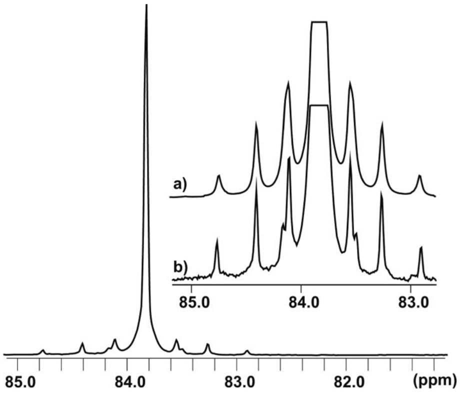
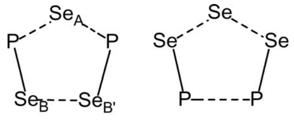


Figure 1. $^{31}P\{^1H\}$ NMR spectrum of **1** in $C_6D_6$. a) Simulated spectrum (WIN-DAISY) with $J_{P,P} = 56$, $J_{P,Se(A)} = 100$, $J_{P,Se(B)} = 50$, and $J_{P,Se(B')} = 225$ Hz; b) experimental spectrum.

The $^{31}P$ MAS NMR spectrum of **1** shows a singlet at $\delta = 91.5$ ppm, which is in agreement with the existence of only one isomer in the solid state. DFT calculations with the 3-21G* basis set revealed a structure analogous to $[Cp^*_2Mo_2P_2S_3]$[13] with isomer **A** (Scheme 1) being more stable by 9.7 kcal than isomer **B**. The chemical shifts of the isostructural $[Cp^*_2Mo_2P_2S_3]$ and $[(tBuMe_2C_5H_2)_2Mo_2P_2S_3]$ are observed at $\delta = -38.6$[11,13] and $-58.4$ ppm, respectively.[7]



**A** **B**

Scheme 1. Energetically favored distributions of P and Se in the *cyclo*-$P_2Se_3$ middle deck of **1**.

### $[(Cp^*_2Mo_2P_2Se_3)_2(CuBr)_2]$

Layering of a solution of **1** in $CH_2Cl_2$ with a solution of CuCl or CuBr in $CH_3CN$ gave dark insoluble crystals of $[(Cp^*_2Mo_2P_2Se_3)_2(CuX)_2]$ (**2**; X = Cl: **a**; Br: **b**). Only a few crystals of **2a** could be isolated preventing closer examination. Thus, its identity was only established by X-ray diffraction analysis.[14] By contrast, **2b** was formed in 73% yield and its composition was confirmed by elemental analysis and X-ray diffraction.

The central structural feature of **2b** is a four-membered $Cu_2Br_2$ ring linking two tripledecker complexes (Figure 2). The geometry of the five-membered ring, which corresponds to that of isomer **A** (Scheme 1), is defined by P–Se bonds of 2.25 Å (mean), P···Se interactions of 2.60 Å (mean), and a Se···Se distance of 3.164(1) Å. The coordination of each $P_2Se_3$ middle deck occurs through P1, which is part of one of two $\eta^2$-PSe dumb-bells. This was confirmed by analysis of the $^{31}P$ MAS NMR spectrum, which reveals a singlet at $\delta = 78.8$ ppm and a multiplet at $\delta = 31.3$ ppm in a 1:1 ratio. The splitting of the latter is caused by coupling with $^{63/65}Cu$ ($J_{P,Cu} = 1830$ Hz). Moreover, weak interactions [$d$(Se···Se) = 3.79 Å] between the bridging atom Se1 and the atoms Se2 and Se3 of a neighboring tripledecker complex were observed. This leads to the formation of a two-dimensional polymer (Figure 3), which may explain the insolubility of **2b**. Compound **2a** is isostructural with **2b**.[14]

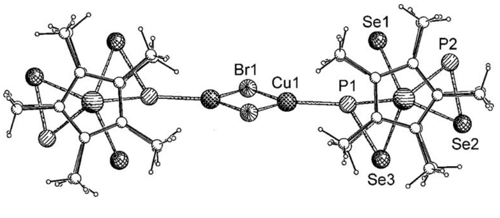


Figure 2. Repeating unit of the crystal structure of **2b**. Selected distances [Å]: Mo1–Mo2 2.612(1), Mo1–Se1 2.619(1), Mo1–Se2 2.610(1), Mo1–Se3 2.635(1), Mo1–P1 2.402(1), Mo1–P2 2.466(1), P1···Se1 2.499(1), P1–Se3 2.273(1), P2···Se1 2.692(1), P2–Se2 2.230(1), Cu1–P1 2.176(1), Br1–Cu1 2.405(1), Br1–Cu1a 2.404(1), Se2···Se3 3.164(1), Cu1···Cu1a 2.736(1).

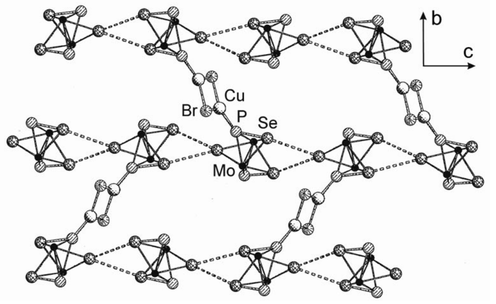


Figure 3. Section of the crystal structure of **2b** (projection on the *bc* plane). Intermolecular Se···Se interactions are indicated by dashed lines. Cp* rings have been omitted for clarity.

### Reaction of 1 with CuI

The reaction of **1** with CuI gave a mixture of bright-red plates of **3** and dark prisms of **4**, both with a composition $[Cp^*_2Mo_2P_2Se_3(CuI)_3(CH_3CN)]_n$. The ratio of these constitutional isomers seems to be temperature-dependent. Thus, the amount of **3** can be increased by cooling the reaction mixture to –20 °C whereas at room temperature **4** appears to be the main product. Nevertheless, a complete separation has so far not been achieved. Owing to their identical composition and completely overlapping signals in the $^{31}$P MAS NMR spectrum it was not possible to determine the ratio of the two compounds by spectroscopic means.

X-ray diffraction analysis of **3** revealed a broad one-dimensional ribbon composed of short twisted chains consisting of three planar $Cu_2I_2$ four-membered rings. These alternate with two tripledecker molecules of **1** (Figure 4). Similar chains are known.[15] Polymer **3** contains tetrahedral (Cu2, Cu3) and trigonal planar (Cu1) coordination sites. Cu1 and Cu2 coordinate the P atoms of adjacent middle deck dumb-bells. The coordination sphere of Cu3 is formed by a bridging Se3 and acetonitrile. As in **2b**, weak Se···Se interactions may be considered because of mean distances of 3.67 Å between Se atoms of adjacent strands. This is significantly less than the sum (4.0 Å) of the van der Waals radii. The resulting 2D polymer is constructed of stepped layers that are arranged in a parallel manner along the *b* axis (Figure 5). Note that **3** is the first example of a tripledecker-derived compound in which all main group atoms of the five-membered middle deck are coordinated either to Cu or to Se.

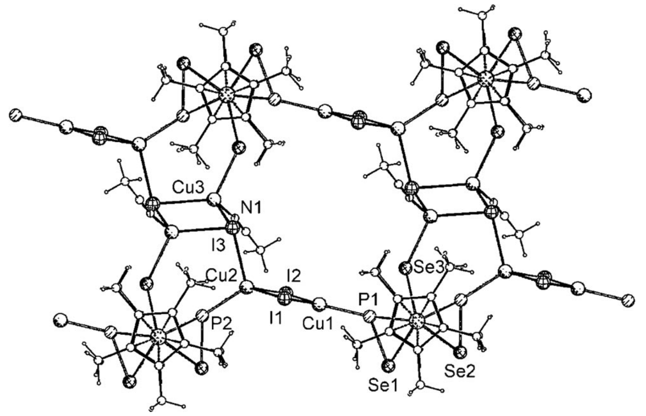


Figure 4. Section of the 2D polymer **3**. Selected distances [Å]: Mo1–Mo2 2.610(1), Mo1–Se1 2.615(1), Mo1–Se2 2.618(1), Mo1–Se3 2.646(1), Mo1–P1 2.432(1), Mo1–P2, 2.458(1), Se1–P1 2.243(2), Se2–P2 2.214(2), Se3···P1 2.559(2), Se3–Cu3 2.477(1), Cu1–P1 2.221(2), Cu2–P2 2.251(2), Cu3–N1 1.991(6), I1–Cu1 2.544(1), I1–Cu2 2.679(1), I2–Cu1 2.550(1), I2–Cu2 2.662(1), I3–Cu2 2.628(1), I3–Cu3 2.665(1), Cu1···Cu2 3.201(1), Cu3···Cu3a 3.128(1).

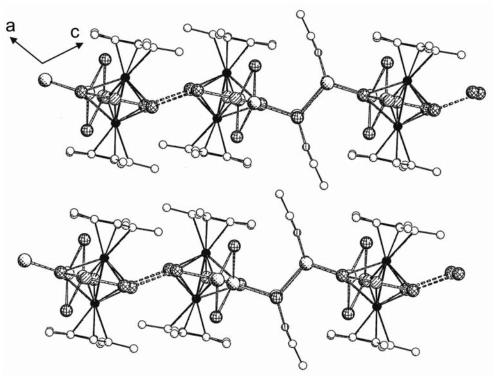


Figure 5. Parallel layers in the crystal structure of **3**. Intermolecular Se···Se-interactions are indicated by dashed lines. H atoms have been omitted for clarity.

Owing to its incommensurate nature, the crystal structure of **4** is only discussed briefly. The superspace description is needed to resolve the disorder of the average (based only on main reflections) structure. The modulated structure of **4** is constructed of one-dimensional strands in which four tripledecker moieties are connected by a $(CuI)_6$ cage (Figure 6). Thus, both phosphorus positions of **1** are coordinated by copper atoms. Further, an acetonitrile molecule coordinates to one of the non-phosphorus-bound copper positions.[16]

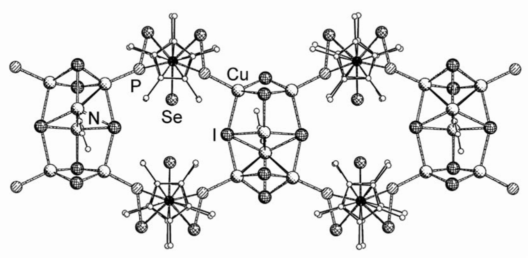


Figure 6. Modulated structure of **4**.[16] H atoms have been omitted for clarity.

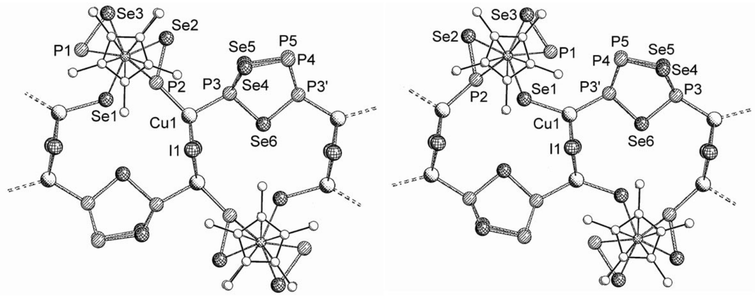


Figure 7. Section of the crystal structure of **5** showing both sets of disordered main group elements, revealing a distribution of 50:50. H atoms have been omitted for clarity. Selected distances [Å]: Mo1–Mo2 2.614(1), Mo1–Se1 2.659(1), Mo1–Se2 2.575(2), Mo1–Se3 2.629(1), Mo1–P1 2.527(3), Mo1–P2 2.393(2), Se1–Cu1 2.404(1), Se1···P2 2.613(2), Se2···Se3 3.143(2), Se2–P2 2.221(3), Se3–P1 2.222(4), Se4–P3 2.301(2), Se4–P4 2.246(4), Se5–P3 2.303(2), Se5–P5 2.243(4), Se6–P3 2.230(1), P3–P4 2.153(3), P3–P5 2.160(3), P4–P5 2.230(5), Cu1–P2 2.279(2), Cu1–P3 2.272(1), I1–Cu1 2.628(1), I1–Cu1a 2.628(1).

### The 1/$P_4Se_3$/CuI System

Reaction of an equimolar mixture of **1** and $P_4Se_3$ with CuI using the interdiffusion technique gave the organometallic–inorganic hybrid polymer $[(Cp^*_2Mo_2P_2Se_3)(P_4Se_3)(CuI)_2]_n$ (**5**) according to X-ray diffraction analysis. The composition was confirmed by elemental analysis after assuming half a molecule of $CH_2Cl_2$ and one molecule of $CH_3CN$ per formula unit. The crystal structure of **5** is composed of $Cu_2I_2$ four-membered rings bearing *trans*-coordinated $P_4S_3$ and tripledecker building blocks. Each $P_4Se_3$ cage bridges two $Cu_2I_2$ rings by its apical P atom and one of the basal P atoms. The organometallic unit employs P2 of one of the $\eta^2$-PSe dumb-bells for coordination (Figure 7). This results in two sinoidal strands forming a 1D ribbon. These ribbons form a channel along the *c* axis (Figure 8) that contain solvent molecules (see Crystallographic section). Furthermore, the $P_4Se_3$ cage shows two different orientations in the crystal structure.

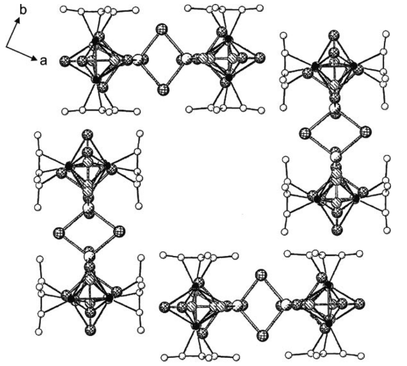


Figure 8. Crystal structure of **5**. The view along the *c* axis shows stacks of ribbons forming channels. Disordered solvent molecules and hydrogen atoms are not shown.

## Conclusion

We have shown that $[Cp^*_2Mo_2(\mu,\eta^{2:2}\text{-PSe})_2(\mu\text{-Se})]$ (**1**) represents a further member of mixed group 15/16 element sandwich building blocks for the construction of copper(I) halide coordination polymers. The coordination behavior of **1** extends our knowledge to that already observed for complexes with the *cyclo*-$P_2S_3$[7] or *cyclo*-$As_2S_3$[8] middle deck. The competitive coordination of copper towards P and Se sites is completed by weak intermolecular Se···Se interactions leading to the formation of two-dimensional networks. Although the coordination behavior of $P_4S_3$[17] and $P_4Se_3$[18] towards copper(I) halides has been investigated, the simultaneous coordination of **1** and $P_4Se_3$ at $Cu^I$ centers opens a new route to the formation of organometallic–inorganic frameworks. It demonstrates that the $P_4Se_3$ cage is able to serve as a cross-linking ligand similar to multiple N-donor ligands in metal–organic frameworks.[19] This strategy may find further applications in the synthesis of hybrid polymers from organometallic and inorganic cage building blocks exhibiting main group donor sites.

## Experimental Section

**General:** All manipulations were carried out under an inert atmosphere using Schlenk-line techniques and dry solvents. Elemental analyses were performed by the Mikroanalytisches Laboratorium, University of Regensburg. IR spectra were obtained with a Varian Digilab Scimitar FTS800 spectrometer. FD mass spectra were measured with a Finnigan MAT 95 instrument. The $^1H$ and $^{31}P$ NMR spectra were recorded with Bruker Avance 300 and 400 instruments, respectively. $^{31}P$ MAS NMR spectra were recorded with a Bruker Advance 300 spectrometer using double resonance 2.5 or 4.0 mm MAS probes. The $^{31}P$ resonance was 121.495 MHz. The spectra were acquired at MAS rotation frequencies of 12 (**1**) or 35 kHz (**2**), a 90° pulse length of 3 (**1**) or 2.3 µs (**2**), and with a delay time of 30 (**1**) or 200 s (**2**). For spectrum simulation the program WinDaisy, version 4.05, was used. $P_4Se_3$ was synthesized by cautiously melting together red phosphorus and grey selenium under $N_2$ followed by Soxhlet extraction and recrystallization from $CH_2Cl_2$.[20]

**$[Cp^*_2Mo_2(PSe)_2Se]$ (1):** A mixture of $[Cp^*Mo(CO)_2]_2$ (1.59 g, 2.77 mmol) and $P_4Se_3$ (0.91 g, 2.52 mmol) was stirred in boiling toluene (100 mL) for 17 h. After evaporating the solvent, the dark-brown residue was dissolved in toluene/pentane (1:2) and filtered over $SiO_2$ (3 × 10 cm). The concentrated filtrate was purified by chromatography on $SiO_2$ (column 20 × 4 cm). With toluene/pentane (1:2) first a dark-red band was eluted and then a bright-red band containing **1** (493 mg, 26%). Repeated chromatography of the dark-red band gave $[Cp^*Mo(CO)_2P_3]$ (145 mg, 7%) followed by traces of $[Cp^*_2Mo_2(CO)_4P_2]$ and $[Cp^*_2Mo_2P_4Se]$, which were identified by $^{31}P$ NMR spectroscopy. **1**: $^1H$ NMR (300 MHz, $C_6D_6$): $\delta = 2.10$ (s) ppm. $^{31}P\{^1H\}$ NMR (121 MHz, $C_6D_6$): $\delta = 83.8$ [m, $J_{P,P} = 56$, $J_{P,Se(A)} = 100$, $J_{P,Se(B)} = 50$, $J_{P,Se(B')} = 225$ Hz] ppm. $^{31}P$ MAS NMR (121 MHz): $\delta = 91.5$ (s) ppm. $^{77}Se$ NMR (76 MHz, $C_6D_6$): $\delta = 68.7$ (t, A), –259.0 (dd, B, B′) ppm. FD-MS (toluene): $m/z = 761$ $[M]^+$. $C_{20}H_{30}Mo_2P_2Se_3$ (761.17): calcd. C 31.56, H 3.97; found C 31.85, H 3.96.

**Reaction of 1 with CuX (X = Cl, Br, I):** A solution of **1** (100 mg, 0.13 mmol) in $CH_2Cl_2$ (10 mL) was layered with a solution of CuX (2 equiv.) in $CH_3CN$ (10 mL). Red prisms of $[(Cp^*_2Mo_2P_2Se_3)_2(CuCl)_2]$ (**2a**; few crystals, identified by X-ray diffraction), $[(Cp^*_2Mo_2P_2Se_3)_2(CuBr)_2]$ (**2b**) or a mixture of dark prisms and red plates of $[Cp^*_2Mo_2P_2Se_3(CuI)_3(CH_3CN)]_n$ (**3/4**) were isolated. **2b**: yield 86 mg (73%). $^{31}P$ MAS NMR (121 MHz): $\delta = 78.8$ (s), 31.3 (m, $J_{P,Cu} = 1830$ Hz) ppm. $C_{40}H_{60}Br_2Cu_2Mo_4P_4Se_6$ (1809.23): calcd. C 26.55, H 3.34; found C 26.66, H 3.33. **3/4**: yield 65 mg (36%). $^{31}P\{^1H\}$ NMR MAS NMR (121 MHz): $\delta = 20$ (br. m,) ppm. $C_{22}H_{33}Cu_3I_3Mo_2NP_2Se_3$ (1373.56): calcd. C 19.24, H 2.42, N 1.0; found C 18.81, H 2.41, N 0.6.

**$[Cp^*_2Mo_2P_2Se_3(P_4Se_3)(CuI)_2]_n$ (5):** A solution of **1** (68 mg, 0.09 mmol) and $P_4Se_3$ (32 mg, 0.09 mmol) in $CH_2Cl_2$ (10 mL) was layered with CuI (2 equiv.) in $CH_3CN$ (10 mL). Bright-red needles of **5** (66 mg, 49%) were obtained. $C_{23}H_{34}ClCu_2I_2Mo_2NP_6Se_6$ (1586.3): calcd. C 17.02, H 2.16; found C 16.98, H 2.19.

**Crystal Structure Analysis:** Crystal structure analyses were performed with an Oxford Diffraction Gemini R Ultra CCD. Semi-empirical absorption corrections from equivalents (multi-scan) were applied.[21] The structures were solved by direct methods with the SIR-97 program[22] and full-matrix least-square refinement on $F^2$ in SHELXL-97[23] was performed with anisotropic displacements for non-hydrogen atoms. Hydrogen atoms were located in idealized positions and refined isotropically according to the riding model. In the structure of **2b**, residual electron density is located

Table 1. Crystallographic data and details of X-ray experiments for **2b**, **3**, and **5**.

| | **2b** | **3** | **5**·($CH_2Cl_2$,$CH_3CN$) |
|---|---|---|---|
| Formula | $C_{40}H_{60}Br_2Cu_2Mo_4P_4Se_6$ | $C_{24}H_{36}Cu_3I_3Mo_2N_2P_2Se_3$ | $C_{23}H_{34}ClCu_2I_2Mo_2NP_6Se_6$ |
| $M_w$ | 1809.18 | 1414.60 | 793.15 |
| Crystal size [mm] | 0.23 × 0.18 × 0.17 | 0.08 × 0.05 × 0.02 | 0.48 × 0.03 × 0.02 |
| $T$ [K] | 123(1) | 123(1) | 123(1) |
| Space group | $P2_1/c$ | $P2_1/n$ | $I4/m$ |
| Crystal system | monoclinic | monoclinic | tetragonal |
| $a$ [Å] | 11.9616(2) | 18.0560(9) | 25.2814(12) |
| $b$ [Å] | 15.5610(2) | 11.1157(5) | |
| $c$ [Å] | 14.6724(2) | 19.8852(1) | 13.7407(6) |
| $\beta$ [°] | 105.202(2) | 115.003(6) | |
| $V$ [Å$^3$] | 2635.47(7) | 3617.0(4) | 8782.4(7) |
| $Z$ | 2 | 4 | 8 |
| $\rho_{calcd.}$ [g cm$^{-3}$] | 2.280 | 2.598 | 2.399 |
| $\mu$ [mm$^{-1}$] | 7.525 | 32.015 | 25.167 |
| $\lambda$ (Mo-$K_\alpha$) [Å] | 0.71073 | | |
| $\lambda$ (Cu-$K_\alpha$) [Å] | | 1.54178 | 1.54178 |
| Scan range | $2.95 < \Theta < 32.74$ | $4.35 < \Theta < 66.91$ | $3.5 < \Theta < 66.72$ |
| Reflections collected | 8807 | 6311 | 4024 |
| Reflections observed, $I > 2\sigma(I)$ | 6512 | 5440 | 3406 |
| Parameters | 272 | 363 | 223 |
| GOF in $F^2$ | 0.979 | 0.970 | 1.012 |
| Residual density [e Å$^{-3}$] | 4.469, –1.424 | 1.469, –1.174 | 1.447, –0.789 |
| $R_1/wR_2$ ($I > 2\sigma$) | 0.0368, 0.0951 | 0.0326, 0.0757 | 0.0361, 0.0955 |
| $R_1/wR_2$ (all data) | 0.0524, 0.0979 | 0.0387, 0.0781 | 0.0425, 0.0986 |

close to heavy atoms and clearly does not belong to a solvent molecule. In **5**, a large solvent-accessible void was found but due to severe disorder only four semi-occupied and eight quarter-occupied chlorine positions could be found. Thus, the SQUEEZE function of the PLATON software was used to determine the size (938 Å$^3$) and number of electrons (170) in the void.[24] These data indicate the presence of two molecules of $CH_2Cl_2$ and four acetonitrile molecules in each void and are further in good agreement with the elemental analysis of the compound. In addition, several P and Se positions are disordered in **5** with 50% occupancy for each position. Further crystallographic details are summarized in Table 1.

CCDC-782269 (for **2b**), -782290 (for **3**), and -782271 (for **5**) 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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