# Discrete and Polymeric Organometallic-Organic Assemblies Based on the Diarsene Complex [(C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>Mo<sub>2</sub>(CO)<sub>4</sub>(μ,η<sup>2</sup>-As<sub>2</sub>)], AgPF<sub>6</sub> and Organic N-donor Molecules

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# **Supporting Information**

#### General

All experiments were performed under an atmosphere of dry argon using standard Schlenk and glovebox techniques. All used solvents were taken from the solvent drying machine MB SPS-800 of the company MBRAUN. The precursor  $[Cp_2Mo_2(CO)_4(\mu,\eta^{2:2}-As_2)]$  (**B**) was prepared according to literature procedures.<sup>[1]</sup> AgPF<sub>6</sub> (abcr), 1,2-di(4-pyridyl)ethylene (**L1**) (TCI), 1,2-di(4-pyridyl)ethyne (**L2**) (TCI), 2,2'-bipyrimidine (**L3**) (TCI), 1,3-di(4-pyridyl)propane (**L4**) (TCI) and 4,4'-bipyridine (**L5**) (TCI) were used as received without further purification. Solution NMR spectra were recorded on a Bruker Avance III HD 400 spectrometer (<sup>1</sup>H: 400 MHz, <sup>31</sup>P: 161 MHz, <sup>13</sup>C: 100 MHz, <sup>19</sup>F: 376 MHz) with acetonitrile-d<sub>3</sub> as solvent at room temperature. The chemical shifts  $\delta$  are presented in parts per million ppm and coupling constants *J* in Hz. The following samples were used as external reference: TMS (<sup>1</sup>H, <sup>13</sup>C), CFCl<sub>3</sub> (<sup>19</sup>F), H<sub>3</sub>PO<sub>4</sub> 85 % (<sup>31</sup>P). The spectra were processed and analyzed using the software Bruker TopSpin 3.0. IR spectra were recorded as solids with an ATR-Ge disc on a Thermo Fisher Nicolet iS5 spectrometer. Elemental analyses were performed on an Elementar Vario MICRO cube apparatus. Mass spectra were recorded on an Agilent Q-TOF 6540 UHD mass spectrometer with acetonitrile as solvent.

### Synthesis of [{(n<sup>2</sup>-B)<sub>2</sub>Ag}<sub>2</sub>(L1)][PF<sub>6</sub>]<sub>2</sub>(1):



AgPF<sub>6</sub> (7 mg, 0.025 mmol), complex **B** (29 mg, 0.05 mmol) and **L1** (4.6 mg, 0.025 mmol) were dissolved in 10 mL CH<sub>2</sub>Cl<sub>2</sub>:CH<sub>3</sub>CN 1:1 and stirred for 3 h at room temperature. The red solution was filtered and carefully layered with the threefold amount of *n*-pentane and stored at room temperature in the dark. After several days, compound **1** was obtained as clear red blocks. The supernatant was decanted off, the remaining crystals were washed with *n*-pentane and dried *in vacuo*. Yield = (28 mg, 74%).

<sup>1</sup>H NMR (CD<sub>3</sub>CN):  $\delta$ /ppm = 8.57 (m, 4H, H<sub>a</sub>), 7.54 (m, 4H, H<sub>b</sub>), 7.42 (s, 2H, H<sub>d</sub>), 5.33 (s, 40H, H<sub>Cp</sub>).

<sup>13</sup>C {<sup>1</sup>H} NMR (CD<sub>3</sub>CN):  $\delta$ /ppm = 225.11 (s, C<sub>CO</sub>), 151.41 (s, C<sub>a</sub>), 131.64 (s, C<sub>b</sub>), 122.38 (s, C<sub>d</sub>), 86.53 (s, C<sub>Cp</sub>).

<sup>31</sup>P {<sup>1</sup>H} NMR (CD<sub>3</sub>CN):  $\delta$ /ppm = -143.13 (sept, <sup>1</sup>J<sub>P,F</sub> = 705.3 Hz).

<sup>19</sup>F {<sup>1</sup>H} NMR (CD<sub>3</sub>CN):  $\delta$ /ppm = -71.76 (d, <sup>1</sup>J<sub>F,P</sub> = 705.3 Hz).

Positive ion ESI-MS (CH<sub>3</sub>CN, r. t.): m/z (%) = 1276.33 (100) [{Cp<sub>2</sub>(CO)<sub>4</sub>Mo<sub>2</sub>As<sub>2</sub>}<sub>2</sub>Ag]<sup>+</sup>, 731.65 (19) [{Cp<sub>2</sub>(CO)<sub>4</sub>Mo<sub>2</sub>As<sub>2</sub>}Ag(CH<sub>3</sub>CN)]<sup>+</sup>, 690.62 (5) [{Cp<sub>2</sub>(CO)<sub>4</sub>Mo<sub>2</sub>As<sub>2</sub>}Ag]<sup>+</sup>, 183.09 (6) [N<sub>2</sub>C<sub>12</sub>H<sub>10</sub>]<sup>+</sup>.

Negative ion ESI-MS (CH<sub>3</sub>CN, r. t.): m/z (%) = 144.97 (100) PF<sub>6</sub>.

Elemental analysis, calcd (%) for  $C_{68}H_{50}Ag_2As_8F_{12}Mo_8N_2O_{16}P_2$  (3023.71 g/mol): C, 27.01; H, 1.67; N, 0.93; found: C, 26.93; H, 1.78; N, 1.03;

IR (solid, CO bands):  $\tilde{v}$ /cm<sup>-1</sup>: 1953.42 (w), 1912.22 (w).

#### Synthesis of $[{(\eta^2-B)_2Ag}_2(L2)][PF_6]_2(2):$



AgPF<sub>6</sub> (7 mg, 0.025 mmol), complex **B** (29 mg, 0.05 mmol) and **L2** (4.6 mg, 0.025 mmol) were dissolved in 10 mL CH<sub>2</sub>Cl<sub>2</sub>:CH<sub>3</sub>CN 1:1 and stirred for 3 h at room temperature. The red solution was filtered and carefully layered with the threefold amount of *n*-pentane and stored at room temperature in the dark. After several days, compound **2** was obtained as clear red blocks. The supernatant was decanted off, the remaining crystals washed with *n*-pentane and dried *in vacuo*. Yield = (25 mg, 66%).

<sup>1</sup>H NMR (CD<sub>3</sub>CN):  $\delta$ /ppm = 8.64 (m, 4H, H<sub>a</sub>), 7.49 (m, 4H, H<sub>b</sub>), 5.32 (s, 40H, H<sub>Cp</sub>).

<sup>13</sup>C {<sup>1</sup>H} NMR (CD<sub>3</sub>CN):  $\delta$ /ppm = 225.39 (s, C<sub>CO</sub>), 151.12 (s, C<sub>a</sub>), 126.57 (s, C<sub>b</sub>), 86.47 (s, C<sub>Cp</sub>). <sup>31</sup>P {<sup>1</sup>H} NMR (CD<sub>3</sub>CN):  $\delta$ /ppm = -143.08 (sept, <sup>1</sup>J<sub>P,F</sub> = 706.3 Hz). <sup>19</sup>F {<sup>1</sup>H} NMR (CD<sub>3</sub>CN):  $\delta$ /ppm = -71.76 (d, <sup>1</sup>J<sub>F,P</sub> = 706.7 Hz).

Positive ion ESI-MS (CH<sub>3</sub>CN, r. t.): m/z (%) = 1276.33 (100) [{Cp<sub>2</sub>(CO)<sub>4</sub>Mo<sub>2</sub>As<sub>2</sub>}<sub>2</sub>Ag]<sup>+</sup>, 731.65 (28) [{Cp<sub>2</sub>(CO)<sub>4</sub>Mo<sub>2</sub>As<sub>2</sub>}Ag(CH<sub>3</sub>CN)]<sup>+</sup>, 690.62 (7) [{Cp<sub>2</sub>(CO)<sub>4</sub>Mo<sub>2</sub>As<sub>2</sub>}Ag]<sup>+</sup>, 181.08 (19) [N<sub>2</sub>C<sub>12</sub>H<sub>8</sub>]<sup>+</sup>.

Negative ion ESI-MS (CH<sub>3</sub>CN, r. t.): m/z (%) = 144.97 (100) PF<sub>6</sub><sup>-</sup>.

Elemental analysis, calcd (%) for C<sub>68</sub>H<sub>48</sub>Ag<sub>2</sub>As<sub>8</sub>F<sub>12</sub>Mo<sub>8</sub>N<sub>2</sub>O<sub>16</sub>P<sub>2</sub> (3021.69 g/mol): C, 27.03; H, 1.60; N, 0.93; found: C, 27.27; H, 1.84; N, 1.22;

IR (solid, CO bands):  $\tilde{v}$ /cm<sup>-1</sup>: 1951.88 (s), 1917.12 (s).

## Synthesis of [{(n<sup>2</sup>-B)Ag}(L3)]n[PF<sub>6</sub>]n (3):



AgPF<sub>6</sub> (7 mg, 0.025 mmol), complex **B** (29 mg, 0.05 mmol) and **L3** (4 mg, 0.025 mmol) were dissolved in 10 mL CH<sub>2</sub>Cl<sub>2</sub>:CH<sub>3</sub>CN 1:1 and stirred for 3 h at room temperature. The red solution was filtered and carefully layered with the threefold amount of *n*-pentane and stored at room temperature in the dark. After several days, compound **3** was obtained as dark red blocks. The supernatant was decanted off, the remaining crystals washed with *n*-pentane and dried *in vacuo*. Yield = 10 mg (40%).

<sup>1</sup>H NMR (CD<sub>3</sub>CN): δ/ppm = 9.03 (d, *J*<sub>HH</sub> = 4.91 Hz, 4H, H<sub>b</sub>), 7.64 (t, *J*<sub>HH</sub> = 4.92 Hz, 2H, H<sub>a</sub>), 5.31 (s, 10H, H<sub>Cp</sub>).

<sup>13</sup>C {<sup>1</sup>H} NMR (CD<sub>3</sub>CN):  $\delta$ /ppm = 225.03 (s, C<sub>CO</sub>), 161.56 (s, C<sub>c</sub>), 159.49 (s, C<sub>b</sub>), 123.65 (s, C<sub>a</sub>), 86.51 (s, C<sub>Cp</sub>).

<sup>31</sup>P {<sup>1</sup>H} NMR (CD<sub>3</sub>CN):  $\delta$ /ppm = = -143.14 (sept, <sup>1</sup>J<sub>P,F</sub> = 706.9 Hz).

<sup>19</sup>F {<sup>1</sup>H} NMR (CD<sub>3</sub>CN):  $\delta$ /ppm = -71.76 (d, <sup>1</sup>J<sub>F,P</sub> = 705.5 Hz).

Positive ion ESI-MS (CH<sub>3</sub>CN, r. t.): m/z (%) = 1276.33 (12) [{Cp<sub>2</sub>(CO)<sub>4</sub>Mo<sub>2</sub>As<sub>2</sub>}<sub>2</sub>Ag]<sup>+</sup>, 848.68 (100) [Ag[Cp<sub>2</sub>(CO)<sub>4</sub>Mo<sub>2</sub>As<sub>2</sub>](N<sub>2</sub>C<sub>10</sub>H<sub>8</sub>)]<sup>+</sup>, 423.02 (18) [Ag(N<sub>4</sub>C<sub>8</sub>H<sub>6</sub>)<sub>2</sub>]<sup>+</sup>, 147.93 (8) [Ag(CH<sub>3</sub>CN)]<sup>+</sup>. Negative ion ESI-MS (CH<sub>3</sub>CN, r. t.): m/z (%) = 144.97 (100) PF<sub>6</sub><sup>-</sup>.

Elemental analysis, calcd (%) for  $C_{22}H_{16}AgAs_2F_6Mo_2N_4O_4P$  (994.95 g/mol): C, 26.56; H, 1.62; N, 5.63; found: C, 26.50; H, 1.44; N, 5.53;

IR (solid, CO bands):  $\tilde{v}$ /cm<sup>-1</sup>: 1942.85 (s), 1915.93 (vs), 1900.98 (vs).

### Synthesis of [{(n<sup>1</sup>:n<sup>2</sup>-B)<sub>2</sub>(CH<sub>3</sub>CN)<sub>2</sub>Ag<sub>2</sub>}(L4)]n[PF<sub>6</sub>]<sub>2n</sub> (4):



AgPF<sub>6</sub> (7 mg, 0.025 mmol), complex **B** (29 mg, 0.05 mmol) and **L4** (5 mg, 0.025 mmol) were dissolved in 10 mL CH<sub>2</sub>Cl<sub>2</sub>:CH<sub>3</sub>CN 1:1 and stirred for 3 h at room temperature. The red solution was filtered and carefully layered with the threefold amount of *n*-pentane and stored at room temperature in the dark. After 3-5 weeks, compound **4** was obtained as clear orange blocks. The supernatant was decanted off, the remaining crystals washed with *n*-pentane and dried *in vacuo*. Yield = (9 mg, 35%).

<sup>1</sup>H NMR (CD<sub>3</sub>CN):  $\delta$ /ppm = 8.44 (d,  $J_{HH}$  = 4.85 Hz, 4H, H<sub>a</sub>), 7.22 (d,  $J_{HH}$  = 4.85 Hz, 4H, H<sub>b</sub>), 5.34 (s, 20H, H<sub>Cp</sub>), 2.67 (t,  $J_{HH}$  = 7.7 Hz, 4H, H<sub>d</sub>), 1.98 (d,  $J_{HH}$  = 7.7 Hz, 2H, H<sub>e</sub>).

<sup>13</sup>C {<sup>1</sup>H} NMR (CD<sub>3</sub>CN):  $\delta$ /ppm = 224.60 (s, C<sub>CO</sub>), 153.85 (s, C<sub>c</sub>), 150.27 (s, C<sub>a</sub>), 125.54(s, C<sub>b</sub>), 86.64 (s, C<sub>Cp</sub>), 35.13 (s, C<sub>d</sub>), 31.33 (s, C<sub>e</sub>).

<sup>31</sup>P {<sup>1</sup>H} NMR (CD<sub>3</sub>CN):  $\delta$ /ppm = -143.08 (sept, <sup>1</sup>J<sub>P,F</sub> = 705.8 Hz).

<sup>19</sup>F {<sup>1</sup>H} NMR (CD<sub>3</sub>CN):  $\delta$ /ppm = -71.74 (d, <sup>1</sup>J<sub>F,P</sub> = 707.2Hz).

Positive ion ESI-MS (CH<sub>3</sub>CN, r. t.): m/z (%) = 1276.3 (15) [{Cp<sub>2</sub>(CO)<sub>4</sub>Mo<sub>2</sub>As<sub>2</sub>}<sub>2</sub>Ag]<sup>+</sup>, 731.6 (33) [{Cp<sub>2</sub>(CO)<sub>4</sub>Mo<sub>2</sub>As<sub>2</sub>}Ag(CH<sub>3</sub>CN)]<sup>+</sup>, 147.9 (100) [Ag(CH<sub>3</sub>CN)]<sup>+</sup>, 198.0 (24) [N<sub>2</sub>C<sub>13</sub>H<sub>14</sub>]<sup>+</sup>.

Negative ion ESI-MS (CH<sub>3</sub>CN, r. t.): m/z (%) = 144.97 (100) PF<sub>6</sub>.

Elemental analysis, calcd (%) for  $C_{43}H_{37}Ag_2As_4F_{12}Mo_4N_3O_8P_2$  (1913 g/mol): C, 27.00; H, 1.95; N, 2.20; found: C, 27.66; H, 1.80; N, 1.73

IR (solid, CO bands):  $\tilde{v}$ /cm<sup>-1</sup>: 1962 (vs), 1919 (vs).

### Synthesis of $[{(\eta^1:\eta^2-B)_2(CH_3CN)_2Ag_2}(L_5)]_n[PF_6]_{2n}$ (5):



AgPF<sub>6</sub> (7 mg, 0.025 mmol), complex **B** (29 mg, 0.05 mmol) and **L5** (4 mg, 0.025 mmol) were dissolved in 10 mL CH<sub>2</sub>Cl<sub>2</sub>:CH<sub>3</sub>CN 1:1 and stirred for 3 h at room temperature. The red solution was filtered and carefully layered with the threefold amount of *n*-pentane and stored at room

temperature in the dark. After several days, compound **5** was obtained as clear orange blocks. The supernatant was decanted off, the remaining crystals washed with *n*-pentane and dried *in vacuo*. Yield = (6 mg, 22%).

<sup>1</sup>H NMR (CD<sub>3</sub>CN):  $\delta$ /ppm = 8,76 (dd, 4H, <sup>4</sup>*J*<sub>H,H</sub> = 1.7 Hz, <sup>3</sup>*J*<sub>H,H</sub> = 4,5 Hz, H<sub>a</sub>), 7.91 (dd, 4H, <sup>4</sup>*J*<sub>H,H</sub> = 1.7 Hz, <sup>3</sup>*J*<sub>H,H</sub> = 4,5 Hz, H<sub>b</sub>), 5.33 (s, 20H, H<sub>Cp</sub>).

<sup>13</sup>C {<sup>1</sup>H} NMR (CD<sub>3</sub>CN):  $\delta$ /ppm = 224.15 (s, C<sub>CO</sub>), 148.83 (s, C<sub>a</sub>), 123.49 (s, C<sub>b</sub>), 86.25 (s, C<sub>Cp</sub>) <sup>31</sup>P {<sup>1</sup>H} NMR (CD<sub>3</sub>CN):  $\delta$ /ppm = -143.11 (sept, <sup>1</sup>J<sub>P,F</sub> = 706.2 Hz).

<sup>19</sup>F NMR (CD<sub>3</sub>CN):  $\delta$ /ppm = -71.73 (d, <sup>1</sup>*J*<sub>F,P</sub> = 706.3 Hz).

Positive ion ESI-MS (CH<sub>3</sub>CN, RT): m/z (%) = 1276.33 (43) [{Cp<sub>2</sub>(CO)<sub>4</sub>Mo<sub>2</sub>As<sub>2</sub>}<sub>2</sub>Ag]<sup>+</sup>, 731.65 (100) [{Cp<sub>2</sub>(CO)<sub>4</sub>Mo<sub>2</sub>As<sub>2</sub>}Ag(CH<sub>3</sub>CN)]<sup>+</sup>, 690.62 (25) [{Cp<sub>2</sub>(CO)<sub>4</sub>Mo<sub>2</sub>As<sub>2</sub>}Ag]<sup>+</sup>,147.93 (69) Ag(CH<sub>3</sub>CN)<sup>+</sup>.

Negative ion ESI-MS (CH<sub>3</sub>CN, RT): m/z (%) = 144.97 (100) PF<sub>6</sub><sup>-</sup>.

Elemental analysis, calcd (%) for  $C_{39.2}H_{29.8}Ag_2As_4F_{12}Mo_4N_{2.6}O_8P_2$  (1854.43 g/mol): C, 25.39; H, 1.62; N, 1.96; found: C, 26.13; H, 1.39; N, 1.46.

IR (solid, CO bands):  $\tilde{v}$ /cm<sup>-1</sup>: 1990 (s), 1971 (vs), 1935 (s), 1912 (vs).

### <u>Synthesis of $[{(n^1:n^2-B)_2(n^1:n^1-B)Ag_2}(L_5)]_n[PF_6]_{2n}$ (6):</u>



AgPF<sub>6</sub> (7 mg, 0.025 mmol), complex **B** (29 mg, 0.05 mmol) and **L5** (4 mg, 0.025 mmol) were dissolved in 10 mL CH<sub>2</sub>Cl<sub>2</sub>:CH<sub>3</sub>CN (8:2) and stirred for 3 h at room temperature. The red solution was filtered and carefully layered with the threefold amount of *n*-pentane and stored at room temperature in the dark. After several days, compound **6** was obtained as red blocks. The supernatant was decanted off, the remaining crystals washed with *n*-pentane and dried *in vacuo*. Yield = (17 mg, 57%).

<sup>1</sup>H NMR (CD<sub>3</sub>CN):  $\delta$ /ppm = 8.71 (dd, 4H, <sup>4</sup>*J*<sub>H,H</sub> = 1.7, <sup>3</sup>*J*<sub>H,H</sub> = 4.6 Hz, H<sub>a</sub>), 7.71 (m, 4H, H<sub>b</sub>), 5.34 (s, 30H, H<sub>Cp</sub>).

<sup>13</sup>C {<sup>1</sup>H} NMR (CD<sub>3</sub>CN):  $\delta$ /ppm = 224.44 (s, C<sub>CO</sub>), 151.74 (s, C<sub>a</sub>), 122.69 (s, C<sub>b</sub>), 86.62 (s, C<sub>Cp</sub>). <sup>31</sup>P {<sup>1</sup>H} NMR (CD<sub>3</sub>CN):  $\delta$ /ppm = -143.13 (sept, <sup>1</sup>J<sub>P,F</sub> = 705.2 Hz).

<sup>19</sup>F NMR (CD<sub>3</sub>CN):  $\delta$ /ppm = -71.75 (d, <sup>1</sup>*J*<sub>F,P</sub> = 705.3 Hz).

Positive ion ESI-MS (CH<sub>3</sub>CN, r. t.): m/z (%) = 1276.3 (100) [{Cp<sub>2</sub>(CO)<sub>4</sub>Mo<sub>2</sub>As<sub>2</sub>}<sub>2</sub>Ag]<sup>+</sup>, 731.7 (82) [{Cp<sub>2</sub>(CO)<sub>4</sub>Mo<sub>2</sub>As<sub>2</sub>}Ag(CH<sub>3</sub>CN)]<sup>+</sup>, 690.6 (22) [{Cp<sub>2</sub>(CO)<sub>4</sub>Mo<sub>2</sub>As<sub>2</sub>}Ag]<sup>+</sup>, 147.9 (22) [Ag(CH<sub>3</sub>CN)]<sup>+</sup>.

Negative ion ESI-MS (CH<sub>3</sub>CN, r. t.): m/z (%) = 144.97 (100) PF<sub>6</sub><sup>-</sup>. Elemental analysis, calcd (%) for C<sub>52</sub>H<sub>38</sub>Ag<sub>2</sub>As<sub>6</sub>F<sub>12</sub>Mo<sub>6</sub>N<sub>2</sub>O<sub>12</sub>P<sub>2</sub> (2413.72 g/mol): C, 25.88; H, 1.59; N, 1.16; found: C, 25.49; H, 1.61; N, 1.16.

IR (solid, CO bands):  $\tilde{v}$ /cm<sup>-1</sup>: 1983.19 (s), 1956.80 (s), 1905.60 (vs).

## NMR spectra



Figure S1: <sup>1</sup>H NMR spectrum of complex 1 in CD<sub>3</sub>CN at 400 MHz.  $*CH_2Cl_2$  solvent.



Figure S2: <sup>1</sup>H NMR spectrum of complex 2 in CD<sub>3</sub>CN at 400 MHz.



Figure S3: <sup>1</sup>H NMR spectrum of complex 3 in CD<sub>3</sub>CN at 400 MHz.







Figure S7:  $^{13}\text{C}\{^{1}\text{H}\}$  NMR spectrum of complex 1 in CD\_3CN at 100.61 MHz.











Figure S11: <sup>13</sup>C{<sup>1</sup>H} NMR spectrum of complex 5 in CD<sub>3</sub>CN at 100.61 MHz.



Figure S12:  $^{13}\text{C}\{^{1}\text{H}\}$  NMR spectrum of complex 6 in CD\_3CN at 100.61 MHz.



Figure S13:  $^{31}\text{P}\{^{1}\text{H}\}$  NMR spectrum of complex 1 in CD\_3CN at 161.98 MHz.



Figure S14:  $^{31}\text{P}\{^{1}\text{H}\}$  NMR spectrum of complex 2 in CD\_3CN at 161.98 MHz.



Figure S15: <sup>31</sup>P{<sup>1</sup>H} NMR spectrum of complex 3 in CD<sub>3</sub>CN at 161.98 MHz.



Figure S16:  $^{31}\mathsf{P}\{^{1}\mathsf{H}\}$  NMR spectrum of complex 4 in CD<sub>3</sub>CN at 161.98 MHz.



Figure S16:  $^{31}\text{P}\{^{1}\text{H}\}$  NMR spectrum of complex 5 in CD\_3CN at 161.98 MHz.







Figure S18:  $^{19}\text{F}\{^{1}\text{H}\}$  NMR spectrum of complex 1 in CD\_3CN at 376.50 MHz.







Figure S20:  $^{19}\text{F}\{^1\text{H}\}$  NMR spectrum of complex 3 in CD\_3CN at 376.50 MHz.



Figure S21: <sup>19</sup>F{<sup>1</sup>H} NMR spectrum of complex 4 in CD<sub>3</sub>CN at 376.50 MHz.



Figure S22:  $^{19}\text{F}\{^{1}\text{H}\}$  NMR spectrum of complex 5 in CD\_3CN at 376.50 MHz.



Figure S23: <sup>19</sup>F{<sup>1</sup>H} NMR spectrum of complex 6 in CD<sub>3</sub>CN at 376.50 MHz.

## **ESI-MS** spectra















Figure S27: Positive ion ESI-MS spectrum of complex 4 in CD<sub>3</sub>CN at room temperature.







Figure S29: Positive ion ESI-MS spectrum of complex 6 in CD<sub>3</sub>CN at room temperature.

#### **Crystallographic Data**

Crystals of **1-6** were taken from a Schlenk flask under a stream of argon and immediately covered with mineral oil to prevent a loss of solvent. The quickly chosen single crystals covered by a thin oil/Fomblin layer were taken to the pre-centered goniometer head with MiTeGen MicroLoops and directly attached to the diffractometer into a stream of cold nitrogen.

The diffraction experiments for **1-6** were collected on a GV50 diffractometer (CuK $\alpha$  radiation,  $\lambda = 1.54178$  Å (**1-4,6**); CuK $\beta$  radiation,  $\lambda = 1.39222$  Å (**5**)) from Rigaku Oxford Diffraction equipped with a TitanS2 detector. The crystals were kept at *T* = 123(1) K during data collection. Data collection and reduction were performed with *CrysAlisPro* [Version V1.171.40.14a, 2018 (**1**), V1.171.38.41h, 2015 (**2**, **3**, **6**), V1.171.41.54a, 2020 (**4**, **5**)].<sup>[2]</sup> For all compounds a numerical absorption correction based on gaussian integration over a multifaceted crystal model and an empirical absorption correction using spherical harmonics as implemented in SCALE3 ABSPACK scaling algorithm was applied.

Using  $Olex2^{[3]}$ , the crystal structures were solved with  $SHELXT^{[4]}$  and refined by full-matrix least-squares method against  $|F|^2$  in anisotropic approximation using multiprocessor versions of SHELXL.<sup>[5]</sup> Hydrogen atoms were refined in calculated positions using riding on pivot atom model. In case of the disorder, the site occupancies of the disordered components were refined with their U<sub>iso</sub> fixed at average U<sub>eq</sub> for fully occupied atoms in given structure in order to avoid correlations. After refinement, occupancies were fixed at the resulting values and the refinement of the atomic displacement parameters was performed.

The  $PF_6^-$  molecule in **1** is disorder over two positions (65:35). Further, the two  $CH_2CI_2$  solvent molecules are only partly occupied one with an occupation of 0.75 and the second one with an occupation of 0.6. However, the second  $CH_2CI_2$  molecule is also disordered over two positions (40:20). Compound **2** shows an anion disordered over two positions (54:46). Further, 1.5  $CH_2CI_2$  solvent were heavily disordered. Therefore, a solvent mask was calculated and 69 electrons were found in a volume of 245 Å<sup>3</sup> in 1 void per unit cell. This is consistent with the

presence of 1.5  $CH_2CI_2$  molecules per asymmetric unit, which account for 63 electrons per unit cell. In compound **6** one As atom, two CO ligands and a Cp ligand coordinated to a Mo atom, as well as one  $CH_2CI_2$  molecule show positional disorder (50:50; 65:35). The [CpMo(CO)<sub>2</sub>]<sub>2</sub> fragment (58:42), as well as the  $PF_6^-$  molecule (40:35:25) and one linker molecule (63:37) in compound **5** demonstrate positional disorder, related to different mutual orientation. Additionally, there were 1.5  $CH_3CN$  molecules, which were heavily disordered. Therefore, a solvent mask was calculated and 66 electrons were found in a volume of 262Å<sup>3</sup> in 1 void per unit cell. This is consistent with the presence of 1.5  $CH_3CN$  molecules per asymmetric unit, which account for 66 electrons per unit cell. All ORTEP drawings for **1-6** were made with the Olex2 software.<sup>[3]</sup>

CCDC-2048099 (1), CCDC-2048100 (2), CCDC-2048101 (3), CCDC-2048102 (4), CCDC-2048103 (5), and CCDC-2048104 (6), contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at <u>www.ccdc.cam.ac.uk/conts/retrieving.html</u> (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: + 44-1223-336-033; e-mail: <u>deposit@ccdc.cam.ac.uk</u>).

Compound	1 · 1.35 CH <sub>2</sub> Cl <sub>2</sub> /	2 · CH₃CN/	2
compound	1 CH₃CN	1.5 CH <sub>2</sub> Cl <sub>2</sub>	3
Data set	ems_405_aP_	ems_407_aP_	ems_542f_mP_
(internal naming)	abs_gaus	abs	abs
Formula	C74.7H61.4Ag2As8Cl5.4	Ag2As8C75Cl6F12H60	$C_{22}H_{16}AgAs_2F_6Mo_2$
	F12M08N4O16P2	M08N4O16P2	N4O4P
D <sub>calc.</sub> / g ⋅ cm <sup>-3</sup>	2.142	2.162	2.348
µ/mm <sup>-1</sup>	15.754	15.937	16.591
Formula Weight	3335.06	3358.53	994.95
Colour	red	red	red
Shape	block	block	block
Size/mm <sup>3</sup>	0.33×0.25×0.21	0.35×0.23×0.15	0.20×0.14×0.10
T/K	122.97(13)	123.0(2)	123.01(10)
Crystal System	triclinic	triclinic	monoclinic
Space Group	PĪ	$P\overline{1}$	P21/c
<i>a</i> /Å	12.9052(4)	12.8682(7)	12.5558(3)
<i>b</i> /Å	12.9624(3)	13.0664(6)	21.4306(5)
c/Å	16.0579(5)	15.9420(8)	10.6865(2)
α/°	97.822(2)	98.621(4)	90
β/°	103.366(3)	103.144(4)	101.817(2)
γ/°	91.281(2)	90.062(4)	90
V/Å <sup>3</sup>	2585.09(13)	2579.1(2)	2814.56(11)
Ζ	1	1	4
Ζ'	0.5	0.5	1
Wavelength/Å	1.54184	1.54184	1.54184
Radiation type	Cu Kα	Cu Ka	CuKα
$\Theta_{min}/^{\circ}$	2.859	2.881	3.596
$\Theta_{max}$	74.232	74.868	74.231
Measured Refl.	24671	16268	15640
Independent Refl.	10080	9907	5559
Reflections with I > 2(I)	9574	9310	5096

 Table S1. Crystallographic details for 1, 2 and 3.

Rint	0.0347	0.0359	0.0547
Parameters	696	615	379
Restraints	130	150	18
Largest Peak	1.132	0.917	2.640
Deepest Hole	-1.386	-1.075	-1.871
GooF	1.050	1.031	1.056
$wR_2$ (all data)	0.0971	0.1015	0.1588
wR <sub>2</sub>	0.0955	0.0996	0.1532
R₁ (all data)	0.0372	0.0375	0.0628
R <sub>1</sub>	0.0355	0.0359	0.0590

#### Table S2. Crystallographic details for 4, 5 and 6.

Compound	4	5 · 2.5 CH₃CN	$6\cdot CH_2CI_2$
Data set (internal naming)	js2016_aP_abs_gaus	js233_aP_abs_gaus	ems_404_mC_abs
Formula	C90H80Ag4As8F24M08N8 O16P4	C <sub>26</sub> AgAs <sub>2</sub> F <sub>6</sub> H <sub>24.5</sub> Mo <sub>2</sub> N4.5O4P	C27H21AgAs3Cl2F6 M03NO6P
D <sub>calc.</sub> / g ⋅ cm <sup>-3</sup>	2.273	1.891	2.371
µ/mm <sup>-1</sup>	16.312	9.962	18.091
Formula Weight	3907.86	996.98	1291.77
Colour	clear orange	clear orange	red
Shape	block	block	block
Size/mm <sup>3</sup>	0.15×0.12×0.11	0.15×0.07×0.06	0.18×0.09×0.07
<i>T</i> /K	122.97(12)	123.00(10)	123.11(10)
Crystal System	triclinic	triclinic	monoclinic
Space Group	PĪ	PĪ	C2/c
a/Å	10.7861(2)	10.8770(2)	24.8486(4)
b/Å	20.7482(4)	13.3926(2)	18.8751(3)
c/Å	26.5944(5)	13.6762(2)	15.5925(3)
α/°	79.429(2)	100.5570(10)	90
β/°	87.128(2)	111.5570(10)	98.2656(17)
γ/°	77.470(2)	100.6310(10)	90
V/Å <sup>3</sup>	5710.9(2)	1751.07(5)	7237.2(2)
Ζ	2	2	8
Ζ'	1	1	1
Wavelength/Å	1.54184	1.39222	1.54184
Radiation type	Cu Ka	Cu K <sub>β</sub>	Cu Kα
$\Theta_{min}$ /°	3.381	3.153	2.951
$\Theta_{max}$	74.148	69.506	74.254
Measured Refl.	63285	21688	21960
Independent Refl.	22500	8567	7156
Reflections with I > 2(I)	20378	7586	6547
Rint	0.0468	0.0324	0.0305
Parameters	1463	705	559
Restraints	0	342	234
Largest Peak	1.064	1.020	0.868
Deepest Hole	-0.742	-1.200	-0.760
GooF	1.047	1.034	1.038
$wR_2$ (all data)	0.0754	0.0746	0.0650
wR <sub>2</sub>	0.0730	0.0718	0.0627
R₁ (all data)	0.0348	0.0350	0.0286
R <sub>1</sub>	0.0306	0.0301	0.0254



Figure S30. Molecular structure in the solid state of compound 1. Thermal ellipsoids are depicted at 50% probability level. <sup>i</sup> symmetry codes: -x, -y, 1-z.

Ag1—As1	2.6823(5)	Ag1—N1	2.302(3)
Ag1—As2	2.7393(5)	As1—As2	2.3858(6)
Ag1—As3	2.7164(5)	As3—As4	2.3726(6)
Ag1—As4	2.7637(6)		
As1—Ag1—As2	52.201(13)	As3—Ag1—As4	51.302(14)
As1—Ag1—As3	118.165(16)	N1—Ag1—As1	127.19(9)
As1—Ag1—As4	105.770(16)	N1—Ag1—As2	109.78(9)
As2—Ag1—As4	149.395(16)	N1—Ag1—As3	114.12(9)
As3—Ag1—As2	115.542(17)	N1—Ag1—As4	100.60(9)

Table S3. Selected geometric parameters (Å, °) for 1.



Figure S31. Molecular structure in the solid state of compound 2. Thermal ellipsoids are depicted at 50% probability level. <sup>i</sup> symmetry codes: 2-x, 2-y, 1-z.

Ag1—As1	2.6764(5)	Ag1—N1	2.324(4)
Ag1—As2	2.7230(6)	As1—As2	2.3842(7)
Ag1—As3	2.7246(6)	As3—As4	2.3749(7)
Ag1—As4	2.7230(6)		
As1—Ag1—As2	52.398(15)	As4—Ag1—As3	51.693(15)
As1—Ag1—As3	108.037(19)	N1—Ag1—As1	127.01(10)
As1—Ag1—As4	119.285(18)	N1—Ag1—As2	107.58(10)
As2—Ag1—As3	151.525(19)	N1—Ag1—As3	100.85(10)
As4—Ag1—As2	115.296(19)	N1—Ag1—As4	113.55(10)

Table S4. Selected geometric parameters (Å, °) for 2.



**Figure S32.** Part of the polymeric structure in the solid state of compound **3**. Thermal ellipsoids are depicted at 50% probability level. <sup>i</sup> symmetry codes: x, 1/2-y, 1/2+z.

Ag1—As1	2.7298(8)	Ag1—N3 <sup>i</sup>	2.596(5)
Ag1—As2	2.6314(8)	Ag1—N4 <sup>i</sup>	2.423(5)
Ag1—N1	2.553(5)	As1—As2	2.3777(8)
Ag1—N2	2.387(5)		
As2—Ag1—As1	52.61(2)	N4 <sup>i</sup> —Ag1—As1	124.83(13)
N3 <sup>i</sup> —Ag1—As1	84.29(12)	N4 <sup>i</sup> —Ag1—As2	101.77(14)
N3 <sup>i</sup> —Ag1—As2	118.01(12)	N4 <sup>i</sup> —Ag1—N3 <sup>i</sup>	65.51(17)
N2—Ag1—As1	128.78(12)	N4 <sup>i</sup> —Ag1—N1	94.12(18)
N2—Ag1—As2	154.87(12)	N1—Ag1—As1	130.07(14)
N2—Ag1—N3 <sup>i</sup>	85.81(16)	N1—Ag1—As2	93.45(13)
N2—Ag1—N4 <sup>i</sup>	95.30(18)	N1—Ag1—N3 <sup>i</sup>	144.67(18)
N2—Ag1—N1	66.81(17)		

Table S5. Selected geometric parameters (Å, °) for 3.

<sup>i</sup> Symmetry code: *x*, 1/2-*y*, 1/2+*z*.



**Figure S33.** Part of the polymeric structure in the solid state of compound **4**. Thermal ellipsoids are depicted at 50% probability level.

Ag2—Ag3	2.9690(4)	Ag3—N5	2.463(4)
Ag2—As5	2.7177(4)	Mo4—Mo3	3.0704(4)
Ag2—As6	2.6953(4)	Mo4—As3	2.5518(5)
Ag2—As3	2.7257(5)	Mo4—As4	2.6589(5)
Ag2—N3	2.274(3)	Mo5—As5	2.5498(5)
Ag2—N4	2.482(4)	Mo5—As6	2.6216(5)
Ag3—As6	2.8073(4)	Mo6—Mo5	3.0644(4)
Ag3—As3	2.6912(5)	Mo6—As5	2.6632(4)
Ag3—As4	2.7096(5)	Mo6—As6	2.5569(4)
Ag3—N6	2.267(3)		
As5—Ag2—Ag3	111.542(12)	N4—Ag2—Ag3	121.41(10)
As5—Ag2—As3	155.758(15)	N4—Ag2—As5	93.18(9)
As6—Ag2—Ag3	59.186(11)	N4—Ag2—As6	121.59(9)
As6—Ag2—Ag3	52.407(11)	N4—Ag2—As3	79.43(10)
As3—Ag2—Ag3	56.207(11)	As6—Ag3—Ag2	55.544(10)
N3—Ag2—Ag3	126.56(8)	As3—Ag3—Ag2	57.323(11)
N3—Ag2—As5	105.17(8)	As3—Ag3—As6	109.941(14)
N3—Ag2—As6	136.56(8)	As3—Ag3—As4	52.595(12)
N3—Ag2—As3	98.30(8)	As4—Ag3—Ag2	109.798(12)
N3—Ag2—N4	92.96(13)	As4—Ag3—As6	158.611(16)

Table S6. Selected geometric parameters (Å, °) for 4.



Figure S34. Part of polymeric structure in the solid state of compound 5 (left). Disordered molecular structure of the [Cp<sub>2</sub>(CO)<sub>4</sub>Mo<sub>2</sub>As<sub>2</sub>] moiety (right). Thermal ellipsoids are depicted at 50% probability level.

Table S7. Selected geometric parameters (Å, °) for 5.

Ag1—Ag1 <sup>i</sup>	2.9798(4)	Mo2A—As1	2.583(3)
Ag1—As2	2.6599(4)	Mo1A—As2	2.5180(13)
Ag1—As2 <sup>i</sup>	2.7437(4)	Mo1A—As1	2.7055(11)
Ag1—As1	2.7235(4)	As2—As1	2.3734(4)
Ag1—N1	2.309(2)	As2—Mo1B	2.615(4)
Ag1—N2	2.393(3)	As2—Mo2B	2.685(3)
Mo2A—Mo1A	3.108(3)	As1—Mo1B	2.450(3)
Mo2A—As2	2.543(3)	As1—Mo2B	2.511(3)
As2 <sup>i</sup> —Ag1—Ag1 <sup>i</sup>	55.199(9)	As1—Ag1—Ag2 <sup>i</sup>	164.634(13)
As2—Ag1—Ag1 <sup>i</sup>	57.888(9)	N1—Ag1—Ag1 <sup>i</sup>	131.56(7)
As2—Ag1—As2 <sup>i</sup>	113.087(10)	N1—Ag1—As2	145.00(7)
As2—Ag1—Ag1	52.302(10)	N1—Ag1—As2 <sup>i</sup>	85.77(7)
As1—Ag1—Ag1 <sup>i</sup>	109.998(12)	N1—Ag1—As1	104.49(7)
N1—Ag1—N2	94.78(10)	N2—Ag1—As2	114.17(7)
N2—Ag1—Ag1 <sup>i</sup>	109.69(8)	N2—Ag1—As1	102.03(8)
N2—Ag1—As2 <sup>i</sup>	88.23(8)		
• _			

<sup>i</sup> Symmetry code: 2-*x*, 1-*y*, 1-*z*.



**Figure S35.** Part of the polymeric structure in the solid state of compound **6** (left). Disordered  $[Ag_2B_3]^{2+}$  unit (right). Thermal ellipsoids are depicted at 50% probability level. <sup>i</sup> symmetry codes: 1-x, y, 3/2-z.

Mo1—Mo2	3.0653(3)	Ag1—Ag1 <sup>i</sup>	2.7866(6)
Mo1—As1	2.5787(4)	Ag1—As1	2.6997(4)
Mo1—As2	2.6464(4)	Ag1—As1 <sup>i</sup>	3.0965(5)
Mo2—As1	2.6364(4)	Ag1—As2	2.7515(4)
Mo2—As2	2.5599(4)	Ag1—As3	2.9209(14)
Mo3—Mo3 <sup>i</sup>	3.0745(5)	Ag1—N1	2.254(3)
Mo3—As3	2.6399(13)	As1—As2	2.3908(5)
Mo3—As4	2.6361(13)	As3—As4	2.350(3)
As1—Mo1—Mo2	54.878(10)	As2—Ag1—As1 <sup>i</sup>	121.065(16)
As1—Mo1—As2	54.440(12)	As2—Ag1—As3	126.36(3)
As2—Mo1—Mo2	52.633(10)	As3—Ag1—As1 <sup>i</sup>	110.95(3)
As1—Mo2—Mo1	53.133(10)	N1—Ag1—Ag1 <sup>i</sup>	138.87(9)
As2—Mo2—Mo1	55.249(10)	N1—Ag1—As1	150.00(9)
As2—Mo2—As1	54.763(12)	N1—Ag1—As1 <sup>i</sup>	85.95(10)
Ag1 <sup>i</sup> —Ag1—As1 <sup>i</sup>	54.324(13)	N1—Ag1—As2	99.50(8)
Ag1 <sup>i</sup> —Ag1—As3	89.73(3)	N1—Ag1—As3	96.09(9)
As1—Ag1—Ag1 <sup>i</sup>	68.697(13)	Ag1—As1—Ag1 <sup>i</sup>	56.979(12)
As1—Ag1—As2	52.016(11)	As2—As1—Ag1 <sup>i</sup>	110.353(16)
As1—Ag1—As3	95.36(3)	As2—As1—Ag1	65.107(13)
As2—Ag1—Ag1 <sup>i</sup>	109.492(13)	As4—As3—Ag1	79.70(5)

Table S8. Selected geometric parameters (Å, °) for 6.

<sup>i</sup> Symmetry code: 1-*x*, *y*, 3/2-*z*.

#### References

- [1] P. J. Sullivan, A. L. Rheingold, Organometallics **1982**, *1*, 1547-1549.
- [2] CrysAlisPro Software System, Rigaku Oxford Diffraction, (2020).
- [3] O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, Olex2: A complete structure solution, refinement and analysis program, *J. Appl. Cryst.* 2009, *42*, 339-341.
- [4] G. M. Sheldrick, ShelXT-Integrated space-group and crystal-structure determination, *Acta Cryst.* **2015**, *A71*, 3-8.
- [5] M. Sheldrick, Crystal structure refinement with ShelXL, Acta Cryst. 2015, C71, 3-8.