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Supporting Information

The Potential of the Diarsene Complex $[(C_5H_5)_2Mo_2(CO)_4(\mu,\eta^2\text{-}As_2)]$ as a Connector Between Silver Ions

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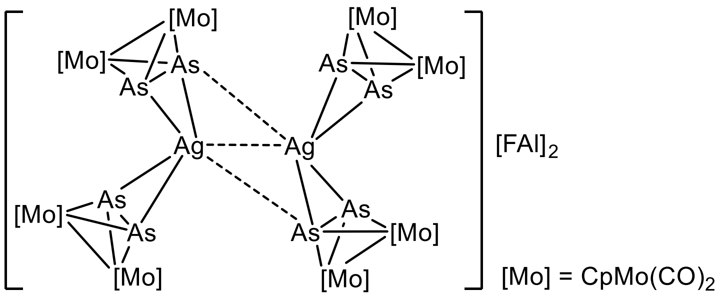
General

All manipulations were carried out under an inert atmosphere of dry nitrogen using standard glove-box and Schlenk techniques. The ligand complex $[Cp_2Mo_2(CO)_4(\mu,\eta^2\text{-}As_2)]$ (**B**)[1] and the Ag(I) salts $Ag[FAl\{OC(C_6F_5)(C_6F_{10})\}_3]$[2] and $Ag[Al\{OC(CF_3)_3\}_4]$[3] were prepared according to literature procedures. Solvents were freshly distilled under argon from CaH_2 (CH_2Cl_2) and from Na/K alloy (n-pentane). IR spectra were recorded as solids using a ThermoFisher Nicolet iS5 FT-IR spectrometer with an ATR-Ge disc. ^1H and ^{13}C spectra were recorded on a Bruker Avance 400 spectrometer. ^1H and ^{13}C chemical shifts were reported in parts per million (ppm) relative to Me_4Si as external standard. ^{13}C NMR chemical shifts were decoupled from the protons. For the ESI-MS a Finnignan Thermoquest TSQ 7000 mass spectrometer was used. Elemental analyses were performed on an Elementar Vario EL III apparatus by the microanalytical laboratory of the University of Regensburg.

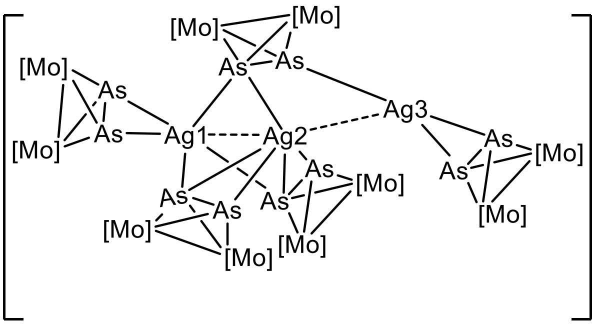
Synthesis of $[\{\{CpMo(CO)_2\}_2\{\eta^2{:}\eta^2\text{-}As_2\}\}_4Ag_2][FAl\{OC(C_6F_5)(C_6F_{10})\}_3]_2$ (4):



A solution of Ag[FAl] (76 mg, 0.05 mmol, 1 eq.) in 5 mL of CH_2Cl_2 and slowly added to a stirred solution of $[CpMo_2(CO)_4(\eta^2\text{-}As_2)]$ (**B**) (58 mg, 0.1 mmol, 2 eq.) in 10 ml of CH_2Cl_2. The red solution was stirred for 1 h at room temperature, after which, it was carefully layered with 30 ml of n-pentane. In two days, red crystals of **4** were obtained, collected, washed with n-pentane (5 ml × 2) and dried in vacuum. Yield (48 mg, 36%).

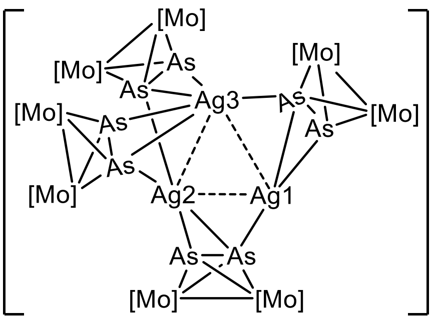
^1H NMR (400 MHz, CD_3CN): δ = 5.34 ppm (s, H_{Cp}). $^{13}C\{^1H\}$ NMR (100 MHz, CD_3CN): δ = 86.7 (s, C_{Cp}), 224.5 ppm (s, C_{CO}). Positive ion ESI-MS (CH_3CN, RT): m/z (%) = 1276.3 (100) $[\{Cp_2(CO)_4Mo_2As_2\}_2Ag]^+$, 731.6 (80) $[\{Cp_2(CO)_4Mo_2As_2\}Ag(CH_3CN)]^+$, 690.6 (30) $[\{Cp_2(CO)_4Mo_2As_2\}Ag]^+$, 583.7 (7) $[Cp_2(CO)_4Mo_2As_2]^+$. Negative ion ESI-MS (CH_3CN, RT): *m/z* (%) = 1380.9 $[FAl\{OC_6F_{10}(C_6F_5)\}_3]^-$. Elemental analysis, calcd (%) for $C_{128}H_{40}Ag_2Al_2As_8F_{92}Mo_8O_{22}$ (5314.16): C, 28.93; H, 0.76; found: C, 28.69; H, 0.79; IR (solid, CO bands): $\tilde{\nu}$/cm^{-1}: 1971 (vs), 1933 (vs), 1921 (vs).

Synthesis of $[\{\{CpMo(CO)_2\}_2\{\eta^2{:}\eta^2\text{-}As_2\}\}_2\{\{CpMo(CO)_2\}_2\{\eta^1{:}\eta^2{:}\eta^2\text{-}As_2\}\}_3Ag_3][Al\{OC(CF_3)_3\}_4]_3$ (5):



A solution of Ag[TEF] (54 mg, 0.05 mmol, 1 eq.) in 5 mL of CH_2Cl_2 and slowly added to a stirred solution of [$CpMo_2(CO)_4(\eta^2$-$As_2)$] (**B**) (58 mg, 0.1 mmol, 2 eq.) in 10 ml of CH_2Cl_2. The red solution was stirred for 1 h at room temperature, after which, it was carefully layered with 30 ml of n-pentane. In one week, red crystals of **5** were obtained, collected, washed with n-pentane (5 ml × 2) and dried in vacuum. Yield (61 mg, 60%).
^{1}H NMR (400 MHz, CD_3CN): δ = 5.34 ppm (s, H_{Cp}). $^{13}C\{^1H\}$ NMR (100 MHz, CD_3CN): δ = 86.7 (s, C_{Cp}), 224.5 ppm (s, C_{CO}). Positive ion ESI-MS (CH_3CN, RT): m/z (%) = 1276.3 (42) $[\{Cp_2(CO)_4Mo_2As_2\}_2Ag]^+$, 731.7 (100) $[\{Cp_2(CO)_4Mo_2As_2\}Ag(CH_3CN)]^+$, 690.6 (16) $[\{Cp_2(CO)_4Mo_2As_2\}Ag]^+$. Negative ion ESI-MS ($CH_3CN$, RT): *m/z* (%) = 966.9 (100) $[Al\{OC(CF_3)_3\}_4]^-$. Elemental analysis, calcd (%) for $C_{118}H_{50}Ag_3Al_3As_{10}F_{108}Mo_{10}O_{32}$ (6144.67): C, 23.07; H, ;0.82 found: C, 23.11; H, 0.93; IR (solid, CO bands): $\tilde{\nu}$/cm^{-1}: 1980 (vs), 1949 (vs).

Synthesis of $[\{\{CpMo(CO)_2\}_2\{\eta^1:\eta^2:\eta^2\text{-}As_2\}\}_4Ag_3][Al\{OC(CF_3)_3\}_4]_3$ (6):



A solution of Ag[TEF] (54 mg, 0.05 mmol, 1 eq.) in 5 mL of CH_2Cl_2 and slowly added to a stirred solution of [$CpMo_2(CO)_4(\eta^2$-$As_2)$] (**B**) (29 mg, 0.05 mmol, 1 eq.) in 5 ml of CH_2Cl_2. The red solution was stirred for 1 h at room temperature, after which, it was carefully layered with 30 ml of n-pentane. In four days, red crystals of **6** were obtained, collected, washed with n-pentane (5 ml × 2) and dried in vacuum. Yield (65 mg, 71%).
^{1}H NMR (400 MHz, CD_3CN): δ = 5.34 ppm (s, H_{Cp}). $^{13}C\{^1H\}$ NMR (100 MHz, CD_3CN): δ = 86.7 (s, C_{Cp}), 224.5 ppm (s, C_{CO}). Positive ion ESI-MS (CH_3CN, RT): m/z (%) = 1276.3 (100) $[\{Cp_2(CO)_4Mo_2As_2\}_2Ag]^+$, 731.7 (79) $[\{Cp_2(CO)_4Mo_2As_2\}Ag(CH_3CN)]^+$, 690.6 (37) $[\{Cp_2(CO)_4Mo_2As_2\}Ag]^+$, 583.7 (14) $[Cp_2(CO)_4Mo_2As_2]^+$. Negative ion ESI-MS (CH_3CN, RT): *m/z* (%) = 966.9 (100) $[Al\{OC(CF_3)_3\}_4]^-$. Elemental analysis, calcd (%) for $C_{104}H_{40}Ag_3Al_3As_8F_{108}Mo_8O_{28}$ (5560.72): C, 23.06; H, 0.82; found: C, 22.82; H, 0.68; IR (solid, CO bands): $\tilde{\nu}$/cm^{-1}: 1977 (vs), 1942 (vs).

Crystallographic details:

Crystals of **4**-**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 layer were taken to the pre-centered goniometer head with CryoMount® and directly attached to the diffractometer into a stream of cold nitrogen.

The diffraction experiments for **4**-**6** were collected on a Gemini ultra (**4, 5**) or a SuperNova diffractometers (Rigaku Oxford Diffraction) equipped with fine-focus tube (MoKα radiation, λ = 0.71073 Å) and Atlas^{S2} CCD detectors, using ω scans of 0.75° or 0.5° frames, respectively. The diffraction experiment for **6** was collected on a SuperNova diffractometer (Rigaku Oxford Diffraction) equipped with micro-focus SuperNova source (CuKα radiation, λ = 1.54178 Å) and Atlas^{S2} CCD detectors, using ω scans of 1° frames. The measurements for **4**-**6** were performed at 123 K. Absorption corrections were applied analytically using *CrysAlisPRO* Software.[4] The crystal structures were solved by direct methods with *SHELXT*[5] or *Olex*[6] programs and refined by full-matrix least-squares method against $|F|^2$ in anisotropic approximation using multiprocessor versions of SHELXTL.[5] 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_{iso} fixed at average U_{eq} 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 light atoms with site occupation factors less than 0.5 were refined isotropically.

The $Cp_2Mo_2P_2(CO)_4$ dimers in **4**, **5** and **6** demonstrate different type of disorder. It can be rotational caused by re-orientations of Cp groups about the direction of π-bond (the tendency can be seen in **5**), or positional, related to different mutual orientation of the CO, Cp ligands coordinated to Mo atoms (**4**, **5**, **6**). In the case of 6 the introduction of the minor (refined to 0.03) disorder of the three of 5 {Mo_2P_2} dimers allowed to describe otherwise meaningless electron density (2.40-3.23 e·Å^{-2}) and improve quality factors from R_1 = 0.0384, wR_2 = 0.0905 to R_1 = 0.0271, wR_2 = 0.0522 and maximal ED peak of 0.82 e·Å^{-2}

In all structures with the weakly coordinating anion [TEF], it is disordered. The disorder patterns varied according to different orientations or conformations of the [TEF] anion caused by rotation around O-*tert*C (**4**, **5**, **6**) or C-C(F_3) bonds of OC_4F_9 groups (**5**, **6**). In all structures the solvent CH_2Cl_2 molecules are also either disordered or partly occupied. The disorder patterns are illustrated in the Figures S6, S8 and S10.

The supplementary crystallographic data for this publication (Tables S1-S2: CCDC-1985242 (**4**), CCDC-1985244 (**5**), CCDC-1985245 (**6**)) can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: + 44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

All ORTEP drawings for **4**-**6** were made in Olex2 software.[6]

Table 1S. Crystallographic details for 4 and 5.

Compound	**4**	**5**
CCDC Code	CCDC-1985242	CCDC-1985244
Crystal data		
Structural formula	$[Ag_2(Cp_2Mo_2As_2(CO)_4)_4](FAlO_3C_{36}H_{45})\cdot 1.675(CH_2Cl_2)$	$[Ag_3(Cp_2Mo_2As_2(CO)_4)_5](AlO_4C_{16}F_{36})_3\cdot 4CH_2Cl_2$
Chemical formula	$C_{129.68}H_{43.35}Ag_2Al_2As_8Cl_{3.35}F_{92}Mo_8O_{22}$	$C_{122}H_{58}Ag_3Al_3As_{10}Cl_8F_{108}Mo_{10}O_{32}$
M_r	5456.43	6484.43
Crystal system, space group	Orthorhombic, *Pccn*	Monoclinic, $P2_1/n$
Temperature (K)	123	123
a, *b*, *c* (Å)	18.5126 (3), 33.8843 (8), 25.6612 (6)	20.20026(19), 30.0466(3), 31.0089(3)
β (°)	90, 90, 90	103.4982 (10)
V (Å^3)	16096.9 (6)	18301.0 (3)
Z	4	4
F(000)	10409	12336
D_x (Mg m^{-3})	2.252	2.353
Radiation type	Mo $K\alpha$	Mo $K\alpha$
μ (mm^{-1})	2.71	3.07
Crystal shape	Prism	prism
Colour	Red	red
Crystal size (mm)	0.73 × 0.68 × 0.51	0.71 × 0.62 × 0.38
Data collection		
Diffractometer	Xcalibur, Atlas^{S2}, Gemini ultra	Xcalibur, Atlas^{S2}, Gemini ultra
Absorption correction	Analytical	Analytical
T_{min}, T_{max}	0.273, 0.398	0.221, 0.431
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	82022, 26113, 12482	169943, 58279, 38192
R_{int}	0.042	0.029
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.756	0.744
Range of *h*, *k*, *l*	$h = -27\rightarrow16$, $k = -50\rightarrow32$, $l = -21\rightarrow38$	$h = -29\rightarrow28$, $k = -40\rightarrow44$, $l = -46\rightarrow43$
Refinement		
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.044, 0.101, 0.90	0.027, 0.054, 0.90
No. of reflections	26110	58279
No. of parameters	1359	2975
No. of restraints	0	0
H-atom treatment	H-atom parameters constrained	H-atom parameters constrained
$\Delta\rangle_{max}$, $\Delta\rangle_{min}$ (e Å^{-3})	1.78, -1.47	1.26, -1.19

Computer programs: *CrysAlis PRO* 1.171.38.41, 1.171.38.46 (Rigaku OD, 2015), *SHELXT2015*/7 (Sheldrick, 2015), *SHELXL2014*/7 (Sheldrick, 2014).

Table 2S. Crystallographic details for 6

Compound	**6**
CCDC Code	CCDC-1985245
Crystal data	
Structural formula	$[Ag_3(Cp_2Mo_2As_2(CO)_4)_4](AlO_4C_{16}F_{36})_3 \cdot CH_2Cl_2$
Chemical formula	$C_{105}H_{42}Ag_3Al_3As_8Cl_2F_{108}Mo_8O_{28}$
M_r	5645.71
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	123
a, *b*, *c* (Å)	22.6469(5), 23.0028(4), 30.4515(4)
β (°)	91.9714(16)
V ($Å^3$)	15854.1(5)
Z	4
F(000)	10728
D_x (Mg m^{-3})	2.365
Radiation type	Cu $K\alpha$
μ (mm^{-1})	12.025
Crystal shape	plate
Colour	red
Crystal size (mm)	0.32 × 0.17 × 0.05
Data collection	
Diffractometer	Atlas^{S2}, SuperNova
Absorption correction	Analytical
T_{min}, T_{max}	0.143, 0.650
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	69104, 32402, 26756
R_{int}	0.0353
$(\sin \theta/\lambda)_{max}$ ($Å^{-1}$)	0.746
Range of *h*, *k*, *l*	$h = -28 \rightarrow 27$, $k = -25 \rightarrow 29$, $l = -38 \rightarrow 29$
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.0634, 0.1804, 1.02
No. of reflections	32402
No. of parameters	4201
No. of restraints	7150
H-atom treatment	H-atom parameters constrained
$\Delta\rangle_{max}$, $\Delta\rangle_{min}$ (e $Å^{-3}$)	1.67, -1.18

Computer programs: *CrysAlis PRO* 1.171.38.41 and 1.171.39.45g (Rigaku OD, 2018), *SHELXL2014*/7 (Sheldrick, 2014), Olex2 (Dolomanov *et al.*, 2009).

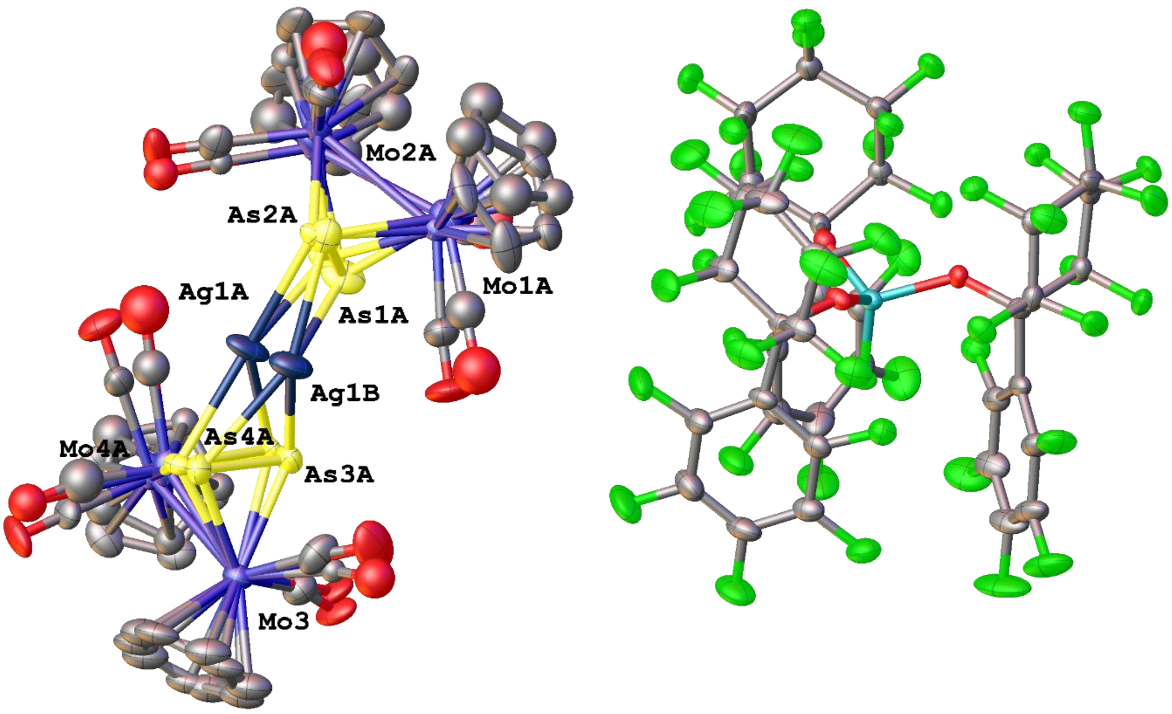


Figure S1. Molecular structure of the compound **4** (a.d.p. ellipsoids at 50% probability)

Table 3S. Selected geometric parameters (Å, º) for **4**

Ag1A—As4A	2.6188 (15)	Ag1B—Ag1B^{i}	2.655 (4)
Ag1A—As2A	2.678 (3)	Ag1B—As1B	2.656 (8)
Ag1A—As1A	2.705 (2)	Ag1B—As4B	2.718 (5)
Ag1A—As3A	2.706 (2)	Ag1B—As3B	2.726 (7)
Ag1A—Ag1A^{i}	2.8583 (12)	Ag1B—As4B^{i}	2.919 (6)
Mo1A—As2A	2.553 (5)	Mo1B—As2B	2.549 (15)
Mo1A—As1A	2.629 (4)	Mo1B—As1B	2.607 (12)
Mo2A—As1A	2.545 (2)	Mo2B—As1B	2.559 (7)
Mo2A—As2A	2.623 (3)	Mo2B—As2B	2.664 (12)
Mo4A—As3A	2.5510 (18)	Mo4B—As3B	2.550 (6)
Mo4A—As4A	2.6546 (17)	Mo4B—As4B	2.603 (6)
As1A—As2A	2.413 (4)	As1B—As2B	2.331 (14)
As3A—As4A	2.414 (2)	As3B—As4B	2.346 (9)
Ag1B—As2B	2.613 (10)	As4B—Ag1B^{i}	2.919 (6)
As4A—Ag1A—As2A	164.27 (8)	As1B—Ag1B—As4B	127.2 (2)
As4A—Ag1A—As1A	142.24 (6)	As2B—Ag1B—As3B	138.7 (3)
As2A—Ag1A—As1A	53.27 (9)	Ag1B^{i}—Ag1B—As3B	116.47 (16)
As4A—Ag1A—As3A	53.88 (5)	As1B—Ag1B—As3B	86.2 (2)
As2A—Ag1A—As3A	138.18 (10)	As4B—Ag1B—As3B	51.05 (18)

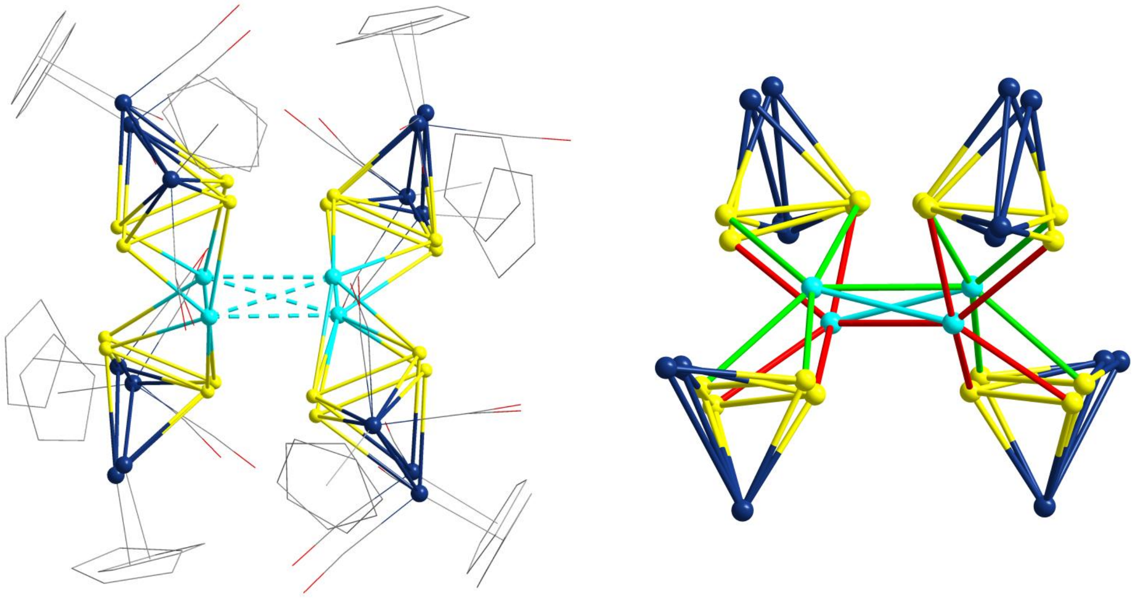
As1A—Ag1A—As3A	90.92 (6)	As2B—Ag1B—As4B^{i}	91.0 (3)
As4A—Ag1A—Ag1A^{i}	92.18 (4)	Ag1B^{i}—Ag1B—As4B^{i}	58.15 (12)
As2A—Ag1A—Ag1A^{i}	72.23 (7)	As1B—Ag1B—As4B^{i}	131.75 (18)
As1A—Ag1A—Ag1A^{i}	125.49 (5)	As4B—Ag1B—As4B^{i}	99.69 (12)
As3A—Ag1A—Ag1A^{i}	137.24 (4)	As3B—Ag1B—As4B^{i}	122.51 (13)
As2A—As1A—Ag1A	62.79 (9)	As2B—As1B—Ag1B	62.8 (3)
Mo2A—As1A—Ag1A	116.34 (10)	Mo2B—As1B—Ag1B	120.6 (3)
Mo1A—As1A—Ag1A	107.36 (9)	Mo1B—As1B—Ag1B	105.1 (3)
As1A—As2A—Ag1A	63.94 (8)	As1B—As2B—Ag1B	64.7 (3)
Mo1A—As2A—Ag1A	110.47 (14)	Mo1B—As2B—Ag1B	108.0 (5)
Mo2A—As2A—Ag1A	114.61 (11)	Ag1B—As2B—Mo2B	118.3 (4)
As4A—As3A—Ag1A	61.21 (6)	As4B—As3B—Ag1B	64.3 (2)
Mo4A—As3A—Ag1A	105.44 (7)	Mo3—As3B—Ag1B	117.1 (2)
Mo3—As3A—Ag1A	115.24 (7)	Mo4B—As3B—Ag1B	109.8 (2)
As3A—As4A—Ag1A	64.90 (6)	As3B—As4B—Ag1B	64.6 (2)
Mo3—As4A—Ag1A	120.91 (6)	Mo3—As4B—Ag1B	120.05 (18)
Ag1A—As4A—Mo4A	105.00 (6)	Mo4B—As4B—Ag1B	108.5 (2)
As2B—Ag1B—Ag1B^{i}	101.2 (3)	As3B—As4B—Ag1B^{i}	120.3 (2)
As2B—Ag1B—As1B	52.5 (3)	Mo3—As4B—Ag1B^{i}	146.48 (15)
Ag1B^{i}—Ag1B—As1B	146.34 (14)	Mo4B—As4B—Ag1B^{i}	143.3 (2)
As2B—Ag1B—As4B	153.8 (3)	Ag1B—As4B—Ag1B^{i}	56.06 (12)
Ag1B^{i}—Ag1B—As4B	65.79 (14)		

Symmetry code(s): (i) -*x*+1/2, -*y*+3/2, *z*.

Interpretation of the disorder of the core in the cationic complex 4

The cationic complex $[Ag_3(Cp_2Mo_2As_2(CO)_4)_5]^{3+}$ (**4**) is disordered over two close positions with occupancies 0.75 and 0.25. It occupies special position on the 2-fold axis along *z* direction. The half of each two disordered components is located in the asymmetric unit. The symmetrically generated disordered complex is depicted in Figure S2.

If symmetry operation of 2_z axis is applied only to the major (0.75) part of the complex **4**, the resulting core will include only 'green-bonded' atoms in the Figure S2b, if the same procedure is repeated for the minor part (0.25) – the 'red-bonded' atoms. This would be the easiest and straightforward interpretation of the disorder. However, it is also possible, that the red part in the asymmetric part combines with the green part of the symmetrically generated part of the disorder. Then two more combinations 'green-red' and 'red-green' are allowed, which correspond to potentially different cores of the complex **4** (Figure S3).



a b

Figure S2. (a) Disordered cationic part in **4** and (b) the view of the disordered core with highlighted major (0.75, green bonds) and minor (0.25, red bonds).

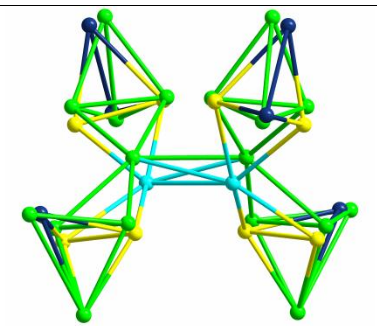
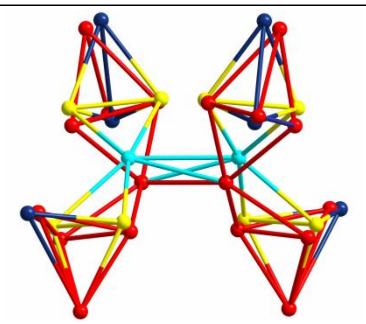
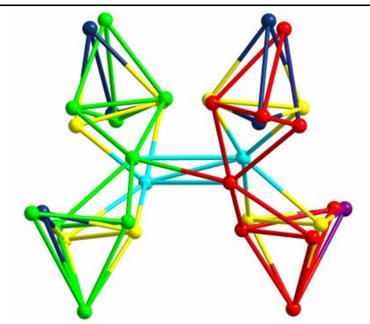
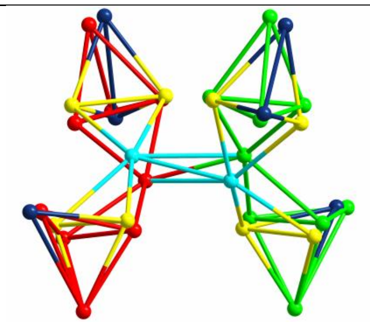
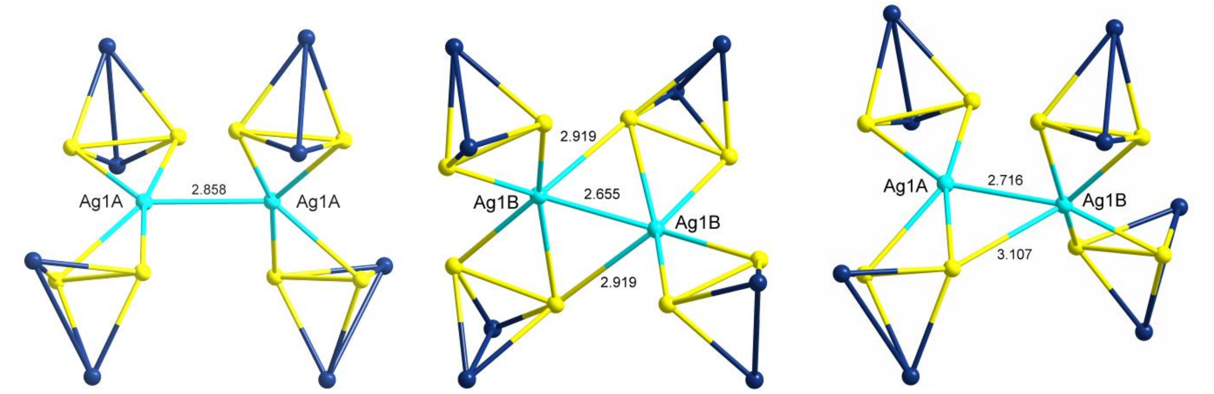
 occupancy 0.75 Core **4a** based on the major part only	 occupancy 0.25 Core **4b** based on the minor part only	 occupancy 0.25 Core **4c** based on the major unique part and minor part rotated by the 2_z axis
Same result as above	Same result as above	 occupancy 0.25 Core **4c** (2) based on the minor unique part and major part rotated by the 2_z axis

Figure S3. (a) Disordered cationic part in **4** and (b) the view of the disordered core with highlighted major (0.75, green bonds) and minor (0.25, red bonds). Occupancies are equal to the occupancy of the smallest contributing part.

There is no unambiguous interpretation of the structure model, as it is impossible to distinguish if it is either cores **4a** and **4b** co-exist (and have local rotational symmetry as they can be generated by 2-fold axis) or the core **4c** (which has no rotational symmetry) is disordered by the 2-fols axis and co-exists with the core **4a** (Figure S4). Obviously, co-existence of **4b** and **4c** is less probable if the occupancies are taken into account.



max occupancy 0.75	max occupancy 0.25	max occupancy 0.50
Core **4a** rotational symmetry	Core **4b** rotational symmetry	Core **4c** asymmetric

Figure S4. Possible inorganic cores of the complex **4**.

Two (simplest) possible situations: in the crystal structure co-exist different complexes:

Situation 1: 0.75×(Core I) + 0.25×(Core II)

Situation 2: 0.5×(Core III) + 0.5×(Core I)

or **any mixture** of all three complexes with a ratio that does not contradict crystallographic occupancies of the atoms. As one of possible examples, the solid solution of 0.25×(core **4a**) + 0.25×(core **4b**) + 0.5×(core **4c**) is non-contradicting to the experimental data. More possible compositions can also be devised. Therefore, the answer to the question as to which of these alternatives do really exist, cannot be obtained from the X-ray structural data as the symmetry of the special position hides the initial forms.

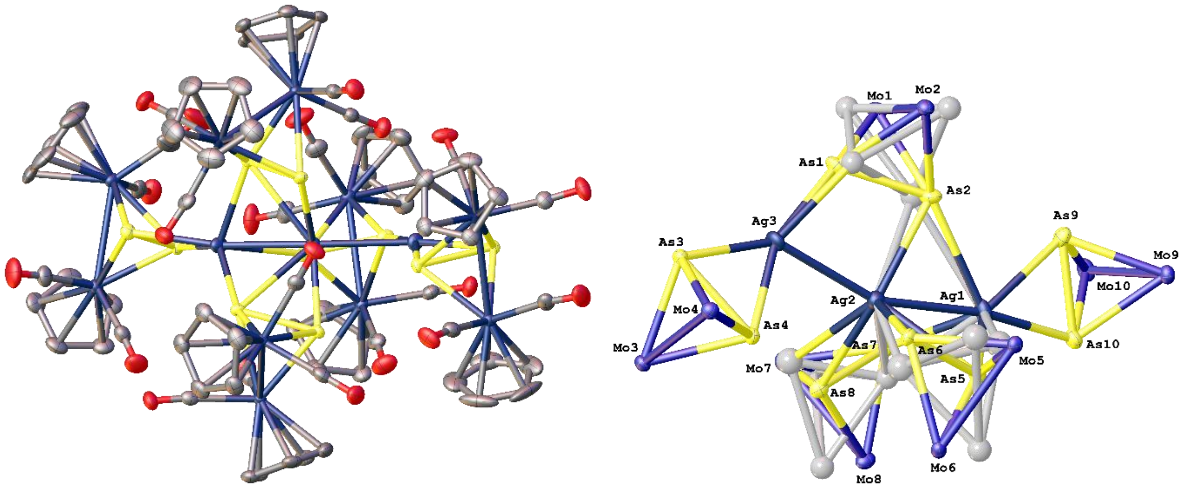


Figure S5. (left) Molecular structure of the cation of the compound **5** (H atoms are omitted); (right) the disorder of the {Mo_2As_2} units with a ratio of 0.97:0.03 (a.d.p. ellipsoids at 50% probability)

Table 4S. Selected geometric parameters (Å) for **5**

Ag1—As10	2.6709 (3)	Mo1A—As2A	2.537 (15)
Ag1—As5A	2.694 (11)	Mo1A—Mo2A	3.036 (13)
Ag1—As9	2.7340 (3)	Mo2A—As1A	2.542 (15)
Ag1—As5	2.7382 (3)	Mo2A—As2A	2.664 (14)
Ag1—As7	2.7541 (3)	As1A—As2A	2.400 (17)
Ag1—As7A	2.826 (10)	Mo5A—As5A	2.560 (15)
Ag1—Ag2	2.8376 (3)	Mo5A—As6A	2.615 (15)
Ag1—As2	3.0218 (4)	Mo5A—Mo6A	3.057 (13)
Ag1—As2A	3.123 (11)	Mo6A—As5A	2.600 (14)
Ag2—As6A	2.438 (12)	Mo6A—As6A	2.609 (15)
Ag2—As8	2.7204 (3)	As5A—As6A	2.387 (16)
Ag2—As6	2.7513 (3)	Mo7A—As8A	2.553 (14)
Ag2—As2	2.7566 (3)	Mo7A—As7A	2.565 (13)
Ag2—As2A	2.858 (11)	Mo7A—Mo8A	2.989 (12)
Ag2—Ag3	2.9053 (3)	Mo8A—As7A	2.524 (13)
Ag2—As7A	2.942 (10)	Mo8A—As8A	2.594 (14)
Ag2—As8A	2.995 (11)	As7A—As8A	2.321 (15)
Ag2—As7	3.0159 (3)	Mo1—As1	2.5144 (4)
Ag2—As5	3.0225 (3)	Mo1—As2	2.6539 (4)
Ag3—As1	2.4642 (3)	Mo1—Mo2	3.0689 (3)
Ag3—As4	2.5699 (3)	Mo2—As2	2.5635 (3)
Ag3—As1A	2.604 (12)	Mo2—As1	2.6140 (4)
Ag3—As3	2.6519 (3)	Mo5—As6	2.5716 (3)
Mo3—As4	2.5824 (3)	Mo5—As5	2.6271 (3)
Mo3—As3	2.6023 (3)	Mo5—Mo6	3.0641 (3)

Mo3—Mo4	3.1375 (3)	Mo6—As5	2.5636 (3)
Mo4—As3	2.5511 (3)	Mo6—As6	2.6665 (3)
Mo4—As4	2.5940 (3)	Mo7—As7	2.5587 (3)
Mo9—As9	2.5514 (3)	Mo7—As8	2.6519 (3)
Mo9—As10	2.6323 (3)	Mo7—Mo8	3.0465 (3)
Mo9—Mo10	3.0480 (3)	Mo8—As8	2.5792 (3)
Mo10—As10	2.5589 (3)	Mo8—As7	2.6359 (3)
Mo10—As9	2.6304 (3)	As1—As2	2.3748 (4)
As3—As4	2.4585 (3)	As5—As6	2.3693 (4)
As9—As10	2.3968 (4)	As7—As8	2.3738 (4)
Mo1A—As1A	2.536 (16)		

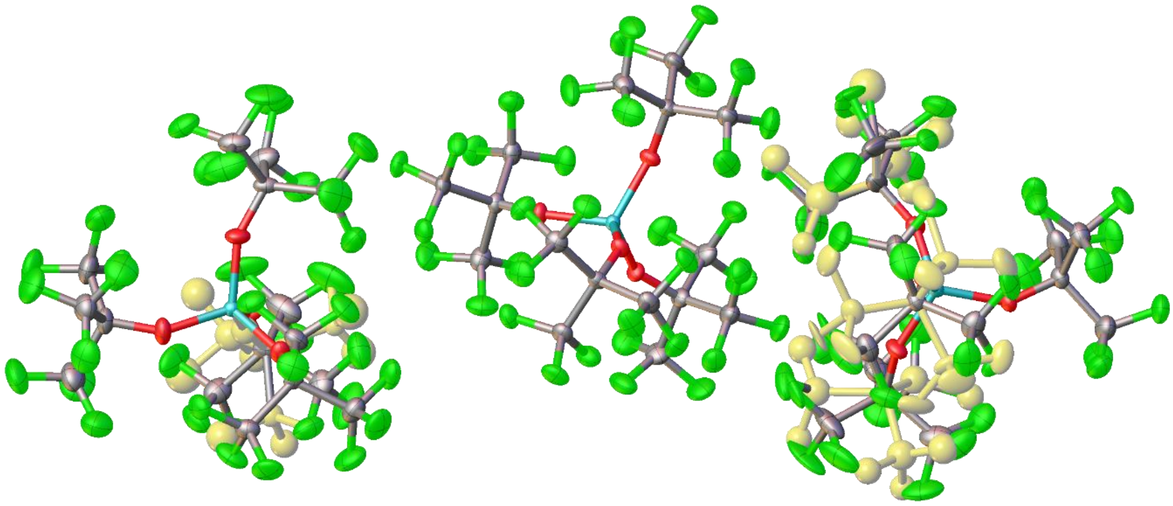


Figure S6. The TEF anions (disordered groups are shown in pale yellow) in the structure of the compound **5** (a.d.p. ellipsoids at 50% probability).

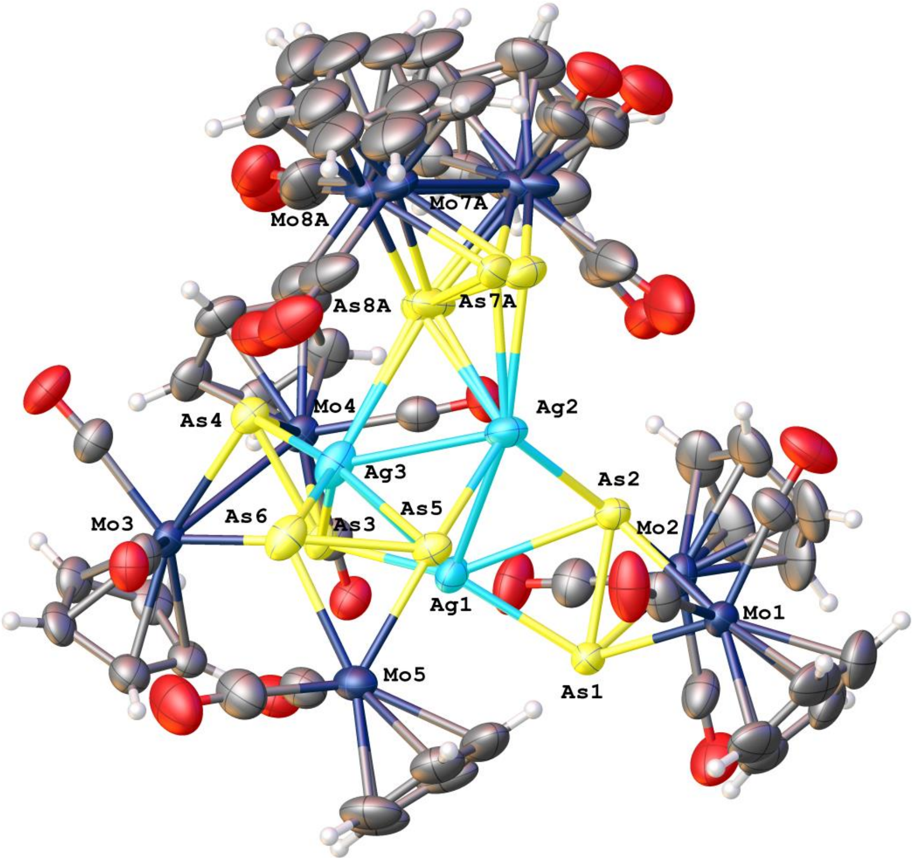


Figure S7. The structure of the cationic complex in the compound **6** (a.d.p. ellipsoids at 50% probability).

Table 5S. Selected geometric parameters (Å) for **6**

Ag1—Ag3	2.8904 (8)	Mo1—Mo2	3.0627 (9)
Ag1—Ag2	2.9800 (8)	Mo1—As2	2.6069 (9)
Ag1—As3	2.5738 (8)	Mo1—As1	2.5643 (10)
Ag1—As2	2.7923 (9)	Mo2—As2	2.5357 (10)
Ag1—As1	2.6133 (9)	Mo2—As1	2.6413 (10)
Mo3—Mo4	3.0759 (8)	Mo5—As5	2.5566 (10)
Mo3—As3	2.5424 (9)	Mo5—As6	2.6267 (11)
Mo3—As4	2.6345 (10)	As3—As4	2.4066 (10)
Ag3—Ag2	2.8625 (9)	Mo7A—As8A	2.540 (9)
Ag3—As3	2.8582 (9)	Mo7A—Mo8A	3.064 (7)
Ag3—As4	2.6054 (9)	Mo7A—As7A	2.649 (5)
Ag3—As5	2.8190 (9)	As2—As1	2.4095 (11)
Ag3—As8A	2.989 (8)	As5—As6	2.4066 (12)
Ag3—As6	2.6312 (11)	As8A—Mo8A	2.596 (7)
Ag2—As2	2.6718 (10)	As8A—As7A	2.378 (5)
Ag2—As5	2.7041 (10)	Mo8A—As7A	2.529 (4)

Ag2—As8A	2.737 (7)	Mo8B—As7B	2.579 (5)
Ag2—As7A	2.730 (5)	Mo8B—Mo7B	3.029 (8)
Ag2—As7B	2.680 (4)	Mo8B—As8B	2.627 (9)
Ag2—As8B	2.683 (9)	As7B—Mo7B	2.585 (5)
Mo4—As3	2.6042 (9)	As7B—As8B	2.365 (6)
Mo4—As4	2.5564 (9)	Mo7B—As8B	2.550 (11)

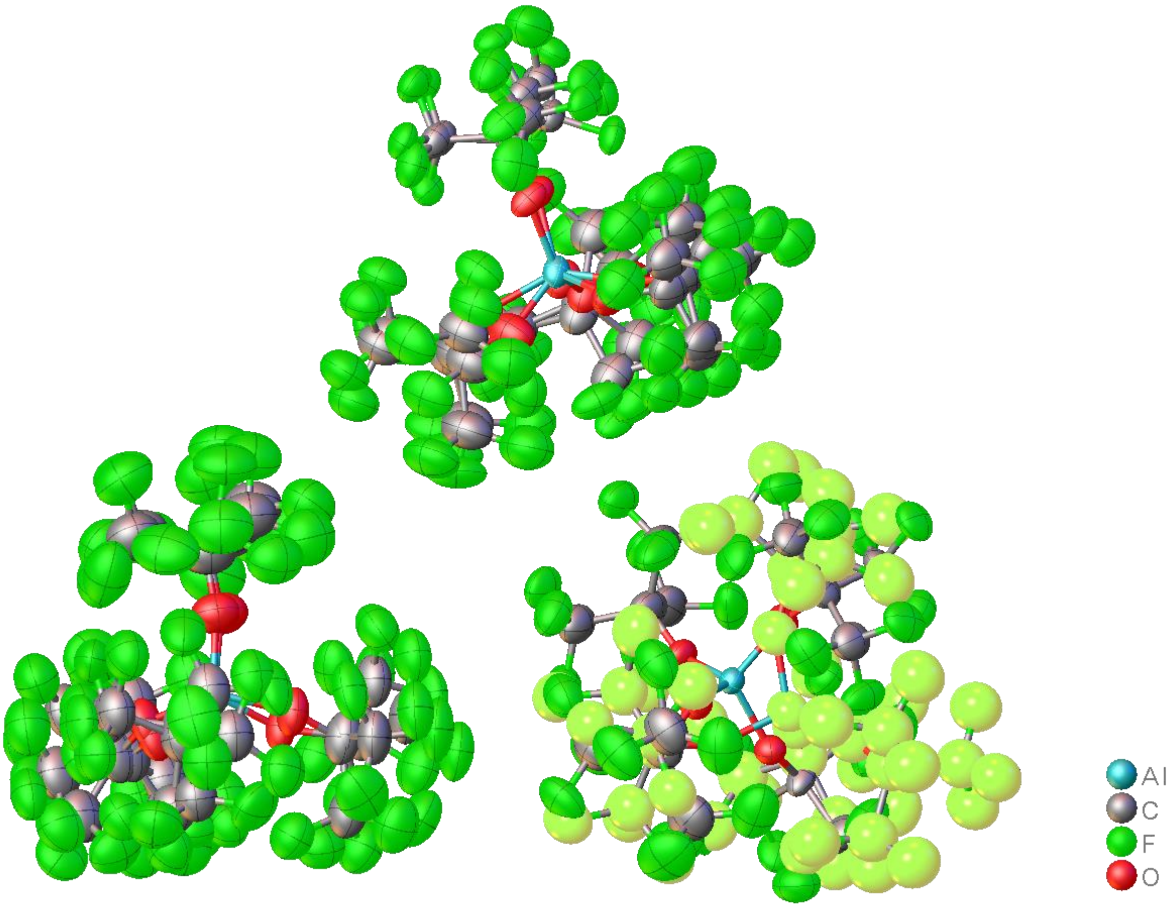


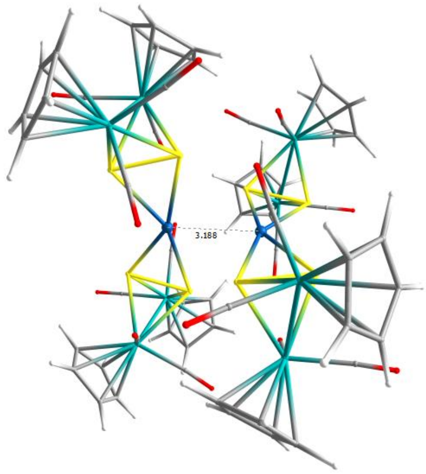
Figure S8. The TEF anions (disordered groups are shown in pale yellow) in the structure of the compound **6** (a.d.p. ellipsoids at 50% probability).

DFT calculations

The DFT calculations have been performed with Gaussian 09[7] at the ωB97XD[8]/def2-SVP[9] (for $[\{(Cp(CO)_2Mo)_2(As_2)\}_4Ag_2]^{2+}$ and $[\{(Cp(CO)_2Mo)_2(As_2)\}_2Ag]^{1+}$) and B3LYP[10]/Def2-TZVP[9] (for $[\{CpMo(CO)_2\}_2(\eta^2\text{-}P_2)]$ and $[\{CpMo(CO)_2\}_2(\eta^2\text{-}As_2)]$) level of theory. For the calculation of reaction energies, the SCF energies were used without corrections for zero point vibrations. Natural Bonding Orbitals (NBOs) for orbital energy diagram were generated using NBO7 program package.[11]

Table 6S. Cartesian coordinates of the gas-phase optimized geometry of $[\{(Cp(CO)_2Mo)_2(As_2)\}_4Ag_2]^{2+}$ at the ωB97XD/def2-SVP level of theory. E = -22083.8841414 Hartree.

Atom	x	y	z
Ag	-0.000866000	-1.594029000	-0.026443000
Ag	0.000866000	1.594029000	-0.026443000
As	1.515199000	-3.335603000	-1.450448000
As	1.940414000	-1.007319000	-1.853091000
As	-1.485453000	-3.253201000	1.573342000
As	-1.989238000	-0.908669000	1.693120000
Mo	4.011374000	-2.496227000	-1.554668000
Mo	2.028208000	-2.703223000	-3.871395000
Mo	-3.977864000	-2.658945000	1.536702000
Mo	-2.108387000	-2.198671000	3.906483000
As	-1.515199000	3.335603000	-1.450448000
As	-1.940414000	1.007319000	-1.853091000
As	1.485453000	3.253201000	1.573342000
As	1.989238000	0.908669000	1.693120000
Mo	-4.011374000	2.496227000	-1.554668000
Mo	-2.028208000	2.703223000	-3.871395000
Mo	3.977864000	2.658945000	1.536702000
Mo	2.108387000	2.198671000	3.906483000
C	2.137965000	1.836553000	6.160565000
H	1.446672000	2.321408000	6.846963000
C	3.436039000	2.309748000	5.803808000
H	3.895788000	3.228895000	6.163348000
C	4.049441000	1.343001000	4.964910000
H	5.061819000	1.392809000	4.574991000
C	3.133166000	0.269675000	4.782761000
H	3.312079000	-0.644116000	4.219765000
C	1.958637000	0.570148000	5.523407000
H	1.102040000	-0.089282000	5.628433000
C	-4.035706000	4.483947000	-1.476566000
O	-4.140102000	5.625976000	-1.439355000
C	2.039701000	4.173861000	4.147826000
O	2.020450000	5.298045000	4.371097000
O	-3.506698000	2.412349000	1.534924000
O	0.835362000	1.492291000	-4.203163000
O	-3.329851000	0.104952000	-5.050037000
O	-1.014673000	2.140633000	4.055659000
O	3.671416000	1.982062000	-1.499321000
C	4.791278000	0.897744000	1.940526000
O	5.365354000	-0.068671000	2.183406000
C	-3.663634000	2.454078000	0.399227000
C	-5.672044000	0.961928000	-1.128553000
H	-5.614794000	0.251313000	-0.309565000
C	-6.233031000	2.276416000	-1.062093000
H	-6.690288000	2.740207000	-0.190582000
C	-6.161403000	2.836110000	-2.371345000
H	-6.541719000	3.813383000	-2.664713000
C	-5.564384000	1.882530000	-3.235458000
H	-5.417659000	1.997185000	-4.305624000
C	-5.254702000	0.725909000	-2.464895000
H	-4.816164000	-0.194462000	-2.842525000
C	-0.223648000	1.906145000	-4.050847000
C	-2.834605000	1.016441000	-4.563595000
C	-3.368750000	4.510205000	-4.607539000
H	-4.335878000	4.788716000	-4.198830000
C	-3.146476000	3.614524000	-5.685412000
H	-3.915933000	3.085321000	-6.245211000



C	-1.746838000	3.580772000	-5.960551000
H	-1.266107000	3.038048000	-6.771746000
C	-1.106409000	4.462432000	-5.033525000
H	-0.044126000	4.697235000	-5.003289000
C	-2.108387000	5.029717000	-4.199787000
H	-1.950632000	5.777757000	-3.425804000
C	0.128432000	2.179253000	3.960998000
C	3.753381000	2.181520000	-0.371441000
C	4.335219000	4.963335000	1.855081000
H	3.550494000	5.711708000	1.942721000
C	4.968597000	4.289587000	2.937328000
H	4.759019000	4.437565000	3.992551000
C	5.977552000	3.447856000	2.400934000
H	6.667555000	2.832619000	2.975993000
C	5.983246000	3.601909000	0.982584000
H	6.685846000	3.143380000	0.289874000
C	4.961357000	4.545535000	0.650231000
H	4.735621000	4.919792000	-0.346645000
C	-2.137965000	-1.836553000	6.160565000
H	-1.446672000	-2.321408000	6.846963000
C	-3.436039000	-2.309748000	5.803808000
H	-3.895788000	-3.228895000	6.163348000
C	-4.049441000	-1.343001000	4.964910000
H	-5.061819000	-1.392809000	4.574991000
C	-3.133166000	-0.269675000	4.782761000
H	-3.312079000	0.644116000	4.219765000
C	-1.958637000	-0.570148000	5.523407000
H	-1.102040000	0.089282000	5.628433000
C	4.035706000	-4.483947000	-1.476566000
O	4.140102000	-5.625976000	-1.439355000
C	-2.039701000	-4.173861000	4.147826000
O	-2.020450000	-5.298045000	4.371097000
O	3.506698000	-2.412349000	1.534924000
O	-0.835362000	-1.492291000	-4.203163000
O	3.329851000	-0.104952000	-5.050037000
O	1.014673000	-2.140633000	4.055659000
O	-3.671416000	-1.982062000	-1.499321000
C	-4.791278000	-0.897744000	1.940526000
O	-5.365354000	0.068671000	2.183406000
C	3.663634000	-2.454078000	0.399227000
C	5.672044000	-0.961928000	-1.128553000
H	5.614794000	-0.251313000	-0.309565000
C	6.233031000	-2.276416000	-1.062093000
H	6.690288000	-2.740207000	-0.190582000
C	6.161403000	-2.836110000	-2.371345000
H	6.541719000	-3.813383000	-2.664713000
C	5.564384000	-1.882530000	-3.235458000
H	5.417659000	-1.997185000	-4.305624000
C	5.254702000	-0.725909000	-2.464895000
H	4.816164000	0.194462000	-2.842525000
C	0.223648000	-1.906145000	-4.050847000
C	2.834605000	-1.016441000	-4.563595000
C	3.368750000	-4.510205000	-4.607539000
H	4.335878000	-4.788716000	-4.198830000
C	3.146476000	-3.614524000	-5.685412000
H	3.915933000	-3.085321000	-6.245211000
C	1.746838000	-3.580772000	-5.960551000
H	1.266107000	-3.038048000	-6.771746000
C	1.106409000	-4.462432000	-5.033525000
H	0.044126000	-4.697235000	-5.003289000
C	2.108387000	-5.029717000	-4.199787000
H	1.950632000	-5.777757000	-3.425804000
C	-0.128432000	-2.179253000	3.960998000
C	-3.753381000	-2.181520000	-0.371441000
C	-4.335219000	-4.963335000	1.855081000
H	-3.550494000	-5.711708000	1.942721000
C	-4.968597000	-4.289587000	2.937328000
H	-4.759019000	-4.437565000	3.992551000
C	-5.977552000	-3.447856000	2.400934000
H	-6.667555000	-2.832619000	2.975993000
C	-5.983246000	-3.601909000	0.982584000
H	-6.685846000	-3.143380000	0.289874000
C	-4.961357000	-4.545535000	0.650231000
H	-4.735621000	-4.919792000	-0.346645000

Table 7S. Cartesian coordinates of the gas-phase optimized geometry of $[\{(Cp(CO)_2Mo)_2(As_2)\}_2Ag]^{1+}$ at the ωB97XD/def2-SVP level of theory. E = -11041.940186 Hartree.

Atom	x	y	z
Ag	-0.001021000	-0.000373000	-0.000068000
As	-2.389062000	0.689827000	0.979702000
As	-2.389157000	-0.690014000	-0.979720000
As	2.388013000	-0.507348000	1.085472000
As	2.388002000	0.507102000	-1.085535000
Mo	-4.110070000	-1.297193000	0.812890000
Mo	-4.109837000	1.297286000	-0.812948000
Mo	4.110057000	1.352855000	0.722413000
Mo	4.110387000	-1.352761000	-0.722338000
C	5.439321000	-2.757969000	-1.939482000
H	5.424200000	-3.826150000	-1.800533000
C	6.303621000	-1.838899000	-1.283998000
H	7.049807000	-2.093328000	-0.548626000
C	6.056987000	-0.547839000	-1.803828000
H	6.582604000	0.352158000	-1.537103000
C	5.030178000	-0.655264000	-2.775011000
H	4.637282000	0.152315000	-3.369879000
C	4.648856000	-2.014941000	-2.862652000
H	3.915319000	-2.420661000	-3.540100000
C	-4.597070000	-0.220722000	2.413801000
O	-4.948873000	0.339837000	3.344968000
C	4.602556000	-2.200638000	1.009759000
O	4.957763000	-2.726334000	1.959653000
O	-1.825962000	-2.664274000	2.455528000
O	-1.825444000	2.664102000	-2.455410000
O	-4.949052000	-0.339771000	-3.344871000
O	1.829594000	-3.463927000	-1.071768000
O	1.828835000	3.463587000	1.071682000
C	4.602211000	2.200817000	-1.009642000
O	4.957454000	2.726608000	-1.959471000
C	-2.636072000	-2.127611000	1.861583000
C	-4.647424000	-3.479372000	0.304268000
H	-3.909407000	-4.264748000	0.305450000
C	-5.429545000	-3.062832000	1.419839000
H	-5.404108000	-3.486511000	2.409983000
C	-6.303793000	-2.037931000	0.967480000
H	-7.045893000	-1.535027000	1.566606000
C	-6.069732000	-1.829034000	-0.410380000
H	-6.605868000	-1.146293000	-1.045986000
C	-5.042368000	-2.715990000	-0.819696000
H	-4.657119000	-2.817376000	-1.820632000
C	-2.635695000	2.127467000	-1.861632000
C	-4.596974000	0.220906000	-2.413879000
C	-6.069430000	1.829426000	0.410297000
H	-6.605688000	1.146764000	1.045887000
C	-6.303438000	2.038376000	-0.967564000
H	-7.045611000	1.535597000	-1.566705000
C	-5.429025000	3.063146000	-1.419899000
H	-5.403507000	3.486834000	-2.410038000
C	-4.646852000	3.479548000	-0.304312000
H	-3.908715000	4.264810000	-0.305475000
C	-5.041935000	2.716218000	0.819638000
H	-4.656689000	2.817537000	1.820582000
C	2.638969000	-2.678678000	-0.909237000
C	2.638360000	2.678489000	0.909169000
C	5.029821000	0.655638000	2.775198000
H	4.637012000	-0.151966000	3.370089000
C	6.056711000	0.548311000	1.804090000
H	6.582485000	-0.351622000	1.537453000
C	6.303174000	1.839375000	1.284189000
H	7.049373000	2.093874000	0.548853000
C	5.438679000	2.758352000	1.939550000
H	5.423392000	3.826521000	1.800530000
C	4.648271000	2.015260000	2.862716000
H	3.914628000	2.420909000	3.540092000

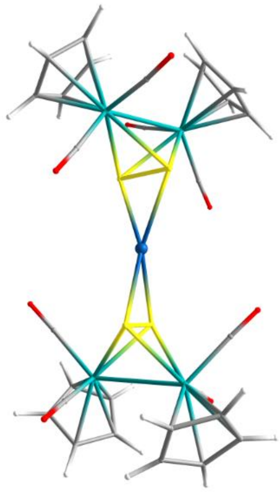


Table 8S. Cartesian coordinates of the gas-phase optimized geometry of [{CpMo(CO)$_2$}$_2$(η^2-P$_2$)] (**A**) at the B3LYP/def2-TZVP level of theory (E^0 = -1660.18758083 a.u.)

Atom	x	y	z
Mo	1.546765000	0.078822000	0.030094000
Mo	-1.546984000	-0.079047000	0.029774000
P	0.141107000	-1.034867000	1.757351000
P	-0.141067000	1.025672000	1.762769000
C	3.270524000	-1.471824000	-0.413286000
H	3.923563000	-1.816618000	0.371676000
C	3.476965000	-0.317249000	-1.227864000
H	4.318947000	0.353094000	-1.181150000
C	2.403884000	-0.252659000	-2.157512000
H	2.281970000	0.491842000	-2.927459000
C	1.547592000	-1.356364000	-1.923876000
H	0.663008000	-1.600453000	-2.485764000
C	2.081116000	-2.107449000	-0.841520000
H	1.662621000	-3.012830000	-0.435765000
C	-3.476562000	0.323734000	-1.227006000
H	-4.318538000	-0.346894000	-1.184436000
C	-2.403096000	0.264406000	-2.156571000
H	-2.280742000	-0.475797000	-2.930590000
C	-1.547082000	1.366934000	-1.916608000
H	-0.662499000	1.614394000	-2.477059000
C	-2.081092000	2.111969000	-0.830304000
H	-1.662989000	3.015236000	-0.419462000
C	-3.270595000	1.473853000	-0.406045000
H	-3.924080000	1.814311000	0.380439000
O	3.476992000	1.037483000	2.304253000
O	1.214850000	3.083379000	-0.791439000
O	-3.477105000	-1.049829000	2.298875000
O	-1.214795000	-3.079328000	-0.807527000
C	2.727094000	0.703982000	1.502688000
C	1.291522000	1.985222000	-0.450432000
C	-2.727285000	-0.711976000	1.499060000
C	-1.291689000	-1.983010000	-0.460719000

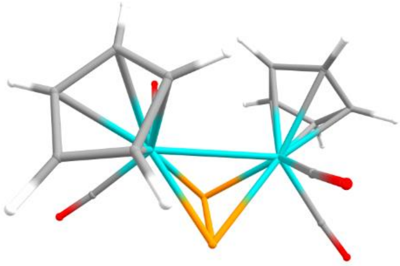
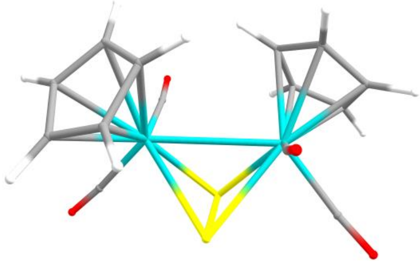


Table 9S. Cartesian coordinates of the gas-phase optimized geometry of [{CpMo(CO)$_2$}$_2$(η^2-As$_2$)] (**B**) at the B3LYP/def2-TZVP level of theory (E^0 = -5449.28758843 a.u.)

Atom	x	y	z
Mo	-1.564482000	0.209398000	-0.086630000
Mo	1.564497000	0.209407000	0.086665000
As	-0.158528000	-1.605754000	1.149006000
As	0.158561000	-1.605541000	-1.149298000
C	-3.282143000	0.718768000	1.440902000
H	-3.961108000	-0.042357000	1.788999000
C	-3.454711000	1.524474000	0.275696000
H	-4.291604000	1.494258000	-0.401781000
C	-2.352546000	2.420476000	0.209198000
H	-2.203133000	3.178497000	-0.542430000
C	-1.514551000	2.177621000	1.325216000
H	-0.618209000	2.717938000	1.574157000
C	-2.086105000	1.120960000	2.083859000
H	-1.691353000	0.718920000	3.001412000
C	3.454705000	1.524581000	-0.275410000
H	4.291594000	1.494260000	0.402068000
C	2.352523000	2.420551000	-0.208761000
H	2.203089000	3.178436000	0.543000000
C	1.514548000	2.177884000	-1.324834000
H	0.618201000	2.718232000	-1.573688000
C	2.086125000	1.121364000	-2.083657000
H	1.691390000	0.719479000	-3.001285000



C	3.282163000	0.719079000	-1.440760000
H	3.961144000	-0.041973000	-1.788986000
O	-3.545622000	-2.045765000	-0.976932000
O	-1.254277000	1.027658000	-3.093687000
O	3.545483000	-2.046084000	0.976526000
O	1.254177000	1.026919000	3.093924000
C	-2.768474000	-1.257533000	-0.671223000
C	-1.318043000	0.673636000	-1.997560000
C	2.768511000	-1.257606000	0.671007000
C	1.318029000	0.673309000	1.997669000

Table 10S. Energy diagram of selected Natural Bond Orbitals (NBOs) for compounds [Cp_2Mo_2(CO)4(η^2−E_2)] (E = P (**A**), As (**As**)), calculated at the B3LYP/def2-TZVP level of theory. BD stands for sigma bonds; LP stands for lone pairs.

[Cp_2Mo_2(CO)4(η^2−P_2)] (**A**)		[Cp_2Mo_2(CO)4(η^2−P_2)] (**B**)	
Orbital	Energy, eV	Orbital	Energy, eV
LP (1) P 3	-10.747	LP (1)As 3	-11.614
LP (1) P 4	-10.747	LP (1)As 4	-11.614
BD (1) P 3- P 4	-10.191	BD (1)As 3-As 4	-8.766
BD (1)Mo 1- P 3	-6.680	BD (1)Mo 1-As 3	-7.068
BD (1)Mo 1- P 4	-4.689	BD (1)Mo 1-As 4	-5.947
BD (1)Mo 2- P 3	-4.689	BD (1)Mo 2-As 3	-5.946
BD (1)Mo 2- P 4	-6.679	BD (1)Mo 2-As 4	-7.068
BD (1)Mo 1-Mo 2	-4.109	LP (2)Mo 2 †	7.585
BD*(1)Mo 1-Mo 2	1.757	LV (2)Mo 2 †	7.585
BD*(1)Mo 1- P 3	4.426	BD*(1)Mo 1-As 3	1.846
BD*(1)Mo 1- P 4	5.205	BD*(1)Mo 1-As 4	1.652
BD*(1)Mo 2- P 3	5.203	BD*(1)Mo 2-As 3	1.652
BD*(1)Mo 2- P 4	4.423	BD*(1)Mo 2-As 4	1.846
BD*(1) P 3- P 4	3.500	BD*(1)As 3-As 4	1.411

† for [Cp_2Mo_2(CO)4(η^2−P_2)] (**B**) we were unable to localize the Mo-Mo bond. Corresponding orbital, though having density on both Molybdenum atoms, was designated as molybdenum lone pair (LP and LV respectively).

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