

Chemistry–A European Journal

Supporting Information

Synthesis of Tetrahedranes Containing the Unique Bridging Hetero-Dipnictogen Ligand EE' ($E \neq E' = P, As, Sb, Bi$)

Luis Dütsch, Christoph Riesinger, Gábor Balázs, and Manfred Scheer*

Contents

General considerations.....	2
Experimental details.....	2
Synthesis of the complexes of the type $[\{\text{CpMo}(\text{CO})_2\}_2(\mu,\eta^2:\eta^2\text{-EE}')] (EE' = \text{PAs (1), PSb (2), AsSb (3a), AsBi (4), SbBi (5)})$ and $[\{\text{CpMo}(\text{CO})_2\}_2(\mu,\eta^2:\eta^2\text{-E}_2)] (E = \text{P ("Mo}_2\text{P}_2"), \text{As ("Mo}_2\text{As}_2"), \text{Sb ("Mo}_2\text{Sb}_2"), \text{Bi ("Mo}_2\text{Bi}_2"))$ – General procedure.....	2
Synthesis of 1 using NaPH_2	7
Synthesis of the complexes $[\{\text{Cp}'\text{Mo}(\text{CO})_2\}_2(\mu,\eta^2:\eta^2\text{-EE}')] (EE' = \text{AsSb (3b), As}_2\text{ (7), Sb}_2\text{ (8); Cp}' = \eta^5\text{-C}_5\text{H}_4\text{tBu})$ – General procedure.....	7
Synthesis of the intermediates $\text{M}[\{\text{CpMo}(\text{CO})_2\}_2\{\mu,\eta^2\text{-E}(\text{SiMe}_3)_2\}]$ (6a-d) for X-ray analysis	10
NMR spectra	12
IR Spectra.....	22
X-ray crystallography.....	23
Details of DFT Calculations	32
References.....	42

General considerations

All manipulations were carried out under an inert atmosphere of dried nitrogen/argon using standard Schlenk and glovebox techniques. The starting materials $[\text{CpMo}(\text{CO})_2]_2$,^[1] $[\text{Cp}'\text{Mo}(\text{CO})_2]_2$,^[2] $\text{LiP}(\text{SiMe}_3)_2$,^[3] $\text{LiAs}(\text{SiMe}_3)_2$,^[4] $\text{MSb}(\text{SiMe}_3)_2$ ($\text{M} = \text{Li}, \text{K}$),^[5] $\text{KBi}(\text{SiMe}_3)_2$ ^[6] and NaPH_2 ^[7] were synthesized via the respective literature procedures. The reagents PCl_3 , AsCl_3 , SbCl_3 , BiCl_3 and the crown-ethers (12-crown-4 and 18-crown-6) are commercially available and were used after purification by distillation or sublimation, respectively. Solvents were freshly distilled under nitrogen after drying over CaH_2 (CH_2Cl_2 , CD_2Cl_2), or over K or Na/K alloy (alkanes, THF = tetrahydrofuran). Dried solvents were also taken from a solvent purification system from MBraun. Silica for column chromatography was dried under vacuum at 200 °C for 7 days. NMR spectra were recorded on a Bruker Avance 300 MHz NMR spectrometer (^1H : 300.132 MHz, ^{31}P : 121.495 MHz, ^{13}C : 75.468 MHz) or a Bruker Avance 400 MHz NMR spectrometer (^1H : 400.130 MHz, ^{31}P : 161.976 MHz, ^{13}C : 100.613 MHz) with external references of SiMe_4 (^1H , ^{13}C) and H_3PO_4 (85%, ^{31}P). The chemical shifts δ are presented in parts per million (ppm) and coupling constants J in Hz. The measurements were performed at 300 K. LIFDI-MS and FD-MS spectra were measured on a Jeol AccuTOF GCX by the mass spectrometry department of the University of Regensburg. The respective molecular ion peaks of the desired products **1–8** are assigned as $[\text{M}^+]$ in each case. IR spectra were recorded either as solids using a ThermoFisher Nicolet iS5 FT-IR spectrometer with an iD7 ATR module and an ITX Germanium or ITX Diamond crystal, or grinded together with dried KBr and pressed to pellets and measured on a VARIAN FTS-800 FR-IR spectrometer. Elemental analyses (EA) were performed by the micro analytical laboratory of the University of Regensburg.

Experimental details

Synthesis of the complexes of the type $[\{\text{CpMo}(\text{CO})_2\}_2(\mu,\eta^2:\eta^2\text{-EE}')]$ ($\text{EE}' = \text{PAs}$ (1**), PSb (**2**), AsSb (**3a**), AsBi (**4**), SbBi (**5**)) and $[\{\text{CpMo}(\text{CO})_2\}_2(\mu,\eta^2:\eta^2\text{-E}_2)]$ ($\text{E} = \text{P}$ (" Mo_2P_2 "), As (" Mo_2As_2 "), Sb (" Mo_2Sb_2 "), Bi (" Mo_2Bi_2 ") – General procedure**

The synthesis for all complexes of the type $[\{\text{CpMo}(\text{CO})_2\}_2(\mu,\eta^2:\eta^2\text{-EE}')]$ are similar and, therefore, a general procedure is provided. The data (amount of substances, colour changes, work-up methods and yields) for the specific reactions are given in Table S1.

Dark orange-brown solutions of $[\text{Cp}(\text{CO})_2\text{Mo}]_2$ (**A**) in 30 mL THF were reacted with $\text{LiP}(\text{SiMe}_3)_2$ (**E1**), $\text{LiAs}(\text{SiMe}_3)_2$ (**E2**), $\text{KSb}(\text{SiMe}_3)_2$ (**E3**) or $\text{KBi}(\text{SiMe}_3)_2$ (**E4**), respectively, in 10 mL THF leading to colour changes to dark greenish red (**E1**, **E2**), dark greenish brown (**E3**) or dark bronze-coloured (**E4**). These solutions were stirred for 30 minutes. Subsequently, $\text{E}'\text{Cl}_3$ ($\text{E}' = \text{P}, \text{As}, \text{Sb}, \text{Bi}$) was added, either as pure liquid (PCl_3 and AsCl_3) or dissolved in 10 mL THF (SbCl_3 and BiCl_3), and stirred for another 30 minutes. After evaporation of the solvent, the residue was mixed with silica, redissolved in 10 mL CH_2Cl_2 and evaporated to dryness. The free-flowing powder was subjected to a column chromatography (silica, 20x4 cm). Elution with a mixture of *n*-hexane and toluene (3:1) leads to a orange red (**1**, **2**), red (**3a**) or dark red (**4**, **5**) fraction containing the desired tetrahedral compounds. For Mo_2P_2 and Mo_2As_2 sometimes a small yellow fraction can be observed, which

elutes already with pure *n*-hexane or *n*-pentane, containing the respective **MoE₃** compounds [CpMo(CO)₂(η³-E₃)]. The solvent of the main fraction was removed *in vacuo* and the residue dried in vacuum for 3 hours. Crystals suitable for single crystal X-ray diffraction analyses could be obtained by cooling saturated CH₂Cl₂ solutions from room temperature to -30 °C.

Table S1: Data for the syntheses of the complexes **Mo₂P₂**, **Mo₂As₂**, **Mo₂Sb₂**, **Mo₂Bi₂**, **1**, **2**, **3a**, **4** and **5**.

Product	Amount of A	Amount of ME(SiMe ₃) ₂	Amount of E'Cl ₃	Colour change after 2 nd reaction step	Column chromatography	Yield
Mo₂P₂	5.60 g 12.9 mmol 1.0 eq.	<u>LiP(SiMe₃)₂(thf)_{1.6}</u> 3.80 g 12.7 mmol 1.0 eq.	<u>PCl₃</u> 1.2 mL 13.7 mmol 1.1 eq.	dark orange red	orange fraction	3.56 g (7.2 mmol = 57 %)
Mo₂As₂	4.00 g 9.2 mmol 1.0 eq.	<u>LiAs(SiMe₃)₂(thf)_{1.6}</u> 3.10 g 9.0 mmol 1.0 eq.	<u>AsCl₃</u> 0.8 mL 9.5 mmol 1.0 eq.	dark orange red	orange red fraction	2,7 g (4.7 mmol = 52 %)
Mo₂Sb₂	1.00 g 2.3 mmol 1.0 eq.	<u>KSb(SiMe₃)₂(thf)_{0.4}</u> 724 mg 2.15 mmol 0.95 eq.	<u>SbCl₃</u> 525 mg 2.3 mmol 1.0 eq.	dark red	red fraction	526 mg (0.8 mmol = 37 %)
Mo₂Bi₂	2.00 g 4.57 mmol 1.0 eq.	<u>KBi(SiMe₃)₂(thf)_{0.3}</u> 1.90 g 4.95 mmol 1.1 eq.	<u>BiCl₃</u> 1.43 g 4.57 mmol 1.0 eq.	dark brown	brown fraction	965 mg (1.1 mmol = 25 %)
1 – Method A –	556 mg 1.28 mmol 1.2 eq.	<u>LiP(SiMe₃)₂(thf)_{1.6}</u> 384 mg 1.28 mmol 1.2 eq.	<u>AsCl₃</u> 0.09 mL 1.07 mmol 1.0 eq.	dark orange red	orange red fraction	400 mg (0.74 mmol = 69 %)
1 – Method B –	3.30 g 7.6 mmol 1.0 eq.	<u>LiAs(SiMe₃)₂(thf)_{1.6}</u> 2.55 g 7.4 mmol 1.0 eq.	<u>PCl₃</u> 0.7 mL 8.0 mmol 1.1 eq.	dark orange red	orange red fraction	1.99 g (3.69 mmol = 50 %)
2 – Method A –	1.30 g 3.0 mmol 1.0 eq.	<u>LiP(SiMe₃)₂(thf)_{1.8}</u> 942 mg 3.0 mmol 1.0 eq.	<u>SbCl₃</u> 684 mg 3.0 mmol 1.0 eq.	dark orange red	orange red fraction	400 mg (0.74 mmol = 69 %)

Product	Amount of A	Amount of ME(SiMe ₃) ₂	Amount of E'Cl ₃	Colour change after 2 nd reaction step	Column chromatography	Yield
2 – Method B –	434 mg 1.0 mmol 1.0 eq.	<u>KSb(SiMe₃)₂(thf)_{1.8}</u> 437 mg 1.0 mmol 1.0 eq.	<u>P</u> Cl ₃ 87 μL 1.0 mmol 1.0 eq.	dark orange red	orange red fraction	105 mg (0.18 mmol = 18 %)
3a – Method A –	434 mg 1.0 mmol 1.0 eq.	<u>LiAs(SiMe₃)₂(thf)_{1.8}</u> 358 mg 1.0 mmol 1.0 eq.	<u>Sb</u> Cl ₃ 181 mg 1.0 mmol 1.0 eq.	dark red	red fraction	298 mg (0.51 mmol = 51 %)
3a – Method B –	152 mg 0.35 mmol 1.0 eq.	<u>KSb(SiMe₃)₂</u> 107 mg 0.35 mmol 1.0 eq.	<u>As</u> Cl ₃ 0.03 mL 0.35 mmol 1.0 eq.	dark red	red fraction	136 mg (0.22 mmol = 63 %)
4 – Method A –	174 mg 0.4 mmol 1.0 eq.	<u>LiAs(SiMe₃)₂(thf)_{1.8}</u> 143 mg 0.4 mmol 1.0 eq.	<u>Bi</u> Cl ₃ 126 mg 0.4 mmol 1.0 eq.	dark red	dark red	166 mg (0.23 mmol = 58 %)
4 – Method B –	A + KBi(SiMe₃)₂(thf)_{0.3} + AsCl₃ unsuccessful (only traces of Mo₂As₂ and MoAs₃)!					
5 – Method A –	217 mg 0.50 mmol 1.0 eq.	<u>KSb(SiMe₃)₂(thf)_{0.4}</u> 168 mg 0.50 mmol 1.0 eq.	<u>Bi</u> Cl ₃ 173 mg 0.55 mmol 1.1 eq.	dark red brown	dark red fraction	136 mg (0.22 mmol = 63 %)
5 – Method B –	A + KBi(SiMe₃)₂(thf)_{0.3} + SbCl₃ unsuccessful!					
Mo₂PBi	A + LiP(SiMe₃)₂(thf)_{1.6} + BiCl₃ unsuccessful!					
	A + KBi(SiMe₃)₂(thf)_{0.3} + PCl₃ unsuccessful!					

Analytical Data:

Mo₂P₂:^[8]

¹H NMR (CD₂Cl₂): δ /ppm = 5.20 (s, Cp)

³¹P NMR (CD₂Cl₂): δ /ppm = -43.7 (s, P₂), -351.9 (traces, [CpMo(CO)₂(η^3 -P₃)])

Mo₂As₂:^[9]

¹H NMR (acetone-d₆): δ /ppm = 5.36 (s, Cp)

Mo₂Sb₂:^[10]

EA: calcd. (%) for [C₁₄H₁₀Mo₂O₄Sb₂]: C: 24.81, H: 1.49

found (%): C: 24.92, H: 1.47

FD-MS (THF): Cation *m/z* (%): 677.57 (100) [**M**⁺]

Mo₂Bi₂:^[11]

FD-MS (toluene): Cation *m/z* (%): 851.79 (100) [**M**⁺]

Mo₂PAs (1):^[12]

¹H NMR (CD₂Cl₂): δ /ppm = 5.20 (s, Cp)

¹H NMR (C₆D₆): δ /ppm = 4.51 (s, Cp)

³¹P NMR (C₆D₆/CD₂Cl₂): δ /ppm = 30.2 (s, **1**),

³¹P NMR (C₆D₆): δ /ppm = 34.5 (s, **1**), -44.5 (traces, **Mo₂P₂**)

³¹P NMR (CD₂Cl₂): δ /ppm = 30.1 (s, **1**), -43.2 (traces < 5 %, **Mo₂P₂**)

¹³C{¹H} NMR (CD₂Cl₂): δ /ppm = 85.87 (s, Cp), 226.37 (s, CO), 226.85 (s, CO)

ESI-MS (MeCN/H₂O): Cation *m/z* (%) = 485.8 (33) [**M**⁺-2·CO], 457.8 (100) [**M**⁺-3·CO], 429.8 (55) [**M**⁺-4·CO]

EA: calcd. (%) for [C₁₄H₁₀Mo₂O₄PAs]: C: 30.90, H: 1.85

found (%): C: 30.80, H: 1.95

IR (KBr): $\tilde{\nu}$ /cm⁻¹ = 2058 (w), 1946 (vs), 1900 (vs), 1420 (w), 1060 (vw), 1007 (w), 819 (m), 567 (m), 531 (m), 498 (m), 456 (m)

Mo₂PSb (2):^[12]

¹ H NMR (CD ₂ Cl ₂):	δ/ppm = 5.18 (s, Cp), 5.23 (traces, Cp of Mo₂P₂)
¹ H NMR (CDCl ₃):	δ/ppm = 5.15 (s, Cp), 5.21 (traces, Cp of Mo₂P₂)
¹ H NMR (C ₆ D ₆):	δ/ppm = 4.48 (s, Cp), 4.54 (traces, Cp of Mo₂P₂)
³¹ P NMR (CD ₂ Cl ₂):	δ/ppm = 90.7 (s, 1), -43.1 (traces < 5 %, Mo₂P₂)
³¹ P NMR (CDCl ₃):	δ/ppm = 90.9 (s, 1), -47.0 (traces < 3 %, Mo₂P₂)
³¹ P NMR (C ₆ D ₆):	δ/ppm = 98.8 (s, 1), -44.4 (traces < 5 %, Mo₂P₂)
EA:	calcd. (%) for [C ₁₄ H ₁₀ Mo ₂ O ₄ PSb]: C: 28.63, H: 1.72
	found (%): C: 29.20, H: 1.80
FD-MS (toluene):	Cation <i>m/z</i> (%): 585.75 (100) [M ⁺]

"Mo₂PBi":

FD-MS (toluene):	Cation <i>m/z</i> (%): 495.77 (100) [Mo₂P₂], 467.82 (68) [Mo₂P₂-CO], several unidentified decomposition products
³¹ P{ ¹ H} NMR (CD ₂ Cl ₂):	δ/ppm = -43.3 (Mo₂P₂)

Mo₂AsSb (3a):

¹ H NMR (CDCl ₃):	δ/ppm = 5.11 (s, Cp), 5.14/5.30 (traces, Cp of Mo₂As₂/Mo₂Sb₂)
¹³ C{ ¹ H} NMR (CDCl ₃):	δ/ppm = 83.51 (s, Cp), 226.33 (s, CO), 226.93 (s, CO)
EA:	calcd. (%) for [C ₁₄ H ₁₀ Mo ₂ O ₄ AsSb]·(toluene) _{0.06} : C: 27.22, H: 1.66
	found (%): C: 27.34, H: 1.62
FD-MS (toluene):	Cation <i>m/z</i> (%): 629.70 (100) [M ⁺], 677.67 (3) [Mo₂Sb₂], 583.71 (14) [Mo₂As₂]

Mo₂AsBi (4):

¹ H NMR (CD ₂ Cl ₂):	δ/ppm = 5.13 (s, Cp)
¹³ C{ ¹ H} NMR (CD ₂ Cl ₂):	δ/ppm = 83.08 (s, Cp), 84.53 (s, traces, Cp of Mo₂As₂), 225.35 (s, CO), 226.49 (s, CO)
EA:	calcd. (%) for [C ₁₄ H ₁₀ Mo ₂ O ₄ AsBi]·(toluene) _{0.05} : C: 23.85, H: 1.45

	found (%):	C: 23.95, H: 1.30
FD-MS (toluene):	Cation m/z (%):	717.74 (100) [\mathbf{M}^+], 583.65 (5) [$\mathbf{Mo}_2\mathbf{As}_2$]

Mo₂SbBi (5):

¹H NMR (CD₂Cl₂): δ /ppm = 5.07 (traces, s, Cp of **Mo₂Bi₂**) 5.09 (s, Cp), 5.10 (traces, s, Cp of **Mo₂Sb₂**)

¹³C{¹H} NMR (CD₂Cl₂): δ /ppm = 81.49 (s, traces, Cp of **Mo₂Bi₂**), 81.93 (s, Cp), 82.50 (s, traces, Cp of **Mo₂Sb₂**), 226.31 (s, CO), 226.92 (s, CO)

EA: calcd. (%) for [C₁₄H₁₀Mo₂O₄SbBi]·(toluene)_{0.15}: C: 23.21, H: 1.45

found (%): C: 23.26, H: 1.30

FD-MS (toluene): Cation m/z (%): 763.65 (100) [\mathbf{M}^+], 677.57 (31) [**Mo₂Sb₂**]

Synthesis of 1 using NaPH₂

A dark orange-brown solution of [Cp(CO)₂Mo]₂ (**A**; 2.0 g, 4.61 mmol, 1 eq.) in 30 mL THF was reacted with NaPH₂ (280 mg, 5.00 mmol, 1 eq.) in 50 mL THF leading to a colour change to dark purple. The solution was stirred for 30 minutes. Subsequently, AsCl₃ (0.45 mL, 4.60 mmol, 1 eq.) was added as a pure liquid. The resulting orange suspension was stirred for another 15 hours. After evaporation of the solvent, the residue was mixed with silica, redissolved in 10 mL CH₂Cl₂ and evaporated to dryness. The free-flowing powder was subjected to a column chromatography (silica, 30 x 3.5 cm). Elution with a mixture of *n*-hexane and CH₂Cl₂ (1:1) leads to an orange red fraction containing **1**. An additional orange fraction could be observed, which could not be further characterised. The solvent was removed and the residue dried in vacuum for 3 hours.

Yield 398 mg (0.75 mmol, 16.4 %)

³¹P NMR (C₆D₆) δ /ppm = 33.7 (traces of [{CpMo(CO)₂]₂(μ -H)(μ -PH₂)}), 34.7 (s, **1**)

Synthesis of the complexes [{Cp'Mo(CO)₂]₂(μ , η^2 : η^2 -EE')] (EE' = AsSb (3b**), As₂ (**7**), Sb₂ (**8**); Cp' = η^5 -C₅H₄^tBu) – General procedure**

The synthesis for the complexes **3b**, **7** and **8** are similar and, therefore, a general procedure is provided. The data (amount of substances, colour changes, work-up method and yield) for the specific reactions are given in Table S2.

Dark orange-brown solutions of [Cp'(CO)₂Mo]₂ in 30 mL THF were reacted with LiAs(SiMe₃)₂ (**E2**) or LiSb(SiMe₃)₂ (**E3**), respectively, in 10 mL THF leading to colour changes to dark greenish red (**E2**) or dark greenish brown (**E3**). These solutions were stirred for 30 minutes. Subsequently, E'Cl₃ (E' = As, Sb) was added, either as pure liquid (AsCl₃) or dissolved in 10 mL THF (SbCl₃), and stirred for another 30 minutes. After

evaporation of the solvent, the residue was mixed with silica, redissolved in 10 mL CH₂Cl₂ and evaporated to dryness. The free-flowing powder was subjected to a column chromatography (silica, 20x4 cm). Elution with a mixture of *n*-hexane and toluene (5:1) leads to a fraction containing the desired tetrahedral compounds. In the case of **7** a yellow first fraction can be observed, which eluates already with pure *n*-pentane, containing the respective **MoE₃** compound [Cp'¹Mo(CO)₂(η³-As₃)]. The solvent was removed *in vacuo* and the residue dried in vacuum for 3 hours. Crystals suitable for single crystal X-ray diffraction analyses could be obtained by cooling saturated CH₂Cl₂ solutions from room temperature to -30 °C.

Table S2: Data for the syntheses of the complexes **3b**, **7** and **8**; dme = dimethoxyethane.

Product	Amount of [Cp' ¹ (CO) ₂ Mo] ₂	Amount of ME(SiMe ₃) ₂	Amount of E' ¹ Cl ₃	Colour change after 2 nd reaction step	Column chromatography	Yield
3b	500 mg 0.9 mmol 1.0 eq.	<u>LiAs(SiMe₃)₂(thf)_{2,3}</u> 355 mg 0.9 mmol 1.0 eq.	<u>SbCl₃</u> 204 mg 0.9 mmol 1.0 eq.	dark orange red	dark red fraction	325 mg (0.44 mmol = 49 %)
7	2.00 g 3.66 mmol 1.0 eq.	<u>LiAs(SiMe₃)₂(thf)_{2,0}</u> 1.44 g 3.84 mmol 1.05 eq.	<u>AsCl₃</u> 0.32 mL 3.84 mmol 1.05 eq.	dark orange red	dark red fraction	1.40 g (2.01 mmol = 55 %)
8	500 mg 0.9 mmol 1.0 eq.	<u>LiSb(SiMe₃)₂(dme)</u> 328 mg 0.9 mmol 1.0 eq.	<u>SbCl₃</u> 226 mg 1.0 mmol 1.1 eq.	dark orange red	dark red fraction	208 mg (0.26 mmol = 29 %)

Analytical Data:

(Cp'¹)Mo₂AsSb (**3b**):

¹H NMR (CD₂Cl₂): δ/ppm = 1.27 (s, tBu, 18H), 5.00 (m, Cp, 2H), 5.06 (m, Cp, 4H), 5.15 (m, Cp, 2H)

¹³C{¹H} NMR (CD₂Cl₂): δ/ppm = 31.77 (s, tBu (quart.)), 32.03 (s, tBu (Me)), 81.63 (s, Cp (C-H)), 82.74 (s, Cp (C-H)), 83.11 (s, Cp (C-H)), 83.90 (s, Cp (C-H)), 118.26 (s, Cp (quart.)), 228.03 (s, CO), 228.51 (s, CO)

EA: calcd. (%) for [C₂₂H₂₆Mo₂O₄AsSb]: C: 35.56, H: 3.53
found (%): C: 35.70, H: 3.41

FD-MS (toluene): Cation *m/z* (%): 741.79 (100) [M⁺], 695.81 (9) [Cp'₂(CO)₄Mo₂As₂]

(Cp')Mo₂As₂ (7):

¹H NMR (C₆D₆): δ/ppm = 1.06 (s, tBu, 18H), 4.61 (t, 2.4 Hz, Cp, 4H), 4.75 (t, 2.4 Hz, Cp, 4H)

¹³C{¹H} NMR (C₆D₆): δ/ppm = 31.3 (s, tBu (quart.)), 31.8 (s, tBu (Me)), 83.0 (s, Cp (C-H)), 84.8 (s, Cp (C-H)), 119.0 (s, Cp (quart.)), 228.5 (s, CO)

EA: calcd. (%) for [C₂₂H₂₆As₂Mo₂O₄]: C: 37.96, H: 3.76
found (%): C: 37.42, H: 3.5

FD-MS (CH₂Cl₂): Cation *m/z* (%): 695.86 (100) [M⁺]; 789.72 (58) [Cp'₂Mo₂As₄(CO)₂]

IR (ATR): $\tilde{\nu}/\text{cm}^{-1}$ = 3098 (w), 2955 (m), 2864 (w), 1965 (vs), 1934 (vs), 1893 (vs), 1872 (vs), 1478 (m), 1461 (m), 1444 (w), 1398 (w), 1360 (m), 1269 (m), 1197 (w), 1148 (m), 1060 (w), 1040 (w), 1019 (w), 921 (w), 906 (w), 880 (w), 842 (m), 830 (m), 815 (s), 801 (s), 673 (w)

(Cp')Mo₂Sb₂ (8):

¹H NMR (C₆D₆): δ/ppm = 1.08 (s, tBu, 9H), 4.43 (t, 2.4 Hz, Cp, 2H), 4.75 (t, 2.4 Hz, Cp, 2H)

¹³C{¹H} NMR (C₆D₆): δ/ppm = 31.4 (s, tBu (quart.)), 31.9 (s, tBu (Me)), 81.1 (s, Cp (C-H)), 81.4 (s, Cp (C-H)), 116.8 (s, Cp (quart.)), 228.7 (s, CO)

EA: calcd. (%) for [(C₉H₁₃)(CO)₂Mo]₂Sb₂: C: 33.45, H: 3.32
found (%): C: 33.61, H: 3.34

LIFDI-MS (toluene): Cation *m/z* (%): 789.78 (100) [M⁺]

IR (ATR): $\tilde{\nu}/\text{cm}^{-1}$ = 2983 (w), 2965 (w), 2943 (w), 2902 (w), 1918 (vs), 1890 (vs), 1866 (vs), 1842 (w), 1476 (w), 1462 (w), 1443 (w), 1400 (w), 1362 (w), 1269 (w), 1147 (w), 1058 (w), 1041 (w), 1020 (w), 904 (w), 883 (w), 842 (w), 831 (w), 818 (w), 804 (w), 682 (w)

Synthesis of the intermediates $M\{[CpMo(CO)_2]_2\{\mu,\eta^2-E(SiMe_3)_2\}\}$ (**6a-d**) for X-ray analysis

The syntheses of crystalline sample of the salts **6a-d** are similar and, therefore, a general procedure is provided. The amount of substances, which are used in the specific reactions are given in Table S3.

Dark orange-brown solutions of $[Cp(CO)_2Mo]_2$ (**A**) in 5 mL THF were reacted with $LiP(SiMe_3)_2$ (**E1**), $LiAs(SiMe_3)_2$ (**E2**), $KSb(SiMe_3)_2$ (**E3**) or $KBi(SiMe_3)_2$ (**E4**), respectively, in 5 mL THF leading to colour changes to dark greenish red (**E1, E2**), dark greenish brown (**E3**) or dark bronze-coloured (**E4**). To this solution the respective crown-ether was added, either as a stock solution in DME (12-crown-4 for Li) or as a solid dissolved in 5 mL THF (18-crown-6 for K). After stirring for 30 minutes the solution was layered with *n*-hexane and stored at -30 °C under exclusion from light. After several days the products **6a-c** can be obtained as crystals suitable for single crystal X-ray diffraction. Crystallisation of **6d**, however, was unsuccessful, maybe due to low stability of **6d**.

For NMR characterization of **6a** compound **A** (84 mg, 0.2 mmol) and $LiP(SiMe_3)_2(thf)_{1.6}$ (65 mg, 0.2 mmol) are both solved in 15 mL toluene and the solutions were combined. After few minutes, **6a** precipitates and the slightly orange coloured mother liquid was decanted off. The residue was dried for 10 minutes and subjected to 1H , ^{31}P and $^{31}P\{^1H\}$ NMR spectroscopy without further purification (Figure S15-S17).

Table S3: Data for the syntheses of the complexes **6a-d** for X-ray analysis.

Product	Amount of A	Amount of $ME(SiMe_3)_2$	Amount of crown-ether
6a	87 mg 0.2 mmol 1.0 eq.	<u>$LiP(SiMe_3)_2(thf)_{2.3}$</u> 65 mg 0.2 mmol 1.0 eq.	<u>12-crown-4</u> 0.25 mL of a 0.81 M solution in DME 0.2 mmol 1.0 eq.
6b	87 mg 0.2 mmol 1.0 eq.	<u>$LiAs(SiMe_3)_2(thf)_{1.6}$</u> 69 mg 0.2 mmol 1.0 eq.	<u>12-crown-4</u> 0.25 mL of a 0.81 M solution in DME 0.2 mmol 1.0 eq.
6c	87 mg 0.2 mmol 1.0 eq.	<u>$KSb(SiMe_3)_2$</u> 61 mg 0.2 mmol 1.0 eq.	<u>18-crown-6</u> 58 mg 0.2 mmol 1.0 eq.
6d	87 mg 0.2 mmol 1.0 eq.	<u>$KBi(SiMe_3)_2(thf)_{0.3}$</u> 83 mg 0.2 mmol 1.0 eq.	<u>18-crown-6</u> 58 mg 0.2 mmol 1.0 eq.

Analytical Data:

- 6a:** ^1H NMR (CD_2Cl_2): $\delta/\text{ppm} = 0.28$ (s, 9H, SiMe_3), 0.30 (s, 9H, SiMe_3), $1.79/3.66$ (t, 16H, two THFs coordinating the lithium cation), 5.22 (s, 10H, Cp)
- ^1H NMR (CD_3CN): $\delta/\text{ppm} = 0.18$ (s, 9H, SiMe_3), 0.20 (s, 9H, SiMe_3), $1.80/3.64$ (t, 4H, half THF coordinating the lithium cation), 4.95 (s, 10H, Cp)
- $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2): $\delta/\text{ppm} = 4.0$ (s, $\text{P}(\text{SiMe}_3)_2$), the signal is broadening in the proton coupled ^{31}P NMR spectrum upon coupling to the methyl groups of SiMe_3
- $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_3CN): $\delta/\text{ppm} = 11.4$ (s, $\text{P}(\text{SiMe}_3)_2$)
- ^{31}P NMR (CD_3CN): $\delta/\text{ppm} = 11.4$ (s, $\text{P}(\text{SiMe}_3)_2$)
- $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_3CN): $\delta/\text{ppm} = 4.07$ (s, SiMe_3), 4.15 (s, SiMe_3), 25.83 (s, THF), 67.88 (s, THF), 89.54 (s, Cp); the signals of the CO ligands were too weak and could not be observed

NMR spectra

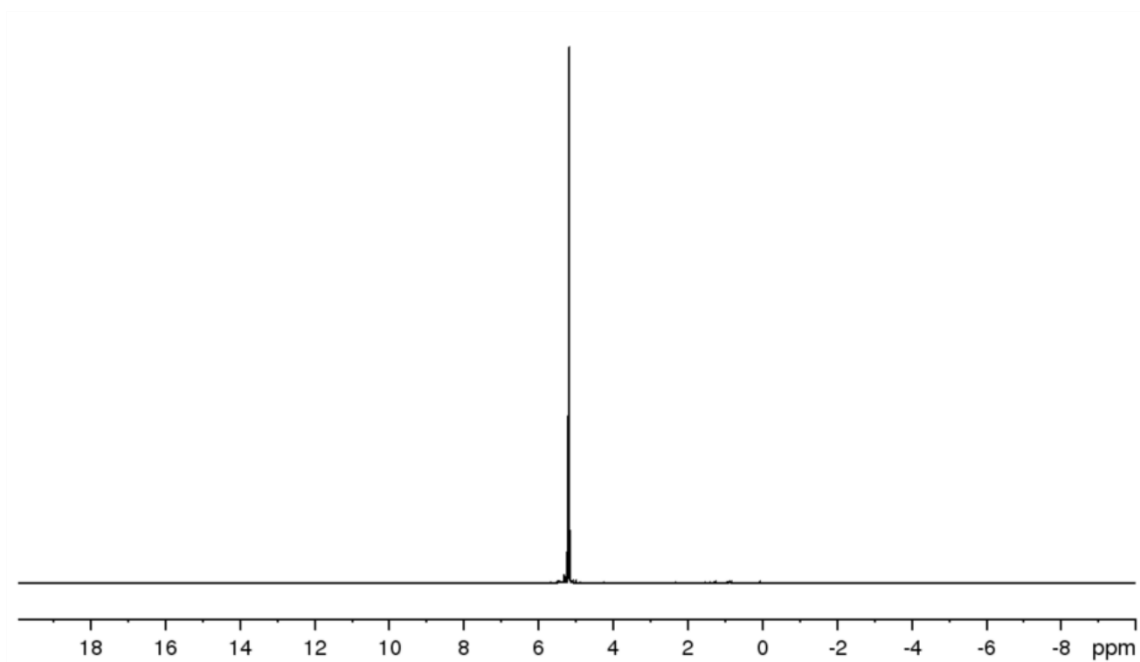


Figure S1: ^1H NMR spectrum of $[(\text{CpMo}(\text{CO})_2)_2(\mu,\eta^2:\eta^2\text{-PAs})]$ (**1**) in CD_2Cl_2 .

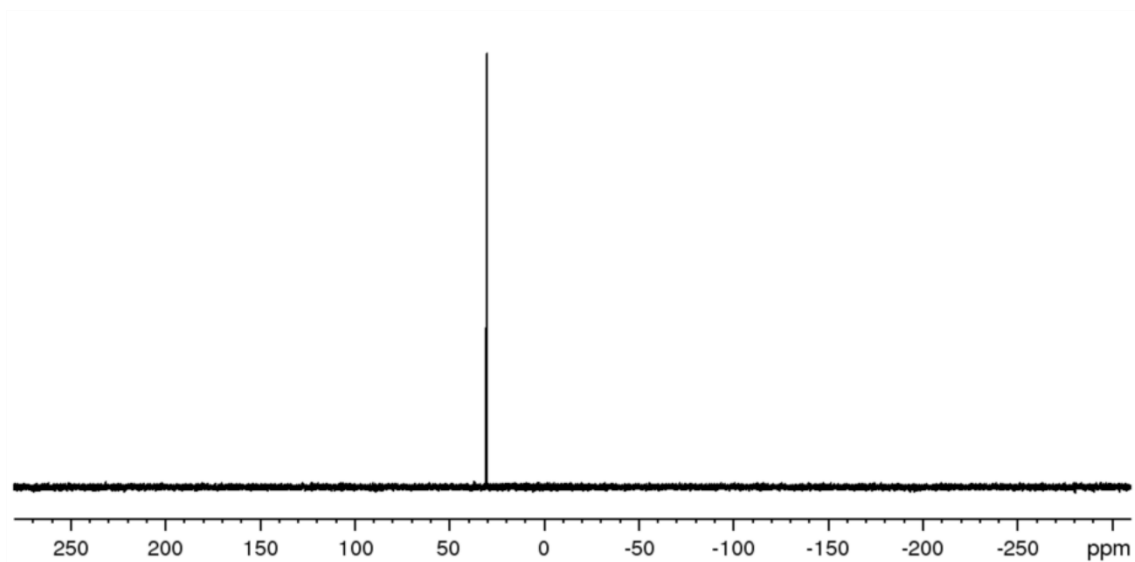


Figure S2: ^{31}P NMR spectrum of $[(\text{CpMo}(\text{CO})_2)_2(\mu,\eta^2:\eta^2\text{-PAs})]$ (**1**) in C_6D_6 .

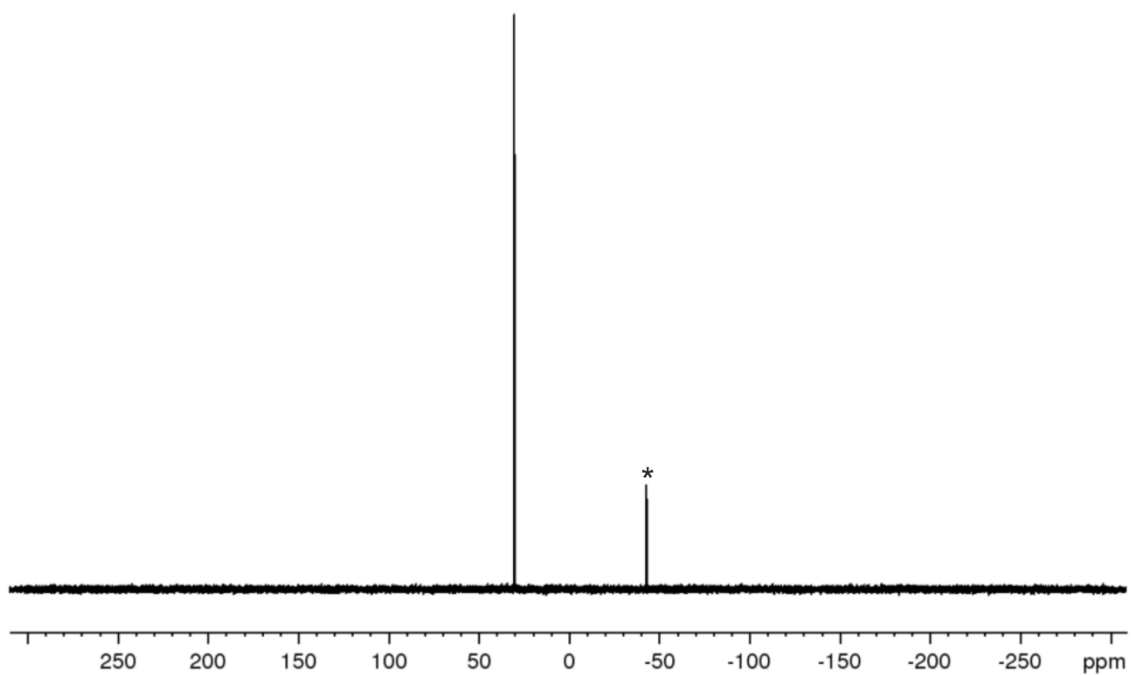


Figure S3: ^{31}P NMR spectrum of $[(\text{CpMo}(\text{CO})_2)_2(\mu,\eta^2:\eta^2\text{-PAs})]$ (**1**) in CD_2Cl_2 with additional formed traces of Mo_2P_2 (*; < 5%).

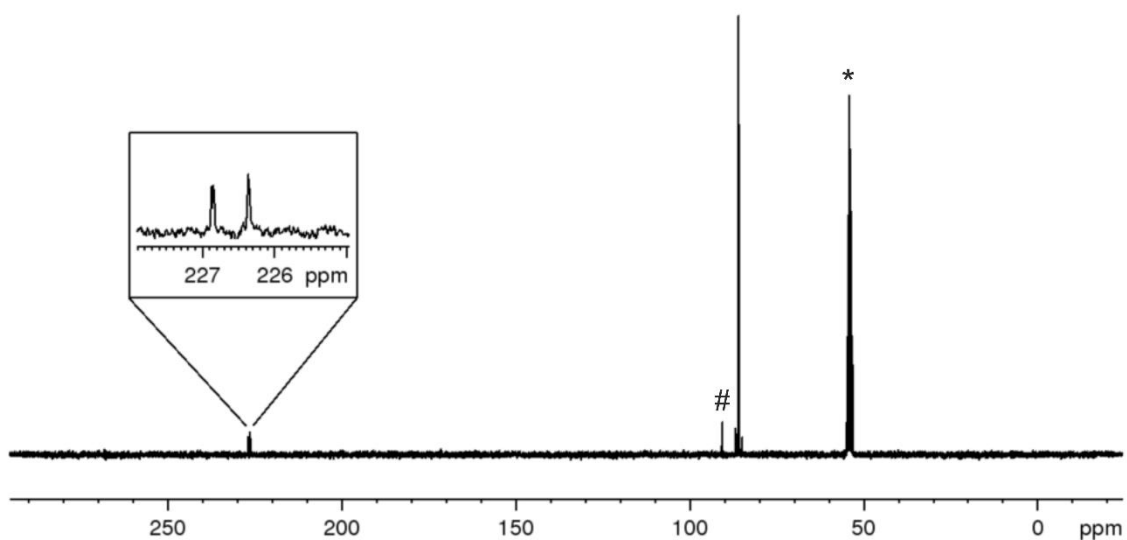


Figure S4: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of $[(\text{CpMo}(\text{CO})_2)_2(\mu,\eta^2:\eta^2\text{-PAs})]$ (**1**) in CD_2Cl_2 ; * = CD_2Cl_2 , # = Cp of traces of Mo_2P_2 .

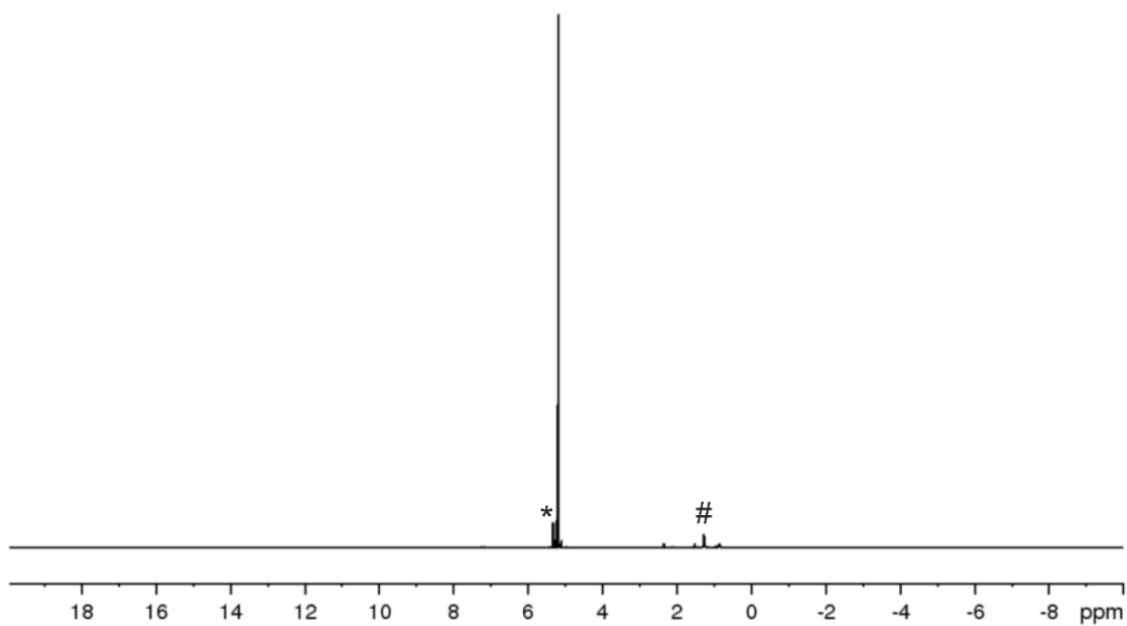


Figure S5: ^1H NMR spectrum of $[(\text{CpMo}(\text{CO})_2)_2(\mu,\eta^2:\eta^2\text{-PSb})]$ (**2**) in CD_2Cl_2 ; * = CD_2Cl_2 , # = H grease.

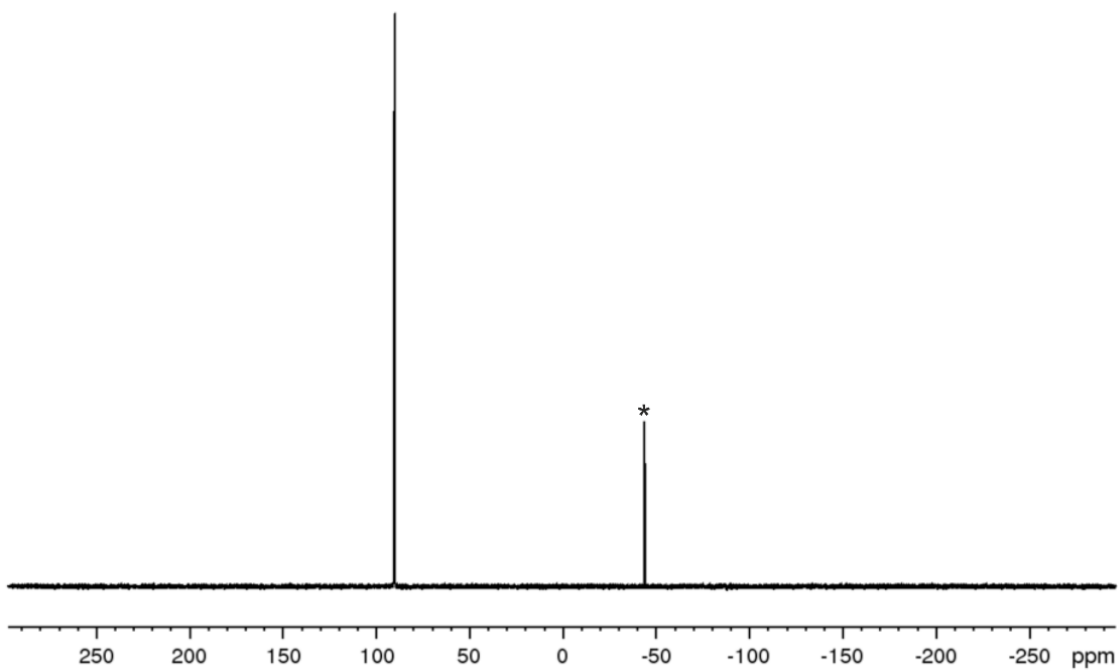


Figure S6: ^{31}P NMR spectrum of $[(\text{CpMo}(\text{CO})_2)_2(\mu,\eta^2:\eta^2\text{-PSb})]$ (**2**) in CD_2Cl_2 ; * = traces of Mo_2P_2 (< 5 %).

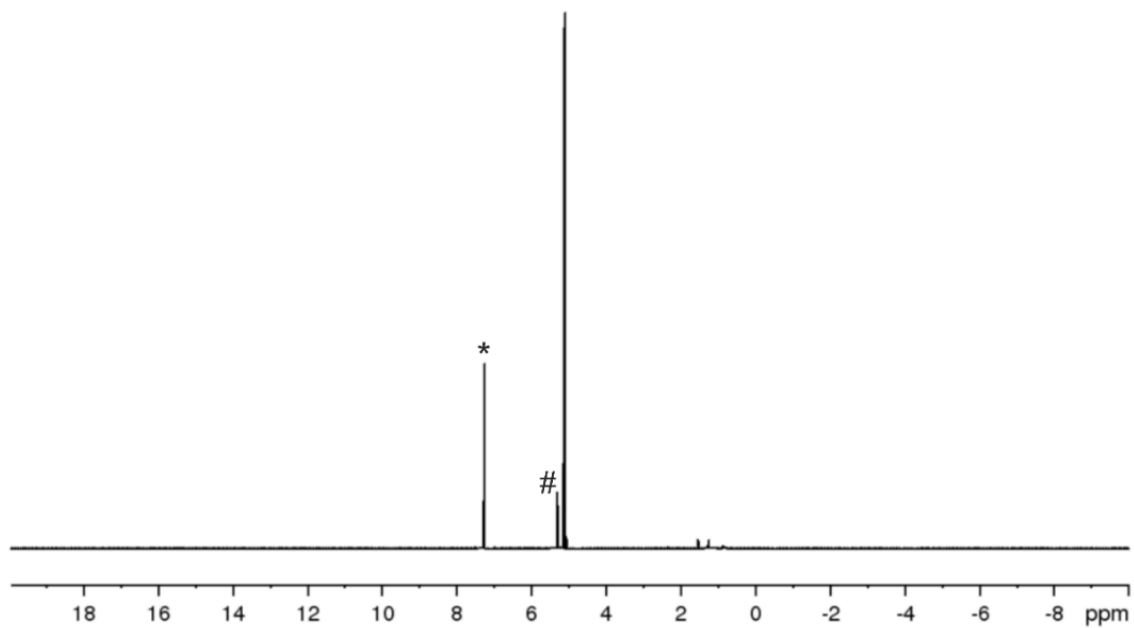


Figure S7: ^1H NMR spectrum of $[(\text{CpMo}(\text{CO})_2)_2(\mu,\eta^2:\eta^2\text{-AsSb})]$ (**3a**) in CDCl_3 ; * = CDCl_3 , # = Cp of traces of $\text{Mo}_2\text{As}_2/\text{Mo}_2\text{Sb}_2$.

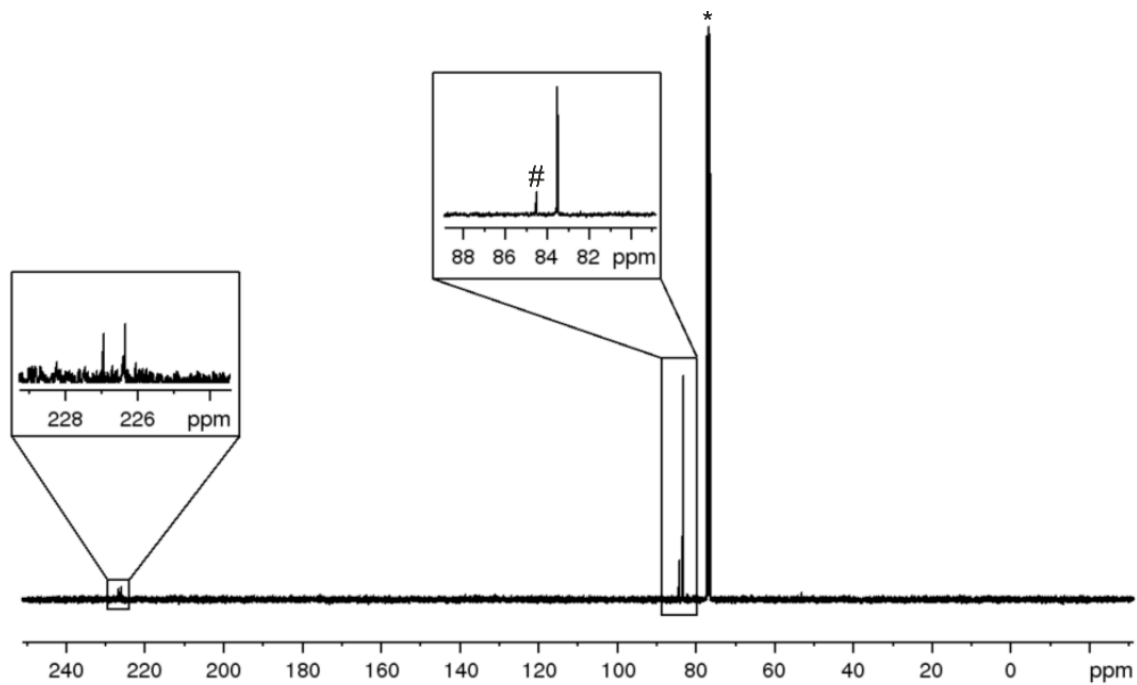


Figure S8: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of $[(\text{CpMo}(\text{CO})_2)_2(\mu,\eta^2:\eta^2\text{-AsSb})]$ (**3a**) in CDCl_3 ; * = CDCl_3 , # = Cp of traces of $\text{Mo}_2\text{As}_2/\text{Mo}_2\text{Sb}_2$.

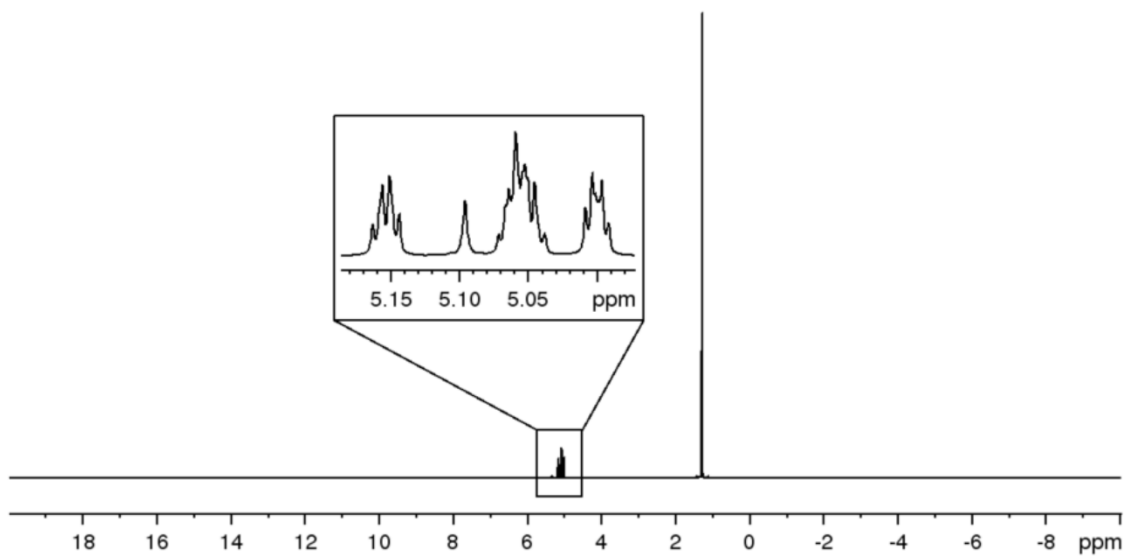


Figure S9: ^1H NMR spectrum of $[(\text{Cp}'\text{Mo}(\text{CO})_2)_2(\mu, \eta^2:\eta^2\text{-AsSb})]$ (**3b**) in CD_2Cl_2 .

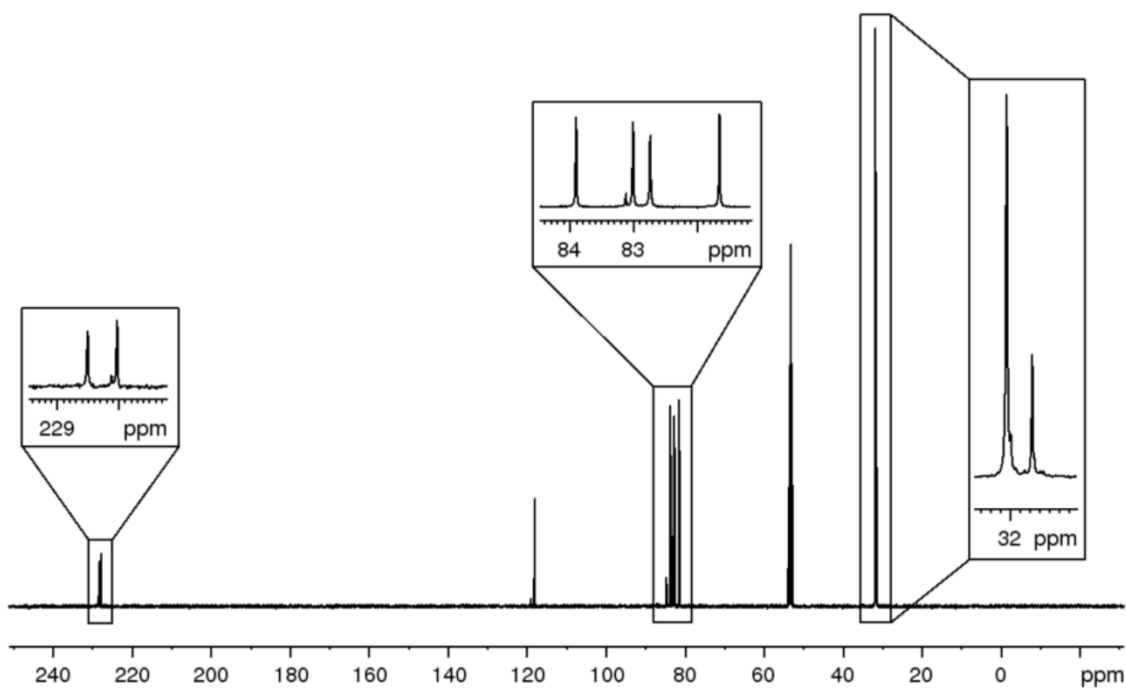


Figure S10: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of $[(\text{Cp}'\text{Mo}(\text{CO})_2)_2(\mu, \eta^2:\eta^2\text{-AsSb})]$ (**3b**) in CD_2Cl_2 .

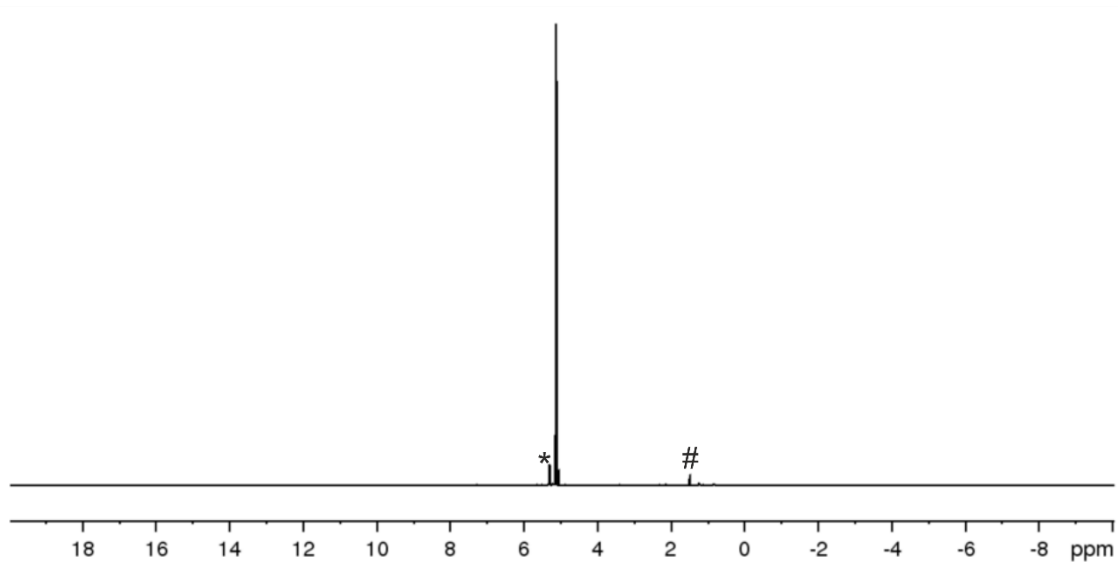


Figure S11: ^1H NMR spectrum of $[(\text{CpMo}(\text{CO})_2)_2(\mu,\eta^2:\eta^2\text{-AsBi})]$ (**4**) in CD_2Cl_2 ; * = CD_2Cl_2 , # = H_2O .

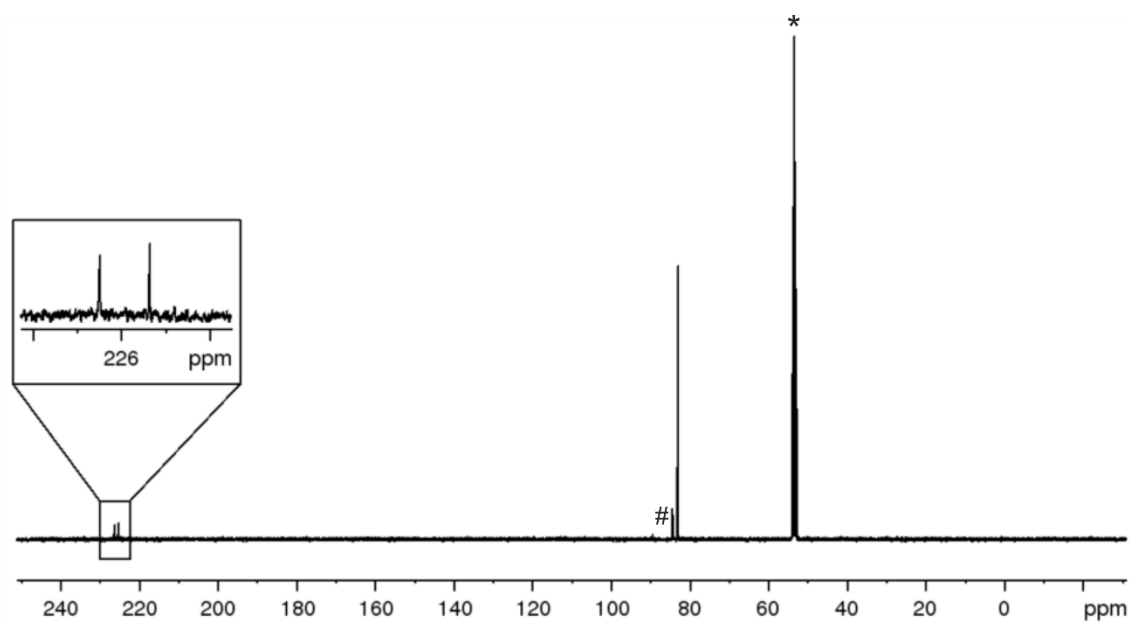


Figure S12: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of $[(\text{CpMo}(\text{CO})_2)_2(\mu,\eta^2:\eta^2\text{-AsBi})]$ (**4**) in CD_2Cl_2 ; * = CD_2Cl_2 , # = traces of Mo_2As_2 .

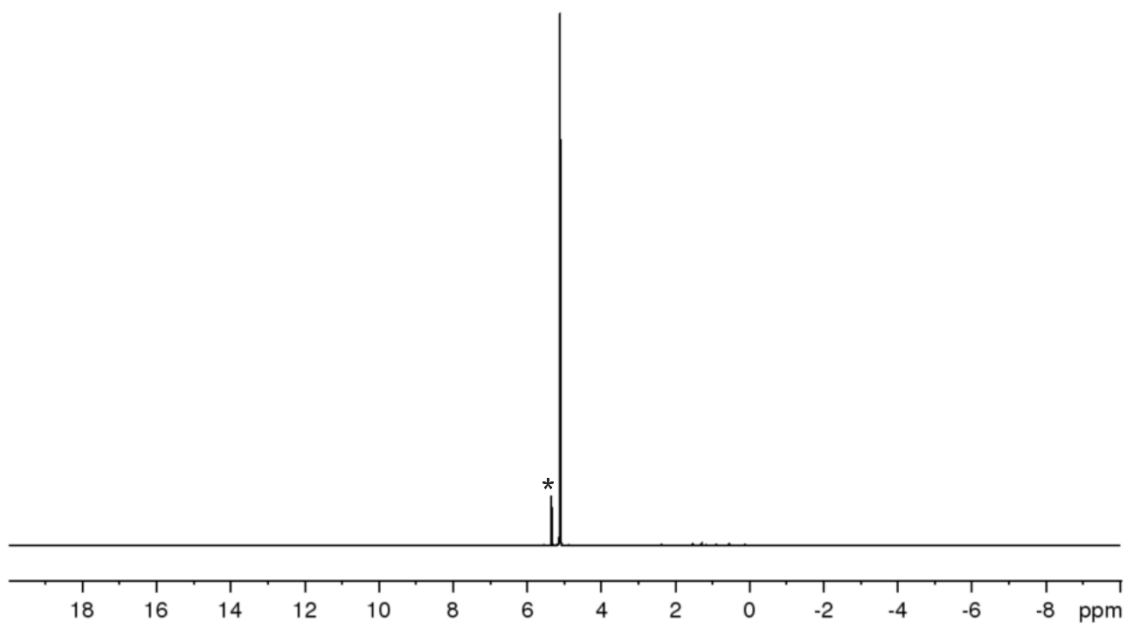


Figure S13: ^1H NMR spectrum of $[(\text{CpMo}(\text{CO})_2)_2(\mu,\eta^2:\eta^2\text{-SbBi})]$ (**5**) in CD_2Cl_2 ; * = CD_2Cl_2 .

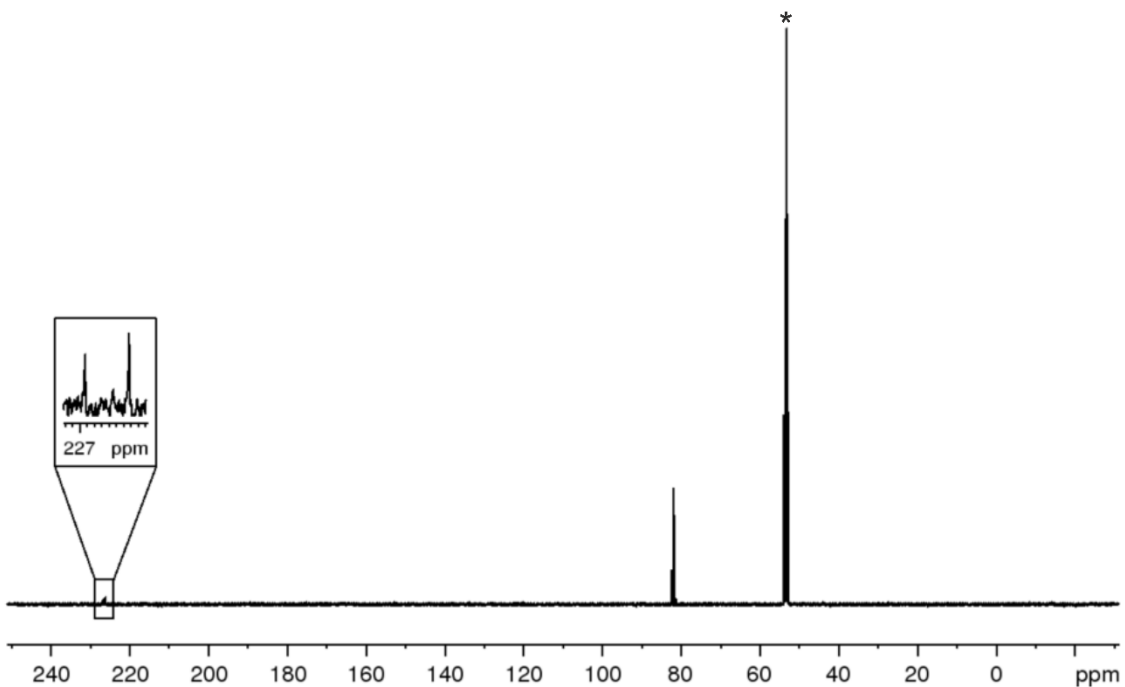


Figure S14: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of $[(\text{CpMo}(\text{CO})_2)_2(\mu,\eta^2:\eta^2\text{-SbBi})]$ (**5**) in CD_2Cl_2 ; * = CD_2Cl_2 .

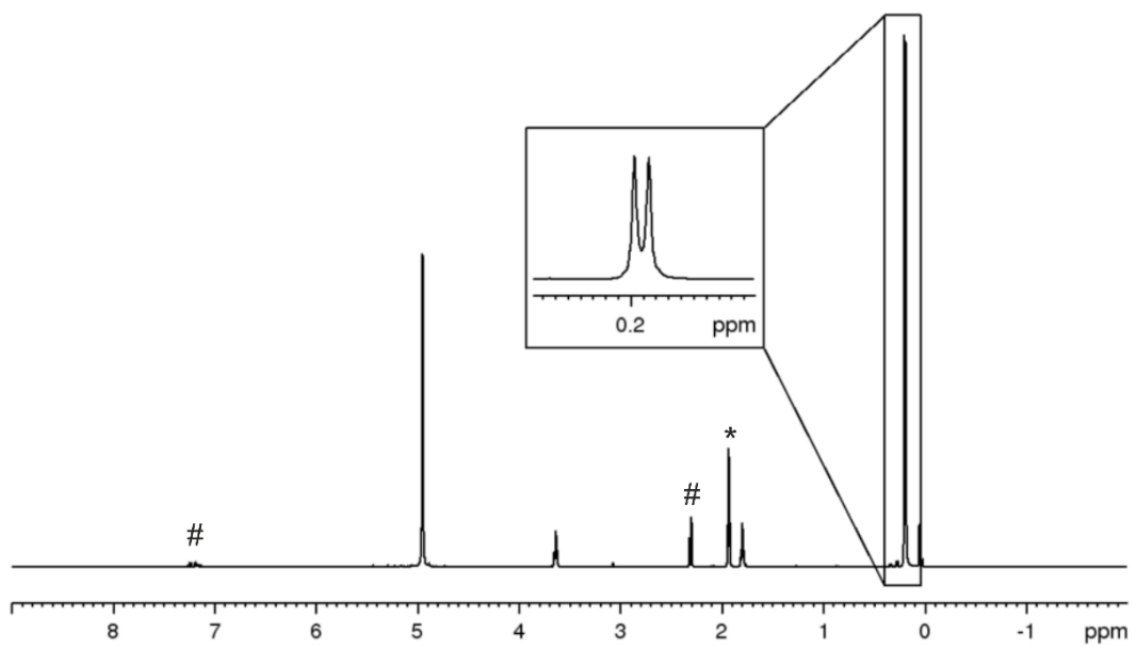


Figure S15: ^1H NMR spectrum of $\text{Li}[\{\text{CpMo}(\text{CO})_2\}_2\{\mu,\eta^2\text{-P}(\text{SiMe}_3)_2\}]$ (**6a**) in CD_3CN ; * = CD_3CN , # = toluene.

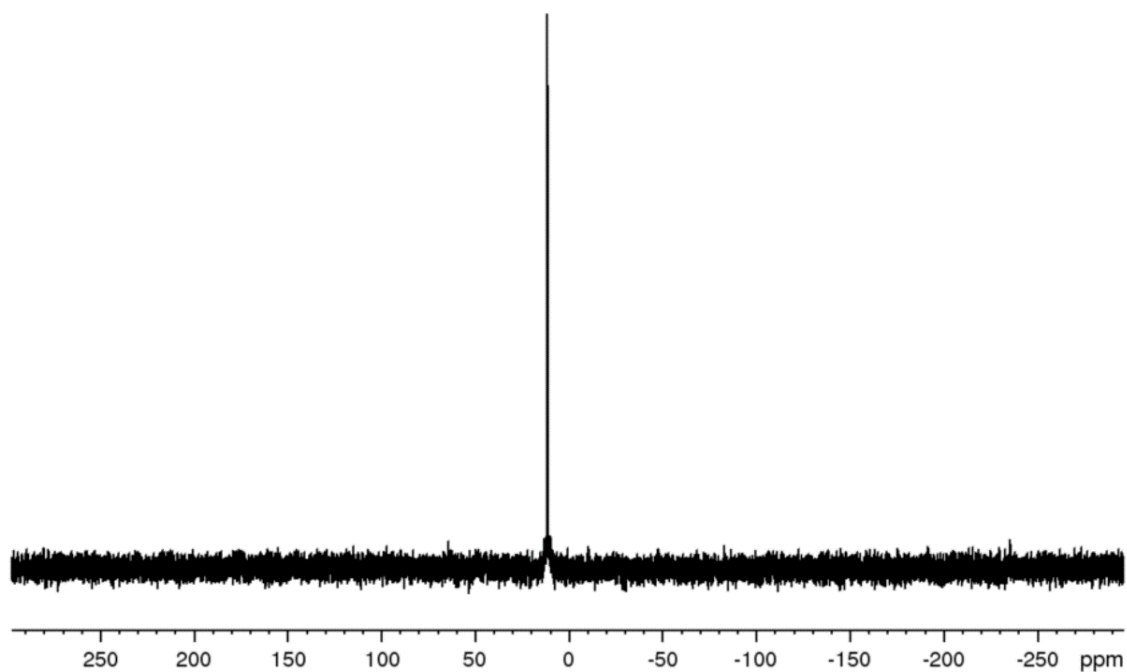


Figure S16: ^{31}P NMR spectrum of $\text{Li}[\{\text{CpMo}(\text{CO})_2\}_2\{\mu,\eta^2\text{-P}(\text{SiMe}_3)_2\}]$ (**6a**) in CD_3CN .

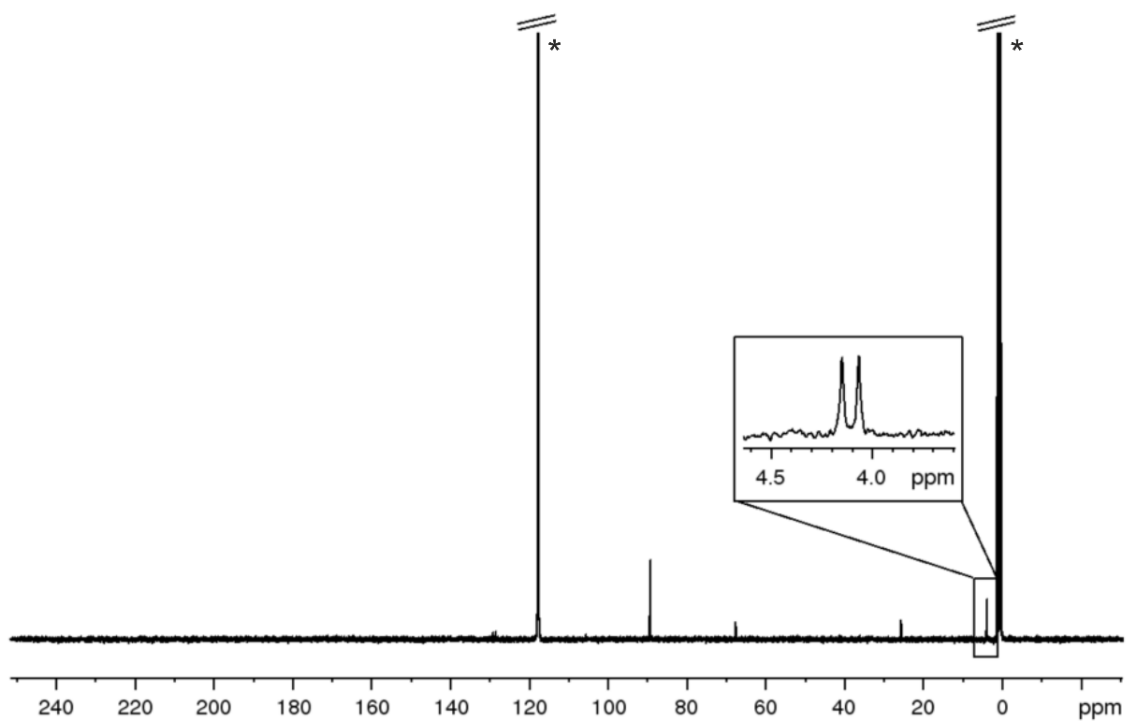


Figure S17: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of $\text{Li}[\{\text{CpMo}(\text{CO})_2\}_2\{\mu,\eta^2\text{-P}(\text{SiMe}_3)_2\}]$ (**6a**) in CD_3CN ; * = CD_3CN .

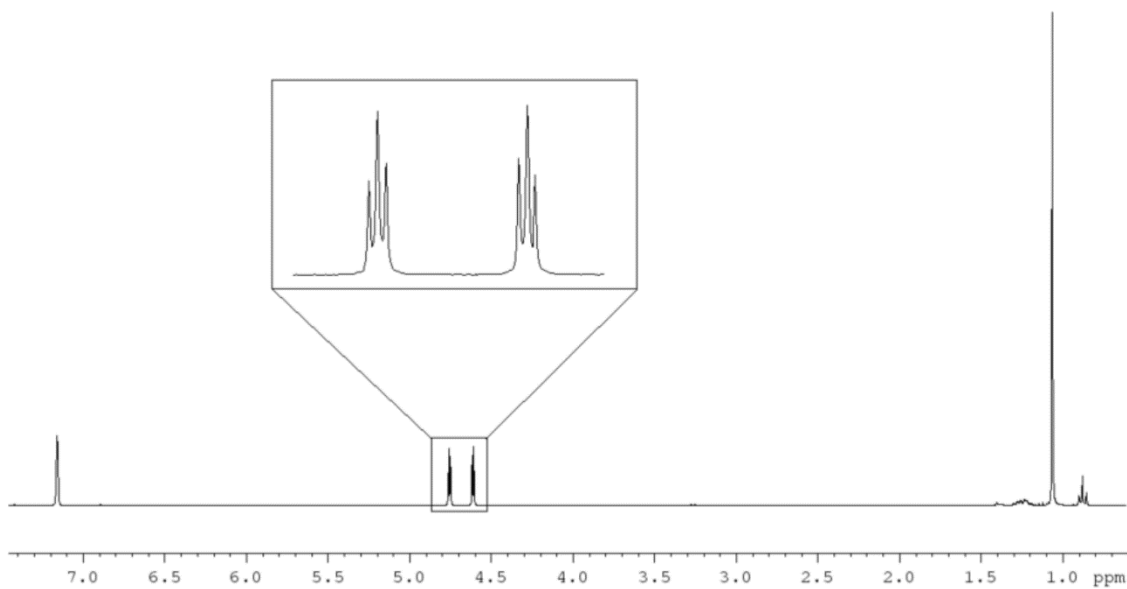


Figure S18: ^1H NMR spectrum of $[(\text{Cp}'\text{Mo}(\text{CO})_2)_2(\mu,\eta^2:\eta^2\text{-As}_2)]$ (**7**) in C_6D_6 .

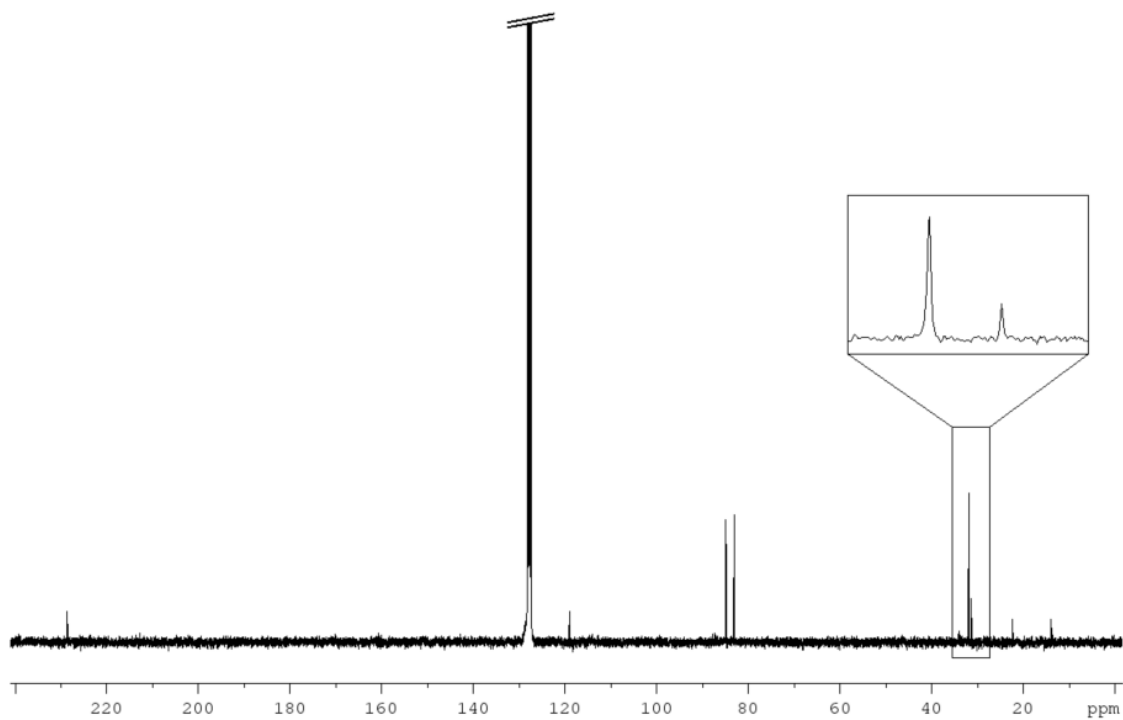


Figure S19: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of $[(\text{Cp}'\text{Mo}(\text{CO})_2)_2(\mu,\eta^2:\eta^2\text{-As}_2)]$ (**7**) in C_6D_6 .

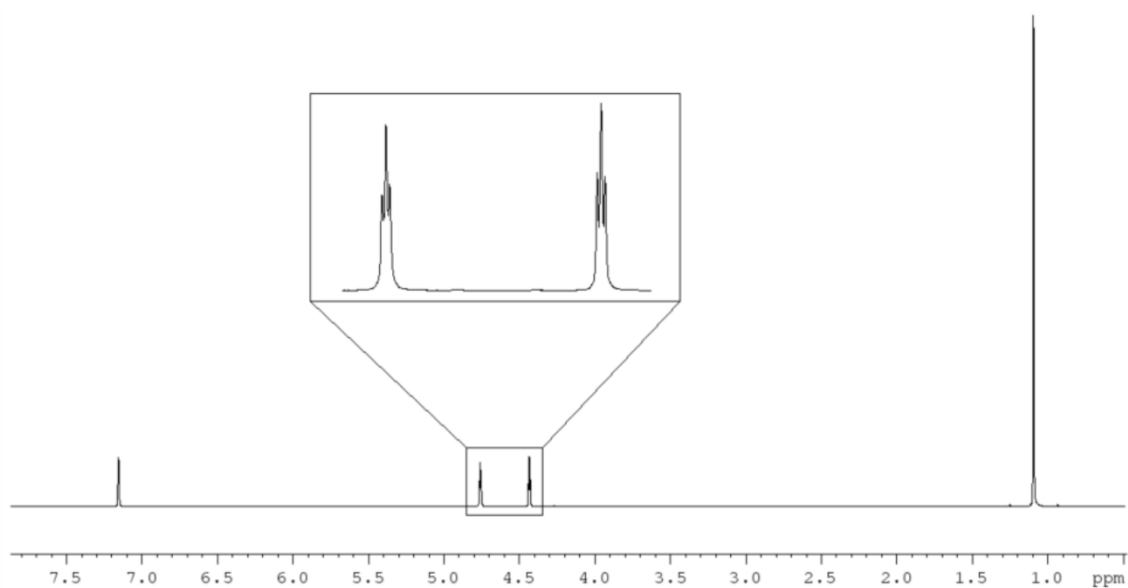


Figure S20: ^1H NMR spectrum of $[(\text{Cp}'\text{Mo}(\text{CO})_2)_2(\mu,\eta^2:\eta^2\text{-Sb}_2)]$ (**8**) in C_6D_6 .

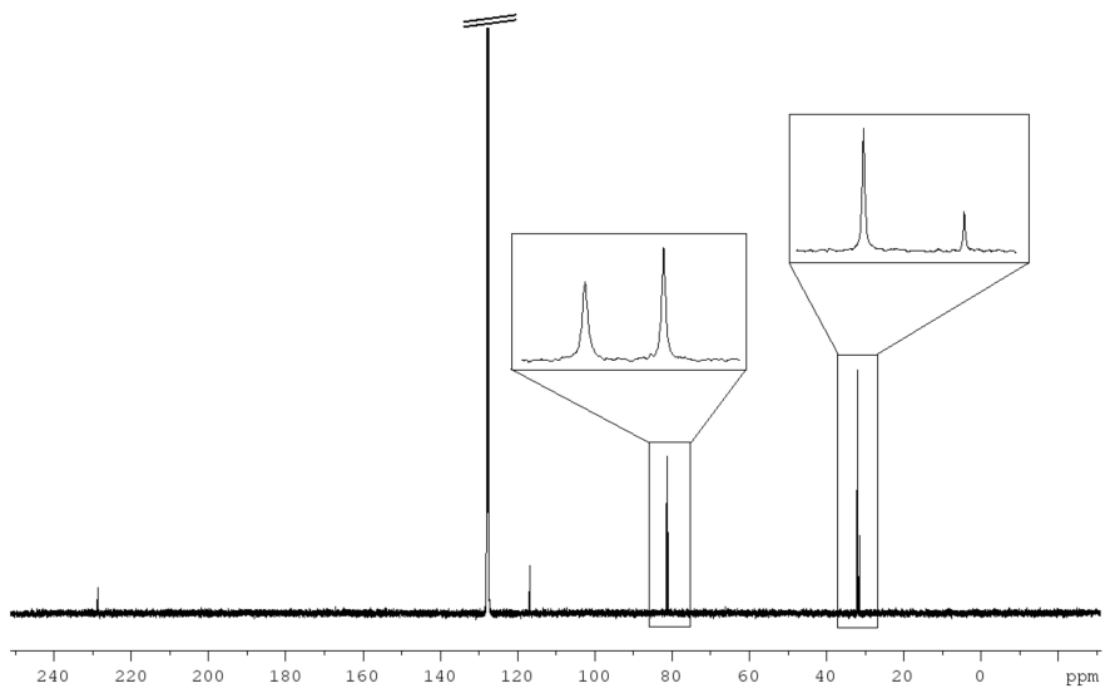


Figure S21: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of $[(\text{Cp}^*\text{Mo}(\text{CO})_2)_2(\mu,\eta^2:\eta^2\text{-Sb}_2)]$ (**8**) in C_6D_6 .

IR Spectra

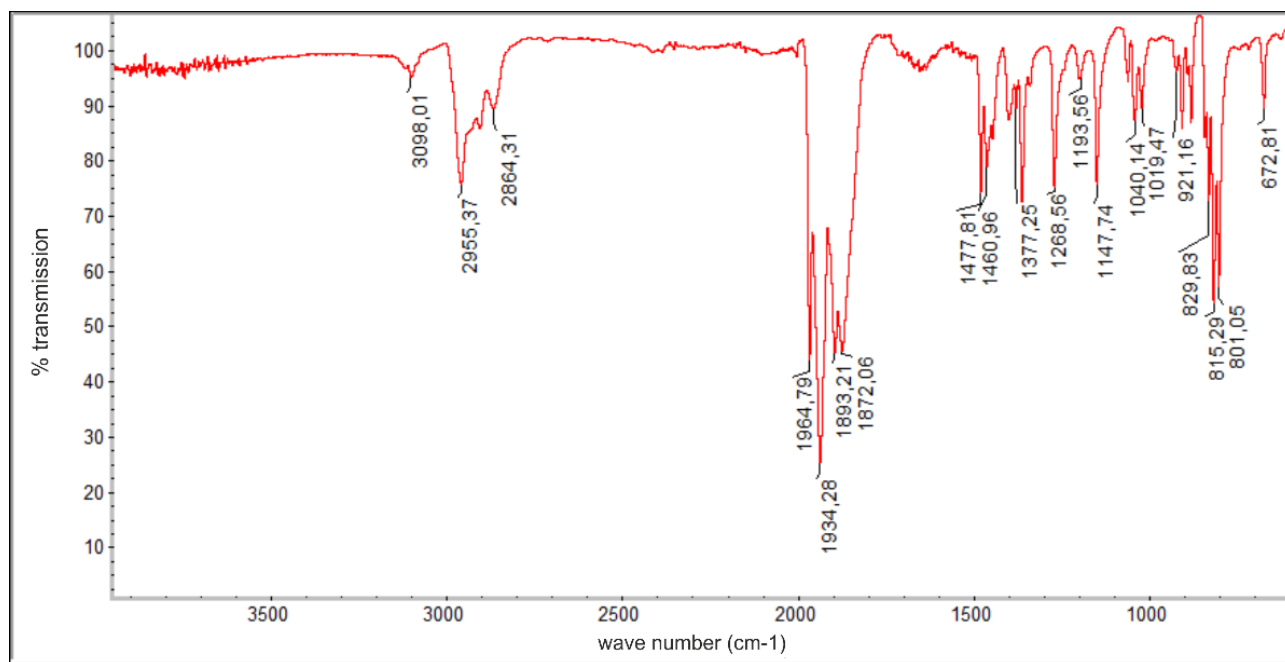


Figure S22: IR spectrum of $[(\text{Cp}^*\text{Mo}(\text{CO})_2)_2(\mu,\eta^2:\eta^2\text{-As}_2)]$ (**7**).

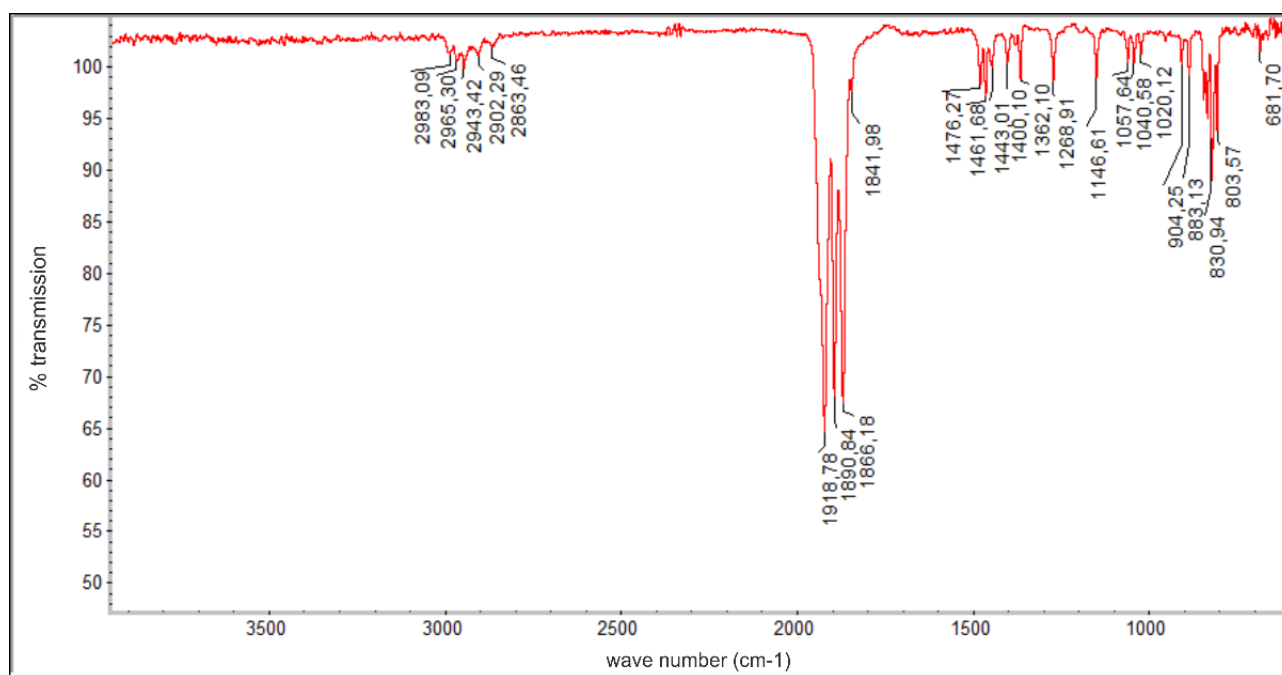


Figure S23: IR spectrum of $[(\text{Cp}'\text{Mo}(\text{CO})_2)_2(\mu,\eta^2:\eta^2\text{-Sb}_2)]$ (**8**).

X-ray crystallography

All crystal manipulations were performed under mineral oil. The diffraction experiments were performed at 123 K on a Rigaku (former Agilent Technologies or Oxford Diffraction) Gemini Ultra with an AtlasS2 detector, on a GV50 diffractometer with a TitanS2 detector or on a SuperNova Single Source diffractometer using Cu-K_α , Cu-K_β or Mo-K_α radiation. Crystallographic data together with the details of the experiments are given in Table S4 and Table S5. The cell determination, data reduction and absorption correction for all compounds were performed with the help of the CrysAlis PRO software.^[13] All structures were solved by using the programs SHELXT^[14] and Olex2.^[15] The full-matrix least-squares refinement against F^2 was done using SHELXL^[16] and Olex2.^[15] If not stated otherwise, all atoms except hydrogen atoms were refined anisotropically. The H atoms were calculated geometrically and a riding model was used during the refinement process.

CIF files with comprehensive information on the details of the diffraction experiments and full tables of bond lengths and angles for **2-8** and $[\text{Cp}'\text{Mo}(\text{CO})_2(\eta^3\text{-As}_3)]$ are deposited in Cambridge Crystallographic Data Centre (CCDC) under the deposition codes CCDC-2061901 (**2**), CCDC-2061902 (**3a**), CCDC-2061903 (**3b**), CCDC-2061904 (**4**), CCDC-2061905 (**5**), CCDC-2061906 (**6a**), CCDC-2061907 (**6b**), CCDC-2061908 (**6c**), CCDC-2061909 (**7**), CCDC-2061910 (**8**) and CCDC-2072587 ($[\text{Cp}'\text{Mo}(\text{CO})_2(\eta^3\text{-As}_3)]$).

Crystallographic Data for Compound **2** was already provided by Mays *et. al.* in 1998 under the CCDC deposition code CCDC-100650.^[12]

Table S4: Crystallographic details for the compounds **2**,^[17] **3a**, **3b**, **4**, and **5**.

	2 ^[17]	3a	3b	4	5
formula	C ₁₄ H ₁₀ O ₄ PMo ₂ Sb	C ₁₄ H ₁₀ AsMo ₂ O ₄ Sb	C ₂₂ H ₂₆ AsMo ₂ O ₄ Sb	C ₁₄ H ₁₀ O ₄ AsMo ₂ Bi	C ₁₄ H ₁₀ BiMo ₂ O ₄ Sb
weight [g·mol ⁻¹]	586.82	630.77	742.98	718.00	764.83
Temperature [K]	123	123	122.9(3)	123(1)	123(2)
crystal system	monoclinic	monoclinic	orthorhombic	monoclinic	monoclinic
space group	<i>P2/n</i>	<i>P2/n</i>	<i>P2₁2₁2</i>	<i>P2₁</i>	<i>I2/a</i>
<i>a</i> [Å]	13.4669(2)	13.5271(2)	15.0805(5)	8.8466(2)	16.6083(9)
<i>b</i> [Å]	7.5991(1)	7.6095(1)	10.1597(3)	7.8968(2)	7.6109(3)
<i>c</i> [Å]	15.7859(2)	15.7703(3)	7.8995(2)	11.5419(3)	14.4656(7)
α [°]	90	90	90	90	90
β [°]	95.047(1)	94.625(2)	90	101.576(2)	115.955(6)
γ [°]	90	90	90	90	90
Volume [Å ³]	1609.21(4)	1618.02(4)	1210.31(6)	789.91(3)	1644.1(2)
<i>Z</i>	4	4	2	2	4
ρ_{calc} [g·cm ⁻³]	2.422	2.589	2.039	3.019	3.090
μ [mm ⁻¹]	26.861	28.052	14.150	36.782	13.799
<i>F</i> (000)	1104.0	1176.0	716.0	652.0	1376.0
crystal size [mm ³]	0.218 × 0.152 × 0.069	0.126 × 0.097 × 0.072	0.427 × 0.277 × 0.162	0.197 × 0.095 × 0.073	0.703 × 0.306 × 0.281
diffractometer	Gemini Ultra	Gemini Ultra	GV50	GV50	Gemini Ultra
absorption correction	gaussian	gaussian	gaussian	gaussian	analytical
<i>T</i> _{min} / <i>T</i> _{max}	0.343 / 0.668	0.575 / 0.678	0.003 / 0.234	0.023 / 0.277	0.014 / 0.122
radiation [Å]	Cu-K α (λ = 1.54184)	Cu-K α (λ = 1.54184)	Cu-K β (λ = 1.39222)	Cu-K α (λ = 1.54184)	Mo-K α (λ = 0.71073)
2 θ range [°]	8.278 to 133.49	8.288 to 133.458	9.478 to 120.36	7.818 to 147.3	7.3 to 62.908
completeness [%]	99.3	99.4	99.9	98.6	99.7
reflns collected / unique	8840 / 2827	8891 / 2846	6312 / 2418	7411 / 3149	7351 / 2599
<i>R</i> _{int} / <i>R</i> _{sigma}	0.0330 / 0.0336	0.0315 / 0.0307	0.1318 / 0.0866	0.0455 / 0.0344	0.0333 / 0.0303
data / restraints / parameters	2827 / 66 / 210	2846 / 72 / 217	2418 / 0 / 139	3149 / 146 / 218	2599 / 0 / 100
GOF on <i>F</i> ²	1.185	1.100	1.056	1.097	1.093
<i>R</i> ₁ / <i>wR</i> ₂ [<i>I</i> ≥ 2 σ (<i>I</i>)]	0.0331 / 0.0850	0.0263 / 0.0617	0.0746 / 0.1934	0.0468 / 0.1212	0.0317 / 0.0801
<i>R</i> ₁ / <i>wR</i> ₂ [all data]	0.0349 / 0.0864	0.0306 / 0.0636	0.0761 / 0.1944	0.0476 / 0.1215	0.0336 / 0.0812
max / min $\Delta\rho$ [e·Å ⁻³]	1.02 / -1.59	0.68 / -1.30	2.88 / -1.54	2.34 / -2.15	0.96 / -2.22
identification code	LD185_CR003_abs	LD190_CR008_abs	LD153_F1_abs	CR492_Cua	LD233_abs

Table S5: Crystallographic details for the compounds **6a**, **6b**, **6c**, **7** and **8**.

	6a	6b	6c	7	8
formula	C ₃₆ H ₆₀ LiMo ₂ O ₁₂ PSi ₂	C ₃₆ H ₆₀ AsLiMo ₂ O ₁₂ Si ₂	C ₄₂ H ₇₁ KMo ₂ O _{12.5} SbSi ₂	C ₂₂ H ₂₆ As ₂ Mo ₂ O ₄	C ₂₂ H ₂₆ O ₄ Mo ₂ Sb ₂
weight [g·mol ⁻¹]	970.81	1014.76	1184.89	696.15	789.81
Temperature [K]	123(1)	123(1)	123(1)	123(1)	123.0(1)
crystal system	monoclinic	monoclinic	triclinic	monoclinic	orthorhombic
space group	<i>P2₁/n</i>	<i>P2₁/c</i>	<i>P-1</i>	<i>P2₁/c</i>	<i>P2₁2₁2</i>
<i>a</i> [Å]	23.081(1)	12.4933(1)	9.7702(2)	10.3882(3)	15.1466(4)
<i>b</i> [Å]	9.2777(3)	18.7395(2)	14.1024(3)	14.8930(3)	10.2347(3)
<i>c</i> [Å]	12.4744(6)	18.9341(2)	19.0574(5)	15.2218(3)	7.8972(3)
α [°]	90	90	85.172(2)	90	90
β [°]	125.121(7)	92.476(1)	84.141(2)	90.911(2)	90
γ [°]	90	90	85.419(2)	90	90
Volume [Å ³]	2185.0(2)	4428.68(8)	2596.1(1)	2354.7(1)	1224.23(7)
<i>Z</i>	2	4	2	4	2
ρ_{calc} [g·cm ⁻³]	1.476	1.522	1.516	1.964	2.143
μ [mm ⁻¹]	6.037	6.445	7.165	3.880	19.358
<i>F</i> (000)	1004.0	2080.0	1210.0	1360.0	752.0
crystal size [mm ³]	0.211 × 0.127 × 0.064	0.474 × 0.231 × 0.129	0.414 × 0.338 × 0.085	0.958 × 0.553 × 0.381	0.235 × 0.143 × 0.048
diffractometer	Gemini Ultra	Gemini Ultra	GV50	Gemini Ultra	GV50
absorption correction	analytical	analytical	gaussian	analytical	gaussian
<i>T</i> _{min} / <i>T</i> _{max}	0.497 / 0.730	0.140 / 0.480	0.219 / 1.000	0.494 / 0.741	0.298 / 0.858
radiation [Å]	Cu-K α (λ = 1.54184)	Cu-K α (λ = 1.54184)	Cu-K β (λ = 1.39222)	Mo-K α (λ = 0.71073)	Cu-K β (λ = 1.39222)
2 θ range [°]	7.092 to 132.046	7.082 to 148.448	5.694 to 149.958	7.134 to 70.64	9.416 to 120.458
completeness [%]	99.5	99.4	99.2	99.9	99.7
reflns collected / unique	11658 / 3794	27585 / 8866	41532 / 14134	88121 / 10042	4114 / 2248
<i>R</i> _{int} / <i>R</i> _{sigma}	0.0272 / 0.0284	0.0291 / 0.0257	0.0562 / 0.0454	0.0535 / 0.0283	0.0333 / 0.0479
data / restraints / parameters	3794 / 693 / 465	8866 / 156 / 602	14134 / 0 / 529	10042 / 0 / 307	2248 / 0 / 139
GOF on <i>F</i> ²	1.061	1.055	1.136	1.105	1.031
<i>R</i> ₁ / <i>wR</i> ₂ [<i>I</i> ≥ 2 σ (<i>I</i>)]	0.0235 / 0.0570	0.0341 / 0.0932	0.0793 / 0.1999	0.0255 / 0.0554	0.0337 / 0.0821
<i>R</i> ₁ / <i>wR</i> ₂ [all data]	0.0268 / 0.0588	0.0374 / 0.0964	0.0892 / 0.2061	0.0331 / 0.0578	0.0366 / 0.0849
max / min $\Delta\rho$ [e·Å ⁻³]	0.72 / -0.43	1.02 / -0.52	4.86 / -2.23	0.73 / -1.03	0.60 / -1.50
identification code	CR326_GemCua	CR327_Cua	LD370_CR328	LD444_Fr2_abs	LD151_2_abs

Refinement details for 2:

Compound **2** can be regarded as isostructural to the compounds **1**, **3a**, **4** and **5**. It crystallizes in the monoclinic space group $P2/n$ with two half molecules in the asymmetric unit. The refinement of the crystal structure could be done without any difficulty. The **PSb** ligands within the tetrahedral complexes exhibit a disorder over the two sites in a ratio of 50:50 (Figure S24). The anisotropic displacement parameters (ADP) of one Cp ring and one **PSb** ligand were restrained by SIMU commands.

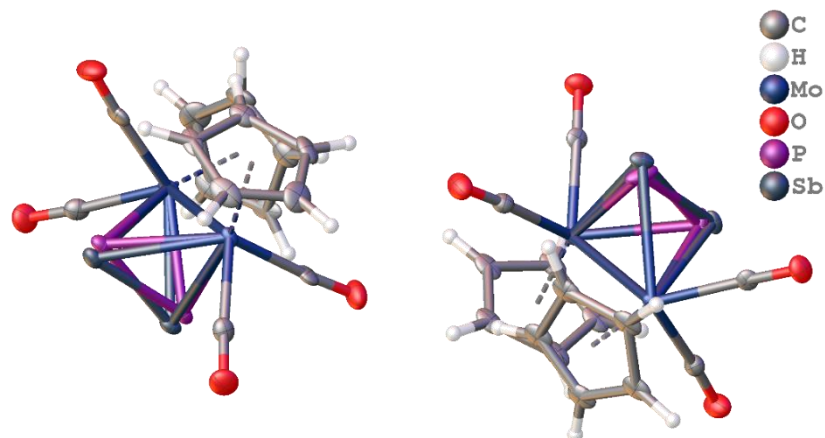


Figure S24: X-ray structure of **2**. The grown structure of the asymmetric unit, which contains two half molecules of **2**, is shown.

Refinement details for 3a:

Compound **3a** can be regarded as isostructural to the compounds **1**, **2**, **4** and **5**. It crystallizes in the monoclinic space group $P2/n$ with two half molecules in the asymmetric unit. The refinement of the crystal structure could be done without any difficulty. The **AsSb** ligands within the tetrahedral complexes exhibit a disorder over the two sites in a ratio of 50:50 (Figure S25). The ADPs of one Cp ring and the two **AsSb** ligands were restrained by SIMU commands.

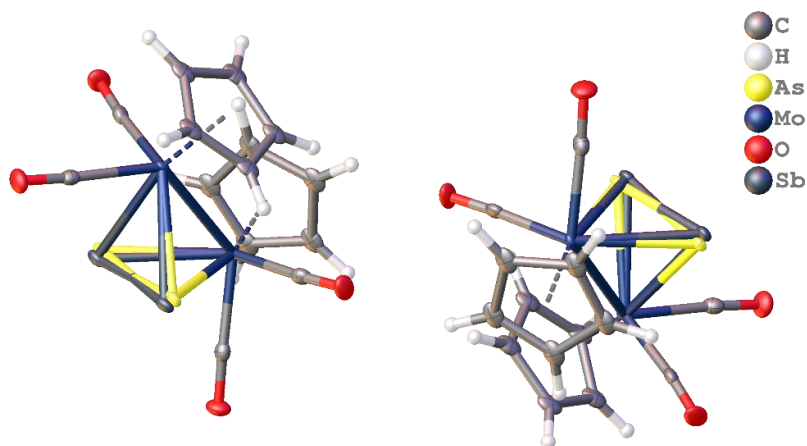


Figure S25: X-ray structure of **3a**. The grown structure of the asymmetric unit, which contains two half molecules of **2**, is shown.

Refinement details for 3b:

Compound **3b** can be regarded as isostructural to the compounds **7** and **8**. It crystallizes in the orthorhombic space group $P2_12_12$ with one half molecule in the asymmetric unit. The refinement of the crystal structure could be done without any difficulty. The **AsSb** ligand within the tetrahedral complexes exhibits a disorder over the two sites in a ratio of 50:50 (Figure S26). The disorder was refined by using a EXYZ command as the As and Sb atoms sit on the same position.

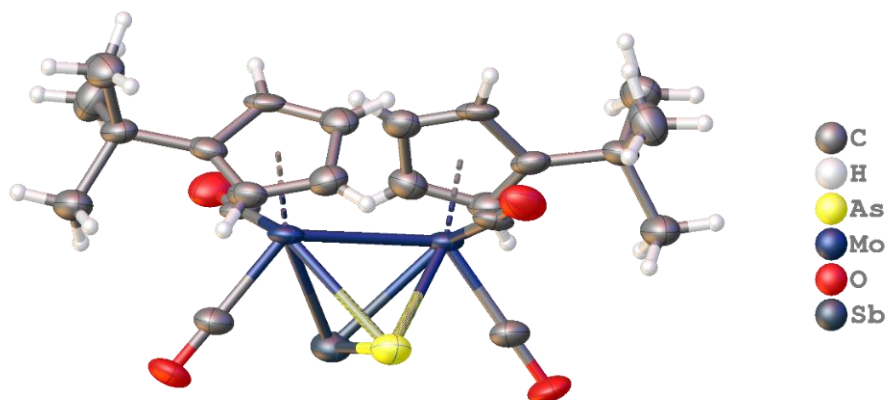


Figure S26: X-ray structure of **3b**. The grown structure of the asymmetric unit, which contains a half molecule of **3b**, is shown.

Refinement details for 4:

Compound **4** can be regarded as isostructural to the compounds **1**, **2**, **3a** and **5**. It crystallizes in the monoclinic space group $P2_1$ with one molecule in the asymmetric unit. The refinement of the crystal structure could be done without any difficulty. The **AsBi** ligand within the tetrahedral complex exhibits a disorder over the two sites in ratio of 76:24 (Figure S27). The ADPs of the Cp rings, the two **AsSb** ligands and two CO ligands were restrained by SIMU commands. The **AsBi** ligands were restrained with a SADI command.

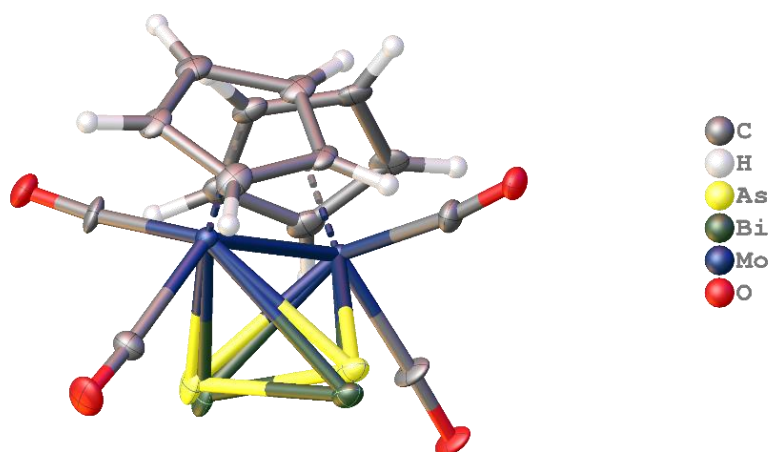


Figure S27: X-ray structure of **4**.

Refinement details for 5:

Compound **5** can be regarded as isostructural to the compounds **1**, **2**, **3a** and **4**. It crystallizes in the monoclinic space group $I2/a$ with one half molecule in the asymmetric unit. The refinement of the crystal structure could be done without any difficulty. The **SbBi** ligand within the tetrahedral complex exhibits a disorder over the two sites in ratio of 50:50 (Figure S27). The disorder was refined by using a EXYZ command as the Sb and Bi atoms sit on the same position.

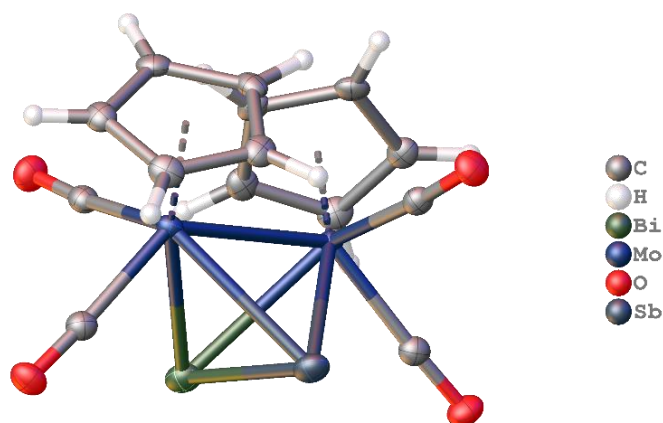


Figure S28: X-ray structure of **5**. The grown structure of the asymmetric unit, which contains one half molecule of **5**, is shown.

Refinement details for 6a:

Compound **6a** can be regarded as isostructural to the compounds **6b** and **6c**. It crystallizes in the monoclinic space group $P2/n$ with one half anion $[\{\text{CpMo}(\text{CO})_2\}_2\{\mu\text{-P}(\text{SiMe}_3)_2\}]^-$, one half Li^+ cation and one crown-ether (12-crown-4) in the asymmetric unit. The refinement of the crystal structure could be done without any difficulty. Overall, two crown-ethers are coordinating the lithium ion and each exhibits a threefold disorder in a ratio of 50:33:17 (Figure S29). The disordered crown-ethers were restrained by several DFIX, and the ADPs with SIMU commands.

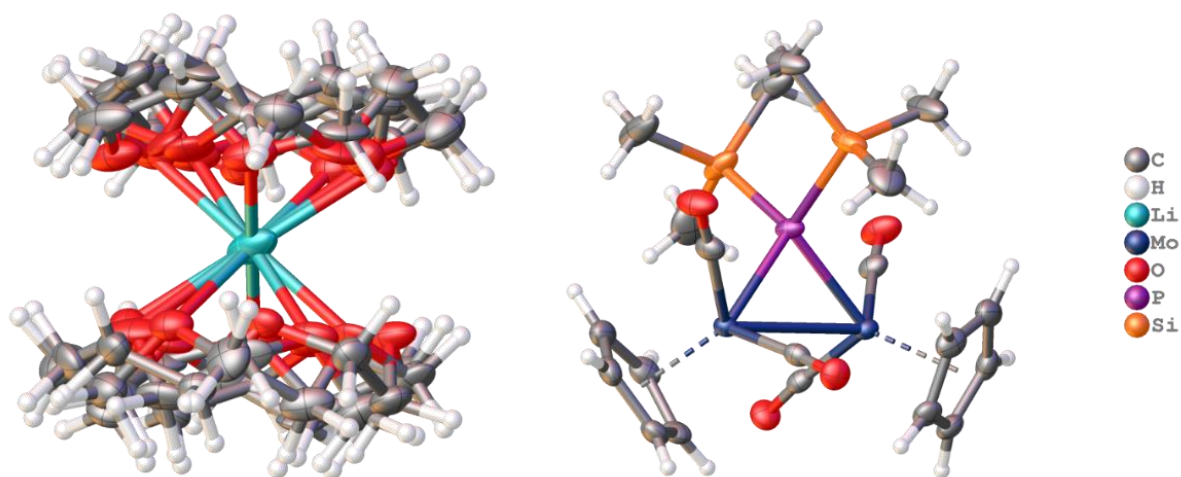


Figure S29: X-ray structure of **6a**. Left: Lithium cation coordinated by two disordered crown-ethers (12-crown-4); right: anionic part of **6a**.

Refinement details for 6b:

Compound **6b** can be regarded as isostructural to the compounds **6a** and **6c**. It crystallizes in the monoclinic space group $P2_1/c$ with one anion $[\{\text{CpMo}(\text{CO})_2\}_2\{\mu\text{-As}(\text{SiMe}_3)_2\}]^-$, one Li^+ cation and two crown-ethers (12-crown-4) in the asymmetric unit. The refinement of the crystal structure could be done without any difficulty. The two crown-ethers are coordinating the lithium ion. One of them exhibits a disorder in a ratio of 70:30 (Figure S30). The ADPs of the disordered crown-ether were restrained by SIMU and RIGU commands.

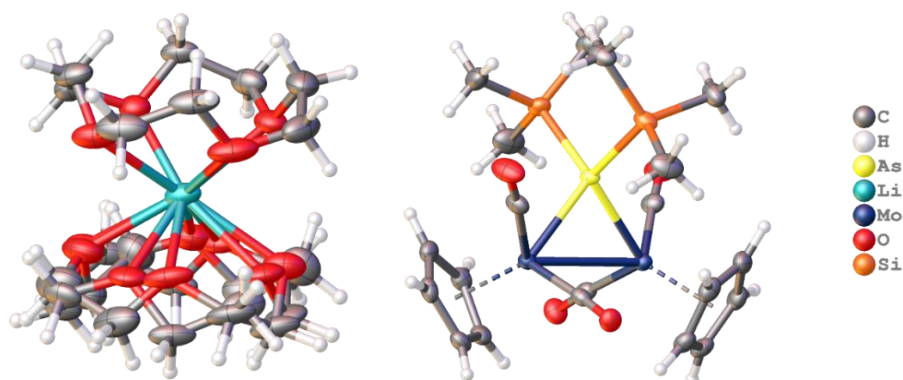


Figure S30: X-ray structure of **6b**. Left: Lithium cation coordinated by one ordered and one disordered crown-ether (12-crown-4); right: anionic part of **6b**.

Refinement details for 6c:

Compound **6c** can be regarded as isostructural to the compounds **6a** and **6b**. It crystallizes in the triclinic space group $P-1$ with one anion $[\{\text{CpMo}(\text{CO})_2\}_2\{\mu\text{-Sb}(\text{SiMe}_3)_2\}]^-$, one K^+ cation, one crown-ether (18-crown-6) and two THF molecules in the asymmetric unit. The refinement of the crystal structure could be done without any difficulty. The potassium cation is coordinated by the crown-ether and the two THF molecules (Figure S31). A solvent mask was calculated and 41 electrons were found in a volume of 171 \AA^3 in two voids per unit cell. This is consistent with the presence of half THF per asymmetric unit, which accounts for 40 electrons per unit cell.

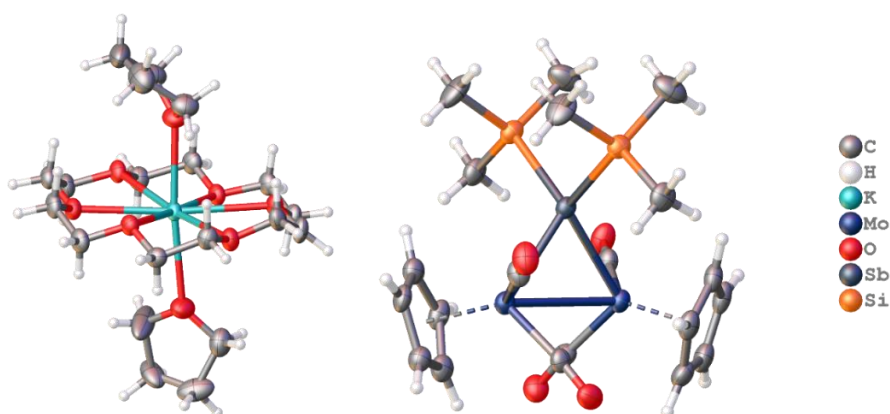


Figure S31: X-ray structure of **6c**. Left: Potassium cation coordinated by one crown-ether (18-crown-6) and two THF molecules; right: anionic part of **6c**.

Refinement details for 7:

Compound **7** can be regarded as isostructural to the compounds **3b** and **8**. It crystallizes in the monoclinic space group $P2_1/c$ with one molecule in the asymmetric unit. The refinement of the crystal structure could be done without any difficulty. One of the *tert*-butyl-groups shows a rotational disorder with a ratio of 78:22 (Figure S32).

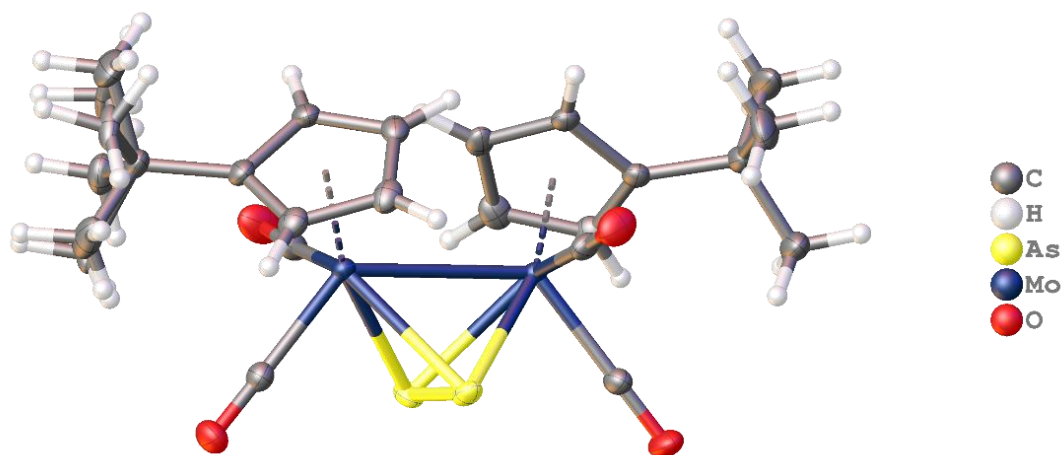


Figure S32: X-ray structure of **7**.

Refinement details for 8:

Compound **8** can be regarded as isostructural to the compounds **3b** and **7**. It crystallizes in the orthorhombic space group $P2_12_12$ with one half molecule in the asymmetric unit. The refinement of the crystal structure could be done without any difficulty (Figure S33).

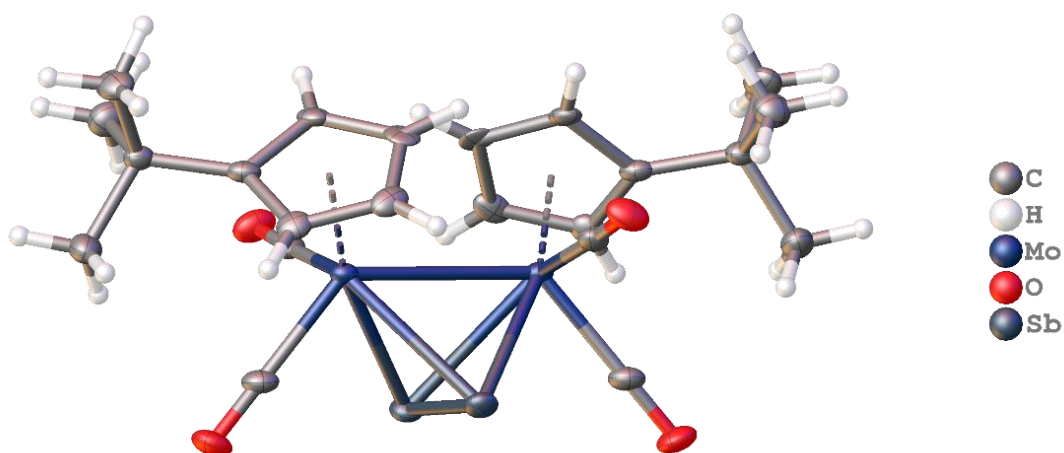


Figure S33: X-ray structure of **8**. The grown structure of the asymmetric unit, which contains one half molecule of **8**, is shown.

Refinement details for [Cp'Mo(CO)₂(η³-As₃)]:

During the synthesis of **7** also minor amounts of the side product [Cp'Mo(CO)₂(η³-As₃)] could be received. [Cp'Mo(CO)₂(η³-As₃)] is already known in the literature,^[27] however, it is not crystallographically characterised yet. By cooling a saturated CH₂Cl₂ solution of [Cp'Mo(CO)₂(η³-As₃)] from room temperature to -30 °C yellow crystalline plates can be obtained, which are suitable for single crystal X-ray diffraction. [Cp'Mo(CO)₂(η³-As₃)] crystallizes in the orthorhombic space group *Fdd2* with one molecule in the asymmetric unit. The refinement of the crystal structure could be done without any difficulty (Figure 34). The *tert*-butyl group of the Cp' ligand shows a rotational disorder in a ratio of 74:26. Crystallographic details for [Cp'Mo(CO)₂(η³-As₃)] are given in Table S6.

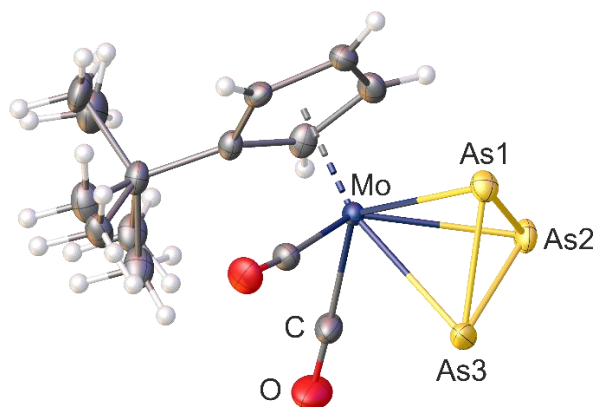


Figure S34: X-ray structure of [Cp'Mo(CO)₂(η³-As₃)]; selected bond lengths [Å]: As1–As2 2.3978(6), As2–As3 2.3588(7), As3–As1 2.3648(6), Mo–As1 2.6519(5), Mo–As2 2.6506(5), Mo–As3 2.7036(5).

Table S6: Crystallographic details for [Cp'Mo(CO)₂(η³-As₃)].

formula	C ₁₁ H ₁₃ As ₃ MoO ₂	crystal size [mm ³]	0.47 x 0.192 x 0.049
weight [g·mol ⁻¹]	497.91	diffractometer	SuperNova
Temperature [K]	123.0	absorption correction	gaussian
crystal system	orthorhombic	<i>T</i> _{min} / <i>T</i> _{max}	0.054 / 1.000
space group	<i>Fdd2</i>	radiation [Å]	Mo-Kα (λ = 0.71073)
<i>a</i> [Å]	21.6834(3)	2θ range [°]	6.022 to 69.264
<i>b</i> [Å]	17.3149(2)	completeness [%]	0.999
<i>c</i> [Å]	15.3030(2)	reflns collected / unique	42209 / 5974
α [°]	90	<i>R</i> _{int} / <i>R</i> _{sigma}	0.0633 / 0.0329
β [°]	90	data / restraints / parameters	5974 / 19 / 187
γ [°]	90	<i>GOF</i> on <i>F</i> ²	1.087
Volume [Å ³]	5747.5(1)	<i>R</i> ₁ / <i>wR</i> ₂ [I ≥ 2σ(I)]	0.0279 / 0.0639
<i>Z</i>	16	<i>R</i> ₁ / <i>wR</i> ₂ [all data]	0.0302 / 0.0659
<i>ρ</i> _{calc} [g·cm ⁻³]	2.302	max / min Δρ [e·Å ⁻³]	0.69 / -0.64
μ [mm ⁻¹]	7.758	identification code	LD444_Fr1_abs
<i>F</i> (000)	3776.0		

Details of DFT Calculations

The geometry of the molecules has been optimized using ORCA,^[18] version 4.2 at the B3LYP^[19] level together with the def2-TZVP basis set for all atoms.^[20] The dispersion effects have been incorporated via the D3 corrections together with the Beke-Johnson damping.^[21] Additionally, for the complexes **6a-d**, the solvent effects has been incorporated via the Conductor-like Polarizable Continuum Model (C-PCM)^[22] with THF as solvent. The calculation of the Wiberg bond indices in the Löwdin orthogonal orbital basis,^[23] which are known to be less basis set dependent have been calculated using the Multiwfn program (version 3.8)^[24] It has to be noted that the WBIs computed using the Löwdin orbitals, are slightly overestimated for polar bonds.^[24] The Intrinsic Bonding Orbitals^[25] have been generated using the IboWiew program.^[26]

Table S7: Total energies calculated at the B3LYP-D3J/def2-TZVP level and additional C-PCM correction for **6a-d**.

Compound	Total Energy (a.u.)
1	-3554.101344105
2	-1558.568042740
[[CpMo(CO) ₂] ₂ (PBi)]	-1532.946515369
3a	-3453.050397049
4	-3427.430176249
5	-1431.904231562
6a	-2136.881020368
6b	-4031.346794109
6c	-2035.799910774
6d	-2010.160724327

Table S8: Selected bond lengths (Å) and the corresponding Wiberg bond order in Löwdin orthogonalized basis.

Compound	E-E' bond length (Å)	WBI	Mo-Mo bond length (Å)	WBI
1	2.209	1.48	3.048	0.53
2	2.412	1.41	3.073	0.52
[[CpMo(CO) ₂] ₂ (PBi)]	2.504	1.35	3.080	0.51
3a	2.515	1.40	3.095	0.51
4	2.600	1.35	3.102	0.51
5	2.772	1.36	3.138	0.50
6a	n. a.	n. a.	3.199	0.45
6b	n. a.	n. a.	3.231	0.44
6c	n. a.	n. a.	3.305	0.43
6d	n. a.	n. a.	3.320	0.42

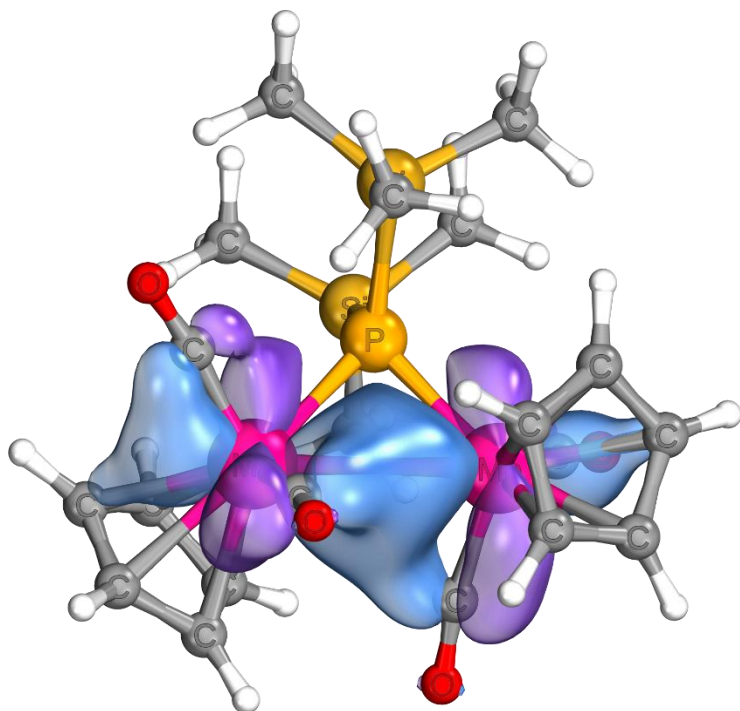
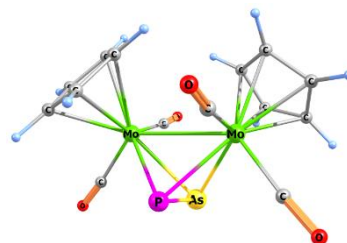


Figure S35: Intrinsic Bonding Orbital representing the Mo-Mo bond in **6a**. AO contributions: Mo2 0.763, Mo1 0.763, C9 0.136, C13 0.136, C12 0.052, C8 0.052 (other: 0.098).

Table S9: Cartesian coordinates of the optimized geometry of $[(\text{CpMo}(\text{CO})_2)_2(\text{PAs})]$ (**1**).

As	-0.619448173	-2.484514211	-0.859089129
P	-1.765412690	-1.657004630	0.838565293
Mo	0.779481442	-1.152782602	0.869319661
Mo	-1.384649976	0.097642499	-0.875305199
C	-0.948918290	2.105542138	0.373157870
H	-0.115877234	2.220854217	1.042614638
C	-3.055385252	1.680323644	-0.430266584
H	-4.097081094	1.410423048	-0.480791604
C	-2.258776948	2.152645410	-1.517171517
H	-2.592929221	2.319795180	-2.527023866
C	-0.954665166	2.407766262	-1.010776353
H	-0.122375091	2.788826208	-1.579317602
C	-2.246959838	1.650850912	0.731227598
H	-2.558670350	1.348253345	1.715645128
C	-2.766739448	-0.783199515	-1.995664350
C	-0.117981210	-0.130400853	-2.376455789
O	-3.606594419	-1.206221087	-2.653284477
O	0.605996614	-0.159802619	-3.274137103
C	2.301319083	0.225935207	-0.378803841
H	1.988266329	0.997529711	-1.058524522
C	2.990663319	-1.800099418	0.449936066
H	3.285104791	-2.834515623	0.512201124
C	2.986085799	-0.864826135	1.528407201
H	3.292595530	-1.058915082	2.542177457
C	2.551798216	0.385445797	1.006019319
H	2.457157504	1.301662760	1.565227522
C	2.567106552	-1.127443460	-0.722262565
H	2.475840172	-1.555956070	-1.705075649



C	0.689286564	-2.794136830	1.983350384
C	-0.045299462	-0.176654705	2.375092027
O	0.726440315	-3.735568907	2.637279230
O	-0.439378364	0.428543408	3.273730634

Table S10: Cartesian coordinates of the optimized geometry of $[(\text{CpMo}(\text{CO})_2)_2(\text{PSb})]$ (**2**).

Sb	-0.661486242	-2.690099957	-0.951297907
P	-1.787107348	-1.614468545	0.891215896
Mo	0.785204403	-1.170398080	0.871804175
Mo	-1.399650513	0.088817255	-0.885169074
C	-0.927632734	2.090918918	0.363016608
H	-0.088391613	2.195172491	1.026376827
C	-3.044885034	1.692443672	-0.424658445
H	-4.090120213	1.435193535	-0.467184900
C	-2.250998726	2.156299021	-1.516770606
H	-2.590612778	2.327061230	-2.524214427
C	-0.940077128	2.393221963	-1.021016012
H	-0.107693038	2.764053115	-1.596170696
C	-2.227843614	1.652941411	0.730575732
H	-2.536131793	1.353246189	1.716955111
C	-2.802579224	-0.755964584	-1.999604063
C	-0.134442042	-0.134645108	-2.387637037
O	-3.665378701	-1.137227193	-2.656810603
O	0.593369822	-0.131500790	-3.285175853
C	2.284789039	0.233870299	-0.374844268
H	1.962967350	0.995843131	-1.061128764
C	3.007623758	-1.774785465	0.469307528
H	3.323794421	-2.802317014	0.538601845
C	2.978592789	-0.834868225	1.541880595
H	3.282751377	-1.017524565	2.558476473
C	2.522927257	0.404117521	1.009941127
H	2.408217123	1.321089551	1.564181042
C	2.578501755	-1.115755365	-0.710287212
H	2.513949872	-1.545914969	-1.694390052
C	0.708989346	-2.816926265	1.974125465
C	-0.038873374	-0.202631242	2.382664893
O	0.763021158	-3.758675202	2.628274465
O	-0.420795457	0.399413064	3.288962237

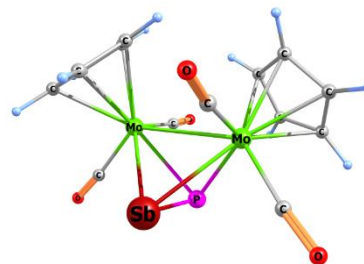
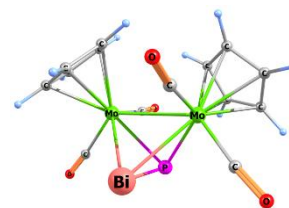


Table S11: Cartesian coordinates of the optimized geometry of $[(\text{CpMo}(\text{CO})_2)_2(\text{PBi})]$.

Bi	-0.675044218	-2.783171593	-0.996347412
P	-1.788910107	-1.595617908	0.905495401
Mo	0.785074061	-1.175563511	0.873346569
Mo	-1.402907712	0.086724193	-0.888650558
C	-0.917953559	2.083713866	0.361567153
H	-0.078182633	2.180588169	1.025231236
C	-3.036808098	1.698928731	-0.428221600
H	-4.083378479	1.447362239	-0.471622851
C	-2.239989974	2.159549414	-1.519178773
H	-2.577795776	2.332255762	-2.526843588
C	-0.927873192	2.387373266	-1.022388416
H	-0.092876895	2.753028944	-1.597056828



C	-2.220782287	1.653473992	0.727779185
H	-2.531613778	1.354455016	1.713547615
C	-2.816760147	-0.750304952	-1.992486627
C	-0.140259308	-0.136928692	-2.393893618
O	-3.691291458	-1.118935727	-2.643298629
O	0.591120178	-0.120990912	-3.289564727
C	2.274079689	0.239386725	-0.373676111
H	1.948438536	0.996381288	-1.063459267
C	3.012301078	-1.760039178	0.479669306
H	3.337997323	-2.784287859	0.553273090
C	2.970850619	-0.817857335	1.549255241
H	3.272810330	-0.994943273	2.567427298
C	2.505333701	0.415292493	1.011733123
H	2.380144483	1.332544836	1.563202394
C	2.581918330	-1.108080517	-0.703990794
H	2.528055517	-1.540006183	-1.687896206
C	0.712696021	-2.828220855	1.964466076
C	-0.036651272	-0.217689006	2.389482743
O	0.772977895	-3.772797502	2.615279625
O	-0.414718368	0.384376069	3.297819552

Table S12: Cartesian coordinates of the optimized geometry of $[(\text{CpMo}(\text{CO})_2)_2(\text{AsSb})]$ (**3a**).

Sb	-0.621511743	-2.686393251	-0.987272421
As	-1.882932640	-1.697473478	0.950648591
Mo	0.787851894	-1.178969691	0.882115728
Mo	-1.410789010	0.088554978	-0.888633901
C	-0.922002562	2.078541311	0.369196833
H	-0.090344104	2.171482184	1.043331842
C	-3.035226867	1.711571960	-0.446059333
H	-4.083821894	1.470955199	-0.501391564
C	-2.221803109	2.163286860	-1.528035621
H	-2.546467737	2.340714555	-2.539140094
C	-0.912845735	2.379899607	-1.015099639
H	-0.068652523	2.740093553	-1.579608775
C	-2.232845280	1.659389966	0.720491832
H	-2.558719592	1.371053947	1.704586167
C	-2.824100719	-0.755204301	-1.989711602
C	-0.156064195	-0.132709203	-2.397377959
O	-3.694286906	-1.134674357	-2.638231630
O	0.569619117	-0.120833285	-3.297027582
C	2.267610144	0.237368331	-0.373237656
H	1.936526900	0.996055307	-1.058510516
C	3.010731476	-1.764691151	0.469089827
H	3.334861337	-2.789774088	0.537440538
C	2.978262949	-0.824872690	1.541525893
H	3.286899042	-1.005000726	2.557142993
C	2.509568959	0.410004761	1.011013496
H	2.388767119	1.325890214	1.565699285
C	2.571481870	-1.109660062	-0.709404018
H	2.508951603	-1.540181995	-1.693421694
C	0.737136667	-2.829626263	1.978509513
C	-0.036567966	-0.209489906	2.391808779
O	0.815256482	-3.775188362	2.625907336
O	-0.404543176	0.409879677	3.293655452

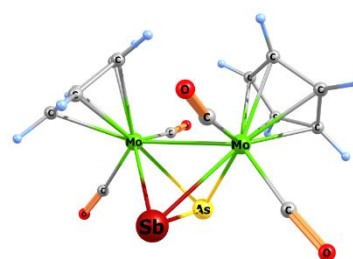


Table S13: Cartesian coordinates of the optimized geometry of $[(\text{CpMo}(\text{CO})_2)_2(\text{AsBi})]$ (**4**).

Bi	-0.637790539	-2.778159050	-1.029057149
As	-1.886491304	-1.674702313	0.967345041
Mo	0.787888208	-1.183504176	0.884180177
Mo	-1.414477929	0.087286021	-0.892549322
C	-0.915153003	2.073771547	0.366762926
H	-0.082151750	2.162012094	1.039800811
C	-3.030875787	1.716073891	-0.445944656
H	-4.080400833	1.479305006	-0.499964287
C	-2.217381395	2.165803910	-1.528458851
H	-2.542661940	2.344706690	-2.539092569
C	-0.906798038	2.376075708	-1.017420444
H	-0.061924699	2.732877419	-1.583063682
C	-2.227007523	1.659798834	0.719519297
H	-2.552936957	1.372629656	1.703932313
C	-2.834159863	-0.747209542	-1.990009928
C	-0.157989411	-0.135683900	-2.400521466
O	-3.712780155	-1.112795420	-2.637173124
O	0.568743150	-0.112101762	-3.300360958
C	2.259900070	0.240488992	-0.372711262
H	1.926594784	0.995152339	-1.061188227
C	3.014728394	-1.754133616	0.477471688
H	3.346878566	-2.776393522	0.549562054
C	2.972592315	-0.812160035	1.547145031
H	3.279886450	-0.987358478	2.564000188
C	2.496095181	0.417889551	1.011871006
H	2.367774314	1.334345129	1.563882808
C	2.574543055	-1.104950749	-0.704555480
H	2.521272117	-1.536592584	-1.688562203
C	0.739666978	-2.837882992	1.972738693
C	-0.029866401	-0.219501507	2.398850097
O	0.824105595	-3.784601898	2.618958968
O	-0.389821850	0.399514358	3.304612610

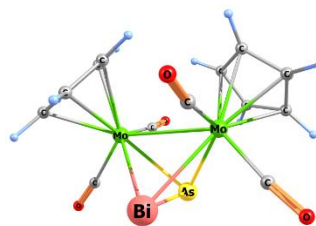


Table S14: Cartesian coordinates of the optimized geometry of $[(\text{CpMo}(\text{CO})_2)_2(\text{SbBi})]$ (**5**).

Bi	0.570368021	6.150784767	7.829125897
Sb	1.397801809	6.038588560	5.186141550
Mo	-0.472497009	4.092782531	5.922350761
Mo	2.446345042	4.093750995	7.074374521
O	-1.475366939	3.256647878	8.758436831
O	-2.696976196	6.275887649	5.710745033
C	-1.064794733	3.654579213	7.752022495
C	-1.835274458	5.523485399	5.841532526
O	3.463679708	3.248116889	4.248683681
O	4.664998399	6.284980646	7.263036423
C	3.049401888	3.645439341	5.252990329
C	3.806059371	5.528200056	7.143706248
C	1.688831822	2.124214318	8.225505394
H	0.747158214	1.641475905	8.039398880
C	2.912593270	1.851002721	7.567855107
H	3.063904232	1.123949583	6.787063223
C	3.923421632	2.672252912	8.141841350
H	4.968808758	2.668437097	7.884388801
C	3.304829742	3.465942004	9.151772073
H	3.801949939	4.182275717	9.784487242
C	1.927886561	3.127952380	9.201801796
H	1.196730770	3.526735457	9.882839341
C	0.280000974	2.114816866	4.783297426
H	1.218766988	1.629486993	4.977585591
C	-0.948649707	1.849528697	5.435241571
H	-1.107404814	1.126833321	6.218631606
C	-1.952027579	2.673378665	4.852763175
H	-2.998623801	2.676389524	5.105313412
C	-1.324171831	3.460505302	3.843061392
H	-1.813721283	4.177880995	3.205670060
C	0.050958579	3.116000796	3.801994531
H	0.787612633	3.511896825	3.125141734

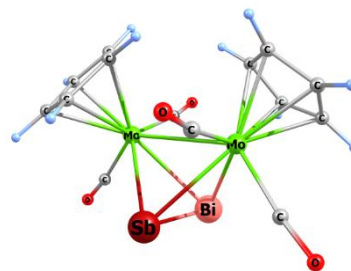


Table S15: Cartesian coordinates of the optimized geometry of $[(\text{CpMo}(\text{CO})_2)_2\text{P}(\text{SiMe}_3)_2]^-$ (**6a**).

Mo	1.421806855	-1.847380882	0.663419393
Mo	-1.421951642	-1.847188120	-0.663605785
P	0.000011820	0.032252906	-0.000016799
Si	0.617011103	1.469304391	-1.690479471
Si	-0.616819772	1.469241777	1.690571352
O	2.463234293	-2.893585023	-2.023854882
O	3.700952159	0.120059569	0.029107539
C	2.775880836	-0.577390138	0.245010739
C	1.960349955	-2.447902944	-1.048503593
O	-2.463492698	-2.893430245	2.023612632
O	-3.700847188	0.120546011	-0.029281974
C	-2.775876660	-0.577033243	-0.245189423
C	-1.960567409	-2.447741965	1.048283899
C	2.000270601	-3.923912925	1.525611493
H	2.175337180	-4.764194156	0.861826945
C	0.773076351	-3.603960077	2.161321660
H	-0.154238247	-4.153943437	2.071046254
C	2.968165767	-2.955754465	1.917554206
H	4.010574960	-2.937265241	1.617693571
C	0.966921221	-2.431381157	2.944682001
H	0.216790063	-1.958644775	3.564815949
C	2.320367725	-2.027478378	2.792924567
H	2.795547245	-1.180864600	3.277255019
C	-1.669778654	0.639879139	3.023775240
H	-2.638141810	0.311786852	2.638673489
H	-1.847496194	1.379785417	3.817251565
H	-1.175876271	-0.224468038	3.472137578
C	-1.636556902	2.978218911	1.141645442
H	-1.114776108	3.628880875	0.433931935
H	-1.873421163	3.578169051	2.032341262
H	-2.582556444	2.662493225	0.690638305
C	0.934532895	2.120306162	2.571942191
H	1.477603169	1.298173334	3.049845039
H	0.637998581	2.833977019	3.354031468
H	1.629398506	2.627369152	1.895856562
C	-2.000831889	-3.923558297	-1.525927068
H	-2.176209169	-4.763801470	-0.862176847
C	-0.773460515	-3.603892126	-2.161436886
H	0.153703409	-4.154110002	-2.071035305
C	-2.968420058	-2.955147886	-1.917989643
H	-4.010869195	-2.936403346	-1.618282563
C	-0.966894349	-2.431244777	-2.944803967
H	-0.216541835	-1.958687116	-3.564805957
C	-2.320262868	-2.027018361	-2.793253697
H	-2.795156981	-1.180275567	-3.277639399
C	1.671374573	0.640316692	-3.022805362
H	2.639681788	0.312880058	-2.637007129
H	1.849157467	1.380154509	-3.816329755
H	1.178262364	-0.224425572	-3.471299714
C	1.635367547	2.979057070	-1.141139831
H	1.112628352	3.629521481	-0.433951447
H	1.872504902	3.578975972	-2.031783113
H	2.581238942	2.664044762	-0.689373509
C	-0.934183772	2.119119625	-2.573047220
H	-1.476365787	1.296501511	-3.051129215
H	-0.637599666	2.832811247	-3.355098873
H	-1.629857383	2.625857612	-1.897558867

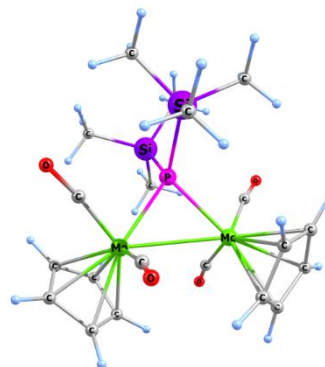


Table S16: Cartesian coordinates of the optimized geometry of $[(\text{CpMo}(\text{CO})_2)_2\text{As}(\text{SiMe}_3)_2]^-$ (**6b**).

Mo	0.301974320	2.024631398	-1.595205595
Mo	-0.431844853	1.991742054	1.551624209
As	0.009704221	0.038067008	-0.024329655
Si	1.911630152	-1.314165476	0.342014832
Si	-1.784555468	-1.453501744	-0.393924802
O	2.062018267	4.262847268	-0.369979962
O	-2.361652846	4.087411871	0.330382108
O	3.096031622	0.995029500	-2.413715943
O	-3.135974560	0.744653072	2.369525981
C	1.377176074	3.383130719	-0.738411512
C	2.036023599	1.341766639	-2.035530500
C	-2.106800061	1.174300674	1.991509161
C	-1.610316803	3.262989761	0.697264048
C	-0.312976251	1.854651826	-3.878128363
H	0.311210316	1.312028145	-4.569764133
C	1.328067209	1.420259450	3.118277544
H	1.746974055	0.430437276	3.172847351
C	-1.411083083	1.320661750	-3.158986988
H	-1.754980390	0.302361046	-3.212018607
C	-0.030972121	3.234510298	3.502472146
H	-0.802647424	3.868214479	3.907930013
C	-0.191484358	3.230581654	-3.547091674
H	0.530685691	3.919382453	-3.953896676
C	0.962887762	3.616282433	2.557151373
H	1.072956666	4.587901495	2.106361560
C	-1.210713826	3.538660024	-2.601837014
H	-1.392478064	4.500120886	-2.152363293
C	-1.965162680	2.358852109	-2.365866793
H	-2.802229891	2.269072809	-1.696724360
C	-2.101372606	-2.437190819	1.178329942
H	-1.239854073	-3.043928714	1.457608430
H	-2.954490111	-3.105737313	1.026090112
H	-2.334587733	-1.767507089	2.006794927
C	2.301750350	-2.266049441	-1.233499661
H	1.492360694	-2.941908940	-1.510183018
H	3.208009853	-2.861779908	-1.086106114
H	2.475000528	-1.578534575	-2.062121578
C	0.192527106	1.872059589	3.835678061
H	-0.390199796	1.285310800	4.527469749
C	-3.350128942	-0.502177686	-0.821097483
H	-3.453701458	0.392590940	-0.210561451
H	-4.211867444	-1.148465105	-0.628812790
H	-3.377779053	-0.211879857	-1.870617402
C	1.803140511	2.495408490	2.323078189
H	2.644813371	2.467254693	1.654234289
C	1.627767286	-2.541741426	1.742967264
H	1.235933566	-2.046199807	2.633462646
H	2.573653074	-3.024004014	2.007724385
H	0.922813494	-3.322333525	1.452804451
C	-1.409496586	-2.651600485	-1.798927807
H	-1.050644542	-2.125515512	-2.685771866
H	-2.317870316	-3.198574812	-2.069230099
H	-0.652092444	-3.381603979	-1.509158553
C	3.400811132	-0.249620365	0.773461616
H	3.443978729	0.647171286	0.158642902
H	4.308115737	-0.833189459	0.590180018
H	3.400342401	0.047166159	1.821476384

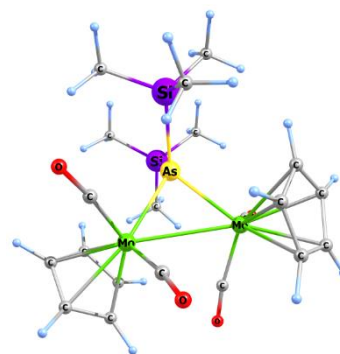


Table S17: Cartesian coordinates of the optimized geometry of $[(\text{CpMo}(\text{CO})_2)_2\text{Sb}(\text{SiMe}_3)_2]^-$ (**6c**).

Sb	0.022750682	-0.045185096	0.051254708
Mo	-1.437555806	1.777884551	1.396953355
Mo	0.385750420	-0.679629566	2.645426641
Si	2.008039687	0.796494643	-1.336130307
Si	-1.155691859	-1.752417518	-1.455258683
O	-2.264210944	-0.725638845	4.259964501
O	0.096536543	3.034723885	3.783599254
O	0.138268341	3.950087564	-0.138261640
O	-0.562570489	-3.533415842	1.925363116
C	-0.414262142	3.082093353	0.436640817
C	1.665922475	0.316639918	4.364947747
H	1.197785962	0.972657423	5.078881346
C	2.283398230	0.719434126	3.152028372
H	2.347977845	1.727083114	2.779783799
C	-0.424814667	2.481817221	2.889132927
C	1.786200390	-1.099265884	4.474320085
H	1.445860481	-1.706360508	5.297085785
C	-1.305628409	-0.647240520	3.587141945
C	2.787813473	-0.443269761	2.510551190
H	3.317037561	-0.476997227	1.573620802
C	2.472631858	-1.563688604	3.320108718
H	2.725361800	-2.589056155	3.103153440
C	3.049707439	1.964525562	-0.294202994
H	2.427039614	2.735171366	0.159656424
H	3.790036100	2.453906294	-0.934924632
H	3.583919296	1.440641887	0.497989421
C	-3.494119014	1.175515477	0.277333613
H	-3.505307609	0.647845889	-0.660979473
C	-1.577727026	-0.986406201	-3.123240609
H	-2.174366991	-0.079787316	-3.002359195
H	-2.150428118	-1.695260991	-3.729195599
H	-0.673267871	-0.723440032	-3.675200857
C	-3.459494023	2.881475861	1.819277073
H	-3.464611334	3.866215270	2.256962045
C	-0.231344369	-2.424830297	2.150180222
C	-2.727873729	-2.346450836	-0.613049878
H	-2.517464749	-2.685755643	0.401058598
H	-3.143689863	-3.186693728	-1.178043530
H	-3.485610788	-1.564858452	-0.565217314
C	-3.511288334	1.644569855	2.525444544
H	-3.538730636	1.522966274	3.594900120
C	-3.439902822	2.583973317	0.430177482
H	-3.405412057	3.304093059	-0.371417990
C	-3.531054046	0.593010857	1.572385570
H	-3.558386057	-0.459942917	1.793329885
C	1.340609850	1.739473691	-2.821846578
H	0.717774817	1.104133070	-3.453522520
H	2.168378906	2.118995224	-3.429209307
H	0.740184690	2.588442143	-2.490571656
C	-0.005924744	-3.220914168	-1.707188584
H	0.931476319	-2.919570415	-2.177495312
H	-0.484332676	-3.969000347	-2.347138807
H	0.225762092	-3.686684945	-0.747811954
C	3.067112975	-0.644374738	-1.927648193
H	3.407435847	-1.255847178	-1.089299847
H	3.948118705	-0.270337160	-2.458377583
H	2.509678776	-1.288550007	-2.610360507

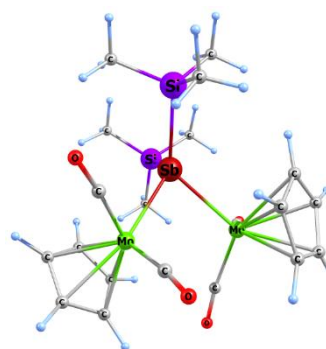
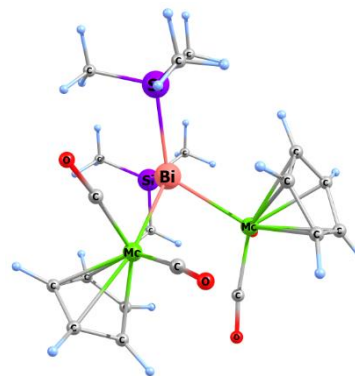


Table S18: Cartesian coordinates of the optimized geometry of $[(\text{CpMo}(\text{CO})_2)_2\text{Bi}(\text{SiMe}_3)_2]^-$ (**6d**).

Bi	0.024139401	-0.048531959	0.058948552
Mo	-1.454846698	1.816407404	1.478397505
Mo	0.357966413	-0.661387172	2.741324985
Si	2.070276663	0.824132096	-1.365153764
Si	-1.194143012	-1.814546710	-1.480836423
O	-2.288481455	-0.667876638	4.360106297
O	0.061204025	3.052442340	3.886015577
O	0.152402871	3.981281732	-0.037346067
O	-0.624346528	-3.506435202	2.026709274
C	-0.415675536	3.117914013	0.530549050
C	1.634759037	0.335588209	4.457964055
H	1.164922857	0.989971370	5.172222897
C	2.253392093	0.741095618	3.246642493
H	2.317239122	1.749244415	2.875138225
C	-0.452348320	2.507111569	2.981779618
C	1.754560231	-1.081001222	4.564779155
H	1.416496016	-1.689093522	5.387654064
C	-1.330679685	-0.605851603	3.683786220
C	2.759630271	-0.420408492	2.603834822
H	3.291244787	-0.450463179	1.667969049
C	2.444209151	-1.542903685	3.410617593
H	2.699182421	-2.567508409	3.192767160
C	3.103127992	1.974476700	-0.296287232
H	2.478826895	2.756104829	0.137292317
H	3.873470223	2.450060899	-0.911824204
H	3.600110062	1.440493989	0.513694958
C	-3.504818142	1.195255333	0.357022184
H	-3.513709913	0.656075560	-0.574876393
C	-1.604773077	-1.049574327	-3.151391548
H	-2.229310468	-0.161448296	-3.034849434
H	-2.144683226	-1.768931048	-3.775141865
H	-0.696254087	-0.756466991	-3.681268674
C	-3.473453632	2.919035073	1.880139550
H	-3.483355413	3.908526230	2.306683511
C	-0.277655146	-2.401993265	2.251771504
C	-2.764384278	-2.384437991	-0.620061838
H	-2.539058762	-2.748730902	0.382569488
H	-3.217830805	-3.201319265	-1.190614939
H	-3.496972870	-1.581505327	-0.538298166
C	-3.528067606	1.689410182	2.599817088
H	-3.557821065	1.579272880	3.670397037
C	-3.451145861	2.605487325	0.493698695
H	-3.416059745	3.316420426	-0.315982502
C	-3.545061512	0.627195939	1.658661482
H	-3.571220403	-0.423437565	1.890974365
C	1.393370199	1.782021503	-2.836518368
H	0.768096061	1.150606090	-3.470271772
H	2.216197886	2.169534859	-3.445869213
H	0.792479147	2.626254420	-2.493728896
C	-0.040953136	-3.283089348	-1.713801086
H	0.896581666	-2.983014291	-2.185322509
H	-0.514570795	-4.040700517	-2.346328063
H	0.191121188	-3.737162452	-0.748744297
C	3.116150269	-0.620612019	-1.968804157
H	3.479214990	-1.221359876	-1.132338274
H	3.982533528	-0.252103693	-2.527148597
H	2.540516713	-1.272955591	-2.628537516



References

- [1] R. J. Klingler, W. Butler, M. D. Curtis, *J. Am. Chem. Soc.* **1975**, *97*, 3535-3536.
- [2] M. Scheer, K. Schuster, K. Schenzel, E. Herrmann, P. G. Jones, *Z. Anorg. Allg. Chem.* **1991**, *600*, 109-119.
- [3] G. Fritz, W. Hölderich, *Z. Anorg. Allg. Chem.* **1976**, *422*, 104-114.
- [4] a) R. L. Wells, M. F. Self, J. D. Johansen, J. A. Laske, S. R. Aubuchon, L. J. Jones III, A. H. Cowley, S. Kamepalli, in *Inorg. Synth.*, **1996**, pp. 150-158; b) G. Becker, C. Witthauer, *Z. Anorg. Allg. Chem.* **1982**, *492*, 28-36.
- [5] a) G. Becker, A. Münch, C. Witthauer, *Z. Anorg. Allg. Chem.* **1982**, *492*, 15-27; b) E. Amberger, R. W. Salazar G, *J. Organomet. Chem.* **1967**, *8*, 111-114; c) C. Marquardt, O. Hegen, M. Hautmann, G. Balázs, M. Bodensteiner, A. V. Virovets, A. Y. Timoshkin, M. Scheer, *Angew. Chem. Int. Ed.* **2015**, *54*, 13122-13125.
- [6] a) O. Mundt, G. Becker, M. Rössler, C. Witthauer, *Z. Anorg. Allg. Chem.* **1983**, *506*, 42-58; b) T. M. Rookes, E. P. Wildman, G. Balázs, B. M. Gardner, A. J. Wooles, M. Gregson, F. Tuna, M. Scheer, S. T. Liddle, *Angew. Chem. Int. Ed.* **2018**, *57*, 1332-1336; c) G. Becker, M. Roessler, *Z. Naturforsch. B.* **1982**, *37b*, 91-96.
- [7] A. Johannis, *Ann. Chim. Phys.* **1906**, *7*, 106.
- [8] O. J. Scherer, H. Sitzmann, G. Wolmershäuser, *J. Organomet. Chem.* **1984**, *268*, C9-C12.
- [9] M. L. Ziegler, K. Blechschmitt, B. Nuber, T. Zahn, *Chem. Ber.* **1988**, *121*, 159-171.
- [10] J. R. Harper, A. L. Rheingold, *J. Organomet. Chem.* **1990**, *390*, c36-c38.
- [11] W. Clegg, N. A. Compton, R. J. Errington, G. A. Fisher, N. C. Norman, T. B. Marder, *J. Chem. Soc., Dalton Trans.* **1991**, 2887-2895.
- [12] J. E. Davies, L. C. Kerr, M. J. Mays, P. R. Raithby, P. K. Tompkin, A. D. Woods, *Angew. Chem. Int. Ed.* **1998**, *37*, 1428-1429.
- [13] Agilent (2014). CrysAlis PRO. Agilent Technologies Ltd., Yarnton, Oxfordshire, England.
- [14] G. Sheldrick, *Acta Crystallographica Section A* **2015**, *71*, 3-8.
- [15] O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, *J. Appl. Cryst.* **2009**, *42*, 339-341.
- [16] G. Sheldrick, *Acta Crystallographica Section C* **2015**, *71*, 3-8.
- [17] Crystallographic Data for Compound **2** was already provided by Mays *et. al.* in 1998 under the CCDC deposition code CCDC-100650.
- [18] F. Neese "The ORCA program system" Wiley Interdisciplinary Reviews: Computational Molecular Science, **2012**, Vol. 2, Issue 1, Pages 73–78.
- [19] a) A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648-5652; b) C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B* **1988**, *37*, 785-789; c) A. D. Becke, *Phys. Rev. A* **1988**, *38*, 3098-3100; d) S. H. Vosko, L. Wilk, M. Nusair, *Can. J. Phys.* **1980**, *58*, 1200-1211; e) J. C. Slater, *Phys. Rev.* **1951**, *81*, 385-390; f) P. A. M. Dirac, *Proc. Royal Soc. A* **1929**, *123*, 714-733.
- [20] a) A. Schäfer, C. Huber, R. Ahlrichs, *J. Chem. Phys.* **1994**, *100*, 5829; b) K. Eichkorn, F. Weigend, O. Treutler, R. Ahlrichs, *Theor. Chem. Acc.* **1997**, *97*, 119; c) F. Weigend, R. Ahlrichs, *Phys. Chem. Chem. Phys.* **2005**, *7*, 3297; d) F. Weigend, *Phys. Chem. Chem. Phys.* **2006**, *8*, 1057.
- [21] S. Grimme, S. Ehrlich, L. Goerigk, *J. Comput. Chem.* **2011**, *32*, 1456-1465.
- [22] V. Barone, M. Cossi, *M. J. Phys. Chem. A*, **1998**, *102*, 1995-2001.
- [23] O. V. Sizova, L. V. Skripnikov, A. Y. Sokolov, *J. Molec. Struct.: THEOCHEM* **2008**, *870*, 1-9.
- [24] T. Lu, F. Chen, *J. Comput. Chem.* **2012**, *33*, 580-592.
- [25] G. Knizia, *J. Chem. Theory Comput.* **2013**, *9*, 4834-4843.
- [26] IboView v20150427. <http://www.iboview.org/>
- [27] N. Reinfandt, C. Schoo, L. Dütsch, R. Köppe, S. Konchenko, M. Scheer, P. Roesky, *Chem. Eur. J.* **2021**, *27*, 3974-3978.