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Reactivity of [Cp*Mo(CO)$_3$Me] with chalcogenated borohydrides Li[BH$_2$E$_3$] and Li[BH$_3$EFc] (Cp* = (η^5-C$_5$Me$_5$); E = S, Se or Te; Fc = (C$_5$H$_5$-Fe-C$_5$H$_4$))

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Abstract. Reactivity of [Cp*Mo(CO)$_3$Me], **1** with various chalcogenide ligands such as Li[BH$_2$E$_3$] and Li[BH$_3$EFc] (E = S, Se or Te; Fc = (C$_5$H$_5$-Fe-C$_5$H$_4$)) has been described. Room temperature reaction of **1** with Li[BH$_2$E$_3$] (E = S and Se) yielded metal chalcogenide complexes [Cp*Mo(CO)$_2$(η^2-S$_2$CCH$_3$)], **2** and [Cp*Mo(CO)$_2$(η^1-SeC$_2$H$_5$)], **3**. In compound **2**, {Cp*Mo(CO)$_2$} fragment adopts a four-legged piano-stool geometry with a η^2-dithioacetate moiety. In contrast, treatment of **1** with Li[BH$_3$(EFc)] (E = S, Se or Te; Fc = C$_5$H$_5$-Fe-C$_5$H$_4$) yielded borate complexes [Cp*Mo(CO)$_2$(μ-H)(μ-EFc)BH$_2$], **4-6** in moderate yields. Compounds **4-6** are too unstable and gradual conversion to [{Cp*Mo(CO)$_2$}$_2$(μ-H)(μ-EFc] (**7**: E = S; **8**: Se) and [{Cp*Mo(CO)$_2$}$_2$(μ-TeFc)$_2$], **9** happened by subsequent release of BH$_3$. All the compounds have been characterized by mass spectrometry, IR, multinuclear NMR spectroscopy and structures were unequivocally established by crystallographic analysis for compounds **2**, **3** and **7**.

Keywords. Molybdenum; thioacetate; sulfur; borate; ferrocene.

1. Introduction

The chalcogen chemistry of transition metals received significant attention due to their potential applications in photovoltaic materials, industrial materials and magnetic resonance imaging.[1–3] Furthermore, sulfur based ligands such as monothio- and dithiocarboxylates have often been reported as mono metal and polynuclear complexes.[4–6] Moreover, reactivity of chalcogenide ligands present in metal dithiolate complexes are well documented.[7–9] For example, [(tppme)M(η^2-S$_2$CSMe)] (BPh$_4$)][7a] (M = Co, Ni; tppme = 1,1,1-tris(diphenylphosphinomethyl)ethane), [(triphos)Rh(η^2-S$_2$CH(PEt$_3$)] (BPh$_4$)$_2$][7c] (triphos = MeC(CH$_2$PPh$_2$)$_3$), [(CpW(CO)$_2$ (η^2-S$_2$CCH$_3$)][8] and [Cp*(PMe$_3$)Ir(η^2-S$_2$CMe$_2$)][9] have been studied widely and remain useful in organometallics due to electrophilic/nucleophilic nature of the metal centre (chart 1).

On the other hand, metal-sulfur bond is relatively strong and these ligands are frequently used to form metal complexes. However, mononuclear complexes with simple thiolate ligands are rare. Recently, these complexes have been received immense interest due to their studies towards the organic substrate.[10] For example, the rhodium complex [(triphos)RhCl S$_2$C(PEt$_3$)],[7c] act as a good reducing agent on the course of reaction with oxidizers and electrophiles. Apart from this, the transition metal-selenide and telluride complexes represent a wide range of structural varieties[11a–b] and recent investigations focus on their cluster growth reactions.[11] Thus, in search of alternative mono metal precursors for the synthesis of chalcogenide complexes, we have found [Cp*Mo(CO)$_3$Me], **1** as a good precursor. As a result, we have explored the reactivity of **1** with various preformed chalcogenated borohydrides as well as chalcogeno-borate ligands.

2. Experimental

2.1 *General considerations*

All the operations were conducted under an Ar/N$_2$ atmosphere using standard Schlenk techniques or glove box. Solvents were distilled prior to use under Argon. Compounds **1**,[12] Li[BH$_2$E$_3$][13,14] (E = S, Se or Te) and [Fc$_2$E$_2$] (E = S, Se or Te)[15] were prepared according to the literature procedure. [LiBH$_4$.thf], [Mo(CO)$_6$], S powder, Se powder, Te powder and ferrocene were obtained commercially and used as received. The external reference for the ^{11}B{^{1}H} NMR, [Bu$_4$N(B$_3$H$_8$)] was synthesized according to literature method.[16] Thin layer chromatography was carried on 250 mm dia

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*For correspondence

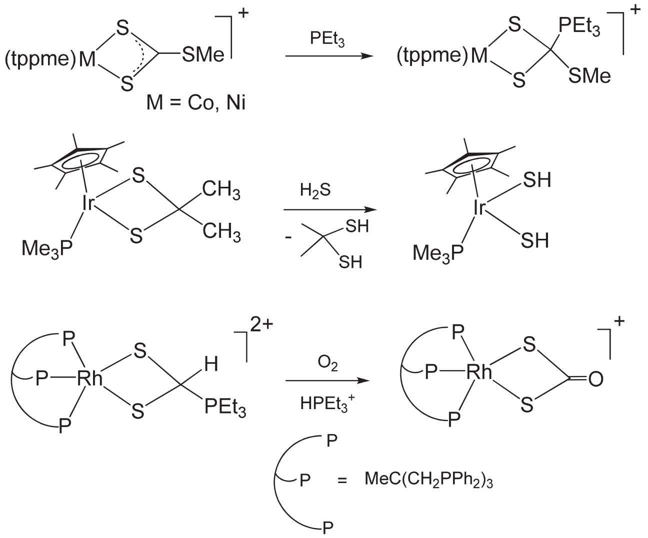


Chart 1. Reactivity of various dithio-metal complexes.

aluminium supported silica gel TLC plates (MERCK TLC plates). The residual solvent protons were used as reference (δ, ppm, d$_6$-benzene, 7.16, $CDCl_3$, 7.26), while a sealed tube containing [$Bu_4N(B_3H_8)$] in d$_6$-benzene (δ, ppm, −30.07) was used as an external reference for the $^{11}B\{^1H\}$ NMR. Infrared spectra were recorded on a Nicolet iS10 spectrometer. Microanalyses for C, H and N were performed on Perkin Elmer Instruments series II model 2400. Mass spectra were recorded on Bruker MicroTOF-II mass spectrometer in ESI ionization mode.

2.2 *Synthesis of compounds 2-3*

In a flame-dried Schlenk tube, [$Cp^*Mo(CO)_3Me$], **1** (0.1 g, 0.3 mmol) dissolved in toluene (10 mL) and allowed to stir at room temperature for 12 h in presence of Li[BH_2S_3] (0.034 g, 0.3 mmol). The solvent was removed under vacuum and the residue was extracted into hexane and passed through Celite. The mother liquor was concentrated and the residue was subjected to chromatographic work up using silica-gel TLC plates. Elution with a hexane/CH_2Cl_2 (80:20) mixture afforded red **2** (0.056 g, 49%). Compound **3** has been synthesized under similar reaction conditions, compound **1** (0.1 g, 0.3 mmol) reacted with Li[BH_2Se_3] (0.076 g, 0.3 mmol) and thus yielded yellow **3** (0.012 g, 10%).

Note that, Li[BH_2S_3] was prepared from the reaction of [$LiBH_4$.thf] with sulfur powder (1:3).[13] In a similar fashion, the Se and Te analogues were prepared using the literature method.[14]

2: MS (ESI$^+$): calculated mass for $^{12}C_{14}{}^{1}H_{18}{}^{96}Mo_1{}^{32}S_2{}^{16}O_2{}^{39}K_1$, 417.4798; found: 417.93; ^1H NMR (400 MHz, $CDCl_3$, 22°C): δ = 1.84 (s, 15H, Cp*), 2.56 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$, 22°C): δ = 104.3 (s, C_5Me_5), 41.8 (s, *C*), 28.6 (s, CH_3), 9.6 (s, C_5Me_5); IR (hexane): νbar = 2951 (CH_3), 1956, 1887 cm^{-1} (CO). Elemental analysis calcd (%) for $C_{14}H_{18}MoS_2O_2$: C, 44.47; H, 4.80; found (%): C, 43.78; H, 4.98.

3: MS (ESI$^+$): calculated mass for $^{12}C_{14}{}^{1}H_{20}{}^{96}Mo_1{}^{79}Se_1{}^{16}O_2$, 395.2274; found: 395.00; ^1H NMR (400 MHz, $CDCl_3$, 22°C): δ = 1.88 (s, 15H, Cp*), 1.26 (s, 2H, CH_2), 0.85 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$, 22°C): δ = 105.3 (s, C_5Me_5), 29.0 (s, CH_2), 16.6 (s, CH_3), 10.8 (s, C_5Me_5); IR (hexane): νbar = 1945, 1860 cm^{-1} (CO). Elemental analysis calcd (%) for $C_{14}H_{20}MoSeO_2$: C, 42.55; H, 5.10; found (%): C, 41.67; H, 5.23.

2.3 *Synthesis of compounds 4-6*

In a flame-dried Schlenk tube, compound **1** (0.1 g, 0.3 mmol) was dissolved in toluene (15 mL) and Li[$H_3B(SFc)$] (in thf) (Fc = C_5H_5-Fe-C_5H_4) (0.107 g, 0.3 mmol) was transferred to the solution, allowed to stir for 14 h at room temperature. The solvent was removed under vacuum and the residue was extracted into hexane and was passed through Celite. The mother liquor was concentrated and the residue was subjected to chromatographic work up using silica-gel TLC plates. Elution with a hexane/CH_2Cl_2 (75:25) mixture afforded yellow **4** (0.031 g, 19.9%). Under same conditions, compound **1** (0.1 g, 0.3 mmol) reacted with Li[$H_3B(EFc)$] [E = Se (0.121 g, 0.3 mmol), E = Te (0.136 g, 0.3 mmol)] yielded yellow **5** (0.025 g, 14.7%) and orange **6,** respectively.

Note that due to instability, compound **6** was not isolated, thus it was characterized based on comparision with the combined spectroscopic data of [$Cp^*Mo(CO)_2(\mu\text{-}H)(\mu\text{-}TePh)BH_2$].[17] The experimental details of Li[BH_3EFc] (E = S, Se or Te) are given in the supplementary information.

4: MS (ESI$^+$): calculated mass for $^{12}C_{22}{}^{1}H_{27}{}^{56}Fe_1{}^{96}Mo_1{}^{11}B_1{}^{32}S_1{}^{16}O_2$: 518.1296; found: 519; $^{11}B\{^1H\}$ NMR (128 MHz, $CDCl_3$, 22°C): δ = −30.5 ppm (s, 1B); ^1H NMR (400 MHz, $CDCl_3$, 22°C): δ = 4.20 (s, 5H, C_5H_5), 4.15-4.05 (m, 4H, C_5H_4), 1.87 (s, 15H, Cp*), 1.55 (br, 2H, BH_t), –8.41 ppm (br, 1H, Mo-H-B); ^{13}C NMR (100 MHz, $CDCl_3$, 22°C): δ = 105.8 (s, C_5Me_5), 71.2, 69.6, 68.4 (m, C_5H_4), 70.3 (s, C_5H_5), 10.8 ppm (s, C_5Me_5); IR (hexane): νbar = 2419, 2376 (w, BH_t), 1951, 1866 cm^{-1} (CO).

5: MS (ESI$^+$): calculated mass for $^{12}C_{22}{}^{1}H_{27}{}^{56}Fe_1{}^{96}Mo_1{}^{11}B_1{}^{79}Se_1{}^{16}O_2$: 565.0246; found: 567; $^{11}B\{^1H\}$

NMR (128 MHz, $CDCl_3$, 22°C): $\delta = -28.3$ ppm (s, 1B); ^{1}H NMR (400 MHz, $CDCl_3$, 22°C): $\delta =$ 4.18 (s, 5H, C_5H_5), 4.30-4.05 (m, 4H, C_5H_4), 1.88 (s, 15H, Cp*), 1.35 (br, 2H, BH_t), -8.97 ppm (br, 1H, Mo-H-B); ^{13}C NMR (100 MHz, $CDCl_3$, 22°C): $\delta = 95.1$ (s, C_5Me_5), 70.2, 69.4, 65.5 (m, C_5H_4), 61.2 (s, C_5H_5), 10.8 ppm (s, $C_5\mathit{Me}_5$); ^{77}Se NMR (95.38 MHz, $CDCl_3$, 22°C): $\delta = -111.2$ ppm (s, SeFc); IR (hexane): νbar = 2372 (w, BH_t), 1944, 1866 cm^{-1}(CO).

6: MS (ESI$^+$): calculated mass for $^{12}C_{20}{}^1H_{27}{}^{56}Fe_1{}^{96}Mo_1{}^{11}B_1{}^{128}Te_1{}^{16}O_2$: 589.6432; found: 561.0 [M-CO]$^+$; $^{11}B\{^1H\}$ NMR (128 MHz, $CDCl_3$, 22°C): $\delta = -26.7$ ppm (s, 1B); ^{1}H NMR (400 MHz, $CDCl_3$, 22°C): $\delta =$ 3.65-3.56 (m, 4H, C_5H_4), 3.38 (s, 5H, C_5H_5), 2.02 (s, 15H, Cp*), 1.05 (br, 2H, BH_t), -10.17 ppm (br, 1H, Mo-H-B); ^{13}C NMR (100 MHz, $CDCl_3$, 22°C): $\delta = 103.1$ (s, C_5Me_5), 78.9, 78.9, 69.3 (m, C_5H_4), 69.3 (s, C_5H_5), 10.4 ppm (s, $C_5\mathit{Me}_5$); ^{125}Te NMR (157.8 MHz, $CDCl_3$, 22°C): $\delta = 621.7$ ppm (s, TeFc); IR (hexane): νbar = 2379 (w, BH_t), 1831 cm^{-1} (CO).

2.4 *Isolation of compounds 7-9*

In a 25 mL Schlenk tube, containing 0.3 g (0.58 mmol) of **4**, 4 mL of hexane was added and kept at 3°C for 4 days. The solvent was dried slowly and the residue was extracted into hexane and passed through Celite. After removal of solvent, the residue was subjected to chromatographic work up using silica gel TLC plates. Elution with a hexane/CH_2Cl_2 (95:05 v/v) mixture yielded green **7** (0.078 g, 17%). Under similar conditions, **5** (0.2 g, 0.35 mmol) and **6** (0.2 g, 0.32 mmol) yielded **8** (0.045 g, 15%) and **9** (0.059 g, 14.5%), respectively. Note that the optimized reaction time for the generation of chalcogenolate complexes **7**-**9** from **4**-**6** is approximately 4 days.

7: MS (ESI$^+$): calculated mass for $^{12}C_{34}{}^1H_{40}{}^{56}Fe_1{}^{96}Mo_2{}^{16}O_4{}^{32}S_1$, 792.5090; found: 792; ^{1}H NMR (400 MHz, $CDCl_3$, 22°C): $\delta =$ 4.40-4.07 (m, 9H, C_5H_5 & C_5H_4), 1.99 (s, 30H, 2Cp*), –10.04 (s, 1H, Mo-H-Mo); ^{13}C NMR (100 MHz, $CDCl_3$, 22°C): $\delta = 102.3$ (s, C_5Me_5), 69.8 (s, C_5H_5), 61.6, 57.9, 53.5 (m, C_5H_4), 11.7 (s, $C_5\mathit{Me}_5$); IR (hexane): νbar = 1962 cm^{-1} (CO).

8: MS (ESI$^+$): calculated mass for $^{12}C_{34}{}^1H_{40}{}^{56}Fe_1{}^{96}Mo_2{}^{16}O_4{}^{79}Se_1$, 839.4040; found: 840.0; ^{1}H NMR (400 MHz, $CDCl_3$, 22°C): $\delta =$ 3.66-3.38 (m, 9H, C_5H_5 & C_5H_4), 2.00 (s, 30H, 2Cp*), –11.03 (s, 1H, Mo-H-Mo); ^{13}C NMR (100 MHz, $CDCl_3$, 22°C): $\delta = 100.1$ (s, C_5Me_5), 73.4, 71.6, 71.6 (m, C_5H_4), 69.1 (s, C_5H_5), 10.4 (s, $C_5\mathit{Me}_5$); IR (hexane): νbar = 1876 cm^{-1} (CO).

9: MS (ESI$^+$): calculated mass for $^{12}C_{44}{}^1H_{48}{}^{56}Fe_2{}^{96}Mo_2{}^{128}Te_2{}^{16}O_4$, 1199.6595; found: 1199.6; ^{1}H NMR (400 MHz, $CDCl_3$, 22°C): $\delta =$ 3.64-3.57 (m, 8H, C_5H_4), 3.49 (s, 10H, C_5H_5), 2.23 (s, 30H, Cp*); ^{13}C NMR (100 MHz, $CDCl_3$, 22°C): $\delta =$ 103.6 (s, C_5Me_5), 79.3, 72.9, 41.1 (m, C_5H_4), 69.3 (s, C_5H_5), 10.8 ppm (s, $C_5\mathit{Me}_5$); IR (hexane): νbar = 1962 cm^{-1} (CO).

2.5 *X-ray structure determination*

Crystallographic information for compounds **2**, **3** and **7** are shown in table 1. The crystal data for **2** and **7** were collected and integrated using a Bruker Axs kappa apex2 CCD diffractometer, with graphite monochromated Mo-Kα ($\lambda = 0.71073$ Å) radiation. The crystal data for **3** were collected and integrated using Oxford Diffraction SuperNova CCD system equipped with graphite-monochromated Cu-Kα ($\lambda = 1.54184$ Å) radiation at 293 K. The structures were solved by heavy atom methods using SHELXS-97 or SIR92 and refined using SHELXL-97 (G.M. Sheldrick, University of Göttingen).[18]

3. Results and Discussion

3.1 *Reactivity of [Cp*Mo(CO)$_3$Me], 1, with Li[BH$_2$E$_3$] (E = S, Se or Te)*

We have previously synthesized various metallaboranes,[19–24] metallaheteroboranes[25] of Group 5 to 9 using boranes (BH_3.thf, $LiBH_4$.thf, $BHCl_2.SMe_2$, etc.), diorganyl dichalcogenides or elemental chalcogens with monopentamethylcyclopentadienyl metal halides [Cp*MCl$_n$]. In an effort to synthesize homometallic molybdaheteroboranes, room temperature reaction of **1**, with Li[BH$_2$S$_3$] generated molybdenum thiolate complex [Cp*Mo(CO)$_2$(η^2-S$_2$CCH$_3$)], **2**, in good yield. In contrast to Li[BH$_2$S$_3$], we have observed quite different behaviour when compound **1** is treated with Li[BH$_2$Se$_3$], which yielded [Cp*Mo(CO)$_2$(η^1-SeC$_2$H$_5$)], **3**. However, the Te analogue is very unstable compared to S and Se analogues and led to decomposition of starting material (scheme 1).

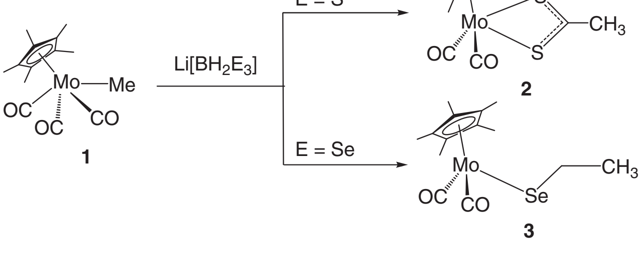
Compound **2** was isolated as red air-stable solid and characterized spectroscopically as well as by single-crystal X-ray diffraction analysis. The IR spectrum of **2** shows bands at 1956 and 1887 cm^{-1}, which are characteristics of carbonyl groups and a strong band at 2951 cm^{-1} attributed to the C−H stretching of methyl group.

Table 1. Crystal data and structure refinement details for compounds **2**, **3** and **7**.

	2	3	7
CCDC No.	1431592	1431593	1431591
Empirical formula	$C_{14}H_{18}MoO_2S_2$	$C_{14}H_{20}MoO_2Se$	$C_{34}H_{40}FeMo_2O_4S$
Formula weight	378.34	395.20	792.45
Crystal system	Orthorhombic	Triclinic	Triclinic
Space group	*Pnma*	*P-1*	*P-1*
a (Å)	16.775(4)	8.2825(5)	10.6795(2)
b (Å)	13.183(3)	9.3544(6)	17.4769(3)
c (Å)	7.3879(19)	12.0173(5)	18.8871(3)
α (°)	90.00	83.319(5)	90.1370(10)
β (°)	90.00	70.903(5)	98.7960(10)
γ (°)	90.00	80.102(5)	104.8870(10)
V(Å^3)	1633.7(7)	864.93(9)	3363.57(10)
Z	4	2	4
D_{calc}(g/cm^3)	1.538	1.517	1.565
$F(000)$	768	392	1608
μ (mm^{-1})	1.053	8.551	1.257
θ Range (°)	2.43-28.00	3.901-64.984	1.207-25.498
no. of reflections collected	2040	5002	12498
no. of unique reflections [$I > 2\sigma(I)$]	1755	4807	9706
goodness-of-fit on F^2	1.099	1.082	1.014
R1, wR2 [$I > 2\sigma(I)$]	0.0363, 0.0925	0.0529, 0.1591	0.0296, 0.0612
R1, wR2 (all data)	0.0429, 0.0925	0.0539, 0.1608	0.0459, 0.0686

The $^{11}B\{^1H\}$ NMR spectrum shows no chemical shift, whereas the ^{13}C NMR spectrum displays upfield signals at $\delta = 41.8$ and 28.6 ppm which signifies the formation of transition metal-dithioacetate complexes. The ^1H NMR spectrum of **2** shows methyl signal at $\delta = 2.56$ ppm and Cp* signal at $\delta = 1.84$ ppm, which is further confirmed by ^{13}C NMR spectrum. The solid state X-ray structure of **2**, shown in figure 1, is found to be isostructural with the W analogue, $[CpW(CO)_2(\eta^2\text{-}S_2CCH_3)]$.[8]

The molecular structure of **2** shows that the Mo atom is bonded with one Cp* and two carbonyl ligands and thus adopts four-legged piano stool geometry with a η^2-dithioacetate moiety (figure 1). A series of η^2-dithioacetate complexes with different transition metals, listed in table 2, corroborate the M-S bond distances and S-M-S angles. The Mo-S separation of 2.469(11) Å is slightly shorter than that observed in $[CpMo(CO)_2\{\eta^2\text{-}(S_2CCH_2{}^tBu)\}]$ (2.477(1) Å).[26] The C8-S1 bond length is 1.666(3) Å, comparatively shorter than that observed for these types of complexes. Also, complex **2** possesses almost exact mirror symmetry (excluding Cp* ring). The molecular structure of **2** displays planar Mo-S-C-S four membered ring having corresponding Mo1-S1 (2.4694(11) Å) and C8-S1 (1.666(3) Å) bond distances, with preferential delocalization. The S1-Mo1-S1 angle of 67.86(6)° is lesser



Scheme 1. Synthesis of metal-chalcogenide complexes **2** and **3**.

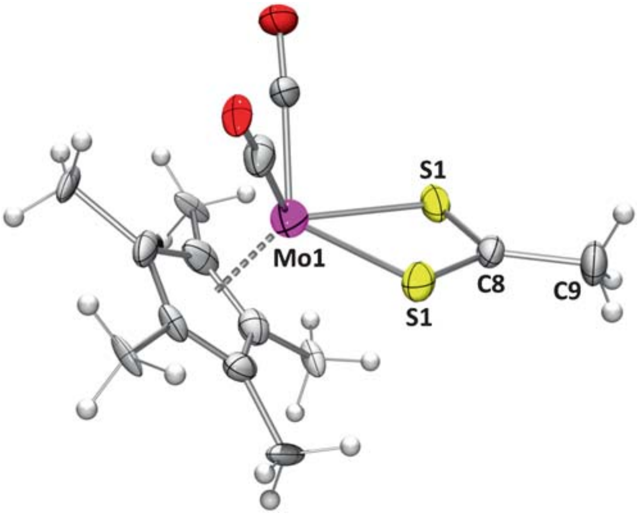
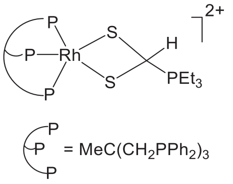
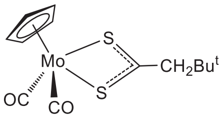
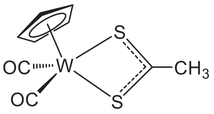
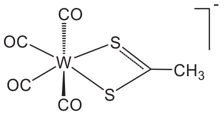
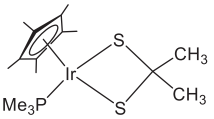
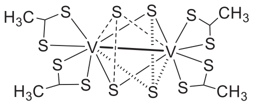
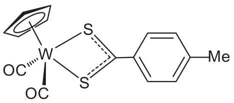
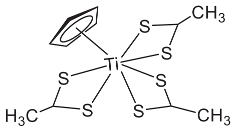
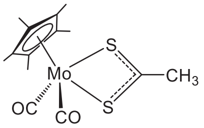
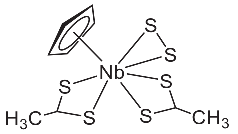


Figure 1. Molecular structure of **2**. Selected bond lengths (Å) and angles (°): Mo1-S1 2.4694(11), S1-C8 1.666(3), C8-C9 1.503(7); Mo1-S1-C8 90.24(14), S1-C8-C9 124.12(13), S1-Mo1-S1 67.86(6).

Table 2. Structural data of various η^2-dithioacetate complexes of transition metals.

Compound	d(M-S) (Å)[a]	S-M-S angle (°)[b]	Compound	d(M-S) (Å)[a]	S-M-S angle (°)[b]
 7c[d]	2.352(7)	75.1(3)	 26	2.477(1)	67.7(1)
 8a	–[c]	–[c]	 27	2.557(5)	67.0(1)
 9	2.358(2)	73.58(5)	 28	2.473(3)	68.57(9)
 26	2.473(3)	67.8(1)	 6d	2.624(3)	65.12(8)
 This work	2.469(11)	67.86(6)	 6d	2.564(1)	65.78(3)

[a] The average M−S distance. [b] The average S-M-S angle. [c] Structural data not available. [d] Reference.

and S1-C8-S1 angle of 111.7(3)° is greater than those observed in other dithioacetate complexes (table 2).

Compound **3** was obtained as yellow solid in modest yield and allowed us to characterize it spectroscopically in solution state. The spectroscopic data of **3** are in full agreement with its solid state X-ray structure (figure 2).

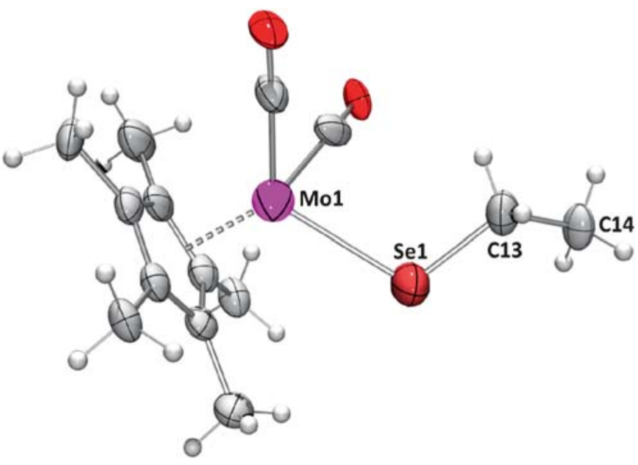


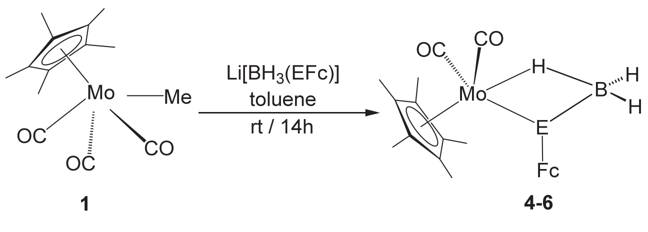
Figure 2. Molecular structures of **3**. Selected bond lengths (Å) and angles (°): Mo1-Se1 2.5763(15), Se1-C13 1.869(15), C13-C14 1.519(17); Mo1-Se1-C13 110.9(7), Se1-C13-C14 122(2).

The mass spectrum of **3** shows molecular ion peak at m/z 395 and thus confirms the formulation of $C_{14}H_{20}MoSeO_2$. The ^{13}C NMR spectrum of **3** shows two distinct carbon environments, along with Cp* ligand at $\delta = 29.0$ and 16.6 ppm for CH_2 and CH_3 groups, respectively. Furthermore, ^{1}H NMR spectrum implies the presence of Cp* ligand at $\delta = 1.88$ ppm. The Mo-Se separation of 2.5763(15) Å is shorter than corresponding bond lengths in $[Cp(CO)_3Mo(C_7H_7Se)]$ (2.6294(4) Å),[29] $[Cp(CO)_2Mo\{\mu\text{-}SeCH_2C(CH_3)CH_3\}]_2$ (2.6327(8) Å),[30] $[Cp(CO)_2MoSe_2(NEt_4)]$ (2.598(1) Å and 2.596(1) Å).[31] These bond lengths lie in the range of observed Mo-Se single bond (2.4-2.7 Å), which is strongly influenced by the bonding mode of Se-containing ligands.

3.2 *Reactivity of [Cp*Mo(CO)$_3$Me], 1, with Li[BH$_3$(EFc)] (E = S, Se or Te) ligands*

The study of heteronuclear transition metal-sulfur complexes has been found to be very useful models for homo- and heterogeneous catalysis and the active sites of natural enzymes. For example, M/M′/S cores are very important in biological systems, such as the Mo/Fe/S core in nitrogenase process.[32] Thus, motivated by our earlier work,[17] we investigated the reaction of Li[BH_3(EFc)] (E = S, Se or Te; Fc = C_5H_5-Fe-C_5H_4) with **1**. By changing the substitution on the chalcogenides from phenyl to ferrocenyl group, we have isolated analogous compounds [Cp*Mo$(CO)_2$(μ-H)(μ-EFc)BH_2], (E = S, Se or Te) **4-6**, in moderate yields (scheme 2). The novel ferrocenyl chalcogeno-borate ligands Li[BH_3(EFc)], were prepared from treatment of [$LiBH_4$.thf] with diferrocenyl dichalcogenides at low temperature (see Supplementary Information). Details of spectroscopic characterization of all compounds **4-6** using IR, ^{1}H, ^{11}B{^{1}H}, ^{13}C NMR spectroscopy and mass spectrometry studies are given below.

Reaction of **1** with Li[BH_3(SFc)] generated hydroborate complex [Cp*Mo$(CO)_2$(μ-H)(μ-SFc)BH_2], **4** as an air sensitive yellow solid in 19.9% yield. In a similar fashion, reaction of **1** with Se and Te analogues of Li[BH_3SFc] produced [Cp*Mo$(CO)_2$(μ-H)(μ-EFc)BH_2], **5** (E = Se) and **6** (E = Te), respectively. The ^{11}B{^{1}H} NMR spectra of **4-6** display sharp singlet at $\delta = -30.5$, -28.3 and -26.7 ppm, respectively, which are significantly shifted to upfield region compared to their corresponding phenyl analogues.[17] In addition to the presence of Cp* protons, the ^{1}H NMR spectra of **4-6**, indicate the presence of Mo-H-B protons appeared in the range of $\delta = -8.41 - -10.99$ ppm, respectively. Further, the existence of ferrocenyl moiety in **4-6** is confirmed by observing the corresponding peaks in ^{1}H and ^{13}C NMR spectra. A single peak in ^{77}Se and ^{125}Te NMR spectra is observed at $\delta = -111.2$ and 621.7 ppm, respectively, which validates the presence of Se and Te in **5** and **6**. They are shifted upfield compared to those of [Cp*Mo$(CO)_2$(μ-H)BH_2EPh] (E = Se or Te). The molecular ion peaks for compounds **4-6**, appeared at m/z 519, 565 and 589, respectively, correspond to [Cp*Mo$(CO)_2$(μ-H)(μ-EFc)BH_2] (E= S, Se or Te). Note that the characterization of **4-6** were achieved by IR, NMR spectroscopy and mass spectrometry that followed similar trend as that of [Cp*Mo$(CO)_2$(μ-H)(μ-EPh)BH_2] (E = S, Se or Te).[17] Several attempts to grow suitable X-ray quality crystals of **4-6** were unsuccessful.

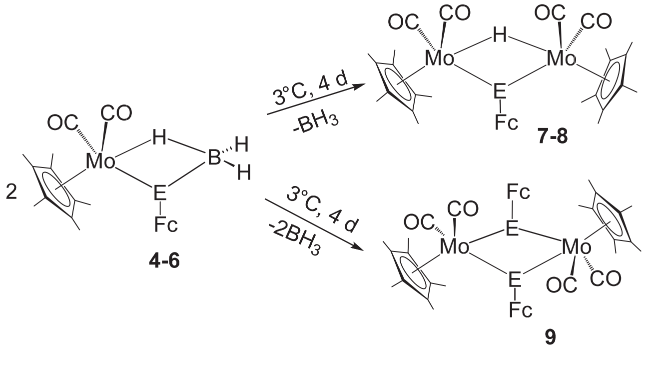


Scheme 2. Synthesis of hydroborate complexes **4-6** (**4**: E = S, **5**: E = Se, **6**: E = Te).

3.3 *Reaction pathway for the formation of 7-9 from 4-6*

During the course of reaction of **1** with Li[BH_3(EFc)] (E = S, Se or Te), we have successfully isolated compounds **4-6**, which are unstable and sensitive to both air and moisture. As a result, the solution of **4-6** slowly converted to corresponding chalcogenolate complexes [{Cp*Mo$(CO)_2$}$_2$(μ-H)(μ-EFc)] (E = S, Se) **7-8** and [{Cp*Mo$(CO)_2$}$_2$(μ-TeFc)$_2$] **9**, even at low temperature (scheme 3). Compound **7** was isolated as green solid in 17% yield. The mass spectrum of compound **7** shows isotropic distribution that is in good agreement with the molecular weight of cationic species. The IR spectrum features bands at 1962 cm^{-1} attributed to the terminal CO ligands. The ^{11}B{^{1}H} NMR shows no ^{11}B chemical shift, whereas the ^{1}H NMR spectrum signifies a sharp upfield resonance at $\delta = -10.04$ ppm, which is assigned for Mo-H-Mo bridging hydrogen. In addition, the ^{1}H and ^{13}C NMR spectra of compound **7** rationalize the presence of Cp* and Cp (ferrocenyl unit) environment. The mass spectra of **8-9** display a molecular ion peak at m/z 840 and 1199 corresponding to $C_{34}H_{40}FeMo_2O_4Se$ and $C_{44}H_{48}Fe_2Mo_2Te_2O_4$, respectively. Apart from Cp* protons, the ^{1}H NMR spectrum of **8** suggests the presence Mo-H-Mo proton ($\delta = -11.03$ ppm). The ^{13}C NMR and IR spectra of **8-9** indicate the presence of Cp*, Cp and CO groups.

In order to confirm the spectroscopic assignments and to determine the molecular structure of compound **7**, X-ray diffraction analysis was undertaken. The solid state structure of **7** reveals two identical {Cp*Mo$(CO)_2$} fragments which are linked through a bridging μ-SFc group (figure 3). Compound **7** has plane of symmetry that passes through the bridging H and S atoms. Inter atomic bond distances of Mo1-S1 (2.4486(8) Å) and Mo2-S1 (2.4546(8) Å) are longer than the sum of the van der Waals radii of the corresponding atoms. The Mo1-S1-Mo2 bond angle of (82.15(2)°) is in good agreement with the reported



Scheme 3. Reaction pathway for the formation of **7-9** from **4-6** (**7**: E = S, **8**: E = Se, **9**: E = Te).

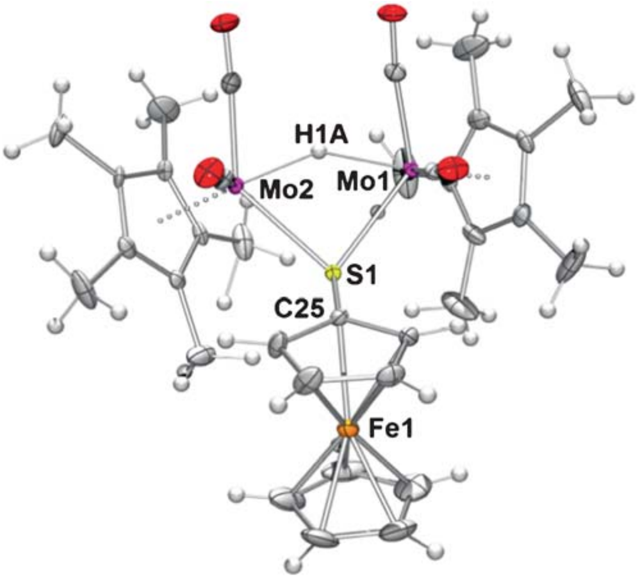


Figure 3. Molecular structure of **7**: Selected bond lengths (Å) and angles (°): Mo1-S1 2.4486(8), Mo2-S1 2.4546(8), Mo1-H1A 1.92(3), Mo2-H1A 1.84(3), C25-S1 1.778(3), Mo1-Mo2 3.221, Mo1-C11 1.961(3), Mo2-C13 1.957(3), Fe1-C25 2.048(3); Mo1-S1-Mo2 82.15(2), C25-S1-Mo1 114.95(10), C25-S1-Mo2 116.81(10), Fe1- C25-S1 125.12(16), C12-Mo1-S1 87.09(9), C13-Mo2-S1 87.60(9).

sulfur bridged molybdenum complex [(Cp)$_2$Mo$_2$(CO)$_3$ (μ-S)(μ-CO)C$_4$H$_6$O] (81.92(5)°).[33]

4. Conclusions

In this article, we have elucidated the synthesis and characterization of molybdenum-chalcogenide complexes. Moreover, the synthetic strategy of ferrocenyl chalcogeno-borate ligands which bind with metal in an interesting fashion have been documented. In the molybdenum thiolate complex **2**, an interesting η^2-dithioacetate linkage has been observed. The [Cp*Mo(CO)$_3$Me], **1** is proved to be a good precursor for the preparation of novel σ-borate complexes by the ligation of chalcogeno-hydroborate ligands.

Supplementary Information (SI)

Supplementary data contains the X-ray crystallographic files in CIF format for **2**, **3**, **7** and CCDC 1431592 (**2**), 1431593 (**3**), 1431591 (**7**) for this work. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_-request/cif. All additional information pertaining to characterization of the complexes **2-9** using ESI-MS technique, IR spectra and multinuclear NMR spectra and ^{1}H coupled ^{11}B spectra of Li[H$_3$B(EFc)] (E = S, Se, Te), (figures S1–S40) are given in the Supplementary Information, available at www.ias.ac.in/chemsci.

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