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Hydride, halide, methyl, carbonyl, and chalcogenido derivatives of permethylmolybdenocene

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Dedicated with respect to Professor Brian James on the occasion of his 70th birthday.

Abstract

$Cp^*_2MoCl_2$ ($Cp^* = C_5Me_5$) is obtained via reaction of $MoCl_5$ with a mixture of Cp*K and $NaBH_4$ followed by treatment with $CHCl_3$. $Cp^*_2MoCl_2$ provides access to a large variety of other permethylmolybdenocene complexes which include $Cp^*_2MoH_2$, $Cp^*_2MoMe_2$, Cp^*_2MoCO, Cp^*_2MoO, $Cp^*_2Mo(Me)Cl$, $Cp^*_2Mo(H)I$, $Cp^*_2Mo(EPh)H$ (E = S, Se, Te), $Cp^*_2Mo(\eta^2\text{-}E_2)$ (E = S, Se, Te), $Cp^*_2Mo(\eta^2\text{-}E_4)$ (E = S, Se), $Cp^*_2Mo(OSiMe_3)CN$, $Cp^*_2Mo(NCS)_2$, and $Cp^*_2Mo(N_3)_2$.

Keywords: Permethylmolybdenocene; Molybdenum; Hydride; Methyl; Carbonyl; Oxo; Chalcogenido

1. Introduction

Molybdenocene and tungstenocene complexes, first prepared in 1954 [1], have played a prominent role in the development of organometallic chemistry following the synthesis of the dihydrides Cp_2MH_2 (M = Mo, W) in 1959 [2].[4] In addition to extensive studies on the parent molybdenocene system [4,5], the chemistry of monosubstituted ring derivatives such as $(Cp^{Me})_2MoX_2$ [6] and $(Cp^{Bu^t})_2MoX_2$ [7], mixed-ring and indenyl complexes [8], and *ansa* molybdenocene compounds [9] have also been investigated, although the complete development of this area has been hampered by synthetic difficulties. In particular, the chemistry of peralkylated- and perarylatedmolybdenocene systems is rather poorly developed due to inefficient and inconvenient synthetic methods. For example, the novel perphenylmolybdenocene complex $\{(C_5Ph_5)_2Mo\}$ is obtained in very low yield (7%) via reaction of $Mo(CO)_6$ with Ph_2C_2 [10]. The first report of the permethylmolybdenocene system appeared in 1973 with the synthesis of $Cp^*_2MoH_2$ ($Cp^* = C_5Me_5$) and several other derivatives [11], but there were no subsequent reports

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[4] A certain degree of confusion exists with the first report of the dihydrides Cp_2MH_2. Specifically, some authors [3a,3b] cite the first report as being 1961 [3c], while others [3d] believe that the 1959 [3e] report involved the reaction of $MoCl_5$, NaCp, and $NaBH_4$. The 1959 synthesis actually involved the reaction of "di-π-cyclopentadienyl halides of molybdenum" with $NaBH_4$ [3e]. Although the specific "di-π-cyclopentadienyl halides of molybdenum" used for the first synthesis were not explicitly stated, examination of the references indicates that the term refers to either $[Cp_2MoCl][Cr(CNS)_4(NH_3)_2] \cdot H_2O$ or $[Cp_2MoCl_2]_2[PtCl_6]$ [3f]. The first synthesis of Cp_2MoH_2 using $MoCl_5$ as the molybdenum reagent was reported in 1960 and involved reaction with only NaCp [3g]; the reaction that involved the use of $NaBH_4$ as an additional hydride reagent was reported in 1961 [3c]. Thus, it is evident that the first report of Cp_2MoH_2 was in 1959 [3e], but the first synthesis involving the reaction of $MoCl_5$, NaCp, and $NaBH_4$ was in 1961 [3c].

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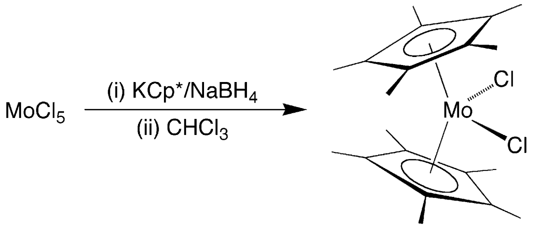
until 1991 when Cloke et al. synthesized $Cp^*_2MoH_2$ by using metal vapor synthesis techniques [12]. The lack of studies on the permethylmolybdenocene system during the period 1973–1991 may be attributed to the fact that other researchers were unable to substantiate the 1973 synthesis of $Cp^*_2MoH_2$ [11], while Ito has noted that a modified method of synthesis gives $Cp^*_2MoH_2$ in insufficient yield for it to be useful as a starting material for subsequent derivitization [3a,13]. Furthermore, Cloke et al. have also questioned the formulation of the proposed permethylmolybdenocene compound $\{Cp^*_2Mo\}$ described in the 1973 paper [12]. In this paper, we report the preparation of the dichloride $Cp^*_2MoCl_2$ by using conventional synthetic methods, and thereby provide a convenient entry point for a variety of permethylmolybdenocene derivatives.

2. Results and discussion

2.1. Synthesis and reactivity of $Cp^*_2MoCl_2$

Access to permethylmolybdenocene chemistry is conveniently provided by $Cp^*_2MoCl_2$ which is obtained via a two step sequence involving (i) the reaction of $MoCl_5$ with a mixture of Cp*K and $NaBH_4$ to give crude $Cp^*_2MoH_2$, followed by (ii) addition of $CHCl_3$ (Scheme 1) [14]. The latter step is an important improvement over the previous method because the lower solubility of $Cp^*_2MoCl_2$ in pentane compared to $Cp^*_2MoH_2$ facilitates isolation of the permethylmolybdenocene derivative. The tetramethylethylcyclopentadienyl counterpart $(Cp^{Me_4Et})_2MoCl_2$ has also been obtained in an analogous manner, and the molecular structures of $Cp^*_2MoCl_2$ and $(Cp^{Me_4Et})_2MoCl_2$ as determined by X-ray diffraction are illustrated in Figs. 1 and 2.

$Cp^*_2MoCl_2$ is a useful precursor for a variety of other permethylmolybdenocene derivatives which include hydride, alkyl, carbonyl and oxo complexes (Scheme 2). Thus, $Cp^*_2MoCl_2$ reacts with: (i) $LiAlH_4$ to give $Cp^*_2MoH_2$, (ii) MeLi to give $Cp^*_2MoMe_2$, (iii) Na(Hg) in the presence of CO to give Cp^*_2MoCO and (iv) LiOH to give Cp^*_2MoO, as illustrated in Scheme 2. The molecular structures of $Cp^*_2MoH_2$, $Cp^*_2MoMe_2$, Cp^*_2MoCO and Cp^*_2MoO have been determined by X-ray diffraction, as shown in Figs. 3–6. The oxo complex has been previously reported but has only been obtained as a minor impurity resulting from the work-up procedure following the reaction of molybdenum atoms with Cp*H [12].



Scheme 1.

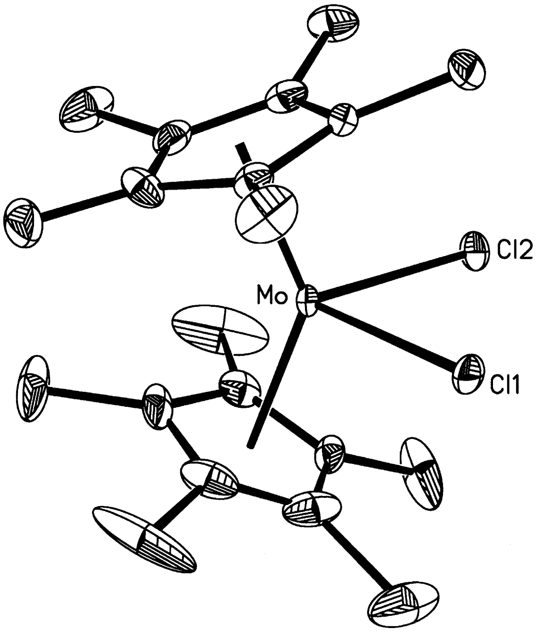


Fig. 1. Molecular structure of $Cp^*_2MoCl_2$. Selected bond lengths (Å) and angles (°): Mo–Cl(1) 2.462(2), Mo–Cl(2) 2.466(2); Cl(1)–Mo–Cl(2) 81.00(9).

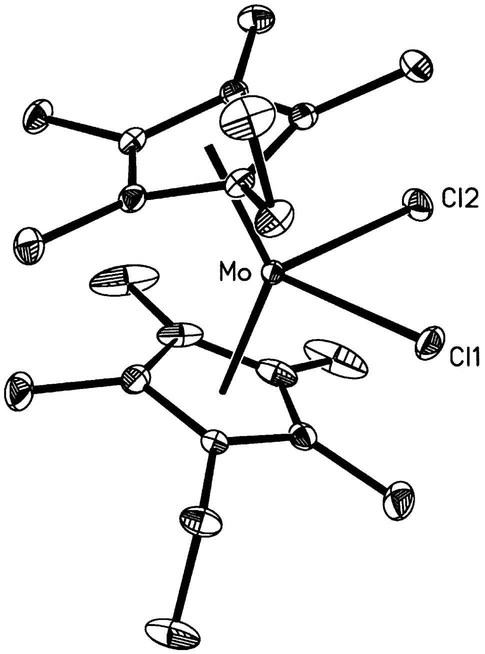
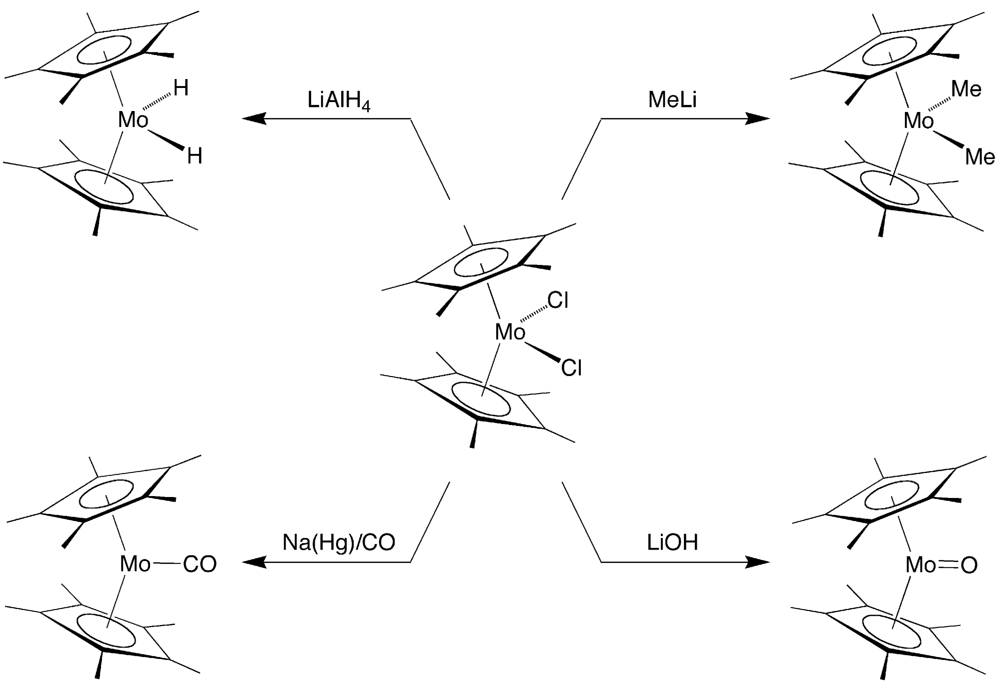


Fig. 2. Molecular structure of $(Cp^{Me_4Et})_2MoCl_2$. Selected bond lengths (Å) and angles (°): Mo–Cl(1) 2.477(1), Mo–Cl(2) 2.475(1); Cl(1)–Mo–Cl(2) 80.63(3).

2.2. Reactivity of $Cp^*_2MoH_2$, $Cp^*_2MoMe_2$ and $Cp^*_2Mo(CO)$

The dihydride, dimethyl and carbonyl complexes, $Cp^*_2MoH_2$, $Cp^*_2MoMe_2$ and $Cp^*_2Mo(CO)$, provide a means to obtain permethylmolybdenocene compounds that feature more than one substituent. For example, the



Scheme 2.

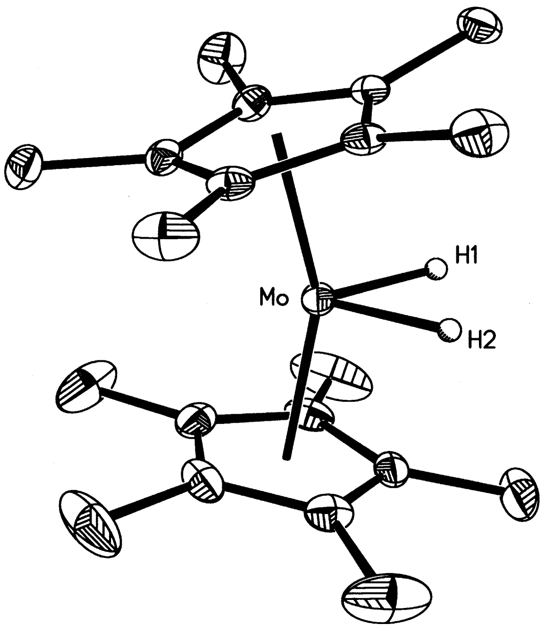


Fig. 3. Molecular structure of $Cp^*_2MoH_2$. Selected bond lengths (Å) and angles (°): Mo–H(1) 1.61(4), Mo–H(2) 1.64(4); H(1)–Mo–H(2) 70.3(18).

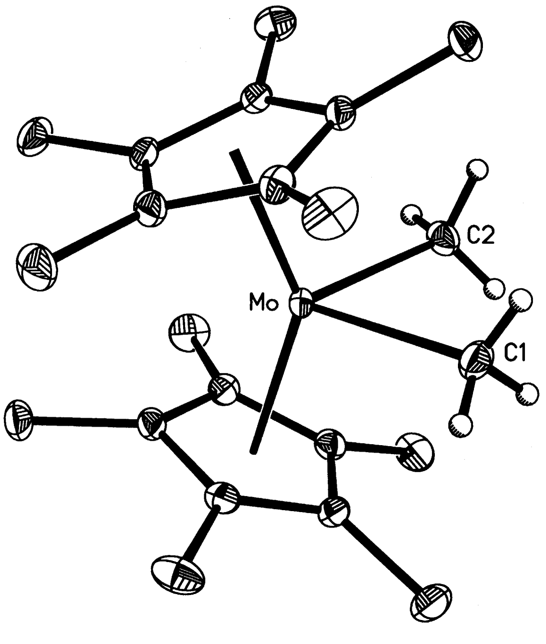


Fig. 4. Molecular structure of $Cp^*_2MoMe_2$. Selected bond lengths (Å) and angles (°): Mo–C(1) 2.234(3), Mo–C(2) 2.239(3); C(1)–Mo–C(2) 78.4(1).

dimethyl $Cp^*_2MoMe_2$ reacts with HCl to yield the methyl-chloride $Cp^*_2Mo(Me)Cl$ (Scheme 3) while the dihydride $Cp^*_2MoH_2$ reacts with MeI to give the hydride-iodide $Cp^*_2Mo(H)I$ (Scheme 4), which has been structurally characterized by X-ray diffraction (Fig. 7). The isolation of the latter complex is noteworthy in view of the fact that reaction of $Cp^*_2MoH_2$ with ICH_2CH_2I yields the diiodide $Cp^*_2MoI_2$ [12]. An asymmetric permethylmolybdenocene derivative, namely the carbonyl–methyl compound $\{Cp^*_2Mo(CO)Me\}I$ may be obtained via treatment of $Cp^*_2Mo(CO)$ with MeI (Scheme 5).

The methyl-chloride complex $Cp^*_2Mo(Me)Cl$ reacts with $LiAlH_4$ to yield the "tuck-in" complex $Cp^*(\eta^5,\eta^1\text{-}C_5Me_4CH_2)MoH$ (Scheme 3) which has previously been obtained via photolysis of $Cp^*_2MoH_2$ [12]. The "tuck-in" complex $Cp^*(\eta^5,\eta^1\text{-}C_5Me_4CH_2)MoH$ is presumably obtained as a consequence of facile elimination of methane from the undetected methyl-hydride intermediate,

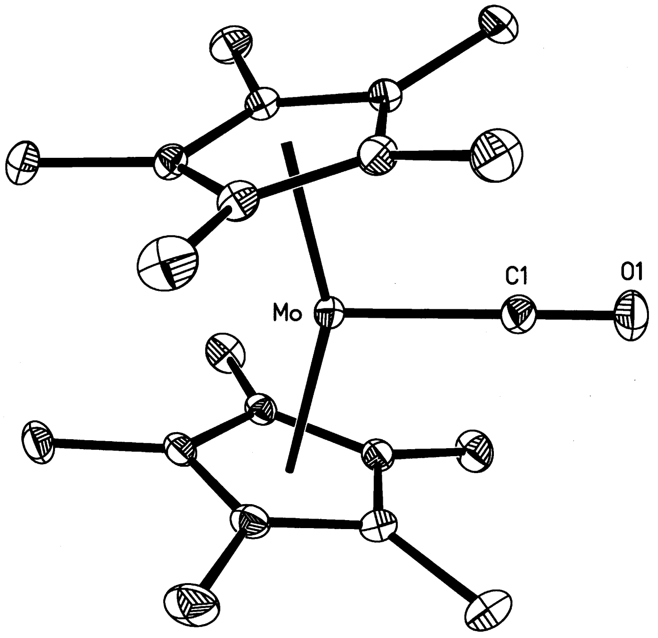


Fig. 5. Molecular structure of $Cp^*_2Mo(CO)$. Selected bond lengths (Å) and angles (°): Mo–C(1) 1.954(2), C(1)–O(1) 1.154(3); Mo–C(1)–O(1) 179.5(3).

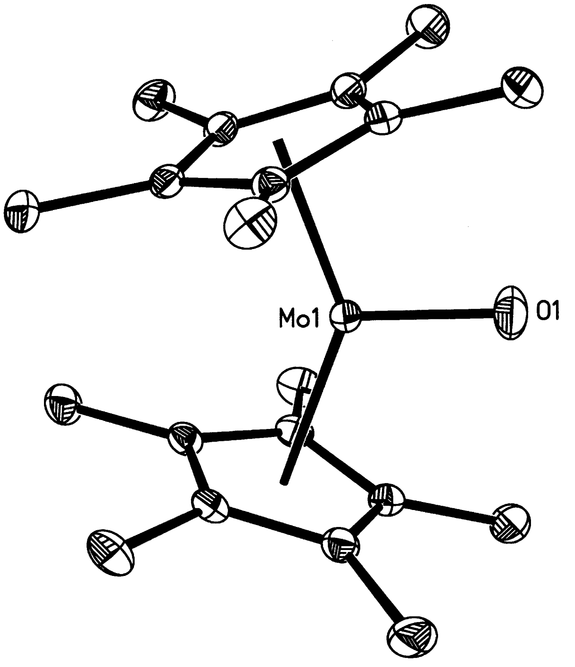


Fig. 6. Molecular structure of Cp^*_2MoO (only one of the two crystallographically independent molecules shown). Selected bond lengths (Å): Mo(1)–O(1) 1.723(2), Mo(2)–O(2) 1.720(2).

$Cp^*_2Mo(Me)H$. The inability to isolate the methyl-hydride $Cp^*_2Mo(Me)H$ in this system is in marked contrast to the isolation of the tungsten analogue, $Cp^*_2W(Me)H$ [14,15], but is not surprising in view of the fact that elimination of RH from a {[M](R)(H)} complex is typically more facile for molybdenum than for tungsten. For example, reductive elimination of benzene from $[Me_2Si(C_5Me_4)_2]Mo(Ph)H$ has a substantially smaller activation barrier ($\Delta G^\ddagger = 27.9$ kcal mol^{-1} at 80 °C) than that for the tungsten counterpart, $[Me_2Si(C_5Me_4)_2]W(Ph)H$ ($\Delta G^\ddagger = 40.1$ kcal mol^{-1} at 182 °C) [9d]. If reductive elimination of methane from $Cp^*_2Mo(Me)H$ and $Cp^*_2W(Me)H$ were to exhibit a similar difference in activation barrier to that for reductive elimination of benzene from $[Me_2Si(C_5Me_4)_2]Mo(Ph)H$ and $[Me_2Si(C_5Me_4)_2]W(Ph)H$ ($\Delta\Delta G^\ddagger \approx 12$ kcal mol^{-1}), the barrier for reductive elimination of methane from $Cp^*_2Mo(Me)H$ is estimated to be $\Delta G^\ddagger \approx 17$ kcal mol^{-1}. This activation barrier corresponds to a half-life of ≈7 s at 0 °C, a value that is in accord with our inability to observe $Cp^*_2Mo(Me)H$.

The dihydride $Cp^*_2MoH_2$ also provides a means to synthesize a series of phenylchalcogenolate–hydride complexes $Cp^*_2Mo(EPh)H$ (E = S, Se, Te)[5] and chalcogenido complexes, namely $Cp^*_2Mo(\eta^2\text{-}E_2)$ (E = S, Se, Te)[6] and $Cp^*_2Mo(\eta^2\text{-}E_4)$ (E = S, Se), as illustrated in Scheme 4. Thus, $Cp^*_2Mo(EPh)H$ is obtained via reaction of $Cp^*_2MoH_2$ with Ph_2E_2, while $Cp^*_2Mo(\eta^2\text{-}E_2)$ and $Cp^*_2Mo(\eta^2\text{-}E_4)$ are obtained by reaction of $Cp^*_2MoH_2$ with 2 and 4 equivalents of the elemental chalcogen, respectively. The molecular structures of $Cp^*_2Mo(\eta^2\text{-}E_2)$ (E = S, Se, Te) and $Cp^*_2Mo(\eta^2\text{-}Se_4)$ have been determined by X-ray diffraction, as illustrated in Figs. 8–11.

Although $Cp^*_2Mo(EPh)H$ have not been structurally characterized by X-ray diffraction, low-temperature ^1H NMR spectroscopic studies demonstrate that the complexes exist as two conformers that are distinguished according to whether the phenyl group occupies an *endo* or *exo* position relative to the hydride ligand (Fig. 12). NOESY studies enable the two isomers to be identified by virtue of the fact that the *endo* isomer exhibits a cross peak between the molybdenum-hydride and the *ortho* hydrogen atoms of the phenyl group, whereas a corresponding cross peak does not exist for the *exo* isomer.[7] Measurement of the equilibrium constant as a function of temperature demonstrates that the *exo* isomer is identified as the more stable. The existence of *endo* and *exo* isomers is not unprecedented, as illustrated by the fact that X-ray diffraction studies demonstrate that the EPh ligands of $(Cp^{Bu^t})_2Mo(EPh)H$ (E = Se, Te) and $(Cp^{Bu^t})_2Mo(SPh)_2$ exhibit *endo* and *exo* conformations, respectively [7a,16]. The *exo* conformation is the geometry that minimizes (i) destabilizing interactions between the lone pairs of electrons on the chalcogen and the d^2 pair of electrons on the molybdenum and (ii) steric interactions between the phenyl group and the other substituent on molybdenum, while the *endo* conformation is the geometry which

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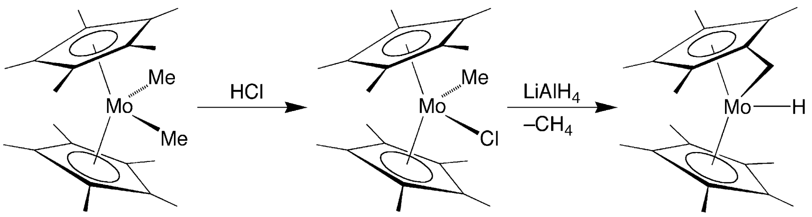
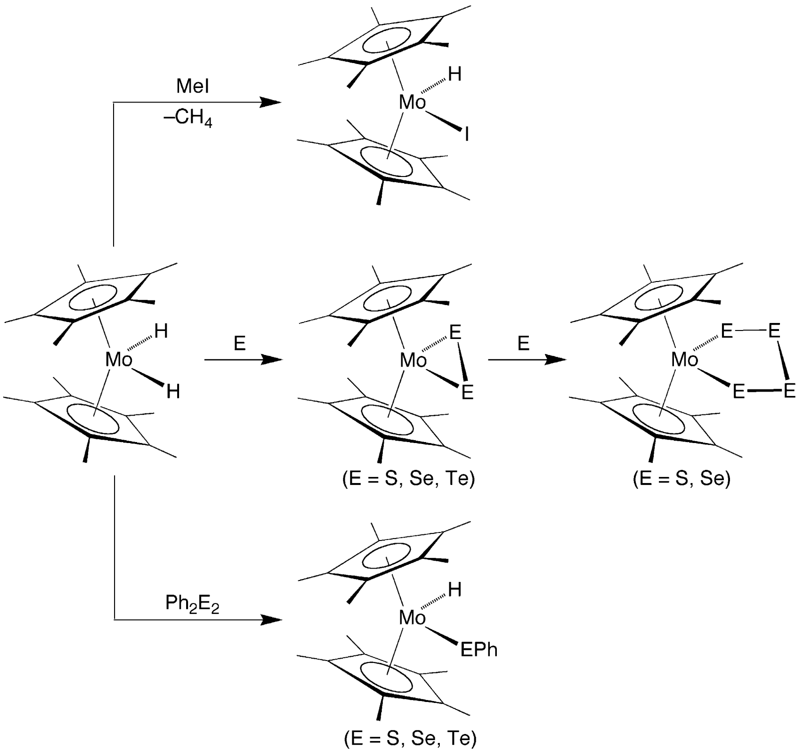
[5] The counterparts $(Cp^{Bu^t})_2Mo(EPh)H$ have also been synthesized. See Ref. [7a].

[6] The counterparts $(Cp^{Bu^t})_2Mo(\eta^2\text{-}E_2)$ have also been synthesized. See Ref. [7a].

[7] It is also noteworthy that the hydride ligand of the *exo* isomers of $Cp^*_2Mo(EPh)H$ (E = Se, Te) exhibit coupling to selenium and tellurium at low temperature (230 K): $J_{Se-H} = 26$ Hz and $J_{Te-H} = 79$ Hz.



Scheme 3.



Scheme 4.

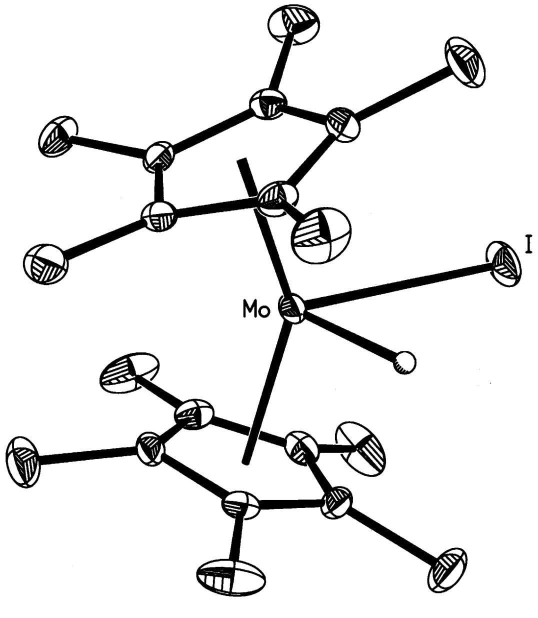
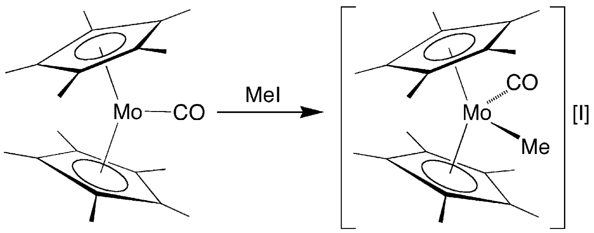


Fig. 7. Molecular structure of $Cp^*_2Mo(H)I$ (the hydride ligand is disordered and only one position is shown). Selected bond lengths (Å): Mo–I 2.8100(5).



Scheme 5.

minimizes steric interactions between the phenyl and cyclopentadienyl ligands.

The interconversion between the *endo* and *exo* conformers of $Cp^*_2Mo(EPh)H$ is facile on the NMR timescale, as illustrated in Fig. 13 for $Cp^*_2Mo(SPh)H$. Analysis of the data demonstrates that the barrier decreases in the sequence $S > Se > Te$ (Table 1). In principle, the interconversion of the *endo* and *exo* conformers may be achieved by either rotation of the phenyl group about the Mo–E bond or by inversion at the chalcogen. However, the observation that the barrier decreases in the sequence

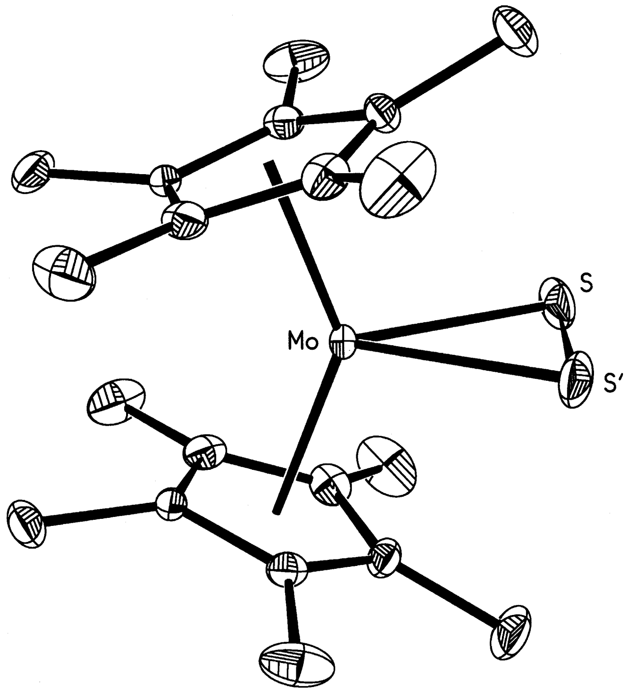


Fig. 8. Molecular structure of $\mathrm{Cp}_2^*\mathrm{Mo}(\eta^2\text{-}\mathrm{S}_2)$. Selected bond lengths (Å) and angles (°): Mo–S 2.434(1), S–S′ 2.091(2); S–Mo–S′ 50.88(5).

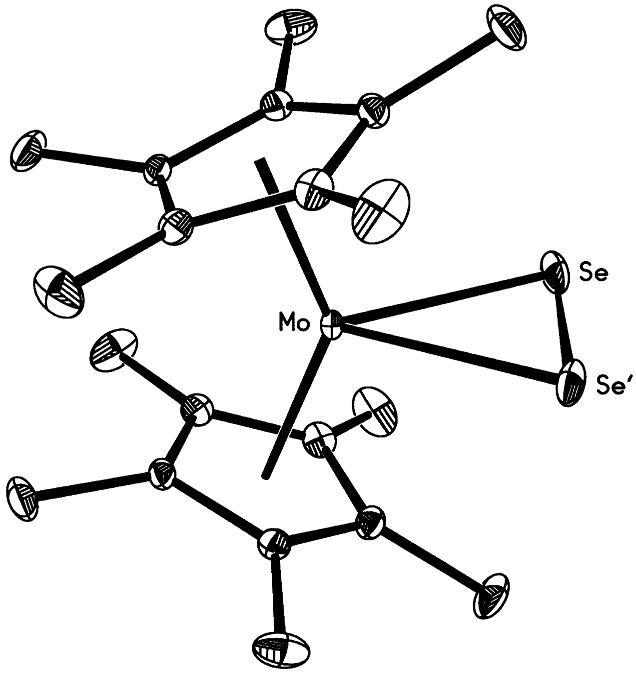


Fig. 9. Molecular structure of $\mathrm{Cp}_2^*\mathrm{Mo}(\eta^2\text{-}\mathrm{Se}_2)$. Selected bond lengths (Å) and angles (°): Mo–Se 2.590(1), Se–Se′ 2.335(1); Se–Mo–Se′ 53.59(2).

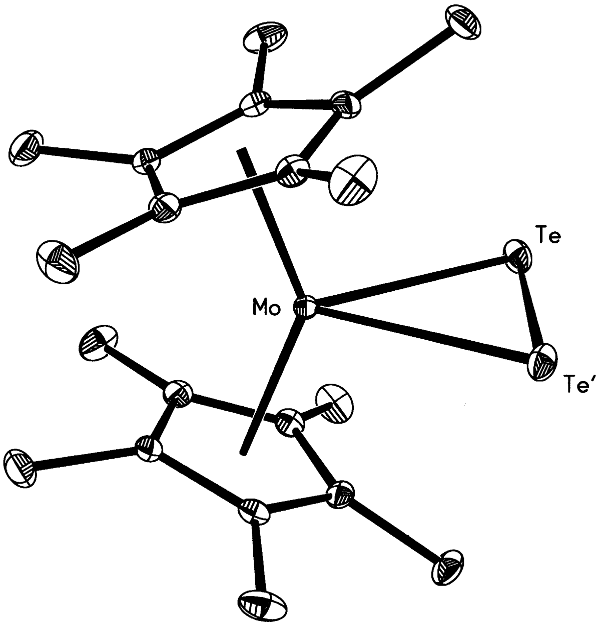


Fig. 10. Molecular structure of $\mathrm{Cp}_2^*\mathrm{Mo}(\eta^2\text{-}\mathrm{Te}_2)$. Selected bond lengths (Å) and angles (°): Mo–Te 2.804(1), Te–Te′ 2.696(1); Te–Mo–Te′ 57.48(3).

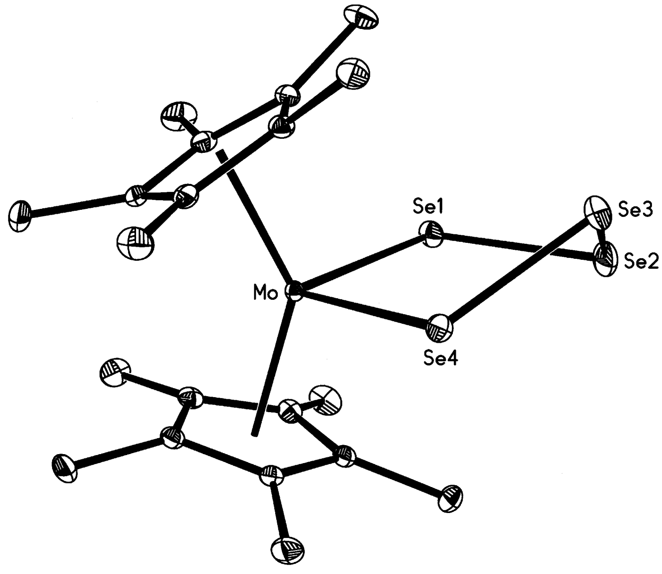


Fig. 11. Molecular structure of $\mathrm{Cp}_2^*\mathrm{Mo}(\eta^2\text{-}\mathrm{Se}_4)$. Selected bond lengths (Å) and angles (°): Mo–Se(1) 2.527(1), Mo–Se(4) 2.550(1), Se(1)–Se(2) 2.409(1), Se(2)–Se(3) 2.307(1), Se(3)–Se(4) 2.380(1); Se(1)–Mo–Se(4) 90.30(2).

$\mathrm{S} > \mathrm{Se} > \mathrm{Te}$ suggests that the mechanism for interconversion merely corresponds to rotation about the Mo–E bond. Specifically, the barrier for rotation about the Mo–E bond should be reduced as the Mo–E bond length increases because this would reduce the interaction between the phenyl group and the Cp* ligand in the transition state. In further support of the notion that the fluxionality within $\mathrm{Cp}_2^*\mathrm{Mo(EPh)H}$ pertains to rotation about the Mo–E bond, the fluxional process that causes the two $\mathrm{Cp}^{\mathrm{Bu}^t}$ ligands of $[\mathrm{Cp}^{\mathrm{Bu}^t}\mathrm{Mo(PhEMe)H}]^+$ to become equivalent requires inversion at the chalcogen and the barrier for this process varies in the opposite sequence, i.e., $\mathrm{S} < \mathrm{Se} < \mathrm{Te}$ [7a].

2.3. Reactivity of $\mathrm{Cp}_2^*\mathrm{MoO}$

The oxo complex $\mathrm{Cp}_2^*\mathrm{MoO}$ is also a useful precursor for other derivatives via reactions with $\mathrm{Me_3SiX}$ reagents. For example, $\mathrm{Cp}_2^*\mathrm{MoO}$ reacts with (i) $\mathrm{Me_3SiCN}$ to give

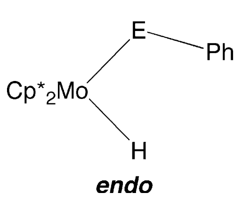


Fig. 12. *Endo* and *exo* conformers of Cp$^*_2$Mo(EPh)H.

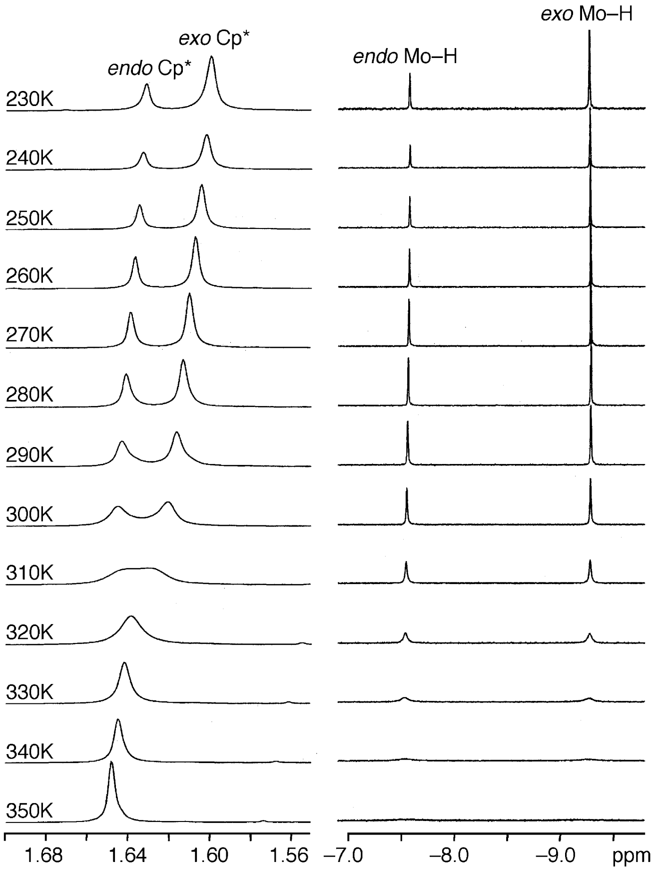
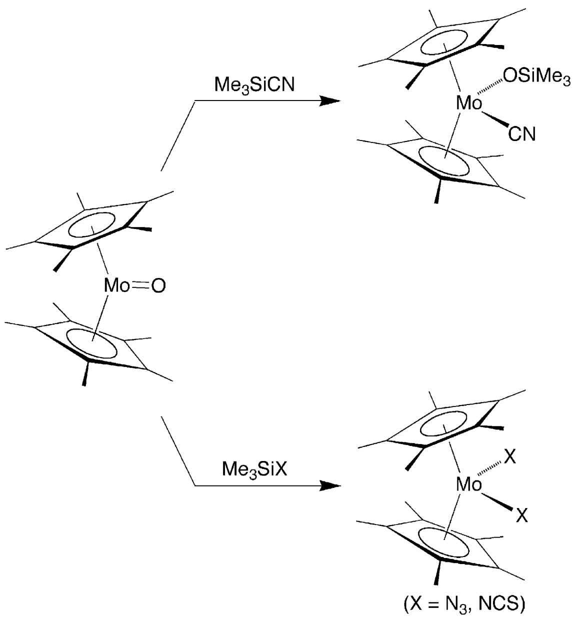


Fig. 13. Variable temperature ^{1}H NMR spectra of Cp$^*_2$Mo(SPh)H (Cp* and hydride region).



Scheme 6.

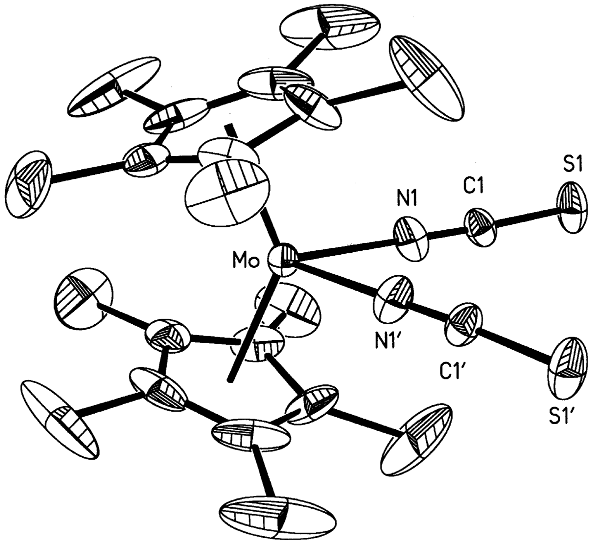


Fig. 14. Molecular structure of Cp$^*_2$Mo(NCS)$_2$ (the NCS ligands are disordered and only one configuration is shown). Selected bond lengths (Å): Mo–N(1) 2.107(2), N(1)–C(1) 1.153(2), C(1)–S(1) 1.631(2).

Cp$^*_2$Mo(OSiMe$_3$)CN and (ii) Me$_3$SiX (X = NCS, N$_3$) to give Cp$^*_2$MoX$_2$ [17], as illustrated in Scheme 6; precedents for these transformations are provided by the reactions of (Cp$^{\mathrm{Bu}^t}$)$_2$MoO with Me$_3$SiX [7a]. Thiocyanate is an ambidentate ligand and may coordinate to a metal center via either sulfur (M–SCN, thiocyanate) or nitrogen (M–NCS, isothiocyanate). ^{13}C NMR spectroscopy has been used to distinguish the two coordination modes, with the chemical shift for M–NCS moieties being comparable to, or greater than, that for NCS$^-$ (ca. 134 ppm), whereas M–SCN moieties are

Table 1
Thermodynamic quantities pertaining to interconversion of *endo* and *exo* Cp$^*_2$Mo(EPh)H

	Cp$^*_2$Mo(SPh)H	Cp$^*_2$Mo(SePh)H	Cp$^*_2$Mo(TePh)H
$\Delta H_{\mathrm{endo}\rightarrow\mathrm{exo}}$/kcal mol^{-1}	−1.64(6)	−2.19(5)	−2.21(9)
$\Delta S_{\mathrm{endo}\rightarrow\mathrm{exo}}$/e.u.	−5.2(2)	−5.5(2)	−5.2(4)
$\Delta H^{\ddagger}_{\mathrm{endo}\rightarrow\mathrm{exo}}$/kcal mol^{-1}	17.6(7)	14.2(6)	12.2(7)
$\Delta S^{\ddagger}_{\mathrm{endo}\rightarrow\mathrm{exo}}$/e.u.	3(2)	−2(2)	0(3)
$\Delta G_{\mathrm{endo}\rightarrow\mathrm{exo}}$/kcal mol^{-1} (25 °C)	−0.09	−0.55	−0.66
$\Delta G^{\ddagger}_{\mathrm{endo}\rightarrow\mathrm{exo}}$/kcal mol^{-1} (25 °C)	16.7	14.8	12.2

characterized by chemical shifts less than that for NCS^- (i.e., $\delta_{M-SCN} < \delta_{NCS^-} \leqslant \delta_{M-NCS}$) [18]. On this basis, $Cp^*_2Mo(NCS)_2$, with a chemical shift of 147.4 ppm, is clearly identified as a *N*-bound isothiocyanate derivative. X-ray diffraction studies also support this coordination mode (Fig. 14), although the NCS ligands are disordered over two positions.

3. Conclusions

In summary, convenient access to permethylmolybdenocene compounds is provided via the synthesis of $Cp^*_2MoCl_2$ which involves the reaction of $MoCl_5$ with a mixture of Cp*K and $NaBH_4$ followed by treatment with $CHCl_3$. $Cp^*_2MoCl_2$ provides access to a large variety of other derivatives, such as $Cp^*_2MoH_2$, $Cp^*_2MoMe_2$, Cp^*_2MoCO, Cp^*_2MoO, $Cp^*_2Mo(Me)Cl$, $Cp^*_2Mo(H)I$, $Cp^*_2Mo(EPh)H$ (E = S, Se, Te), $Cp^*_2Mo(\eta^2\text{-}E_2)$ (E = S, Se, Te), $Cp^*_2Mo(\eta^2\text{-}E_4)$ (E = S, Se), $Cp^*_2Mo(OSiMe)_3CN$, $Cp^*_2Mo(NCS)_2$, and $Cp^*_2Mo(N)_3$, many of which have been structurally characterized by X-ray diffraction.

4. Experimental

4.1. General considerations

All manipulations were performed using a combination of glovebox and Schlenk techniques [19]. Solvents were purified and degassed by standard procedures. All commercially available reagents were used as received without any further purification. IR spectra were recorded as KBr pellets on a Perkin–Elmer Paragon 1000 FT-IR spectrometer and are reported in cm^{-1}. Carbon, hydrogen and nitrogen elemental analyses were performed on a Perkin–Elmer 2400 CHN Elemental Analyzer. NMR spectra were recorded on Bruker Avance DPX 300, DRX 300, and DMX 500 spectrometers. ^1H and ^{13}C resonance chemical shifts are reported in ppm relative to $SiMe_4$ (δ 0) and were referenced internally to the residual protio resonance (δ 7.15 for C_6D_5H and 7.26 for $CHCl_3$) and the ^{13}C resonance (δ 128.0 for C_6D_6 and 77.0 for $CDCl_3$) of the solvent. ^{77}Se chemical shifts are reported in ppm relative to neat Me_2Se ($\delta = 0$) and were referenced using a solution of Ph_2Se_2 in C_6D_6 ($\delta = 460$) as external standard [20]. ^{125}Te chemical shifts are reported in ppm relative to neat Me_2Te ($\delta = 0$) and were referenced using a solution of Ph_2Te_2 in $CDCl_3$ ($\delta = 420.8$) as external standard [21].

4.2. Synthesis of $Cp^*_2MoCl_2$ and $(Cp^{Me_4Et})_2MoCl_2$

A solution of $MoCl_5$ (4.02 g, 14.7 mmol) in toluene (10 mL)/THF (50 mL) at −78 °C was slowly added to a mixture of Cp*K (15.70 g, 90.1 mmol) and $NaBH_4$ (1.49 g, 39.4 mmol) in THF (150 mL) at −78 °C. The resulting mixture was allowed to warm to room temperature and stirred for 3 h. After this period, the mixture was heated for 24 h at 65 °C. The volatile components were removed from the mixture and the residue was dried in vacuo overnight. The residue was extracted into pentane (200 mL), concentrated to 100 mL, and treated with $CHCl_3$ (5 mL). The mixture was stirred overnight at room temperature and the resulting precipitate was isolated by filtration, washed with pentane (2 × 30 mL), and dried in vacuo to give $Cp^*_2MoCl_2$ as a brown[8] solid (4.13 g, 64%). Anal. Calc. for $C_{20}H_{30}Cl_2Mo$: C, 54.9; H, 6.9. Found: C, 54.3; H, 7.2%. IR data (KBr disk, cm^{-1}): 2959 (s), 2904 (vs), 1456 (vs), 1374 (vs), 1069 (m), 1019 (vs), 804 (w), 679 (w), 609 (w), 415 (w). ^1H NMR (C_6D_6): 1.46 [s, $C_5(CH_3)_5$]. ^{13}C NMR (C_6D_6): 11.3 [q, $^1J_{C-H} = 128$, $C_5(CH_3)_5$], 108.9 [s, $C_5(CH_3)_5$]. $(Cp^{Me_4Et})_2MoCl_2$ was prepared by an analogous procedure. IR data (KBr disc, cm^{-1}): 2963 (vs), 2905 (vs), 1636 (m), 1457 (vs), 1376 (vs),1022 (vs), 970 (m). ^1H NMR (C_6D_6): 0.92 [t, $^3J_{H-H} = 8$, 6H, $2C_5(CH_3)_4CH_2CH_3$], 1.52 [s, 12H, $2C_5(CH_3)_4CH_2CH_3$], 1.54 [s, 12H, $2C_5(CH_3)_4CH_2CH_3$], 1.78 [q, $^3J_{H-H} = 8$, 4H, $2C_5(CH_3)_4CH_2CH_3$]. ^{13}C NMR (C_6D_6): 11.3 [q, $^1J_{C-H} = 128$, 4C, $2C_5(CH_3)_4CH_2CH_3$], 11.8 [q, $^1J_{C-H} = 128$, 4C, $2C_5(CH_3)_4CH_2CH_3$], 14.3 [q, $^1J_{C-H} = 127$, 2C, $2C_5(CH_3)_4CH_2CH_3$], 19.3 [t, $^1J_{C-H} = 128$, 2C, $2C_5(CH_3)_4CH_2CH_3$], 107.7 [s, 4C, 2 $C_5(CH_3)_4CH_2CH_3$], 111.3 [s, 4C, 2 $C_5(CH_3)_4CH_2CH_3$], 111.6 [s, 2C, $2C_5(CH_3)_4CH_2CH_3$].

4.3. Synthesis of $Cp^*_2MoH_2$

A stirred suspension of $Cp^*_2MoCl_2$ (1.00 g, 2.29 mmol) in ether (30 mL) was treated with $LiAlH_4$ (14 mL, 1.0 M solution in ether) at −78 °C and then allowed to warm slowly to room temperature and stirred overnight. After this period, the mixture was cooled to 0 °C and treated dropwise with degassed water (2 mL). The mixture was allowed to warm to room temperature and stirred for 1 h. The volatile components were removed in vacuo, and the residue was extracted into pentane. The filtrate was concentrated to ca. 2 mL and cooled to −78 °C, thereby depositing $Cp^*_2MoH_2$ as a green-brown solid[9] which was isolated by filtration and dried in vacuo (0.52 g, 62%). Anal. Calc. for $C_{20}H_{32}Mo$: C, 65.2; H, 8.8. Found: C, 65.3; H, 9.2%. IR data (KBr disk, cm^{-1}): 2975 (vs), 2898 (vs), 2712 (m), 1864 (s) [ν(Mo–H)], 1478 (s), 1452 (s), 1426 (s), 1375 (vs), 1069 (m), 1028 (vs), 908 (w), 884 (w), 792 (w), 670 (w), 590 (w), 414 (w). ^1H NMR (C_6D_6): −8.35 [s, MoH_2], 1.85 [s, $C_5(CH_3)_5$]. ^{13}C NMR (C_6D_6): 12.2 [q, $^1J_{C-H} = 126$, $C_5(CH_3)_5$], 92.9 [s, $C_5(CH_3)_5$].

4.4. Synthesis of $Cp^*_2Mo(CO)$

A mixture of $Cp^*_2MoCl_2$ (500 mg, 1.14 mmol), Na (55 mg, 2.39 mmol) and Hg (2 mL) in THF (100 mL) was

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[8] It should be noted that the brown color of $Cp^*_2MoCl_2$ is in marked contrast to the bright blue color that was reported previously (Ref. [11]).

[9] Sublimation of the green-brown solid gives $Cp^*_2MoH_2$ as a yellow solid upon sublimation (C. Limberg, S. Roggan and C. Jankowski, unpublished results).

stirred under CO (1 atm) overnight at room temperature. After this period, the volatile components were removed and the residue was extracted into pentane. The extract was concentrated to ca. 2 mL and cooled to −78 °C, thereby depositing $Cp^*_2Mo(CO)$ as a green solid which was isolated by filtration and dried in vacuo (290 mg, 64%). Anal. Calc. for $C_{21}H_{30}OMo$: C, 64.0; H, 7.7. Found: C, 63.0; H, 7.8%. IR data (KBr disk, cm^{-1}): 2972 (m), 2952 (m), 2899 (s), 2716 (w), 1867 (vs) [ν(CO)], 1458 (m), 1376 (s), 1067 (w), 1025 (m), 909 (w), 884 (w), 801 (vw), 682 (vw), 620 (vw), 590 (vw), 512 (w), 483 (vw), 404 (vw). IR data (pentane): 1890 [ν(CO)]. ^1H NMR (C_6D_6): 1.72 [s, $C_5(C\mathit{H}_3)_5$]. ^{13}C NMR (C_6D_6): 11.7 [q, $^1J_{C–H} = 127$, $C_5(\mathit{C}H_3)_5$], 90.5 [s, $\mathit{C}_5(CH_3)_5$], 254.8 [s, $\mathit{C}O$].

4.5. Synthesis of $Cp^*_2Mo(H)(I)$

A solution of $Cp^*_2MoH_2$ (200 mg, 0.54 mmol) in toluene (10 mL) was treated with CH_3I (200 mg, 1.41 mmol) for 2 days at room temperature. After this period, the volatile components were removed, and the residue was washed with pentane (1 mL) and dried in vacuo to give $Cp^*_2Mo(H)(I)$ as a green solid (210 mg, 78%). Anal. Calc. for $C_{20}H_{31}IMo$: C, 48.6; H, 6.3. Found: C, 48.4; H, 6.5%. IR data (KBr disk, cm^{-1}): 2956 (s), 2891 (vs), 1869 (m) [ν(Mo–H)], 1462 (vs), 1373 (vs), 1159 (w), 1070 (m), 1021 (vs), 844 (w), 798 (w), 669 (w), 613 (w), 544 (vw), 412 (w). ^1H NMR (C_6D_6): −9.49 [s, $Mo\mathit{H}$], 1.75 [s, $C_5(C\mathit{H}_3)_5$]. ^{13}C NMR (C_6D_6): 13.1 [q, $^1J_{C–H} = 127$, $C_5(\mathit{C}H_3)_5$], 99.0 [s, $\mathit{C}_5(CH_3)_5$].

4.6. Synthesis of $Cp^*_2Mo(CH_3)_2$

A mixture of $Cp^*_2MoCl_2$ (500 mg, 1.14 mmol) and CH_3Li (75 mg, 3.41 mmol) in toluene (20 mL) was stirred at room temperature for 3 h. After this period, the volatile components were removed in vacuo, and the residue was extracted into pentane. The extract was concentrated to ca. 2 mL and cooled to −78 °C, thereby depositing $Cp^*_2Mo(CH_3)_2$ as a red-brown solid which was isolated by filtration and dried in vacuo (275 mg, 61%). Anal. Calc. for $C_{22}H_{36}Mo$: C, 66.6; H, 9.2. Found: C, 65.8; H, 9.5%. IR data (KBr disk, cm^{-1}): 2948 (vs), 2899 (vs), 2859 (vs), 2716 (m), 1481 (s), 1425 (s), 1374 (vs), 1167 (m), 1065 (m), 1021 (vs), 800 (w), 743 (w), 612 (w), 543 (w), 468 (w), 410 (w). ^1H NMR (C_6D_6): −0.66 [s, $Mo(C\mathit{H}_3)_2$], 1.42 [s, $C_5(C\mathit{H}_3)_5$]. ^{13}C NMR (C_6D_6): 6.9 [q, $^1J_{C–H} = 125$, $Mo(\mathit{C}H_3)_2$], 10.1 [q, $^1J_{C–H} = 126$, $C_5(\mathit{C}H_3)_5$], 96.2 [s, $\mathit{C}_5(CH_3)_5$].

4.7. Synthesis of $Cp^*_2Mo(CH_3)Cl$

A solution of $Cp^*_2Mo(CH_3)_2$ (110 mg, 0.28 mmol) in toluene (10 mL) was treated with HCl (0.27 mL, 1.0 M solution in Et_2O) and the mixture was stirred at room temperature for 2 h. After this period, the volatile components were removed in vacuo and the residue was washed with pentane (2 mL) and dried in vacuo to give $Cp^*_2MoCH_3Cl$ as a brown solid (90 mg, 78%). Anal. Calc. for $C_{21}H_{33}ClMo$: C, 60.5; H, 8.0. Found: C, 59.7; H, 7.9%. IR data (KBr disk, cm^{-1}): 2962 (vs), 2901 (vs), 2715 (m), 1481 (s), 1433 (s), 1374 (vs), 1262 (w), 1154 (m), 1067 (m), 1021 (vs), 954 (m), 803 (m), 696 (w), 675 (w), 653 (w), 611 (w), 541 (w), 469 (w). ^1H NMR (C_6D_6): −0.41 [s, $Mo(C\mathit{H}_3)$], 1.44 [s, $C_5(C\mathit{H}_3)_5$]. ^{13}C NMR (C_6D_6): 4.6 [q, $^1J_{C–H} = 129$, $Mo(\mathit{C}H_3)$], 10.6 [q, $^1J_{C–H} = 127$, $C_5(\mathit{C}H_3)_5$], 102.3 [s, $\mathit{C}_5(CH_3)_5$].

4.8. Reaction of $Cp^*_2Mo(CH_3)Cl$ with $LiAlH_4$

A solution of $Cp^*_2Mo(Me)Cl$ (ca. 10 mg) in benzene-d^6 was treated with $LiAlH_4$ and monitored by ^1H NMR spectroscopy, thereby demonstrating the formation of $Cp^*(\eta^5,\eta^1\text{-}C_5Me_4CH_2)MoH$ *inter alia* by comparison with the ^1H NMR spectrum of a sample prepared by the literature method [12]. Specifically, a solution of $Cp^*_2MoH_2$ (200 mg, 0.54 mmol) in cyclohexane (10 mL) was photolyzed for one day. After this period, the volatile components were removed in vacuo, and the residue was extracted into pentane and filtered. The filtrate was concentrated to 1 mL, cooled at −78 °C, filtered and dried in vacuo to give $Cp^*(\eta^6\text{-}C_5Me_4CH_2)MoH$ as a yellow-brown solid (95 mg, 48%). Anal. Calc. for $C_{20}H_{30}Mo$: C, 65.6; H, 8.3. Found: C, 65.7; H, 8.5%. IR data (KBr disk, cm^{-1}): 2951 (vs), 2897 (vs), 2717 (m), 1858 (m) [ν(Mo–H)], 1458 (s), 1374 (vs), 1160 (w), 1080 (m), 1024 (vs), 949 (w), 908 (m), 879 (m), 843 (m), 773 (w), 750 (w), 623 (m), 589 (w), 541 (vw), 425 (w). ^1H NMR (C_6D_6): −9.69 [q, $^4J_{H–H} = 3.5$, 1H, $Mo\mathit{H}$], 1.40 [s, 3H of $C_5(C\mathit{H}_3)_4CH_2$], 1.55 [s, 3H of $C_5(C\mathit{H}_3)_4CH_2$], 1.75 [s, 15H, $C_5(C\mathit{H}_3)_5$], 1.85 [s, 3H of $C_5(C\mathit{H}_3)_4CH_2$], 1.97 [d, $^4J_{H–H} = 3.5$, 3H of $C_5(C\mathit{H}_3)_4CH_2$], 2.69 [br, 1H of $C_5(CH_3)_4C\mathit{H}_2$], 3.29 [br, 1H of $C_5(CH_3)_4C\mathit{H}_2$]. ^{13}C NMR (C_6D_6): 8.6 [q, $^1J_{C–H} = 126$, 1C of $C_5(\mathit{C}H_3)_4CH_2$], 9.5 [q, $^1J_{C–H} = 126$, 1C of $C_5(\mathit{C}H_3)_4CH_2$], 11.3 [q, $^1J_{C–H} = 126$, 1C of $C_5(\mathit{C}H_3)_4CH_2$], 11.8 [q, $^1J_{C–H} = 126$, 5C of $C_5(\mathit{C}H_3)_5$], 15.5 [q, $^1J_{C–H} = 127$, 1C of $C_5(\mathit{C}H_3)_5CH_2$], 49.5 [t, $^1J_{C–H} = 155$, 1C of $C_5(CH_3)_4\mathit{C}H_2$], 90.3 [s, 1C of $\mathit{C}_5(CH_3)_4CH_2$], 92.8 [s, 1C of $\mathit{C}_5(CH_3)_4CH_2$], 95.3 [s, 5C of $\mathit{C}_5(CH_3)_5$], 97.9 [s, 1C of $\mathit{C}_5(CH_3)_4CH_2$], 101.5 [s, 1C of $\mathit{C}_5(CH_3)_4CH_2$], 109.0 [s, 1C of $\mathit{C}_5(CH_3)_4CH_2$].

4.9. Synthesis of Cp^*_2MoO

A mixture of $Cp^*_2MoCl_2$ (1.00 g, 2.29 mmol) and LiOH (0.84 g, 35.08 mmol) in toluene (50 mL) was stirred at 80 °C for 2 days. After this period, the volatile components were removed in vacuo, and the residue was extracted into pentane (50 mL). The extract was concentrated to ca. 2 mL and cooled to −78 °C, thereby depositing Cp^*_2MoO as a green solid which was isolated by filtration and dried in vacuo (0.56 g, 64%). Anal. Calc. for $C_{20}H_{30}OMo$: C, 62.8; H, 7.9. Found: C, 62.6; H, 8.2%. IR data (KBr disk, cm^{-1}): 2973 (s), 2949 (s), 2902 (vs), 2717 (w), 1478 (m), 1440 (s), 1373 (vs), 1159 (w), 1065 (m), 1024 (s), 915 (m), 885 (m), 834 (vs) [*ν*(Mo=O)], 799 (m), 713 (vw), 682 (vw), 621 (vw), 600 (vw), 546 (vw), 437 (w), 405 (vw). ^{1}H NMR (C_6D_6): 1.70 [s, $C_5(CH_3)_5$]. ^{13}C NMR (C_6D_6): 11.8 [q, $^1J_{C–H}$ = 126, $C_5(CH_3)_5$], 109.2 [s, $C_5(CH_3)_5$].

4.10. Synthesis of $Cp^*_2Mo(\eta^2\text{-}S_2)$

A mixture of $Cp^*_2MoH_2$ (200 mg, 0.54 mmol) and sulfur (35 mg, 1.09 mmol) in toluene (10 mL) was stirred at room temperature for 2 h. After this period, the volatile components were removed in vacuo and the residue was washed with pentane (2 × 2 mL) and dried in vacuo to give $Cp^*_2Mo(\eta^2\text{-}S_2)$ as a red-brown solid (150 mg, 64%). Anal. Calc. for $C_{20}H_{30}S_2Mo$: C, 55.8; H, 7.0. Found: C, 55.4; H, 7.3%. IR data (KBr disk, cm^{-1}): 2970 (s), 2946 (s), 2894 (vs), 2708 (w), 1473 (s), 1371 (vs), 1068 (m), 1019 (vs), 802 (m), 728 (w), 608 (w), 526 (m), 457 (w), 413 (w). ^{1}H NMR (C_6D_6): 1.58 [s, $C_5(CH_3)_5$]. ^{13}C NMR (C_6D_6): 11.3 [q, $^1J_{C–H}$ = 127, $C_5(CH_3)_5$], 101.8 [s, $C_5(CH_3)_5$].

4.11. Synthesis of $Cp^*_2Mo(\eta^2\text{-}S_4)$

A mixture of $Cp^*_2Mo(\eta^2\text{-}S_2)$ (90 mg, 0.21 mmol) and sulfur (20 mg, 0.62 mmol) in toluene (5 mL) was stirred at 80 °C for 2 days. After this period, the mixture was cooled to room temperature and pentane (5 mL) was added, thereby depositing $Cp^*_2Mo(\eta^2\text{-}S_4)$ as a red solid which was isolated by filtration, washed with pentane (2 × 5 mL) and dried in vacuo (70 mg, 68%). Anal. Calc. for $C_{20}H_{30}S_4Mo$: C, 48.6; H, 6.1. Found: C, 48.8; H, 6.4%. IR data (KBr disk, cm^{-1}): 2987 (m), 2948 (m), 2899 (vs), 2713 (w), 1483 (vs), 1449 (s), 1374 (vs), 1157 (w), 1065 (w), 1018 (vs), 802 (w), 741 (w), 678 (w), 580 (w), 528 (w), 495 (w), 462 (w), 434 (w), 408 (vw). ^{1}H NMR ($CDCl_3$): 1.74 [s, $C_5(CH_3)_5$]. ^{13}C NMR ($CDCl_3$): 11.2 [q, $^1J_{C–H}$ = 128, $C_5(CH_3)_5$], 107.2 [s, $C_5(CH_3)_5$].

4.12. Synthesis of $Cp^*_2Mo(\eta^2\text{-}Se_2)$

A mixture of $Cp^*_2MoH_2$ (200 mg, 0.54 mmol) and selenium (85 mg, 1.08 mmol) in toluene (10 mL) was stirred at 80 °C for 2 h. After this period, the mixture was filtered and the volatile components were removed in vacuo. The residue was washed with pentane (2 × 5 mL) and dried in vacuo to give $Cp^*_2Mo(\eta^2\text{-}Se_2)$ as a green solid (210 mg, 74%). Anal. Calc. for $C_{20}H_{30}Se_2Mo$: C, 45.8; H, 5.8. Found: C, 45.9; H, 6.1%. IR data (KBr disk, cm^{-1}): 2968 (m), 2888 (vs), 2707 (w), 1471 (s), 1370 (vs), 1161 (w), 1067 (m), 1017 (vs), 804 (m), 696 (w), 601 (w), 543 (w), 411 (w). ^{1}H NMR ($CDCl_3$): 1.82 [s, $C_5(CH_3)_5$]. ^{13}C NMR ($CDCl_3$): 12.1 [q, $^1J_{C–H}$ = 128, $C_5(CH_3)_5$], 101.4 [s, $C_5(CH_3)_5$]. ^{77}Se{^{1}H} NMR ($CDCl_3$): 73 [s].

4.13. Synthesis of $Cp^*_2Mo(\eta^2\text{-}Se_4)$

A mixture of $Cp^*_2MoH_2$ (200 mg, 0.54 mmol) and selenium (175 mg, 2.22 mmol) in toluene (20 mL) was stirred at 80 °C for 3 h. After this period, the volatile components were removed and the residue was extracted into THF (50 mL). The solvent was removed from the extract to give $Cp^*_2Mo(\eta^2\text{-}Se_4)$ as a red-purple solid which was washed with toluene (2 × 20 mL) and pentane (2 × 10 mL) and dried in vacuo (160 mg, 43%). Anal. Calc. for $C_{20}H_{30}Se_4Mo$: C, 35.2; H, 4.4. Found: C, 34.4; H, 4.6%. IR data (KBr disk, cm^{-1}): 2985 (m), 2945 (m), 2893 (vs), 2712 (w), 1480 (vs), 1447 (vs), 1372 (vs), 1065 (m), 1017 (vs), 804 (w), 590 (w), 547 (w), 491 (w), 408 (w). ^{1}H NMR ($CDCl_3$): 1.82 [s, $C_5(CH_3)_5$]. ^{13}C NMR ($CDCl_3$): 12.0 [q, $^1J_{C–H}$ = 128, $C_5(CH_3)_5$], 106.1 [s, $C_5(CH_3)_5$]. ^{77}Se{^{1}H} NMR ($CDCl_3$): 376 [s, $^1J_{Se–Se}$ = 195 (satellite), 2Se of $Mo(\eta^2\text{-}Se_4)$], 997 [s, $^1J_{Se–Se}$ = 195 (satellite), 2Se of $Mo(\eta^2\text{-}Se_4)$].

4.14. Synthesis of $Cp^*_2Mo(\eta^2\text{-}Te_2)$

A mixture of $Cp^*_2MoH_2$ (150 mg, 0.41 mmol) and tellurium (210 mg, 1.65 mmol) in toluene (10 mL) was stirred at 120 °C for 4 days. After this period, the mixture was filtered and the volatile components were removed in vacuo. The residue was washed with pentane (2 × 5 mL) and dried in vacuo to give $Cp^*_2Mo(\eta^2\text{-}Te_2)$ as a red solid (150 mg, 59%). Anal. Calc. for $C_{20}H_{30}Te_2Mo$: C, 38.6; H, 4.9. Found: C, 38.0; H, 4.8%. IR data (KBr disk, cm^{-1}): 2965 (m), 2943 (s), 2879 (vs), 1468 (s), 1372 (vs), 1262 (w), 1067 (m), 1016 (vs), 956 (w), 803 (w), 653 (w), 603 (w), 539 (w), 497 (w), 469 (w), 411 (w). ^{1}H NMR (C_6D_6): 1.88 [s, $C_5(CH_3)_5$]. ^{13}C NMR (C_6D_6): 14.5 [q, $^1J_{C–H}$ = 127, $C_5(CH_3)_5$], 99.3 [s, $C_5(CH_3)_5$]. ^{125}Te NMR (C_6D_6): −225 [s].

4.15. Synthesis of $[Cp^*_2Mo(CO)CH_3]I$

A solution of $Cp^*_2Mo(CO)$ (70 mg, 0.18 mmol) in toluene (10 mL) was treated with CH_3I (200 mg, 1.41 mmol) and the mixture was stirred for 1 h at room temperature. After this period, the mixture was filtered and the precipitate was washed with toluene (5 mL) and pentane (2 × 5 mL) and dried in vacuo to give $[Cp^*_2Mo(CO)CH_3]I$ as a brown solid (50 mg, 53%). Anal. Calc. for $C_{22}H_{33}OIMo$: C, 49.3; H, 6.2. Found: C, 50.2; H, 6.4%. IR data (KBr disk, cm^{-1}): 2985 (w), 2954 (w), 2904 (w), 1946 (vs) [*ν*(CO)], 1493 (w), 1468 (m), 1428 (w), 1386 (m), 1184 (vw), 1075 (vw), 1024 (m), 514 (w), 494 (w), 433 (vw), 410 (vw). ^{1}H NMR ($CDCl_3$): −0.62 [s, $Mo(CH_3)$], 1.86 [s, $C_5(CH_3)_5$]. ^{13}C NMR ($CDCl_3$): −1.6 [q, $^1J_{C–H}$ = 133, $Mo(CH_3)$], 10.6 [q, $^1J_{C–H}$ = 129, $C_5(CH_3)_5$], 105.2 [s, $C_5(CH_3)_5$], 234.0 [s, CO].

4.16. Synthesis of $Cp^*_2Mo(OSiMe_3)CN$

A solution of Cp^*_2MoO (100 mg, 0.26 mmol) in toluene (10 mL) was treated with Me_3SiCN (100 mg, 1.01 mmol) for 1 h at room temperature. After this period, the volatile components were removed and the residue was washed with pentane (5 mL) and dried in vacuo to give $Cp^*_2Mo(OSiMe_3)CN$ as a red-brown solid (90 mg, 71%). Anal. Calc. for $C_{24}H_{39}NOSiMo$: C, 59.9; H, 8.2; N, 2.9. Found: C, 59.9; H, 8.5; N, 2.8%. IR data (KBr disk, cm^{-1}): 2961 (m), 2942 (m), 2905 (s), 2098 (s) [$\nu(C\equiv N)$], 1461 (m), 1378 (m), 1251 (m), 1235 (s), 1074 (w), 1025 (s), 965 (vs), 821 (s), 745 (m), 650 (w), 447 (w), 410 (w). ^1H NMR (C_6D_6): 0.51 [s, $OSi(CH_3)_3$], 1.49 [s, $C_5(CH_3)_5$]. ^{13}C NMR (C_6D_6): 8.4 [q, $^1J_{C–H} = 116$, $OSi(CH_3)_3$], 11.5 [q, $^1J_{C–H} = 128$, $C_5(CH_3)_5$], 107.8 [s, $C_5(CH_3)_5$], 153.4 [s, CN].

4.17. Synthesis of $Cp^*_2Mo(NCS)_2$

A solution of Cp^*_2MoO (100 mg, 0.26 mmol) in toluene (10 mL) was treated with Me_3SiNCS (340 mg, 2.59 mmol) for 1 day at room temperature. After this period, the mixture was filtered and the residue was washed with toluene (5 mL) and pentane (2 × 5 mL) and dried in vacuo to give $Cp^*_2Mo(NCS)_2$ as a purple solid (65 mg, 52%). Anal. Calc. for $C_{22}H_{30}N_2S_2Mo$: C, 54.8; H, 6.3; N, 5.8. Found: C, 54.8; H, 6.7; N, 5.4%. IR data (KBr disk, cm^{-1}): 2992 (vw), 2959 (vw), 2910 (w), 2092 (vs) [$\nu(NC)$], 1477 (w), 1437 (w), 1380 (m), 1070 (vw), 1017 (m), 829 (m), 734 (vw), 427 (vw). ^1H NMR ($CDCl_3$): 1.82 [s, $C_5(CH_3)_5$]. ^{13}C NMR ($CDCl_3$): 10.9 [q, $^1J_{C–H} = 129$, $C_5(CH_3)_5$], 112.2 [s, $C_5(CH_3)_5$], 147.4 [s, $Mo(NCS)_2$].

4.18. Synthesis of $Cp^*_2Mo(N_3)_2$

A solution of Cp^*_2MoO (220 mg, 0.58 mmol) in toluene (20 mL) was treated with Me_3SiN_3 (220 mg, 1.91 mmol) for 2 h at room temperature. After this period, the volatile components were removed, and the residue was washed with pentane (3 × 2 mL) and dried in vacuo to give $Cp^*_2Mo(N_3)_2$ as a green solid (190 mg, 73%) [*Caution: certain azide compounds may decompose explosively*]. Anal. Calc. for $C_{20}H_{30}N_6Mo$: C, 53.3; H, 6.7; N, 18.7. Found: C, 52.5; H, 6.5; N, 18.0%. IR data (KBr disk, cm^{-1}): 2992 (vw), 2960 (vw), 2911 (w), 2040 (vs) [$\nu(N_3)$], 1486 (w), 1458 (w), 1380 (m), 1337 (w), 1285 (w), 1068 (vw), 1021 (w), 804 (vw), 644 (vw), 601 (vw), 420 (vw). ^1H NMR (C_6D_6): 1.45 [s, $C_5(CH_3)_5$]. ^{13}C NMR (C_6D_6): 9.9 [q, $^1J_{C–H} = 128$, $C_5(CH_3)_5$], 110.1 [s, $C_5(CH_3)_5$].

4.19. Synthesis of $Cp^*_2Mo(SPh)H$

A mixture of $Cp^*_2MoH_2$ (150 mg, 0.41 mmol) and PhSSPh (85 mg, 0.39 mmol) in toluene (10 mL) was stirred for 1 day at 80 °C. After this period, the volatile components were removed and the residue was washed with cold pentane (3 mL) and dried in vacuo to give $Cp^*_2Mo(SPh)H$ as a brown solid (110 mg, 57%). ^1H NMR (C_6D_6, 300 K): *exo* isomer −9.23 [s, 1H of Mo–H], 1.62 [s, 30H, $C_5(CH_3)_5$], 6.92 [t, $^3J_{H–H} = 7$, 1H of SC_6H_5], 7.09 [t, $^3J_{H–H} = 8$, 2H of SC_6H_5], 8.24 [d, $^3J_{H–H} = 8$, 2H of SC_6H_5]; *endo* isomer −7.52 [s, 1H of Mo–H], 1.64 [s, 30H, $C_5(CH_3)_5$], 6.97 [t, $^3J_{H–H} = 7$, 1H of SC_6H_5], 7.22 [t, $^3J_{H–H} = 8$, 2H of SC_6H_5] (2H of SC_6H_5 not located). ^{13}C NMR (C_6D_6), both isomers: 11.2 [q, $^1J_{C–H} = 127$, $C_5(CH_3)_5$], 11.6 [q, $^1J_{C–H} = 127$, $C_5(CH_3)_5$], 99.5 [s, $C_5(CH_3)_5$], 99.6 [s, $C_5(CH_3)_5$], 120.6 [d, $^1J_{C–H} = 156$, SC_6H_5], 120.9 [d, $^1J_{C–H} = 158$, SC_6H_5], 126.9 [d, $^1J_{C–H} = 155$, SC_6H_5], 127.6 [d, $^1J_{C–H} = 155$, $2SC_6H_5$], 132.3 [d, $^1J_{C–H} = 158$, SC_6H_5], 132.7 [d, $^1J_{C–H} = 157$, SC_6H_5], 150.0 [s, SC_6H_5], 151.0 [s, SC_6H_5].

4.20. Synthesis of $Cp^*_2Mo(SePh)H$

A mixture of $Cp^*_2MoH_2$ (200 mg, 0.54 mmol) and PhSeSePh (170 mg, 0.54 mmol) in toluene (10 mL) was stirred for 2 h at room temperature. After this period, the volatile components were removed, and the residue was washed with pentane (2 × 5 mL) and dried in vacuo to give $Cp^*_2Mo(SePh)H$ as a red-brown solid (210 mg, 74%). ^1H NMR (C_6D_6, 300 K): *exo* isomer −9.43 [br. s, 1H of Mo–H], 1.66 [br. s, 30H, $C_5(CH_3)_5$], 7.02 [br, 2H of SeC_6H_5], 7.46 [br, 1H of SeC_6H_5], [2H of SeC_6H_5 not located]; *endo* isomer: −7.71 [br, 1H of Mo–H], 1.66 [br, 30H, $C_5(CH_3)_5$], 7.02 [br. s, 2H of SeC_6H_5], 7.46 [br. s, 1H of SeC_6H_5] 8.36 [br. s, 2H of SeC_6H_5]. ^{13}C NMR (C_6D_6): 11.9 [q, $^1J_{C–H} = 127$, $C_5(CH_3)_5$], 98.8 [s, $C_5(CH_3)_5$], 122.1 [br. d, $^1J_{C–H} = 159$, 1C of SeC_6H_5], 127.3 [br. d, $^1J_{C–H} = 154$, 2C of SeC_6H_5], 134.4 [br. d, $^1J_{C–H} = 157$, 2C of SeC_6H_5], 139.9 [br. s, 1C of SeC_6H_5]. $^{77}Se\{^1H\}$ NMR (C_6D_6): 179 [s], 217 [s] (3:1).

4.21. Synthesis of $Cp^*_2Mo(TePh)H$

A mixture of $Cp^*_2MoH_2$ (150 mg, 0.41 mmol) and PhTeTePh (170 mg, 0.42 mmol) in toluene (10 mL) was stirred for 1 h at room temperature. After this period, the volatile components were removed, and the residue was washed with pentane (2 × 3 mL) and dried in vacuo to give $Cp^*_2Mo(TePh)H$ as a brown solid (160 mg, 69%). ^1H NMR (C_6D_6, 300 K): −9.4 [br, Mo–H], 1.75 [s, 30H, $C_5(CH_3)_5$], 6.96 [t, $^3J_{H–H} = 7$, 2H of TeC_6H_5], 7.07 [t, $^3J_{H–H} = 7$, 1H of TeC_6H_5], 7.83 [br, 2H of TeC_6H_5]. ^{13}C NMR (C_6D_6): 12.8 [q, $^1J_{C–H} = 127$, $C_5(CH_3)_5$], 97.5 [s, $C_5(CH_3)_5$], 112.5 [br, 1C of TeC_6H_5], 123.8 [dt, $^1J_{C–H} = 159$, $^2J_{C–H} = 7$, 1C of TeC_6H_5], 127.6 [dd, $^1J_{C–H} = 156$, $^2J_{C–H} = 8$, 2C of TeC_6H_5], 138.6 [dt, $^1J_{C–H} = 159$, $^2J_{C–H} = 7$, 2C of TeC_6H_5]. $^{125}Te\{^1H\}$ NMR (C_6D_6): 416 [s].

4.22. X-ray structure determinations

Single-crystal X-ray diffraction data were collected on a Bruker P4 diffractometer equipped with a SMART CCD detector and crystal data, data collection and refinement parameters are summarized in Table 2. The structures were solved using direct methods and standard difference map techniques, and were refined by full-matrix least-squares procedures on F^2 with SHELXTL (Version 5.10) [22]. The crystallographic data for $Cp^*_2MoCl_2$ (CCDC #289487), $(Cp^{Me_4Et})_2MoCl_2$ (CCDC #289486), $Cp^*_2MoH_2$ (CCDC

Table 2
Crystal, intensity collection, and refinement data

Compound	$Cp^*_2MoCl_2$	$(Cp^{Me_4Et})_2MoCl_2$	$Cp^*_2MoH_2$
Formula	$C_{20}H_{30}MoCl_2$	$C_{22}H_{34}MoCl_2$	$C_{20}H_{32}Mo$
Formula weight	437.28	465.33	368.40
System	monoclinic	monoclinic	monoclinic
Space group	*Cc*	$P2_1/n$	$P2_1/n$
a (Å)	8.267(1)	8.406(1)	8.5210(6)
b (Å)	17.913(1)	17.556(1)	24.875(2)
c (Å)	13.686(1)	14.385(1)	9.7734(6)
α (°)	90	90	90
β (°)	107.020(1)	90.921(1)	114.266(1)
γ (°)	90	90	90
V (Å^3)	1938.0(3)	2122.5(3)	1888.5(2)
Z	4	4	4
T (K)	203	223	203
Radiation (λ, Å)	0.71073	0.71073	0.71073
μ(Mo Kα) (mm^{-1})	0.950	0.873	0.688
θ Maximum (°)	28.3	28.3	28.3
Number of data	3112	4927	4353
Number of parameters	220	236	208
R_1	0.0410	0.0292	0.0339
wR_2	0.1029	0.0651	0.0713
Goodness-of-fit	1.118	1.005	1.040
	$Cp^*_2MoMe_2$	Cp^*_2MoO	Cp^*_2MoCO
Formula	$C_{22}H_{36}Mo$	$C_{20}H_{30}MoO$	$C_{21}H_{30}MoO$
Formula weight	396.45	382.38	394.39
System	monoclinic	monoclinic	monoclinic
Space group	*Cc*	$P2_1/n$	$P2_1/c$
a (Å)	8.4126(6)	12.922(1)	8.539(1)
b (Å)	18.360(1)	18.951(1)	24.943(2)
c (Å)	13.239(1)	16.096(1)	9.929(1)
α (°)	90	90	90
β (°)	106.793(1)	108.912(1)	114.082(1)
γ (°)	90	90	90
V (Å^3)	1957.7(2)	3728.8	1930.7(2)
Z	4	8	4
T (K)	203	203	213
Radiation (λ, Å)	0.71073	0.71073	0.71073
μ(Mo Kα) (mm^{-1})	0.669	0.704	0.682
θ Maximum (°)	28.3	28.3	28.3
Number of data	3951	8612	4444
Number of parameters	244	417	218
R_1	0.0191	0.0309	0.0258
wR_2	0.0477	0.0757	0.0598
Goodness-of-fit	1.043	1.029	1.100
	$Cp^*_2Mo(H)I$	$Cp^*_2Mo(NCS)_2$	$Cp^*_2Mo(\eta^2\text{-}S_2)$
Formula	$C_{20}H_{31}MoI$	$C_{22}H_{30}MoN_2S_2$	$C_{20}H_{30}MoS_2$
Formula weight	494.29	482.54	430.50
System	monoclinic	monoclinic	orthorhombic
Space group	$P2_1/n$	*C2/c*	*Fdd2*
a (Å)	8.564(1)	17.584(1)	17.187(1)
b (Å)	14.040(1)	9.399(1)	26.657(2)
c (Å)	17.121(1)	15.588(1)	8.688(1)
α (°)	90	90	90
β (°)	102.872(1)	118.004(1)	90
γ (°)	90	90	90
V (Å^3)	2006.9(2)	2274.6(3)	3980.1(5)
Z	4	4	8
T (K)	213	223	213
Radiation (λ, Å)	0.71073	0.71073	0.71073
μ(Mo Kα) (mm^{-1})	2.188	0.769	0.867
θ Maximum (°)	28.4	28.3	28.3
Number of data	4637	2633	2299
Number of parameters	217	161	112

Table 2 (*continued*)

Compound	$\text{Cp}^*_2\text{Mo(H)I}$	$\text{Cp}^*_2\text{Mo(NCS)}_2$	$\text{Cp}^*_2\text{Mo}(\eta^2\text{-S}_2)$
R_1	0.0405	0.0510	0.0199
wR_2	0.0768	0.1264	0.0481
Goodness-of-fit	1.017	1.062	1.071
	$\text{Cp}^*_2\text{Mo}(\eta^2\text{-Se}_2)$	$\text{Cp}^*_2\text{Mo}(\eta^2\text{-Te}_2)$	$\text{Cp}^*_2\text{Mo}(\eta^2\text{-Se}_4)$
Formula	$C_{20}H_{30}MoSe_2$	$C_{20}H_{30}MoTe_2$	$C_{20}H_{30}MoSe_4$
Formula weight	524.30	621.58	682.22
System	orthorhombic	orthorhombic	monoclinic
Space group	*Fdd*2	*Fdd*2	$P2_1/n$
a (Å)	16.887(1)	16.754(8)	10.675(1)
b (Å)	26.771(2)	27.241(12)	14.658(1)
c (Å)	8.872(1)	9.146(5)	13.963(1)
α (°)	90	90	90
β (°)	90	90	92.642(1)
γ (°)	90	90	90
V (Å^3)	4010.9(5)	4175(3)	2182.5(1)
Z	8	8	4
T (K)	203	203	223
Radiation (λ, Å)	0.71073	0.71073	0.71073
μ(Mo Kα) (mm^{-1})	4.282	3.367	7.274
θ Maximum (°)	28.3	28.2	28.3
Number of data	1718	2341	5047
Number of parameters	112	111	236
R_1	0.0194	0.0198	0.0304
wR_2	0.0510	0.0499	0.0792
Goodness-of-fit	1.107	1.042	1.050

#289480), $\text{Cp}^*_2\text{MoMe}_2$ (CCDC #289481), $\text{Cp}^*_2\text{Mo(CO)}$ (CCDC #289478), Cp^*_2MoO (CCDC #289489), $\text{Cp}^*_2\text{Mo(H)I}$ (CCDC #289488), $\text{Cp}^*_2\text{Mo}(\eta^2\text{-S}_2)$ (CCDC #289485), $\text{Cp}^*_2\text{Mo}(\eta^2\text{-Se}_2)$ (CCDC #289484), $\text{Cp}^*_2\text{Mo}(\eta^2\text{-Te}_2)$ (CCDC #289483), $\text{Cp}^*_2\text{Mo}(\eta^2\text{-Se}_4)$ (CCDC #289482), and $\text{Cp}^*_2\text{Mo(NCS)}_2$ (CCDC #289479) have been deposited with the Cambridge Crystallographic Data Centre.

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Supplementary data

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