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The syntheses, structures and reactivity of bis(*tert*-butylcyclopentadienyl)molybdenum derivatives: nitrogen alkylation of an η^2-acetonitrile ligand and influence of the chalcogen on the barrier to inversion of chalcogenoether adducts

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An investigation of the chemistry of the *tert*-butyl-substituted molybdenocene system, $\{(Cp^{Bu^t})_2Mo\}$ $(Cp^{Bu^t} = C_5H_4Bu^t)$, has demonstrated that the η^2-acetonitrile ligand in $(Cp^{Bu^t})_2Mo(\eta^2\text{-}MeCN)$ may be alkylated by RI (R = Me, Et) at nitrogen to give iminoacyl derivatives, $[(Cp^{Bu^t})_2Mo(\eta^2\text{-}MeC{=}NR)]^+$, which is a new type of reactivity for mononuclear acetonitrile complexes. A series of chalcogenolate–hydride complexes $(Cp^{Bu^t})_2Mo(EPh)H$ (E = S, Se, Te) have been obtained by reaction of $(Cp^{Bu^t})_2MoH_2$ with Ph_2E_2, and may be alkylated by MeI to give the chalcogenoether adducts $[(Cp^{Bu^t})_2Mo(PhEMe)H]I$. Dynamic NMR studies on $[(Cp^{Bu^t})_2Mo(PhEMe)H]^+$ indicate that the barrier to inversion at the chalcogen increases in the sequence S < Se < Te. The oxo complex $(Cp^{Bu^t})_2MoO$ reacts with 2 equivalents of Me_3SiX (X = Cl, Br, I, O_2CMe, O_3SMe) to yield $(Cp^{Bu^t})_2MoX_2$; for X = CN and NCS, $(Cp^{Bu^t})_2Mo(OSiMe_3)X$, the product of reaction with 1 equivalent may be isolated. $(Cp^{Bu^t})_2Mo(OSiMe_3)X$ (X = CN, NCS) reacts with Me_3SiNCS to give the thiocyanate complex $(Cp^{Bu^t})_2Mo(SCN)X$, rather than the isocyanate isomer, $(Cp^{Bu^t})_2Mo(NCS)X$, thereby indicating that the reactions do not involve a simple metathesis of the Si–NCS bond. Other complexes that are reported include: $(Cp^{Bu^t})_2MoX_2$ (X = H, Cl, Br, I, Me, CH_2Ph, CH_2SiMe_3), $(Cp^{Bu^t})_2MoL$ (L = CO, C_2H_4, C_2H_2, MeCN, PMe_3), $[(Cp^{Bu^t})_2Mo(\mu\text{-}E)]_2$, $(Cp^{Bu^t})_2Mo(\eta^2\text{–}E_2)$ and $(Cp^{Bu^t})_2Mo(EPh)_2$ (E = S, Se, Te).

Introduction

Although the first molybdenocene and tungstenocene complexes, $[Cp_2MoCl][Cr(CNS)_4(NH_3)_2]\cdot H_2O$ and $[Cp_2MCl_2]_2[PtCl_6]$ (M = Mo and W), were prepared by Cotton and Wilkinson in 1954,[1] the development of molybdenocene and tungstenocene chemistry awaited the synthesis of the dihydrides, Cp_2MH_2, in 1959.[2] By comparison to the extensive chemistry of the parent molybdenocene system,[3,4] the chemistry of ring-substituted molybdenocene complexes is poorly developed, an observation that has been attributed to synthetic difficulties.[5] Unsubstituted molybdenocene complexes typically exhibit poor solubility which hampers certain studies. For example, Marks has noted how the low solubility of the parent system complicates thermochemical studies, necessitating the use of methylated molybdenocene complexes.[6] In this paper, we report the chemistry of molybdenocene complexes that feature a bulky *tert*-butyl substituent on the cyclopentadienyl ring and thus exhibit improved solubility in organic solvents and also provides a useful probe for ^1H NMR spectroscopic studies. Specific issues that are discussed include: (*i*) nitrogen alkylation of an η^2-acetonitrile ligand and (*ii*) the influence of the chalcogen on the barrier to inversion of chalcogenoether adducts.

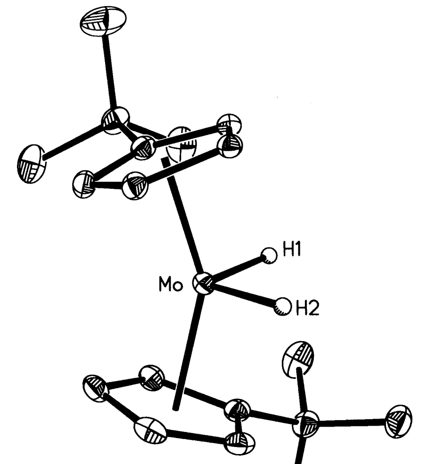

Fig. 1 Molecular structure of $(Cp^{Bu^t})_2MoH_2$ (the hydride ligands were not located, and their positions are illustrative and are based on those in Cp_2MoH_2).

Results and discussion

Dihydride, dihalide and dialkyl complexes

$(Cp^{Bu^t})_2MoH_2$, the key starting material for development of the chemistry of the $[(Cp^{Bu^t})_2Mo]$ system, is readily obtained by reaction of $MoCl_5$ with a mixture of $NaBH_4$ and $(Cp^{Bu^t})Li$ (Scheme 1), a procedure that is analogous to the synthesis of other molybdenocene dihydrides,[7] *e.g.* Cp_2MoH_2,[8] $(Cp^{Me})_2MoH_2$,[5b,6,9] $(Cp^{Bu^n})_2MoH_2$,[9] and $Cp^*{}_2MoH_2$.[10,11] The molecular structure of $(Cp^{Bu^t})_2MoH_2$ has been determined by X-ray diffraction (Fig. 1) and the Cp_{cent}–Mo–Cp_{cent} angle of 150.6° is slightly greater than that in the parent complex, Cp_2MoH_2 (145.8°).[12] Although the hydride ligands were not located, the $[MoH_2]$ moiety of $(Cp^{Bu^t})_2MoH_2$ is characterized by a signal at δ −8.78 ppm in the ^1H NMR spectrum and by ν(Mo–H) absorptions at 1823 and 1866 cm^{-1} in the solution IR spectrum. For comparison, spectroscopic data for other molybdenocene dihydrides are summarized in Table 1.

The dihydride complex $(Cp^{Bu^t})_2MoH_2$ is readily converted to

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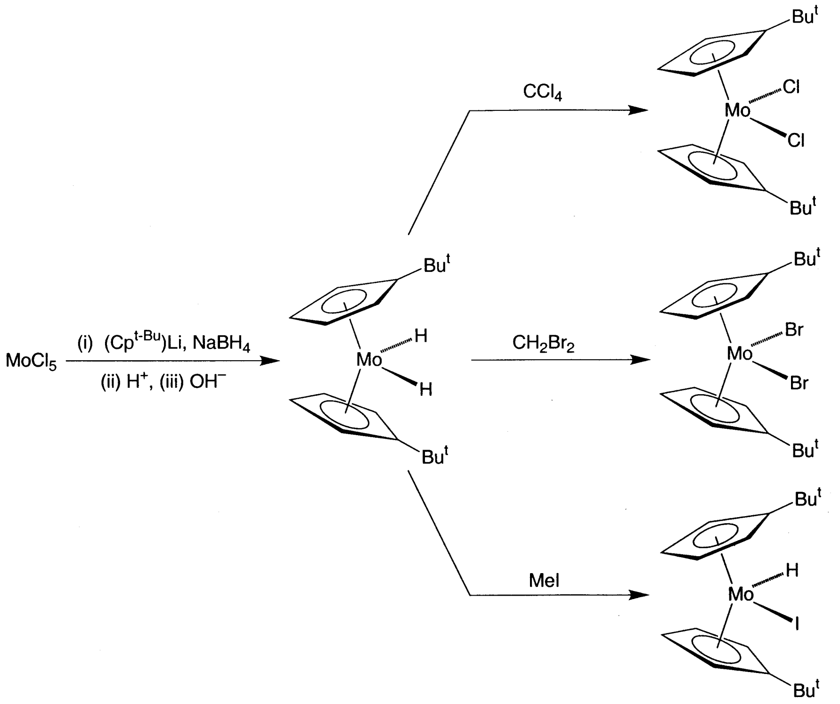
Table 1 ^{1}H NMR and IR spectral data of [Mo–H] moieties of molybdenum dihydride complexes

Complex	^{1}H NMR/ppm	ν(Mo–H)/cm^{-1}	Reference
Cp_2MoH_2	−8.80	1826 (1847)	7
$(Cp^{Me})_2MoH_2$	−8.25	1835 (1840)	7
$(Cp^{Bu^t})_2MoH_2$	−8.78	1823, 1866[a] 1852, 1906[b]	This work
$(Cp^{Bu^n})_2MoH_2$	−8.70	1830	9
$Cp^*{}_2MoH_2$	−8.38	1862	83
$Me_2C(C_5H_4)_2MoH_2$	−4.77	1750, 1760	84, 85
$[(C_4H_8)(C_5H_4)_2]MoH_2$	−4.74		84
$Me_2Si(C_5Me_4)_2MoH_2$	−6.18	1830	86
$O\{Me_2Si(C_5H_4)\}_2MoH_2$	−8.70	1818	5

[a] Pentane solution. [b] KBr disk.



Scheme 1

halide derivatives which, in turn, are useful precursors to other molybdenocene complexes. For example, $(Cp^{Bu^t})_2MoH_2$ is converted to the dichloride, $(Cp^{Bu^t})_2MoCl_2$ by reaction of $(Cp^{Bu^t})_2MoH_2$ with CCl_4 (Scheme 1).[13,14] The bromide analogue, $(Cp^{Bu^t})_2MoBr_2$ may likewise be obtained by treatment of $(Cp^{Bu^t})_2MoH_2$ with CH_2Br_2. In contrast, the reaction of $(Cp^{Bu^t})_2MoH_2$ with CH_3I yields the hydride–iodide complex, $(Cp^{Bu^t})_2Mo(H)I$, rather than the diiodide. The diiodide may, nevertheless, be obtained by treatment of $(Cp^{Bu^t})_2MoO$ with Me_3SiI (*vide infra*). The molecular structures of $(Cp^{Bu^t})_2MoCl_2$ and $(Cp^{Bu^t})_2MoBr_2$ have been determined by X-ray diffraction as shown in Fig. 2.

The dialkyl complexes $(Cp^{Bu^t})_2MoR_2$ are readily obtained by reactions of $(Cp^{Bu^t})_2MoCl_2$ with a variety of alkylating agents, *e.g.* CH_3Li, CH_3MgI, Me_3SiCH_2MgCl and $PhCH_2MgCl$ (Scheme 2). The molecular structures of $(Cp^{Bu^t})_2Mo(CH_2Ph)_2$ and $(Cp^{Bu^t})_2Mo(CH_2SiMe_3)_2$ have been determined by X-ray diffraction as shown in Figs. 3 and 4. Comparison of the data for the halide and alkyl derivatives, $(Cp^{Bu^t})_2MoX_2$, and also those described below (Table 2), indicates that the X–Mo–X angles in $(Cp^{Bu^t})_2MoX_2$ (*ca.* 73–81°) are relatively insensitive to the nature of X and are similar to that of Cp_2MoCl_2 (82°); in contrast, it is well established that the d^n count has a pronounced effect on X–M–X angle, as illustrated by the value of 100.8° for the Mo^{VI} complex, $[Cp_2MoCl_2]^{2+}$ (Table 2).

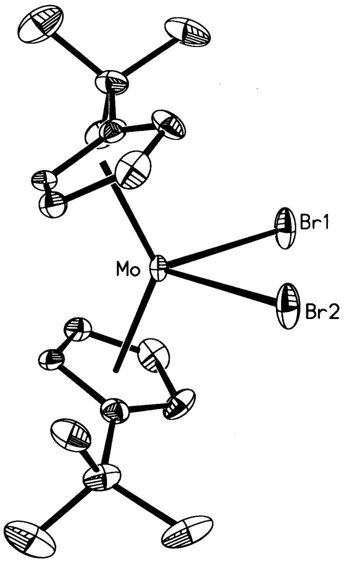
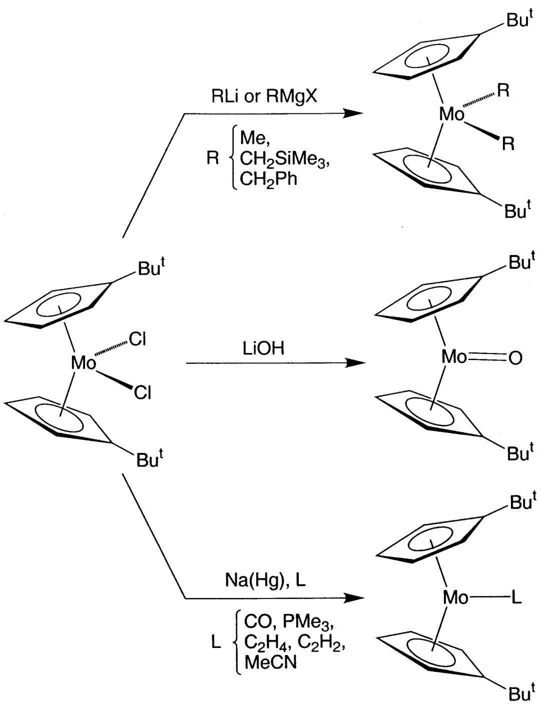


Fig. 2 Molecular structure of $(Cp^{Bu^t})_2MoBr_2$ (the chloride analogue is similar). Selected bond lengths (Å) and angles (°): Mo–Cl 2.493(2), Cl–Mo–Cl 80.6(1); Mo–Br 2.650(2), Br–Mo–Br 80.7(1).

Table 2 Structurally characterized $(Cp^{Bu^t})_2Mo(X)(Y)$ complexes

Complex	d(Mo–X)/Å	X–Mo–Y/°	Reference
$(Cp^{Bu^t})_2MoCl_2$	2.493(2)	80.6(1)	This work
$(Cp^{Bu^t})_2MoBr_2$	2.650(1)	80.7(1)	This work
$(Cp^{Bu^t})_2Mo(CH_2Ph)_2$	2.347(3)	77.0(1)	This work
$(Cp^{Bu^t})_2Mo(CH_2SiMe_3)_2$	2.304(3)	78.4(2)	This work
$(Cp^{Bu^t})_2Mo[OS(O)_2Me]_2$	2.148(2), 2.117(2)	76.24(9)	This work
$(Cp^{Bu^t})_2(SPh)_2$	2.504(1)	73.3(1)	This work
$[(Cp^{Bu^t})_2Mo(PMe_3)Me]^+$	2.491(2),[a] 2.287(7)[b]	77.4(2)	This work
Cp_2MoCl_2	2.464(6), 2.470(5)	82.0(2)	
$[Cp_2MoCl_2][BF_4]$	2.382(4)	87.9(1)	87
	2.400(3)	87.07(10)	88
$[Cp_2MoCl_2][AsF_6]_2$	2.286(4)	100.8	89

[a] Mo–P. [b] Mo–C(1).



Scheme 2

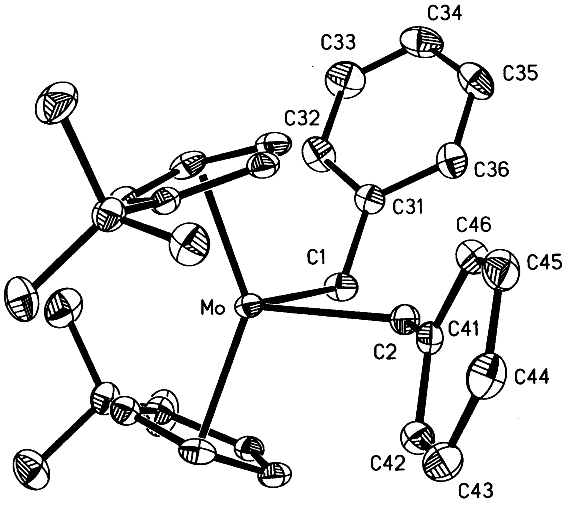


Fig. 3 Molecular structure of $(Cp^{Bu^t})_2Mo(CH_2Ph)_2$. Selected bond lengths (Å) and angles (°): Mo–C(1) 2.347(3), Mo–C(2) 2.309(3), C(1)–C(31) 1.483(4), C(2)–C(41) 1.488(4); C(1)–Mo–C(2) 77.0(1), Mo–C(1)–C(31) 122.8(2), Mo–C(2)–C(41) 121.0(2).

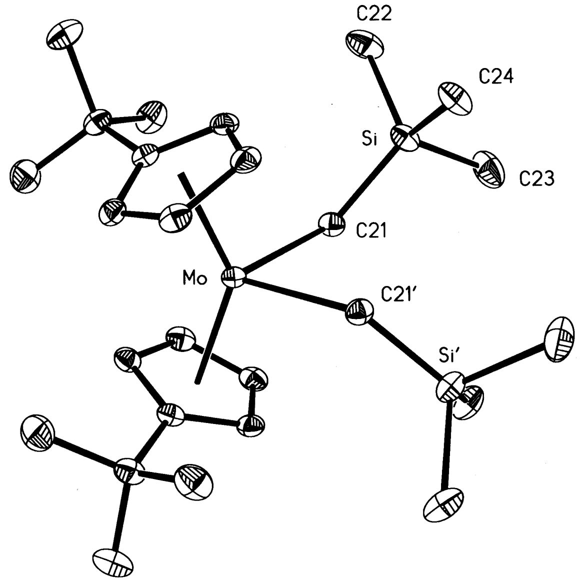


Fig. 4 Molecular structure of $(Cp^{Bu^t})_2Mo(CH_2SiMe_3)_2$. Selected bond lengths (Å) and angles (°): Mo–C(21) 2.304(3), Si–C(21) 1.863(3); C(21)–Mo–C(21′) 78.4(2), Mo–C(21)–Si 134.3(2).

Molybdenocene adducts $(Cp^{Bu^t})_2MoL$ (L = CO, C_2H_4, C_2H_2, MeCN, PMe_3)

Reduction of $(Cp^{Bu^t})_2MoCl_2$ using Na(Hg) in the presence of a donor ligand, *e.g.* L = CO, C_2H_4, C_2H_2, MeCN, PMe_3, yields the corresponding adducts $(Cp^{Bu^t})_2MoL$ (Scheme 2),[15] with the molecular structure of $(Cp^{Bu^t})_2MoPMe_3$ shown in Fig. 5. The acetonitrile adduct $(Cp^{Bu^t})_2Mo(\eta^2\text{-MeCN})$ is characterized by a ν(CN) IR absorption at 1777 cm^{-1}, which is indicative of the rather rare η^2-coordination mode, analogous to that for $Cp_2Mo(\eta^2\text{-MeCN})$.[16–18] Specifically, whereas η^1-coordination is characterized by a small increase in ν(CN) stretching frequency, the uncommon η^2-coordination mode is associated with a large decrease in ν(CN) stretching frequency of up to *ca.* 500 cm^{-1} lower than that of free acetonitrile (2250 cm^{-1}),[19] due to extensive back-bonding.[20] η^2-Acetonitrile ligands may be classified as either two-electron or four-electron donors (analogous to alkynes), which may be distinguished on the basis of the ^{13}C NMR chemical shift for the nitrile carbon atom.[21] Thus, two-electron donor MeCN ligands are characterized by ^{13}C NMR chemical shifts in the range *ca.* δ 165–180 ppm, whereas four-electron donors are characterized by shifts in the range *ca.* δ 230–240 ppm.[22,23] Hence, with a chemical shift of 168.1 ppm, the acetonitrile ligand in $(Cp^{Bu^t})_2Mo(\eta^2\text{-MeCN})$ is better described as two-electron donor, in accord with the 16-electron configuration of the molybdenocene fragment.

Facile displacement of the carbonyl ligand allows the monocarbonyl $(Cp^{Bu^t})_2Mo(CO)$ to be a useful precursor for other

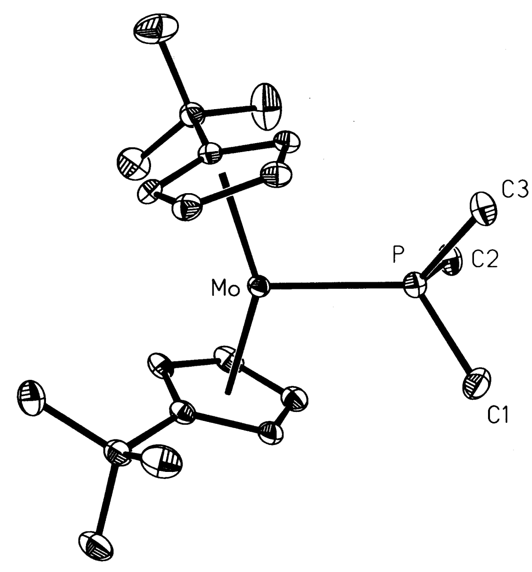
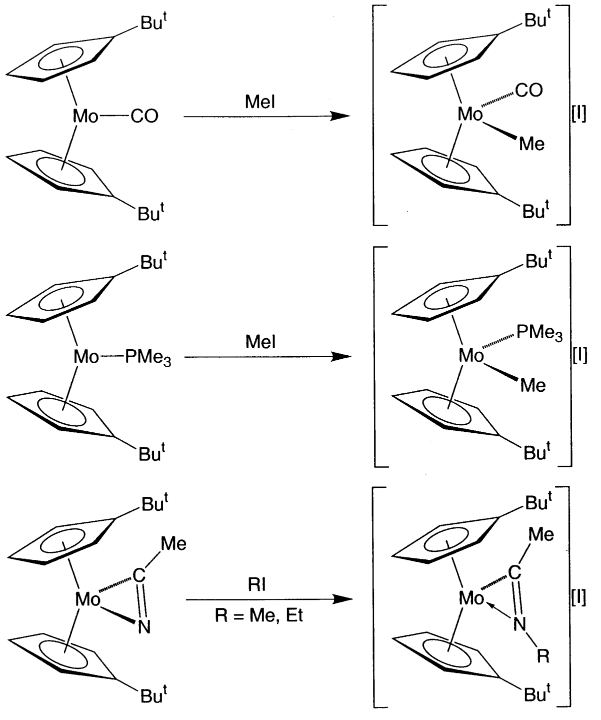


Fig. 5 Molecular structure of $(\mathrm{Cp^{Bu^t}})_2\mathrm{Mo(PMe_3)}$. Selected bond length (Å): Mo–P 2.459(1) Å.

molybdenocene derivatives, *e.g.* $(\mathrm{Cp^{Bu^t}})_2\mathrm{Mo}(\eta^2\text{-}\mathrm{E_2})$ and $(\mathrm{Cp^{Bu^t}})_2\mathrm{Mo(EPh)_2}$ (E = S, Se, Te) by reaction with the elemental chalcogen and $\mathrm{Ph_2E_2}$, as described in detail below.[24] It is also noteworthy that these reactions are considerably more facile than the corresponding reactions of the dihydride $(\mathrm{Cp^{Bu^t}})_2\mathrm{MoH_2}$.

In addition to displacement reactions, the carbonyl and trimethylphosphine adducts $(\mathrm{Cp^{Bu^t}})_2\mathrm{MoL}$ (L = CO, PMe$_3$) are readily alkylated by MeI to give the corresponding methyl complex, $[(\mathrm{Cp^{Bu^t}})_2\mathrm{Mo(L)Me}]^+$ (Scheme 3). The molecular structure of $[(\mathrm{Cp^{Bu^t}})_2\mathrm{Mo(PMe_3)Me}]\mathrm{I}$[25] has been determined by X-ray diffraction (Fig. 6), while the carbonyl complex $[(\mathrm{Cp^{Bu^t}})_2\mathrm{Mo(CO)Me}]\mathrm{I}$ is characterized by a ν(CO) stretch of 2011 cm^{-1}. This value is *ca.* 100 cm^{-1} higher than that of the neutral d^4 precursor, $(\mathrm{Cp^{Bu^t}})_2\mathrm{Mo(CO)}$ (1907 cm^{-1}), in accord with the reduction of metal-to-ligand π-backbonding expected for the cationic species.[26]



Scheme 3

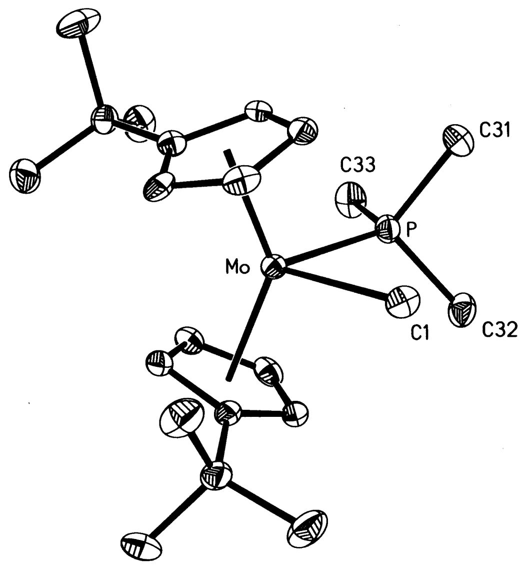


Fig. 6 Molecular structure of $[(\mathrm{Cp^{Bu^t}})_2\mathrm{Mo(PMe_3)Me}]^+$. Selected bond lengths (Å) and angles (°): Mo–P 2.491(2), Mo–C(1) 2.287(7); P–Mo–C(1) 77.4(2).

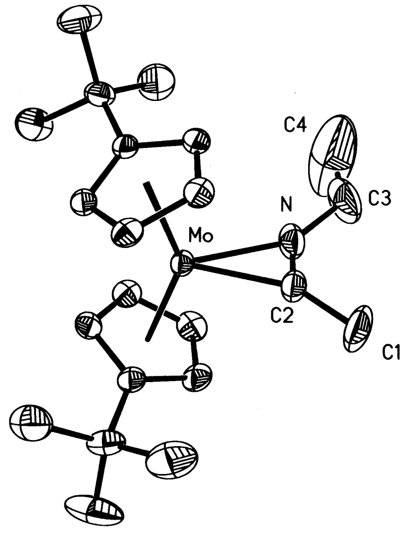


Fig. 7 Molecular structure of $[(\mathrm{Cp^{Bu^t}})_2\mathrm{Mo}(\eta^2\text{-MeC=NEt})]^+$. Selected bond lengths (Å) and angles (°): Mo–C(2) 2.105(9), Mo–N 2.113(8), C(1)–C(2) 1.523(14), C(2)–N 1.177(12), C(3)–C(4) 1.11(3), C(3)–N 1.52(2); C(2)–Mo–N 32.4(3), N–C(2)–C(1) 133.9(11), N–C(2)–Mo 74.2(6), C(1)–C(2)–Mo 151.9(9), C(4)–C(3)–N 127(2), C(2)–N–C(3) 137.0(12), C(2)–N–Mo 73.4(6), C(3)–N–Mo 149.6(10).

In contrast to the formation of a simple methyl complex, the reaction of MeI with the acetonitrile adduct $(\mathrm{Cp^{Bu^t}})_2\mathrm{Mo}(\eta^2\text{-MeCN})$ yields the iminoacyl complex $[(\mathrm{Cp^{Bu^t}})_2\mathrm{Mo}(\eta^2\text{-MeC=NMe})]\mathrm{I}$ (Scheme 3). Likewise, EtI reacts with $(\mathrm{Cp^{Bu^t}})_2\mathrm{Mo}(\eta^2\text{-MeCN})$ to yield $[(\mathrm{Cp^{Bu^t}})_2\mathrm{Mo}(\eta^2\text{-MeC=NEt})]\mathrm{I}$. The iminoacyl moiety (MeC=NMe) in $[(\mathrm{Cp^{Bu^t}})_2\mathrm{Mo}(\eta^2\text{-MeC=NMe})]\mathrm{I}$ is characterized by ^{1}H NMR signals at δ 3.00 (q, $^5J_{\mathrm{H-H}} = 1$ Hz, CCH$_3$) and 3.56 (q, $^5J_{\mathrm{H-H}} = 1$ Hz, NCH$_3$) ppm attributable to the methyl groups attached to carbon and nitrogen, respectively; these signals have been assigned by comparison with the ^{1}H NMR spectrum of the deuterated derivative $[(\mathrm{Cp^{Bu^t}})_2\mathrm{Mo}(\eta^2\text{-MeC=NCD_3})]\mathrm{I}$. Interestingly, the ν(CN) stretching frequency for the iminoacyl $[(\mathrm{Cp^{Bu^t}})_2\mathrm{Mo}(\eta^2\text{-MeC=NMe})]^+$ (1747 cm^{-1}) is comparable to that of the acetonitrile adduct $(\mathrm{Cp^{Bu^t}})_2\mathrm{Mo}(\eta^2\text{-MeCN})$ (1777 cm^{-1}). The molecular structure of $[(\mathrm{Cp^{Bu^t}})_2\mathrm{Mo}(\eta^2\text{-MeC=NEt})]\mathrm{I}$ has been determined by X-ray diffraction as shown in Fig. 7. Of particular note, the C(2)–N bond length [1.177(12) Å] in

$[(Cp^{Bu^t})_2Mo(\eta^2\text{-}MeC{=}NEt)]^+$ is short compared to those of other iminoacyl derivatives [1.19 – 1.35 Å; mean 1.27 Å].[27] Furthermore, the C–N bond length is short compared to compounds with uncoordinated C=N double bonds (1.29–1.31 Å),[28] but is comparable to the MeC≡N triple bond length of free acetonitrile [1.158(2) Å].[29] For additional comparison, the C–N bond length in the acetonitrile complex, $Cp_2Mo(\eta^2\text{-}MeCN)$ is 1.20(1) Å.[16a]

The formation of the iminoacyl complexes $[(Cp^{Bu^t})_2Mo(\eta^2\text{-}MeC{=}NR)]^+$ by the room temperature alkylation of $(Cp^{Bu^t})_2Mo(\eta^2\text{-}MeCN)$ with RI is noteworthy because it represents an unprecedented reaction of acetonitrile coordinated to a single metal center; furthermore, such alkylation is of interest since acetonitrile is not particularly basic.[30] Thus, acetonitrile complexes typically react by either (*i*) displacement, (*ii*) electrophilic or nucleophilic attack at carbon, or (*iii*) direct reaction at the metal center. For example, the acetonitrile ligand in $Cp_2Mo(\eta^2\text{-}MeCN)$ is readily displaced by Bu^tNC to give $Cp_2MoCNBu^t$,[31] and by $(PhCOO)_2$, Et_2S_2, and Ph_2Se_2 to give $Cp_2Mo(ER)_2$ (E = O, S or Se).[15a] Another example of displacement of an acetonitrile ligand is provided by the reaction of $[Cp_2Ti(\eta^1\text{-}NCMe)Me]^+$ with Me_3SiCN to give $[Cp_2Ti(\eta^2\text{-}MeC{=}NSiMe_3)(CNSiMe_3)]^+$; the reaction is proposed to occur *via* insertion of equilibrium amounts of the isomeric isocyanide, Me_3SiNC, into the Ti–Me bond.[32] Illustrative of electrophilic attack at carbon, $(dppe)_2Re(NCR)Cl$ is protonated to give $[(dppe)_2Re\{NC(H)R\}Cl]^+$.[33] $Cp_2Mo(\eta^2\text{-}MeCN)$ is also protonated by HBF_4 to yield $Cp_2Mo(\eta^1\text{-}NH{=}CHMe)(\eta^1\text{-}NCMe)$; however, rather than direct attack at the acetonitrile ligand, the reaction has been postulated to occur *via* initial protonation at the metal center, followed by insertion of the acetonitrile ligand.[20a,34] Another example of electrophilic attack at carbon is provided by the formation of the acetylimido complex $[Tp^{Me_2}]W\{NC(O)Me\}(CO)I$ by reaction of $[Tp^{Me_2}]W\{NCMe\}(CO)I$ with oxo transfer reagents such as DMSO, propylene oxide and pyridine *N*-oxide.[21b] Examples of nucleophilic attack at carbon involve reactions with $[Et_3BH]^-$, H_2O, ROH and RNH_2.[20]

Alkylation of the nitrogen atom of $(Cp^{Bu^t})_2Mo(\eta^2\text{-}MeCN)$ also represents an alternative synthesis of iminoacyl derivatives, which have otherwise been obtained by insertion of an isocyanide RNC into a M–Me bond.[27] For example, $[Cp_2Mo(\eta^2\text{-}MeC{=}NR)]^+$ (R = Me, Et) has been obtained by thermal isomerization of the isocyanide adduct $[Cp_2Mo(CNR)Me]^+$.[35] Two possibilities exist for the formation of $[(Cp^{Bu^t})_2Mo(\eta^2\text{-}MeC{=}NR)]^+$ from $(Cp^{Bu^t})_2Mo(\eta^2\text{-}MeCN)$: (*i*) direct nucleophilic attack of the nitrogen atom with RI, and (*ii*) initial methylation of the metal center to give $[(Cp^{Bu^t})_2Mo(NCMe)Me]^+$, accompanied by subsequent rearrangement. Of these two possibilities, the former is considered to be the more likely in view of the observation that other $[(Cp^R)_2M(NCMe)R]^+$ complexes show no tendency to convert to the corresponding iminoacyl derivatives.[36,37] Furthermore, the reactions of $[Cp_2Ti(NCMe)Me]^+$ with CO and $CNBu^t$ give $[Cp_2Ti(NCMe)(\eta^2\text{-}COMe)]^+$ and $[Cp_2Ti(\eta^2\text{-}Bu^tN{=}CMe)(CNBu^t)]^+$, respectively, with no evidence for coupling of the methyl and acetonitrile ligands.[38] The enhanced nucleophilic character of the nitrogen atom in $(Cp^{Bu^t})_2Mo(\eta^2\text{-}MeCN)$, compared to that of other η^1-MeCN adducts is undoubtedly a manifestation of the uncommon η^2-coordination mode. Thus, whereas the nitrogen atom of an η^1-coordinated acetonitrile is unlikely to act in a nucleophilic manner because the nitrogen lone pair is directly involved in bonding with the metal, the lone pair of the nitrogen atom of an η^2-coordinated acetonitrile ligand is not involved in bonding to the metal and is thus susceptible to electrophilic attack.

Chalcogenido complexes

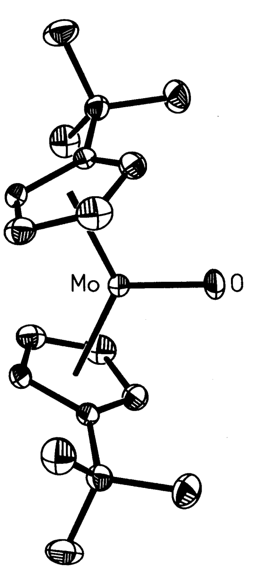
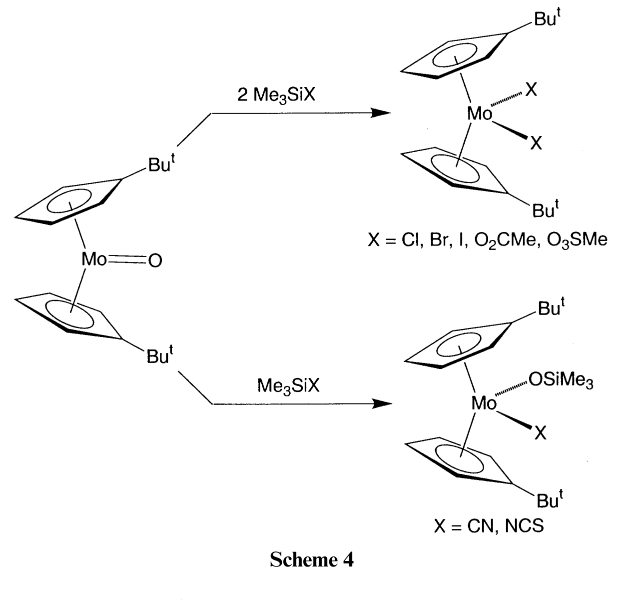


Fig. 8 Molecular structure of $(Cp^{Bu^t})_2MoO$. Selected bond length (Å): Mo–O 1.705(4).

(a) The oxo complex $(Cp^{Bu^t})_2MoO$. The molybdenum oxo complex $(Cp^{Bu^t})_2MoO$, may be synthesized by the reaction of $(Cp^{Bu^t})_2MoCl_2$ with excess LiOH (Scheme 2). The molecular structure of $(Cp^{Bu^t})_2MoO$ has been determined by X-ray diffraction (Fig. 8); the Mo=O bond length in $(Cp^{Bu^t})_2MoO$ [1.706(4) Å] is similar to that in the $(Cp^{Me})_2MoO$ counterpart [1.721(2) Å].[39] The [Mo=O] moiety in $(Cp^{Bu^t})_2MoO$ is also characterized by an IR absorption at 838 cm^{-1}, a value that is comparable to those in, Cp_2MoO (800 cm^{-1}) and $(Cp^{Me})_2MoO$ (827 cm^{-1}).[40] Although the ν(Mo=O) frequencies are low and the Mo=O bond lengths are long in comparison to those for other molybdenum oxo complexes,[41] it is recognized that this is a common feature of metallocene oxo complexes due to the orbital description of the metallocene fragment disfavoring the triply bonded $[\overset{-}{M}{\equiv}\overset{+}{O}]$ resonance structure.[42,43]

As with $(Cp^{Bu^t})_2MoCl_2$, $(Cp^{Bu^t})_2MoO$ is also a useful reagent for the synthesis of other $(Cp^{Bu^t})_2MoX_2$ derivatives. For example, $(Cp^{Bu^t})_2MoO$ reacts with Me_3SiX (X = Cl, Br, I, O_2CMe, O_3SMe)[44] to yield $(Cp^{Bu^t})_2MoX_2$ (Scheme 4), with the structure of $(Cp^{Bu^t})_2Mo[OS(O)_2Me]_2$ illustrated in Fig. 9. The first step of these transformations is proposed to involve the formal 1,2-addition[45] of the Si–X bond across the Mo=O double bond, generating $(Cp^{Bu^t})_2Mo(OSiMe_3)X$; subsequent metathesis of the Mo–OSiMe$_3$ and Me$_3$Si–X bonds yields $(Cp^{Bu^t})_2MoX_2$ and $(Me_3Si)_2O$. Although the intermediates



Scheme 4

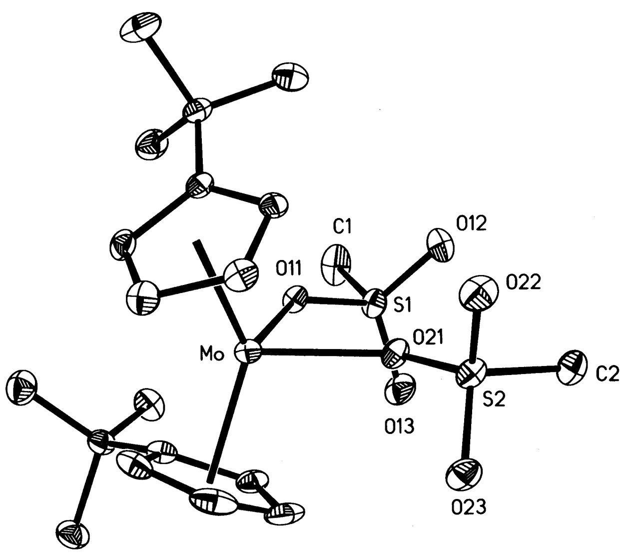


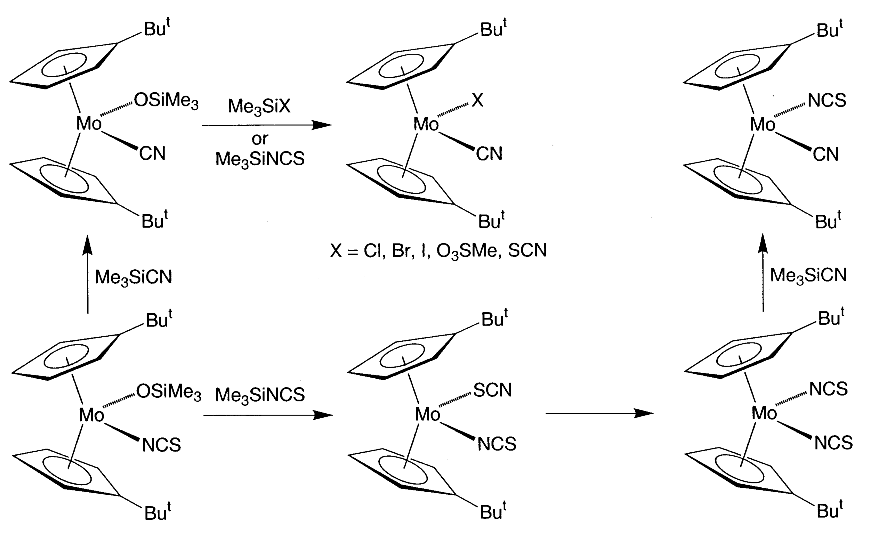
Fig. 9 Molecular structure of $(Cp^{Bu^t})_2Mo[OS(O)_2Me]_2$. Selected bond lengths (Å) and angles (°): Mo–O(11) 2.148(2), Mo–O(21), 2.117(2), S(1)–O(11) 1.500(2), S(2)–O(21), 1.498(2); O(11)–Mo–O(21) 76.24(9), Mo–O(11)–S(1) 137.23(14), Mo–O(21)–S(2) 135.7(2).

$(Cp^{Bu^t})_2Mo(OSiMe_3)X$ were not generally isolated, examples of such species, namely $(Cp^{Bu^t})_2Mo(OSiMe_3)(CN)$ and $(Cp^{Bu^t})_2Mo(OSiMe_3)(NCS)$, have been obtained from the reactions of $(Cp^{Bu^t})_2MoO$ with one equivalent of Me_3SiCN and Me_3SiNCS (Scheme 4). The thiocyanate ligand is ambidentate 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 characterized by chemical shifts less than that for NCS^- (*i.e.* $\delta_{M\text{-}SCN} < \delta_{NCS^-} \leqslant \delta_{M\text{-}NCS}$).[46] Thus, with a chemical shift of 150.2 ppm, $(Cp^{Bu^t})_2Mo(OSiMe_3)(NCS)$ is clearly identified as a *N*-bound isothiocyanate derivative. In contrast to the use of ^{13}C NMR spectroscopy, the ν(CN) stretching frequency is not capable of definitively identifying the thiocyanate coordination mode.[47] For example, [M–NCS] moieties are characterized by ν(CN) stretching frequencies in the range *ca.* 2025–2100 cm^{-1},[48] while [M–SCN] moieties are characterized by ν(CN) stretching frequencies in the range 2090–2125 cm^{-1}.[49,50] Thus, with a ν(CN) stretching frequency of 2102 cm^{-1}, IR spectroscopy is inconclusive with respect to the coordination mode in $(Cp^{Bu^t})_2Mo(OSiMe_3)(NCS)$. Furthermore, while the mixed complex $(Cp^{Bu^t})_2Mo(NCS)(SCN)$ (*vide infra*) is characterized by a single ν(CN) absorption at 2072 cm^{-1}, it is characterized by two very distinct ^{13}C NMR spectroscopic signals at δ 153.0 and 124.6 ppm which are assignable to the carbons of the [Mo–NCS] and the [Mo–SCN] moieties, respectively, on the basis of the criteria described above.

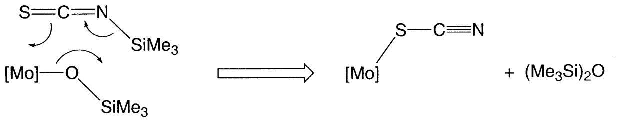
The ability to isolate the trimethylsiloxy species $(Cp^{Bu^t})_2Mo(OSiMe_3)X$ for derivatives in which X = CN or NCS, but not for those in which X = Cl, Br, I, O_2CMe, or O_3SMe is a particularly noteworthy observation since it indicates that the reactivity of the Mo–$OSiMe_3$ linkage of $(Cp^{Bu^t})_2Mo(OSiMe_3)X$ towards Me_3SiX is strongly dependent on the nature of X. In this regard, Marks and co-workers have also reported that the related chloride species $(Cp^{Me})_2Mo(OSiMe_3)Cl$ can not be isolated from the reaction of $(Cp^{Me})_2MoO$ with Me_3SiCl.[6] The tungsten analogue $(Cp^{Me})_2W(OSiMe_3)Cl$ could be isolated,[6] however, and $Cp_2W(OSiMe_3)Cl$[51] and $Cp^*{}_2W(OSiMe_3)Cl$[52] have also been spectroscopically identified.

Interestingly, the stability of the cyanide complex $(Cp^{Bu^t})_2Mo(OSiMe_3)(CN)$ is sufficiently great that it shows no further reaction towards Me_3SiCN, even at 80 °C. The isothiocyanate complex $(Cp^{Bu^t})_2Mo(OSiMe_3)(NCS)$ does, nevertheless, react further with Me_3SiNCS to give sequentially $(Cp^{Bu^t})_2Mo(NCS)(SCN)$ and $(Cp^{Bu^t})_2Mo(NCS)_2$ (Scheme 5). The two isomers may be cleanly isolated on the basis of their solubility differences; thus, $(Cp^{Bu^t})_2Mo(NCS)_2$ is completely insoluble in benzene and toluene, while $(Cp^{Bu^t})_2Mo(NCS)(SCN)$ is soluble in both solvents. The observation that the asymmetric isomer $(Cp^{Bu^t})_2Mo(NCS)(SCN)$ is formed initially is particularly important, because it indicates that the reaction does not involve a simple metathesis of the Mo–$OSiMe_3$ and Me_3Si–NCS bonds. One possibility is that the terminal sulfur atom interacts with the molybdenum center and facilitates the overall reaction, as illustrated in Scheme 6.

Although $(Cp^{Bu^t})_2Mo(OSiMe_3)(CN)$ is unreactive towards Me_3SiCN at 80 °C, it does react with other Me_3SiX derivatives at room temperature to yield $(Cp^{Bu^t})_2Mo(X)(CN)$ (X = Cl, Br, I, O_3SCH_3). $(Cp^{Bu^t})_2Mo(OSiMe_3)(CN)$ also reacts with Me_3SiNCS to yield $(Cp^{Bu^t})_2Mo(SCN)(CN)$, rather than $(Cp^{Bu^t})_2Mo(NCS)(CN)$, which may be obtained by reaction of $(Cp^{Bu^t})_2Mo(NCS)_2$ with Me_3SiCN (Scheme 5). $(Cp^{Bu^t})_2Mo(SCN)(CN)$ and $(Cp^{Bu^t})_2Mo(NCS)(CN)$ may be readily distinguished on the basis of the ^{13}C NMR resonances for the [NCS] ligand: 124.6 and 150.2 ppm, respectively. The formation of $(Cp^{Bu^t})_2Mo(SCN)(CN)$, rather than $(Cp^{Bu^t})_2Mo(NCS)(CN)$, in the reaction of $(Cp^{Bu^t})_2Mo(OSiMe_3)(CN)$ with Me_3SiNCS is in accord with the above formation of $(Cp^{Bu^t})_2Mo(NCS)(SCN)$ in the reaction of $(Cp^{Bu^t})_2Mo(OSiMe_3)(NCS)$ with Me_3SiNCS. Thus, it is evident that the reactivity displayed by $(Cp^{Bu^t})_2Mo(OSiMe_3)$-



Scheme 5



Scheme 6

(CN) towards a variety of $\mathrm{Me_3SiX}$ derivatives indicates that $\mathrm{Me_3SiCN}$ is unique by showing little tendency to displace an $\mathrm{OSiMe_3}$ group. Furthermore, $\mathrm{Me_3SiCN}$ does react with $(\mathrm{Cp^{Bu^t}})_2\mathrm{Mo(OSiMe_3)(NCS)}$, but rather than displace the $\mathrm{Me_3SiO}$ ligand, it is the NCS ligand that is displaced giving $(\mathrm{Cp^{Bu^t}})_2\mathrm{Mo(OSiMe_3)(CN)}$. The preferential displacement of the NCS ligand, rather than the $\mathrm{Me_3SiO}$ ligand, in the reaction of $(\mathrm{Cp^{Bu^t}})_2\mathrm{Mo(OSiMe_3)(NCS)}$ with $\mathrm{Me_3SiCN}$ presumably reflects the different nucleophilic tendencies of the oxygen and nitrogen atoms of the two molybdenum-bound ligands. The greater nucleophilic character of the [Mo–NCS] moiety is likely associated with increased availability of the nitrogen lone pair of the bent Mo–NCS ligand, compared to that of oxygen in the more bulky $\mathrm{Me_3SiO}$ ligand. It is also possible that displacement of the NCS ligand is favored due to the Mo–NCS bond being weaker than the Mo–$\mathrm{OSiMe_3}$ bond, although these values are unknown.

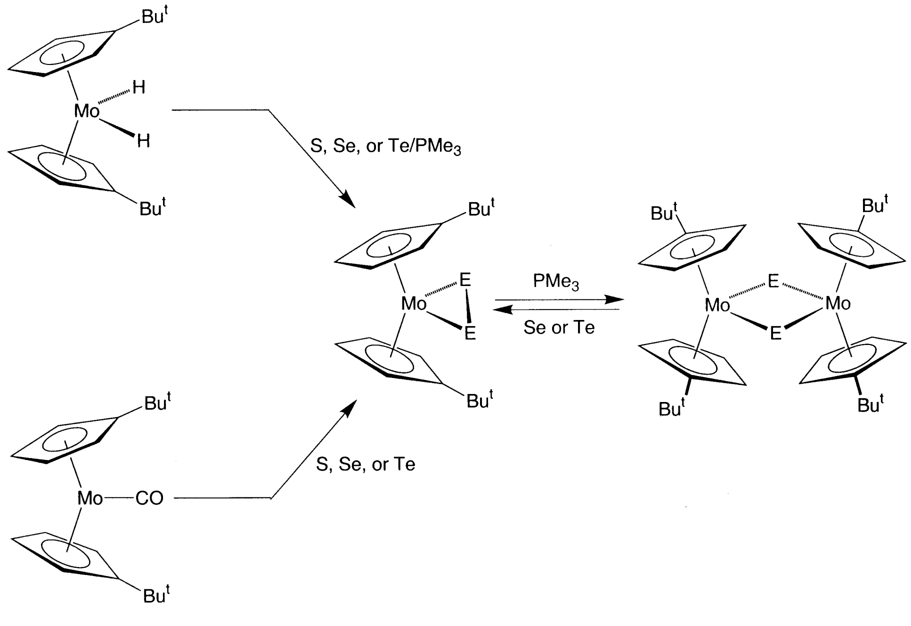
The fact that $(\mathrm{Cp^{Bu^t}})_2\mathrm{Mo(OSiMe_3)(CN)}$ reacts with other $\mathrm{Me_3SiX}$ derivatives indicates that the inertness of $(\mathrm{Cp^{Bu^t}})_2\mathrm{Mo(OSiMe_3)(CN)}$ towards $\mathrm{Me_3SiCN}$ is not so much associated with a special stability of $(\mathrm{Cp^{Bu^t}})_2\mathrm{Mo(OSiMe_3)(CN)}$, but rather is associated with $\mathrm{Me_3SiCN}$. A possible rationalization for the inability of $\mathrm{Me_3SiCN}$ to displace a Mo–$\mathrm{OSiMe_3}$ group is provided by the above observation that it is the terminal sulfur atom of the $\mathrm{Me_3Si}$–NCS molecule that initially becomes coordinated to the molybdenum center. Extending this notion to the reaction of $(\mathrm{Cp^{Bu^t}})_2\mathrm{Mo(OSiMe_3)(CN)}$ towards $\mathrm{Me_3SiCN}$, the initial product would be predicted to be an unprecedented *isocyanide* species, $(\mathrm{Cp^{Bu^t}})_2\mathrm{Mo(NC)X}$. As such, a mechanism of this type would not be expected to be facile, in accord with the observations.

(b) Sulfido, selenido, and tellurido complexes. Whereas the oxo derivative $(\mathrm{Cp^{Bu^t}})_2\mathrm{MoO}$ is readily obtained from $(\mathrm{Cp^{Bu^t}})_2\mathrm{MoCl_2}$, heavier chalcogenido complexes are more conveniently obtained from either the dihydride or carbonyl complexes, $(\mathrm{Cp^{Bu^t}})_2\mathrm{MoH_2}$ and $(\mathrm{Cp^{Bu^t}})_2\mathrm{Mo(CO)}$. Thus, $(\mathrm{Cp^{Bu^t}})_2\mathrm{MoH_2}$ reacts readily with elemental sulfur or selenium to give the dichalcogenido complexes, $(\mathrm{Cp^{Bu^t}})_2\mathrm{Mo}(\eta^2\text{-}\mathrm{E_2})$ (E = S, Se) as illustrated in Scheme 7.[53]

The ditellurido complex $(\mathrm{Cp^{Bu^t}})_2\mathrm{Mo}(\eta^2\text{-}\mathrm{Te_2})$ may also be isolated, but the reaction requires the presence of $\mathrm{PMe_3}$ as a catalyst which generates $\mathrm{Me_3PTe}$ as the active transfer agent.[54,55] The carbonyl complex $(\mathrm{Cp^{Bu^t}})_2\mathrm{Mo(CO)}$ also reacts with the elemental chalcogens to give $(\mathrm{Cp^{Bu^t}})_2\mathrm{Mo}(\eta^2\text{-}\mathrm{E_2})$ (E = S, Se, Te), as illustrated in Scheme 7,[56] but the reactions are more facile than those of $(\mathrm{Cp^{Bu^t}})_2\mathrm{MoH_2}$; for example the reaction between $(\mathrm{Cp^{Bu^t}})_2\mathrm{Mo(CO)}$ and tellurium does not require the presence of catalytic $\mathrm{PMe_3}$, unlike the reaction of $(\mathrm{Cp^{Bu^t}})_2\mathrm{MoH_2}$.

Ligand exchange is observed between $(\mathrm{Cp^{Bu^t}})_2\mathrm{Mo}(\eta^2\text{-}\mathrm{Se_2})$ and $(\mathrm{Cp^{Bu^t}})_2\mathrm{Mo}(\eta^2\text{-}\mathrm{Te_2})$ to give the mixed chalcogenido complex $(\mathrm{Cp^{Bu^t}})_2\mathrm{Mo}(\eta^2\text{-}\mathrm{SeTe})$ as a component in an equilibrium mixture which has been characterized by ^{1}H, ^{77}Se and ^{125}Te NMR spectroscopy. The ^{1}H NMR spectrum of $(\mathrm{Cp^{Bu^t}})_2\mathrm{Mo}(\eta^2\text{-}\mathrm{SeTe})$ shows a singlet and four multiplets[57] consistent with an asymmetric structure, while those of each symmetric dichalcogenido complex show a singlet and two "triplets". Also, the ^{77}Se and ^{125}Te NMR spectra shows signals at −430 ($^1J_{\mathrm{Se-Te}}$ = 522 Hz) and −459 ppm,[58] respectively, and the values differ by 170–340 ppm from those of the dichalcogenido complexes.

The diselenido and ditellurido complexes $(\mathrm{Cp^{Bu^t}})_2\mathrm{Mo}(\eta^2\text{-}\mathrm{Se_2})$ and $(\mathrm{Cp^{Bu^t}})_2\mathrm{Mo}(\eta^2\text{-}\mathrm{Te_2})$ are characterized by ^{77}Se and ^{125}Te NMR signals at δ −254 and δ −803 ppm, respectively, while the molecular structures of $(\mathrm{Cp^{Bu^t}})_2\mathrm{Mo}(\eta^2\text{-}\mathrm{S_2})$ and $(\mathrm{Cp^{Bu^t}})_2\mathrm{Mo}(\eta^2\text{-}\mathrm{Se_2})$ have been determined by X-ray diffraction (Fig. 10); selected bond lengths and angles are compared in Table 3. The $[\mathrm{Mo}(\eta^2\text{-}\mathrm{E_2})]$ moieties of $(\mathrm{Cp^{Bu^t}})_2\mathrm{Mo}(\eta^2\text{-}\mathrm{E_2})$ may be described by two extreme resonance forms (Fig. 11). The issue of which resonance form is most appropriate may be decided by comparing the [E–E] bond lengths in $(\mathrm{Cp^{Bu^t}})_2\mathrm{Mo}(\eta^2\text{-}\mathrm{E_2})$ with other [E–E] and [E=E] bond length data. For example, the S–S bond length of 2.043(4) Å in $(\mathrm{Cp^{Bu^t}})_2\mathrm{Mo}(\eta^2\text{-}\mathrm{S_2})$ is comparable to the S–S single bonds in $\mathrm{S_8}$ (2.060 Å)[59] and $\mathrm{S_2}^{2-}$ (*e.g.* 2.08 Å in $\mathrm{SrS_2}$[60] and 2.13 Å in $\mathrm{Na_2S_2}$[61]), but is much longer than that of the S=S bond in the gas phase (1.887 Å).[59,62] Likewise, the Se–Se bond length of 2.322(6) Å in $(\mathrm{Cp^{Bu^t}})_2\mathrm{Mo}(\eta^2\text{-}\mathrm{Se_2})$ is much closer to those in the $\mathrm{Se_8}$ molecule (2.34 Å)[59] and $\mathrm{Na_2Se_2}$ [2.38(5) Å][61] than that of the Se=Se bond in the gas phase (2.19 Å).[59] On the basis of these bond length comparisons, it is evident that the dichalcogenido complexes, $(\mathrm{Cp^{Bu^t}})_2\mathrm{Mo}(\eta^2\text{-}\mathrm{E_2})$ (E = S, Se), have a Mo(IV) metallacyclopropane type structure rather than a Mo(II) dichalcogen



Scheme 7

Table 3 Comparison of bond lengths (Å) and angles (°) for $(\mathrm{Cp}^{\mathrm{Bu}^t})_2\mathrm{Mo}(\eta^2\text{-}\mathrm{E}_2)$ (E = S, Se)

	E = S	E = Se
Mo–E(1)	2.459(2)	2.598(4)
Mo–E(2)	2.449(2)	2.586(4)
E(1)–E(2)	2.043(4)	2.322(6)
E(1)–Mo–E(2)	49.2(1)	53.2(2)
Mo–E(1)–E(2)	65.1(1)	63.1(2)
Mo–E(2)–E(1)	65.7(1)	63.6(2)

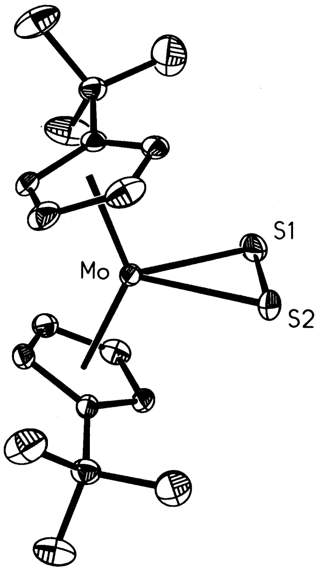


Fig. 10 Molecular structure of $(\mathrm{Cp}^{\mathrm{Bu}^t})_2\mathrm{Mo}(\eta^2\text{-}\mathrm{S}_2)$ (the selenium analogue has a similar structure).

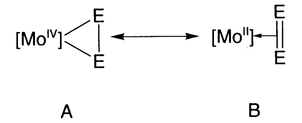


Fig. 11 Resonance structures for $\mathrm{Mo}(\eta^2\text{-}\mathrm{E}_2)$ interactions.

resonance form which would have more double bond character between both chalcogen atoms.[63]

Dinuclear monochalcogenido complexes $[(\mathrm{Cp}^{\mathrm{Bu}^t})_2\mathrm{Mo}(\mu\text{-}\mathrm{E})]_2$ (E = S, Se, Te) may be obtained by treatment of the dichalcogenido complexes $(\mathrm{Cp}^{\mathrm{Bu}^t})_2\mathrm{Mo}(\eta^2\text{-}\mathrm{E}_2)$ with PMe_3 as illustrated in Scheme 7. The observation that the sulfido, selenido, and tellurido ligands in $[(\mathrm{Cp}^{\mathrm{Bu}^t})_2\mathrm{Mo}(\mu\text{-}\mathrm{E})]_2$ bridge two metal centers, whereas the oxo ligand in $(\mathrm{Cp}^{\mathrm{Bu}^t})_2\mathrm{MoO}$ is terminal, is in line with previous studies on chalcogenido complexes of the transition elements, which indicate that the occurrence of terminal chalcogenido complexes decreases rapidly in the order $\mathrm{O} \gg \mathrm{S} > \mathrm{S} > \mathrm{Te}$.[42] The molecular structure of $[(\mathrm{Cp}^{\mathrm{Bu}^t})_2\mathrm{Mo}(\mu\text{-}\mathrm{Se})]_2$ has been determined by X-ray diffraction (Fig. 12). The Mo–Se bond length [2.611(2) Å] is comparable to those in $(\mathrm{Cp}^{\mathrm{Bu}^t})_2\mathrm{Mo}(\eta^2\text{-}\mathrm{Se}_2)$ [2.598(4) and 2.586(4) Å]. The $[\mathrm{Mo}(\mu\text{-}\mathrm{E})_2\mathrm{Mo}]$ moieties of $[(\mathrm{Cp}^{\mathrm{Bu}^t})_2\mathrm{Mo}(\mu\text{-}\mathrm{E})]_2$ (E = Se, Te) derivatives are characterized by $^{77}\mathrm{Se}$ and $^{125}\mathrm{Te}$ NMR signals at δ −996 and δ −1664 ppm, respectively.

The abstraction of a chalcogen atom from $(\mathrm{Cp}^{\mathrm{Bu}^t})_2\mathrm{Mo}(\eta^2\text{-}\mathrm{E}_2)$ is reversible, in the sense that $[(\mathrm{Cp}^{\mathrm{Bu}^t})_2\mathrm{Mo}(\mu\text{-}\mathrm{E})]_2$ (E = Se, Te) regenerate $(\mathrm{Cp}^{\mathrm{Bu}^t})_2\mathrm{Mo}(\eta^2\text{-}\mathrm{E}_2)$ upon heating with elemental Se or Te.[64] The reaction of $[(\mathrm{Cp}^{\mathrm{Bu}^t})_2\mathrm{Mo}(\mu\text{-}\mathrm{Se})]_2$ with tellurium gives not only $(\mathrm{Cp}^{\mathrm{Bu}^t})_2\mathrm{Mo}\{\eta^2\text{-}(\mathrm{SeTe})\}$, but also $(\mathrm{Cp}^{\mathrm{Bu}^t})_2\mathrm{Mo}(\eta^2\text{-}\mathrm{Se}_2)$ and $(\mathrm{Cp}^{\mathrm{Bu}^t})_2\mathrm{Mo}(\eta^2\text{-}\mathrm{Te}_2)$ as a result of chalcogen scrambling.

Chalcogenolate complexes

The reactions of $(\mathrm{Cp}^{\mathrm{Bu}^t})_2\mathrm{MoH}_2$ with $\mathrm{Ph}_2\mathrm{E}_2$ (E = S, Se, Te) provide a convenient method for generating phenylchalcogenolate derivatives.[65] Thus, reaction of $(\mathrm{Cp}^{\mathrm{Bu}^t})_2\mathrm{MoH}_2$ with $\mathrm{Ph}_2\mathrm{E}_2$ (E = S, Se, Te) gives sequentially $(\mathrm{Cp}^{\mathrm{Bu}^t})_2\mathrm{Mo}(\mathrm{EPh})\mathrm{H}$ and $(\mathrm{Cp}^{\mathrm{Bu}^t})_2\mathrm{Mo}(\mathrm{EPh})_2$, with the exception that the tellurium derivative $(\mathrm{Cp}^{\mathrm{Bu}^t})_2\mathrm{Mo}(\mathrm{TePh})_2$ is not obtained in the presence of excess $\mathrm{Ph}_2\mathrm{Te}_2$ at 120 °C (Scheme 8). $(\mathrm{Cp}^{\mathrm{Bu}^t})_2\mathrm{Mo}(\mathrm{TePh})_2$ is, nevertheless, readily obtained by the reaction of $(\mathrm{Cp}^{\mathrm{Bu}^t})_2\mathrm{Mo}(\mathrm{CO})$ with $\mathrm{Ph}_2\mathrm{Te}_2$ at room temperature (Scheme 8); likewise, $(\mathrm{Cp}^{\mathrm{Bu}^t})_2\mathrm{Mo}(\mathrm{SPh})_2$ and $(\mathrm{Cp}^{\mathrm{Bu}^t})_2\mathrm{Mo}(\mathrm{SePh})_2$ may be obtained from the reactions of $(\mathrm{Cp}^{\mathrm{Bu}^t})_2\mathrm{Mo}(\mathrm{CO})$ with $\mathrm{Ph}_2\mathrm{E}_2$ (E = S, Se).[66]

The molecular structures of $(\mathrm{Cp}^{\mathrm{Bu}^t})_2\mathrm{Mo}(\mathrm{EPh})\mathrm{H}$ (E = Se, Te) and $(\mathrm{Cp}^{\mathrm{Bu}^t})_2\mathrm{Mo}(\mathrm{SPh})_2$ have been determined by X-ray diffraction as shown in Figs. 13 and 14. Selected metrical data listed in Table 4, which indicate that the angle at the chalcogen decreases in the sequence S > Se > Te. For the sulfido complex, $(\mathrm{Cp}^{\mathrm{Bu}^t})_2$-

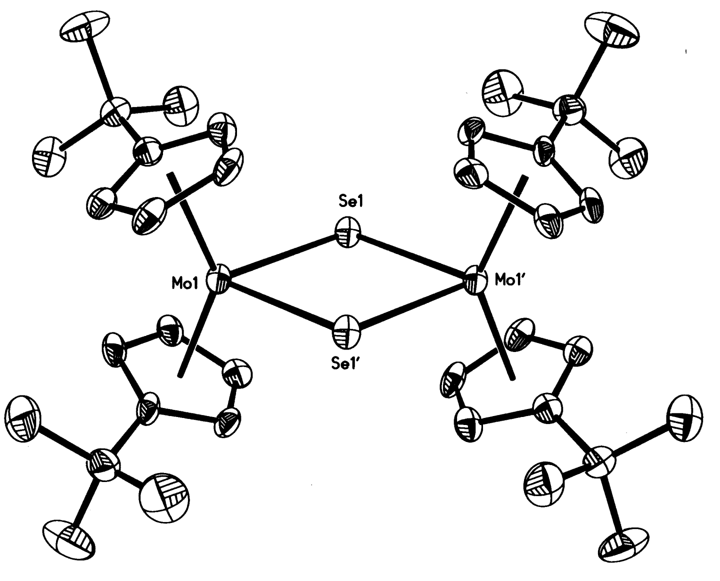
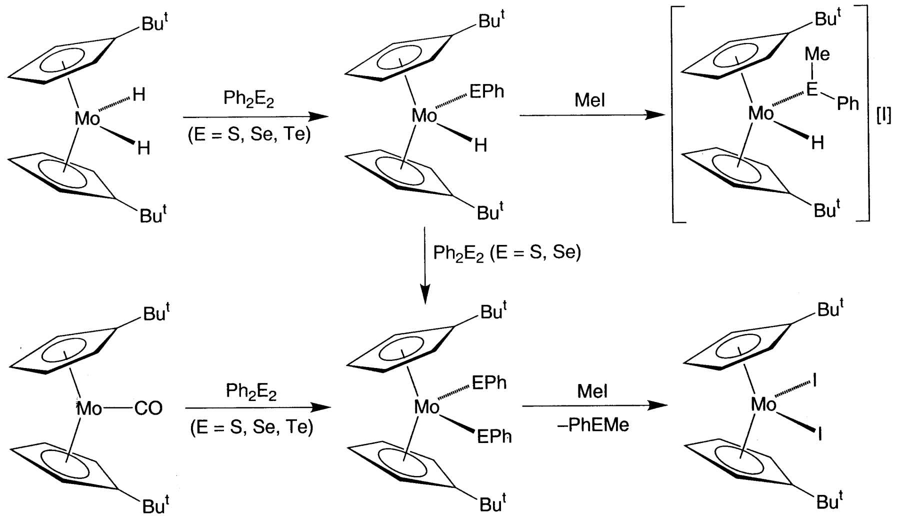


Fig. 12 Molecular structure of $[(\mathrm{Cp}^{\mathrm{Bu}^t})_2\mathrm{Mo}(\mu\text{-}\mathrm{Se})]_2$. There are two crystallographically independent half-molecules in the asymmetric unit, one of which is disordered. Selected bond lengths (Å) and angles (°) are only listed for the ordered molecule: Mo(1)–Se(1) 2.611(2) Å; Se(1)–Mo(1)–Se(1′) 74.24(6), Mo(1)–Se(1)–Mo(1′) 105.76(6).

Table 4 Selected bond lengths and angles for $(Cp^{Bu^t})_2Mo(SPh)_2$, $(Cp^{Bu^t})_2Mo(EPh)H$ and (E = Se, Te)

Complex	*d*(Mo–E)/Å	*d*(E–C)/Å	Mo–E–C/°	E–Mo–X/°
$(Cp^{Bu^t})_2Mo(SPh)_2$	2.504(1)	1.782(3)	113.6(1)	73.3
$(Cp^{Bu^t})_2Mo(SePh)H$	2.620(1)	1.914(10)	105.8(3)	84.4
$(Cp^{Bu^t})_2Mo(TePh)H$	2.799(1)	2.146(10)	102.9(3)	77.3



Scheme 8

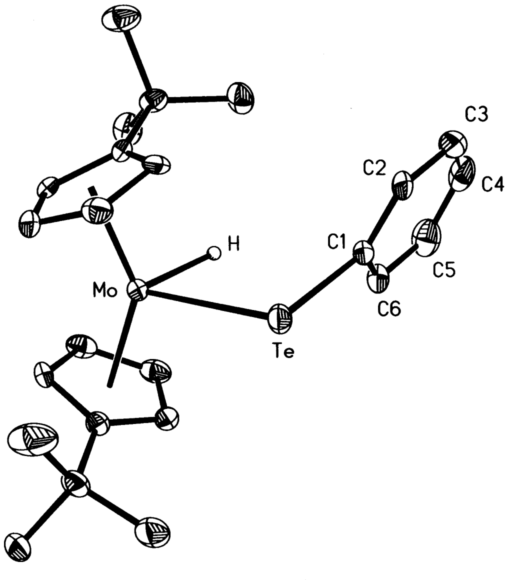


Fig. 13 Molecular structure of $(Cp^{Bu^t})_2Mo(TePh)H$ (the selenium analogue is similar).

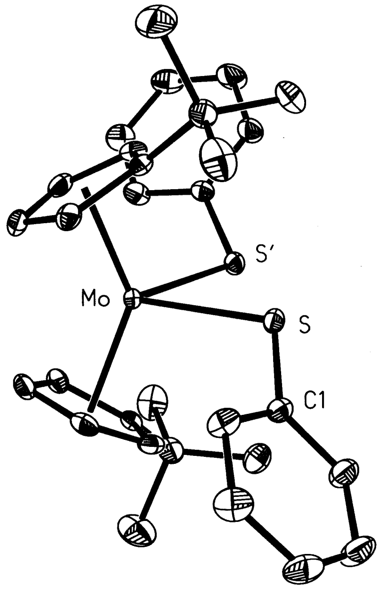


Fig. 14 Molecular structure of $(Cp^{Bu^t})_2Mo(SPh)_2$.

$Mo(SPh)_2$, the phenyl groups adopt an *exo* conformation which minimizes (*i*) destabilizing interactions between the lone pairs of electrons and the d^2 pair of electrons on the molybdenum center,[67] and (*ii*) steric interactions between the two phenyl groups. In contrast, the phenyl groups of $(Cp^{Bu^t})_2Mo(EPh)H$ (E = Se, Te) are directed toward the hydride ligand. Presumably, in the presence of the small hydride ligand, the phenyl group adopts an endo conformation to minimize steric interactions with the *tert*-butyl substituents of the cyclopentadienyl ligands.

The chalcogenolate complexes $(Cp^{Bu^t})_2Mo(EPh)_2$ (E = S, Se, Te) react readily with MeI to yield $(Cp^{Bu^t})_2MoI_2$ and PhEMe, a transformation that has precedence.[68] Of substantially more interest, the corresponding reactions of the hydride derivatives $(Cp^{Bu^t})_2Mo(EPh)H$ (E = S, Se, Te) with MeI give the chalcogenoether adducts $[(Cp^{Bu^t})_2Mo(PhEMe)H]I$, rather than $(Cp^{Bu^t})_2Mo(H)(I)$ (Scheme 8).[69] The [Mo–H] moieties in $[(Cp^{Bu^t})_2Mo(PhEMe)H]I$ are characterized by ^1H NMR signals at δ −8.80 (E = S), −9.12 (E = Se, $^2J_{Se-H}$ = 14 Hz) and −9.39 ppm (E = Te, $^2J_{Te-H}$ = 38 Hz), and by ν(Mo–H) IR absorptions at 1898 (E = S), 1895 (E = Se) and 1893 cm^{-1} (E = Te). The [Mo(PhEMe)] moieties in $[(Cp^{Bu^t})_2Mo(PhSeMe)H]I$ and $[(Cp^{Bu^t})_2Mo(PhTeMe)H]I$ are also characterized by ^{77}Se NMR and ^{125}Te NMR spectroscopic signals at δ 244 ppm ($w_{1/2}$ = 42 Hz) and δ 547 ppm ($w_{1/2}$ = 102 Hz), respectively. These values are shifted substantially downfield from the signals of both (*i*) the parent chalcogenolate–hydride complexes, $(Cp^{Bu^t})_2Mo(SePh)H$ (−117 ppm) and $(Cp^{Bu^t})_2Mo(TePh)H$ (−213 ppm), and (*ii*) the bis(chalcogenolate) complexes $(Cp^{Bu^t})_2Mo(SePh)_2$ (−83 ppm) and $(Cp^{Bu^t})_2Mo(TePh)_2$ (−195 ppm).

The ^1H NMR spectra of $[(Cp^{Bu^t})_2Mo(PhEMe)H]I$ show interesting differences in the range 4–6 ppm, *i.e.* that of the $C_5H_4Bu^t$ ring protons (Fig. 15). Specifically, the ^1H NMR

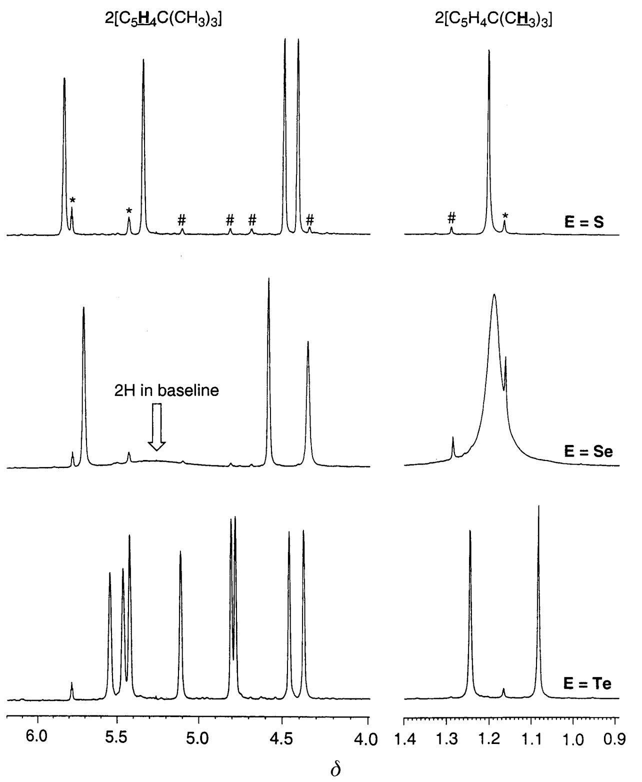
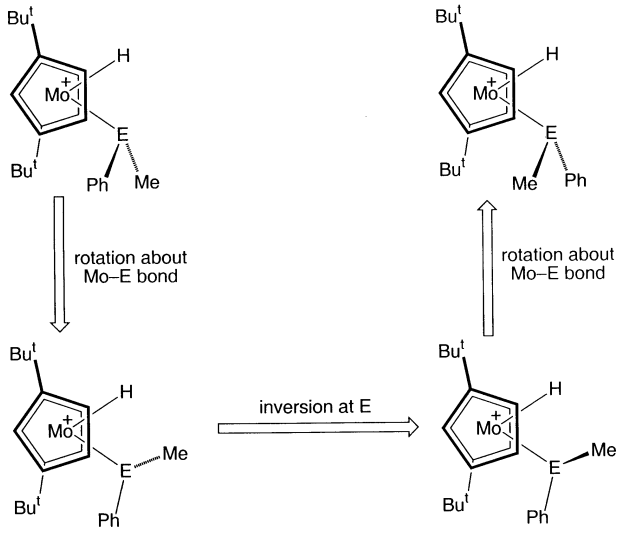


Fig. 15 ^{1}H NMR spectra of $[(\mathrm{Cp}^{\mathrm{Bu}^t})_2\mathrm{Mo(PhEMe)H}]\mathrm{I}$ (E = S, Se, Te); resonances marked * and # correspond to $(\mathrm{Cp}^{\mathrm{Bu}^t})_2\mathrm{MoI}_2$ and $(\mathrm{Cp}^{\mathrm{Bu}^t})_2\mathrm{Mo(H)I}$ impurities that are formed due to dissociation of PhEMe. For clarity, the hydride resonances are not illustrated.

spectrum of $[(\mathrm{Cp}^{\mathrm{Bu}^t})_2\mathrm{Mo(PhSMe)H}]\mathrm{I}$ shows four signals for the ring protons, while that of $[(\mathrm{Cp}^{\mathrm{Bu}^t})_2\mathrm{Mo(PhTeMe)H}]\mathrm{I}$ exhibits eight signals. The selenium analogue $[(\mathrm{Cp}^{\mathrm{Bu}^t})_2\mathrm{Mo(PhSeMe)H}]\mathrm{I}$, exhibits intermediate characteristics, with the ^{1}H NMR spectrum showing four signals, one of which is very broad (Fig. 15).[70] Furthermore, two of the eight ^{1}H NMR signals for $[(\mathrm{Cp}^{\mathrm{Bu}^t})_2\mathrm{Mo(PhTeMe)H}]\mathrm{I}$ in the range 4–6 ppm coalesce at 60 °C (Fig. 15), consistent with an exchange process.[71] The room temperature static ^{1}H NMR spectrum of $[(\mathrm{Cp}^{\mathrm{Bu}^t})_2\mathrm{Mo(PhTeMe)H}]\mathrm{I}$, consisting of eight ring proton signals and two *tert*-butyl signals demonstrates clearly that the two $\mathrm{Cp}^{\mathrm{Bu}^t}$ ligands are inequivalent. Although none of the complexes has been structurally characterized, the inequivalence of the two $\mathrm{Cp}^{\mathrm{Bu}^t}$ ligands is reasonably attributed to the pyramidal chalcogen center of the E(Ph)Me ligand—thus, regardless of the location of the phenyl and methyl groups, the two $\mathrm{Cp}^{\mathrm{Bu}^t}$ ligands can never be related by a mirror plane. Chemical exchange of the two $\mathrm{Cp}^{\mathrm{Bu}^t}$ ligands requires inversion at the chalcogen and, depending upon the location of the phenyl and methyl groups, rotation about the Mo–E bond (see, for example, Scheme 9). Specifically, rotation is required unless the phenyl and methyl groups are located in positions that are related to those of the inverted configuration by reflection of the E(Ph)Me ligand in the molybdenocene coordination plane. For all other conformations, partial rotation about the Mo–E bond is also required to effect exchange. The observation that exchange is more facile for $[(\mathrm{Cp}^{\mathrm{Bu}^t})_2\mathrm{Mo(PhSMe)H}]\mathrm{I}$ than $[(\mathrm{Cp}^{\mathrm{Bu}^t})_2\mathrm{Mo(PhTeMe)H}]\mathrm{I}$ is consistent with the observation that inversion barriers tend to increase as one descends the Periodic Table. For example, the inversion barrier of NH_3 is considerably lower than that of PH_3 due to the reduced tendency of phosphorus to rehybridize and obtain a planar transition state.[72] Likewise, inversion at the three-coordinate oxygen in the bis(pyrazolyl)borato complex $[(\mathrm{Ph_2CHO})\mathrm{Bp}^{\mathrm{Bu}^t,\mathrm{Pr}^i}]\mathrm{ZnI}$ is more facile than that at sulfur in $[(\mathrm{Ph_2CHS})\mathrm{Bp}^{\mathrm{Bu}^t,\mathrm{Pr}^i}]\mathrm{ZnI}$.[73]



Scheme 9 Chemical exchange between the two $\mathrm{Cp}^{\mathrm{Bu}^t}$ ligands of $[(\mathrm{Cp}^{\mathrm{Bu}^t})_2\mathrm{Mo(PhEMe)H}]^+$. Unless the structure of $[(\mathrm{Cp}^{\mathrm{Bu}^t})_2\mathrm{Mo(PhEMe)H}]^+$ is one in which the phenyl and methyl groups are located in positions that are related to those of the inverted configuration by reflection of the E(Ph)Me ligand in the molybdenocene coordination plane, chemical exchange between the two $\mathrm{Cp}^{\mathrm{Bu}^t}$ ligands requires *both* rotation about the M–E bond and inversion at the chalcogen (rotation of the $\mathrm{Cp}^{\mathrm{Bu}^t}$ about the Mo–$\mathrm{Cp}^{\mathrm{Bu}^t}$ centroid is assumed to be facile). Other sequences of rotation and inversion are also feasible.

The more facile exchange for the $[(\mathrm{Cp}^{\mathrm{Bu}^t})_2\mathrm{Mo(PhSMe)H}]\mathrm{I}$ derivative also indicates that inversion, and not rotation about the M–E bond, is the rate determining factor. Specifically, rotation about the Mo–E(Ph)Me bond would be expected to more facile for the tellurium derivative, $[(\mathrm{Cp}^{\mathrm{Bu}^t})_2\mathrm{Mo(PhTeMe)H}]\mathrm{I}$, due to the longer Mo–Te bond minimizing interactions between the telluroether substituents and the $\mathrm{Cp}^{\mathrm{Bu}^t}$ ligand during rotation. Finally, it should be noted that chemical exchange of the two $\mathrm{Cp}^{\mathrm{Bu}^t}$ ligands can also be achieved by dissociation of the chalcogenoether. However, if this were to be the mechanism for exchange then one would expect the opposite trend to that observed, *i.e.* the $[(\mathrm{Cp}^{\mathrm{Bu}^t})_2\mathrm{Mo(PhSMe)H}]\mathrm{I}$ derivative, with the expected stronger Mo–E(Ph)Me bond, would be the derivative that should exhibit eight ring proton signals. Thus, the available evidence suggests that the facility of chemical exchange of the two $\mathrm{Cp}^{\mathrm{Bu}^t}$ ligands in $[(\mathrm{Cp}^{\mathrm{Bu}^t})_2\mathrm{Mo(PhEMe)H}]\mathrm{I}$ is dictated by the barrier to inversion of the chalcogen. In support of this suggestion, calculations on a series of sulfonium, selenonium, and telluronium ylides, $\mathrm{R_2E(CR'_2)}$, indicate that the barrier to inversion increases in the sequence S < Se < Te.[74,75]

Experimental section

General considerations

All manipulations were performed using a combination of glovebox, high-vacuum or Schlenk techniques.[76] Solvents were purified and degassed by standard procedures and all commercially available reagents were used as received, unless otherwise noted in the experimental procedures. IR spectra were recorded as KBr pellets or neat samples on Perkin-Elmer 1430 or 1600 spectrophotometers and are reported in cm^{-1}. Mass spectra were obtained on a Nermag R10-10 mass spectrometer using chemical ionization (CH_4) techniques. Elemental analyses were measured using a Perkin-Elmer 2400 CHN Elemental Analyzer. ^{1}H NMR spectra were recorded on Varian VXR-200 (200.057 MHz), VXR-300 (299.943 MHz), and VXR-400 (399.95 MHz) spectrometers. ^{13}C, ^{31}P, ^{77}Se and ^{125}Te NMR spectra were recorded on a Varian VXR-300 spectrometer. ^{1}H and ^{13}C chemical shifts are reported in ppm

Table 5 Crystal, intensity collection and refinement data

	$(Cp^{Bu^t})_2MoH_2$	$(Cp^{Bu^t})_2MoCl_2$	$(Cp^{Bu^t})_2MoBr_2$	$(Cp^{Bu^t})_2Mo(CH_2Ph)_2$	$(Cp^{Bu^t})_2Mo(CH_2SiMe_3)_2$	$(Cp^{Bu^t})_2MoO$	$(Cp^{Bu^t})_2Mo(O_3SMe)_2$	$(Cp^{Bu^t})_2Mo(PMe_3)$
Lattice	Monoclinic	Orthorhombic	Orthorhombic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Formula	$C_{18}H_{28}Mo$	$C_{18}H_{26}Cl_2Mo$	$C_{18}H_{26}Br_2Mo$	$C_{32}H_{40}Mo$	$C_{26}H_{48}MoSi_2$	$C_{18}H_{26}MoO$	$C_{20}H_{32}O_6S_2$	$C_{21}H_{35}MoP$
Formula weight	340.34	409.23	498.15	520.58	512.76	354.33	528.52	414.40
Space group	$P2_1/c$	$P22_12_1$	$P22_12_1$	$P2_1/c$	$C2/c$	$C2/c$	$P2_1/n$	$C2/c$
a/Å	10.066(3)	6.7510(10)	7.0120(10)	9.7203(6)	17.528(2)	15.601(3)	8.6263(6)	9.705(2)
b/Å	20.509(5)	10.571(4)	10.538(2)	11.8270(7)	19.861(2)	6.2830(10)	17.0614(12)	10.997(2)
c/Å	8.180(2)	12.660(5)	12.562(3)	23.325(2)	9.0166(11)	17.732(3)	15.7394(10)	19.599(4)
α/°	90	90	90	90	90	90	90	90
β/°	107.066(6)	90	90	100.519(5)	119.619(7)	101.21(2)	90.674(6)	92.07(2)
γ/°	90	90	90	90	90	90	90	90
V/Å^3	1614.4(7)	903.5(5)	928.2(3)	2636.4(3)	2728.7(5)	1704.9(5)	2316.3(3)	2090.4(7)
Z	4	2	2	4	4	4	4	4
Temperature/K	238	293	293	298	298	293	298	293
Radiation (λ/Å)	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
D_c/g cm^{-3}	1.400	1.504	1.782	1.312	1.248	1.380	1.516	1.317
μ(Mo-Kα)/mm^{-1}	0.799	1.014	5.004	0.515	0.579	0.764	0.779	0.703
θ_{max}/°	28.13	29.99	25.00	25.00	25.00	25.00	22.49	25.05
No. of data	3620	1535	976	4609	2301	1490	3024	3694
No. of parameters	178	99	100	299	133	94	263	210
R_1	0.0235	0.0359	0.0358	0.0322	0.0315	0.0293	0.0288	0.0299
wR_2	0.0644	0.0820	0.0843	0.0786	0.0789	0.0701	0.0655	0.0681
GOF	1.101	1.021	1.126	1.060	1.060	1.063	1.050	1.027

	$(Cp^{Bu^t})_2Mo(\eta^2\text{-}S_2)$	$(Cp^{Bu^t})_2Mo(\eta^2\text{-}Se_2)$	$[(Cp^{Bu^t})_2Mo(\mu\text{-}Se)]_2$	$[(Cp^{Bu^t})_2Mo(PMe_3)Me]\text{-}I\cdot CH_2Cl_2$	$[(Cp^{Bu^t})_2Mo(\eta^2\text{-}MeC{=}NEt)]I\cdot 2CHCl_3$	$(Cp^{Bu^t})_2Mo\text{-}(SPh)_2$	$(Cp^{Bu^t})_2Mo(SePh)H$	$(Cp^{Bu^t})_2Mo(TePh)H$
Lattice	Monoclinic	Monoclinic	Triclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Formula	$C_{18}H_{26}MoS_2$	$C_{18}H_{26}MoSe_2$	$C_{36}H_{52}Mo_2Se_2$	$C_{23}H_{40}Cl_2IMoP$	$C_{24}H_{36}Cl_6IMoN$	$C_{30}H_{36}MoS_2$	$C_{24}H_{32}MoSe$	$C_{24}H_{32}MoTe$
Formula weight	402.45	496.25	834.58	641.26	774.08	556.65	495.40	544.04
Space group	$P2_1/n$	$P2_1/n$	$P\bar{1}$	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P2_1/c$	$P2_1/c$
a/Å	10.739(3)	10.814(6)	11.023(3)	8.4901(7)	8.9300(10)	21.214(7)	8.5880(10)	8.665(2)
b/Å	13.953(3)	14.229(8)	11.239(3)	16.0746(10)	20.396(2)	7.0890(10)	15.9170(10)	16.169(3)
c/Å	12.357(2)	12.368(6)	14.012(4)	20.617(2)	18.2470(10)	18.633(3)	16.169(2)	16.242(3)
α/°	90	90	92.13(2)	90	90	90	90	90
β/°	91.80(2)	91.45(4)	92.25(2)	101.198(7)	92.110(10)	102.45(2)	93.070(10)	93.43(2)
γ/°	90	90	94.92(2)	90	90	90	90	90
V/Å^3	1850.7(7)	1902.5(18)	1726.9(8)	2760.2(4)	3321.2(5)	2736.2(11)	2207.1(4)	2271.5(8)
Z	4	4	2	4	4	4	4	4
Temperature/K	293	293	293	298	298	293	298	298
Radiation (λ/Å)	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
D_c/g cm^{-3}	1.444	1.733	1.605	1.543	1.548	1.351	1.491	1.591
μ(Mo-Kα)/mm^{-1}	0.927	4.508	2.857	1.853	1.821	0.648	2.248	1.841
θ_{max}/°	22.51	21.04	22.50	25.0	22.50	22.50	23.99	22.50
No. of data	2394	2011	4446	4852	4309	1781	3377	2950
No. of parameters	191	102	359	254	299	150	240	240
R_1	0.0401	0.0946	0.0678	0.0539	0.0506	0.0290	0.0560	0.0514
wR_2	0.0844	0.2287	0.1441	0.0929	0.1287	0.0712	0.1247	0.1094
GOF	1.077	1.004	1.040	1.017	1.036	1.099	1.056	1.020

relative to $SiMe_4$ ($\delta = 0$) and were referenced internally with respect to the protio solvent impurity ($\delta = 7.15$ for C_6D_5H and $\delta = 7.26$ for $CHCl_3$) and the ^{13}C resonances ($\delta = 128.0$ for C_6D_6 and $\delta = 77.0$ for $CDCl_3$) respectively. ^{31}P NMR chemical shifts are reported in ppm relative to 85% H_3PO_4 ($\delta = 0$) and were referenced using $P(OMe_3)$ ($\delta = 141.0$) as external standard. ^{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.[77] ^{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 $CDCl_3$ ($\delta = 420.8$)[78] or a solution of $Te(OH)_6$ (1.74 M in D_2O, $\delta = 712$)[79,80] as external standard. All coupling constants are reported in Hz.

Synthesis of $(Cp^{Bu^t})_2MoH_2$

A mixture of $MoCl_5$ (16.5 g, 60.39 mmol), $NaBH_4$ (11.4 g, 301.34 mmol) and $(Cp^{Bu^t})Li$[81] (31.0 g, 241.92 mmol) was treated with toluene (100 mL) and THF (300 mL) at −78 °C. The mixture was allowed to warm to room temperature and refluxed overnight. After this period, all the volatile components were removed *in vacuo*. The residue was dissolved in THF (100 mL) and HCl(aq) (1000 mL of 0.5 M) was added very slowly at 0 °C (**CAUTION!!** H_2 is liberated vigorously). The mixture was allowed to warm to room temperature and the THF was removed *in vacuo* and the aqueous mixture was filtered, retaining the filtrate. The sticky residue was dissolved in THF (*ca.* 50 mL) and HCl(aq) (*ca.* 200 mL of 0.5 M) was added. The THF was removed *in vacuo* and the aqueous mixture was filtered, retaining the filtrate. The THF/HCl(aq) extraction procedure was repeated one more time, and the combined filtrate was adjusted to pH 7–8 with NaOH solution (6 M), thereby depositing a gray–green solid. The solid was isolated by filtration and dried overnight *in vacuo*. The gray–green residue was extracted into THF until the filtrate was colorless (*ca.* 300 mL), and the solvent was removed from the combined filtrate *in vacuo*. The yellow–brown residue was extracted into pentane (*ca.* 500 mL) and filtered. The solvent was removed from the filtrate to give $(Cp^{Bu^t})_2MoH_2$ as a yellow–brown solid (9.1 g, 44%). Analysis calcd. for $C_{18}H_{28}Mo$: C, 63.5%; H, 8.3%. Found: C, 63.2%; H, 7.9%. MS: $m/z = 339$ ($M^+ - 3$). IR Data (KBr disk, cm^{-1}): 3097 (w), 3077 (m), 2960 (vs), 2903 (s), 2864 (s), 1906 (m) [ν(Mo–H)], 1852 (br, w) [ν(Mo–H)], 1483 (s), 1457 (s), 1389 (s), 1357 (s), 1270 (s), 1194 (m), 1145 (m), 1067 (w), 1038 (s), 1015 (s), 909 (s), 859 (w), 832 (m), 801 (m), 762 (vs), 678 (m), 600 (w), 544 (w), 468 (w), 405 (w). ^1H NMR (C_6D_6): −8.78 [s, $Mo(H)_2$], 1.18 [s, $C_5H_4\{C(CH_3)_3\}$], 4.23 [br s, 2 H of $C_5H_4\{C(CH_3)_3\}$], 4.40 [br s, 2 H of $C_5H_4\{C(CH_3)_3\}$]. ^{13}C NMR (C_6D_6): 30.6 [s, $C_5H_4\{C(CH_3)_3\}$], 32.0 [q, $^1J_{C-H} = 126$, $C_5H_4\{C(CH_3)_3\}$], 72.3 [d, $^1J_{C-H} = 177$, 2 C of $C_5H_4\{C(CH_3)_3\}$], 74.9 [d, $^1J_{C-H} = 175$, 2 C of $C_5H_4\{C(CH_3)_3\}$], 116.8 [s, 1 C of $C_5H_4\{C(CH_3)_3\}$].

Synthesis of $(Cp^{Bu^t})_2MoCl_2$

A solution of $(Cp^{Bu^t})_2MoH_2$ (2.04 g, 5.99 mmol) in toluene (40 mL) was treated with CCl_4 (5.00 g, 32.50 mmol) at room temperature for 1 day, giving a brown precipitate. After this period, the mixture was cooled to 0 °C and filtered. The precipitate obtained was washed with pentane (3 × 10 mL) and dried *in vacuo* to give $(Cp^{Bu^t})_2MoCl_2$ as a brown solid (2.25 g, 92%). Analysis calcd. for $C_{18}H_{26}Cl_2Mo$: C, 52.8%; H, 6.4%. Found: C, 52.8%; H, 5.9%. MS: $m/z = 410$ (M^+). IR Data (KBr disk, cm^{-1}): 3109 (m), 3066 (vs), 2957 (vs), 2907 (vs), 2868 (s), 1486 (s), 1461 (s), 1394 (s), 1361 (s), 1267 (s), 1206 (w), 1152 (m), 1045 (m), 1024 (m), 976 (w), 934 (w), 906 (m), 860 (w), 835 (vs), 666 (m), 589 (w), 479 (w), 449 (w), 412 (w). ^1H NMR ($CDCl_3$): 1.16 [s, $C_5H_4\{C(CH_3)_3\}$], 5.34 [t, $^3J_{H-H} = 2.5$, 2 H of $C_5H_4\{C(CH_3)_3\}$], 5.82 [t, $^3J_{H-H} = 2.5$, 2 H of $C_5H_4\{C(CH_3)_3\}$]. ^{13}C NMR ($CDCl_3$): 31.0 [q, $^1J_{C-H} = 127$, $C_5H_4\{C(CH_3)_3\}$], 33.3 [s, $C_5H_4\{C(CH_3)_3\}$], 99.2 [d, $^1J_{C-H} = 185$, 2 C of $C_5H_4\{C(CH_3)_3\}$], 105.0 [d, $^1J_{C-H} = 184$, 2 C of $C_5H_4\{C(CH_3)_3\}$], 120.7 [s, 1 C of $C_5H_4\{C(CH_3)_3\}$].

Synthesis of $(Cp^{Bu^t})_2MoBr_2$

A solution of $(Cp^{Bu^t})_2MoH_2$ (200 mg, 0.59 mmol) in toluene (15 mL) was treated with CH_2Br_2 (800 mg, 10.01 mmol) for 4 hours at 80 °C. After this period, the mixture was concentrated to *ca.* 1 mL and filtered. The precipitate obtained was washed with pentane (2 × 5 mL) and dried *in vacuo* to give $(Cp^{Bu^t})_2MoBr_2$ as a brown solid (130 mg, 44%). Analysis calcd. for $C_{18}H_{26}Br_2Mo$: C, 43.4%; H, 5.3%. Found: C, 44.0%; H, 5.0%. IR Data (KBr disk, cm^{-1}): 3111 (w), 3064 (vs), 2959 (vs), 2907 (s), 2867 (s), 1486 (m), 1461 (m), 1395 (s), 1360 (m), 1266 (m), 1207 (w), 1152 (m), 1061 (w), 1045 (w), 1024 (w), 972 (w), 932 (w), 906 (w), 859 (w), 837 (vs), 663 (w), 588 (w), 478 (w), 448 (w), 414 (w). ^1H NMR ($CDCl_3$): 1.15 [s, $C_5H_4\{C(CH_3)_3\}$], 5.39 [t, $^3J_{H-H} = 2.5$, 2 H of $C_5H_4\{C(CH_3)_3\}$], 5.88 [t, $^3J_{H-H} = 2.5$, 2 H of $C_5H_4\{C(CH_3)_3\}$]. ^{13}C NMR ($CDCl_3$): 31.1 [q, $^1J_{C-H} = 126$, $C_5H_4\{C(CH_3)_3\}$], 33.2 [s, $C_5H_4\{C(CH_3)_3\}$], 97.5 [d, $^1J_{C-H} = 184$, 2 C of $C_5H_4\{C(CH_3)_3\}$], 104.3 [d, $^1J_{C-H} = 178$, 2 C of $C_5H_4\{C(CH_3)_3\}$], 117.1 [s, 1 C of $C_5H_4\{C(CH_3)_3\}$].

Synthesis of $(Cp^{Bu^t})_2MoI_2$

A solution of $(Cp^{Bu^t})_2MoO$ (150 mg, 0.42 mmol) in toluene (15 mL) was treated with Me_3SiI (212 mg, 1.06 mmol) for 30 minutes at room temperature. After this period, the mixture was concentrated to 1 mL and filtered. The precipitate was washed with pentane (2 × 5 mL) and dried *in vacuo* to give $(Cp^{Bu^t})_2MoI_2$ as a brown solid (220 mg, 88%). Analysis calcd. for $C_{18}H_{26}I_2Mo$: C, 36.5%; H, 4.4%. Found: C, 36.9%; H, 5.0%. IR Data (KBr disk, cm^{-1}): 3092 (vs), 2953 (vs), 2898 (vs), 2907 (s), 2863 (s), 1478 (s), 1459 (s), 1414 (s), 1365 (vs), 1273 (s), 1193 (m), 1152 (s), 1074 (m), 1023 (w), 951 (w), 904 (m), 880 (vs), 840 (m), 804 (s), 658 (m), 595 (w), 472 (w), 407 (w). ^1H NMR (C_6D_6): 0.77 [s, $C_5H_4\{C(CH_3)_3\}$], 4.94 [br s, 2 H of $C_5H_4\{C(CH_3)_3\}$], 5.51 [br s, 2 H of $C_5H_4\{C(CH_3)_3\}$]. ^{13}C NMR (C_6D_6): 31.0 [q, $^1J_{C-H} = 126$, $C_5H_4\{C(CH_3)_3\}$], 32.7 [s, $C_5H_4\{C(CH_3)_3\}$], 92.3 [d, $^1J_{C-H} = 187$, 2 C of $C_5H_4\{C(CH_3)_3\}$], 99.5 [d, $^1J_{C-H} = 180$, 2 C of $C_5H_4\{C(CH_3)_3\}$], 114.5 [s, 1 C of $C_5H_4\{C(CH_3)_3\}$].

Synthesis of $(Cp^{Bu^t})_2Mo(H)(I)$

A solution of $(Cp^{Bu^t})_2MoH_2$ (500 mg, 1.47 mmol) in toluene (10 mL) was treated with CH_3I (1.00 g, 7.05 mmol) for 3 days at room temperature. After this period, the volatile components were removed, and the residue was washed with pentane (3 × 10 mL) and dried *in vacuo* to give $(Cp^{Bu^t})_2Mo(H)(I)$ as a dark brown solid (545 mg, 80%). Analysis calcd. for $C_{18}H_{27}IMo$: C, 46.4%; H, 5.8%. Found: C, 46.2%; H, 5.9%. MS: $m/z = 468$ (M^+). IR Data (KBr disk, cm^{-1}): 3083 (m), 2958 (vs), 2901 (s), 2865 (s), 1876 (w) [ν(Mo–H)], 1484 (s), 1459 (s), 1390 (m), 1361 (s), 1268 (s), 1197 (m), 1148 (m), 1038 (s), 901 (m), 843 (m), 770 (s), 694 (w), 652 (m), 595 (w), 477 (w), 406 (w). ^1H NMR (C_6D_6): −8.93 [s, Mo–H], 1.19 [s, $C_5H_4\{C(CH_3)_3\}$], 3.85 [br s, 1 H of $C_5H_4\{C(CH_3)_3\}$], 3.97 [br s, 1 H of $C_5H_4\{C(CH_3)_3\}$], 4.72 [br s, 1 H of $C_5H_4\{C(CH_3)_3\}$], 4.80 [br s, 1 H of $C_5H_4\{C(CH_3)_3\}$]. ^{13}C NMR (C_6D_6): 31.6 [s, $C_5H_4\{C(CH_3)_3\}$], 32.2 [q, $^1J_{C-H} = 126$, $C_5H_4\{C(CH_3)_3\}$], 75.0 [d, $^1J_{C-H} = 183$, 1 C of $C_5H_4\{C(CH_3)_3\}$], 81.9 [d, $^1J_{C-H} = 177$, 1 C of $C_5H_4\{C(CH_3)_3\}$], 82.0 [d, $^1J_{C-H} = 179$, 1 C of $C_5H_4\{C(CH_3)_3\}$], 94.8 [d, $^1J_{C-H} = 177$, 1 C of $C_5H_4\{C(CH_3)_3\}$], 123.0 [s, 1 C of $C_5H_4\{C(CH_3)_3\}$].

Synthesis of $(Cp^{Bu^t})_2MoMe_2$

A solution of $(Cp^{Bu^t})_2MoCl_2$ (300 mg, 0.73 mmol) in Et_2O (20 mL) was treated with MeMgI (0.98 mL of 3.0 M in Et_2O, 2.94 mmol). The mixture was stirred at room temperature for 1 hour, after which period the volatile components were removed *in vacuo*. The residue was extracted into pentane, filtered, concentrated and cooled to −78 °C to give $(Cp^{Bu^t})_2MoMe_2$ as a red solid (190 mg, 74%). Analysis calcd. for $C_{20}H_{32}Mo$: C, 65.2%; H, 8.8%. Found: C, 64.9%; H, 9.1%. IR Data (KBr disk, cm^{-1}): 3109 (w), 2951 (vs), 2900 (vs), 2870 (vs), 1481 (s), 1458 (s), 1410 (s), 1391 (m), 1360 (vs), 1273 (vs), 1197 (m), 1176 (m), 1150 (s), 1069 (m), 1043 (s), 914 (s), 882 (vs), 855 (s), 812 (m), 660 (m), 598 (w), 472 (m), 404 (m). ^1H NMR (C_6D_6): 0.08 [s, $Mo(CH_3)_2$], 1.02 [s, $C_5H_4\{C(CH_3)_3\}$], 4.02 [br s, 2 H of $C_5H_4\{C(CH_3)_3\}$], 4.29 [br s, 2 H of $C_5H_4\{C(CH_3)_3\}$]. ^{13}C NMR (C_6D_6): −9.7 [q, $^1J_{C-H} = 128$, $Mo(CH_3)_2$], 31.6 [q, $^1J_{C-H} = 126$, $C_5H_4\{C(CH_3)_3\}$], 32.5 [s, $C_5H_4\{C(CH_3)_3\}$], 89.0 [d, $^1J_{C-H} = 176$, 2 C of $C_5H_4\{C(CH_3)_3\}$], 91.0 [d, $^1J_{C-H} = 170$, 2 C of $C_5H_4\{C(CH_3)_3\}$], 109.4 [s, 1 C of $C_5H_4\{C(CH_3)_3\}$].

Synthesis of $(Cp^{Bu^t})_2Mo(CH_2SiMe_3)_2$

A solution of $(Cp^{Bu^t})_2MoCl_2$ (200 mg, 0.49 mmol) in Et_2O (15 mL) was treated with Me_3SiCH_2MgCl (1.5 mL of 1.0 M in Et_2O, 1.50 mmol). The mixture was stirred at room temperature for 1 hour, after which period the volatile components were removed *in vacuo*. The residue was extracted into pentane, filtered, concentrated and cooled to −78 °C to give $(Cp^{Bu^t})_2Mo(CH_2SiMe_3)_2$ as a red solid (140 mg, 56%). Analysis calcd. for $C_{26}H_{48}Si_2Mo$: C, 60.9%; H, 9.4%. Found: C, 60.6%; H, 9.1%. IR Data (KBr disk, cm^{-1}): 2946 (vs), 2901 (s), 2873 (s), 2838 (s), 2703 (w), 1480 (m), 1461 (m), 1437 (w), 1411 (w), 1395 (w), 1363 (s), 1271 (s), 1256 (s), 1245 (s), 1201 (w), 1152 (w), 1047 (w), 1013 (w), 968 (m), 922 (w), 886 (s), 854 (vs), 820 (vs), 785 (s), 746 (s), 730 (s), 671 (s), 608 (w), 561 (w), 461 (w). ^1H NMR (C_6D_6): −0.34 [s, $CH_2Si(CH_3)_3$], 0.29 [s, $CH_2Si(CH_3)_3$], 1.02 [s, $C_5H_4\{C(CH_3)_3\}$], 4.35 [t, $^3J_{H-H} = 2.5$, 2 H of $C_5H_4\{C(CH_3)_3\}$], 4.56 [br s, 2 H of $C_5H_4\{C(CH_3)_3\}$]. ^{13}C NMR (C_6D_6): −15.0 [t, $^1J_{C-H} = 114$, $CH_2Si(CH_3)_3$], 4.5 [q, $^1J_{C-H} = 117$, $CH_2Si(CH_3)_3$], 31.6 [q, $^1J_{C-H} = 126$, $C_5H_4\{C(CH_3)_3\}$], 33.0 [s, $C_5H_4\{C(CH_3)_3\}$], 85.5 [d, $^1J_{C-H} = 181$, 2 C of $C_5H_4\{C(CH_3)_3\}$], 91.3 [d, $^1J_{C-H} = 173$, 2 C of $C_5H_4\{C(CH_3)_3\}$], 116.0 [s, 1 C of $C_5H_4\{C(CH_3)_3\}$].

Synthesis of $(Cp^{Bu^t})_2Mo(CH_2Ph)_2$

A solution of $(Cp^{Bu^t})_2MoCl_2$ (250 mg, 0.61 mmol) in Et_2O (15 mL) was treated with $PhCH_2MgCl$ (1.8 mL of 1.0 M in Et_2O, 1.80 mmol). The mixture was stirred at room temperature for 1 hour, after which period the volatile components were removed *in vacuo*. The residue was extracted into pentane, filtered, concentrated and cooled to −78 °C to give $(Cp^{Bu^t})_2Mo(CH_2Ph)_2$ as a red solid (220 mg, 69%). Analysis calcd. for $C_{32}H_{40}Mo$: C, 73.8%; H, 7.7%. Found: C, 72.9%; H, 7.7%. IR Data (KBr disk, cm^{-1}): 3115 (m), 3063 (s), 3011 (s), 2950 (vs), 2900 (vs), 2864 (vs), 1591 (vs), 1482 (vs), 1458 (vs), 1419 (s), 1393 (s), 1359 (vs), 1309 (m), 1267 (vs), 1205 (vs), 1178 (s), 1150 (s), 1074 (m), 1028 (vs), 994 (m), 946 (m), 917 (s), 894 (vs), 868 (s), 854 (s), 841 (s), 810 (m), 784 (vs), 756 (vs), 698 (vs), 598 (m), 546 (vs), 460 (m), 405 (s). ^1H NMR (C_6D_6): 0.76 [s, $C_5H_4\{C(CH_3)_3\}$], 2.36 [s, CH_2Ph], 4.20 [t, $^3J_{H-H} = 2$, 2 H of $C_5H_4\{C(CH_3)_3\}$], 4.30 [t, $^3J_{H-H} = 2$, 2 H of $C_5H_4\{C(CH_3)_3\}$], 6.99 [t, $^3J_{H-H} = 7$, 1 H of $CH_2C_6H_5$], 7.08 [d, $^3J_{H-H} = 7$, 2 H of $CH_2C_6H_5$], 7.19 [t, $^3J_{H-H} = 8$, 2 H of $CH_2C_6H_5$]. ^{13}C NMR (C_6D_6): 16.8 [t, $^1J_{C-H} = 132$, CH_2Ph], 31.5 [q, $^1J_{C-H} = 126$, $C_5H_4\{C(CH_3)_3\}$], 32.6 [s, $C_5H_4\{C(CH_3)_3\}$], 88.9 [d, $^1J_{C-H} = 180$, 2 C of $C_5H_4\{C(CH_3)_3\}$], 94.8 [d, $^1J_{C-H} = 176$, 2 C of $C_5H_4\{C(CH_3)_3\}$], 116.9 [s, 1 C of $C_5H_4\{C(CH_3)_3\}$], 122.4 [dt, $^1J_{C-H} = 160$, $^2J_{C-H} = 7$, 1 C of $CH_2C_6H_5$], 127.6 [dt, $^1J_{C-H} = 154$, $^2J_{C-H} = 7$, 2 C of $CH_2C_6H_5$], 128.1 [dd, $^1J_{C-H} = 157$, $^2J_{C-H} = 8$, 2 C of $CH_2C_6H_5$], 157.4 [s, 1 C of $CH_2C_6H_5$].

Synthesis of $(Cp^{Bu^t})_2Mo(CO)$

A mixture of $(Cp^{Bu^t})_2MoCl_2$ (300 mg, 0.73 mmol), Na (36 mg, 1.57 mmol) and Hg (1 mL) in THF (30 mL) was stirred under CO (1 atm) for 1.5 hours at room temperature. After this period, the volatile components were removed, and the residue was extracted into pentane. The solvent was removed from the filtrate, and the residue was dried *in vacuo* to give $(Cp^{Bu^t})_2Mo(CO)$ as a green solid (235 mg, 88%). Analysis calcd. for $C_{19}H_{26}OMo$: C, 62.3%; H, 7.2%. Found: C, 61.4%; H, 7.5%. IR Data (KBr disk, cm^{-1}): 3095 (w), 2956 (vs), 2900 (s), 2863 (m), 1907 (vs) [$\nu(C\equiv O)$], 1479 (m), 1459 (m), 1359 (m), 1263 (m), 1200 (w), 1138 (w), 1083 (w), 1042 (w), 1010 (w), 903 (m), 871 (w), 809 (w), 787 (w), 654 (w), 598 (w), 576 (w), 482 (s). ^1H NMR (C_6D_6): 1.10 [s, $C_5H_4\{C(CH_3)_3\}$], 3.76 [t, $^3J_{H-H} = 2$, 2 H of $C_5H_4\{C(CH_3)_3\}$], 4.37 [t, $^3J_{H-H} = 2$, 2 H of $C_5H_4\{C(CH_3)_3\}$]. ^{13}C NMR (C_6D_6): 30.8 [s, $C_5H_4\{C(CH_3)_3\}$], 32.1 [q, $^1J_{C-H} = 125$, $C_5H_4\{C(CH_3)_3\}$], 74.3 [d, $^1J_{C-H} = 172$, 2 C of $C_5H_4\{C(CH_3)_3\}$], 74.6 [d, $^1J_{C-H} = 178$, 2 C of $C_5H_4\{C(CH_3)_3\}$], 111.2 [s, 1 C of $C_5H_4\{C(CH_3)_3\}$], 246.9 [s, $Mo(CO)$]. ^1H NMR (C_6D_6): 1.10 [s, $C_5H_4\{C(CH_3)_3\}$], 3.76 [t, $^3J_{H-H} = 2$, 2 H of $C_5H_4\{C(CH_3)_3\}$], 4.37 [t, $^3J_{H-H} = 2$, 2 H of $C_5H_4\{C(CH_3)_3\}$]. ^{13}C NMR (C_6D_6): 30.8 [s, $C_5H_4\{C(CH_3)_3\}$], 32.1 [q, $^1J_{C-H} = 125$, $C_5H_4\{C(CH_3)_3\}$], 74.3 [d, $^1J_{C-H} = 172$, 2 C of $C_5H_4\{C(CH_3)_3\}$], 74.6 [d, $^1J_{C-H} = 178$, 2 C of $C_5H_4\{C(CH_3)_3\}$], 111.2 [s, 1 C of $C_5H_4\{C(CH_3)_3\}$], 246.9 [s, $Mo(CO)$].

Synthesis of $(Cp^{Bu^t})_2Mo(PMe_3)$

A mixture of $(Cp^{Bu^t})_2MoCl_2$ (200 mg, 0.49 mmol), Na (25 mg, 1.09 mmol) and Hg (1 mL) in THF (20 mL) was treated with PMe_3 (0.5 mL) and stirred for 4 hours at room temperature. After this period, the volatile components were removed, and the residue was extracted into pentane. The solvent was removed from the filtrate, and the residue was dried *in vacuo* to give $(Cp^{Bu^t})_2Mo(PMe_3)$ as a red–orange solid (145 mg, 72%). Analysis calcd. for $C_{21}H_{35}PMo$: C, 60.9%; H, 8.5%. Found: C, 60.3%; H, 8.6%. IR Data (KBr disk, cm^{-1}): 3094 (m), 2955 (vs), 2902 (vs), 1458 (s), 1421 (m), 1357 (s), 1265 (s), 1193 (m), 1136 (m), 1040 (m), 1002 (m), 944 (vs), 830 (vs), 761 (s), 703 (s), 657 (s), 462 (w), 413 (m). ^1H NMR (C_6D_6): 0.98 [d, $^2J_{P-H} = 7$, $P(CH_3)_3$], 1.24 [s, $C_5H_4\{C(CH_3)_3\}$], 3.34 [dt, $^3J_{P-H} = 6$, $^3J_{H-H} = 2$, 2 H of $C_5H_4\{C(CH_3)_3\}$], 4.15 [br s, 2 H of $C_5H_4\{C(CH_3)_3\}$]. ^{13}C NMR (C_6D_6): 23.9 [qd, $^1J_{C-H} = 127$, $^1J_{P-C} = 23$, $P(CH_3)_3$], 31.4 [s, $C_5H_4\{C(CH_3)_3\}$], 32.2 [q, $^1J_{C-H} = 125$, $C_5H_4\{C(CH_3)_3\}$], 67.1 [d, $^1J_{C-H} = 172$, 2 C of $C_5H_4\{C(CH_3)_3\}$], 72.1 [d, $^1J_{C-H} = 174$, 2 C of $C_5H_4\{C(CH_3)_3\}$], 107.1 [s, 1 C of $C_5H_4\{C(CH_3)_3\}$]. ^{31}P NMR (C_6D_6): 8.5 [s].

Synthesis of $(Cp^{Bu^t})_2Mo(\eta^2\text{-}C_2H_4)$

A mixture of $(Cp^{Bu^t})_2MoCl_2$ (200 mg, 0.49 mmol), Na (25 mg, 1.09 mmol) and Hg (1 mL) in THF (15 mL) was stirred under C_2H_4 (0.1 atm) for 1 day at room temperature. After this period, the volatile components were removed, and the residue was extracted into pentane. The solvent was removed from the filtrate, and the residue was dried *in vacuo* to give $(Cp^{Bu^t})_2Mo(\eta^2\text{-}C_2H_4)$ as a dark brown solid (50 mg, 28%). IR Data (KBr disk, cm^{-1}): 3099 (w), 3059 (w), 2954 (vs), 2898 (vs), 2862 (vs), 1479 (s), 1458 (s), 1385 (m), 1357 (s), 1266 (s), 1199 (w), 1145 (s), 1050 (m), 1030 (m), 910 (m), 878 (s), 841 (m), 797 (s), 712 (w), 649 (m), 453 (w), 408 (m). ^1H NMR (C_6D_6): 1.20 [s, $C_5H_4\{C(CH_3)_3\}$], 1.44 [s, $Mo(CH_2CH_2)$], 2.92 [t, $^3J_{H-H} = 2$, 2 H of $C_5H_4\{C(CH_3)_3\}$], 4.48 [t, $^3J_{H-H} = 2$, 2 H of $C_5H_4\{C(CH_3)_3\}$]. ^{13}C NMR (C_6D_6): 13.1 [t, $^1J_{C-H} = 152$, $Mo(CH_2CH_2)$], 31.9 [s, $C_5H_4\{C(CH_3)_3\}$], 32.5 [q, $^1J_{C-H} = 125$, $C_5H_4\{C(CH_3)_3\}$], 80.7 [d, $^1J_{C-H} = 171$, 2 C of $C_5H_4\{C(CH_3)_3\}$], 82.1 [d, $^1J_{C-H} = 176$, 2 C of $C_5H_4\{C(CH_3)_3\}$], 105.9 [s, 1 C of $C_5H_4\{C(CH_3)_3\}$].

Synthesis of $(Cp^{Bu^t})_2Mo(\eta^2\text{-}C_2H_2)$

A mixture of $(Cp^{Bu^t})_2MoCl_2$ (200 mg, 0.49 mmol), Na (25 mg, 1.09 mmol) and Hg (1 mL) in THF (20 mL) was stirred under C_2H_2 (0.7 atm) for 4 hours at room temperature. After this period, the volatile components were removed, and the residue was extracted into pentane. The solvent was removed from the filtrate to give $(Cp^{Bu^t})_2Mo(\eta^2\text{-}C_2H_2)$ as a red–brown oil (140 mg, 79%). Analysis calcd. for $C_{20}H_{28}Mo$: C, 65.9%; H, 7.7%. Found: C, 64.4%; H, 8.1%. IR Data (neat): 3101 (w), 3062 (w), 3022 (w), 2956 (vs), 2899 (s), 2864 (s), 1623 (s) [$\nu(C\equiv C)$], 1482 (s), 1458 (s), 1405 (m), 1391 (m), 1359 (vs), 1271 (s), 1200 (w), 1147 (m), 1049 (m), 1031 (m), 1014 (m), 915 (m), 892 (m), 858 (s), 839 (s), 828 (m), 794 (s), 662 (w), 642 (m), 597 (w), 461 (w). ^1H NMR (C_6D_6): 1.25 [s, $C_5H_4\{C(CH_3)_3\}$], 3.35 [t, $^3J_{H-H} = 2$, 2 H of $C_5H_4\{C(CH_3)_3\}$], 4.53 [t, $^3J_{H-H} = 2$, 2 H of $C_5H_4\{C(CH_3)_3\}$], 7.55 [s, $Mo(CHCH)$]. ^{13}C NMR (C_6D_6): 31.8 [s, $C_5H_4\{C(CH_3)_3\}$], 32.2 [q, $^1J_{C-H} = 125$, $C_5H_4\{C(CH_3)_3\}$], 85.2 [d, $^1J_{C-H} = 172$, 4 C of $C_5H_4\{C(CH_3)_3\}$], 115.3 [s, 1 C of $C_5H_4\{C(CH_3)_3\}$], 118.2 [dd, $^1J_{C-H} = 152$, $^2J_{C-H} = 9$, $Mo(CHCH)$].

Synthesis of $(Cp^{Bu^t})_2Mo(\eta^2\text{-}MeCN)$

A mixture of $(Cp^{Bu^t})_2MoCl_2$ (200 mg, 0.49 mmol), Na (25 mg, 1.09 mmol) and Hg (1 mL) in MeCN (20 mL) was stirred for 10 minutes at room temperature. After this period, the volatile components were removed from the mixture, and the residue was extracted into pentane. The solvent was removed from the filtrate to give $(Cp^{Bu^t})_2Mo(\eta^2\text{-}MeCN)$ as a red–brown oil (150 mg, 81%). Analysis calcd. for $C_{20}H_{29}NMo$: C, 63.3%; H, 7.7%; N, 3.7%. Found: C, 62.1%; H, 7.9%; N, 2.6%. IR Data (neat): 3087 (s), 2958 (vs), 2902 (vs), 2864 (vs), 2707 (w), 1777 (vs) [$\nu(C\equiv N)$], 1485 (vs), 1461 (vs), 1434 (s), 1390 (s), 1359 (vs), 1270 (vs), 1199 (m), 1147 (s), 1052 (vs), 942 (s), 912 (s), 895 (s), 879 (s), 860 (s), 832 (s), 810 (s), 791 (s), 786 (s), 665 (m), 628 (vw), 597 (vw), 551 (s), 482 (vw), 463 (w), 432 (w), 416 (w). ^1H NMR (C_6D_6): 1.24 [s, $C_5H_4\{C(CH_3)_3\}$], 2.53 [s, CH_3CN], 3.16 [q, $^3J_{H-H} = 2$, 1 H of $C_5H_4\{C(CH_3)_3\}$], 3.82 [q, $^3J_{H-H} = 2$, 1 H of $C_5H_4\{C(CH_3)_3\}$], 3.97 [q, $^3J_{H-H} = 2$, 1 H of $C_5H_4\{C(CH_3)_3\}$], 4.98 [q, $^3J_{H-H} = 2$, 1 H of $C_5H_4\{C(CH_3)_3\}$]. ^{13}C NMR (C_6D_6): 21.4 [q, $^1J_{C-H} = 129$, CH_3CN], 31.8 [q, $^1J_{C-H} = 126$, $C_5H_4\{C(CH_3)_3\}$], 31.8 [s, $C_5H_4\{C(CH_3)_3\}$], 79.9 [d, $^1J_{C-H} = 174$, 1 C of $C_5H_4\{C(CH_3)_3\}$], 82.2 [d, $^1J_{C-H} = 178$, 1 C of $C_5H_4\{C(CH_3)_3\}$], 86.6 [d, $^1J_{C-H} = 172$, 1 C of $C_5H_4\{C(CH_3)_3\}$], 87.4 [d, $^1J_{C-H} = 176$, 1 C of $C_5H_4\{C(CH_3)_3\}$], 117.0 [s, 1 C of $C_5H_4\{C(CH_3)_3\}$], 168.1 [s, CH_3CN].

Synthesis of $[(Cp^{Bu^t})_2Mo(CO)Me]I$

A solution of $(Cp^{Bu^t})_2Mo(CO)$ (100 mg, 0.27 mmol) in C_6H_6 (10 mL) was stirred with MeI (400 mg, 2.82 mmol) for 1.5 hours at room temperature to give an orange–brown precipitate. The mixture was filtered, and the residue was washed with toluene (3 × 5 mL) and pentane (3 × 5 mL) and dried *in vacuo* to give $[(Cp^{Bu^t})_2Mo(CO)Me]I$ as an orange–brown solid (125 mg, 90%). Analysis calcd. for $C_{20}H_{29}IOMo$: C, 47.3%; H, 5.8%. Found: C, 47.6%; H, 5.0%. IR Data (KBr disk, cm^{-1}): 3110 (w), 3048 (m), 2965 (m), 2908 (m), 2011 (vs) [$\nu(C\equiv O)$], 1483 (w), 1464 (w), 1397 (w), 1371 (w), 1272 (w), 1194 (w), 1150 (w), 1082 (w), 1035 (w), 951 (w), 887 (w), 863 (w), 838 (w), 678 (w), 512 (w), 452 (m). ^1H NMR ($CDCl_3$): 0.08 [s, $Mo(CH_3)$], 1.37 [s, $C_5H_4\{C(CH_3)_3\}$], 5.42 [q, $^3J_{H-H} = 2.5$, 1 H of $C_5H_4\{C(CH_3)_3\}$], 5.62 [q, $^3J_{H-H} = 2.5$, 1 H of $C_5H_4\{C(CH_3)_3\}$], 5.84 [q, $^3J_{H-H} = 2.5$, 1 H of $C_5H_4\{C(CH_3)_3\}$], 5.96 [q, $^3J_{H-H} = 2.5$, 1 H of $C_5H_4\{C(CH_3)_3\}$]. ^{13}C NMR ($CDCl_3$): −18.6 [q, $^1J_{C-H} = 136$, $Mo(CH_3)$], 31.9 [q, $^1J_{C-H} = 127$, $C_5H_4\{C(CH_3)_3\}$], 32.8 [s, $C_5H_4\{C(CH_3)_3\}$], 90.8 [d, $^1J_{C-H} = 175$, 1 C of $C_5H_4\{C(CH_3)_3\}$], 91.1 [d, $^1J_{C-H} = 183$, 1 C of $C_5H_4\{C(CH_3)_3\}$], 93.1 [d, $^1J_{C-H} = 182$, 1 C of $C_5H_4\{C(CH_3)_3\}$], 95.8 [d, $^1J_{C-H} = 191$, 1 C of $C_5H_4\{C(CH_3)_3\}$], 127.6 [s, 1 C of $C_5H_4\{C(CH_3)_3\}$], 227.0 [s, $Mo(CO)$].

Synthesis of $[(Cp^{Bu^t})_2Mo(PMe_3)Me]I$

A solution of $(Cp^{Bu^t})_2Mo(PMe_3)$ (100 mg, 0.24 mmol) in C_6H_6 (10 mL) was treated with MeI (100 mg, 0.70 mmol) for 0.5 hour at room temperature to give an orange–brown precipitate. The mixture was filtered, and the precipitate was washed with benzene (2 × 5 mL) and pentane (2 × 5 mL) and dried *in vacuo* to give $[(Cp^{Bu^t})_2Mo(PMe_3)Me]I$ as a yellow–orange solid (125 mg, 93%). Analysis calcd. for $C_{22}H_{38}IPMo$: C, 47.5%; H, 6.9%. Found: C, 48.1%; H, 6.1%. IR Data (KBr disk, cm^{-1}): 3050 (vs), 2958 (vs), 2906 (vs), 2869 (s), 1484 (s), 1462 (s), 1422 (m), 1396 (s), 1365 (s), 1293 (m), 1272 (m), 1193 (m), 1152 (m), 1072 (m), 952 (vs), 879 (m), 847 (s), 819 (s), 728 (m), 672 (m), 600 (w), 462 (w), 413 (m). ^1H NMR ($CDCl_3$): −0.09 [d, $^3J_{P-H} = 8$, $Mo(CH_3)$], 1.21 [s, $C_5H_4\{C(CH_3)_3\}$], 1.69 [d, $^2J_{P-H} = 9$, $P(CH_3)_3$], 4.43 [br s, 1 H of $C_5H_4\{C(CH_3)_3\}$], 4.91 [br s, 1 H of $C_5H_4\{C(CH_3)_3\}$], 5.31 [br s, 2 H of $C_5H_4\{C(CH_3)_3\}$]. ^{13}C NMR ($CDCl_3$): −17.4 [qd, $^1J_{C-H} = 130$, $^2J_{P-C} = 16$, $Mo(CH_3)$], 19.2 [qd, $^1J_{C-H} = 130$, $^1J_{P-C} = 31$, $P(CH_3)_3$], 31.5 [q, $^1J_{C-H} = 126$, $C_5H_4\{C(CH_3)_3\}$], 33.0 [s, $C_5H_4\{C(CH_3)_3\}$], 85.4 [d, $^1J_{C-H} = 181$, 1 C of $C_5H_4\{C(CH_3)_3\}$], 86.7 [d, $^1J_{C-H} = 176$, 1 C of $C_5H_4\{C(CH_3)_3\}$], 91.8 [d, $^1J_{C-H} = 183$, 1 C of $C_5H_4\{C(CH_3)_3\}$], 96.3 [d, $^1J_{C-H} = 174$, 1 C of $C_5H_4\{C(CH_3)_3\}$], 119.6 [s, 1 C of $C_5H_4\{C(CH_3)_3\}$]. ^{31}P NMR ($CDCl_3$): 11.3 [s].

Synthesis of $[(Cp^{Bu^t})_2Mo(\eta^2\text{-}MeC{=}NMe)]I$

A solution of $(Cp^{Bu^t})_2Mo(\eta^2\text{-}MeCN)$ (95 mg, 0.18 mmol) in C_6H_6 (10 mL) was treated with MeI (383 mg, 2.70 mmol) for 2 hours at room temperature, resulting in the formation of an orange–brown precipitate. The mixture was filtered, and the precipitate was washed with pentane (2 × 5 mL) and dried *in vacuo* to give $[(Cp^{Bu^t})_2Mo(\eta^2\text{-}MeC{=}NMe)]I$ as an orange–brown solid (75 mg, 57%). Analysis calcd. for $C_{21}H_{32}INMo$: C, 48.4%; H, 6.2%; N, 2.7%. Found: C, 48.2%; H, 6.3%; N, 2.2%. IR Data (KBr disk, cm^{-1}): 3060 (vs), 2962 (vs), 2866 (s), 1747 (s) [$\nu(CN)$], 1479 (s), 1461 (s), 1387 (s), 1363 (s), 1269 (s), 1197 (w), 1149 (m), 1118 (s), 1059 (m), 1033 (m), 935 (m), 904 (s), 883 (s), 844 (s), 822 (s), 734 (w), 670 (w), 626 (w), 466 (w), 424 (w). ^1H NMR ($CDCl_3$): 1.26 [s, $C_5H_4\{C(CH_3)_3\}$], 3.00 [q, $^5J_{H-H} = 1$, $CH_3C{=}NCH_3$], 3.56 [q, $^5J_{H-H} = 1$, $CH_3C{=}NCH_3$], 4.40 [q, $^3J_{H-H} = 2.5$, 1 H of $C_5H_4\{C(CH_3)_3\}$], 4.54 [q, $^3J_{H-H} = 2.5$, 1 H of $C_5H_4\{C(CH_3)_3\}$], 5.25 [q, $^3J_{H-H} = 2.5$, 1 H of $C_5H_4\{C(CH_3)_3\}$], 5.62 [q, $^3J_{H-H} = 2.5$, 1 H of $C_5H_4\{C(CH_3)_3\}$]. ^{13}C NMR ($CDCl_3$): 22.0 [q, $^1J_{C-H} = 132$, $CH_3C{=}NCH_3$], 31.7 [s, $C_5H_4\{C(CH_3)_3\}$], 31.8 [q, $^1J_{C-H} = 126$, $C_5H_4\{C(CH_3)_3\}$], 41.5 [q, $^1J_{C-H} = 142$, $CH_3C{=}NCH_3$], 89.9 [d, $^1J_{C-H} = 177$, 1 C of $C_5H_4\{C(CH_3)_3\}$], 91.0 [d, $^1J_{C-H} = 176$, 1 C of $C_5H_4\{C(CH_3)_3\}$], 93.3 [d, $^1J_{C-H} = 175$, 2 C of $C_5H_4\{C(CH_3)_3\}$], 121.7 [s, 1 C of $C_5H_4\{C(CH_3)_3\}$], 189.5 [s, $CH_3C{=}NCH_3$].

Synthesis of $[(Cp^{Bu^t})_2Mo(\eta^2\text{-}MeC{=}NEt)]I$

A solution of $(Cp^{Bu^t})_2Mo(\eta^2\text{-}MeCN)$ (100 mg, 0.26 mmol) in toluene (10 mL) was treated with EtI (608 mg, 3.90 mmol) for 2 hours at room temperature, resulting in the formation of a brown precipitate. The mixture was filtered, and the residue was washed with pentane (2 × 5 mL) and dried *in vacuo* to give orange–brown solid of $[(Cp^{Bu^t})_2Mo(\eta^2\text{-}MeC{=}NEt)]I$ (30 mg, 21%). Analysis calcd. for $C_{22}H_{34}INMo$: C, 49.4%; H, 6.4%; N, 2.6%. Found: C, 49.0%; H, 6.2%; N, 2.2%. IR Data (KBr disk, cm^{-1}): 3062 (vs), 2963 (vs), 2867 (s), 1764 (s), 1745 (s) [$\nu(C{=}N)$], 1480 (s), 1460 (s), 1381 (s), 1363 (s), 1338 (m), 1270 (s), 1196 (m), 1146 (s), 1113 (s), 1061 (m), 1033 (s), 963 (m), 933 (m), 905 (s), 881 (s), 844 (s), 819 (s), 670 (m), 622 (w), 465 (w), 424 (w). ^1H NMR ($CDCl_3$): 1.21 [t, $^3J_{H-H} = 7$, $CH_3C{=}NCH_2CH_3$], 1.27 [s, $C_5H_4\{C(CH_3)_3\}$], 3.04 [t, $^5J_{H-H} = 1$, $CH_3C{=}NCH_2CH_3$], 3.83 [qq, $^3J_{H-H} = 7$, $^5J_{H-H} = 1$, $CH_3C{=}NCH_2CH_3$], 4.43 [q, $^3J_{H-H} = 2.5$, 1 H of $C_5H_4\{C(CH_3)_3\}$], 4.46 [q, $^3J_{H-H} = 2.5$, 1 H of $C_5H_4\{C(CH_3)_3\}$], 5.29 [q, $^3J_{H-H} = 2.5$, 1 H of $C_5H_4\{C(CH_3)_3\}$], 5.53 [q, $^3J_{H-H} = 2.5$, 1 H of $C_5H_4\{C(CH_3)_3\}$]. ^{13}C NMR ($CDCl_3$): 13.4 [q, $^1J_{C-H} = 128$, $CH_3C{=}NCH_2CH_3$], 22.7 [q, $^1J_{C-H} = 132$, $CH_3C{=}NCH_2CH_3$], 31.7 [q, $^1J_{C-H} = 126$, $C_5H_4\{C(CH_3)_3\}$], 31.8 [s, $C_5H_4\{C(CH_3)_3\}$], 47.5 [t, $^1J_{C-H} = 142$, $CH_3C{=}NCH_2CH_3$], 89.5 [d, $^1J_{C-H} = 183$, 1 C of $C_5H_4\{C(CH_3)_3\}$], 91.3 [d, $^1J_{C-H} = 183$, 1 C of $C_5H_4\{C(CH_3)_3\}$], 91.6 [d, $^1J_{C-H} = 169$, 1 C of $C_5H_4\{C(CH_3)_3\}$], 92.9 [d, $^1J_{C-H} = 180$, 1 C of $C_5H_4\{C(CH_3)_3\}$], 122.0 [s, 1 C of $C_5H_4\{C(CH_3)_3\}$], 188.4 [s, $CH_3C{=}NCH_2CH_3$].

Synthesis of $(\mathrm{Cp^{Bu^t}})_2\mathrm{MoO}$

A mixture of $(\mathrm{Cp^{Bu^t}})_2\mathrm{MoCl_2}$ (450 mg, 1.10 mmol) and LiOH (270 mg, 11.27 mmol) in toluene (20 mL) was stirred for 4 hours at 80 °C. After this period, the mixture was filtered, and the volatile components were removed from the filtrate *in vacuo*. The residue obtained was extracted into pentane, and the filtrate was concentrated to *ca.* 1 mL to give green crystals of $(\mathrm{Cp^{Bu^t}})_2\mathrm{MoO}$, which were isolated by filtration and dried *in vacuo* (290 mg, 74%). Analysis calcd. for $\mathrm{C_{18}H_{26}OMo}$: C, 61.0%; H, 7.4%. Found: C, 61.1%; H, 8.0%. MS: $m/z = 357$ ($\mathrm{M^+}$ + 1). IR Data (KBr disk, $\mathrm{cm^{-1}}$): 3108 (w), 2959 (vs), 2900 (s), 2864 (s), 1480 (m), 1460 (s), 1421 (m), 1359 (s), 1280 (s), 1202 (w), 1155 (m), 1068 (m), 1048 (m), 910 (m), 877 (s), 838 (vs), 796 (s), 662 (m), 461 (w). ^{1}H NMR ($\mathrm{C_6D_6}$): 1.33 [s, $\mathrm{C_5H_4\{C(C\mathit{H}_3)_3\}}$], 4.79 [t, $^3J_{\mathrm{H-H}} = 2$, 2 H of $\mathrm{C_5\mathit{H}_4\{C(CH_3)_3\}}$], 4.97 [t, $^3J_{\mathrm{H-H}} = 2$, 2 H of $\mathrm{C_5\mathit{H}_4\{C(CH_3)_3\}}$]. ^{13}C NMR ($\mathrm{C_6D_6}$): 31.5 [q, $^1J_{\mathrm{C-H}} = 126$, $\mathrm{C_5H_4\{C(\mathit{C}H_3)_3\}}$], 32.0 [s, $\mathrm{C_5H_4\{\mathit{C}(CH_3)_3\}}$], 93.2 [d, $^1J_{\mathrm{C-H}} = 176$, 2 C of $\mathrm{\mathit{C}_5H_4\{C(CH_3)_3\}}$], 100.6 [d, $^1J_{\mathrm{C-H}} = 173$, 2 C of $\mathrm{\mathit{C}_5H_4\{C(CH_3)_3\}}$], 128.0 [s, 1 C of $\mathrm{\mathit{C}_5H_4\{C(CH_3)_3\}}$].

Reactions of $(\mathrm{Cp^{Bu^t}})_2\mathrm{MoO}$ with $\mathrm{Me_3SiX}$ (X = Cl, Br, I)

A solution of $(\mathrm{Cp^{Bu^t}})_2\mathrm{MoO}$ (*ca.* 10 mg) in $\mathrm{C_6D_6}$ (1 mL) was treated with excess $\mathrm{Me_3SiX}$ (X = Cl, Br, I). The sample was monitored by ^{1}H NMR spectroscopy, which demonstrated that the formation of $(\mathrm{Cp^{Bu^t}})_2\mathrm{MoX_2}$ was complete within 30 minutes at room temperature.

Reaction of $(\mathrm{Cp^{Bu^t}})_2\mathrm{MoO}$ with $\mathrm{Me_3SiO_2CMe}$

A solution of $(\mathrm{Cp^{Bu^t}})_2\mathrm{MoO}$ (*ca.* 10 mg) in $\mathrm{C_6D_6}$ (1 mL) was treated with excess $\mathrm{Me_3SiO_2CMe}$. The sample was monitored by ^{1}H NMR spectroscopy, which demonstrated that the formation of $(\mathrm{Cp^{Bu^t}})_2\mathrm{Mo(O_2CMe)_2}$ was complete within 24 hours at 80 °C. ^{1}H NMR ($\mathrm{C_6D_6}$): 0.98 (s, 18H), 2.07 (s, 3H), 5.22 (t, 4H), 5.33 (t, 4H). ^{1}H NMR ($\mathrm{C_6D_6}$): 0.98 [s, $\mathrm{C_5H_4\{C(C\mathit{H}_3)_3\}}$], 2.07 [s, $\mathrm{O_2CC\mathit{H}_3}$], 5.22 [t, $^3J_{\mathrm{H-H}} = 2.5$, 2 H of $\mathrm{C_5\mathit{H}_4\{C(CH_3)_3\}}$], 5.33 [t, $^3J_{\mathrm{H-H}} = 2.5$, 2 H of $\mathrm{C_5\mathit{H}_4\{C(CH_3)_3\}}$].

Synthesis of $(\mathrm{Cp^{Bu^t}})_2\mathrm{Mo(O_3SMe)_2}$

A solution of $(\mathrm{Cp^{Bu^t}})_2\mathrm{MoO}$ (200 mg, 0.56 mmol) in toluene (20 mL) was treated with $\mathrm{Me_3SiO_3SMe}$ (190 mg, 1.13 mmol) for 1 hour at room temperature. After this period, the mixture was concentrated to *ca.* 1 mL and filtered. The precipitate was washed with pentane (2 × 5 mL) and dried *in vacuo* to give $(\mathrm{Cp^{Bu^t}})_2\mathrm{Mo(O_3SMe)_2}$ as an olive-green solid (225 mg, 76%). Analysis calcd. for $\mathrm{C_{20}H_{32}O_6S_2Mo}$: C, 45.5%; H, 6.1%. Found: C, 45.9%; H, 6.4%. IR Data (KBr disk, $\mathrm{cm^{-1}}$): 3107 (s), 2960 (s), 2909 (m), 2876 (m), 1491 (s), 1464 (m), 1419 (m), 1366 (m), 1325 (m), 1271 (vs), 1197 (s), 1141 (vs), 1013 (vs), 981 (vs), 882 (s), 861 (s), 773 (s), 668 (w), 559 (s), 532 (s), 428 (w). ^{1}H NMR ($\mathrm{CDCl_3}$): 1.20 [s, $\mathrm{C_5H_4\{C(C\mathit{H}_3)_3\}}$], 2.69 [s, $\mathrm{O_3SC\mathit{H}_3}$], 5.95 [t, $^3J_{\mathrm{H-H}} = 2.5$, 2 H of $\mathrm{C_5\mathit{H}_4\{C(CH_3)_3\}}$], 6.17 [t, $^3J_{\mathrm{H-H}} = 2.5$, 2 H of $\mathrm{C_5\mathit{H}_4\{C(CH_3)_3\}}$]. ^{13}C NMR ($\mathrm{CDCl_3}$): 30.6 [q, $^1J_{\mathrm{C-H}} = 127$, $\mathrm{C_5H_4\{C(\mathit{C}H_3)_3\}}$], 33.7 [s, $\mathrm{C_5H_4\{\mathit{C}(CH_3)_3\}}$], 40.9 [q, $^1J_{\mathrm{C-H}} = 136$, $\mathrm{O_3S\mathit{C}H_3}$], 98.3 [d, $^1J_{\mathrm{C-H}} = 185$, 2 C of $\mathrm{\mathit{C}_5H_4\{C(CH_3)_3\}}$], 104.4 [d, $^1J_{\mathrm{C-H}} = 180$, 2 C of $\mathrm{\mathit{C}_5H_4\{C(CH_3)_3\}}$], 134.3 [s, 1 C of $\mathrm{\mathit{C}_5H_4\{C(CH_3)_3\}}$].

Synthesis of $(\mathrm{Cp^{Bu^t}})_2\mathrm{Mo(OSiMe_3)(CN)}$

A solution of $(\mathrm{Cp^{Bu^t}})_2\mathrm{MoO}$ (270 mg, 0.76 mmol) in toluene (20 mL) was treated with $\mathrm{Me_3SiCN}$ (100 mg, 1.01 mmol) for 1 hour 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 $(\mathrm{Cp^{Bu^t}})_2\mathrm{Mo(OSiMe_3)(CN)}$ as a purple solid (305 mg, 88%). Analysis calcd. for $\mathrm{C_{22}H_{35}NOSiMo}$: C, 58.3%; H, 7.8%; N, 3.1%. Found: C, 57.5%; H, 6.8%; N, 2.9%. IR Data (KBr disk, $\mathrm{cm^{-1}}$): 3039 (w), 2959 (s), 2906 (m), 2871 (m), 2105 (m) [$\nu(\mathrm{C{\equiv}N})$], 1482 (w), 1461 (m), 1419 (w), 1367 (m), 1277 (m), 1231 (m), 1196 (w), 1152 (w), 1041 (w), 969 (vs), 907 (w), 869 (m), 822 (s), 794 (w), 741 (w), 662 (w), 464 (w). ^{1}H NMR ($\mathrm{CDCl_3}$): −0.13 [s, $\mathrm{OSi(C\mathit{H}_3)_3}$], 1.16 [s, $\mathrm{C_5H_4\{C(C\mathit{H}_3)_3\}}$], 4.87 [q, $^3J_{\mathrm{H-H}} = 2.5$, 1 H of $\mathrm{C_5\mathit{H}_4\{C(CH_3)_3\}}$], 5.05 [q, $^3J_{\mathrm{H-H}} = 2.5$, 1 H of $\mathrm{C_5\mathit{H}_4\{C(CH_3)_3\}}$], 5.31 [q, $^3J_{\mathrm{H-H}} = 2.5$, 1 H of $\mathrm{C_5\mathit{H}_4\{C(CH_3)_3\}}$], 5.93 [q, $^3J_{\mathrm{H-H}} = 2.5$, 1 H of $\mathrm{C_5\mathit{H}_4\{C(CH_3)_3\}}$]. ^{13}C NMR ($\mathrm{CDCl_3}$): 3.4 [q, $^1J_{\mathrm{C-H}} = 117$, $\mathrm{OSi(\mathit{C}H_3)_3}$], 31.1 [q, $^1J_{\mathrm{C-H}} = 126$, $\mathrm{C_5H_4\{C(\mathit{C}H_3)_3\}}$], 32.6 [s, $\mathrm{C_5H_4\{\mathit{C}(CH_3)_3\}}$], 91.9 [d, $^1J_{\mathrm{C-H}} = 185$, 1 C of $\mathrm{\mathit{C}_5H_4\{C(CH_3)_3\}}$], 93.5 [d, $^1J_{\mathrm{C-H}} = 171$, 1 C of $\mathrm{\mathit{C}_5H_4\{C(CH_3)_3\}}$], 97.4 [d, $^1J_{\mathrm{C-H}} = 183$, 1 C of $\mathrm{\mathit{C}_5H_4\{C(CH_3)_3\}}$], 105.8 [d, $^1J_{\mathrm{C-H}} = 178$, 1 C of $\mathrm{\mathit{C}_5H_4\{C(CH_3)_3\}}$], 122.8 [s, 1 C of $\mathrm{\mathit{C}_5H_4\{C(CH_3)_3\}}$], 140.7 [s, $\mathrm{\mathit{C}N}$].

Synthesis of $(\mathrm{Cp^{Bu^t}})_2\mathrm{Mo(OSiMe_3)(NCS)}$

A solution of $(\mathrm{Cp^{Bu^t}})_2\mathrm{MoO}$ (200 mg, 0.56 mmol) in toluene (20 mL) was treated with $\mathrm{Me_3SiNCS}$ (74 mg, 0.56 mmol). The volatile components were removed after stirring for 10 minutes at room temperature, and the residue was washed with pentane (2 × 5 mL) and dried *in vacuo* to give $(\mathrm{Cp^{Bu^t}})_2\mathrm{Mo(OSiMe_3)(NCS)}$ as a dark brown solid (255 mg, 93%). Analysis calcd. for $\mathrm{C_{22}H_{35}NOSSiMo}$: C, 54.4%; H, 7.3%; N, 2.9%. Found: C, 54.6%; H, 7.3%; N, 2.6%. IR Data (KBr disk, $\mathrm{cm^{-1}}$): 3077 (w), 2955 (s), 2905 (m), 2867 (m), 2102 (vs) [$\nu(\mathrm{CN})$], 1485 (w), 1462 (w), 1389 (w), 1360 (w), 1269 (w), 1237 (m), 1202 (w), 1150 (w), 1040 (w), 1023 (w), 964 (vs), 896 (m), 824 (vs), 740 (m), 666 (w), 450 (w), 403 (w). ^{1}H NMR ($\mathrm{C_6D_6}$): 0.34 [s, $\mathrm{OSi(C\mathit{H}_3)_3}$], 0.87 [s, $\mathrm{C_5H_4\{C(C\mathit{H}_3)_3\}}$], 4.34 [q, $^3J_{\mathrm{H-H}} = 2.5$, 1 H of $\mathrm{C_5\mathit{H}_4\{C(CH_3)_3\}}$], 4.64 [q, $^3J_{\mathrm{H-H}} = 2.5$, 1 H of $\mathrm{C_5\mathit{H}_4\{C(CH_3)_3\}}$], 4.69 [q, $^3J_{\mathrm{H-H}} = 2.5$, 1 H of $\mathrm{C_5\mathit{H}_4\{C(CH_3)_3\}}$], 5.13 [q, $^3J_{\mathrm{H-H}} = 2.5$, 1 H of $\mathrm{C_5\mathit{H}_4\{C(CH_3)_3\}}$]. ^{13}C NMR ($\mathrm{C_6D_6}$): 4.0 [q, $^1J_{\mathrm{C-H}} = 116$, $\mathrm{OSi(\mathit{C}H_3)_3}$], 31.0 [q, $^1J_{\mathrm{C-H}} = 126$, $\mathrm{C_5H_4\{C(\mathit{C}H_3)_3\}}$], 32.7 [s, $\mathrm{C_5H_4\{\mathit{C}(CH_3)_3\}}$], 97.0 [d, $^1J_{\mathrm{C-H}} = 181$, 1 C of $\mathrm{\mathit{C}_5H_4\{C(CH_3)_3\}}$], 102.4 [d, $^1J_{\mathrm{C-H}} = 180$, 1 C of $\mathrm{\mathit{C}_5H_4\{C(CH_3)_3\}}$], 102.9 [d, $^1J_{\mathrm{C-H}} = 178$, 1 C of $\mathrm{\mathit{C}_5H_4\{C(CH_3)_3\}}$], 103.3 [d, $^1J_{\mathrm{C-H}} = 184$, 1 C of $\mathrm{\mathit{C}_5H_4\{C(CH_3)_3\}}$], 123.6 [s, 1 C of $\mathrm{\mathit{C}_5H_4\{C(CH_3)_3\}}$], 150.2 [s, $\mathrm{N\mathit{C}S}$)].

Reaction of $(\mathrm{Cp^{Bu^t}})_2\mathrm{Mo(OSiMe_3)(CN)}$ with $\mathrm{Me_3SiNCS}$

A solution of $(\mathrm{Cp^{Bu^t}})_2\mathrm{Mo(OSiMe_3)(CN)}$ (*ca.* 10 mg) in $\mathrm{C_6D_6}$ (1 mL) was treated with $\mathrm{Me_3SiNCS}$ (excess) at room temperature. The sample was monitored by ^{1}H NMR spectroscopy, which demonstrated the formation of $(\mathrm{Cp^{Bu^t}})_2\mathrm{Mo(SCN)CN}$ to be complete within 5 hours. ^{1}H NMR ($\mathrm{CDCl_3}$): 1.28 [s, $\mathrm{C_5H_4\{C(C\mathit{H}_3)_3\}}$], 5.30 [q, $^3J_{\mathrm{H-H}} = 2.5$, 1 H of $\mathrm{C_5\mathit{H}_4\{C(CH_3)_3\}}$], 5.34 [q, $^3J_{\mathrm{H-H}} = 2.5$, 1 H of $\mathrm{C_5\mathit{H}_4\{C(CH_3)_3\}}$], 5.48 [q, $^3J_{\mathrm{H-H}} = 2.5$, 1 H of $\mathrm{C_5\mathit{H}_4\{C(CH_3)_3\}}$], 5.71 [q, $^3J_{\mathrm{H-H}} = 2.5$, 1 H of $\mathrm{C_5\mathit{H}_4\{C(CH_3)_3\}}$]. ^{13}C{^{1}H} NMR ($\mathrm{CDCl_3}$): 31.2 [$\mathrm{C_5H_4\{C(\mathit{C}H_3)_3\}}$], 33.2 [$\mathrm{C_5H_4\{\mathit{C}(CH_3)_3\}}$], 89.7 [1 C of $\mathrm{\mathit{C}_5H_4\{C(CH_3)_3\}}$], 95.3 [1 C of $\mathrm{\mathit{C}_5H_4\{C(CH_3)_3\}}$], 97.6 [1 C of $\mathrm{\mathit{C}_5H_4\{C(CH_3)_3\}}$], 98.7 [1 C of $\mathrm{\mathit{C}_5H_4\{C(CH_3)_3\}}$], 124.6 [s, $\mathrm{Mo(S\mathit{C}N)}$], 125.5 [1 C of $\mathrm{\mathit{C}_5H_4\{C(CH_3)_3\}}$], 137.1 [$\mathrm{Mo{-}\mathit{C}N}$].

Reaction of $(\mathrm{Cp^{Bu^t}})_2\mathrm{Mo(OSiMe_3)(NCS)}$ with $\mathrm{Me_3SiCN}$

A solution of $(\mathrm{Cp^{Bu^t}})_2\mathrm{Mo(OSiMe_3)(NCS)}$ (*ca.* 10 mg) in $\mathrm{C_6D_6}$ (1 mL) was treated with $\mathrm{Me_3SiCN}$ (excess) at room temperature. The sample was monitored by ^{1}H NMR spectroscopy, which demonstrated that formation of $(\mathrm{Cp^{Bu^t}})_2\mathrm{Mo(OSiMe_3)(CN)}$ was complete within 30 minutes.

Reaction of $\mathrm{Cp^{Bu^t}}_2\mathrm{Mo(NCS)_2}$ with $\mathrm{Me_3SiCN}$

A solution of $\mathrm{Cp^{Bu^t}}_2\mathrm{Mo(NCS)_2}$ (*ca.* 20 mg) in $\mathrm{CDCl_3}$ (1 mL) was treated with $\mathrm{Me_3SiCN}$ (*ca.* 20 mg) and heated at 80 °C. The reaction was monitored by ^{1}H NMR spectroscopy, and the formation of $\mathrm{Cp^{Bu^t}}_2\mathrm{Mo(NCS)(CN)}$ was complete over 6 days. ^{1}H NMR ($\mathrm{CDCl_3}$): 1.24 [s, $\mathrm{C_5H_4\{C(C\mathit{H}_3)_3\}}$], 5.15 [q, $^3J_{\mathrm{H-H}} = 2.5$, 1 H of $\mathrm{C_5\mathit{H}_4\{C(CH_3)_3\}}$], 5.46 [q, $^3J_{\mathrm{H-H}} = 2.5$, 1 H of $\mathrm{C_5\mathit{H}_4\{C(CH_3)_3\}}$], 5.50 [q, $^3J_{\mathrm{H-H}} = 2.5$, 1 H of $\mathrm{C_5\mathit{H}_4\{C(CH_3)_3\}}$], 5.75 [q, $^3J_{H-H} = 2.5$, 1 H of $C_5\mathit{H}_4\{C(CH_3)_3\}$]. $^{13}C\{^1H\}$ NMR ($CDCl_3$): 30.9 [$C_5H_4\{C(\mathit{C}H_3)_3\}$], 33.0 [$C_5H_4\{\mathit{C}(CH_3)_3\}$], 90.8 [1 C of $\mathit{C}_5H_4\{C(CH_3)_3\}$], 91.6 [1 C of $\mathit{C}_5H_4\{C(CH_3)_3\}$], 92.0 [1 C of $\mathit{C}_5H_4\{C(CH_3)_3\}$], 102.3 [1 C of $\mathit{C}_5H_4\{C(CH_3)_3\}$], 130.2 [1 C of $\mathit{C}_5H_4\{C(CH_3)_3\}$], 134.7 [Mo-$\mathit{C}$N], 150.2 [Mo(N$\mathit{C}$S)].

Syntheses of $(Cp^{Bu^t})_2Mo(NCS)(SCN)$ and $(Cp^{Bu^t})_2Mo(NCS)_2$

A solution of $(Cp^{Bu^t})_2MoO$ (200 mg, 0.56 mmol) in benzene (15 mL) was treated with Me_3SiNCS (180 mg, 1.37 mmol) for 3 hours at room temperature. After this period, the mixture was filtered, and the precipitate was washed with toluene (2 × 5 mL) and pentane (2 × 5 mL) and dried *in vacuo* to give $(Cp^{Bu^t})_2Mo(NCS)_2$ as a purple solid (90 mg, 35%). Analysis calcd. for $C_{20}H_{26}N_2S_2Mo$: C, 52.9%; H, 5.8%; N, 6.2%. Found: C, 52.2%; H, 5.2%; N, 6.0%. IR Data (KBr disk, cm^{-1}): 3127 (w), 3087 (m), 2963 (s), 2906 (m), 2875 (m), 2076 (vs) [ν(CN)], 1492 (m), 1460 (m), 1385 (m), 1365 (m), 1270 (m), 1189 (w), 1150 (m), 1049 (w), 1013 (w), 958 (w), 931 (w), 911 (w), 880 (w), 830 (m), 684 (w), 579 (w), 481 (w). ^1H NMR ($CDCl_3$): 1.25 [s, $C_5H_4\{C(C\mathit{H}_3)_3\}$], 5.45 [t, $^3J_{H-H} = 2.5$, 2 H of $C_5\mathit{H}_4\{C(CH_3)_3\}$], 5.56 [t, $^3J_{H-H} = 2.5$, 2 H of $C_5\mathit{H}_4\{C(CH_3)_3\}$]. ^{13}C NMR ($CDCl_3$): 30.9 [q, $^1J_{C-H} = 127$, $C_5H_4\{C(\mathit{C}H_3)_3\}$], 33.5 [s, $C_5H_4\{\mathit{C}(CH_3)_3\}$], 96.1 [d, $^1J_{C-H} = 185$, 2 C of $\mathit{C}_5H_4\{C(CH_3)_3\}$], 100.3 [d, $^1J_{C-H} = 181$, 2 C of $\mathit{C}_5H_4\{C(CH_3)_3\}$], 133.7 [s, 1 C of $\mathit{C}_5H_4\{C(CH_3)_3\}$], 149.9 [s, Mo(N$\mathit{C}$S)]. The volatile components were removed from the reaction filtrate, and the residue obtained was washed with pentane (2 × 5 mL) and dried *in vacuo* to give $(Cp^{Bu^t})_2Mo(NCS)(SCN)$ as a dark brown solid (150 mg, 59%). Analysis calcd. for $C_{20}H_{26}N_2S_2Mo$: C, 52.9%; H, 5.8%; N, 6.2%. Found: C, 53.6%; H, 5.6%; N, 6.0%. IR Data (KBr disk, cm^{-1}): 3086 (m), 2960 (s), 2904 (m), 2873 (m), 2072 (vs) [ν(CN)], 1488 (m), 1460 (m), 1389 (m), 1363 (m), 1269 (m), 1192 (w), 1150 (m), 1045 (w), 1017 (w), 928 (w), 912 (w), 843 (s), 694 (m), 684 (m), 594 (w), 485 (w), 432 (w), 408 (w). ^1H NMR ($CDCl_3$): 1.28 [s, $C_5H_4\{C(C\mathit{H}_3)_3\}$], 5.01 [q, $^3J_{H-H} = 2$, 1 H of $C_5\mathit{H}_4\{C(CH_3)_3\}$], 5.15 [q, $^3J_{H-H} = 2$, 1 H of $C_5\mathit{H}_4\{C(CH_3)_3\}$], 5.79 [q, $^3J_{H-H} = 2$, 1 H of $C_5\mathit{H}_4\{C(CH_3)_3\}$], 5.92 [q, $^3J_{H-H} = 2$, 1 H of $C_5\mathit{H}_4\{C(CH_3)_3\}$]. ^{13}C NMR ($CDCl_3$): 30.7 [q, $^1J_{C-H} = 127$, $C_5H_4\{C(\mathit{C}H_3)_3\}$], 33.5 [s, $C_5H_4\{\mathit{C}(CH_3)_3\}$], 87.9 [d, $^1J_{C-H} = 178$, 1 C of $\mathit{C}_5H_4\{C(CH_3)_3\}$], 91.9 [d, $^1J_{C-H} = 181$, 1 C of $\mathit{C}_5H_4\{C(CH_3)_3\}$], 97.2 [d, $^1J_{C-H} = 185$, 1 C of $\mathit{C}_5H_4\{C(CH_3)_3\}$], 109.7 [d, $^1J_{C-H} = 181$, 1 C of $\mathit{C}_5H_4\{C(CH_3)_3\}$], 124.6 [s, Mo(S$\mathit{C}$N)], 135.5 [s, 1 C of $\mathit{C}_5H_4\{C(CH_3)_3\}$], 153.0 [s, Mo(N$\mathit{C}$S)].

Synthesis of $(Cp^{Bu^t})_2Mo(CN)Cl$

A solution of $(Cp^{Bu^t})_2Mo(OSiMe_3)(CN)$ (200 mg, 0.44 mmol) in toluene (20 mL) was treated with Me_3SiCl (96 mg, 0.88 mmol) and stirred for 1 day at room temperature. After this period, the mixture was cooled at 0 °C and filtered. The precipitate was washed with pentane (2 × 5 mL) and dried *in vacuo* to give $(Cp^{Bu^t})_2Mo(CN)Cl$ as a brown solid (150 mg, 85%). Analysis calcd. for $C_{19}H_{26}ClNMo$: C, 57.1%; H, 6.6%; N, 3.5%. Found: C, 56.8%; H, 6.8%; N, 3.5%. IR Data (KBr disk, cm^{-1}): 3098 (s), 3071 (vs), 2959 (vs), 2909 (vs), 2871 (vs), 2106 (vs) [ν(C≡N)], 1487 (s), 1463 (s), 1394 (s), 1363 (s), 1269 (s), 1205 (w), 1152 (m), 1077 (w), 1044 (m), 1024 (m), 972 (w), 933 (w), 908 (m), 842 (vs), 732 (w), 669 (w), 597 (w), 463 (w), 435 (w), 420 (w). ^1H NMR ($CDCl_3$): 1.22 [s, $C_5H_4\{C(C\mathit{H}_3)_3\}$], 5.28 [q, $^3J_{H-H} = 2.5$, 1 H of $C_5\mathit{H}_4\{C(CH_3)_3\}$], 5.36 [q, $^3J_{H-H} = 2.5$, 1 H of $C_5\mathit{H}_4\{C(CH_3)_3\}$], 5.42 [q, $^3J_{H-H} = 2.5$, 1 H of $C_5\mathit{H}_4\{C(CH_3)_3\}$], 5.88 [q, $^3J_{H-H} = 2.5$, 1 H of $C_5\mathit{H}_4\{C(CH_3)_3\}$]. ^{13}C NMR ($CDCl_3$): 31.1 [q, $^1J_{C-H} = 126$, $C_5H_4\{C(\mathit{C}H_3)_3\}$], 32.9 [s, $C_5H_4\{\mathit{C}(CH_3)_3\}$], 91.5 [d, $^1J_{C-H} = 185$, 1 C of $\mathit{C}_5H_4\{C(CH_3)_3\}$], 94.7 [d, $^1J_{C-H} = 183$, 1 C of $\mathit{C}_5H_4\{C(CH_3)_3\}$], 97.2 [d, $^1J_{C-H} = 191$, 1 C of $\mathit{C}_5H_4\{C(CH_3)_3\}$], 103.2 [d, $^1J_{C-H} = 178$, 1 C of $\mathit{C}_5H_4\{C(CH_3)_3\}$], 122.3 [s, 1 C of $C_5H_4\{C(CH_3)_3\}$], 137.9 [s, CN].

Synthesis of $(Cp^{Bu^t})_2Mo(CN)Br$

A solution of $(Cp^{Bu^t})_2Mo(OSiMe_3)(CN)$ (200 mg, 0.44 mmol) in toluene (20 mL) was stirred with Me_3SiBr (135 mg, 0.88 mmol) for 1 day at room temperature. After this period, the mixture was cooled at 0 °C and filtered. The precipitate was washed with toluene (2 × 5 mL) and pentane (2 × 5 mL) and dried *in vacuo* to give $(Cp^{Bu^t})_2Mo(CN)Br$ as a brown solid (180 mg, 92%). Analysis calcd. for $C_{19}H_{26}BrNMo$: C, 51.4%; H, 5.9%; N, 3.2%. Found: C, 50.2%; H, 5.4%; N, 2.9%. IR Data (KBr disk, cm^{-1}): 3122 (m), 3091 (s), 2959 (vs), 2905 (s), 2870 (m), 2108 (s) [ν(C≡N)], 1484 (s), 1463 (s), 1417 (m), 1397 (m), 1276 (s), 1196 (w), 1153 (m), 1078 (w), 1041 (m), 1025 (m), 968 (w), 907 (m), 889 (s), 844 (m), 813 (m), 733 (w), 697 (w), 666 (w), 631 (w), 602 (w), 534 (w), 513 (w), 480 (w), 438 (w), 415 (w). ^1H NMR ($CDCl_3$): 1.21 [s, $C_5H_4\{C(C\mathit{H}_3)_3\}$], 5.34 [br s, 2 H of $C_5\mathit{H}_4\{C(CH_3)_3\}$], 5.52 [br s, 1 H of $C_5\mathit{H}_4\{C(CH_3)_3\}$], 5.77 [br s, 1 H of $C_5\mathit{H}_4\{C(CH_3)_3\}$]. ^{13}C NMR ($CDCl_3$): 31.2 [q, $^1J_{C-H} = 126$, $C_5H_4\{C(\mathit{C}H_3)_3\}$], 32.8 [s, $C_5H_4\{\mathit{C}(CH_3)_3\}$], 90.9 [d, $^1J_{C-H} = 184$, 1 C of $\mathit{C}_5H_4\{C(CH_3)_3\}$], 95.3 [d, $^1J_{C-H} = 178$, 1 C of $\mathit{C}_5H_4\{C(CH_3)_3\}$], 96.9 [d, $^1J_{C-H} = 185$, 1 C of $\mathit{C}_5H_4\{C(CH_3)_3\}$], 101.5 [d, $^1J_{C-H} = 178$, 1 C of $\mathit{C}_5H_4\{C(CH_3)_3\}$], 120.2 [s, 1 C of $\mathit{C}_5H_4\{C(CH_3)_3\}$], [not located, CN].

Synthesis of $(Cp^{Bu^t})_2Mo(CN)I$

A solution of $(Cp^{Bu^t})_2Mo(OSiMe_3)CN$ (200 mg, 0.44 mmol) in toluene (20 mL) was stirred with Me_3SiI (110 mg, 0.55 mmol) for 1 day at room temperature. After this period, the mixture was cooled at 0 °C and filtered. The precipitate was washed with toluene (2 × 5 mL) and pentane (2 × 5 mL) and dried *in vacuo* to give $(Cp^{Bu^t})_2Mo(CN)I$ as a brown solid (120 mg, 55%). Analysis calcd. for $C_{19}H_{26}INMo$: C, 46.5%; H, 5.3%; N, 2.9%. Found: C, 47.2%; H, 5.6%; N, 3.2%. IR Data (KBr disk, cm^{-1}): 3089 (vs), 2957 (vs), 2903 (vs), 2868 (s), 2106 (vs) [ν(C≡N)], 1482 (s), 1462 (s), 1414 (s), 1367 (vs), 1274 (s), 1196 (m), 1152 (s), 1077 (m), 1041 (m), 965 (m), 888 (s), 842 (s), 812 (s), 734 (w), 666 (w), 598 (w), 475 (w), 441 (w), 414 (m). ^1H NMR ($CDCl_3$): 1.22 [s, $C_5H_4\{C(C\mathit{H}_3)_3\}$], 5.27 [q, $^3J_{H-H} = 2.5$, 1 H of $C_5\mathit{H}_4\{C(CH_3)_3\}$], 5.50 [m, 2 H of $C_5\mathit{H}_4\{C(CH_3)_3\}$], 5.76 [q, $^3J_{H-H} = 2.5$, 1 H of $C_5\mathit{H}_4\{C(CH_3)_3\}$]. ^{13}C NMR ($CDCl_3$): 31.3 [q, $^1J_{C-H} = 127$, $C_5H_4\{C(\mathit{C}H_3)_3\}$], 32.7 [s, $C_5H_4\{\mathit{C}(CH_3)_3\}$], 88.7 [d, $^1J_{C-H} = 185$, 1 C of $\mathit{C}_5H_4\{C(CH_3)_3\}$], 94.0 [d, $^1J_{C-H} = 185$, 1 C of $\mathit{C}_5H_4\{C(CH_3)_3\}$], 94.5 [d, $^1J_{C-H} = 178$, 1 C of $\mathit{C}_5H_4\{C(CH_3)_3\}$], 98.0 [d, $^1J_{C-H} = 180$, 1 C of $\mathit{C}_5H_4\{C(CH_3)_3\}$], 119.1 [s, 1 C of $\mathit{C}_5H_4\{C(CH_3)_3\}$], 136.1 [s, CN].

Synthesis of $(Cp^{Bu^t})_2Mo(CN)(O_3SMe)$

A solution of $(Cp^{Bu^t})_2Mo(OSiMe_3)(CN)$ (200 mg, 0.44 mmol) in toluene (20 mL) was stirred with Me_3SiO_3SMe (89 mg, 0.53 mmol) for 4 hours at room temperature. After this period, the mixture was concentrated to 5 mL and filtered at 0 °C. The precipitate was washed with pentane (2 × 5 mL) and dried *in vacuo* to give $(Cp^{Bu^t})_2Mo(CN)(O_3SMe)$ as a brown solid (150 mg, 74%). Analysis calcd. for $C_{20}H_{29}NO_3SMo$: C, 52.3%; H, 6.4%; N, 3.1%. Found: C, 51.5%; H, 6.3%; N, 3.1%. IR Data (KBr disk, cm^{-1}): 3102 (s), 2958 (s), 2909 (m), 2874 (m), 2116 (s) [ν(C≡N)], 1489 (m), 1465 (m), 1392 (m), 1366 (m), 1328 (w), 1273 (vs), 1198 (m), 1151 (vs), 1081 (m), 1011 (vs), 908 (w), 849 (m), 769 (m), 672 (w), 599 (w), 558 (m), 531 (m), 467 (w), 423 (w). ^1H NMR ($CDCl_3$): 1.23 [s, $C_5H_4\{C(C\mathit{H}_3)_3\}$], 2.70 [s, $O_3SC\mathit{H}_3$], 5.56 [q, $^3J_{H-H} = 2.5$, 1 H of $C_5\mathit{H}_4\{C(CH_3)_3\}$], 5.59 [q, $^3J_{H-H} = 2.5$, 1 H of $C_5\mathit{H}_4\{C(CH_3)_3\}$], 5.88 [q, $^3J_{H-H} = 2.5$, 1 H of $C_5\mathit{H}_4\{C(CH_3)_3\}$], 5.99 [q, $^3J_{H-H} = 2.5$, 1 H of $C_5\mathit{H}_4\{C(CH_3)_3\}$]. ^{13}C NMR ($CDCl_3$): 31.0 [q, $^1J_{C-H} = 127$, $C_5H_4\{C(\mathit{C}H_3)_3\}$], 33.2 [s, $C_5H_4\{\mathit{C}(CH_3)_3\}$], 40.0 [q, $^1J_{C-H} = 137$, $O_3S\mathit{C}H_3$], 91.5 [d, $^1J_{C-H} = 185$, 1 C of $\mathit{C}_5H_4\{C(CH_3)_3\}$], 98.2 [d, $^1J_{C-H} = 182$, 1 C of $\mathit{C}_5H_4\{C(CH_3)_3\}$], 98.7 [d, $^1J_{C-H} = 182$, 1 C of $\mathit{C}_5H_4\{C(CH_3)_3\}$], 99.6 [d, $^1J_{C-H} = 185$, 1 C of $\mathit{C}_5H_4\{C(CH_3)_3\}$], 127.8 [s, 1 C of $\mathit{C}_5H_4\{C(CH_3)_3\}$], 137.7 [s, CN].

Synthesis of $(Cp^{Bu^t})_2Mo(\eta^2\text{-}S_2)$

A mixture of $(Cp^{Bu^t})_2MoH_2$ (300 mg, 0.88 mmol) and sulfur (85 mg, 2.65 mmol of "S") in toluene (20 mL) was stirred at room temperature for 1 hour. The volatile components were removed and the residue was washed with pentane (2 × 5 mL) and dried *in vacuo* to give $(Cp^{Bu^t})_2Mo(\eta^2\text{-}S_2)$ as an orange solid (310 mg, 87%). Analysis calcd. for $C_{18}H_{26}S_2Mo$: C, 53.7%; H, 6.5%. Found: C, 53.5%; H, 6.5%. MS: $m/z = 404$ (M^+). IR Data (KBr disk, cm^{-1}): 3077 (s), 2956 (vs), 2865 (s), 1459 (s), 1390 (s), 1361 (s), 1267 (s), 1199 (w), 1150 (m), 1037 (m), 896 (s), 823 (s), 663 (w), 582 (w), 533 (m), 466 (w). ^1H NMR (C_6D_6): 1.08 [s, $C_5H_4\{C(C\mathit{H}_3)_3\}$], 3.95 [t, $^3J_{H-H} = 2$, 2 H of $C_5\mathit{H}_4\{C(CH_3)_3\}$], 4.85 [t, $^3J_{H-H} = 2$, 2 H of $C_5\mathit{H}_4\{C(CH_3)_3\}$]. ^{13}C NMR (C_6D_6): 32.2 [q, $^1J_{C-H} = 126$, $C_5H_4\{C(\mathit{C}H_3)_3\}$], 32.3 [s, $C_5H_4\{\mathit{C}(CH_3)_3\}$], 88.8 [d, $^1J_{C-H} = 176$, 2 C of $\mathit{C}_5H_4\{C(CH_3)_3\}$], 93.0 [d, $^1J_{C-H} = 180$, 2 C of $\mathit{C}_5H_4\{C(CH_3)_3\}$], 113.9 [s, 1 C of $\mathit{C}_5H_4\{C(CH_3)_3\}$].

Synthesis of $(Cp^{Bu^t})_2Mo(\eta^2\text{-}Se_2)$

A mixture of $(Cp^{Bu^t})_2MoH_2$ (220 mg, 0.65 mmol) and selenium powder (170 mg, 2.15 mmol of "Se") in toluene (20 mL) was stirred at 120 °C for 1 hour. The mixture was filtered, and the volatile components were removed from the filtrate. The residue was washed with pentane (2 × 5 mL) and dried *in vacuo* to give $(Cp^{Bu^t})_2Mo(\eta^2\text{-}Se_2)$ as a brown solid (270 mg, 84%). Analysis calcd. for $C_{18}H_{26}Se_2Mo$: C, 43.6%; H, 5.3%. Found: C, 42.8%; H, 5.4%. MS: $m/z = 497$ ($M^+ - 1$). IR Data (KBr disk, cm^{-1}): 3075 (s), 2957 (vs), 2899 (s), 2863 (s), 1478 (m), 1458 (s), 1390 (s), 1360 (s), 1267 (s), 1200 (w), 1149 (m), 1038 (m), 937 (w), 896 (s), 828 (vs), 660 (w), 575 (w), 457 (w), 412 (w). ^1H NMR (C_6D_6): 1.00 [s, $C_5H_4\{C(C\mathit{H}_3)_3\}$], 4.14 [t, $^3J_{H-H} = 2$, 2 H of $C_5\mathit{H}_4\{C(CH_3)_3\}$], 4.93 [t, $^3J_{H-H} = 2$, 2 H of $C_5\mathit{H}_4\{C(CH_3)_3\}$]. ^{13}C NMR (C_6D_6): 32.2 [q, $^1J_{C-H} = 126$, $C_5H_4\{C(\mathit{C}H_3)_3\}$], 32.3 [s, $C_5H_4\{\mathit{C}(CH_3)_3\}$], 87.7 [d, $^1J_{C-H} = 181$, 2 C of $\mathit{C}_5H_4\{C(CH_3)_3\}$], 91.4 [d, $^1J_{C-H} = 178$, 2 C of $\mathit{C}_5H_4\{C(CH_3)_3\}$], 111.0 [s, 1 C of $\mathit{C}_5H_4\{C(CH_3)_3\}$]. ^{77}Se NMR (C_6D_6): −254 [s].

Synthesis of $(Cp^{Bu^t})_2Mo(\eta^2\text{-}Te_2)$

A mixture of $(Cp^{Bu^t})_2MoH_2$ (335 mg, 0.98 mmol) and tellurium powder (390 mg, 3.06 mmol of "Te") in toluene (20 mL) was treated with PMe_3 (0.5 mL) at −78 °C. The mixture was warmed to room temperature and heated at 80 °C for 1 day. After this period, the mixture was filtered and the volatile components were removed from the filtrate. The residue was dissolved in toluene (20 mL) and stirred with Hg (1 mL) for 1.5 hours at room temperature to convert PMe_3PTe to HgTe, which was removed by filtration. The volatile components were removed from the filtrate, giving a mixture of $(Cp^{Bu^t})_2Mo(\eta^2\text{-}Te_2)$ and $[(Cp^{Bu^t})_2Mo(\mu\text{-}Te)]_2$ (due to tellurium abstraction by PMe_3). The residue was extracted into toluene and tellurium powder was added to the extracted filtrate, and the mixture was allowed to stir for 2.5 hours at 120 °C to convert $[(Cp^{Bu^t})_2Mo(\mu\text{-}Te)]_2$ to $(Cp^{Bu^t})_2Mo(\eta^2\text{-}Te_2)$. After this period, the mixture was filtered, and the volatile components were removed from the filtrate. The residue was extracted into toluene again and the volatile components were removed. The extraction was repeated until no tellurium powder was observed from the residue. The final residue was washed with pentane (2 × 5 mL) and dried *in vacuo* to give $(Cp^{Bu^t})_2Mo(\eta^2\text{-}Te_2)$ as a dark-brown solid (390 mg, 67%). Analysis calcd. for $C_{18}H_{26}Te_2Mo$: C, 36.4%; H, 4.4%. Found: C, 37.0%; H, 4.7%. MS: $m/z = 593$ ($M^+ - 1$). IR Data (KBr disk, cm^{-1}): 3108 (m), 3071 (w), 2953 (vs), 2899 (s), 2862 (s), 1477 (s), 1458 (s), 1361 (vs), 1269 (s), 1196 (w), 1148 (m), 1025 (m), 937 (m), 907 (m), 889 (s), 836 (vs), 796 (s), 729 (w), 659 (m), 591 (w), 466 (w), 405 (w). ^1H NMR (C_6D_6): 0.86 [s, $C_5H_4\{C(C\mathit{H}_3)_3\}$], 4.62 [t, $^3J_{H-H} = 2$, 2 H of $C_5\mathit{H}_4\{C(CH_3)_3\}$], 5.06 [t, $^3J_{H-H} = 2$, 2 H of $C_5\mathit{H}_4\{C(CH_3)_3\}$]. ^{13}C NMR (C_6D_6): 31.8 [q, $^1J_{C-H} = 126$, $C_5H_4\{C(\mathit{C}H_3)_3\}$], 32.0 [s, $C_5H_4\{\mathit{C}(CH_3)_3\}$], 83.7 [d, $^1J_{C-H} = 181$, 2 C of $\mathit{C}_5H_4\{C(CH_3)_3\}$], 87.2 [d, $^1J_{C-H} = 176$, 2 C of $\mathit{C}_5H_4\{C(CH_3)_3\}$], 108.1 [s, 1 C of $\mathit{C}_5H_4\{C(CH_3)_3\}$]. ^{125}Te NMR (C_6D_6): −803 [s].

Chalcogen exchange between $(Cp^{Bu^t})_2Mo(\eta^2\text{-}Se_2)$ and $(Cp^{Bu^t})_2Mo(\eta^2\text{-}Te_2)$

A mixture of $(Cp^{Bu^t})_2Mo(\eta^2\text{-}Se_2)$ (*ca.* 30 mg) and $(Cp^{Bu^t})_2Mo(\eta^2\text{-}Te_2)$ (*ca.* 30 mg) in C_6D_6 (1 mL) was heated at 80 °C. The sample was monitored by ^1H NMR spectroscopy, which demonstrated that $(Cp^{Bu^t})_2Mo\{\eta^2\text{-}(SeTe)\}$ was formed as the major product over a period of 1 day. ^1H NMR (C_6D_6): 0.94 [s, $C_5H_4\{C(C\mathit{H}_3)_3\}$], 4.16 [q, $^3J_{H-H} = 2$, 1 H of $C_5\mathit{H}_4\{C(CH_3)_3\}$], 4.60 [q, $^3J_{H-H} = 2$, 1 H of $C_5\mathit{H}_4\{C(CH_3)_3\}$], 4.66 [q, $^3J_{H-H} = 2$, 1 H of $C_5\mathit{H}_4\{C(CH_3)_3\}$], 5.32 [q, $^3J_{H-H} = 2$, 1 H of $C_5\mathit{H}_4\{C(CH_3)_3\}$]. ^{77}Se NMR (C_6D_6): −430 [s, $^1J_{Se-Te} = 522$]. ^{125}Te NMR (C_6D_6): −459 [s, $^1J_{Te-Se}$ not observed].

Reactions of $(Cp^{Bu^t})_2Mo(CO)$ with the elemental chalcogens

A solution of $(Cp^{Bu^t})_2Mo(CO)$ (*ca.* 10 mg) in C_6D_6 (1 mL) was treated with elemental chalcogen (excess). ^1H NMR spectroscopy was used to monitor the formation of $(Cp^{Bu^t})_2Mo(\eta^2\text{-}E_2)$ (E = S, 1 hour at room temperature; E = Se, 5 hours at 80 °C; E = Te, 1 day at 120 °C).

Synthesis of $[(Cp^{Bu^t})_2Mo(\mu\text{-}S)]_2$

A solution of $(Cp^{Bu^t})_2Mo(\eta^2\text{-}S_2)$ (*ca.* 10 mg) in C_6D_6 (1 mL) was treated with PMe_3. The sample was monitored by ^1H NMR spectroscopy, which demonstrated that the formation of $[(Cp^{Bu^t})_2Mo(\mu\text{-}S)]_2$ was complete after 1 day at room temperature, accompanied by the formation of Me_3PS. ^1H NMR (C_6D_6): 1.24 [s, $C_5H_4\{C(C\mathit{H}_3)_3\}$], 3.34 [m, 2 H of $C_5\mathit{H}_4\{C(CH_3)_3\}$], 4.15 [br s, 2 H of $C_5\mathit{H}_4\{C(CH_3)_3\}$].

Synthesis of $[(Cp^{Bu^t})_2Mo(\mu\text{-}Se)]_2$

A solution of $(Cp^{Bu^t})_2Mo(\eta^2\text{-}Se_2)$ (300 mg, 0.60 mmol) in toluene (20 mL) was treated with PMe_3 (0.5 mL) for 6 hours at room temperature. After this period, the volatile components were removed *in vacuo* and the residue obtained was extracted into pentane (50 mL). The filtrate was concentrated to *ca.* 3 mL and placed at −78 °C, thereby depositing a red–brown solid that was isolated by filtration. The Me_3PSe by-product was removed by vacuum sublimation at 50 °C, giving pure red–brown $[(Cp^{Bu^t})_2Mo(\mu\text{-}Se)]_2$ (170 mg, 60%). Analysis calcd. for $C_{36}H_{52}Se_2Mo_2$: C, 51.8%; H, 6.3%. Found: C, 51.8%; H, 5.8%. MS: $m/z = 835$ ($M^+ - 1$). IR Data (KBr disk, cm^{-1}): 3123 (w), 2956 (vs), 2899 (vs), 2864 (s), 1480 (s), 1458 (s), 1391 (m), 1360 (s), 1273 (s), 1195 (w), 1150 (m), 1041 (m), 917 (m), 871 (m), 821 (vs), 783 (vs), 655 (w), 587 (w), 459 (w). ^1H NMR (C_6D_6): 1.05 [s, $C_5H_4\{C(C\mathit{H}_3)_3\}$], 4.80 [br s, 2 H of $C_5\mathit{H}_4\{C(CH_3)_3\}$], 5.68 [br s, 2 H of $C_5\mathit{H}_4\{C(CH_3)_3\}$]. ^{13}C NMR (C_6D_6): 31.8 [q, $^1J_{C-H} = 126$, $C_5H_4\{C(\mathit{C}H_3)_3\}$], 32.7 [s, $C_5H_4\{\mathit{C}(CH_3)_3\}$], 91.4 [d, $^1J_{C-H} = 176$, 2 C of $\mathit{C}_5H_4\{C(CH_3)_3\}$], 95.8 [d, $^1J_{C-H} = 175$, 2 C of $\mathit{C}_5H_4\{C(CH_3)_3\}$], 110.1 [s, 1 C of $\mathit{C}_5H_4\{C(CH_3)_3\}$]. ^{77}Se NMR (C_6D_6): −996 [s].

Synthesis of $[(Cp^{Bu^t})_2Mo(\mu\text{-}Te)]_2$

A mixture of $(Cp^{Bu^t})_2Mo(\eta^2\text{-}Te_2)$ (390 mg, 0.66 mmol) and Hg (2 mL) in benzene (20 mL) was treated with PMe_3 (0.5 mL) and stirred for 1 day at room temperature. The mixture was filtered after this period, and the volatile components were removed slowly from the filtrate. The residue was dried *in vacuo* to give $[(Cp^{Bu^t})_2Mo(\mu\text{-}Te)]_2$ as a brown solid (290 mg, 95%). IR Data (KBr disk, cm^{-1}): 3074 (w), 2957 (vs), 2901 (s), 2865 (s), 1480 (s), 1460 (s), 1394 (m), 1362 (s), 1271 (s), 1195 (w), 1149 (m), 1039 (m), 914 (m), 874 (s), 825 (s), 788 (s), 658 (w), 588 (w), 473 (w), 409 (w). ^1H NMR (C_6D_6): 1.04 [s, $C_5H_4\{C(C\mathit{H}_3)_3\}$], 4.87 [br s, 2 H of $C_5\mathit{H}_4\{C(CH_3)_3\}$], 5.69 [br s, 2 H of $C_5\mathit{H}_4\{C(CH_3)_3\}$]. ^{13}C NMR (C_6D_6): 31.8 [q, $^1J_{C-H} = 126$, $C_5H_4\{C(\mathit{C}H_3)_3\}$], 32.5 [s,

$\mathrm{C_5H_4\{\mathit{C}(CH_3)_3\}}$], 85.2 [d, $^1J_{\mathrm{C-H}} = 180$, 2 C of $\mathrm{\mathit{C}_5H_4\{C(CH_3)_3\}}$], 89.9 [d, $^1J_{\mathrm{C-H}} = 176$, 2 C of $\mathrm{\mathit{C}_5H_4\{C(CH_3)_3\}}$], 108.7 [s, 1 C of $\mathrm{\mathit{C}_5H_4\{C(CH_3)_3\}}$]. ^{125}Te NMR ($\mathrm{C_6D_6}$): −1664 [s].

Reaction of $\mathbf{[(Cp^{Bu^t})_2Mo(\mu\text{-}Te)]_2}$ with Te

A mixture of $\mathrm{[(Cp^{Bu^t})_2Mo(\mu\text{-}Te)]_2}$ (*ca.* 10 mg) and tellurium powder (*ca.* 5 mg) in $\mathrm{C_6D_6}$ (1 mL) was heated at 120 °C. The sample was monitored by ^{1}H NMR spectroscopy, which demonstrated that the formation of $\mathrm{(Cp^{Bu^t})_2Mo(\eta^2\text{-}Te_2)}$ was complete after 5 hours.

Reaction of $\mathbf{[(Cp^{Bu^t})_2Mo(\mu\text{-}Te)]_2}$ with Se

A mixture of $\mathrm{[(Cp^{Bu^t})_2Mo(\mu\text{-}Te)]_2}$ (*ca.* 10 mg) and selenium powder (*ca.* 5 mg) in $\mathrm{C_6D_6}$ (1 mL) was heated at 80 °C. The sample was monitored by ^{1}H NMR spectroscopy, which demonstrated that a mixture of $\mathrm{(Cp^{Bu^t})_2Mo(\eta^2\text{-}Te_2)}$, $\mathrm{(Cp^{Bu^t})_2Mo(\eta^2\text{-}Se_2)}$ and $\mathrm{(Cp^{Bu^t})_2Mo(\eta^2\text{-}SeTe)}$ was obtained after 1 hour, then the formation of $\mathrm{(Cp^{Bu^t})_2Mo(\eta^2\text{-}Se_2)}$ was complete within 24 hours.

Reaction of $\mathbf{[(Cp^{Bu^t})_2Mo(\mu\text{-}Se)]_2}$ with Se

A mixture of $\mathrm{[(Cp^{Bu^t})_2Mo(\mu\text{-}Se)]_2}$ (*ca.* 10 mg) and selenium powder (*ca.* 5 mg) in $\mathrm{C_6D_6}$ (1 mL) was heated at 80 °C. The sample was monitored by ^{1}H NMR spectroscopy, which demonstrated that the formation of $\mathrm{(Cp^{Bu^t})_2Mo(\eta^2\text{-}Se_2)}$ was complete within 5 hours.

Reaction of $\mathbf{[(Cp^{Bu^t})_2Mo(\mu\text{-}Se)]_2}$ with Te

A mixture of $\mathrm{[(Cp^{Bu^t})_2Mo(\mu\text{-}Se)]_2}$ (*ca.* 10 mg) and tellurium powder (*ca.* 5 mg) in $\mathrm{C_6D_6}$ (1 mL) was heated at 80 °C. The sample was monitored by ^{1}H NMR spectroscopy, which demonstrated that a mixture of $\mathrm{(Cp^{Bu^t})_2Mo(\eta^2\text{-}Te_2)}$, $\mathrm{(Cp^{Bu^t})_2Mo(\eta^2\text{-}Se_2)}$ and $\mathrm{(Cp^{Bu^t})_2Mo(\eta^2\text{-}SeTe)}$ was obtained after 1 day; the mixture persisted even after 3 days at 80 °C.

Synthesis of $\mathbf{(Cp^{Bu^t})_2Mo(SPh)H}$

A mixture of $\mathrm{(Cp^{Bu^t})_2MoH_2}$ (400 mg, 1.18 mmol) and $\mathrm{Ph_2S_2}$ (256 mg, 1.18 mmol) in toluene (10 mL) was stirred for 1 day at 80 °C. After this period, the volatile components were removed *in vacuo*, and the residue obtained was washed with cold pentane (2 × 5 mL) and dried to give $\mathrm{(Cp^{Bu^t})_2Mo(SPh)H}$ as an orange–brown solid (440 mg, 83%). Analysis calcd. for $\mathrm{C_{24}H_{32}SMo}$: C, 64.3%; H, 7.2%. Found: C, 64.1%; H, 7.1%. IR Data (KBr disk, cm^{-1}): 3127 (w), 3076 (vs), 2957 (vs), 2899 (s), 2863 (s), 1896 (w) [ν(Mo–H)], 1574 (s), 1456 (s), 1393 (m), 1358 (vs), 1272 (s), 1195 (m), 1148 (m), 1076 (m), 1019 (s), 914 (m), 898 (m), 842 (m), 804 (m), 776 (s), 736 (vs), 691 (vs), 595 (w), 486 (m), 407 (w). ^{1}H NMR ($\mathrm{C_6D_6}$): −7.52 [s, Mo–H], 1.21 [s, $\mathrm{C_5H_4\{C(C\mathit{H}_3)_3\}}$], 3.62 [q, $^3J_{\mathrm{H-H}} = 2$, 1 H of $\mathrm{C_5\mathit{H}_4\{C(CH_3)_3\}}$], 3.90 [q, $^3J_{\mathrm{H-H}} = 2$, 1 H of $\mathrm{C_5\mathit{H}_4\{C(CH_3)_3\}}$], 4.53 [q, $^3J_{\mathrm{H-H}} = 2$, 1 H of $\mathrm{C_5\mathit{H}_4\{C(CH_3)_3\}}$], 4.97 [q, $^3J_{\mathrm{H-H}} = 2$, 1 H of $\mathrm{C_5\mathit{H}_4\{C(CH_3)_3\}}$], 6.99 [t, $^3J_{\mathrm{H-H}} = 7$, 1 H of $\mathrm{SC_6\mathit{H}_5}$], 7.18 [t, $^3J_{\mathrm{H-H}} = 7$, 2 H of $\mathrm{SC_6\mathit{H}_5}$], 7.74 [d, $^3J_{\mathrm{H-H}} = 8$, 2 H of $\mathrm{SC_6\mathit{H}_5}$]. ^{13}C NMR ($\mathrm{C_6D_6}$): 31.8 [s, $\mathrm{C_5H_4\{\mathit{C}(CH_3)_3\}}$], 32.2 [q, $^1J_{\mathrm{C-H}} = 126$, $\mathrm{C_5H_4\{C(\mathit{C}H_3)_3\}}$], 77.0 [d, $^1J_{\mathrm{C-H}} = 176$, 1 C of $\mathrm{\mathit{C}_5H_4\{C(CH_3)_3\}}$], 80.3 [d, $^1J_{\mathrm{C-H}} = 181$, 1 C of $\mathrm{\mathit{C}_5H_4\{C(CH_3)_3\}}$], 82.2 [d, $^1J_{\mathrm{C-H}} = 176$, 1 C of $\mathrm{\mathit{C}_5H_4\{C(CH_3)_3\}}$], 101.3 [d, $^1J_{\mathrm{C-H}} = 177$, 1 C of $\mathrm{\mathit{C}_5H_4\{C(CH_3)_3\}}$], 121.7 [d, $^1J_{\mathrm{C-H}} = 160$, 1 C of $\mathrm{S\mathit{C}_6H_5}$], 123.5 [s, 1 C of $\mathrm{\mathit{C}_5H_4\{C(CH_3)_3\}}$], 127.5 [d, $^1J_{\mathrm{C-H}} = 163$, 2 C of $\mathrm{S\mathit{C}_6H_5}$], 132.6 [d, $^1J_{\mathrm{C-H}} = 158$, 2 C of $\mathrm{S\mathit{C}_6H_5}$], 152.3 [s, 1 C of $\mathrm{S\mathit{C}_6H_5}$].

Synthesis of $\mathbf{(Cp^{Bu^t})_2Mo(SePh)H}$

A mixture of $\mathrm{(Cp^{Bu^t})_2MoH_2}$ (300 mg, 0.88 mmol) and $\mathrm{Ph_2Se_2}$ (275 mg, 0.88 mmol) in toluene (10 mL) was stirred for 2 hours at room temperature. After this period, the volatile components were removed *in vacuo*, and the residue obtained was washed with cold pentane (2 × 5 mL) and dried to give $\mathrm{(Cp^{Bu^t})_2Mo(SePh)H}$ as a red–brown solid (200 mg, 46%). Analysis calcd. for $\mathrm{C_{24}H_{32}SeMo}$: C, 58.2%; H, 6.5%. Found: C, 58.9%; H, 5.9%. MS: $m/z = 495$ ($\mathrm{M^+}$ − H). IR Data (KBr disk, cm^{-1}): 3113 (m), 3062 (m), 2959 (vs), 2900 (s), 2864 (s), 1882 (w) [ν(Mo–H)], 1571 (s), 1484 (s), 1459 (s), 1430 (s), 1390 (s), 1359 (vs), 1270 (s), 1194 (m), 1149 (m), 1063 (m), 1019 (s), 909 (m), 879 (s), 838 (s), 779 (vs), 738 (vs), 694 (vs), 664 (s), 473 (s). ^{1}H NMR ($\mathrm{C_6D_6}$): −7.83 [s, $^2J_{\mathrm{Se-H}} = 15$, Mo–H], 1.19 [s, $\mathrm{C_5H_4\{C(C\mathit{H}_3)_3\}}$], 3.66 [br s, 1 H of $\mathrm{C_5\mathit{H}_4\{C(CH_3)_3\}}$], 3.89 [br s, 1 H of $\mathrm{C_5\mathit{H}_4\{C(CH_3)_3\}}$], 4.69 [br s, 1 H of $\mathrm{C_5\mathit{H}_4\{C(CH_3)_3\}}$], 4.91 [br s, 1 H of $\mathrm{C_5\mathit{H}_4\{C(CH_3)_3\}}$], 7.07 [m, 3 H of $\mathrm{SeC_6\mathit{H}_5}$], 7.87 [d, $^3J_{\mathrm{H-H}} = 8$, 2 H of $\mathrm{SeC_6\mathit{H}_5}$]. ^{13}C NMR ($\mathrm{C_6D_6}$): 31.7 [s, $\mathrm{C_5H_4\{\mathit{C}(CH_3)_3\}}$], 32.2 [q, $^1J_{\mathrm{C-H}} = 126$, $\mathrm{C_5H_4\{C(\mathit{C}H_3)_3\}}$], 76.7 [d, $^1J_{\mathrm{C-H}} = 177$, 1 C of $\mathrm{\mathit{C}_5H_4\{C(CH_3)_3\}}$], 79.0 [d, $^1J_{\mathrm{C-H}} = 184$, 1 C of $\mathrm{\mathit{C}_5H_4\{C(CH_3)_3\}}$], 81.8 [d, $^1J_{\mathrm{C-H}} = 177$, 1 C of $\mathrm{\mathit{C}_5H_4\{C(CH_3)_3\}}$], 98.8 [d, $^1J_{\mathrm{C-H}} = 178$, 1 C of $\mathrm{\mathit{C}_5H_4\{C(CH_3)_3\}}$], 123.1 [s, 1 C of $\mathrm{\mathit{C}_5H_4\{C(CH_3)_3\}}$], 123.2 [dt, $^1J_{\mathrm{C-H}} = 159$, $^2J_{\mathrm{C-H}} = 8$, 1 C of $\mathrm{Se\mathit{C}_6H_5}$], 127.7 [dd, $^1J_{\mathrm{C-H}} = 157$, $^2J_{\mathrm{C-H}} = 8$, 2 C of $\mathrm{Se\mathit{C}_6H_5}$], 134.8 [dt, $^1J_{\mathrm{C-H}} = 158$, $^2J_{\mathrm{C-H}} = 7$, 2 C of $\mathrm{Se\mathit{C}_6H_5}$], 140.5 [s, 1 C of $\mathrm{Se\mathit{C}_6H_5}$]. ^{77}Se NMR ($\mathrm{C_6D_6}$): −117 [d, $^2J_{\mathrm{Se-H}} = 15$].

Synthesis of $\mathbf{(Cp^{Bu^t})_2Mo(TePh)H}$

A mixture of $\mathrm{(Cp^{Bu^t})_2MoH_2}$ (300 mg, 0.88 mmol) and $\mathrm{Ph_2Te_2}$ (343 mg, 0.84 mmol) in toluene (15 mL) was stirred for 24 hours at room temperature. After this period, the volatile components were removed *in vacuo*, and the residue obtained was washed with cold pentane (2 × 5 mL) and dried to give $\mathrm{(Cp^{Bu^t})_2Mo(TePh)H}$ as a brown solid (390 mg, 81%). Analysis calcd. for $\mathrm{C_{24}H_{32}TeMo}$: C, 53.0%; H, 5.9%. Found: C, 51.7%; H, 6.2%. IR Data (KBr disk, cm^{-1}): 3106 (m), 3057 (s), 2955 (vs), 2899 (s), 2862 (s), 1869 (w) [ν(Mo–H)], 1567 (m), 1483 (s), 1461 (s), 1429 (m), 1387 (s), 1359 (s), 1269 (s), 1194 (w), 1148 (m), 1039 (m), 1016 (s), 916 (m), 880 (m), 838 (s), 783 (s), 731 (s), 694 (s), 658 (m), 458 (m), 408 (w). ^{1}H NMR ($\mathrm{C_6D_6}$): −8.25 [s, $^2J_{\mathrm{Te-H}} = 39$, Mo–H], 1.11 [s, $\mathrm{C_5H_4\{C(C\mathit{H}_3)_3\}}$], 3.83 [q, $^3J_{\mathrm{H-H}} = 2$, 1 H of $\mathrm{C_5\mathit{H}_4\{C(CH_3)_3\}}$], 3.89 [q, $^3J_{\mathrm{H-H}} = 2$, 1 H of $\mathrm{C_5\mathit{H}_4\{C(CH_3)_3\}}$], 4.82 [q, $^3J_{\mathrm{H-H}} = 2$, 1 H of $\mathrm{C_5\mathit{H}_4\{C(CH_3)_3\}}$], 4.88 [q, $^3J_{\mathrm{H-H}} = 2$, 1 H of $\mathrm{C_5\mathit{H}_4\{C(CH_3)_3\}}$], 6.98 [t, $^3J_{\mathrm{H-H}} = 7$, 2 H of $\mathrm{TeC_6\mathit{H}_5}$], 7.09 [t, $^3J_{\mathrm{H-H}} = 7$, 1 H of $\mathrm{TeC_6\mathit{H}_5}$], 8.04 [d, $^3J_{\mathrm{H-H}} = 8$, 2 H of $\mathrm{TeC_6\mathit{H}_5}$]. ^{13}C NMR ($\mathrm{C_6D_6}$): 31.4 [s, $\mathrm{C_5H_4\{\mathit{C}(CH_3)_3\}}$], 32.2 [q, $^1J_{\mathrm{C-H}} = 126$, $\mathrm{C_5H_4\{C(\mathit{C}H_3)_3\}}$], 76.8 [d, $^1J_{\mathrm{C-H}} = 183$, 1 C of $\mathrm{\mathit{C}_5H_4\{C(CH_3)_3\}}$], 77.6 [d, $^1J_{\mathrm{C-H}} = 181$, 1 C of $\mathrm{\mathit{C}_5H_4\{C(CH_3)_3\}}$], 80.9 [d, $^1J_{\mathrm{C-H}} = 176$, 1 C of $\mathrm{\mathit{C}_5H_4\{C(CH_3)_3\}}$], 92.0 [d, $^1J_{\mathrm{C-H}} = 179$, 1 C of $\mathrm{\mathit{C}_5H_4\{C(CH_3)_3\}}$], 111.5 [s, 1 C of $\mathrm{Te\mathit{C}_6H_5}$], 121.8 [s, 1 C of $\mathrm{\mathit{C}_5H_4\{C(CH_3)_3\}}$], 124.9 [dt, $^1J_{\mathrm{C-H}} = 159$, $^2J_{\mathrm{C-H}} = 7$, 1 C of $\mathrm{Te\mathit{C}_6H_5}$], 127.8 [dd, $^1J_{\mathrm{C-H}} = 157$, $^2J_{\mathrm{C-H}} = 8$, 2 C of $\mathrm{Te\mathit{C}_6H_5}$], 139.9 [dt, $^1J_{\mathrm{C-H}} = 160$, $^2J_{\mathrm{C-H}} = 7$, 2 C of $\mathrm{Te\mathit{C}_6H_5}$]. ^{125}Te NMR ($\mathrm{C_6D_6}$): −213 [d, $^2J_{\mathrm{Te-H}} = 39$].

Synthesis of $\mathbf{(Cp^{Bu^t})_2Mo(SPh)_2}$

Method A: from $\mathbf{(Cp^{Bu^t})_2Mo(SPh)H}$. A mixture of $\mathrm{(Cp^{Bu^t})_2Mo(SPh)H}$ (95 mg, 0.21 mmol) and $\mathrm{Ph_2S_2}$ (50 mg, 0.23 mmol) in toluene (15 mL) was stirred for 2 days at 80 °C. After this period, the volatile components were removed, and the residue was washed with cold pentane (2 × 5 mL) and dried *in vacuo* to give $\mathrm{(Cp^{Bu^t})_2Mo(SPh)_2}$ as a red solid (90 mg, 76%).

Method B: from $\mathbf{(Cp^{Bu^t})_2Mo(CO)}$. A mixture of $\mathrm{(Cp^{Bu^t})_2Mo(CO)}$ (150 mg, 0.41 mmol) and $\mathrm{Ph_2S_2}$ (90 mg, 0.41 mmol) in toluene (10 mL) was stirred for 2 hours at room temperature. After this period, the volatile components were removed from the mixture, and the residue was washed with pentane (3 × 5 mL) and dried *in vacuo* to give $\mathrm{(Cp^{Bu^t})_2Mo(SPh)_2}$ as a red solid (140 mg, 61%). Analysis calcd. for $\mathrm{C_{30}H_{36}S_2Mo}$: C, 64.7%; H, 6.5%. Found: C, 64.5%; H, 6.2%. IR Data (KBr disk, cm^{-1}): 3097 (vs), 3065 (s), 2956 (vs), 2902 (s), 2868 (s), 1574 (vs), 1486 (s), 1459 (vs), 1431 (s), 1391 (s), 1358 (vs), 1269 (s), 1190 (w), 1150 (m), 1078 (s), 1048 (s), 1022 (s), 958 (w), 927 (w), 908 (s), 846 (s), 826 (m), 803 (s), 740 (vs), 696 (vs), 676 (m), 488 (m), 403 (w). ^{1}H NMR (C_6D_6): 0.92 [s, $C_5H_4\{C(C\mathit{H}_3)_3\}$], 4.89 [t, $^3J_{H-H} = 2.5$, 2 H of $C_5\mathit{H}_4\{C(CH_3)_3\}$], 5.05 [t, $^3J_{H-H} = 2.5$, 2 H of $C_5\mathit{H}_4\{C(CH_3)_3\}$], 6.99 [t, $^3J_{H-H} = 7$, 1 H of $SC_6\mathit{H}_5$], 7.09 [t, $^3J_{H-H} = 7$, 2 H of $SC_6\mathit{H}_5$], 7.62 [d, $^3J_{H-H} = 7$, 2 H of $SC_6\mathit{H}_5$]. ^{13}C NMR (C_6D_6): 31.0 [q, $^1J_{C-H} = 126$, $C_5H_4\{C(\mathit{C}H_3)_3\}$], 33.8 [s, $C_5H_4\{\mathit{C}(CH_3)_3\}$], 94.5 [d, $^1J_{C-H} = 182$, 2 C of $\mathit{C}_5H_4\{C(CH_3)_3\}$], 98.5 [d, $^1J_{C-H} = 177$, 2 C of $\mathit{C}_5H_4\{C(CH_3)_3\}$], 124.1 [d, $^1J_{C-H} = 159$, 1 C of $S\mathit{C}_6H_5$], 124.7 [s, 1 C of $\mathit{C}_5H_4\{C(CH_3)_3\}$], 127.7 [d, $^1J_{C-H} = 157$, 2 C of $S\mathit{C}_6H_5$], 135.3 [d, $^1J_{C-H} = 157$, 2 C of $S\mathit{C}_6H_5$], 148.9 [s, 1 C of $S\mathit{C}_6H_5$].

Synthesis of $(Cp^{Bu^t})_2Mo(SePh)_2$

Method A: from $(Cp^{Bu^t})_2MoH_2$. A mixture of $(Cp^{Bu^t})_2MoH_2$ (300 mg, 0.88 mmol) and Ph_2Se_2 (605 mg, 1.94 mmol) in toluene (20 mL) was stirred for 6 days at 120 °C. After this period, the volatile components were removed, and the oily residue was washed with pentane (2 × 5 mL) and dried *in vacuo* to give $(Cp^{Bu^t})_2Mo(SePh)_2$ as an olive-green solid (340 mg, 59%).

Method B: from $(Cp^{Bu^t})_2Mo(CO)$. A mixture of $(Cp^{Bu^t})_2Mo(CO)$ (200 mg, 0.55 mmol) and Ph_2Se_2 (171 mg, 0.55 mmol) in toluene (10 mL) was stirred for 1 hour at room temperature. After this period, the volatile components were removed, and the residue obtained was washed with pentane (3 × 5 mL) and dried *in vacuo* to give $(Cp^{Bu^t})_2Mo(SePh)_2$ as an olive-green solid (230 mg, 65%). Analysis calcd. for $C_{30}H_{36}Se_2Mo$: C, 55.4%; H, 5.6%. Found: C, 55.3%; H, 5.6%. IR Data (KBr disk, cm^{-1}): 3087 (m), 3054 (m), 2961 (vs), 2902 (s), 2868 (s), 1573 (s), 1470 (vs), 1432 (s), 1395 (m), 1359 (s), 1295 (w), 1271 (s), 1190 (w), 1150 (s), 1065 (m), 1021 (s), 998 (w), 924 (m), 905 (m), 850 (s), 810 (s), 738 (vs), 694 (vs), 664 (s), 472 (s), 408 (m). ^{1}H NMR (C_6D_6): 0.77 [s, $C_5H_4\{C(C\mathit{H}_3)_3\}$], 4.76 [t, $^3J_{H-H} = 2.5$, 2 H of $C_5\mathit{H}_4\{C(CH_3)_3\}$], 5.20 [t, $^3J_{H-H} = 2.5$, 2 H of $C_5\mathit{H}_4\{C(CH_3)_3\}$], 7.02 [m, 3 H of $SeC_6\mathit{H}_5$], 7.82 [m, 2 H of $SeC_6\mathit{H}_5$]. ^{13}C NMR (C_6D_6): 31.2 [q, $^1J_{C-H} = 126$, $C_5H_4\{C(\mathit{C}H_3)_3\}$], 33.2 [s, $C_5H_4\{\mathit{C}(CH_3)_3\}$], 93.4 [d, $^1J_{C-H} = 183$, 2 C of $\mathit{C}_5H_4\{C(CH_3)_3\}$], 96.7 [d, $^1J_{C-H} = 177$, 2 C of $\mathit{C}_5H_4\{C(CH_3)_3\}$], 119.3 [s, 1 C of $\mathit{C}_5H_4\{C(CH_3)_3\}$], 125.8 [dt, $^1J_{C-H} = 159$, $^2J_{C-H} = 7$, 1 C of $Se\mathit{C}_6H_5$], 127.9 [dt, $^1J_{C-H} = 154$, $^2J_{C-H} = 7$, 2 C of $Se\mathit{C}_6H_5$], 137.5 [t, $^2J_{C-H} = 7$, 1 C of $Se\mathit{C}_6H_5$], 138.0 [dt, $^1J_{C-H} = 160$, $^2J_{C-H} = 7$, 2 C of $Se\mathit{C}_6H_5$]. ^{77}Se NMR (C_6D_6): −83 [s].

Synthesis of $(Cp^{Bu^t})_2Mo(TePh)_2$

A mixture of $(Cp^{Bu^t})_2Mo(CO)$ (100 mg, 0.27 mmol) and Ph_2Te_2 (112 mg, 0.27 mmol) in toluene (15 mL) was stirred for 1 hour at room temperature. After this period, the volatile components were removed and the residue obtained was washed with pentane (2 × 5 mL) and dried *in vacuo* to give $(Cp^{Bu^t})_2Mo(TePh)_2$ as a brown solid (140 mg, 69%). Analysis calcd. for $C_{30}H_{36}Te_2Mo$: C, 48.2%; H, 4.9%. Found: C, 48.2%; H, 5.0%. IR Data (KBr disk, cm^{-1}): 3056 (s), 2958 (vs), 2901 (s), 2866 (s), 1567 (m), 1464 (vs), 1428 (s), 1389 (m), 1362 (s), 1295 (m), 1267 (s), 1183 (w), 1149 (m), 1059 (m), 1015 (s), 912 (m), 883 (m), 834 (s), 796 (vs), 730 (vs), 695 (vs), 657 (m), 595 (w), 458 (s), 409 (m). ^{1}H NMR (C_6D_6): 0.74 [s, $C_5H_4\{C(C\mathit{H}_3)_3\}$], 4.69 [t, $^3J_{H-H} = 2.5$, 2 H of $C_5\mathit{H}_4\{C(CH_3)_3\}$], 5.03 [t, $^3J_{H-H} = 2.5$, 2 H of $C_5\mathit{H}_4\{C(CH_3)_3\}$], 6.92 [t, $^3J_{H-H} = 7$, 2 H of $TeC_6\mathit{H}_5$], 7.07 [t, $^3J_{H-H} = 7$, 1 H of $TeC_6\mathit{H}_5$], 8.00 [d, $^3J_{H-H} = 8$, 2 H of $TeC_6\mathit{H}_5$]. ^{13}C NMR (C_6D_6): 31.4 [q, $^1J_{C-H} = 126$, $C_5H_4\{C(\mathit{C}H_3)_3\}$], 32.7 [s, $C_5H_4\{\mathit{C}(CH_3)_3\}$], 88.0 [d, $^1J_{C-H} = 183$, 2 C of $\mathit{C}_5H_4\{C(CH_3)_3\}$], 91.3 [d, $^1J_{C-H} = 176$, 2 C of $\mathit{C}_5H_4\{C(CH_3)_3\}$], 113.3 [s, 1 C of $Te\mathit{C}_6H_5$], 116.9 [s, 1 C of $\mathit{C}_5H_4\{C(CH_3)_3\}$], 127.0 [dt, $^1J_{C-H} = 160$, $^2J_{C-H} = 8$, 1 C of $Te\mathit{C}_6H_5$], 128.1 [dd, $^1J_{C-H} = 158$, $^2J_{C-H} = 8$, 2 C of $Te\mathit{C}_6H_5$], 141.9 [dt, $^1J_{C-H} = 160$, $^2J_{C-H} = 7$, 2 C of $Te\mathit{C}_6H_5$]. ^{125}Te NMR (C_6D_6): −195 [s].

Reactivity of $(Cp^{Bu^t})_2Mo(TePh)H$ towards Ph_2Te_2

A mixture of $(Cp^{Bu^t})_2Mo(TePh)H$ (*ca.* 10 mg) and Ph_2Te_2 (*ca.* 10 mg) in C_6D_6 (1 mL) was heated at 120 °C. The sample was monitored by ^{1}H NMR spectroscopy, which demonstrated that no reaction had occurred after a period of 4 days.

Reactions of $(Cp^{Bu^t})_2Mo(EPh)_2$ (E = S, Se, Te) with MeI

A solution of $(Cp^{Bu^t})_2Mo(EPh)_2$ (E = S, Se, Te) (*ca.* 10 mg) in C_6D_6 (1 mL) was treated with excess MeI at room temperature. ^{1}H NMR spectroscopy was used to monitor the formation of $(Cp^{Bu^t})_2MoI_2$ (E = S, 1 day; E = Se, 2 hours; E = Te, 0.5 hours).

Synthesis of $[(Cp^{Bu^t})_2Mo(PhSMe)H]I$

A solution of $(Cp^{Bu^t})_2Mo(SPh)H$ (100 mg, 0.22 mmol) in C_6H_6 (10 mL) was treated with excess MeI (625 mg, 4.40 mmol) for 1 hour at room temperature, resulting in the formation of a brown precipitate. The mixture was filtered, and the precipitate was washed with toluene (2 × 5 mL) and pentane (2 × 5 mL) and dried *in vacuo* to give $[(Cp^{Bu^t})_2Mo(\eta^2\text{-}1\text{-}PhSMe)H]I$ as a brown solid (90 mg, 68%). Analysis calcd. for $C_{25}H_{35}ISMo$: C, 50.9%; H, 6.0%. Found: C, 50.4%; H, 5.5%. IR Data (KBr disk, cm^{-1}): 3057 (vs), 2964 (vs), 2870 (s), 1898 (w) [ν(Mo–H)], 1579 (w), 1485 (s), 1382 (s), 1271 (m), 1149 (m), 1080 (m), 1021 (m), 968 (m), 908 (m), 843 (m), 794 (s), 751 (s), 689 (m), 483 (w), 426 (w). ^{1}H NMR ($CDCl_3$): −8.80 [s, Mo–H], 1.18 [s, $C_5H_4\{C(C\mathit{H}_3)_3\}$], 2.81 [s, $C\mathit{H}_3SC_6H_5$], 4.44 [q, $^3J_{H-H} = 2.5$, 1 H of $C_5\mathit{H}_4\{C(CH_3)_3\}$], 4.52 [q, $^3J_{H-H} = 2.5$, 1 H of $C_5\mathit{H}_4\{C(CH_3)_3\}$], 5.30 [q, $^3J_{H-H} = 2.5$, 1 H of $C_5\mathit{H}_4\{C(CH_3)_3\}$], 5.79 [q, $^3J_{H-H} = 2.5$, 1 H of $C_5\mathit{H}_4\{C(CH_3)_3\}$], 7.30 [t, $^3J_{H-H} = 7$, 1 H of $CH_3SC_6\mathit{H}_5$], 7.33 [d, $^3J_{H-H} = 7$, 2 H of $CH_3SC_6\mathit{H}_5$], 7.42 [t, $^3J_{H-H} = 8$, 2 H of $CH_3SC_6\mathit{H}_5$]. ^{13}C NMR ($CDCl_3$): 29.6 [q, $^1J_{C-H} = 142$, $\mathit{C}H_3SC_6H_5$], 31.9 [q, $^1J_{C-H} = 127$, $C_5H_4\{C(\mathit{C}H_3)_3\}$], 32.0 [s, $C_5H_4\{\mathit{C}(CH_3)_3\}$], 79.5 [d, $^1J_{C-H} = 178$, 1 C of $\mathit{C}_5H_4\{C(CH_3)_3\}$], 79.7 [d, $^1J_{C-H} = 187$, 1 C of $\mathit{C}_5H_4\{C(CH_3)_3\}$], 89.4 [d, $^1J_{C-H} = 183$, 1 C of $\mathit{C}_5H_4\{C(CH_3)_3\}$], 94.7 [d, $^1J_{C-H} = 180$, 1 C of $\mathit{C}_5H_4\{C(CH_3)_3\}$], 127.1 [dt, $^1J_{C-H} = 160$, $^2J_{C-H} = 7$, 2 C of $CH_3S\mathit{C}_6H_5$], 128.7 [dt, $^1J_{C-H} = 163$, $^2J_{C-H} = 7$, 1 C of $CH_3S\mathit{C}_6H_5$], 129.7 [dd, $^1J_{C-H} = 164$, $^2J_{C-H} = 8$, 2 C of $CH_3S\mathit{C}_6H_5$], 133.2 [s, 1 C of $\mathit{C}_5H_4\{C(CH_3)_3\}$], 138.3 [t, $^2J_{C-H} = 9$, 1 C of $CH_3S\mathit{C}_6H_5$].

Synthesis of $[(Cp^{Bu^t})_2Mo(PhSeMe)H]I$

A solution of $(Cp^{Bu^t})_2Mo(SePh)H$ (115 mg, 0.23 mmol) in C_6H_6 (10 mL) was treated with excess MeI (330 mg, 2.32 mmol) for 1 hour at room temperature, resulting in the formation of a brown precipitate. The mixture was filtered, and the precipitate was washed with toluene (2 × 5 mL) and pentane (2 × 5 mL) and dried *in vacuo* to give $[(Cp^{Bu^t})_2Mo(PhSeMe)H]I$ as a brown solid (135 mg, 91%). Analysis calcd. for $C_{25}H_{35}ISeMo$: C, 47.1%; H, 5.5%. Found: C, 46.9%; H, 5.4%. IR Data (KBr disk, cm^{-1}): 3056 (vs), 2963 (vs), 2870 (s), 1895 (w) [ν(Mo–H)], 1578 (w), 1485 (vs), 1462 (s), 1381 (s), 1313 (w), 1272 (m), 1193 (w), 1149 (m), 1018 (s), 914 (s), 843 (m), 792 (s), 745 (s), 689 (m), 643 (w), 581 (w), 471 (m), 406 (w). ^{1}H NMR ($CDCl_3$): −9.12 [s, $^2J_{Se-H} = 14$, Mo–H], 1.20 [s, $C_5H_4\{C(C\mathit{H}_3)_3\}$], 2.67 [s, $C\mathit{H}_3SeC_6H_5$], 4.35 [br s, 1 H of $C_5\mathit{H}_4\{C(CH_3)_3\}$], 4.59 [br s, 1 H of $C_5\mathit{H}_4\{C(CH_3)_3\}$], 5.30 [very br, 1 H of $C_5\mathit{H}_4\{C(CH_3)_3\}$], 5.77 [br s, 1 H of $C_5\mathit{H}_4\{C(CH_3)_3\}$], 7.32 [d, $^3J_{H-H} = 7$, 2 H of $CH_3SeC_6\mathit{H}_5$], 7.38 [t, $^3J_{H-H} = 7$, 1 H of $CH_3SeC_6\mathit{H}_5$], 7.45 [t, $^3J_{H-H} = 7$, 2 H of $CH_3SeC_6\mathit{H}_5$]. ^{13}C NMR ($CDCl_3$): 19.8 [q, $^1J_{C-H} = 145$, $\mathit{C}H_3SeC_6H_5$], 31.6 [s, $C_5H_4\{\mathit{C}(CH_3)_3\}$], 31.8 [q, $^1J_{C-H} = 126$, $C_5H_4\{C(\mathit{C}H_3)_3\}$], 78.1 [br d, $^1J_{C-H} = 170$, 1 C of $\mathit{C}_5H_4\{C(CH_3)_3\}$], 79.8 [br d, $^1J_{C-H} = 180$, 1 C of $\mathit{C}_5H_4\{C(CH_3)_3\}$], 88.0 [d, $^1J_{C-H} = 182$, 1 C of $\mathit{C}_5H_4\{C(CH_3)_3\}$], 92.4 [br d, $^1J_{C-H} = 172$, 1 C of $\mathit{C}_5H_4\{C(CH_3)_3\}$], 128.5 [dt, $^1J_{C-H} = 163$, $^2J_{C-H} = 7$, 2 C of $CH_3Se\mathit{C}_6H_5$], 129.0 [dt, $^1J_{C-H} = 163$, $^2J_{C-H} = 7$, 1 C of $CH_3Se\mathit{C}_6H_5$], 129.6 [dd, $^1J_{C-H} = 163$, $^2J_{C-H} = 7$, 2 C of $CH_3Se\mathit{C}_6H_5$], 131.6 [s, 1 C of $\mathit{C}_5H_4\{C(CH_3)_3\}$], 131.8 [s, 1 C of $CH_3Se\mathit{C}_6H_5$]. ^{77}Se NMR ($CDCl_3$): 244 [s].

Synthesis of $[(Cp^{Bu^t})_2Mo(PhTeMe)H]I$

A solution of $(Cp^{Bu^t})_2Mo(TePh)H$ (65 mg, 0.12 mmol) in C_6H_6 (10 mL) was treated with excess MeI (511 mg, 3.60 mmol) for 2 hours at room temperature, resulting in the formation of a brown precipitate. The mixture was filtered, and the residue was washed with toluene (2 × 5 mL) and pentane (2 × 5 mL) and dried *in vacuo* to give $[(Cp^{Bu^t})_2Mo(PhTeMe)H]I$ as a brown solid (75 mg, 92%). Analysis calcd. for $C_{25}H_{35}ITeMo$: C, 43.8%; H, 5.1%. Found: C, 43.5%; H, 5.1%. IR Data (KBr disk, cm^{-1}): 3051 (vs), 2963 (vs), 2870 (s), 1893 (w) [ν(Mo–H)], 1620 (w), 1573 (w), 1484 (vs), 1434 (s), 1382 (s), 1270 (s), 1192 (m), 1148 (m), 1018 (s), 916 (s), 843 (s), 794 (s), 740 (s), 690 (m), 624 (w), 518 (w), 460 (m), 407 (w). ^1H NMR ($CDCl_3$): −9.39 [s, $^2J_{Te\text{-}H} = 38$, Mo-*H*], 1.08 [s, 9 H, 1 Bu^t of 2 $C_5H_4\{C(C\mathit{H}_3)_3\}$], 1.25 [s, 9 H, 1 Bu^t of 2 $C_5H_4\{C(C\mathit{H}_3)_3\}$], 2.48 [s, $C\mathit{H}_3TeC_6H_5$], 4.38 [q, $^3J_{H\text{–}H} = 3$, 1 H of 2 $C_5\mathit{H}_4\{C(CH_3)_3\}$], 4.47 [q, $^3J_{H\text{–}H} = 3$, 1 H of 2 $C_5\mathit{H}_4\{C(CH_3)_3\}$], 4.80 [q, $^3J_{H\text{–}H} = 2$, 1 H of 2 $C_5\mathit{H}_4\{C(CH_3)_3\}$], 4.82 [q, $^3J_{H\text{–}H} = 2$, 1 H of 2 $C_5\mathit{H}_4\{C(CH_3)_3\}$], 5.14 [q, $^3J_{H\text{–}H} = 3$, 1 H of 2 $C_5\mathit{H}_4\{C(CH_3)_3\}$], 5.45 [q, $^3J_{H\text{–}H} = 2$, 1 H of 2 $C_5\mathit{H}_4\{C(CH_3)_3\}$], 5.50 [q, $^3J_{H\text{–}H} = 3$, 1 H of 2 $C_5\mathit{H}_4\{C(CH_3)_3\}$], 5.58 [q, $^3J_{H\text{–}H} = 2$, 1 H of 2 $C_5\mathit{H}_4\{C(CH_3)_3\}$], 7.37 [m, 5 H of $CH_3SC_6\mathit{H}_5$]. ^{13}C NMR ($CDCl_3$): −2.7 [q, $^1J_{C\text{–}H} = 137$, $\mathit{C}H_3TeC_6H_5$], 31.4 [s, 1 C of 2 $C_5H_4\{\mathit{C}(CH_3)_3\}$], 31.5 [s, 1 C of 2 $C_5H_4\{\mathit{C}(CH_3)_3\}$], 31.8 [q, $^1J_{C\text{–}H} = 126$, 3 C of 2 $C_5H_4\{C(\mathit{C}H_3)_3\}$], 32.0 [q, $^1J_{C\text{–}H} = 127$, 3 C of 2 $C_5H_4\{C(\mathit{C}H_3)_3\}$], 75.7 [d, $^1J_{C\text{–}H} = 188$, 1 C of 2 $\mathit{C}_5H_4\{C(CH_3)_3\}$], 76.9 [d, $^1J_{C\text{–}H} = 182$, 1 C of 2 $\mathit{C}_5H_4\{C(CH_3)_3\}$], 80.6 [d, $^1J_{C\text{–}H} = 178$, 1 C of 2 $\mathit{C}_5H_4\{C(CH_3)_3\}$], 80.8 [d, $^1J_{C\text{–}H} = 178$, 1 C of 2 $\mathit{C}_5H_4\{C(CH_3)_3\}$], 85.9 [d, $^1J_{C\text{–}H} = 182$, 1 C of 2 $\mathit{C}_5H_4\{C(CH_3)_3\}$], 86.1 [d, $^1J_{C\text{–}H} = 181$, 1 C of 2 $\mathit{C}_5H_4\{C(CH_3)_3\}$], 87.3 [d, $^1J_{C\text{–}H} = 176$, 1 C of 2 $\mathit{C}_5H_4\{C(CH_3)_3\}$], 87.4 [d, $^1J_{C\text{–}H} = 176$, 1 C of 2 $\mathit{C}_5H_4\{C(CH_3)_3\}$], 114.1 [s, 1 C of 2 $\mathit{C}_5H_4\{C(CH_3)_3\}$], 129.3 [s, 1 C of $CH_3Te\mathit{C}_6H_5$], 129.4 [s, 1 C of 2 $\mathit{C}_5H_4\{C(CH_3)_3\}$], 129.6 [d, $^1J_{C\text{–}H} = 161$, 1 C of $CH_3Te\mathit{C}_6H_5$], 129.9 [d, $^1J_{C\text{–}H} = 162$, 2 C of $CH_3Te\mathit{C}_6H_5$], 133.0 [d, $^1J_{C\text{–}H} = 161$, 2 C of $CH_3Te\mathit{C}_6H_5$]. ^{125}Te NMR ($CDCl_3$): 547 [s].

X-Ray structure determinations

X-Ray diffraction data for $(Cp^{Bu^t})_2MoH_2$ were collected on a Bruker P4 diffractometer equipped with a SMART CCD detector; data for all other complexes were collected using a Siemens P4 diffractometer. Crystal data, data collection and refinement parameters are summarized in Table 5. The structures were solved using direct methods and standard difference map techniques, and were refined by full-matrix least-squares procedures using SHELXTL.[82] Hydrogen atoms on carbon were included in calculated positions.

CCDC reference numbers 161663–161678.

See http://www.rsc.org/suppdata/dt/b1/b100372k/ for crystallographic data in CIF or other electronic format.

Summary

A study of the *tert*-butylmolybdenocene dihydride system has resulted in the synthesis of a series of complexes which include: (*i*) alkyl, hydride, and halide complexes, (*ii*) adducts, $(Cp^{Bu^t})_2MoL$ (L = CO, C_2H_4, C_2H_2, MeCN, PMe_3), (*iii*) iminoacyl complexes $[(Cp^{Bu^t})_2Mo(\eta^2\text{-}MeC{=}NR)]^+$ (R = Me, Et), (*iv*) chalcogenido complexes, $(Cp^{Bu^t})_2MoO$, $[(Cp^{Bu^t})_2Mo(\mu\text{-}E)]_2$, and $(Cp^{Bu^t})_2Mo(\eta^2\text{-}E_2)$ (E = S, Se, Te), (*v*) chalcogenolate complexes, $(Cp^{Bu^t})_2Mo(EPh)H$ and $(Cp^{Bu^t})_2Mo(EPh)_2$ (E = S, Se, Te), and (*vi*) chalcogenoether complexes, $[(Cp^{Bu^t})_2Mo(PhEMe)H]I$ (E = S, Se, Te). Of particular note, the iminoacyl complexes $[(Cp^{Bu^t})_2Mo(\eta^2\text{-}MeC{=}NR)]^+$ are obtained by alkylation of the nitrogen atom of the coordinated acetonitrile, a rather uncommon transformation. Finally, ^1H NMR spectroscopy indicates that the barrier to inversion at the chalcogen in the coordinated chalcogenoether complexes $[(Cp^{Bu^t})_2Mo(PhEMe)H]$ increases in the sequence S < Se < Te.

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70 The position of the broad signal was identified by integration of this region of the spectrum. Also, this signal sharpened as the temperature was raised.

71 It should be noted that the ^1H NMR spectrum of the cyclopentadienyl analogue $[Cp_2Mo(PhTeMe)H]I$ also indicates that the two Cp ligands are inequivalent. $[Cp_2Mo(PhTeMe)H]I$

was prepared by the reaction $Cp_2Mo(TePh)H$ with MeI. ^1H NMR($CDCl_3$) for $[Cp_2Mo(PheMe)H]I$: 7.53 (m, 5H), 5.35 (s, 5H), 5.31 (s, 5H), 2.61 (s, 3H), −9.35 (s, 1H, $^2J_{Te-H} = 47$ Hz).

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