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Controlled nucleophilic activation of different sites in $[Mo_2Cp_2L_2(\mu\text{-}SMe)_2(\mu\text{-}L')]^+$ cations (L = Bu^{t}NC, xylNC, CO; L′ = SMe or PPh_2)

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Abstract

The thiolato-bridged binuclear molybdenum complexes $[Mo_2Cp_2L_2(\mu\text{-}SMe)_2(\mu\text{-}L')]Y$ (Cp = η^5-C_5H_5; L′ = SMe, L = Bu^{t}NC (**1a**), xylNC (**1b**) or CO (**3**); L′ = PPh_2, L = Bu^{t}NC (**16**); Y = BF_4, Cl) react with the anionic reagents $NaBH_4$, $NaBD_4$, LiR (R = Me, Bu^n), R′MgCl (R′ = Me, Pr^i, Bu^n or Ph). The products are unsubstituted (**5**, **7**) or substituted (**8**–**12**) η^4-cyclopentadiene derivatives, $[Mo_2(\eta^5\text{-}C_5H_5)(\eta^4\text{-}C_5H_5R)L_2(\mu\text{-}SMe)_3]$ (L = xylNC, CO), or μ-formimidoyl dinuclear products, $[Mo_2Cp_2L_2(\mu\text{-}SMe)_2(\mu\text{-}L')(\mu\text{-}CHNR)]$ (L′ = SMe, L = Bu^{t}NC (**4**) or xylNC (**6**); L′ = PPh_2, L = Bu^{t}NC (**17**)). Since the reduced dinuclear species $[Mo_2Cp_2(CO)_2(\mu\text{-}SMe)_2]$ and the related oxo-compound $[Mo_2Cp_2(CO)(O)(\mu\text{-}SMe)_2]$ are sometimes isolated as minor products, the anionic reagent can play a secondary role as a reductant in these reactions in addition to its main role as a nucleophile. The electronic properties of the donor carbon atoms of the cyclopentadienyl rings and of the terminal ligands L, together with the nature of the anionic reagent, are the dominant factors controlling selective formation of **4**–**12** and **17**. Tetrafluoroboric acid reacts with the substituted cyclopentadiene derivatives **9**, **11** and **12** to form new functionalised cyclopentadienyl derivatives, $[Mo_2(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4R)(CO)_2(\mu\text{-}SMe)_3](BF_4)$ (R = Me (**13**), Bu^n (**14**) or Ph (**15**)). New complexes have been characterised by spectroscopic and chemical methods, supplemented for **5**, **6** and **12** by X-ray diffraction studies at 100 K.

Keywords: Dimolybdenum complexes; Cyclopentadienyl; Cyclopentadiene; Thiolato-bridged complexes; Crystal structure; Isocyanide liagand; Carbonyl ligand; Formyl ligand; Nucleophilic activation

1. Introduction

Nucleophilic addition to the coordinatively saturated metal ions in $[M_2Cp_2L_2L'_n]Y$ complexes (M = transition metal; Cp = η^5-C_5H_5; L = terminal two electron-donor ligand; L′ = bridging three electron-donor ligand; Y = anion) can lead to scission of the M–M bond. Alternatively, the unsaturated ligands offer several sites at which reaction can occur. In addition, with poly(μ-thiolato) complexes, where L′ = SMe for example, there is the further possibility of C–S bond cleavage promoted by nucleophilic attack [1]. The extent to which these reactions are selective depends to a large extent on the relative Lewis acidities of the metal and ligand sites.

These comments are prompted in part by our earlier study of the action of various nucleophiles on the cations $[Mo_2Cp_2L_2(\mu\text{-}SMe)_3]^+$ (L = RNC (**1**), MeCN

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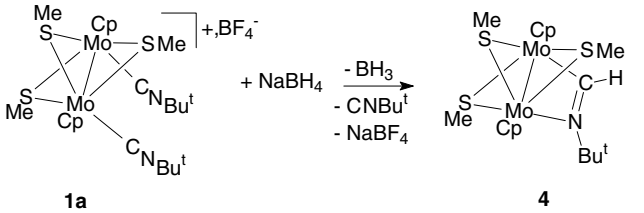
(**2**) or CO (**3**)). Thus, we have shown that **2** reacts with $NaBH_4$ to yield two products: substitution of both terminal MeCN ligands leads to the μ-borohydride derivative $[Mo_2Cp_2(\mu\text{-}BH_4)(\mu\text{-}SMe)_3]$, whereas nucleophilic addition of hydride to one of the nitrile ligands gives the μ-azavinylidene compound $[Mo_2Cp_2(\mu\text{-}N{=}CHMe)(\mu\text{-}SMe)_3]$ [2]. In addition, nucleophilic attack on **1a** (R = Bu^t) by $LiBu^n$ is directed at an isocyanide ligand, subsequent dealkylation giving rise to the terminal cyanide ligand in the product complex $[Mo_2Cp_2(CN)(Bu^tNC)(\mu\text{-}SMe)_3]$ [3].

We now report an extension of these studies on the reactivity of $[M_2Cp_2L'_2(\mu\text{-}SMe)_2(\mu\text{-}L')]^+$ cations. Reactions of $[Mo_2Cp_2L_2(\mu\text{-}SMe)_3]Y$ (L = Bu^tNC (**1a**) [3], xylNC (**1b**) or CO (**3**) [4]; Y = BF_4,Cl) with $NaBH_4$, $LiBu^n$, R′MgCl (R′ = Me, Pr^i, Bu^n, Ph) are first described. Selectivity in these reactions is controlled by varying both the ligands L attached terminally to the Mo(III) centres and the strength of the nucleophile. A rough affinity order is established by determining whether a Cp ring atom or terminal L ligand is the site for nucleophilic addition. The influence of the three-electron-donor μ-L′ ligand on the reactivity of nucleophiles towards $[M_2Cp_2L_2L'_n]^+$ cations has also been assessed by examining the chemistry of the species obtained when one of the μ-thiolate groups in **1a** is replaced by a μ-phosphido ligand. Finally, we have tested the reaction of electrophiles with the η^4-cyclopentadiene derivatives previously obtained by nucleophilic addition.

2. Results

2.1. Reaction of *1a* with $NaBH_4$: synthesis and characterisation of *4*

Treatment of a red solution of **1a** under reflux in acetonitrile with 4.0 equivalents of sodium borohydride over 3 h led to a maroon solution in which only two organometallic products were detected by ^1H NMR analysis. Substantial quantities (70%) of starting compound **1a** were recovered. However, chromatography of the diethyl ether extract produced a new derivative **4** in low yield (~15%) as an orange, analytically pure solid (Reaction (1)). The yield was not improved when the reaction was carried out either for a prolonged time in acetonitrile or under reflux in tetrahydrofuran.

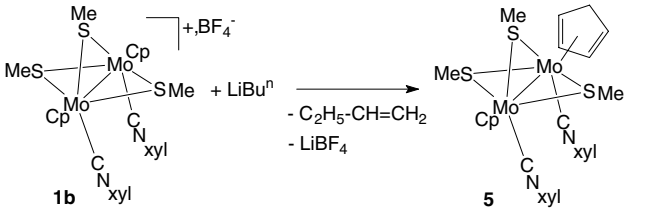


(1)

Formation of **4** requires addition of hydride to an isocyanide carbon atom, thereby generating a formimidoyl ligand which then displaces the second isocyanide. This reaction is driven by the ability of the formimidoyl ligand to participate in a Mo_2CN ring. We previously described the formation of a related μ-formimidoyl dimolybdenum compound $[Mo_2Cp_2(\mu\text{-}SMe)_2(\mu\text{-}PPh_2)(\mu\text{-}CH{=}NBu^t)]$ by the reaction of $[Mo_2Cp_2(\mu\text{-}SMe)_2\ (\mu\text{-}H)(\mu\text{-}PPh_2)]$ with Bu^tNC via the insertion of isonitrile into an Mo–H bond [2]. In Section 2.3, we will show that $[Mo_2Cp_2(\mu\text{-}SMe)_3(\mu\text{-}CH{=}Nxyl)]$ (**6**) is obtained in a way similar to its close analogue **4** by reaction of $[Mo_2Cp_2(\mu\text{-}SMe)_3(xylNC)_2](BF_4)$ (**1b**) with $NaBH_4$. Although crystals of **4** proved unsuitable for a diffraction study, the complex was successfully characterised from analytical and NMR data. The latter show obvious parallels with those of $[Mo_2Cp_2(\mu\text{-}SMe)_2(\mu\text{-}PPh_2)(\mu\text{-}CH{=}NBu^t)]$ and the related dimanganese species $[Mn_2(CO)_6(\mu\text{-}H)(\mu\text{-}Ph_2PCH_2PPh_2)(\mu\text{-}CH{=}N\text{–}C_6H_4\text{-}Me\text{-}4)]$ [2,5]. The ^1H NMR spectra indicate that the solution contains two isomeric forms of the complex, **4a** and **4b**, in 3:1 ratio. The isomers appear to differ only in the orientation (*syn* or *anti*) of the two in-plane "Mo_2S_2" bridging SMe groups. They were inseparable by conventional chromatographic techniques. The presence of a three electron-donor, bridging formimidoyl ligand ($HC{=}NBu^t$) in **4** is mainly supported by the observation of one resonance ($\delta \sim 230$), at low field in the carbene range, corresponding to a carbon atom attached to an H nucleus. This was established by an HMQC ^1H–^{13}C experiment which showed clearly that carbon atoms at $\delta \sim 230$ correlate with hydrogen atoms detected at low field ($\delta \sim 10.6$) in the region typical for formimidoyl protons [5,6]. The results of ^1H–^{15}N correlation NMR experiments are in accord with these assignments. Moreover, both ^1H and ^{13}C NMR spectra exhibit peaks which can be attributed to two inequivalent cyclopentadienyl ligands in agreement with the unsymmetrical geometry proposed for **4**. Finally, NMR spectra show the sets of resonances expected for the $\{Mo_2Cp_2(\mu\text{-}SMe)_3\}$ core and for the Bu^t group.

2.2. Reaction of *1b* with $LiBu^n$: synthesis and molecular structure of *5*

Treatment of a dichloromethane solution of $[Mo_2Cp_2(MeCN)_2(\mu\text{-}SMe)_3](BF_4)$ [7] with excess xylNC at room temperature afforded $[Mo_2Cp_2(xylNC)_2(\mu\text{-}SMe)_3](BF_4)$ (**1b**) as a brown solid in 81% yield. The formulation of **1b** was deduced from the analytical and NMR data (see Section 5). Addition of $LiBu^n$ to **1b** led to the formation of a new compound **5** (Reaction (2)).



(2)

n-Butene is a product of this reaction but no effort was made to detect this volatile species. The ^{1}H NMR spectra of $CDCl_3$ solutions of product taken after reaction was complete indicated that there had been essentially quantitative conversion of **1b** into **5**. Complex **5** was isolated in analytically pure form with a recovered yield of 65%. On the basis of ^{1}H and $^{13}C\{^1H\}$ NMR data **5** was identified as a cyclopentadiene complex arising from hydride addition to a cyclopentadienyl ligand. The ^{1}H NMR spectrum shows evidence for two isomers in the 6.5/1 ratio. These may correspond to *syn* and *anti* orientations of the two in-plane thiolate methyl groups.

The ^{1}H NMR spectrum of the major isomer **5a** shows a singlet for the unchanged cyclopentadienyl ligand (5.17 ppm) and four multiplets for the four vinyl hydrogen atoms of the cyclopentadiene ring (4.91, 4.62, 3.31 and 3.25 ppm). An AB pattern centered at 3.45 ppm is assigned to the geminal hydrogen atoms. The $^{13}C\{^1H\}$ NMR spectrum accords with the formulation proposed according to the ^{1}H NMR data. A second NMR pattern of similar but less intense resonances is assigned to the minor isomer **5b**.

This formulation of **5** as a η^4-cyclopentadiene complex is consistent with X-ray analysis of single crystals obtained from a cooled pentane solution (see Section 5 and Tables 1 and 3). The molecular skeleton (Fig. 1) contains similar (η^4-C_5H_6)Mo(xylNC) and (η^5-C_5H_5)Mo(xylNC) units linked directly by an Mo–Mo bond of 2.797(1) Å and indirectly by three μ-SMe groups. The coordination geometry around each Mo atom is that of a distorted square pyramid, with three sulfur atoms and one isocyanide carbon atom in the basal plane and the centroid of either the η^4-cyclopentadiene or η^5-cyclopentadienyl ring at the apical position. The S(2) and S(3) methyl groups adopt an *anti* orientation relative to the $Mo_2S(2)S(3)$ plane. The aromatic rings of the xylNC ligands are nearly parallel [dihedral angle 8.1(5)°]. Departures from linear coordination at C(4) and C(5) and more especially at N(1) and N(2) [C–N–C = 162(1)° and 168(1)°] ensure that there are no short intramolecular contacts between these rings and give support to the

Table 1
Selected distances and angles (Å and °) in the η^4-C_5H_4R complexes **5** (R = H) and **12** (R = Ph)

	5 – Mo(1)	**5** – Mo(2)	**12A**	**12B**
(a) Bond lengths in the (η^4-C_5H_4R)-MoL(μ-SMe)$_3$ units, L = CNPh (**5**), CO (**12**)				
Mo–L	2.005(7)	2.043(7)	1.951(4)	1.966(3)
Mo–C(9)	2.240(10)	2.265(10)	2.262(3)	2.205(3)
Mo–C(8)	2.229(9)	2.259(9)	2.273(3)	2.231(3)
Mo–C(10)	2.364(11)	2.316(10)	2.308(4)	2.362(4)
Mo–C(7)	2.340(9)	2.330(11)	2.308(4)	2.405(4)
Mo–C(6)	2.712(10)	2.520(9)	2.844(4)	2.926(4)
Mo–S(2)	2.456(2)	2.474(2)	2.493(1)	2.440(1)
Mo–S(3)	2.450(2)	2.479(2)	2.454(1)	2.464(1)
Mo–S(1)	2.516(2)	2.489(2)	2.561(1)	2.546(1)
Mo–Mo	2.797(1)		2.773(1)	2.755(1)
C(6)–C(10)	1.442(13)	1.409(12)	1.516(5)	1.518(5)
C(6)–C(7)	1.438(13)	1.442(13)	1.534(5)	1.528(5)
C(7)–C(8)	1.445(12)	1.414(13)	1.402(5)	1.403(5)
C(8)–C(9)	1.426(13)	1.436(12)	1.444(5)	1.456(5)
C(9)–C(10)	1.389(13)	1.423(12)	1.404(5)	1.410(5)
C(6)–C(Ph)			1.519(5)	1.530(5)
(b) Other bond lengths in **12**				
Mo(2)–CO	1.984(4)–1.994(4)		Mo(2)–S	2.460(1)–2.488(1)
C(Cp)–C(Cp)	1.403(5)–1.433(5)		Mo(2)–C(Cp)	2.260(4)–2.379(3)
	5 – Ring A	**5** – Ring B	**12A**	**12B**
(c) Endocyclic η^4-C_5H_4R ring torsion angles: $\tau(i,j)$ is the C–C(i)–C(j)–C torsion angle				
τ(6,7)	22.8(10)	−10.9(12)	33.7(3)	32.4(4)
τ(7,8)	−15.0(11)	6.0(12)	−23.2(4)	−21.5(4)
τ(8,9)	0.8(12)	1.2(11)	0.7(4)	−0.6(4)
τ(9,10)	13.9(13)	−8.3(11)	22.4(4)	22.6(4)
τ(6,10)	−22.8(12)	11.7(12)	−33.3(3)	−32.6(3)

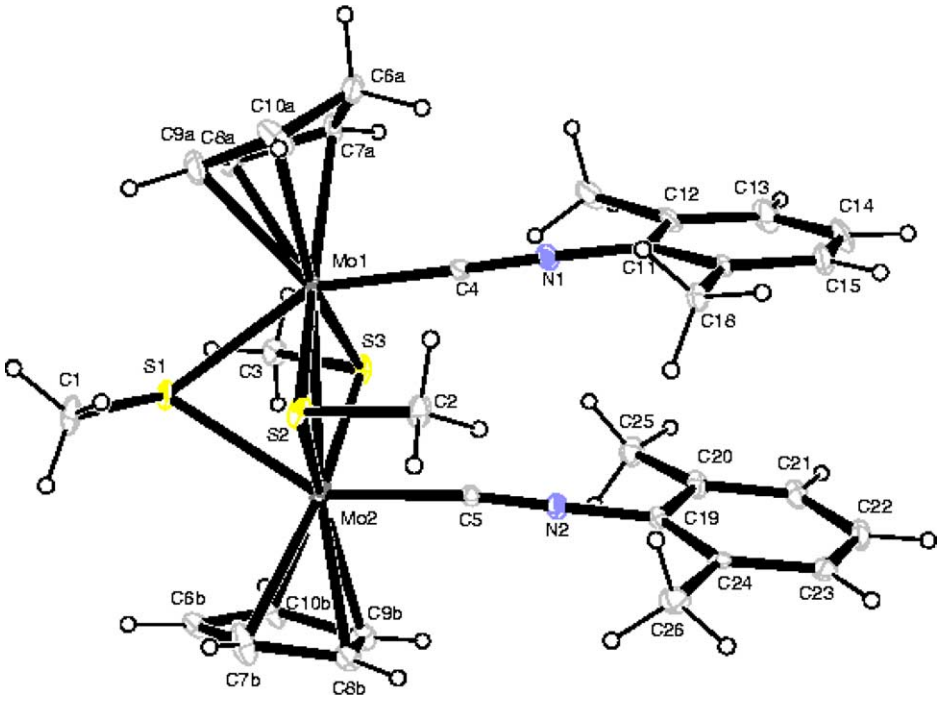


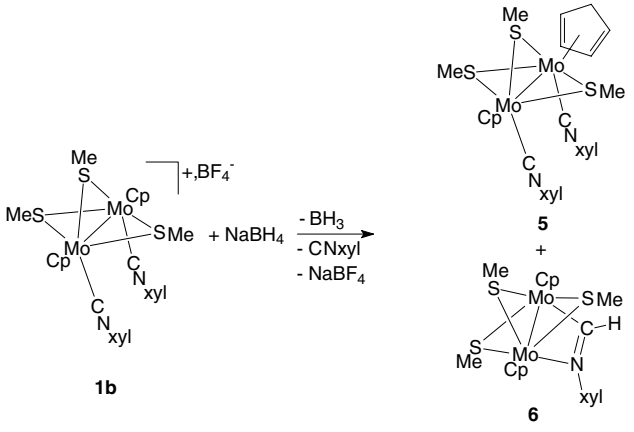
Fig. 1. A view of the structure of **5**. Here and elsewhere 20% probability ellipsoids are shown. There is a ca. 2:1 disorder of the π-rings: Ring A (C6a–C10a) is predominantly η^4-C_5H_6 whereas Ring B (C6b–C10b) is mainly η^5-C_5H_5. Note that a consistent atom numbering scheme is used for **5** and for both rotamers of **12**.

unexpected very low C–N stretches in IR spectrum (see Section 5).

In Section 2.5, the η^4-cyclopentadiene–Mo interactions in **5** and in the related complex **12** will be compared both with each other and with previously characterised [8,9] η^4-C_5R_6 complexes. Here, we anticipate this discussion to note that in **5** there is a roughly 2:1 disorder of the η^4-C_5H_6 and η^5-C_5H_5 rings: Ring A bonded to Mo(1) is predominantly but not exclusively η^4-C_5H_6 and Ring B attached to Mo(2) is mainly η^5-C_5H_5.

2.3. Reaction of *1b* with $NaBH_4$ and Bu^nMgCl: synthesis of *5* and *6*; structure of *6*

Complex **5** was also prepared by reacting **1b** with sodium borohydride in tetrahydrofuran under reflux. Though **5** was the major product of the reaction, approximately 12% of the material was converted into the neutral formimidoyl compound **6**. It is presumed that displaced xylNC is a by-product in the formation of complex **6** (Reaction (3)). Although the neutral derivatives **5** and **6** were difficult to separate, **6** was obtained in pure form, as shown below. Compound **5** was identified by comparing the ^{1}H NMR spectrum of a solution of the two products **5** and **6** of Reaction (3) with that of a pure sample of **5** obtained by the method described in Section 2.2.



(3)

When the reagents **1b** and $NaBH_4$ were heated in tetrahydrofuran at 120 °C in a sealed tube dipped into an oil-bath, complexes **5**, **6** and the known compound $[Mo_2Cp_2(\mu\text{-}SMe)_4]$ [10] were formed; they were detected in about 1:4:1.75 ratio by ^{1}H NMR spectroscopy of the crude products. Work-up of these products gave, after chromatography on silica gel, a mixture of compounds **6** and $[Mo_2Cp_2(\mu\text{-}SMe)_4]$ in about equimolar amounts. Complex **6** was then isolated in pure form as red crystals by recrystallization from a cooled CH_2Cl_2/pentane (1:1) solution of the above mixture.

^{1}H NMR spectroscopy showed that in solution **6** is present in only one isomeric form. The spectrum of **6**

exhibits the sets of resonances expected for the $\{Mo_2Cp_2(\mu\text{-}SMe)_3\}$ core and for the xyl group (see Section 5). A singlet detected at low field (δ 10.40) is typical of a formimidoyl proton [5,6]. The presence of two resonances at 5.29 and 5.02 ppm assigned to the two cyclopentadienyl ligands accords with the unsymmetrical geometry proposed for **6**. These conclusions were confirmed by an X-ray analysis of a single crystal of **6** (see Fig. 2 and Tables 2 and 3). The molecule contains two CpMo fragments which are bridged by three thiolates and by a formimidoyl ligand derived by protonation of an isocyanide ligand. As expected, the Mo–Mo distance [2.681(1) Å] in the quadruply-bridged complex **6** is somewhat shorter than that in the triply-bridged derivative **5** [2.797(1) Å]. The Mo–C(Cp) and Mo–S distances [respective ranges 2.224(5)–2.384(5) and 2.449(1)–2.482(1) Å] show no unusual features. As in **5**, there is an *anti* orientation of the S(1) and S(2) methyl groups relative to the $Mo_2S(1)S(2)$ plane. The four-membered Mo(2)–N(1)–C(4)–Mo(1) ring system is essentially planar, with an internal torsion angle across N(1)–C(4) of 0.9(4)°. The formimidoyl unit thus displays the $\mu\text{-}\eta^2$ coordination mode typical of formimidoyl, imino and diazenido ligands in transition metal complexes [11]. It is, therefore, a 3e donor. This contrasts strongly with its mode of coordination in the only other structurally characterised formimidoyl dimolybdenum derivative, $[Mo_2Cp_2(CO)_2(\mu\text{-}Pcy_2)(\mu\text{-}CHNBu^t)]$ [12], where the C–N axis is perpendicular to the Mo–Mo vector. These different orientations may be a result of orbital requirements but a steric interpretation appears more likely. Steric factors may also explain the weakness of the Mo(2)–N(1) bond in **6**: its length is appreciably greater [cf. 2.223(4) and 2.096(4) Å] than that of the corresponding bond in the isoelectronic diazenido species $[Mo_2Cp_2(\mu\text{-}SMe)_3(\mu\text{-}\eta^2\text{-}N{=}NMe)]$ which has otherwise, apart from *syn*-SMe groups, a

Table 2
Selected distances (Å) and angles (°) for compound **6**

Bonds lengths (Å)	
Mo(1)–Mo(2)	2.681(1)
Mo(1)–S(1)	2.451(1)
Mo(1)–S(2)	2.445(1)
Mo(1)–S(3)	2.474(1)
Mo(1)–C(4)	2.088(5)
N(1)–C(4)	1.312(7)
Mo–C(Cp)	2.224(5)–2.384(5)
Mo(2)–S(1)	2.449(1)
Mo(2)–S(2)	2.482(1)
Mo(2)–S(3)	2.469(1)
Mo(2)–N(1)	2.223(4)
N(1)–C(31)	1.434(6)
Bonds angles (°)	
C(4)–N(1)–Mo(2)	100.7(3)
C(4)–N(1)–Mo(31)	122.7(4)
C(4)–Mo(1)–Mo(2)	70.2(1)
C(31)–N(1)–Mo(2)	135.7(3)
Mo(1)–C(4)–N(1)	116.6(4)
N(1)–Mo(2)–Mo(1)	72.5(1)
Torsion angles (°)	
C(4)–Mo(1)–Mo(2)–S(1)	−83.9(2)
C(4)–Mo(1)–Mo(2)–S(2)	91.3(2)
C(4)–N(1)–C(31)–C(32)	−51.8(7)
C(4)–Mo(1)–Mo(2)–S(3)	−177.8(2)
Mo(2)–N(1)–C(4)–Mo(1)	0.9(4)

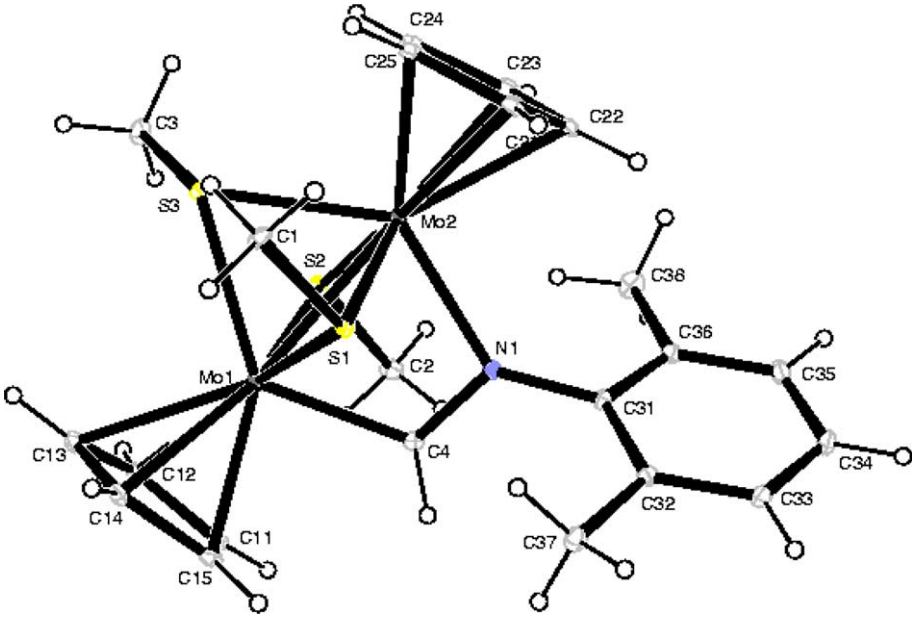


Fig. 2. A view of the structure of **6**.

Table 3
Crystallographic data at 100 K for compounds **5**, **6**, and **12**

	5	**6**	**12**
Empirical formula	$C_{31}H_{38}Mo_2N_2S_3$	$C_{22}H_{29}Mo_2NS_3$	$C_{21}H_{24}Mo_2O_2S_3$
Formula weight	726.69	595.52	596.46
Crystal system	Monoclinic	Triclinic	Triclinic
Space group	$C2/c$	$P\bar{1}$	$P\bar{1}$
a (Å)	33.2989(3)	8.0034(3)	13.2107(4)
b (Å)	8.2747(1)	8.4263(3)	13.2740(4)
c (Å)	23.0429(2)	17.4782(6)	13.9111(5)
α (°)		80.375(3)	103.318(2)
β (°)	108.764(1)	77.039(2)	104.903(2)
γ (°)		77.608(2)	102.334(2)
V (Å^3)	6011.8(1)	1113.1(1)	2195.3(1)
Z	8	2	4
ρ_{calc} (Mg mm^{-3})	1.606	1.777	1.805
μ (mm^{-1})	1.067	1.417	1.443
Crystal size (mm)	$0.35 \times 0.32 \times 0.08$	$0.25 \times 0.10 \times 0.10$	$0.43 \times 0.10 \times 0.09$
Range of θ (°)	1.9–27.5	2.7–30.0	1.7–28.6
Reflections measured	34906	11422	30713
R_{int}	0.049	0.035	0.054
Unique data/parameters	6799/343	6011/258	10531/523
$R(F)$, $wR(F^2)$ (all data)	0.091, 0.190	0.056, 0.134	0.057, 0.099
Goodness-of-fit on F^2	1.36	1.16	1.04
$\|\Delta\rho\|$ maximum (e/Å^3)	1.96	2.62	1.31

$\{Mo_2Cp_2(\mu\text{-}SMe)_3(\mu\text{-}\eta^2\text{-}L)\}$ core strikingly similar to that of **6** [11g]. The formimidoyl function in **6** also shows an interesting difference from other structurally characterised imino complexes [11–13]: it displays extensive delocalization of electrons along the Mo–C(4)–N(1) chain, as is evident from the sequence of distances 2.088(5) and 1.312(7) Å. The former distance is in the range for typical of Mo–C(carbenes) [14], while the latter indicates a C–N bond order of ~1.5 [15]. These results suggest that C(4) has a significant amount of carbene-like character, so that **6** is best represented as a hybrid based on the canonical forms I and II (Chart 1). Finally, ^{1}H and ^{13}C{^{1}H} NMR data for **6** are in accord with this formulation. In particular, the Mo-bound C(4) atom of the formimidoyl moiety appears at low field in the ^{13}C NMR spectrum, as it does in the spectra of closely related bimetallic compounds $[Mo_2Cp_2(\mu\text{-}SMe)_3(\mu\text{-}CH{=}NBu^t)]$ (**4**) (δ 233.3 and 230.0) [see Section 2.1], $[Mo_2Cp_2(\mu\text{-}SMe)_2(\mu\text{-}PPh_2)(\mu\text{-}CH{=}NBu^t)]$ (**17**) (δ 232.5) [2] and $[Mn_2(CO)_6(\mu\text{-}H)(\mu\text{-dppm})(\mu\text{-}CH{=}Np\text{-tolyl})]$ (δ 241.2) [5], none of which have been structurally characterised by X-ray analysis.

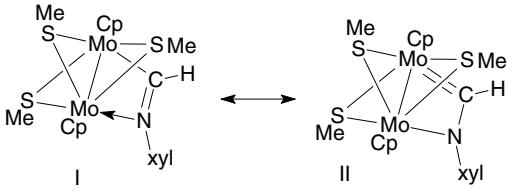
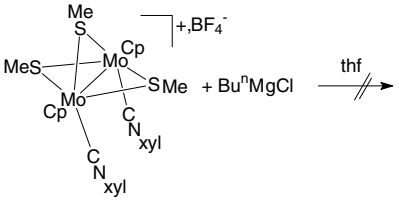


Chart 1.

Thus, reaction of **1b** with borohydride brings about addition of hydride to either a Cp (**5**) or isocyanide (**6**) carbon atom (Reaction (3)). We were interested to see how the stronger nucleophile *n*-butylmagnesium chloride would react with **1b**. However, no reaction (Reaction (4)) was observed under conditions similar to those employed for the corresponding reaction of **1b** with $NaBH_4$.

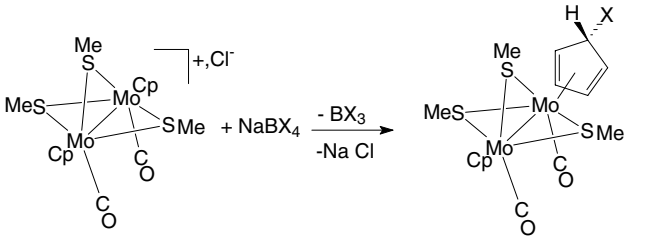


(4)

2.4. Reaction of *3* with $NaBH_4$ and $NaBD_4$: synthesis and characterisation of *7* and *8*

Reaction of the dicarbonyl derivative $[Mo_2Cp_2(CO)_2(\mu\text{-}SMe)_3](BF_4)$ (**3**) with sodium borohydride in tetrahydrofuran at room temperature for 1 h afforded the new η^4-cyclopentadiene compound $[Mo_2Cp(\eta^4\text{-}C_5H_6)(CO)_2(\mu\text{-}SMe)_3]$ (**7**) as the sole organometallic product in good yield (71%) (Reaction (5)). Similar treatment of **3** with $NaBD_4$ gave $[Mo_2Cp(\eta^4\text{-}C_5H_5D)(CO)_2(\mu\text{-}SMe)_3]$ (**8**), also in good overall

yield. Complexes **7** and **8** have been characterised by ^{1}H, ^{13}C NMR and IR spectroscopy and by microanalysis (Section 5). The ^{1}H NMR spectrum of **7** shows evidence for two isomers **7a** and **7b** in 4:1 ratio. These are thought to have different orientations, *syn* and *anti*, of the thiolate methyl groups relative to the Mo_2S_2 plane. NMR analysis indicates that the corresponding derivative **8** exists in solution as a mixture of four isomers **8a**, **8b**, **8c** and **8d** in the ratio 70/17/6/1. These may be *syn* and *anti* isomers of two rotamers (see Section 3).

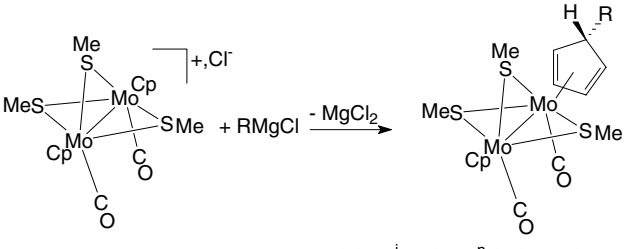


(5)

The NMR spectroscopic characteristics of bis-carbonyl derivatives **7** and **8** closely match those of the bis(isocyanide) analogue **5**. In particular, the ^{1}H NMR spectra of **7** show for each isomer the typical pattern of a $\{(\eta^5\text{-}C_5H_5)M\text{–}M(\eta^4\text{-}C_5H_6)\}$ moiety with a singlet at about 5.4 ppm attributed to the unchanged cyclopentadienyl, and an AB system due to the geminal hydrogen atoms and four multiplets between 5.63 and 3.25 ppm assigned to the four vinyl hydrogen atoms of the cyclopentadiene ring. In the ^{13}C NMR spectrum of **7a** at room temperature, peaks are seen for the four diene carbon atoms (between 82.0 and 70.0 ppm) and for the carbon atom (δ 46.6) of the CH_2 entity of the cyclopentadiene ligand. In addition, resonances for the carbonyl, cyclopentadienyl and thiolate groups are observed. The ^{1}H NMR patterns of each isomer of the corresponding deuterated compound **8** differ from those of the hydrogenated derivative **7** by the absence of an AB resonance due to geminal hydrogen atoms and by the expected presence of five multiplets between 5.63 and 3.17 ppm instead of the four observed for **7**.

2.5. Reaction of 3 with RMgCl (R = Me, Pr^i, Bu^n, Ph): synthesis and characterisation of 9–12. Molecular structure of 12

When a tetrahydrofuran solution of **3** with Grignard reagents, RMgCl, was stirred at room temperature for 15–60 min, the new products $[Mo_2(\eta^5\text{-}C_5H_5)(\eta^4\text{-}C_5H_5R)(CO)_2(\mu\text{-}(SMe)_3]$ [R = Me (**9**), Pr^i (**10**), Bu^n (**11**), Ph (**12**)] were obtained in moderate-to-high yields (68–90%) (Reaction (6)). When R is methyl, isopropyl or phenyl group small amounts of known by-products, $[Mo_2Cp_2(\mu\text{-}SMe)_4]$ [10], *trans–syn/anti*-$[Mo_2Cp_2(CO)_2(\mu\text{-}SMe)_2]$ [16] and $[Mo_2Cp_2(CO)(O)(\mu\text{-}SMe)_2]$ [17] were formed, together with the corresponding η^4-cyclopentadiene derivative **9**, **10** or **12**. It was noted that reaction of **3** with phenylmagnesium chloride in cooled tetrahydrofuran (−60 °C) afforded **12** as the sole product in very high yield (98%).



(6)

NMR analyses reveal that all the products **9**–**12** exist in solution as mixtures of four isomers **a**, **b**, **c** and **d** in variable ratios 20–8:5.5–2.5:3–2:1. These are probably due to *syn* and *anti* isomers of two rotamers (see Section 3). Complexes **9**–**12** show similar patterns of bands which resemble those for the corresponding compound **8**, indicating that all these derivatives have in common a substituted η^4-cyclopentadiene ligand. Accordingly, only complex **9** will be discussed here since it exemplifies the entire series. Its ^{1}H NMR spectrum displays the typical pattern of substituted cyclopentadiene ligands, consisting of four multiplets between 4.90 and 3.94 ppm attributed to the four vinyl hydrogen atoms, and a quartet (δ 3.52) due to the *endo* hydrogen atom of the cyclopentadiene ring which couples with the vicinal methyl group ($^{3}J_{H-H} = 6.0$ Hz). Three other ^{1}H NMR patterns of similar but much less intense resonances in the cyclopentadiene region are assigned to minor isomers **9b**, **9c** and **9d**. However, in the ^{1}H NMR spectra a few of the expected peaks are so weak that they are either not detected or obscured. It should be pointed out that the observed chemical shifts of the *endo* H atoms are in the order Ph > Me > Bu^n > Pr^i (i.e., δ 4.62, 3.52, 3.38 and 3.01, respectively, for major isomers **a**). This parallels closely the electron donating ability of these substituents which increases in the order Ph < Me < Bu^n < Pr^i. The C_5H_5R ring carbons, being diastereotopic, give rise to five distinct signals in the ^{13}C NMR spectra: e.g., for **9a** four vinylic carbon resonances of approximatively equal intensity are observed at 79.4, 78.9, 77.9 and 76.3 ppm, and a methylenic carbon signal appears at 52.5 ppm. In addition, intense resonances due to two carbonyl (δ 243.0, 230.7), one cyclopentadienyl (δ 90.7), one alkyl (R = Me; δ 30.7) and three thiolate (δ 25.4, 25.2 and 6.4) groups are detected in the ^{13}C NMR spectra. Further less intense resonances are also discernible and may be confidently attributed to the three minor isomers **9b**, **9c** and **9d**.

The formulation of **9**, **10**, **11** and **12** as $\eta^4\text{-}C_5H_4R$ cyclopentadiene complexes was confirmed by X-ray

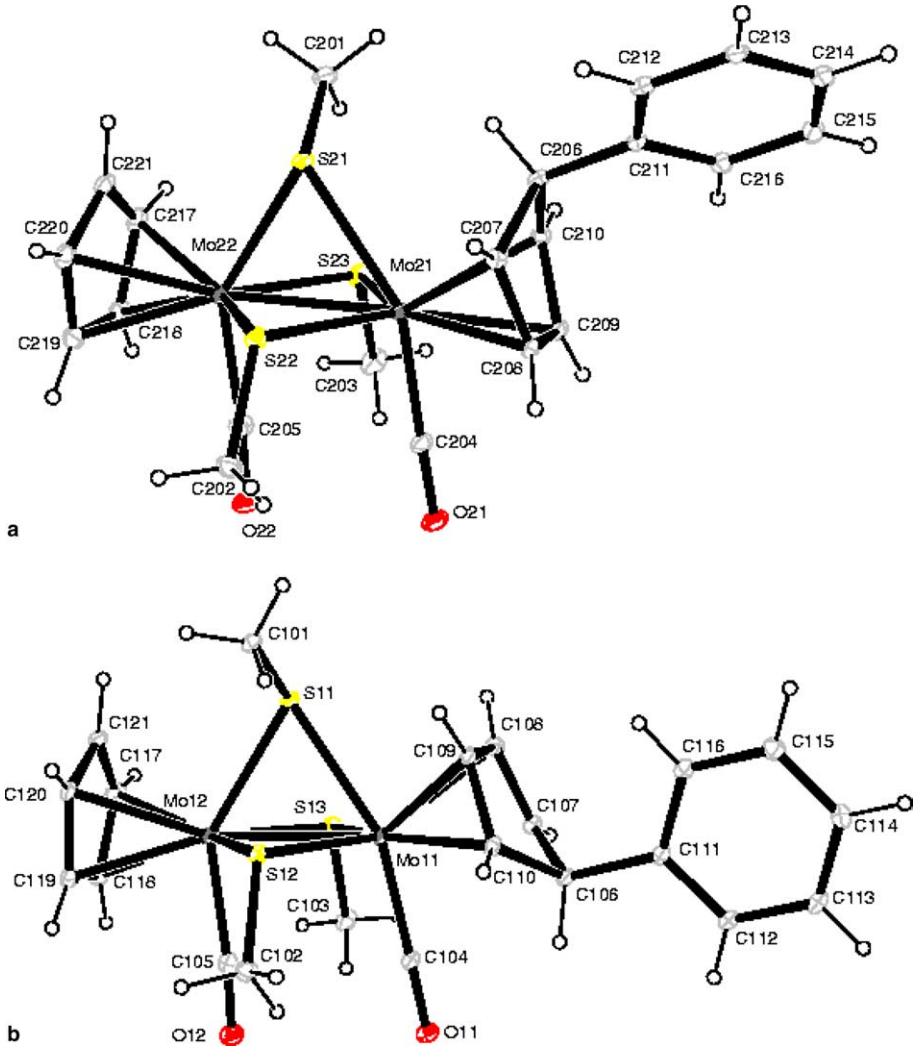


Fig. 3. Views of the two independent molecules of **12** present in the crystal. (a) Rotamer A. (b) Rotamer B.

analysis of a single crystal of **12** obtained from cold diethyl ether (see Section 5, Fig. 3 and Table 1). Two independent molecules, **12A** and **12B**, are present in the crystal of **12**. As can be seen from Fig. 3, these molecules are rotamers: Ph-substituted C(6) is on the same side of the $Mo_2S(2)S(3)$ plane from S(1) in **12A** but on the opposite side in **12B**. Both rotamers have (η^5-C_5H_5)(CO)Mo–Mo(CO)(η^4-C_5H_5Ph) skeletons bridged by three thiolate groups, with an *syn* orientation of the S(2) and S(3) methyl groups, both of which lie on the opposite side of the $Mo_2S(2)S(3)$ plane from S(1). All four independent molybdenum atoms in the crystal of **12** adopt a similar distorted square pyramidal coordination, with a basal S_3C donor set and the centroid of either a η^5-C_5H_5 or η^4-C_5H_5Ph ring occupying the apical site. In both rotamers the η^4-cyclopentadiene ring adopts a symmetrical envelope conformation; C(6) at the flap carries an *exo* Ph substituent. This is consistent with the absence of a C–H stretching frequency near 2780 cm^{-1}, believed to be characteristic of an *exo* C–H group [18,21c], in the IR spectra of **9**–**12**, whereas this peak is present in the spectrum of the related but unsubstituted compound **7**.

The Mo–η^4-C_5H_5Ph bond lengths in **12A** and **12B** show interesting differences: in both the inner Mo–C(8) and –C(9) bonds are shorter than the outer Mo–C(7) and –C(10) bonds but the mean shortening is much more marked in **12B** (0.17 Å) than it is in **12A** (0.04 Å). In other structurally characterised Mo–η^4-C_5R_6 species individual Mo–C distances are quite variable [8] but the mean values (outer 2.297 Å, inner 2.265 Å) agree with those in **12A**. The non-bonded Mo···C(6) distances [2.844(4) and 2.926(4) Å] in **12** fall in the range of 2.747–2.930 Å observed in other Mo–η^4-C_5R_6 species [8]. Despite the differences in Mo(1)–C bond lengths the Mo–S distances in **12A** and **12B** show the same pattern, with Mo(1)–S(1) [2.561(1) and 2.546(1) Å] longer than the other Mo–S bonds [2.440(1)–2.493(1) Å]. The Mo–Mo

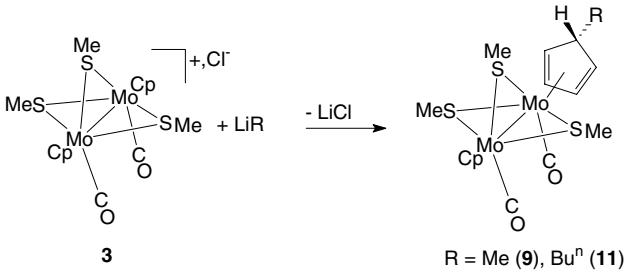
distances [2.773(1) and 2.755(1) Å] are also in agreement.

Like other Mo–η^4-C_5R_6 species [8], the C(6)–C(7) and C(6)–C(10) single bonds in **12** are longer than the other cyclopentadiene ring C–C bonds; however, in **12** the sequence C(7)–C(8)–C(9)–C10 shows significant bond alternation [means 1.403(4), 1.450(4), 1.408(4) Å] not typical of other Mo–η^4-C_5R_6 species [8] where the corresponding bonds are more nearly equal in length (means 1.423, 1.406 and 1.415 Å), though again individual values show much variation. Finally, we note that symmetrical envelope conformations of the η^4-C_5R_6 rings, with C(6) at the flap, are evident from the endocyclic torsion angles in Table 1(c), which agree well with the means for other Mo–η^4-C_5R_6 species; for example the magnitudes of the endocyclic torsion angles across C(6)–C(7) and C(6)–C(10), 32–34° in **12**, compare with a range of 26–39° in related molybdenum complexes [8].

The results for the ordered structure **12** clarify those for the disordered structure **5**, in which xylNC takes the place of CO and η^4-C_5H_6replaces η^4-C_5H_5Ph. Ring A in **5** differs from the η^4-C_5H_5Ph rings in **12** in several ways: it is less puckered, with smaller torsion angles across the C(6)–C(7) and C(6)–C(10) bonds, the ring C–C bonds do not vary so much and C(6) is only 2.712(10) Å from Mo(1). Ring B, bonded to Mo(2), defines an even flatter envelope, again with C(6) at the flap. The longest Mo–S bonds again involve S(1) but the lengthening is not so obvious as in **12**. Disorder of the η^4-C_5H_5Ph and η^5-C_5H_5 rings seems the most probable explanation for these results. This disorder may involve different rotamers, since C(6a) lies on the opposite side of the $Mo_2S(2)S(3)$ plane from S(1), while C(6b) lies on the same side.

2.6. Reaction of *3* with alkyllithium LiR (R = Me, Bu^n): synthesis of *9* and *11*

Complexes **9** and **11**, obtained by reacting **3** with the appropriate alkylmagnesium chloride (see Section 2.5) may also be synthesised by action of the corresponding alkyllithium on the dicarbonyl derivative **3**. Indeed, treatment of a tetrahydrofuran solution of **3** with excess alkyllithium LiR (R = Me, Bu^n) at room temperature for 20 min afforded the η^4-substituted cyclopentadiene derivatives **9** and **11** with improved yields (76% and 82%, respectively) (Reaction (7)). In both cases small amounts of known by-products, *trans-syn/anti*-$[Mo_2Cp_2(CO)_2(\mu\text{-}SMe)_2]$ [16] (in about 13% yield) and *trans-syn/anti*-$[Mo_2Cp_2(CO)(O)(\mu\text{-}SMe)_2]$ [17] (yield: R = Me, 10.5%; R = Bu^n, 5.5%), were formed in addition to the main products **9** or **11**. All the products of these reaction were characterised by comparing their ^{1}H NMR spectra with those of authentic samples obtained by methods already described.

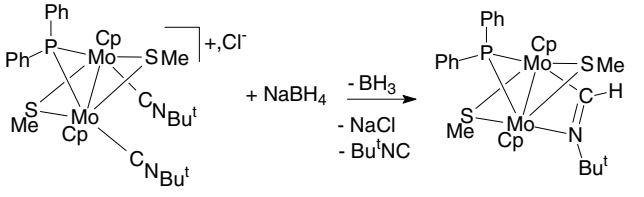


3 R = Me (**9**), Bu^n (**11**)

(7)

2.7. Reaction of *16* with $NaBH_4$: formation of *17*

To evaluate the influence of the bridging 3e-donor ligand L′ upon the reactivity of nucleophiles towards cationic derivatives $[Mo_2Cp_2L_2L'_n]^+$, we synthesised an analogue of **1a** in which one μ-SMe group is replaced by the better electron-donor ligand μ-PPh_2. For this purpose we treated an acetonitrile solution of $[Mo_2Cp_2(\mu\text{-}SMe)_2(\mu\text{-}Cl)(\mu\text{-}PPh_2)]$ [2] with excess Bu^tNC at room temperature to obtain the desired product $[Mo_2Cp_2(Bu^tNC)_2(\mu\text{-}SMe)_2(\mu\text{-}PPh_2)]Cl$ (**16**) as an ochre solid in good yield (79%). The formulation of **16** was deduced from its analytical, ^{1}H and $^{13}C\{^1H\}$ NMR data (see Section 5). Stirring a tetrahydrofuran solution of **16** with excess $NaBH_4$ at ambient temperature afforded **17** in good yield (ca. 80%) (Reaction (8)).



16 **17**

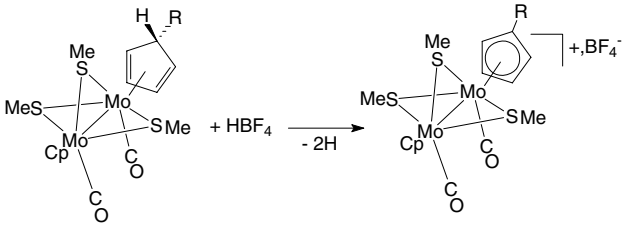
(8)

The NMR spectra of **17** were identical to those of the μ-formimidoyl derivative $[Mo_2Cp_2(\mu\text{-}SMe)_2(\mu\text{-}PPh_2)(\mu\text{-}CH{=}NBu^t)]$ previously obtained in good yield from the reaction of $[Mo_2Cp_2(\mu\text{-}H)(\mu\text{-}SMe)_2(\mu\text{-}PPh_2)]$ with Bu^tNC in tetrahydrofuran [2]. Reaction (8) required addition of hydride onto isocyanide to give a formimidoyl ligand which then displaced the other isocyanide.

2.8. Reaction of *9*, *11*, and *12* with HBF_4: synthesis and characterisation of *13*, *14* and *15*

For metal-bound cyclopentadienyl rings most functionalization reactions involve either Friedel–Crafts electrophilic alkylation or proton abstraction by base, followed by reaction of the resulting anion with an alkyl halide [19]. Hydrogen abstraction from the substituted cyclopentadiene rings present in complexes **9**, **11** and **12** offered us an alternative route to functionalised cyclopentadienyls. Thus, addition of one equivalent of

$HBF_4{\cdot}OEt_2$ to dichloromethane solutions of compounds **9**, **11** or **12** caused their rapid transformation into the corresponding cationic bis(cyclopentadienyl) derivatives **13, 14** or **15** as sole product with respective yields of 49%, 51.5% and 33% (Reaction (9)).



R = Me (**9**), Bu^n (**11**), Ph (**12**) R = Me (**13**), Bu^n (**14**), Ph (**15**)

(9)

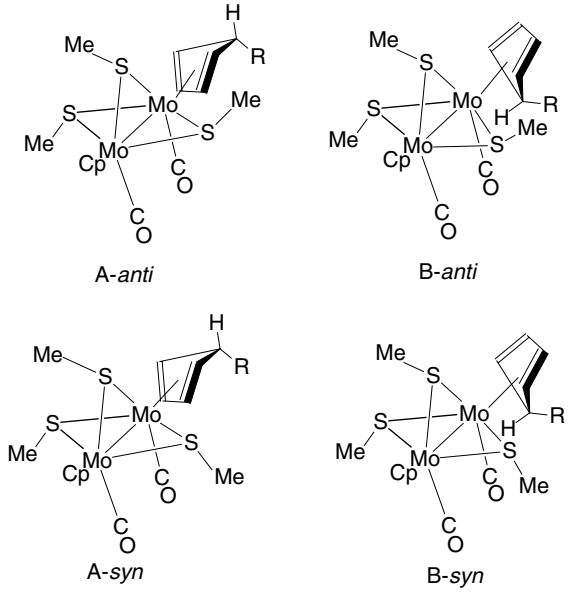
The new compounds **13, 14** and **15** were identified from their analytical and spectroscopic data. Since the NMR and IR spectra suggest a close structural similarity between these three species, only one of them, namely **13**, will be discussed here as an example. A typical broad band between 1100 and 1000 cm^{-1}, attributable to a ν(B–F) absorption, is observed in the IR spectrum of **13** and is indicative of the presence of a tetrafluoroborate anion, suggesting a cationic molybdenum dimer as counter-ion. NMR suggests that two isomeric forms of the cation are present. Since the patterns of resonances of both isomers are similar and the spectra differ only in the chemical shifts of two of the SMe groups, it is likely that *syn* and *anti* isomers **13a** and **13b** are present in solution. These cations exhibit a deshielded ^1H NMR singlet at ca. 6.03 ppm which is assigned to one cyclopentadienyl ligand. Furthermore, both isomers show in the expected region the typical pattern of a monosubstituted cyclopentadienyl ring, consisting of two multiplets of equal intensity at ca 5.95 and 5.84 ppm. Additional resonances due to three thiolates, between 2.65 and 1.75 ppm, and to one ring methyl substituent are observed in the ^1H NMR spectra. The C_5H_5Me ring carbons, being diastereotopic, display five distinct signals in the $^{13}C\{^1H\}$ NMR spectra of **13a** and **13b**, at ca. 97.2, 94.1, 93.3, 90.8 and 89.9 ppm; other resonances due to two carbonyls, one cyclopentadienyl, one methyl and three thiolate groups are also detected.

3. Discussion

3.1. Isomerism in η^4-cyclopentadiene molybdenum derivatives (7–12) and in mono-substituted η^5-cyclopentadienyl molybdenum compounds (13–15)

Reaction of the symmetrical bis(cyclopentadienyl) derivative $[Mo_2Cp_2(CO)_2(\mu\text{-}SMe)_3]Cl$ (**3**) with either $NaBR_4$ (R = H, D), LiR (R = Me, Bu^n) or RMgCl (R = Me, Pr^i, Bu^n, Ph) formally proceeds by nucleophilic attack at a Cp carbon atom by R^- to give a pair of spectroscopically indistinguishable enantiomers $[Mo_2(\eta^5\text{-}C_5H_5)\{\eta^4\text{-}C_5H_5R)\}(CO)_2(\mu\text{-}SMe)_3]$ (**7–12**). Only four isomers characterisable by NMR spectrometry seem stereochemically possible: they result from *syn* or *anti* orientations of the two in plane "Mo_2S_2" bridging SMe groups and two possible rotamer arrangements (A and B) of the η^4-cyclopentadiene ligand (Scheme 1).

As expected, each ^1H NMR spectrum of a η^4-cyclopentadiene derivative showed the presence in solution of four isomers (**a–d**), except in the case of compound **7** for which only two isomers were detected. It should be noted that **7** and the formally oxidised bis(cyclopentadienyl) derivatives **13–15** displayed very similar ^1H NMR patterns in the SMe region, suggesting strongly similar patterns of isomerism. Moreover, ^1H NMR spectroscopy revealed that each of the compounds **13–15** was present in solution as a mixture of two isomers: these may differ either in the orientations (*syn* or *anti*) of the two in-plane "Mo_2S_2" bridging SMe groups or in relative positions (*cis* or *trans*) of the two carbonyl ligands relative to the Mo–Mo axis. However, separate experiments showed that electrochemical oxidation of the *cis*-bis(carbonyl)-η^4-cyclopentadiene derivative $[Mo_2(\eta^5\text{-}C_5H_5)(\eta^4\text{-}C_5H_6)(CO)_2(\mu\text{-}SMe)_3]$ (**7**), formed by addition of H^- to the *cis*-bis(carbonyl) complex $[Mo_2(\eta^5\text{-}C_5H_5)_2(CO)_2(\mu\text{-}SMe)_3]Cl$ (**3**), gave back the starting compound. This observation appears to eliminate the possibility that two isomers are formed by a *cis-trans* rearrangement of the two CO groups in **13–15**. Therefore, from the similarity of the SCH_3 NMR patterns of **7** and **13–15**, we attribute the isomerism observed for **7** to *syn* and *anti* orientations of the SMe groups. Such an assignment is also in accordance



Scheme 1. Possible η^4-cyclopentadiene molybdenum isomers **7–12.**

with the difference in ^{1}H NMR chemical shifts for the SMe resonances in the two isomers (2.53, 2.52 and 1.31 ppm for **7a**, and 2.28, 2.23 and 1.59 ppm for **7b**), which may reflect different methyl orientations in the two derivatives. Interestingly, when a CH(D/R) fragment is present in the η^4-cyclopentadiene group, the two more abundant isomers **a** and **b** of compounds **8**–**12**, and those of bis(η^5-cyclopentadienyl) derivatives **13**–**15** displayed very similar patterns in both cyclopentadienyl and SMe regions in all seven complexes. We, therefore, confidently assign the corresponding resonances to *syn* and *anti* orientations of the two SMe groups of one rotamer in **8**–**12**. The remaining resonances observed in the ^{1}H NMR spectra of **8**–**12** were attributed to the two less abundant isomers **c** and **d**, which accordingly were identified with the other *syn* and *anti* rotamer. While the rotamer isomerization rates are slow in substituted cyclopentadiene dimolybdenum derivatives (**8**–**12**), allowing the characterisation of each of the two rotamers, they are rapid in the unsubstituted cyclopentadiene compounds **7** and **5**, for which only one form has been detected in solution by ^{1}H NMR spectroscopy. Similar trends have been previously observed in Mo(II) and Mo(III) diene derivatives $[MoCp(\eta^4\text{-}C_4H_4)(\eta^3\text{-}C_3H_5)]^{n+}$ ($n = 0$, 1) [20]. It should be noted that *syn-anti* isomerization rates are slow for all the cyclopentadiene complexes of this study (**5**, **7**–**12**), allowing the detection of the expected two conformations.

The existence of a pair of *endo–exo* isomers, resulting from attack of the nucleophile onto the metal followed by its migration to the cyclopentadienyl ligand, has been also considered, but on the basis of the X-ray characterisation of a pair of rotamers for complex **12** this hypothesis has been rejected.

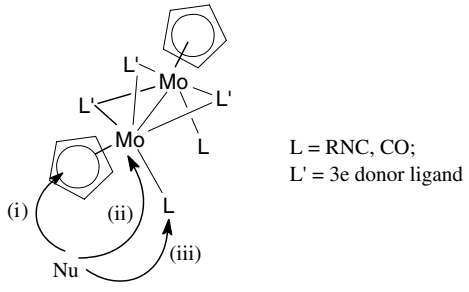
It is worth noting that, until now, there was no evidence from NMR spectra or from diffraction studies for the existence of rotamers for substituted or unsubstituted η^4-cyclopentadiene binuclear complexes [9c,21], whereas a few examples of *prone* and *supine* isomers of mononuclear substituted η^4-cyclopentadiene derivatives have been detected in solution by ^{1}H NMR spectroscopy [22]. Thus, as far as we know, isomers **8**–**12** are the first well-established examples of rotamers of binuclear η^4-cyclopentadiene species.

3.2. Factors influencing the regiochemical control in the reactions of anionic reagents with metal carbonyl and metal carbonyl-like complexes

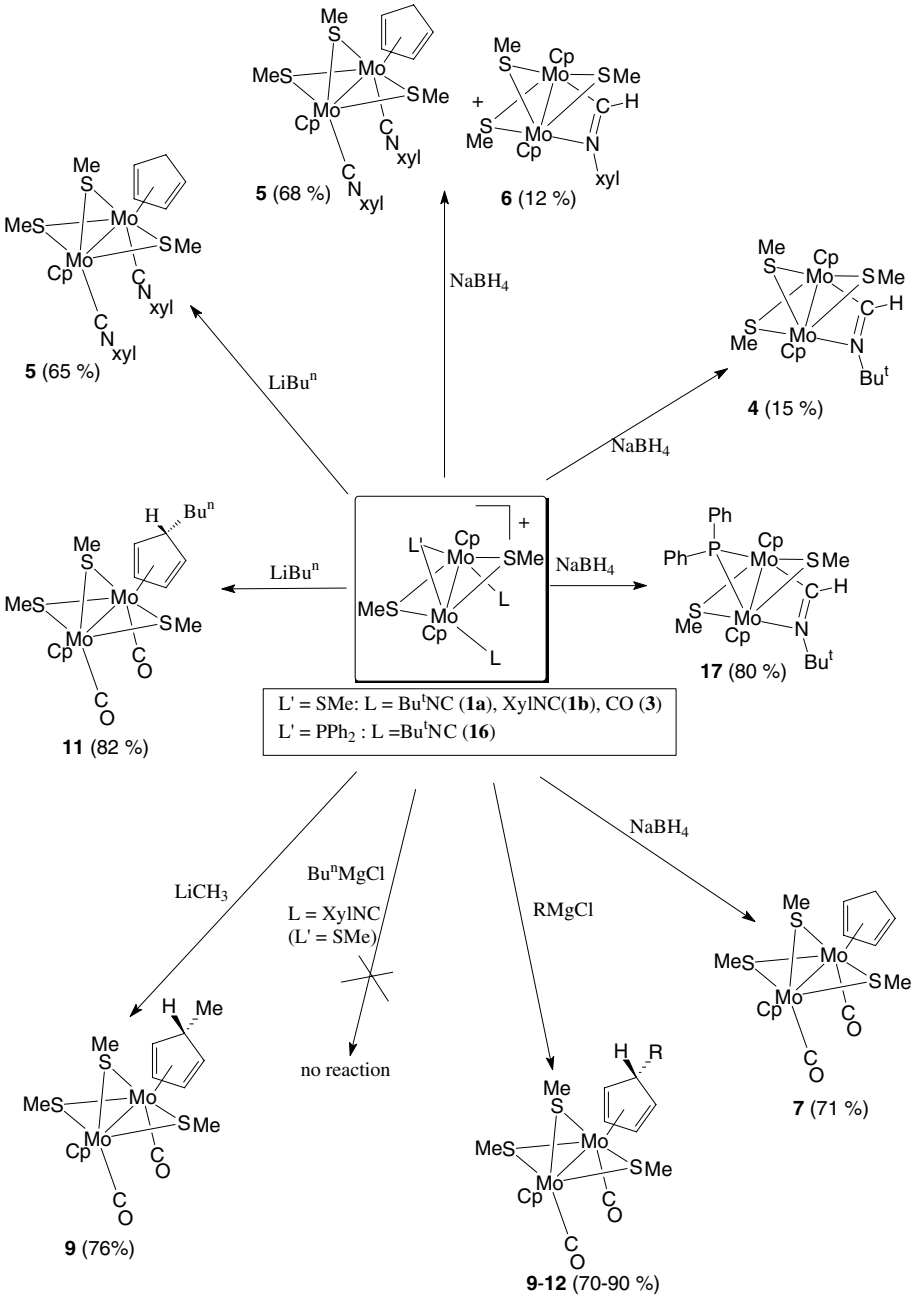
Reactions of nucleophilic reagents, such as sodium borohydride, alkyl- or aryllithium compounds, or alkyl-or arylmagnesium halides, with binuclear cyclopentadienyl transition metal complexes bearing a positive charge proceed by three general pathways determined by the nature of the metal and ligands: (i) attack on a cyclopentadienyl ring, (ii) attack at the metal with formation of a transient metal–nucleophile bond, and (iii) attack at a terminal ligand L with possible displacement of a second ligand L (Scheme 2).

Investigation of the reactivity of binuclear cyclopentadienyl transition metal complexes with anionic reagents, such as hydride, alkyl- or aryl anions or Grignard reagents, described either here or in previous reports [23] reveals that the regioselectivity of the reaction depends on: (i) the nature of the terminal (L) or/and bridging (L′) ligands, (ii) the strength of the nucleophile, (iii) the oxidation state of the metal, (iv) the steric influence of substituents of terminal or bridging ligands, and (v) the temperature. Further complications arise because the anionic reagent can behave as a base or as a reducing agent as well as a nucleophile. In order to appreciate how these factors determine the site of the reagent attack in dinuclear cyclopentadienyl carbonyl and carbonyl-like molybdenum cations, we have summarized in Scheme 3, the set of addition reactions of anionic reagents with $[Mo_2Cp_2L_2(\mu\text{-}SMe)_2(\mu\text{-}L')]^+$.

Examination of the reactions gathered in Scheme 3 suggests that the dominant factor governing regioselectivity is the nature of the terminal ligand L. Indeed, when L has adequate π-acceptor power, e.g., CO or xylNC, irrespective of the anionic reagent the cyclopentadienyl carbon atoms are activated to nucleophilic attack, thus affording cyclopentadiene derivatives. The failure of Bu^{n}MgCl to give any reaction when L = xylNC is the single exception to this rule. However, it must be emphasized that, with BH_4^- as reagent, the selectivity of these nucleophilic additions is higher if the terminal ligands are CO rather than xylNC. Formation of small amounts of the μ-formimidoyl product **6** together with the unsubstituted cyclopentadiene derivative **5** when BH_4^- reacts with **1b** (Scheme 3) supports this statement. Consistently, the higher π-acceptor power of CO relative to xylNC disfavours attack at the CO carbon: thus H^- addition occurs exclusively at the cyclopentadienyl carbon atom when BH_4^- reacts with **3**, whereas some H^- addition also occurs at the iminium carbon in the related reaction of BH_4^- with **1b**.



Scheme 2. Potential electrophilic sites in cationic metal carbonyl-like dinuclear complexes.



Scheme 3. Summary of the reactivity of complexes $[Mo_2Cp_2L_2(\mu\text{-SMe})_2(\mu\text{-L}')]^+$ towards anionic reagents.

Now, it is well known that increased back-donation from the metal to the π-acidic L = CO or CNR terminal ligands increases the polarization of both the C–X (X = O or N) bonds of the terminal ligand and of the Cp C–H bonds. The relative electrophilicity of the donor carbon atoms of the Cp and L ligands depends on the metal, its oxidation state and the charge of the complex. These factors govern the regiochemical control in reactions of nucleophiles with metal carbonyl or carbonyl-like complexes. Previous studies on reactions of nucleophiles with cationic dinuclear carbonyl iron complexes, $[Fe_2Cp_2(CO)_2(\mu\text{-CO/S})(\mu\text{-CSMe})]^+$ and $[Fe_2Cp_2(CO)_2(\mu\text{-CO})(\mu\text{-CNRMe})]^+$ [9c,21b,21c,23e], offer some parallels with our systems, although they involve iron(II) rather than molybdenum(III). This electronic difference may be responsible for the different trends observed in the two series. Thus, the exclusive addition of nucleophile to the C_5H_5 ring of the dicarbonyl complex **3** contrasts with the vulnerability of dinuclear carbonyl iron compounds to nucleophilic attack at the terminal carbonyl group as well as on the Cp ring [9c,21b,21c,23e]. It is also pertinent to note here that Rakowski Dubois et al. [21a] have shown that the dicarbonyl molybdenum cation, $[Mo_2Cp_2(CO)_2(\mu\text{-SMe})$-

(μ-SCH_2S)]$^+$, reacts with $LiEt_3BH$ to give a single cyclopentadiene product resulting from direct addition of H^- to the cyclopentadienyl ring. The reactions between anionic reagents and dimolybdenum complexes with L = CO or xylNC as terminal ligands contrast with those where L = Bu^{t}NC, a poorer π-acceptor group than CO and xylNC but a valuable σ-donor, in which no nucleophilic attack at a Cp carbon atom is observed. This difference in electronic behaviour between Bu^{t}NC and xylNC upon coordination to the {CpMo(μ-SMe)$_3$-MoCp} core is illustrated by the effect of coordination on the ν(CN) bands: for Bu^{t}NC the drop is 18 cm^{-1}, from 2130 cm^{-1} in the free ligand [24] to 2112 cm^{-1} in **1a**, whereas xylNC displays a more substantial drop of 31 cm^{-1}, from 2120 to 2089 cm^{-1} in **1b**.

The nature of the ancillary ligands in [$Mo_2Cp_2L_2$-(μ-SMe)$_2$(μ-L′)]$^+$ determine also the character of the anionic reagent acting either as reducing agent or nucleophile. For example, when the anion reacting with **1b** (L = xylNC) is derived from *n*-butyllithium, it acts as a reducing agent rather than a nucleophile, since the η^4-cyclopentadiene C_5H_6 ligand is formed rather than the substituted cyclopentadiene $C_5H_5Bu^n$. This contrasts with alkyllithium LiR (R = Bu^n) which reacts with the bis-carbonyl derivative **3** mainly as a nucleophile, giving substituted cyclopentadiene complexes as the major products. Nevertheless, small quantities of reduced dimolybdenum derivatives, [$Mo_2Cp_2(CO)_2$(μ-SMe)$_2$] and related oxo-complexes, are also formed, indicating that lithium compounds may also reduce bis(cyclopentadienyl) derivatives. Similar trends are observed when **3** reacts with Grignard reagents at room temperature. However, at low temperature, PhMgCl, for example, acts exclusively as nucleophile, affording quantitatively the Ph-substituted derivative. Evidently, arylmagnesium compounds are less likely to act as reducing agents at low temperature.

In coordinated isonitriles, RNC, the electronic properties of the substituent R gives rise to different modes of activation but the outcome also depends on the anionic reagent. When R is a good electron-donor, such as Bu^t, no activation of the cyclopentadienyl carbon atoms occurs and thus no cyclopentadiene derivative is formed. However, when the anionic compound reacting with **1a** is LiBu^n, a dealkylation reaction, involving ejection of the Bu^t group, is observed (Scheme 3) [3]; this requires that LiBu^n should act as a base. On the other hand, when the anionic reagent is BH_4^-, hydride attack occurs at the isonitrile carbon in **1a** (L = Bu^{t}NC), affording the μ-formimidoyl derivative **4**.

Finally, when the bis(*t*-BuNC) derivative **16**, derived from **1a** by replacement of one μ-SMe ligand by the better σ-donor μ-PPh_2, reacts with $NaBH_4$, one isonitrile undergoes selective hydride addition at an iminium-like carbon. This reaction does not stop at the imino complex but proceeds ultimately to form the more geometrically favoured μ-formimidoyl complex **17** by loss of isonitrile from the second molybdenum atom which then accepts N-co-ordination from the modified isocyanide. Thus, **16** and **1a** show similar reactivity with $NaBH_4$. Both afford μ-formimidoyl products, respectively, **17** and **4**. However, **17** is formed in significantly higher yield than **4**, possibly owing to the higher lability of the isonitrile in **16** compared with **1a**.

3.3. Reactivity of the cyclopentadiene derivatives towards electrophiles: mechanistic considerations

The addition of tetrafluoroboric acid to substituted cyclopentadiene complexes reverses the nucleophile addition. The products are hydrogen and an analogue of the starting complex with different functionality (see Reaction (9)).

The formation of **13**, **14** and **15** implies the oxidation of **9**, **11** and **12** by H^+, promoting a $\eta^4 \rightarrow \eta^5$ rearrangement of the C_5 ring, with concomitant elimination of a radical ($H^{\cdot}$). It is noteworthy that electrochemical oxidation of the η^4-cyclopentadiene compounds **9** and **11** in the absence of protons affords the η^5-cyclopentadienyl derivatives **13** and**14**, respectively. This supports the proposed reaction path. Nevertheless, a second route to the η^5-cyclopentadienyl compounds **13, 14** and **15** from the reaction of η^4-cyclopentadiene derivatives **9**, **11** and **12** with HBF_4 may also be considered. This involves β-elimination in the initial step, then electrophilic attack by H^+ at one Mo atom (second step) and a final loss of dihydrogen via a reductive elimination (third step). However, two observations make this unlikely. First, we have already shown that addition of HBF_4 to related dimolybdenum complexes gave rise to a *face-addition* of the proton to a Mo–C bond, with formation of a α-agostic structure rather than an Mo–H bond [14]. Second, the second step requires a higher coordination number for the molybdenum atom than is usual in these compounds. The radical mechanism for formation of functionalized cyclopentadienyl products thus seems more likely.

4. Conclusions

We have shown that the reactivity of dinuclear molybdenum cationic complexes, [$Mo_2Cp_2L_2$(μ-SMe)$_2$(μ-L′)]$^+$ (L = Bu^{t}NC, xylNC, CO; L′ = SMe, PPh_2), towards anionic reagents affords η^4-cyclopentadiene, μ-formimidoyl and reduced dinuclear dimolybdenum, neutral products, according to the relative influences of the terminal (L) and bridging (L′) ligands, the nature and oxidation state of the metal, the nature of the anionic reagent and the temperature. Attack of the anion, acting mainly as nucleophile but also as reductant, at the carbon atoms of the C_5H_5 ring is favoured

when good π-acceptor terminal ligands L are present in the cationic derivatives, affording new monocyclopentadiene dinuclear molybdenum complexes. When the terminal ligand L is a poor π-acceptor unit, e.g., Bu^tNC, the nucleophile adds at the iminium carbon atom, leading to the formation of new μ-formimidoyl molybdenum complexes. Nucleophilic addition at the C_5H_5 ring, giving cyclopentadiene complexes, is well known in mononuclear derivatives [25] but has been less often seen in dinuclear species [9a,21].

5. Experimental

5.1. General procedures and materials

All reactions were performed under an atmosphere of argon or dinitrogen using conventional Schlenk techniques. Solvents were deoxygenated and dried by standard methods. Some of the starting materials $[Mo_2Cp_2(Bu^tNC)_2(\mu\text{-}SMe)_3](BF_4)$ (**1a**) [3], $[Mo_2Cp_2(MeCN)_2(\mu\text{-}SMe)_3](BF_4)$ [7], $[Mo_2Cp_2(CO)_2(\mu\text{-}SMe)_3]Cl$ (**3**) [4] and $[Mo_2Cp_2(\mu\text{-}SMe)_2(\mu\text{-}Cl)(\mu\text{-}PPh_2)]$ [26] were prepared as described previously. All other reagents were purchased commercially: Bu^tNC (98%), CH_3MgCl (3.0 M solution in tetrahydrofuran), $(CH_3)_2CHMgCl$ and $CH_3(CH_2)_3MgCl$ (2.0 M solution in diethyl ether), $(C_6H_5)MgCl$ (2.0 M solution in tetrahydrofuran), $CH_3(CH_2)_3Li$ (2.5 M solution in hexanes) and HBF_4 (54 wt% solution in Et_2O) from Aldrich, CH_3Li (1.6 M solution in diethyl ether) and $CH_3(CH_2)_3Li$ (2.5 M solution in hexanes) from Acros Organics, and xylNC (98%) from Fluka Chemica. Yields of all products are relative to the starting dimolybdenum complexes. Column chromatography was carried out with either silica gel or Florisil purchased from SDS. Chemical analyses were performed either by the Service de Microanalyse I.C.S.N., Gif sur Yvette (France), or by the Centre de Microanalyses du CNRS, Vernaison (France). IR spectra were recorded on a Nicolet-Nexus FT-IR spectrometer from either KBr pellets or dichloromethane solution. The NMR spectra (^1H, ^{13}C, ^{15}N) were recorded either at room temperature or at 253 K in $CDCl_3$, C_6D_6, toluene-d_8 or $(CD_3)_2CO$ solutions with a Bruker AMX 400 spectrometer and were referenced to $SiMe_4$ (^1H, ^{13}C) and CH_3NO_2 (^{15}N). ^1H–^{13}C and ^1H–^{15}N 2D experiments were carried out on a Bruker DRX 500 spectrometer.

5.2. Reaction of *1a* with $NaBH_4$

The complex **1a** (200 mg, 0.28 mmol) and 4 equiv. of $NaBH_4$ (42mg) were heated in acetonitrile (50 ml) at reflux for 3h. The colour of the solution turned from red to maroon. The solvent was then removed under vacuum, and the ^1H NMR analysis of the crude products showed that 70% of the starting material was recovered. The organometallic derivatives were extracted from the residue with diethylether (2×20 ml). Evaporation of the volatiles gave a solid, which was dissolved in CH_2Cl_2 (20 ml) and chromatographed on silica gel. Elution with hexane–CH_2Cl_2 (1:1) removed an orange band which afforded, after evaporation of solvents, complex **4** as an orange powder (26 mg, 15% yield). Complex **4** was obtained as a mixture of two inseparable *syn* and *anti* isomers by chromatography. Several attempts to improve the yields of **4** by increasing the time of reaction were unsuccessful.

Complex **4**: Anal. Calc. for $C_{18}H_{29}Mo_2NS_3$, CH_2Cl_2: C, 36.1; H, 4.9; N, 2.2. Found: C, 36.2; H, 5.1; N, 2.2%. ^1H NMR δ/ppm (toluene-d_8; 253 K), **4a** (major isomer): 10.60 (s, 1H, C*H*N), 5.15, 5.07 (s, 5H, C_5H_5), 1.81, 1.57, 1.55 (s, 3H, SCH_3), 0.81 (s, 9H, Bu^t); **4b** (minor isomer): 10.63 (s, 1H, C*H*N), 5.23, 5.05 (s, 5H, C_5H_5), 1.64, 1.51, 1.50 (s, 3H, SCH_3), 0.76 (s, 9H, Bu^t). $^{13}C\{^1H\}$ NMR δ/ppm (toluene-d_8; 253 K), **4a**: 230.0 (*C*HN), 91.5, 84.0 (C_5H_5), 29.7 ($C(CH_3)_3$), 18.6, 12.7, 11.5 (SCH_3); **4b**: 233.3 (*C*HN), 92.3, 89.3 (C_5H_5), 29.2 ($C(CH_3)_3$), 17.2, 12.4 (SCH_3). ^{15}N NMR δ/ppm (toluene-d_8; 253 K), **4a**: −129.3 (*N*Bu^t); **4b**: −136.2 (*N*Bu^t).

5.3. Synthesis of *1b*

A solution of $[Mo_2Cp_2(\mu\text{-}SMe)_3(MeCN)_2](BF_4)$ (500 mg, 0.79 mmol) in dichloromethane (50 ml) was stirred in the presence of 2 equiv. of xylNC (206 mg) for 1 h at room temperature. The solution turned readily from red to brown. After evaporation of the solvent, the residue was washed with diethyl ether (2×20 ml) and pentane (2×20 ml), affording complex **1b** as a brown solid (520 mg, 81% yield).

Complex **1b**: Anal. Calc. for $C_{31}H_{37}BF_4Mo_2N_2S_3$, 0.5 CH_2Cl_2: C, 44,2; H, 4.5; N, 3.3. Found: C, 44.2; H, 4.5; N, 3.2%. IR (CH_2Cl_2, cm^{-1}): 2089 s (*ν* CN), 1100–1000 s, br (*ν* BF). ^1H NMR δ/ppm ($(CD_3)_2CO$; 298 K): 6.95 (t, $^3J_{H-H} = 7.6$ Hz, 2H, $C_6H_3Me_2$), 6.82 (d, $^3J_{H-H} = 7.6$ Hz, 4H, $C_6H_3Me_2$), 5.66 (s, 10H, C_5H_5), 2.65 (s, 3H, SCH_3), 2.22 (s, 12H, CH_3), 1.85 (s, 3H, SCH_3), 1.65 (s, 3H, SCH_3).

5.4. Reaction of *1b* with $LiBu^n$

The complex **1b** (200 mg, 0.246 mmol) and 4 equiv. of *n*-butyllithium ($V = 390$ μl) were heated in tetrahydrofuran (30 ml) at reflux for 12h. The solvent was then removed under vacuum and only one organometallic product was extracted with diethylether (2×20 ml). Evaporation of the volatiles afforded complex **5** as an analytically pure, red solid (116 mg, 65% yield). Complex **5** was obtained as a mixture of two inseparable isomers **5a** and **5b** in the 87:13 ratio by chromatography.

Complex **5**: Anal. Calc. for $C_{31}H_{38}Mo_2N_2S_3$: C, 51.2; H, 5.3; N, 3.8. Found: C, 51.3; H, 5.4; N, 3.7%. IR (KBr pellet, cm^{-1}), **5a**: 2052 s and 1933 s (*v* CN); **5b**: 1995 m and 1857 m (*v* CN). ^1H NMR δ/ppm ($CDCl_3$; 298 K), **5a**: 6.83–6.66 (m, 6H, C*H*ar(xyl)), 5.17 (s, 5H, C_5H_5), 4.91, 4.62 (m,1H,C_5H_6), 3.70 (AB, $^2J_{H-H} = 10.4$ Hz, 1H, C_5H_6), 3.31, 3.25 (m,1H, C_5H_6), 3.20 (AB, $^2J_{H-H} = 10.4$ Hz, 1H, C_5H_6), 2.56 (s, 3H, SCH_3), 2.22, 2.11 (s, 6H, CH_3), 1.54, 1.31 (s, 3H, SCH_3); **5b**: 6.80–6.61 (m, 6H, C*H*ar(xyl)), 5.36 (m, 1H, C_5H_6), 5.32 (s, 5H, C_5H_5), 5.14 (m, 1H, C_5H_6), 3.93 (AB, $^2J_{H-H} = 10.8$ Hz, 1H, C_5H_6), 3.24, 3.12 (m, 1H, C_5H_6), 2.27 (s, 3H, SCH_3), 2.06, 2.03 (s, 6H, CH_3), 1.86, 1.64 (s, 3H, SCH_3). $^{13}C\{^1H\}$ NMR δ/ppm (C_6D_6; 298 K), **5a**: 211.7, 199.5 (xylN*C*), 135–125 (*C*ar(xyl)), 89.4 (C_5H_5), 78.5, 77.8, 62.8, 59.8, 46.0 (C_5H_6), 26.0, 19.2, 10.2 (S*C*H_3).

5.5. Reaction of *1b* with $NaBH_4$

Method (a) – *In a Schlenk tube*: The complex **1b** (100 mg, 0.123 mmol) and 4 equiv. of $NaBH_4$ (18 mg) were heated in tetrahydrofuran (30 ml) at reflux for 4h. The solvent was then removed under vacuum and the crude products were characterised in $(CD_3)_2CO$ by ^1H NMR spectroscopy. A valuable amount of the starting material (20%) was recovered. The compounds **5** and **6** were formed in the 85:15 ratio. Attempts to separate the three complexes by chromatography failed.

Complex **6**: ^1H NMR δ/ppm ($CDCl_3$; 298 K): 10.40 (s, 1H, C*H*), 7.0–6.6 (m, 3H, C*H*ar.), 5.29, 5.02 (s, 5H, C_5H_5), 2.13, 2.04 (s, 3H, CH_3), 1.83, 1.57, 1.55 (s, 3H, SCH_3).

Method (b) – *In a sealed tube*: The reaction was carried out as above, but the reagents were heated at 120 °C in a sealed tube dipped into an oil-bath. After complete consumption of the starting material (about 4h), the solvent was removed under vacuum and the crude products were analysed in $(CD_3)_2CO$ by ^1H NMR spectroscopy. Three complexes, **5**, **6** and $[Mo_2Cp_2(\mu\text{-SMe})_4]$, were detected in the 13:55:23 ratio. The organometallic compounds were then extracted with diethyl ether (20 ml). Evaporation of the volatiles gave a solid, which was dissolved in CH_2Cl_2 (3 ml) and chromatographed on silica gel. Elution with hexane–CH_2Cl_2(4:1) removed only one red band, which gave, after evaporation of solvents, a mixture (44 mg) of compounds **6** (yield: 30%) and $[Mo_2Cp_2(\mu\text{-SMe})_4]$ (yield: 35%) (^1H NMR analysis) as a red-brown powder in 1:1 ratio. The complex **5** decomposed onto the silica gel column.

No elemental analysis is available for **6** as a pure sample of this compound was not obtained after chromatography. However, **6** has been fully characterised by X-ray analysis of red crystals picked from a diethyl ether solution of an equimolar (^1H NMR analysis) mixture of **6** and $[Mo_2Cp_2(\mu\text{-SMe})_4]$ at 8 °C.

5.6. Reaction of *1b* with Bu^nMgCl

Several attempts to react complex **1b** (110 mg, 0.135 mmol) with 3.8 equiv. of Bu^nMgCl ($V = 250$ μl) either by stirring at room temperature or by heating in tetrahydrofuran (30 ml) at reflux for 1 h failed. The starting material was fully recovered in each experiment.

5.7. Reaction of *3* with $NaBH_4$ and $NaBD_4$

A mixture of **3** (300 mg, 0.54 mmol) and $NaBH_4$ (82 mg, 2.16 mmol) was stirred in thf (15 ml) until a clear red solution was obtained (about 1 h). The solvent was then removed under vacuum and the organometallic product was extracted from the residue with diethyl ether (20 ml). Evaporation of the volatiles gave a solid, which was washed with pentane (10 ml) to afford complex **7** as an analytically pure red powder (200 mg,71% yield). Complex **7** was obtained as a mixture of two inseparable isomers **7a** and **7b** in 4:1 ratio by chromatography.

Complex **7**: Anal. Calc. for $C_{15}H_{20}Mo_2O_2S_3$: C, 34.6; H, 3.9. Found: C, 34.7; H, 3.9%. IR (CH_2Cl_2, cm^{-1}), **7a**: 2850 w (*v* C–H*endo*), 2780 m (*v* C–H*exo*), 1938 s and 1859 s (*v* CO). ^1H NMR δ/ppm ($CDCl_3$; 298 K), **7a**: 5.37 (s, 5H, C_5H_5), 5.09, 5.02, 3.95, 3.86 (m, 1H, C*H* (C_5H_6)), 3.67 and 3.54 (AB, $^2J_{H-H} = 12.3$ Hz, 2H, CH_2 (C_5H_6)), 2.53, 2.52, 1.31 (s, 3H, SCH_3), **7b**: 5.63, 5.55 (m, 1H, C*H* (C_5H_6)), 5.51 (s, 5H, C_5H_5), 3.31, 3.25 (m, 1H, C*H*(C_5H_6)), obscured peaks and 3.16 (AB, $^2J_{H-H} = 13.6$ Hz, 2H, CH_2(C_5H_6)), 2.28, 2.23, 1.59 (s, 3H, SCH_3). ^{13}C NMR δ/ppm ($CDCl_3$; 298 K), **7a**: 242.9, 231.5 (s, *C*O), 90.7 (dm, $^1J_{C-H} = 179.0$ Hz, C_5H_5), 81.9 (dm, $^1J_{C-H} = 178.5$ Hz, C_5H_6), 81.3 (dm, $^1J_{C-H} = 176.5$ Hz, C_5H_6), 71.7 (dm, $^1J_{C-H} = 170.5$ Hz, C_5H_6), 70.0 (dm, $^1J_{C-H} = 174.0$ Hz, C_5H_6), 46.6 (ddm, $^1J_{C-H} = 141.5$ Hz, *C*H_2 (C_5H_6)), 25.5, 25.2, 6.3 (q, $^1J_{C-H} = 139.0$ Hz, S*C*H_3); **7b**: 242.1, 233.6 (*C*O), 90.4 (C_5H_5), 82.7, 81.0, 66.0, 65.0 (*C*H(C_5H_6)), 41.0 (*C*H_2(C_5H_6)), 26.2, 25.9, 8.4 (S*C*H_3).

Using a similar procedure, a solution of **3** (300 mg, 0.54 mmol) and $NaBD_4$ (91 mg, 2.16 mmol) in thf (15 ml) was stirred at room temperature for 1 h. Work up of the product as described above afforded **8** in good yield. Complex **8** was obtained as a mixture of four inseparable isomers **8a**–**8d** in the ratio 70:17:6:1 by chromatography.

^1H NMR δ/ppm ($CDCl_3$; 298 K), **8a**: 5.36 (s, 5H, C_5H_5), 5.08, 5.01, 3.94, 3.83, 3.51 (m, 1H, C_5H_5D), 2.53, 2.51, 1.31 (s, 3H, SCH_3); **8b**: 5.63 (m, 1H, C_5H_5D), 5.51 (s, 5H, C_5H_5), 3.65, 3.55, 3.32, 3.26 (m, 1H, C_5H_5D), 2.28, 2.23, 1.58 (s, 3H, SCH_3); **8c**: 5.40 (s, 5H, C_5H_5), 5.23, 4.93, 3.67, 3.17 (m, 1H, C_5H_5D), 2.36, 1.44, 1.33 (s, 3H, SCH_3); **8d**: 5.58 (m, 1H, C_5H_5D), 5.55 (s, 5H, C_5H_5), 5.18, 5.13, 3.21 (m, 1H, C_5H_5D), 2.10, 1.78, 1.63 (1, 3H, SCH_3).

5.8. Reaction of **3** with alkyl-arylmagnesium chloride *RMgCl*

(a) – R = CH_3: In a typical procedure ca. 3 equiv. of methylmagnesium chloride ($V = 200$ μl) were added to a suspension of **3** (100 mg, 0.18 mmol) in tetrahydrofuran (30 ml). The solution was stirred at room temperature for 15 min and then was filtered to remove insoluble material. The filtrate was evaporated to yield an oily residue (96.4 mg), which was shown by ^{1}H NMR analysis to contain three compounds: **9** (70%), *trans–syn/anti*-[$Mo_2Cp_2(CO)_2(\mu\text{-}SMe)_2$] (24%) and [$Mo_2Cp_2(\mu\text{-}SMe)_4$] (6%). The residue was dissolved in n-hexane (3ml) and chromatographed on silica gel. Elution with hexane-diethyl ether (95:5) removed an orange band, which afforded, after evaporation of the solvents, compound **9** as a pure sticky orange solid (65.5 mg, 68% yield). Complex **11** was obtained as a mixture of four inseparable isomers **9a**, **9b**, **9c** and **9d** in 10:2.5:2:1 ratio by chromatography.

Complex **9**: IR (CH_2Cl_2, cm^{-1}): 1939 vs and 1862 s (*v* CO). Complex **9** was only obtained as a sticky solid in spite of several attempts to get it as a powder by crystallization from various solvents. For this reason, no elemental analysis is available for **9**. ^{1}H NMR δ/ppm ($CDCl_3$; 298 K), **9a**: 5.37 (s, 5H, C_5H_6), 4.90, 4.83, 4.03, 3.94 (m, 1H, C_5H_5Me), 3.52 (q, $^3J_{H-H} = 6.0$ Hz, 1H, C_5H_5Me), 2.52, 2.50, 1.30 (s, 3H, SCH_3), 0.84 (d, $^3J_{H-H} = 6.0$ Hz, 3H, CH_3); **9b**: 5.51 (s, 1H, C_5H_5), 5.45, 3.38, 3.31, 3.17 (m, 1H, C_5H_5Me), 2.29, 2.24, 1.56 (s, 3H, SCH_3), 0.74 (d, $^3J_{H-H} = 6.1$ Hz, 3H, CH_3); **9c**: 5.40 (s, 5H, C_5H_5), 5.05, 4.76, 3.97, 3.82, 3.04 (m, 1H, C_5H_5Me), 2.36, 1.44, 1.32 (s, 3H, SCH_3), 0.96 (d, $^3J_{H-H} = 6.6$ Hz, 3H, CH_3); **9d**: 5.54 (s, 5H, C_5H_5), 5.11, 4.97, 4.15, 3.26 (m, 1H, C_5H_5Me), 2.10, 1.75, 1.59 (s, 3H, SCH_3), 0.78 (d, $^3J_{H-H} = 6.5$ Hz, 3H, CH_3). ^{13}C {^{1}H} NMR δ/ppm ($CDCl_3$; 298 K), **9a**: 243.0, 230.7 (*C*O), 90.7 (C_5H_5), 79.4, 78.9, 77.9, 76.3 (C_5H_5Me), 52.5 (C_4H_4CHMe), 30.7 (CH_3), 25.4, 25.2, 6.4 (SCH_3); **9b**: 242.4, 233.1 (*C*O), 90.5 (C_5H_5), 78.9, 72.2, 71.3 (C_5H_5Me), 46.8 (C_4H_4CHMe), 29.7 (CH_3), 26.3, 26.0, 8.4 (SCH_3); **9c**: 242.4, 231.1 (*C*O), 90.5 (C_5H_5), 79.6, 76.0, 74.4 (C_5H_5Me), 52.3 (C_4H_4CHMe), 31.9 (CH_3), 8.9, 7.2 (SCH_3); **9d**: 242.0, 232.0 (*C*O), 71.0, 69.0, 65.8, (C_5H_5Me), 47.5 (C_4H_4CHMe), 27.0 (CH_3), 15.3, 11.0, 9.0 (SCH_3).

(b) – R = $CH(CH_3)_2$: A mixture of **3** (110 mg, 0.180 mmol) and 2 equiv. of isopropylmagnesium chloride ($V = 200$ μl) was stirred in tetrahydrofuran (20 ml) until a clear red solution was obtained (about 15 min). The solvent was then removed under vacuum and the organometallic products were extracted from the residue with diethyl ether (2 × 20 ml). Evaporation of the volatiles gave an oily product (105 mg), which was shown by ^{1}H NMR ($CDCl_3$) analysis to contain three compounds: **10** (88%), *trans–syn*-[$Mo_2Cp_2(CO)_2(\mu\text{-}SMe)_2$] (9.5%) and the oxo-derivatives *trans–syn/anti*-[$Mo_2Cp_2(CO)(O)(\mu\text{-}SMe)_2$] (2.5%). The residue was dissolved in *n*-hexane (3 ml) and chromatographed on silica gel. Elution with hexane-diethyl ether (95:5) removed a red band, which gave, after evaporation of the solvents, compound **10** as a pure sticky solid (~95 mg, 85% yield). For the reasons which applied for complex **9** an elemental analysis cannot be provided for **10**. It was obtained as mixture of four inseparable isomers **10a**, **10b**, **10c** and **10d** in the 20:5.5:2.5:1 ratio by chromatography.

Complex **10**: IR (CH_2Cl_2, cm^{-1}): 1939 vs and 1863 s (*v* CO). ^{1}H NMR δ/ppm ($CDCl_3$; 298 K), **10a**: 5.37 (s, 5H, C_5H_5), 4.90, 4.82, 4.09, 4.00 (m, 1H, $C_5H_5CHMe_2$), 3.01 (dm, $^3J_{H-H} = 8.2$ Hz, 1H, $C_5H_5CHMe_2$), 2.52, 2.50, 1.30 (s, 3H, SCH_3), 1.08 (m, 1H, $C_5H_5CHMe_2$), 0.86 (m, 6H, $C_5H_5CHMe_2$); **10b**: 5.50 (s, 5H, C_5H_5), 5.43, 3.40, 3.35, 2.78 (m, 1H, $C_5H_5CHMe_2$), 2.29, 2.24, 1.54 (s, 3H, SCH_3), 0.94 (m, 1H, $C_5H_5CHMe_2$), 0.73 (dm, $^3J_{H-H} = 6.6$ Hz, 6H, $C_5H_5CHMe_2$); **10c**: 5.40 (s, 5H, C_5H_5), 5.05, 4.75, 4.02, 3.87, 2.66 (m, 1H, $C_5H_5CHMe_2$), 2.36, 1.44, 1.32 (s, 3H, SCH_3); **10d**: 5.53 (s, 5H, C_5H_5), 5.08, 5.02, 3.96, 2.88 (m, 1H, $C_5H_5CHMe_2$), 2.10, 1.75, 1.58 (s, 3H, SCH_3).

Trans-syn-[$Mo_2Cp_2(CO)(O)(\mu\text{-}SMe)_2$]: ^{1}H NMR δ/ppm ($CDCl_3$; 298 K): 5.96 (s,5H, C_5H_5), 5.42 (s, 5H, C_5H_5), 2.32 (s, 6H, SCH_3).

Trans-anti-[$Mo_2Cp_2(CO)(O)(\mu\text{-}SMe)_2$]: ^{1}H NMR δ/ppm ($CDCl_3$; 298 K): 6.03 (s, 5H, C_5H_5), 5.40 (s, 5H, C_5H_5), 2.68 (s, 3H, SCH_3), 2.17 (s, 3H, SCH_3).

(c) – R = $(CH_2)_3CH_3$: When a red suspension of **3** (200 mg, 0.36 mmol) in 30 ml of tetrahydrofuran was treated with butylmagnesium chloride (2.5 equiv., $V = 460$ μl), a rapid colour change to dark-red occurred. After stirring for 1 h, the solvents were removed to dryness and the residue was dissolved in hexane (5 ml) and chromatographed on silica gel. Elution with CH_2Cl_2–hexane (1:1) afforded a red band, which gave **11** as a red sticky solid ($m = 170$ mg, 82% yield). Complex **11** was obtained as a mixture of four inseparable isomers **11a**, **11b**, **11c** and **11d** in 19.5:4.5:3:1 ratio by chromatography.

Complex **11**: IR (CH_2Cl_2, cm^{-1}): 1939 vs and 1862 s (*v* CO). ^{1}H NMR δ/ppm ($CDCl_3$; 298 K), **11a**: 5.37 (s, 5H, C_5H_5), 4.91, 4.83, 4.07, 3.97, 3.38 (m, 1H, $C_5H_5Bu^n$), 2.52, 2.50, 1.30 (s, 3H, SCH_3), 1.28 (m, 6H, $(CH_2)_3CH_3$), 0.88 (m, 3H, $(CH_2)_3CH_3$); **11b**: 5.51 (s, 5H, C_5H_5), 5.46, 3.42, 3.38, 3.06 (m, 1H, $C_5H_5Bu^n$), 2.29, 2.24, 1.55 (s, 3H, SCH_3), 1.10 (m, 6H, $(CH_2)_3CH_3$), 0.82 (m, 3H, $(CH_2)_3CH_3$); **11c**: 5.40 (s, 5H, C_5H_5), 5.06, 4.77, 4.01, 3.85 (m, 1H, $C_5H_5Bu^n$), 2.36, 1.44, 1.32 (s, 3H, SCH_3), 1.10 (m, 6H, $(CH_2)_3CH_3$), 0.82 (m, 3H, $(CH_2)_3CH_3$); **11d**: 5.54 (s, 5H, C_5H_5), 5.28, 5.14, 3.60, 3.17 (m, 1H, $C_5H_5Bu^n$), 2.09, 1.75, 1.58 (s, 3H, SCH_3), 1.21 (m, 6H, $(CH_2)_3CH_3$), 0.98 (m, 3H, $(CH_2)_3CH_3$). ^{13}C {^{1}H} NMR δ/ppm ($CDCl_3$; 298 K), **11a**: 243.1, 230.6 (*C*O), 90.8 (C_5H_5), 79.9, 79.3, 76.5, 74.9

($C_5H_5Bu^n$), 58.1 ($C_4H_4CHBu^n$), 45.6, 29.0 (($CH_2)_3CH_3$), 25.4, 25.2 (SCH_3), 23.0 (($CH_2)_3CH_3$), 14.2 (($CH_2)_3CH_3$), 6.4 (SCH_3); **11b**: 242.6, 233.4 (*C*O), 90.5 (C_5H_5), 81.0, 79.2, 71.0, 70.0 ($C_5H_5Bu^n$), 52.2 ($C_4H_4CHBu^n$), 46.6, 28.9 (($CH_2)_3CH_3$), 26.4, 26.3 (SCH_3), 22.8 (($CH_2)_3CH_3$), 14.2 (($CH_2)_3CH_3$), 8.2 (SCH_3); **11c**: 242.6 (*C*O), 90.7 (C_5H_5), 79.5, 78.0, 74.7, 73.1 ($C_5H_5Bu^n$), 57.7 ($C_4H_4CHBu^n$), 29.8 (($CH_2)_3CH_3$), 26.0 (SCH_3), 14.2 (($CH_2)_3CH_3$), 8.9, 7.2 (SCH_3).

(d) – $R = C_6H_5$: A large excess of phenylmagnesium (4 equiv., $V = 720$ μl) was added to a suspension of **3** (200 mg, 0.36 mmol) in tetrahydrofuran (30 ml) at −60 °C. The mixture was stirred until the temperature reached 20 °C, affording a clear red solution. The solvents were then removed under vacuum and the organometallic products were extracted from the residue with diethyl ether (3 × 20 ml). Evaporation of the volatiles gave an oily product (211 mg), which was shown by ^{1}H NMR ($CDCl_3$) analysis to contain only one compound **12** (98% yield). Complex **12** was formed as a mixture of four isomers **12a**, **12b**, **12c** and **12d** in 21:9:2:1 ratio. Red analytically pure crystals of **12** of X-ray quality were obtained from cold diethyl ether by fractional crystallization of the complex. When the above reaction was conducted at ambient temperature *trans–syn* bis (carbonylthiolato) and oxo-derivatives, [$Mo_2Cp_2(CO)_2$-(μ-SMe)$_2$] (8.5%) and [$Mo_2Cp_2(CO)(O)$(μ-SMe)$_2$] (1.5%), were recovered together with compound **12** (90%), which was obtained as a mixture of four isomers **12a**, **12b**, **12c** and **12d** in the 8:3:2:1 ratio.

Complex **12**: Anal. Calc. for $C_{21}H_{24}Mo_2O_2S_3$. C, 42.3; H, 4.05. Found: C, 42.1; H, 4.06%. IR(CH_2Cl_2, cm^{-1}): 1939 s and 1862 s (*v* CO). ^{1}H NMR δ/ppm ($CDCl_3$; 298 K), **12a**: 7.58–7.15 (m, 5H, C_6H_5), 5.37 (m, 5H, C_5H_5), 5.01, 4.94, 4.62, 4.17, 4.08 (m, 1H, C_5H_5Ph), 2.54, 2.52, 1.30 (s, 3H, SCH_3); **12b**: 7.58–7.15 (m, 5H, C_6H_5), 5.52 (s, C_5H_5), 5.43, 4.39, 3.52 (m, 1H, C_5H_5Ph), 2.30, 2.26, 1.62 (s, 3H, SCH_3); **12c**: 7.58–7.15 (m, 5H, C_6H_5), 5.40 (s, 5H, C_5H_5), 5.17, 4.84, 4.11, 3.97 (m, 1H, C_5H_5Ph), 2.38, 1.43, 1.32 (s, 3H, SCH_3); **12d**: 7.58–7.15 (m, 5H, C_6H_5), 5.54 (s, 5H, C_5H_5) 4.48, 3.68, (m, 1H, C_5H_5Ph), 2.11, 1.77, 1.66 (s, 3H, SCH_3).

5.9. Reaction of 3 with alkyllithium LiR (R = CH_3, Bu^n)

A suspension of the red complex **3** (200 mg, 0.36 mmol) in 40 ml of tetrahydrofuran was stirred at room temperature in presence of *n* equiv. of alkyllithium ($R = CH_3$: $n = 2$, $V = 45$ μl; $R = Bu^n$: $n = 4$, $V = 576$ μl) until a clear orange ($R = CH_3$) or red ($R = Bu^n$) solution was obtained (about 20 min). Filtration of the mixture and removal of the solvents gave an oily residue. Organometallic products were extracted from the residue with either dichloromethane or diethyl ether (2 × 30 ml). Evaporation of the volatiles afforded sticky solids ($R = CH_3$: 125 mg; $R = Bu^n$: 133 mg), which were shown by ^{1}H NMR analyses to be a mixture of the η^4-cyclopentadiene compound [$R = CH_3$: **9** (76%); $R = Bu^n$: **11** (82%)], *trans–syn/anti*-[$Mo_2Cp_2(CO)_2$(μ-SMe)$_2$] ($R = CH_3$: 13.5%; $R = Bu^n$: 12.5%) and *trans–syn/anti* oxo-derivatives [$Mo_2Cp_2(CO)(O)$(μ-SMe)$_2$] ($R = CH_3$: 10.5%; $R = Bu^n$: 5.5%). This mixture was dissolved in n-hexane (5 ml) and chromatographed on silica gel. Elution with n-hexane-diethyl ether (95:5) removed either an orange ($R = CH_3$) or red ($R = Bu^n$) band, which gave, after evaporation of the solvents, the η^4-cyclopentadiene complex as a pure sticky orange or red solid [**9** ($R = CH_3$): 95 mg, 49% yield; **11** ($R = Bu^n$): 109 mg, 52.5% yield].

5.10. Preparation of 16

A solution of [Mo_2Cp_2(μ-SMe)$_2$(μ-Cl)(μ-PPh_2)] (300 mg, 0.47 mmol) in acetonitrile (60 ml) was stirred in the presence of 2.5 equiv. of Bu^tNC ($V = 130$ μl) for 1 h at room temperature. The colour of the solution turned from violet to orange. Evaporation of the volatiles gave a solid, which was washed with diethyl ether (2 × 20 ml) and pentane (2 × 20 ml) to afford complex **16** as an analytically pure ochre powder (315 mg, 79% yield).

Complex **16**: Anal. Calc. for $C_{34}H_{44}ClMo_2N_2PS_2$, 0.5 CH_2Cl_2: C, 49.0; H, 5.4, N, 3.3; P, 3.7. Found: C, 48.8; H, 5.4; N, 3.4; P, 4.2%. IR (KBr pellet, cm^{-1}): 2127 s (*v* CN). ^{1}H NMR δ/ppm ($(CD_3)_2CO$; 298 K): 7.4–6.8 (m, 10H, C_6H_5), 5.37 (d, $^3J_{P-H} = 0.7$ Hz, 10H, C_5H_5), 2.45 (s, 6H, SCH_3), 1.66 (s, 18H, $C(CH_3)_3$). $^{13}C\{^1H\}$ NMR δ/ppm ($(CD_3)_2CO$;298 K): 162.0 (d, $^2J_{P-C} = 9.3$ Hz, Bu^tNC), 135.2 (d, $^1J_{P-C} = 40.4$ Hz, *C*ipso(C_6H_5)), 134.0 (d, $J_{P-C} = 7.4$ Hz, C_6H_5), 129.0 (s, *C*para(C_6H_5)), 127.8 (d, $J_{P-C} = 9.9$ Hz, C_6H_5), 89.7 (s, C_5H_5), 59.6 (s, CMe_3), 30.3 (s, $C(CH_3)_3$), 27.6 (d, $^3J_{P-C} = 18$ Hz, SCH_3).

5.11. Reaction of 16 with $NaBH_4$

The complex **16** (200 mg, 0.236 mmol) and 4 equiv. of $NaBH_4$(35 mg) were stirred in tetrahydrofuran (50 ml) at room temperature for 1 h. The solvent was then removed under vacuum and the organometallic product was extracted with diethyl ether (2 × 20 ml). Evaporation of the volatiles gave a solid, which was dissolved in CH_2Cl_2 (5 ml) and chromatographed on florisil. Elution with dichloromethane removed an orange band, which gave, after evaporation of the solvents, compound **17** as an analytically pure, orange powder (134 mg, 80% yield).

5.12. Reactions of η^4-cyclopentadiene compounds 9, 11 and 12 with HBF_4

A dichloromethane (20 ml) solution of **9** (150 mg, 0.28 mmol) or **11** (150 mg, 0.26 mmol) or **12** (210 mg,

0.35 mmol) was treated at room temperature with 1 equiv. of tetrafluoroboric acid (**9**: $V = 38$ μl; **11**: $V = 35$ μl; **12**: $V = 47$ μl). The mixture was stirred for a few minutes, and the solution changed from either orange (**9**) or red (**11**, **12**) to dark-red. The volume of the solution was then reduced under vacuum and diethyl ether was added to precipitate powders that were washed twice with pentane (2×10 ml), affording maroon products **13** (86 mg, 49% yield), **14** (100 mg, 51.5% yield) and **15** (80 mg, 33% yield). Complexes **13**–**15** were each obtained as mixtures of two isomers **13a** and **13b**, **14a** and **14b**, and **15a** and **15b** in 4:1, 3:1 and 7:1 ratios, respectively.

Complex **13**: Anal. Calc. for $C_{16}H_{21}BF_4Mo_2O_2S_3$: C, 30.9; H, 3.4. Found: C, 30.5; H, 3.4%. IR (CH_2Cl_2, cm^{-1}), **13a**: 1999 vs and 1967 sh (*ν* CO), 1100–1000 s, br (*ν* B–F); **13b**: masked peak and 1941 m (*ν* CO), 1100–1000 s, br (*ν* B–F). ^1H NMR *δ*/ppm ($(CD_3)_2CO$; 298 K), **13a**: 6.02 (s, 5H, C_5H_5), 5.93, 5.86 (m, 2H, C_5H_4Me), 2.65, 2.61 (s, 3H, SCH_3), 2.16 (s, 3H, CH_3), 1.75 (s, 3H, SCH_3); **13b**: 6.05 (s, 5H, C_5H_5), 5.98, 5.82 (m, 2H, C_5H_4Me), 2.47, 2.24 (s, 3H, SCH_3), 1.81 (s, 3H, CH_3), 1.75 (s, 3H, SCH_3). $^{13}C\{^1H\}$ NMR *δ*/ppm ($(CD_3)_2CO$; 298 K), **13a**: 233.7, 233.0 (*C*O), 94.1 (C_5H_5), 97.1, 94.7, 93.9, 90.5, 90.4 (C_5H_4Me), 27.3, 26.5 (SCH_3), 15.4 (CH_3), 8.5 (SCH_3); **13b**: 234.0, 233.4 (*C*O), 94.1 (C_5H_5), 97.3 93.5, 92.8, 91.0, 89.4 (C_5H_4Me).

Complex **14**: Anal. Calc.for $C_{19}H_{27}BF_4Mo_2O_2S_2$, CH_2Cl_2: C, 32.1; H, 3.9. Found: C, 32.0; H, 3.8%. IR (CH_2Cl_2, cm^{-1}) 1999vs and 1972 sh (*ν* CO). ^1H NMR *δ*/ppm ($(CD_3)_2CO$; 298 K), **14a**:6.01 (s, 5H, C_5H_5), 5.99, 5.87 (m, 2H, C_5H_4Me), 2.65, 2.60 (s, 3H, SCH_3), 2.35(t, $^3J_{H-H} = 7.6$ Hz, 2H, CH_2-$(CH)_2$–CH_3), 1.74 (s, 3H, SCH_3), 1.65, 1.45 (m, 2H, CH_2-$(CH)_2$–CH_3), 0.92 (t, $^3J_{H-H} = 7.2$ Hz, 3H, $(CH_2)_3CH_3$); **14b**: 6.04 (s, 5H, C_5H_5), 5.92, 5.83 (m, 2H, $C_5H_4Bu^n$), 2.69, 2.62 (s, 3H, SCH_3), 2.41 (t, 2H, $(CH_2)_3CH_3$), 1.79 (s, 3H, SCH_3), 1.72, 1.27 (m, 2H, $(CH_2)_3CH_3$), 0.87 (t, 3H, $(CH_2)_3CH_3$). $^{13}C\{^1H\}$ NMR *δ*/ppm ($(CD_3)_2CO$,298 K), **14a**: 233.9, 233.2 (*C*O), 97.3, 95.2 ($C_5H_4Bu^n$), 94.3 (C_5H_5), 93.6, 91.1, 90.7 ($C_5H_4Bu^n$), 33.8 (CH_2–CH_2–CH_2CH_3), 27.5, 26.7 (SCH_3), 22.9, 15.6 (CH_2–CH_2–CH_2–CH_3), 14.0 ($(CH_2)_3CH_3$), 8.6 (SCH_3); **14b**: 234.4, 233.6 (*C*O), 96.4, 94.4 ($C_5H_4Bu^n$), 94.1 (C_5H_5), 92.7, 91.8, 90.6 ($C_5H_4Bu^n$), 34.3 (CH_2–CH_2–CH_2–CH_3), 28.3 (SCH_3), 9.4 ($(CH_2)_3CH_3$), 8.7 (SCH_3).

Complex **15**: IR (CH_2Cl_2, cm^{-1}): 1999 s and 1951 mw (*ν* CO), 1075–1053 s, br (*ν* B–F). ^1H NMR *δ*/ppm ($(CD_3)_2CO$; 298 K), **15a**: 7.68–7.65 and 7.39–7.37 (m, 5H, C_6H_5), 6.56 (m, 2H, C_5H_4Ph), 6.11 (m, 2H, C_5H_4Ph), 5.96 (s, 5H, C_5H_5), 2.51, 2.49, 1.49 (s, 3H, SCH_3); **15b**: 7.90 and 7.42–7.41 (m, 5H, C_6H_5), 6.67 (m, 2H, C_5H_4Ph), 5.97 (m, 5H, C_5H_5), 2.48, 2.47, 1.44 (s, 3H, SCH_3).

*5.13. X-ray crystallographic studies of **5**, **6** and **12***

All measurements were made at 100 K on a Nonius KappaCCD diffractometer with Mo Kα radiation, $\lambda = 0.71073$ Å. Standard procedures were used to solve and refine each structure [2,27] In general, non-hydrogen atoms were refined with anisotropic displacement tensors. H-atoms were located using stereochemical considerations or from difference maps and subsequently rode on their parent C atoms. Only the H-atoms bonded to C(7) and C(10) in **12** were freely refined. Further details for each structure are given in Table 3. For **5** and **6** the crystals were of poor quality for diffraction analysis; the results presented here are in each case the better of two separate (and consistent) analyses performed with different crystals. For **5** there was the further complication, discussed above, that the C_5H_5 and C_5H_6 rings are disordered. Attempts to model this disorder explicitly were unsuccessful. Apart from systematic errors in bond lengths discussed above, the disorder manifests itself through some physically unreasonable vibration tensors, particularly for the ring carbon atoms.

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Appendix A. Deposited material

Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as CCDC Nos. 268261–268263. Copies can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: (international) +44 1223 336 033; e-mail: deposit@ccdc.com.ac.uk]. Also deposited as supplementary data are tables of crystallographic data atomic parameters and bond lengths and angles. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2005.07.034.

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