DALTON

Control of the reactivity of *trans*-$[Mo_2(cp)_2(CO)(Y{\equiv}Z)(\mu\text{-}SR)_2]$ (cp = $\eta\text{-}C_5H_5$; Y≡Z = CO or CN^-) by the sulfur substituents (R = Me, Pr^i, Bu^t, Ph or CF_3). Crystal structure of *trans*-$[Mo_2(cp)_2(CO)(CNMe)(\mu\text{-}SCF_3)_2]$†

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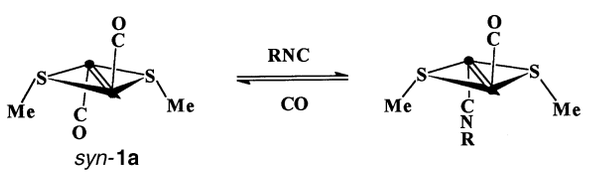
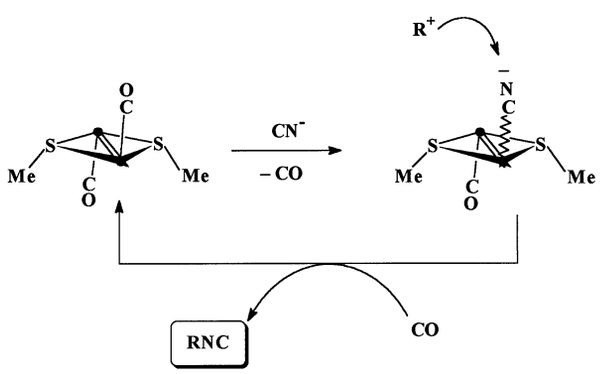
Reaction of *trans*-$[Mo_2(cp)_2(CO)_2(\mu\text{-}SR)_2]$ (cp = $\eta\text{-}C_5H_5$; R = Me, Pr^i, Bu^t, Ph or CF_3; *syn* and *anti* isomers) with cyanide ion gave the corresponding cyanide complexes *trans*-$[Mo_2(cp)_2(CO)(CN)(\mu\text{-}SR)_2]^-$, except with R = Bu^t where no reaction was observed. For R = CF_3, two isomers having a *syn* orientation of the sulfur substituents were obtained. The nature of the R groups is shown to have a crucial influence on the site of the reaction of the cyanide complexes with Me_3O^+. Complexes where R = Me, Pr^i (*syn* and *anti* isomers) or Ph (*anti* isomer) were S-methylated, whereas N-methylation was observed for R = Ph (*syn* isomer) or CF_3 (*anti* and both *syn* isomers). This is ascribed to electronic effects of the R groups which control the site of methylation by switching the reaction from orbital control (S-methylation) to charge control (N-methylation). For R = CF_3, the R groups also affect the reaction of the dicarbonyl precursor with a Y≡Z substrate since the preferred site of attack is different for Y≡Z = CN^- and Y≡Z = RNC.

In previous papers of this series we have shown that reactive intermediates can be generated electrochemically from stable precursors possessing the $\{Mo_2(\mu\text{-}SR)_n\}$ core (n = 2 or 3).[1,2] In the absence of substrates, deactivation of these sites leads to the thermodynamically stable complex *trans*-$[Mo_2(cp)_2(CO)_2(\mu\text{-}SMe)_2]$ (cp = $\eta^5\text{-}C_5H_5$; *trans* relates to the positions of the CO and cp ligands). However, this complex possesses an interesting reactivity. In particular, its reaction with isocyanides produces the substituted $[Mo_2(cp)_2(CO)(CNR)(\mu\text{-}SMe)_2]$ derivatives and the reaction can be reversed by CO (Scheme 1).[2] Furthermore, as we show herein, complex **1a** reacts with cyanide ion. This suggested that *trans*-$[Mo_2(cp)_2(CO)_2(\mu\text{-}SMe)_2]$ might be used as a platform at which various isocyanides could be assembled through the successive reactions of cyanide ions and different electrophilic reagents. Many studies have been concerned with the synthesis of isocyanides in the co-ordination sphere of metal centres and this has been reviewed recently.[3] The interest of *trans*-$[Mo_2(cp)_2(CO)_2(\mu\text{-}SMe)_2]$ in this context lies in the fact that the new isocyanide molecule can be easily released by a reaction of the complex with carbon monoxide, Scheme 1. The crucial question was whether or not electrophilic reagents attack the co-ordinated CN^- group thus enabling a cycle such as that shown in Scheme 2.



Scheme 1 ● = Mo(cp); R = Bu^t, xylyl or CH_2Ph



Scheme 2

The results presented here demonstrate that the cyanide complex $[Mo_2(cp)_2(CO)(CN)(\mu\text{-}SMe)_2]^-$ **2a** does indeed react with Me_3O^+ but that the site of attack is a sulfur lone pair rather than the bound cyanide. We also deduce the factors which control the site of attack by studying the reactions of various new cyanide complexes related to **2a** with Me_3O^+. A preliminary account of this work has been published.[4]

Results

Synthesis and methylation of $[Mo_2(cp)_2(CO)(CN)(\mu\text{-}SMe)_2]^-$ 2a

Synthesis. The complex *trans*-$[Mo_2(cp)_2(CO)_2(\mu\text{-}SMe)_2]$ **1a** exists as two isomers which differ by the relative orientation of the sulfur substituents,[5,‡] *syn* and *anti*, the spectroscopic and redox data for which are listed in Tables 1 and 2 respectively. Cyclic voltammetric monitoring of the stepwise addition of CN^- to a solution of *trans*,*syn*-$[Mo_2(cp)_2(CO)_2(\mu\text{-}SMe)_2]$ *syn*-**1a** in MeCN–$[NBu_4][PF_6]$ shows that the reaction [equation (1)]

† Electrochemistry of dinuclear, thiolate-bridged transition-metal compounds. Part 9. Part 8: F. Y. Pétillon, S. Poder-Guillou, P. Schollhammer and J. Talarmin, *New J. Chem.*, in the press.

‡ The spectroscopic data for *trans*,*syn*-$[Mo_2(cp)_2(CO)_2(\mu\text{-}SMe)_2]$ are in very good agreement with those reported by Li and Curtis.[6] The other isomer was assigned by these authors as *cis*,*syn*-$[Mo_2(cp)_2(CO)_2(\mu\text{-}SMe)_2]$.

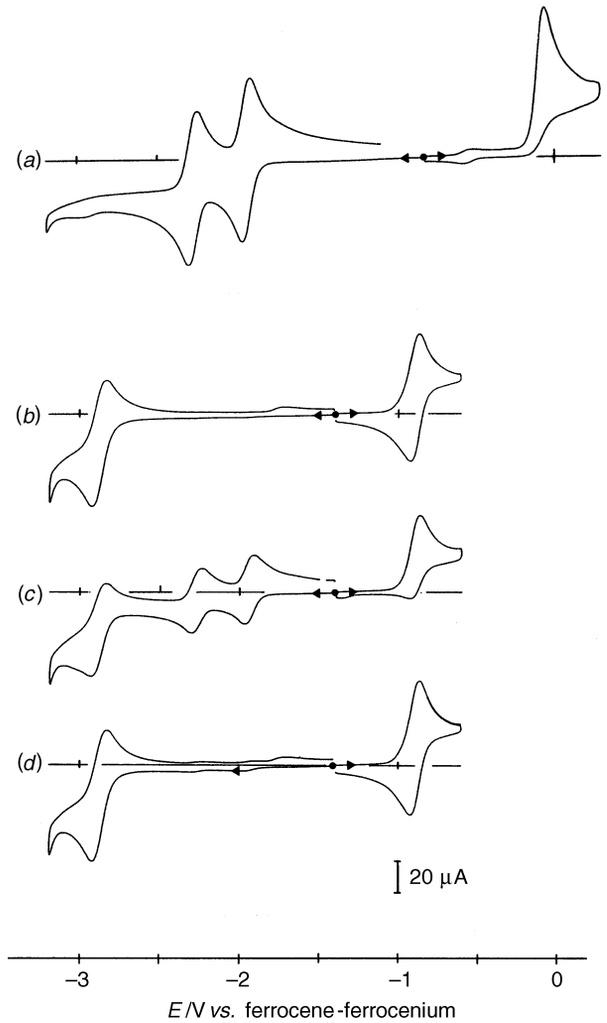


Fig. 1 Cyclic voltammetry of a 2.2 mmol dm^{-3} solution of *trans*-$[Mo_2(cp)_2(CO)_2(\mu\text{-}SMe)_2]$ *syn*-**1a** under N_2 before (*a*) and after (*b*) the addition of 1 equivalent $[NBu_4][CN]$; the curve in (*c*) was recorded after treatment of solution (*b*) with CO; (*d*) was obtained after the solution (*b*) had been flushed with N_2 ($MeCN–[NBu_4][PF_6]$ electrolyte; vitreous carbon electrode, $\nu = 0.2$ V s^{-1})

$$[Mo_2(cp)_2(CO)_2(\mu\text{-}SMe)_2] + CN^- \longrightarrow \underset{\textit{syn}\text{-}\mathbf{1a}}{\underset{\textit{anti}\text{-}\mathbf{1a}}{}} [Mo_2(cp)_2(CO)(CN)(\mu\text{-}SMe)_2]^- + CO \quad (1)$$
$$\underset{\textit{anti}\text{-}\mathbf{2a}}{\underset{\textit{syn}\text{-}\mathbf{2a}}{}}$$

leads to the formation of a 1:1 derivative, resistant to further substitution.[4] The reaction carried out with the *trans,anti* analogue gives similar results.

The assignment of the reaction product as $[Mo_2(cp)_2(CO)(CN)(\mu\text{-}SMe)_2]^-$ **2a** is confirmed by spectroscopic data, Table 1. The ^{13}C NMR spectrum shows the presence of one CO ligand instead of two in the precursor and, although it is not detected in the ^{13}C NMR spectrum, the co-ordination of CN^- is evidenced by infrared spectroscopy. The retention of the *syn* orientation of the methyl groups on the bridging sulfur atoms in *syn*-**2a** is confirmed by the singlet for the methyl protons in the ^1H NMR spectrum (Table 1), and the *trans* geometry of the dicarbonyl precursor is also maintained (see Discussion section).

The cyanide complex *syn*-**2a** is characterized [Fig. 1(*b*)] by reversible oxidation and reduction processes occurring at slightly different potentials for the *syn* and *anti* isomers (Table 2). Whereas the oxidation of the parent dicarbonyl is an irreversible process [Fig. 1(*a*)], that of the cyanide derivative is reversible on the cyclic voltammetry (CV) time-scale; however, in the presence of more than 1 equivalent CN^- the oxidation loses its reversibility. One reduction step (instead of two for the dicarbonyl precursor) is observed in the potential window available in MeCN or tetrahydrofuran (thf) electrolyte. This illustrates the effects of substitution of CN^- for CO: first, the presence of CN^- stabilizes the oxidized form of the complex (formally $Mo^{III}–Mo^{II}$) with respect to CO and secondly, as expected from the substitution of CO by a donor ligand, the redox processes are shifted towards negative potentials with respect to the redox steps of the dicarbonyl precursor, by about 900 mV. The magnitude of the potential shift is attributed, at least in part, to the negative charge carried by the cyanide complex. In agreement with the potential shift, the infrared spectrum of $[Mo_2(cp)_2(CO)(CN)(\mu\text{-}SMe)_2]^-$ shows the band of the remaining CO ligand at 1780 cm^{-1}, that is *ca.* 70 cm^{-1} lower than for the parent dicarbonyl complex (Table 1): this indicates a more important Mo to CO back donation due to the presence of the net donor cyanide ligand at the neighbouring metal centre. The reaction with CN^- can be reversed partially upon treatment of a solution of the cyanide complex with CO: as shown in Fig. 1(*c*), an equilibrium mixture containing the dicarbonyl and the cyanide complexes in a *ca.* 2:1 ratio is obtained under 1 atm (*ca.* 10^5 Pa) CO.§ That CN^- is only partially displaced whereas RNC is totally displaced under similar conditions shows that the cyanide ligand is more strongly retained than isocyanides RNC (R = Bu^t, xylyl or CH_2Ph)[2] by the $\{Mo_2(cp)_2(CO)(\mu\text{-}SMe)_2\}$ core. Flushing the CO-saturated solution with N_2 or Ar regenerates the cyanide complex *syn*-**2a**, Fig. 1(*d*).

A third isomer of $[Mo_2(cp)_2(CO)(CN)(\mu\text{-}SMe)_2]^-$, *syn*-**2a′** can be prepared electrochemically, as described previously for isocyanide complexes.[2] Controlled-potential electrolysis (CPE) of $[Mo_2(cp)_2(CO)_2(\mu\text{-}SMe)_3]^+$ performed in the presence of CN^- produces this new isomer (Figs. 2 and 3), which is accessible only by the electrochemical route. From Figs. 2(*a*) and 2(*b*) it can be seen that the addition of cyanide ions modifies the CV of $[Mo_2(cp)_2(CO)_2(\mu\text{-}SMe)_3]^+$ in much the same way as did the addition of isocyanide:[2] the redox systems of the intermediate *cis*-$[Mo_2(cp)_2(CO)_2(\mu\text{-}SMe)_2]$ are replaced by new peaks due to *syn*-**2a′**. The cyclic voltammogram recorded after electrolysis (1.3–1.7 F mol^{-1} starting material, N_2 purge¶) shows the redox processes of the electrogenerated complex at $E^{1/2}_{red} = -2.77$ V and $E^{1/2}_{ox} = -1.01$ V [Table 2, Fig. 2(*c*)]. No analytical data could be obtained for this complex which could not be separated from the supporting electrolyte. However, that *syn*-**2a′** is a cyanide complex with *syn*-Me substituents is demonstrated by the following experiments. Purging CO through a solution of it [Fig. 3(*a*), 3(*b*)] and flushing the resulting solution with N_2 [Fig. 3(*c*)] converted *syn*-**2a′** into *syn*-**2a**, which can be obtained directly from *trans,syn*-$[Mo_2(cp)_2(CO)_2(\mu\text{-}SMe)_2]$ and CN^- (Scheme 3). Indeed, the cyanide complex in Fig. 3(*b*) is no more *syn*-**2a′** but *syn*-**2a**, as demonstrated by the reduction potential $E^{1/2}_{red} = -2.86$ V, instead of $E^{1/2}_{red} = -2.77$ V in Fig.

§ We thank Dr. J. N. Verpeaux for drawing our attention to the fact that the equilibrium is not shifted by the reduction of the dicarbonyl complex at the electrode. This is shown by the fact that the ratio of the oxidation to reduction peak currents of the cyanide complex is almost the same in Figs. 1(*b*) and 1(*c*). The loss of reversibility of the oxidation of the cyanide complex, in Fig. 1(*c*), is due to the presence of free cyanide (released by co-ordination of CO): when a small excess of cyanide is added to the dicarbonyl complex the oxidation loses reversibility, due to a reaction of the oxidized complex with CN^-.

¶ Nitrogen is purged through the catholyte in order to remove the CO released on binding of CN^- or RNC to *cis*-$[Mo_2(cp)_2(CO)_2(\mu\text{-}SMe)_2]$; CO was shown[2] to catalyse the *cis/trans* isomerization of $[Mo_2(cp)_2(CO)_2(\mu\text{-}SMe)_2]$; therefore, the nitrogen purge during electrolyses prevents the formation of *trans*-$[Mo_2(cp)_2(CO)_2(\mu\text{-}SMe)_2]$ and of products derived therefrom.

Table 1 Spectroscopic data

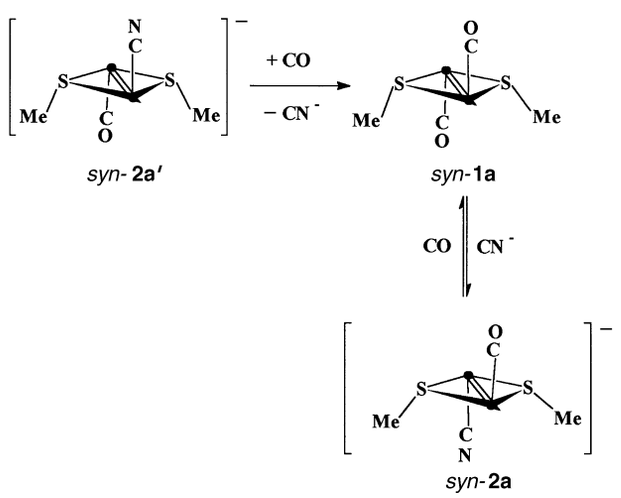
Complex	NMR (δ, *J*/Hz; $CDCl_3$) ^1H	^{13}C-{^1H}	IR (cm^{-1}) (CH_2Cl_2)
Dicarbonyls			
syn -**1a** *syn*-$[Mo_2(cp)_2(CO)_2(\mu\text{-}SMe)_2]$ [a]	5.44 (s, 5 H, cp) 5.29 (s, 5 H, cp) 2.36 (s, 6 H, SMe)	252.0, 246.5 (CO) 91.1 (cp) 32.6 (SCH_3)	ν(CO) 1855, 1885 (sh)
anti-**1a** *anti*-$[Mo_2(cp)_2(CO)_2(\mu\text{-}SMe)_2]$ [a]	5.40 (s, 10 H, cp) 2.29 (s, 6 H, SMe)	249.5 (CO) 91.0 (cp) 34.3 (SCH_3)	ν(CO) 1840
syn-**1b** *syn*-$[Mo_2(cp)_2(CO)_2(\mu\text{-}SPr^i)_2]$	5.47 (s, 5 H, cp) 5.27 (s, 5 H, cp) 2.43 (m, 2 H, CH) 1.49 (d, 6 H, J = 6.7, CH_3) 1.38 (d, 6 H, J = 6.7, CH_3)	250.8, 246.3 (CO) 91.6, 90.7 (cp) 50.1 (SCH) 26.0, 25.8 (CH_3)	ν(CO) 1855
anti-**1b** *anti*-$[Mo_2(cp)_2(CO)_2(\mu\text{-}SPr^i)_2]$	5.40 (s, 10 H, cp) 2.37 (m, 2 H, CH) 1.49 (d, 6 H, J = 6.7, CH_3) 1.29 (d, 6 H, J = 6.7, CH_3)	249.2 (CO) 91.1 (cp) 52.4 (SCH) 26.2, 26.0 (CH_3)	ν(CO) 1845
syn-**1c** *syn*-$[Mo_2(cp)_2(CO)_2(\mu\text{-}SBu^t)_2]$ [b]	5.49 (s, 5 H, cp) 5.15 (s, 5 H, cp) 1.28 [s, 18 H, $C(CH_3)_3$]	261.4, 247.0 (CO) 91.7, 90.5 (cp) 47.3 [$C(CH_3)_3$] 32.6 (CH_3)	ν(CO) 1845, 1880
syn-**1d** *syn*-$[Mo_2(cp)_2(CO)_2(\mu\text{-}SPh)_2]$	7.33–7.17 (m, 10 H, Ph) 5.63 (s, 5 H, cp) 5.28 (s, 5 H, cp)	248.4, 242.9 (CO) 147.6, 130.3, 128.0, 126.3 (C_6H_5) 92.0, 91.6 (cp)	ν(CO) 1855, 1905
anti-**1d** *anti*-$[Mo_2(cp)_2(CO)_2(\mu\text{-}SPh)_2]$	7.37–7.15 (m, 10 H, Ph) 5.42 (s, 10 H, cp)	246.8 (CO) 148.0, 130.6, 128.1, 126.5 (C_6H_5) 92.0 (cp)	ν(CO) 1855
syn-**1e** *syn*-$[Mo_2(cp)_2(CO)_2(\mu\text{-}SCF_3)_2]$	5.58 (s, 5 H, cp) 5.35 (s, 5 H, cp)	241.2, 239.8 (CO) 136.2 (q, J_{CF} = 320, CF_3) 92.0, 91.1 (cp)	ν(CO) 1890, 1950
anti-**1e** *anti*-$[Mo_2(cp)_2(CO)_2(\mu\text{-}SCF_3)_2]$	5.50 (s, 10 H, cp)	241.0 (CO) 136.4 (q, J_{CF} = 320, CF_3) 91.5 (cp)	ν(CO) 1900
Cyanides [c]			
syn-**2a** K[*syn*-$Mo_2(cp)_2(CO)(CN)(\mu\text{-}SMe)_2$]	5.19 (s, 5 H, cp) 4.25 (s, 5 H, cp) 2.13 (s, 6 H, SMe)	243.6 (CO) 89.1, 87.3 (cp) 32.7 (SCH_3)	ν(CN) 2060 ν(CO) 1780
syn-**2e′** K[*syn*-$Mo_2(cp)_2(CO)(CN)(\mu\text{-}SCF_3)_2$]	5.20 (s, 5 H, cp) 4.81 (s, 5 H, cp)	239.6 (CO) 90.0, 89.3 (cp)	
syn-**2e**	5.34 (s, 5 H, cp) 4.53 (s, 5 H, cp)	238.6 (CO) 152.3 (CN) 90.3, 88.8 (cp)	ν(CN) 2040 ν(CO) 1885
anti-**2e** K[*anti*-$Mo_2(cp)_2(CO)(CN)(\mu\text{-}SCF_3)_2$]	5.31 (s, 5 H, cp) 4.63 (s, 5 H, cp)	237.8 (CO) 151.1 (CN) 90.1, 89.2 (cp)	
syn-**2d** [NBu_4][*syn*-$Mo_2(cp)_2(CO)(CN)(\mu\text{-}SPh)_2$]	7.54–6.95 (Ph) 5.04 (s, 5 H, cp) 4.34 (s, 5 H, cp)	244.0 (CO) 89.6, 88.3 (cp)	ν(CN) 2070 ν(CO) 1800
Isocyanides [d]			
4a *syn*-$[Mo_2(cp)_2(CO)(CNMe)(\mu\text{-}SCF_3)_2]$ Brown-yellow	5.31 (s, 5 H, cp) 5.25 (s, 5 H, cp) 3.36 (s, 3 H, MeNC)	239.7 (CO) 138.2 (J_{CF} = 321, CF_3) 90.2, 89.5 (cp) 32.0 (CH_3NC)	
4b *syn*-$[Mo_2(cp)_2(CO)(CNMe)(\mu\text{-}SCF_3)_2]$ Red	5.47 (s, 5 H, cp) 4.94 (s, 5 H, cp) 3.34 (s, 3 H, MeNC)	237.8 (CO) 177.0 ($CNCH_3$) 136.6 (J_{CF} = 322, CF_3) 90.7, 89.5 (cp) 31.05 (CH_3NC)	ν(CN) 2140 ν(CO) 1860
anti-$[Mo_2(cp)_2(CO)(CNMe)(\mu\text{-}SCF_3)_2]$ Green	5.44 (s, 5 H, cp) 5.07 (s, 5 H, cp) 3.38 (s, 3 H, MeNC)	237.8 (CO) 181.8 ($CNCH_3$) 137.6 (J_{CF} = 320, CF_3) 137.0 (J_{CF} = 323, CF_3) 90.3, 89.96 (cp) 31.6 (CH_3NC)	ν(CN) 2120 ν(CO) 1860
syn-$[Mo_2(cp)_2(CO)(CNBu^t)(\mu\text{-}SCF_3)_2]$ Red	5.45 (s, 5 H, cp) 4.87 (s, 5 H, cp) 1.24 (s, 9 H, Bu^tNC)	238.1 (CO) 168.7 ($CNBu^t$) 136.7 (J_{CF} = 322, CF_3) 90.5, 89.4 (cp) 57.5 [$C(CH_3)_3$] 30.1 [$C(CH_3)_3$]	ν(CN) 2125 ν(CO) 1855
anti-$[Mo_2(cp)_2(CO)(CNBu^t)(\mu\text{-}SCF_3)_2]$ Green	5.40 (s, 5 H, cp) 5.03 (s, 5 H, cp) 1.24 (s, 9 H, Bu^tNC)	238.1 (CO) 176.6 ($CNBu^t$) 137.7 (J_{CF} = 321, CF_3) 137.2 (J_{CF} = 323, CF_3) 90.2, 89.8 (cp) 58.3 [$C(CH_3)_3$] 30.6 [$C(CH_3)_3$]	ν(CN) 2110 ν(CO) 1860

[a] See ref. 6. [b] The ^1H NMR data are in agreement with those reported by Benson *et al.*[7] [c] Solvent for NMR was CD_3CN. [d] The δ(^{19}F) values in $CDCl_3$ are: −41.0; −42.9; −39.7, −44.0; −41.8; −39.7, −42.5, respectively.

Table 2 Redox potentials (V *vs.* ferrocene–ferrocenium) as measured from CV experiments ($MeCN–NBu_4PF_6$)

Complex	$E^{1/2}_{red1}$	$E^{1/2}_{red2}$	$E_{p\ ox}$	Ref.
Dicarbonyls				
syn-**1a** *syn*-$[Mo_2(cp)_2(CO)_2(\mu\text{-}SMe)_2]$ Brown	−1.94	−2.27	−0.03	This work
	−1.91	−2.25	−0.10	2
anti-**1a** *anti*-$[Mo_2(cp)_2(CO)_2(\mu\text{-}SMe)_2]$ Green	−1.92	−2.23	−0.05	This work
	−1.95	−2.26	−0.07	2
syn-**1b** *syn*-$[Mo_2(cp)_2(CO)_2(\mu\text{-}SPr^i)_2]$ Brown	−1.93	−2.27	0	This work
anti-**1b** *anti*-$[Mo_2(cp)_2(CO)_2(\mu\text{-}SPr^i)_2]$ Green	−1.97	−2.33	−0.03	This work
syn-**1c** *syn*-$[Mo_2(cp)_2(CO)_2(\mu\text{-}SBu^t)_2]$ Green	−1.94	−2.4	−0.01	This work
syn-**1d** *syn*-$[Mo_2(cp)_2(CO)_2(\mu\text{-}SPh)_2]$ Brown	−1.83	−2.12	−0.04	This work
anti-**1d** *anti*-$[Mo_2(cp)_2(CO)_2(\mu\text{-}SPh)_2]$ Green	−1.83	−2.14	0	This work
syn-**1e** *syn*-$[Mo_2(cp)_2(CO)_2(\mu\text{-}SCF_3)_2]$ Red-brown	−1.58	−2.02	0.50	This work
anti-**1e** *anti*-$[Mo_2(cp)_2(CO)_2(\mu\text{-}SCF_3)_2]$ Green	−1.57	−2.0	0.43	This work
Cyanides				
syn-**2a** *syn*-$[Mo_2(cp)_2(CO)(CN)(\mu\text{-}SMe)_2]^-$	−2.86	—	−0.89 [a]	
anti-**2a** *anti*-$[Mo_2(cp)_2(CO)(CN)(\mu\text{-}SMe)_2]^-$	−2.88	—	−0.96 [a]	
syn **2a′** *syn*-$[Mo_2(cp)_2(CO)(CN)(\mu\text{-}SMe)_2]^-$	−2.77	—	−1.01 [a]	
syn-**2b** *syn*-$[Mo_2(cp)_2(CO)(CN)(\mu\text{-}SPr^i)_2]^-$	−2.95	—	−0.87 [a]	
anti-**2b** *anti*-$[Mo_2(cp)_2(CO)(CN)(\mu\text{-}SPr^i)_2]^-$	−2.95	—	−0.93 [a]	
syn-**2d** *syn*-$[Mo_2(cp)_2(CO)(CN)(\mu\text{-}SPh)_2]^-$	−2.72	—	−0.77 [a]	
anti-**2d** *anti*-$[Mo_2(cp)_2(CO)(CN)(\mu\text{-}SPh)_2]^-$	−2.70	—	−0.85 [a]	
syn-**2e** *syn*-$[Mo_2(cp)_2(CO)(CN)(\mu\text{-}SCF_3)_2]^-$	−2.56 [b]	—	−0.43 [a]	
syn-**2e′** *syn*-$[Mo_2(cp)_2(CO)(CN)(\mu\text{-}SCF_3)_2]^-$	−2.45	—	−0.52 [a]	
anti-**2e** *anti*-$[Mo_2(cp)_2(CO)(CN)(\mu\text{-}SCF_3)_2]^-$	−2.51 [c]	—	−0.48 [a]	
	−2.46 [d]			
S-Methylated cyanides				
3a $[Mo_2(cp)_2(CO)(CN)(\mu\text{-}SMe_2)(\mu\text{-}SMe)]$ [e]	−2.18	−2.78 [c]	−0.28	8
3a′ $[Mo_2(cp)_2(CO)(CN)(\mu\text{-}SMe_2)(\mu\text{-}SMe)]$ [f]	−2.13	−2.76 [c]	−0.37	8
3b $[Mo_2(cp)_2(CO)(CN)\{\mu\text{-}S(Me)Pr^i\}(\mu\text{-}SPr^i)]$ [g]	−2.23	−2.84 [c]	−0.23	This work
3d $[Mo_2(cp)_2(CO)(CN)\{\mu\text{-}S(Me)Ph\}(\mu\text{-}SPh)]$ [h]	−2.07	−2.64 [c]	−0.18	This work
Isocyanides				
4a *syn*-$[Mo_2(cp)_2(CO)(CNMe)(\mu\text{-}SCF_3)_2]$	−1.86	−2.18	+0.02	
4b *syn*-$[Mo_2(cp)_2(CO)(CNMe)(\mu\text{-}SCF_3)_2]$	−1.98	−2.19	+0.13	
anti-$[Mo_2(cp)_2(CO)(CNMe)(\mu\text{-}SCF_3)_2]$	−1.91	−2.16	+0.06	
syn-$[Mo_2(cp)_2(CO)(CNBu^t)(\mu\text{-}SCF_3)_2]$	−2.03	−2.3 [c]	+0.13	
anti-$[Mo_2(cp)_2(CO)(CNBu^t)(\mu\text{-}SCF_3)_2]$	−1.94	−2.15	+0.06	
$[Mo_2(cp)_2(CO)(CNMe)(\mu\text{-}SPh)_2]$	−2.20 [c]	—	−0.24	
$[Mo_2(cp)_2(CO)(CNBu^t)(\mu\text{-}SPh)_2]$	−2.20 [c]	−2.36 [c]	−0.27	

[a] Reversible one-electron oxidation. [b] Ill defined peaks. [c] Irreversible. [d] At −20 °C. [e] $E^{1/2}_{red3}$ −2.87 V. [f] Overlapping reduction peaks around −2.8 V. [g] $E^{1/2}_{red3}$ −2.95 V. [h] $E^{1/2}_{red3}$ −2.73 V.



Scheme 3

3(*a*) [the oxidation in Fig. 3(*b*) is less reversible due to the presence of free cyanide, see above]. This shows that the deco-ordination of CN^- from *syn*-**2a′** is irreversible, and the presence of *syn*-**2a** under CO is a consequence of the equilibrium between this complex and the dicarbonyl *syn*-**1a** [compare Figs. 3(*b*) and 1(*c*)]. Exactly the same processes were observed for the Bu^tNC analogues of *syn*-**2a′** and *syn*-**2a**,[2] and, therefore, we assign to *syn*-**2a′** the same geometry as for the isocyanide analogue, that is *trans-syn* with the cyanide ligand opposite to the methyl groups.

Reaction with Me_3O^+. The addition of the methylating agent $[OMe_3][BF_4]$ to a $MeCN–[NBu_4][PF_6]$ solution of the cyanide complex *syn*-**2a** leads to changes in the CV, characterized by complete loss of the oxidation at $E^{1/2} = -0.89$ V and by the appearance of new reduction ($E^{1/2}_{red1} = -2.18$, $E_{p\ red2} = -2.79$, $E^{1/2}_{red3} = -2.87$ V) and oxidation processes ($E_{p\ ox} = -0.28$ V) (Fig. 4). The primary processes of the methylated product are observed at potentials *ca.* 700 mV more positive than those of the cyanide precursor, which is consistent with neutralization of the negative charge of the latter. The assignment of the methylated product **3a** as the mixed thiolate–thioether-bridged cyanide complex is based upon spectroscopic data, and comparison of the cyclic voltammetry with that of an authentic sample of $[Mo_2(cp)_2(CO)(CN)(\mu\text{-}SMe)(\mu\text{-}SMe_2)]$ **3a** (Table 2), synthesized as shown in Scheme 4.[8]

The ^{13}C NMR spectrum of complex **3a** shows the resonance of the CN ligand at δ 152.6, and the CN band in the infrared is observed at 2080 cm^{-1}.[8] These are diagnostic of cyanide ligands in this type of complexes, and we will show below that isocyanides are characterized by ^{13}C NMR resonances around δ 170–180 and by infrared bands in the range 2100–2140 cm^{-1}. The assignment of the product as $[Mo_2(cp)_2(CO)(CN)(\mu\text{-}SMe)(\mu\text{-}SMe_2)]$ is confirmed by the fact that, unlike $[Mo_2(cp)_2(CO)(CNR)(\mu\text{-}SMe)_2]$ (R = Bu^t, xylyl or CH_2Ph),[2] the methylated

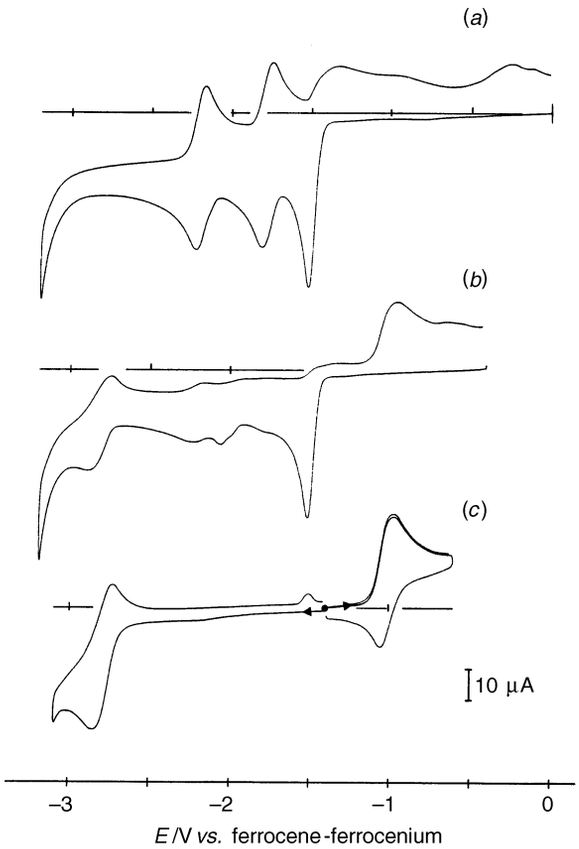
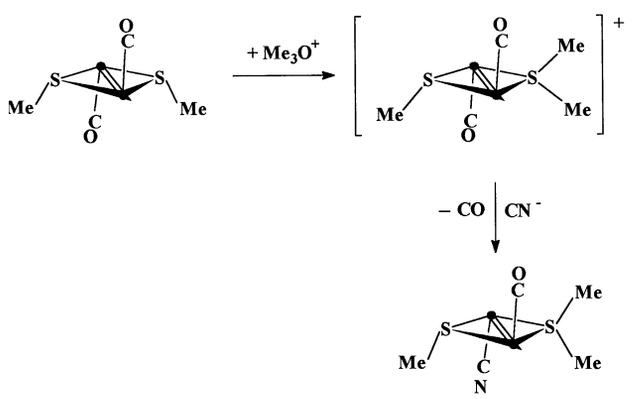


Fig. 2 Cyclic voltammetry of (*a*) a 1.6 mmol dm^{-3} solution of $[Mo_2(cp)_2(CO)_2(\mu\text{-}SMe)_2]^+$, (*b*) in the presence of 1 equivalent $[NBu_4][CN]$ and (*c*) after electrolysis in the presence of 1 equivalent $[NBu_4][CN]$ with a nitrogen purge through the catholyte (mercury-pool cathode; electrolysis potential = −2.1 V) (MeCN–$[NBu_4][PF_6]$ electrolyte; vitreous carbon electrode, $\nu = 0.2$ V s^{-1})



Scheme 4

compound does not regenerate the parent dicarbonyl under a carbon monoxide atmosphere.

There is no detectable difference in the redox potentials of the methylated products obtained from either *syn* or *anti* isomers of the cyanide complex: this suggests that a single product is formed according to Scheme 5. As for *syn*- and *anti*-**2a**, the methylation of *syn*-**2a**′ yields a thiolate–thioether-bridged complex.[8] This is shown by the electrochemical data of the product, **3a**′, which are quite analogous to those of **3a** (Table 2), and totally different from those of an isocyanide complex; furthermore, the reaction of **3a**′ with CO does not generate a dicarbonyl complex.

The question which arises then is: how to favour the alkylation of the cyanide ligand? The first, obvious, answer is to alkylate the sulfur lone pairs before treating the resulting product with cyanide and Me_3O^+. However, as shown elsewhere, the

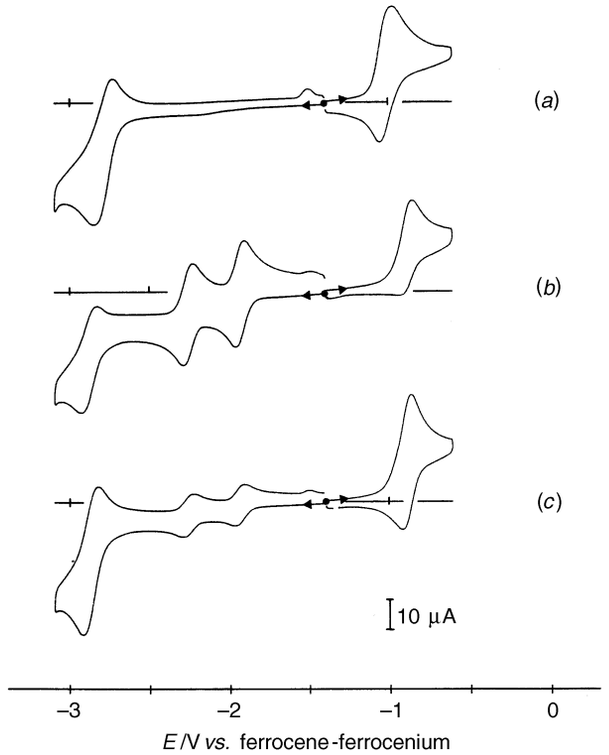
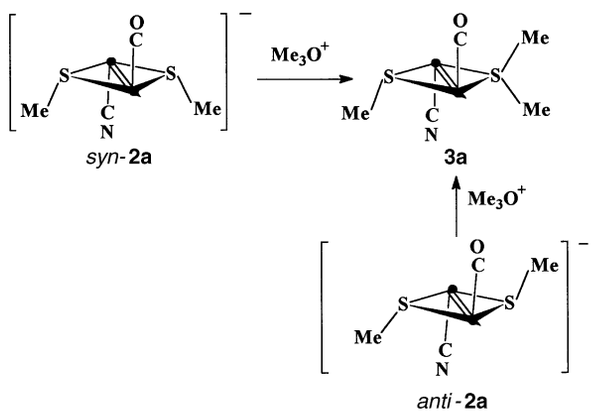


Fig. 3 Cyclic voltammetry of (*a*) a 1.6 mmol dm^{-3} solution of *trans*-$[Mo_2(cp)_2(CO)(CN)(\mu\text{-}SMe)_2]^-$ **2a**′ produced as shown in Fig. 2(*c*), (*b*) after purging CO through the solution in (*a*) (CV under CO) and (*c*) after flushing solution (*b*) with N_2 (MeCN–$[NBu_4][PF_6]$ electrolyte; vitreous carbon electrode, $\nu = 0.2$ V s^{-1})



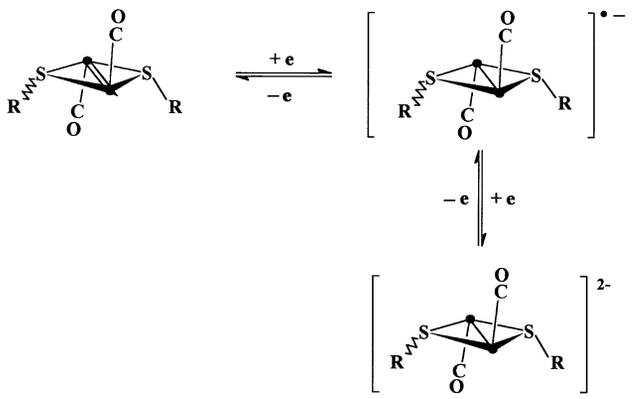
Scheme 5

isocyanide complexes $[Mo_2(cp)_2(CO)(CNR)(\mu\text{-}SMe)(\mu\text{-}SMe_2)]^+$ and $[Mo_2(cp)_2(CO)(CNR)(\mu\text{-}SMe_2)_2]^{2+}$ do not significantly release RNC on reaction with CO.[8] We have consequently looked for other ways of promoting the methylation of the cyanide ligand in thiolate-bridged compounds $[Mo_2(cp)_2(CO)(CN)(\mu\text{-}SR)_2]^-$. In this context, we have investigated the influence of the steric and electronic properties of the R substituents on the site of electrophilic attack.

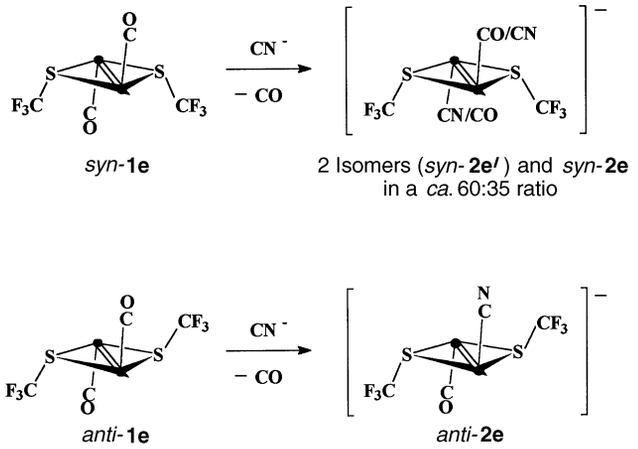
Influence of the nature of the sulfur substituents of $[Mo_2(cp)_2(CO)(CN)(\mu\text{-}SR)_2]^-$ on the site of electrophilic attack by Me_3O^+

The substituents on the bridging sulfur atoms may influence the alkylation of the cyanide complexes, *via* both their steric and their electronic properties. Replacing the methyl groups on the sulfur atoms by bulkier *tert*-butyl or isopropyl substituents may result in a change in the orientation of the reaction of the electrophile.

On the other hand, a modification of the electronic properties of the sulfur substituents may be responsible for a diversion of the electrophilic attack. Fenske and Milletti[9] have reported



Scheme 6 R = Me *syn*- and *anti*-**1a**, Pr^i *syn*- and *anti*-**1b**, Bu^t *syn*-**1c**, Ph *syn*- and *anti*-**1d**, CF_3 *syn*- and *anti*-**1e**



Scheme 7

that the reaction of a complex with a nucleophile can be either orbitally controlled when the energy difference between the HOMO (highest occupied molecular orbital) of the nucleophile and the LUMO (lowest unoccupied molecular orbital) of the complex is negligible, or charge controlled when this energy gap is larger. In the first situation the LUMO (or an orbital close to it in energy and of correct symmetry) of the complex is attacked, in the second the reaction takes place at the site where the charge is localized.

This can be extended to the present case of electrophilic attack of $[Mo_2(cp)_2(CO)(CN)(\mu\text{-}SR)_2]^-$ by Me_3O^+. The alkylation of a sulfur lone pair for R = Me suggests that the reaction is under orbital control, and that the sulfur lone pairs are close to the HOMO in energy and have correct symmetry for an interaction with the electrophile's LUMO. The replacement of the methyl substituents by electron-withdrawing groups such as CF_3 will stabilize the HOMO of the complex as well as the sulfur lone pairs, and will thus increase the energy gap between these orbitals and the LUMO of Me_3O^+: this might switch the reaction from orbitally to charge controlled and consequently favour the alkylation of the cyanide ligand.

In order to discriminate between the steric and the electronic effects of the R substituents, R groups with similar electronic properties are needed to probe the steric influence and *vice versa*, substituents of similar size will be used to check on their electronic effect on the orientation of the reaction. We have therefore prepared the dicarbonyls *trans*-$[Mo_2(cp)_2(CO)_2(\mu\text{-}SR)_2]$ (R = Bu^t or Pr^i) and investigated their redox behaviour in order to check whether or not this substitution induces an important change in the electronic properties of the complexes. We have also synthesized *trans*-$[Mo_2(cp)_2(CO)_2(\mu\text{-}SCF_3)_2]$, since the similar size of the CF_3 and alkyl substituents makes interferences of steric effects unlikely.

Synthesis and electrochemistry of *trans*-$[Mo_2(cp)_2(CO)_2(\mu\text{-}SR)_2]$ (R = Pr^i, Bu^t, CF_3 or Ph). The complexes were obtained from the reaction of the molybdenum dimer $[Mo_2(cp)_2(CO)_n]$ (n = 4 or 6) with the disulfide RSSR or with the thiol in the presence of triethylamine (see Experimental section). The *syn* and *anti* isomers were separated by column chromatography or recrystallization. The Bu^{t}S$^-$ and PhS$^-$ complexes were already known[7,10] but the electrochemical and/or spectroscopic properties of the *syn* and *anti* isomers had not been reported. The complexes with R = CF_3 or Pr^i are new. The ^{1}H, ^{13}C NMR, and infrared data are listed in Table 1. Several X-ray structural studies of $[M_2(cp)_2(CO)_2(\mu\text{-}SR)_2]$ have shown that the complexes are always in a *trans* geometry. From the crystal analysed by X-ray diffraction for M = Mo and R = Bu^t, the R groups were shown to adopt a mutually *syn* orientation,[7,10] whereas for M = Mo, R = Ph[10] and M = W, R = Pr^i[11] the R substituents were found in *anti* positions in the solid.

All the *trans*-$[Mo_2(cp)_2(CO)_2(\mu\text{-}SR)_2]$ complexes undergo two reversible, one-electron reduction steps (Scheme 6) and one irreversible multielectron oxidation in a MeCN electrolyte (Table 2). The addition of two electrons to the Mo–Mo antibonding LUMO[12] leads to cleavage of one metal–metal bond in the dianion, in agreement with the 18-electron rule. There is almost no difference between the reduction potentials of the *syn* and *anti* isomers of these complexes (Table 2), which do not interconvert in solution at room temperature. The redox potentials are sensitive to the nature of R: as expected, complexes with the more electron-withdrawing substituents are easier to reduce (*cf.* Table 2, CF_3 and Ph). The alkanethiolate derivatives all show similar redox potentials, which confirms that the R substituents (R = Me, Bu^t or Pr^i) have similar effects on the redox orbitals of the complexes: the SMe, SPr^i and SBu^t analogues can therefore be used to probe the effect of increasing the size (with no effect of the electronic properties) of the sulfur substituents on the reactivity of the compounds.

Reaction of *trans*-$[Mo_2(cp)_2(CO)_2(\mu\text{-}SR)_2]$ (R = Pr^i, Bu^t, CF_3 or Ph) with CN$^-$. The complexes *trans*-$[Mo_2(cp)_2(CO)_2(\mu\text{-}SR)_2]$ react with 1 equivalent $[NBu_4][CN]$ at room temperature [reaction (2)] except for R = Bu^t where no reaction is detected. The

$$[Mo_2(cp)_2(CO)_2(\mu\text{-}SR)_2] + CN^- \longrightarrow [Mo_2(cp)_2(CO)(CN)(\mu\text{-}SR)_2]^- + CO \quad (2)$$

cyanide complexes were not stable in the solid state and only the compounds with R = CF_3 **2e** or Ph *syn*-**2d** were isolated and characterized spectroscopically (Table 1). The isopropyl derivatives and *anti*-**2d** were formed in the CV cell and their redox potentials are listed in Table 2. The ^{13}C NMR resonance of the cyanide ligand and the infrared ν(CN) are in the region expected for cyanide complexes, and the presence of the remaining CO in the complexes is also evident on the ^{13}C NMR and infrared spectra (Table 1). The substitution of one CO by one cyanide ligand does not affect the disposition of the R substituents. In the ^{13}C NMR spectrum of the benzenethiolate derivative *syn*-**2d** four resonances only are observed in the range δ 125–150, which are characteristic of the equivalent phenyl substituents. The NMR spectrum of the crude product of the reaction of *trans*,*syn*-$[Mo_2(cp)_2(CO)_2(\mu\text{-}SCF_3)_2]$ with 1 equivalent of $[NBu_4][CN]$ shows the presence of two isomers of the cyanide complex (60:35), both different from the single product of the reaction of CN$^-$ with the *trans*,*anti* isomer (Table 1, Scheme 7). The redox potentials of the cyanide complexes (Table 2) are influenced by the nature of the R substituents in the same way as for the dicarbonyl precursors, with a slight difference between the *syn* and *anti* isomers.

Influence of the steric and electronic properties of the substituents R on the site of methylation of $[Mo_2(cp)_2(CO)(CN)(\mu\text{-}SR)_2]^-$ (R = Pr^i, CF_3 or Ph). *Steric effect*. As the bulkiest substituent used in this study, R = Bu^t, prevents the formation of the cyan-

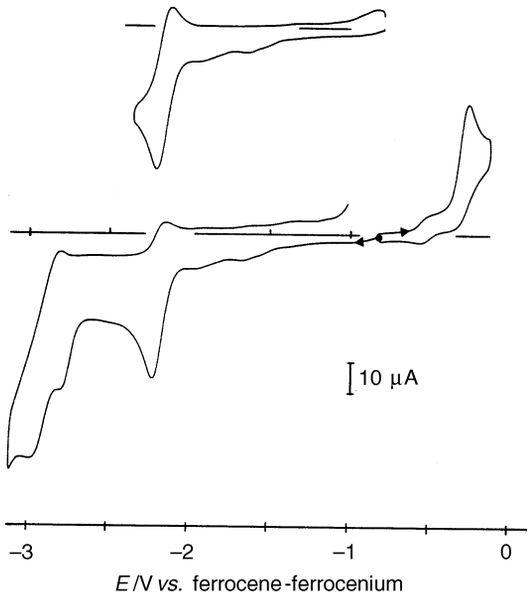


Fig. 4 Cyclic voltammetry of $[Mo_2(cp)_2(CO)(CN)(\mu\text{-}SMe)(\mu\text{-}SMe_2)]$ **3a** obtained by the successive additions of 1 equivalent $[NBu_4][CN]$ and of Me_3O^+ to a 2.2 mmol dm^{-3} solution of *trans*-$[Mo_2(cp)_2(CO)_2(\mu\text{-}SMe)_2]$ *syn*-**1a** (MeCN–$[NBu_4][PF_6]$ electrolyte; vitreous carbon electrode, $\nu = 0.2$ V s^{-1})

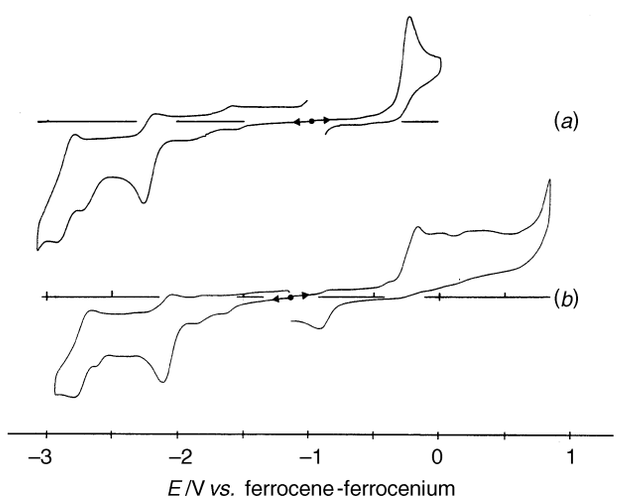


Fig. 5 Cyclic voltammetry of *trans*-$[Mo_2(cp)_2(CO)(CN)\{\mu\text{-}S(Me)R\}(\mu\text{-}SR)]$ obtained by successive additions of 1 equivalent $[NBu_4][CN]$ and of Me_3O^+ to *trans*-$[Mo_2(cp)_2(CO)_2(\mu\text{-}SR)_2]$: (*a*) R = Pr^i **3b**; (*b*) R = Ph **3d** (MeCN–$[NBu_4][PF_6]$ electrolyte; vitreous carbon electrode, ν = 0.2 V s^{-1})

ide complex, the steric effect of R upon the site of alkylation can be estimated only from a comparison of the reaction carried out with the MeS^- and Pr^iS^- analogues. The NMR data (Experimental section) and the electrochemical behaviour (Table 2) of the product formed on addition of Me_3O^+ to $[Mo_2(cp)_2(CO)(CN)(\mu\text{-}SPr^i)_2]^-$ are similar to those of $[Mo_2(cp)_2(CO)(CN)(\mu\text{-}SMe)(\mu\text{-}SMe)_2]$ [compare Figs. 4 and 5(*a*)]. The two-electron reduction of this complex led to S–C bond cleavage[8] giving rise to a product identified as $[Mo_2(cp)_2(CO)(CN)(\mu\text{-}SPr^i)_2]^-$ by its redox processes ($E^{1/2}_{red} = -2.95$, $E^{1/2}_{ox} \approx -0.9$ V). The CN resonance in the ^{13}C NMR spectrum (Experimental section) of the methylated $(Pr^iS)_2$ complex is observed at δ 150.6 and is quite different from that of Bu^tNC (δ 183.4) in $[Mo_2(cp)_2(CO)(CNBu^t)(\mu\text{-}SPr^i)_2]$. This shows that the methylated product is $[Mo_2(cp)_2(CO)(CN)\{\mu\text{-}S(Me)Pr^i\}(\mu\text{-}SPr^i)]$ **3b**. Consistent with the methylation at a sulfur lone pair, the methylated Pr^iS^- complex does not regenerate the parent

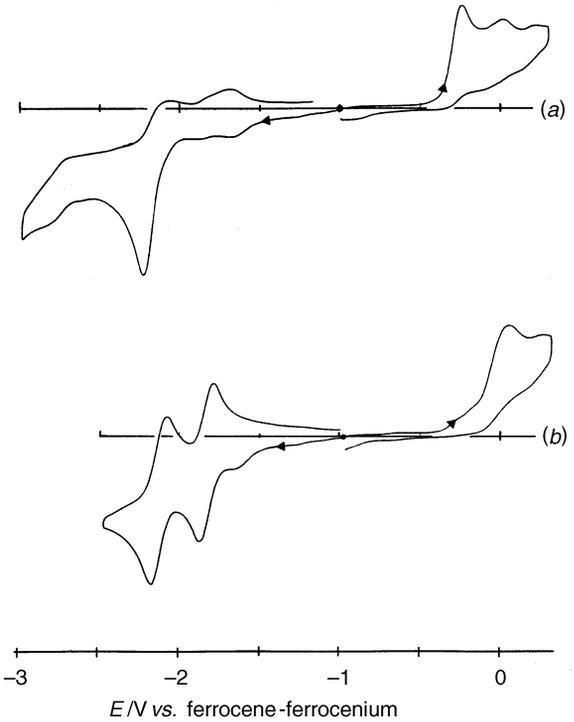


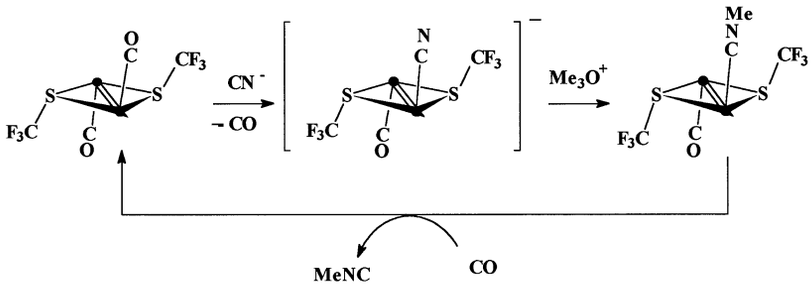
Fig. 6 Cyclic voltammetry of *trans,syn*-$[Mo_2(cp)_2(CO)(CNMe)(\mu\text{-}SPh)_2]$ (*a*) under Ar and (*b*) after flushing solution (*a*) with CO (CV under CO) (MeCN–$[NBu_4][PF_6]$ electrolyte; vitreous carbon electrode, $\nu = 0.2$ V s^{-1})

dicarbonyl on reaction with CO, in contrast with $[Mo_2(cp)_2(CO)(CNBu^t)(\mu\text{-}SPr^i)_2]$.

Electronic effect. This was probed by comparing the reactivity of the *anti* and of both *syn* isomers of $[Mo_2(cp)_2(CO)(CN)(\mu\text{-}SCF_3)_2]^-$ to that of the methanethiolate analogues. The reaction of $[Mo_2(cp)_2(CO)(CN)(\mu\text{-}SPh)_2]^-$ with Me_3O^+ has also been investigated; in this case, both the size and the electronic properties of the sulfur substituents are different from those of the methyl groups, and it is difficult to assess which of these parameters is responsible for the observed reactions.

The addition of Me_3O^+ to $[Mo_2(cp)_2(CO)(CN)(\mu\text{-}SPh)_2]^-$ produces two different species. When the cyanide complex is prepared from *trans,syn*-$[Mo_2(cp)_2(CO)_2(\mu\text{-}SPh)_2]$ *syn*-**1d** the major product of the methylation is an isocyanide derivative: ^1H, ^{13}C NMR [δ 183.5 (CN)] and infrared spectroscopies show the presence of the isocyanide ligand (Table 1). The complex reacts with CO to regenerate the dicarbonyl parent almost quantitatively (90–100%) (Figure 6), and this is diagnostic of isocyanide complexes such as $[Mo_2(cp)_2(CO)(CNR')(\mu\text{-}SR)_2]$ (R′ = Bu^t, xylyl or CH_2Ph; R = Me).[2] In addition, the ^{13}C NMR data and the electrochemical behaviour of the MeNC derivative are similar to those of the authentic isocyanide complex prepared from *syn*-**1d** and 1 equivalent Bu^tNC (Tables 1, 2 and Experimental section). These data demonstrate unambiguously that $[Mo_2(cp)_2(CO)(CN)(\mu\text{-}SPh)_2]^-$ *syn*-**2d** undergoes methylation preferentially at the cyanide nitrogen atom.

The product formed by successive additions of CN^- and Me_3O^+ to *trans,anti*-$[Mo_2(cp)_2(CO)_2(\mu\text{-}SPh)_2]$ *anti*-**1d** was generated in the CV cell only. The formation of a S-methylated compound as the major product is demonstrated by its electrochemical behaviour, which is similar to that of the other $[Mo_2(cp)_2(CO)(CN)\{\mu\text{-}S(Me)R\}(\mu\text{-}SR)]$ compounds described above [R = Me, Pr^i; Figs. 4, 5(*a*) and 5(*b*), Table 2]. This is also confirmed by a comparison of the redox potentials of the methylated complex with those of $[Mo_2(cp)_2(CO)(CN)\{\mu\text{-}S(Me)Ph\}(\mu\text{-}SPh)]$ prepared from the addition of 1 equivalent cyanide to $[Mo_2(cp)_2(CO)_2\{\mu\text{-}S(Me)Ph\}(\mu\text{-}SPh)]^+$, obtained according to a procedure analogous to that described in Scheme 4. The origin of a *syn/anti* dependence of the



Scheme 8

methylation site will be discussed in more detail below (Discussion).

The product resulting from the addition of Me_3O^+ to $[Mo_2(cp)_2(CO)(CN)(\mu\text{-}SCF_3)_2]^-$ *anti*-**2e** displays spectroscopic [^{13}C NMR: δ 181.8 (CN), Table 1] and electrochemical (Table 2) characteristics, as well as the reactivity with CO (Scheme 8) typical of an isocyanide complex. The retention of the *anti* orientation of the CF_3 groups is evidenced by ^{19}F NMR spectroscopy (Table 1). Furthermore, the assignment of the reaction product as $[Mo_2(cp)_2(CO)(CNMe)(\mu\text{-}SCF_3)_2]$ is supported by a comparison of the electrochemical and spectroscopic data for the above complex with those of an isocyanide derivative obtained from the reaction of *trans-anti*-$[Mo_2(cp)_2(CO)_2(\mu\text{-}SCF_3)_2]$ with Bu^{t}NC [^{13}C NMR, δ 176.6 (CN); IR, ν(CN) 2110 cm^{-1}; Tables 1, 2].

The alkylation of the *syn* isomers of $[Mo_2(cp)_2(CO)(CN)(\mu\text{-}SCF_3)_2]^-$ *syn*-**2e** and -**2e**′ also produces *syn* isomers of an isocyanide complex, characterized spectroscopically (Table 1). Again, the CN resonance in the ^{13}C NMR spectrum (δ 177.0) and the infrared band [ν(CN) 2140 cm^{-1}] establish that methylation occurred at the CN ligand. This is supported by a comparison of these data with those of the *single tert*-butyl isocyanide complex obtained from *trans,syn*-$[Mo_2(cp)_2(CO)_2(\mu\text{-}SCF_3)_2]$ with Bu^{t}NC [δ 168.7 (CN), ν(CN) 2125 cm^{-1}, Tables 1, 2].

Cyclic voltammetric monitoring of the reaction of the mixture of complexes *syn*-**2e** and -**2e**′ with Me_3O^+ shows that the initially major isomer of the isocyanide complex, **4a**, reduces reversibly in two separate one-electron steps and undergoes an irreversible oxidation (Table 2). The ^{1}H NMR spectrum of **4a** shows two cp signals with a small separation [Δδ(cp) = 0.06 ppm, Table 1]. A significant amount of a second isomer, **4b**, is also present. The latter is characterized by its redox potentials (Table 2) and by a wider separation of the cp signals with Δδ(cp) = 0.53 ppm (Table 1). Upon treatment of the solution with CO the dicarbonyl precursor is regenerated in 70–80% yield, and a **4a** ⟶ **4b** isomerization is induced as shown by the increase in the oxidation peak due to **4b** at +0.13 V. Flushing the solution with N_2 converts the dicarbonyl complex into the initially minor isomer **4b** whereas **4a** is not restored.

A similar irreversible CO-induced conversion has been observed[2] for two *syn* isomers of $[Mo_2(cp)_2(CO)(CNBu^t)(\mu\text{-}SMe)_2]$, the ^{1}H NMR spectra of which also showed cp separation [Δδ(cp) = 0.06 and 0.52 ppm] very similar to those of **4a** and **4b**. Therefore, there exist two types of $[Mo_2(cp)_2(CO)(CNR')(\mu\text{-}SR)_2]$ complexes with a mutually *syn* orientation of the R groups. Complexes of the first type, by far the more frequent (R = Me, R′ = Bu^t, xylyl or CH_2Ph;[2] R = Pr^i, R′ = Bu^t; R = Ph, R′ = Me or Bu^t; R = CF_3, R′ = Me **4b** or Bu^t), are characterized by a reversible displacement of the isocyanide ligand by CO. Only two complexes of the second type, characterized by the irreversible substitution of R′NC by CO, have been obtained so far (R = Me, R′ = Bu^t;[2] R = CF_3, R′ = Me **4a**). It should be noted that the latter are not formed in the reaction of *trans,syn*-$[Mo_2(cp)_2(CO)_2(\mu\text{-}SR)_2]$ with isocyanides but are obtained from the *cis* isomer of this complex (R = Me, R′ = Bu^t),[2] or *via* the reaction of a cyanide complex with Me_3O^+ (R = CF_3, R′ = Me **4a**, see above). In order to establish the geometry of the isocyanide complexes of the first type mentioned above, we undertook an X-ray structural determination on a crystal of **4b**.

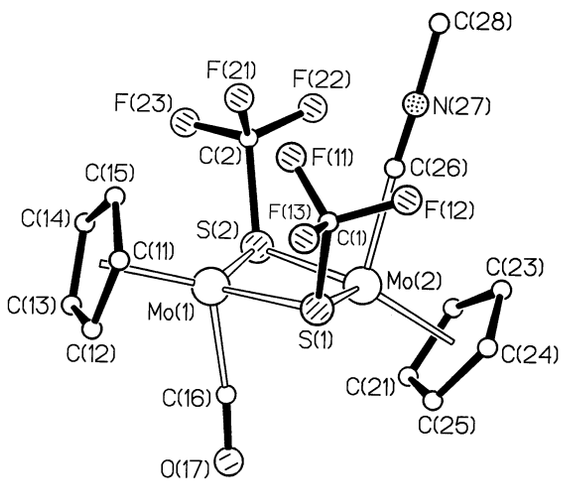


Fig. 7 View of the molecule *trans,syn*-$[Mo_2(cp)_2(CO)(CNMe)(\mu\text{-}SCF_3)_2]$, isomer **4b**, showing the atomic numbering scheme

Crystal structure of $[Mo_2(cp)_2(CO)(CNMe)(\mu\text{-}SCF_3)_2]$, isomer 4b

Although *trans*-$[Mo_2(cp)_2(CO)_2(\mu\text{-}SR)_2]$ complexes have been known for about twenty years,[5,7] their reactivity had not been studied until recently,[2,6,13] and $[Mo_2(cp)_2(CO)(CNMe)(\mu\text{-}SCF_3)_2]$ is the first isocyanide complex derived from the above dicarbonyl to be characterized by X-ray crystallography. A perspective view of the molecule **4b** is shown in Fig. 7, and bond lengths and angles are listed in Table 3. The CO and CNMe ligand are *trans* with respect to the Mo_2S_2 core, with the isocyanide ligand situated on the same side of the core as the *syn*-CF_3 groups. Therefore, the *trans,syn* geometry of the dicarbonyl precursor is maintained in the isocyanide complex. The Mo–Mo separation, 2.597(1) Å, is consistent with a metal–metal double bond which confers a closed-shell configuration on the metal centres and is similar to that found in other *trans*-$[Mo_2(cp)_2(CO)_2(\mu\text{-}SR)_2]$ complexes,[7,10,11] the principal molecular dimensions of which are in Table 4. A comparison of the M–C(O) and C–O bonds in these complexes suggests a more important d_π–π*(CO) back bonding in **4b**. This is consistent with the spectroscopic data [ν(CO) and δ(^{13}CO)] for the different complexes.

As in the structure of *trans,syn*-$[Mo_2(cp)_2(CO)_2(\mu\text{-}SBu^t)_2]$,[7] there is a pseudo-mirror plane of symmetry in the molecule of complex **4b**; the carbonyl and isocyanide ligands lie in this plane, each of the cp rings lies astride the plane, and the two SCF_3 groups are closely related by it. Whereas, however, the cp rings are approximately staggered in orientation with respect to each other in the dicarbonyl complex, they are almost eclipsed in **4b**. The pseudo-symmetry does not extend beyond the

molecule, however; intermolecular contacts are at normal van der Waals distances except perhaps for two shorter F · · · H contacts at 2.38 and 2.49 Å to hydrogen atoms of cp rings.

The *trans*,*anti* complexes in Table 4 adopt a centrosymmetrical arrangement, with a planar Mo_2S_2 core. The *trans*,*syn* complexes, however, normally have a puckered core with the S atoms displaced towards the side of the thiolate ligands, and the degree of non-planarity depending principally on steric factors within the molecule. In *trans*-$[Mo_2(cp)_2(CO)(PMe_3)(\mu\text{-}SMe_2)_2][BF_4]_2$,[13] with bridging thioether ligands, interactions between the ligands appear minimal and the puckering of the core is significant; we measure the puckering by (*i*) the mean (absolute) torsion angle in the Mo_2S_2 ring, here 7.9°, and (*ii*) the mean (absolute) displacement from the mean plane through the four atoms, here 0.076 Å. In *trans*,*syn*-$[Mo_2(cp)_2(CO)_2(\mu\text{-}SBu^t)_2]$ there are short contacts around both carbonyl C atoms and the butyl groups appear forced outwards from the central pseudo-mirror plane; there is very little puckering here, with a mean torsion angle of 1.6° and displacement 0.015 Å. In our complex the interligand distances are marginally longer than in the dicarbonyl complex, *i.e.* a sterically slightly less crowded molecule, and the core is more puckered with a mean torsion angle of 7.5° and displacement 0.071 Å. Another distinctive feature in the thiolate complexes is the mean S · · · S–C angle: in the dicarbonyl complex, this is 124.7(5)° whereas in **4b** there is a tight folding back of the SCF_3 ligands towards the central plane and a mean S · · · S–C angle of 112.2(2)°.

Table 3 Selected bond lengths (Å) and angles (°) in *trans*,*syn*-$[Mo_2(cp)_2(CO)(CNMe)(\mu\text{-}SCF_3)_2]$, isomer **4b** with estimated standard deviations (e.s.d.s) in parentheses[a]

(*a*) About the molybdenum atoms

Mo(1)–Mo(2)	2.597(1)	Mo(2)–S(1)	2.397(2)
Mo(1)–S(1)	2.391(2)	Mo(2)–S(2)	2.378(2)
Mo(1)–S(2)	2.381(2)	Mo(2)–C(21)	2.257(8)
Mo(1)–C(11)	2.311(7)	Mo(2)–C(22)	2.310(9)
Mo(1)–C(12)	2.317(7)	Mo(2)–C(23)	2.369(10)
Mo(1)–C(13)	2.333(7)	Mo(2)–C(24)	2.326(10)
Mo(1)–C(14)	2.361(7)	Mo(2)–C(25)	2.263(8)
Mo(1)–C(15)	2.341(7)	Mo(2)–C(26)	2.069(6)
Mo(1)–C(16)	1.920(6)	Mo(2)–C(2x)	1.99
Mo(1)–C(1x)	2.02		
Mo(2)–Mo(1)–S(1)	57.3[b]	Mo(1)–Mo(2)–S(1)	57.0[b]
Mo(2)–Mo(1)–S(2)	56.9[b]	Mo(1)–Mo(2)–S(2)	57.0[b]
Mo(2)–Mo(1)–C(16)	77.9(2)	Mo(1)–Mo(2)–C(26)	101.8(2)
Mo(2)–Mo(1)–C(1x)	168.0	Mo(1)–Mo(2)–C(2x)	148.1
S(1)–Mo(1)–S(2)	113.7(1)	S(1)–Mo(2)–S(2)	113.6(1)
S(1)–Mo(1)–C(16)	87.5(2)	S(1)–Mo(2)–C(26)	93.5(2)
S(1)–Mo(1)–C(1x)	122.5	S(1)–Mo(2)–C(2x)	121.3
S(2)–Mo(1)–C(16)	86.2(2)	S(2)–Mo(2)–C(26)	92.5(2)
S(2)–Mo(1)–C(1x)	120.1	S(2)–Mo(2)–C(2x)	117.9
C(16)–Mo(1)–C(1x)	114.0	C(26)–Mo(2)–C(2x)	110.1

(*b*) In the CF_3S^- ligands

S(1)–C(1)	1.821(7)	S(2)–C(2)	1.836(7)
C(1)–F(11)	1.315(8)	C(2)–F(21)	1.314(8)
C(1)–F(12)	1.350(10)	C(2)–F(22)	1.316(9)
C(1)–F(13)	1.299(10)	C(2)–F(23)	1.321(10)
Mo(1)–S(1)–Mo(2)	65.7[b]	Mo(1)–S(2)–Mo(2)	66.1[b]
Mo(1)–S(1)–C(1)	110.0(2)	Mo(1)–S(2)–C(2)	110.5(2)
Mo(2)–S(1)–C(1)	113.3(3)	Mo(2)–S(2)–C(2)	113.4(3)
S(1)–C(1)–F(11)	115.1(5)	S(2)–C(2)–F(21)	114.7(5)
S(1)–C(1)–F(12)	111.4(6)	S(2)–C(2)–F(22)	111.3(6)
F(11)–C(1)–F(12)	104.5(6)	F(21)–C(2)–F(22)	107.4(6)
S(1)–C(1)–F(13)	110.5(6)	S(2)–C(2)–F(23)	108.7(5)
F(11)–C(1)–F(13)	108.4(7)	F(21)–C(2)–F(23)	106.6(7)
F(12)–C(1)–F(13)	106.4(6)	F(22)–C(2)–F(23)	107.9(7)

(*c*) In the carbonyl ligand

C(16)–O(17)	1.167(8)	Mo(1)–C(16)–O(17)	173.7(7)

(*d*) In the MeNC ligand

C(26)–N(27)	1.133(8)	Mo(2)–C(26)–N(27)	177.2(5)
N(27)–C(28)	1.412(8)	C(26)–N(27)–C(28)	178.2(7)

[a] C(1x) and C(2x) are the centroids of the cp rings. [b] The e.s.d. is less than 0.05°.

Discussion

Electronic control of the site of methylation by the sulfur substituents: orbital *vs.* charge control of the reaction

The results reported above demonstrate that the nature of the substituents on the bridging sulfur atoms is crucial to the orientation of the reaction of Me_3O^+ with the cyanide complex $[Mo_2(cp)_2(CO)(CN)(\mu\text{-}SR)_2]^-$. The steric effect of the R groups can prevent the formation of the cyanide complex (R = Bu^t), but the orientation of the methylation reaction of $[Mo_2(cp)_2(CO)(CN)(\mu\text{-}SR)_2]^-$ is not modified by the size of the sulfur substituents for R = Me or Pr^i: in both cases, methylation occurs at a sulfur lone pair. On the contrary, the electronic properties of R affect the site of methylation: electron-withdrawing substituents such as CF_3 (and to a lesser extent Ph) promote alkylation at the cyanide ligand. This is consistent with the reaction being switched from orbital to charge control upon substitution of R = CF_3 for Me. The *syn/anti* arrangement of the sulfur substituents has no effect on the site of methylation of the cyanide complexes, except when R = Ph. In this case, an isocyanide complex is obtained as the major product from the *syn* isomer, whereas the *anti* isomer is preferentially methylated at sulfur. Again, the difference may have an electronic origin. The redox potentials in Table 2 show that the *syn* isomer is harder to oxidize than the *anti* analogue by 80 mV: the energy gap between the LUMO of the electrophile and the HOMO of the complex increases on going from the *anti* to the *syn* isomer. Provided the sulfur lone pairs experience a similar shift in energy, this stabilization might be sufficient to switch the alkylation from an

Table 4 Comparison of selected crystallographic dimensions of $[Mo_2(cp)_2(CO)(Y{\equiv}Z)(\mu\text{-}SR)_2]$ complexes

Complex	M–M/Å	M–C(O)/Å	M–S/Å	M–S–M/°	S–M–S/°	Ref.
trans,*syn*-$[Mo_2(cp)_2(CO)_2(\mu\text{-}SBu^t)_2]$	2.616(2)	1.946(3)	2.422(2)	65.43(5)	114.51(6)	7
		1.930(4)	2.415(4)	65.64(5)	114.37(6)	
			2.420(4)			
			2.413(2)			
	2.616(3)		2.422(5)	65.4(1)	114.5(1)	10
			2.413(5)	65.8(1)	114.7(1)	
trans,*anti*-$[Mo_2(cp)_2(CO)_2(\mu\text{-}SPh)_2]$	2.569(6)		2.405(8)	64.4(2)	115.6(2)	10
			2.42(1)			
trans,*anti*-$[W_2(cp)_2(CO)_2(\mu\text{-}SCHMe_2)_2]$	2.602(5)	1.95(1)	2.412(4)	65.3(1)	114.7(1)	11
			2.411(3)			
trans,*syn*-$[Mo_2(cp)_2(CO)(CNMe)(\mu\text{-}SCF_3)_2]$	2.597(1)	1.920(6)	2.391(2)	66.1(1)	113.7(1)	This work
			2.381(2)	65.7(1)	113.6(1)	
			2.397(2)			
			2.378(2)			

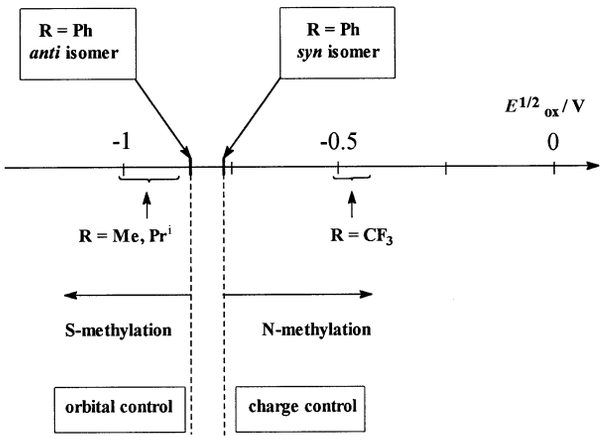


Fig. 8 Schematic representation of the relationship between $E^{1/2}_{ox}$ of *trans*-$[Mo_2(cp)_2(CO)(CN)(\mu\text{-}SR)_2]^-$ complexes and the site of methylation by Me_3O^+

orbital (*anti*) to a charge control (*syn*). The borderline between the two types of control of the methylation of the cyanide complexes by Me_3O^+ would thus be situated in the range where the oxidation potential is between −0.85 and −0.77 V (Fig. 8).

Pertinent to this point, it has been demonstrated that the electronic properties of the sulfur substituents affect the reaction of the $[Mo_2(cp)_2(\mu\text{-}S_2CH_2)(\mu\text{-}SMe)(\mu\text{-}SR)]$ and $[Mo_2(cp)_2(\mu\text{-}S_2CH_2)(\mu\text{-}S_2CRR')]$ complexes with protons.[14] Whereas the reaction led to a one-electron oxidation of $[Mo_2(cp)_2(\mu\text{-}S_2CH_2)(\mu\text{-}SMe)(\mu\text{-}SR)]$ for R = Me or Pr^i, it resulted in rapid S–C bond cleavage in the complexes where R = C_4H_3S, CH(Me)Ph or CH_2Ph.[14a] In the case of $[Mo_2(cp)_2(\mu\text{-}S_2CH_2)(\mu\text{-}S_2CRR')]$ a 110 mV shift of the oxidation potentials is enough to switch the reaction with H^+ from a one-electron oxidation (R = R′ = Me) to a C–S bond cleavage (R = H, R′ = CO_2Me).[14b] For these examples, the concept of orbital *vs.* charge control could still account for the orientation of the reaction with H^+: one-electron oxidation suggested that protonation initially occurred at the metal centre.[14] This is consistent with an orbitally controlled reaction since the HOMO of the complexes is mainly metal in character.[15] Substitution of electron-releasing by withdrawing groups at the bridging sulfur will stabilize the HOMO and therefore increase the gap between this orbital and the electrophile's LUMO: this should favour a charge control of the reaction. The cleavage of S–C bonds suggest that the reaction of complexes possessing electron-withdrawing substituents with H^+ could be charge controlled since these substituents stabilize a carbanionic character in the thiolate carbon.[14]

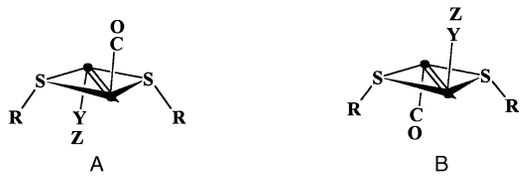
Other examples showing the electronic influence of ligands on the site of protonation or alkylation include $[Fe(CO)_3L(SR)]^-$ and $[Fe(CO)_2L_2(SR)]^-$ complexes [L = CO or P(OEt)$_3$; R = alkyl or aryl],[16] and the protonation of $[FeH(CN)(R_2PCH_2CH_2PR_2)_2]$ (R = Et, Ph or *p*-tolyl).[17]

Site of attack of *trans*-$[Mo_2(cp)_2(CO)_2(\mu\text{-}SR)_2]$ by CN^- and RNC

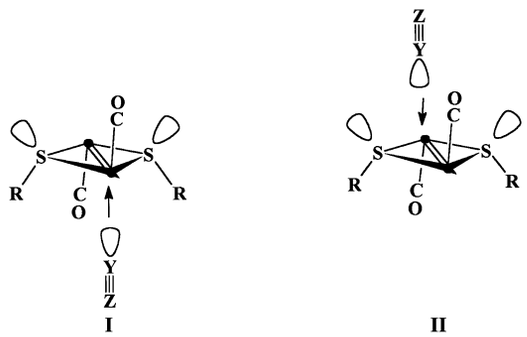
Concerning the geometry of the cyanide and isocyanide complexes, the following information is available.

(*i*) There are two types of isocyanide and cyanide complexes having a *syn* arrangement of the sulfur substituents, while only one for the *anti* analogue. This is due to the fact that in *trans,syn*-$[Mo_2(cp)_2(CO)_2(\mu\text{-}SR)_2]$ the two faces of the Mo_2S_2 core, *e.g.* the two metal sites, are not equivalent; this can lead to isomers **A** and **B**, which differ by the situation of the Y≡Z ligand with respect to the R groups (Scheme 9), whereas in the *trans,anti* derivative, isomers **A** and **B** are identical.

(*ii*) The more common isocyanide and cyanide complexes with *syn* R groups are obtained in the reaction of the substrate with *trans,syn*-$[Mo_2(cp)_2(CO)_2(\mu\text{-}SR)_2]$, which is regenerated



Scheme 9



Scheme 10

by treating the cyanide or isocyanide product, $[Mo_2(cp)_2(CO)(Y{\equiv}Z)(\mu\text{-}SR)_2]$, with CO; although synthesized differently, **4b** and $[Mo_2(cp)_2(CO)(CNMe)(\mu\text{-}SPh)_2]$, which show the same reactivity and similar electrochemical and spectroscopic characteristics as those of the authentic isocyanide complexes, belong to this group. Therefore, all these compounds can be assigned the same geometry as that of the structurally characterized **4b** (**A** in Scheme 9).

(*iii*) The uncommon isocyanide and cyanide complexes (*syn*) are not obtained from *trans,syn*-$[Mo_2(cp)_2(CO)_2(\mu\text{-}SR)_2]$. They undergo an irreversible reaction with CO, which produces this dicarbonyl complex; consistent with (*ii*), flushing the solution with dinitrogen or argon leads to the common isocyanide and cyanide complexes {see Scheme 3, the **4a** ⟶ **4b** conversion, and the similar reaction observed with $[Mo_2(cp)_2(CO)(CNBu^t)(\mu\text{-}SMe)_2]$}.[2] There are only four examples of the uncommon cyanide and isocyanide complexes so far: one isomer of $[Mo_2(cp)_2(CO)(CNBu^t)(\mu\text{-}SMe)_2]$,[2] *syn*-**2a**′, **4a** and its cyanide precursor *syn*-**2e**′. The first two were produced in the reaction of the substrate Y≡Z (Bu^tNC or CN^-) with the electrogenerated *cis*-$[Mo_2(cp)_2(CO)_2(\mu\text{-}SMe)_2]$[2,8] and were assigned a *trans* geometry with the Y≡Z ligand opposite to the Me groups (**B** in Scheme 9). This is consistent with the fact that the reaction of *cis*-$[Mo_2(cp)_2(CO)_2(\mu\text{-}SMe)_2]$ with Y≡Z = CO produces the *trans* isomer.[2] Therefore, the *trans,syn*-$[Mo_2(cp)_2(CO)_2(\mu\text{-}SR)_2]$ complexes appear to favour attack of Y≡Z on the same side of the Mo_2S_2 plane as the R groups (see **I** in Scheme 10), that is on the more crowded face of the complex, which leads to an **A**-type derivative. The attack shown in **II** (Scheme 10), which would produce a compound with a **B** geometry, might be avoided because of a repulsion of the nucleophile by the sulfur lone pairs; this is consistent with the fact that when the attack according to **I** is sterically hindered (R = Bu^t) no cyanide or isocyanide complex is formed at all.

However, when R is CF_3 and Y≡Z = CN^- the approach as **I** appears to be less favourable since the precursor of complex **4b** (*e.g.* a cyanide complex like **A**) is initially the minor product (*ca.* 35%) formed in the reaction of *syn*-**1e** with CN^-. This might be due to the fact that, in this case, the substrate attacking either side of the Mo_2S_2 plane experiences repulsions, by the fluoride ligands or by the sulfur lone pairs. On the contrary, when Y≡Z = CNR, the single product has a **A**-type geometry. Therefore, the *trans,syn*-$[Mo_2(cp)_2(CO)_2(\mu\text{-}SCF_3)_2]$ complex is able to *discriminate* between cyanide and isocyanide substrates. This is yet another type of effect of the sulfur substituents upon the reactivity of *trans*-$[Mo_2(cp)_2(CO)_2(\mu\text{-}SR)_2]$ complexes.

Conclusion

The results reported in this paper lead to the conclusions summarized below.

(1) Our approach to methylate the cyanide ligand rather than the sulfur lone pairs of *trans*-$[Mo_2(cp)_2(CO)(CN)(\mu\text{-}SR)_2]^-$ was based on the concept of orbital *vs.* charge control of a reaction.[9] We have shown that the R groups have a pronounced influence on the reactivity of the *trans*-$[Mo_2(cp)_2(CO)(Y{\equiv}Z)(\mu\text{-}SR)_2]$ complexes (Y≡Z = CO or CN^-). Their steric bulk can prevent the reaction of the complex with cyanide or isocyanide (R = Bu^t, Y≡Z = CO), but more importantly their electronic properties can lead to a completely different orientation of the reaction of the cyanide complex with a methylating agent (R = Me or Pr^i, S-methylation; CF_3, N-methylation), which is consistent with the above concept. In the case of the methylation reaction of *trans*-$[Mo_2(cp)_2(CO)(CN)(\mu\text{-}SPh)_2]^-$ this is even more spectacular, since the *anti* isomer is methylated at sulfur, whereas the *syn* isomer produces an isocyanide complex. The present results demonstrate that the redox potentials of the complexes are largely affected by the electronic properties of the R groups, since the different substituents used allow the oxidation potentials to be varied in a range extending over 0.58 V. Therefore, the sulfur substituents exert a control of the reactivity of the complexes *via* their effect on the redox potentials, and consequently the choice of particular R groups can allow a selective activation of a given site in a complex which has several potentially reactive centres. As the actual site of attack of *trans*-$[Mo_2(cp)_2(CO)(CN)(\mu\text{-}SR)_2]^-$ by an electrophile depends on the energy gap between the HOMO of the complex and the LUMO of the electrophile, it is not certain that other electrophiles would react with *trans*-$[Mo_2(cp)_2(CO)(CN)(\mu\text{-}SR)_2]^-$ as Me_3O^+ was shown to do.

(2) The sulfur substituents make possible a recognition of CN^- and RNC by *trans*,*syn*-$[Mo_2(cp)_2(CO)_2(\mu\text{-}SCF_3)_2]$ since the favoured site of attack of the complex by these substrates is different. For the other *trans*,*syn*-$[Mo_2(cp)_2(CO)_2(\mu\text{-}SR)_2]$ complexes this discrimination is not observed.

(3) The displacement of the isocyanide ligand by CO is typical of all the complexes *trans*-$[Mo_2(cp)_2(CO)(CNR')(\mu\text{-}SR)_2]$ (R′ = Bu^t or xylyl, R = Me; R′ = Bu^t, R = Pr^i, Ph or CF_3; R′ = Me, R = Ph or CF_3) studied so far. It appears to be a convenient way to distinguish an isocyanide complex from its S-alkylated isomer $[Mo_2(cp)_2(CO)(CN)\{\mu\text{-}S(R')R\}(\mu\text{-}SR)]$. Furthermore, whether this reaction is reversible or not is a criterion to assign the complex a geometry of type **B** or **A**, respectively.

Experimental

Methods and materials

All the experiments were carried out under an inert atmosphere, using Schlenk techniques for the syntheses. Tetrahydrofuran (thf) was purified as described previously.[8] Acetonitrile (Carlo Erba or BDH, HPLC grade) was used as received. The preparation and the purification of the supporting electrolyte $[NBu_4][PF_6]$ and the electrochemical equipment were as described previously.[8] Infrared spectra were obtained with a Perkin-Elmer 1430 and ^{1}H and ^{13}C NMR spectra on a Bruker AC300 spectrophotometer. Shifts are relative to tetramethylsilane as internal reference. The mass spectra were obtained on a GC/MS Hewlett-Packard 5995C apparatus. Chemical analyses were performed by the Centre de Microanalyses du CNRS, Vernaison. The complexes $[Mo_2(cp)_2(CO)_4]$,[18] $[Mo_2(cp)_2(CO)_2(\mu\text{-}SMe)(\mu\text{-}SMe_2)][BF_4]$,[13] $[Mo_2(cp)_2(CO)(CN)(\mu\text{-}SMe)(\mu\text{-}SMe_2)]$ **3a**[8] and $[Mo_2(cp)_2(CO)_3(\mu\text{-}SMe_3)][PF_6]$[19] were synthesized as described in the literature.

Syntheses

The complexes *trans*-$[Mo_2(cp)_2(CO)_2(\mu\text{-}SR)_2]$ (R = Me, Bu^t or Ph) have been obtained following different routes.[5,7,10] We prepared them by reaction of $[Mo_2(cp)_2(CO)_6]$ with the disulfides for R = Me and Ph, or with the thiol for R = Bu^t.

***trans*-$[Mo_2(cp)_2(CO)_2(\mu\text{-}SR)_2]$.** *R = Pr^i*. A toluene (30 cm^3) solution of $[Mo_2(cp)_2(CO)_6]$ (1 g, 2.04 mmol) was heated (110 °C) in the presence of an excess of Pr^{i}SSPr^i (2–3 equivalents) for 48 h. The solution was taken to dryness and the residue dissolved in CH_2Cl_2–hexane (1:4) and chromatographed on a silica gel column. The *syn* and *anti* isomers were eluted with CH_2Cl_2–hexane (3:7). The isomers were separated by recrystallization from cold acetonitrile (yield: 55%): *syn*-**1b**, brown; *anti*-**1b**, green (Found: C, 41.3; H, 4.6; S, 10.9. Calc. for $C_{18}H_{24}Mo_2O_2S_2$: C, 40.9; H, 4.6; S, 12.15%). Mass spectrum: *m/z* 528, M^+; 485, $[M - Pr^i]^+$; 457, $[M - Pr^i - CO]^+$; 386, $[M - 2Pr^i - 2CO]^+$; and 321, $[M - 2Pr^i - 2CO - cp]^+$.

R = Me or Ph. The same procedure as described above was followed. The reaction was complete after *ca.* 2 h (yield 70%). *trans*-$[Mo_2(cp)_2(CO)_2(\mu\text{-}SPh)_2]$ *syn*-**1d**: mass spectrum: *m/z* 596, M^+; 568, $[M - CO]^+$; 540, $[M - 2CO]^+$ and 386, $[M - 2CO - 2Ph]^+$.

R = Bu^t, syn-**1c**. A solution of $[Mo_2(cp)_2(CO)_6]$ (0.6 g, 1.22 mmol) in toluene (50 cm^3) was heated at 100 °C in the presence of an excess of Bu^{t}SH and NEt_3 for 72 h under vacuum. The solution was taken to dryness and the residue dissolved in CH_2Cl_2–hexane (3:17) and chromatographed on a silica gel column. The *syn* isomer was eluted with CH_2Cl_2–hexane (1:4). A small amount of the *anti* isomer was eluted with CH_2Cl_2–hexane (1:3) (total yield *ca.* 30%). *syn*-**1c**: green; mass spectrum: *m/z* 556, M^+; 499, $[M - Bu^t]^+$; 471, $[M - Bu^t - CO]^+$; 443, $[M - Bu^t - 2CO]^+$ and 386, $[M - 2Bu^t - 2CO]^+$.

R = CF$_3$, syn- *and* anti-**1e**. A solution of $[Mo_2(cp)_2(CO)_4]$ (1.6 g, 3.74 mmol) in toluene (40 cm^3) was heated (110 °C) in the presence of an excess of CF_3SSCF_3 (2–3 equivalents) for 72 h. The solution was taken to dryness and the residue dissolved in the minimum volume of CH_2Cl_2 and chromatographed on a silica gel column. The *syn* isomer (red-brown) was eluted with CH_2Cl_2–hexane (1:4) and the *anti* isomer (green) with CH_2Cl_2–hexane (3:7) (total yield: 50%) (Found: C, 29.3; H, 1.9. Calc. for $C_{14}H_{10}F_6Mo_2O_2S_2$: C, 29.0; H, 1.75%). *syn*-**1e**: mass spectrum: *m/z* 580, M^+; 511, $[M - CF_3]^+$; 483, $[M - CF_3 - CO]^+$; 455, $[M - CF_3 - 2CO]^+$ and 386, $[M - 2CF_3 - 2CO]^+$. The *anti* isomer gave exactly the same spectrum.

K[*trans*-$Mo_2(cp)_2(CO)(CN)(\mu\text{-}SR)_2$] (R = Me or CF_3) and $[NBu_4]$[*trans*-$Mo_2(cp)_2(CO)(CN)(\mu\text{-}SR)_2$] *syn*-2d (R = Ph). To a solution of *trans*,*syn*-$[Mo_2(cp)_2(CO)_2(\mu\text{-}SR)_2]$ (R = Me, 0.32; CF_3, 0.25 mmol) in acetonitrile (30 cm^3) was added 1 equivalent KCN in a minimum volume of water–MeCN (1:5) at room temperature. The solution instantly turned from brownish to orange. After 15 min of stirring the solvent was evaporated under vacuum and the residue extracted by acetonitrile (20 cm^3). The volume of the solution was reduced to 5 cm^3 and an equivalent volume of diethyl ether was added to precipitate the complex. After filtration, the residue was stirred with pentane (3 × 5 cm^3). *syn*-**2a**: orange solid, yield 80%. *syn*-**2e** and -**2e′**: orange solid, yield 80%; the mass spectral peak corresponding to the complex anion (*m/z* 578, M_a) was not observed, others at *m/z* 455 ($[M_a - CO - CN - CF_3]^+$), 386 ($[M_a - CO - CN - 2CF_3]^+$) and 321 ($[M_a - CO - CN - 2CF_3 - cp]^+$).

A similar procedure was followed to obtain the *anti* analogue of the SCF_3 derivative (orange solid, yield 80%), and also the SPh derivative, except that in this case $[NBu_4][CN]$ was used in place of KCN. *syn*-**2d**: orange solid, yield 80%; the mass spectral peak corresponding to the complex anion (*m/z* 594, M_a) was not observed, others at *m/z* 540 ($[M_a - CO - CN]^+$), 462 ($[M_a - CO - CN - C_6H_6]^+$), 386 ($[M_a - CO - CN - 2Ph]^+$) and 321 ($[M_a - CO - CN - 2Ph - cp]^+$).

The derivatives *syn*- and *anti*-**2b** were generated *in situ* in the electrochemical cell only. Cyclic voltammetric monitoring of a

solution of *trans*,*syn*-$[Mo_2(cp)_2(CO)_2(\mu\text{-}SBu^t)_2]$ in the presence of cyanide showed that no reaction occurred.

The cyanide complexes were found unstable in the solid state under nitrogen or argon and did not give satisfactory microanalyses.

$[Mo_2(cp)_2(CO)(CN)\{\mu\text{-}S(Me)R\}(\mu\text{-}SR)]$ (R = Pr^i or Ph). To a solution of *trans*,*syn*-$[Mo_2(cp)_2(CO)_2(\mu\text{-}SPr^i)_2]$ (0.12 g, 0.23 mmol) in MeCN (25 cm^3) was added 1 equivalent KCN in a minimum volume of water–MeCN (1:5). After 15 min of stirring at room temperature, 1 equivalent $[OMe_3][BF_4]$ (0.034 g) in MeCN (10 cm^3) was added. An instant colour change was observed. After the solvent was evaporated under vacuum, the residue was extracted by thf (2 × 10 cm^3) in order to remove $K[BF_4]$. The volume of the solution was reduced to 4 cm^3 and pentane (8 cm^3) was added to precipitate complex **3b**. After filtration, the residue was washed several times with pentane. Orange-brown solid, yield 60%. NMR ($CDCl_3$): ^{1}H, δ 5.49 (s, 5 H, cp), 4.85 (s, 5 H, cp), 3.25 (m, 1 H, J = 6.9), 2.88 (s, 3 H, SMe), 2.65 (m, 1 H, J = 6.9), 1.72 (d, 3 H, J = 6.9, CH_3), 1.62 (d, 3 H, J = 6.9, CH_3), 1.48 (d, 3 H, J = 6.7, CH_3) and 1.38 (d, 3 H, J = 6.7 Hz, CH_3); ^{13}C-{^{1}H}, δ 233.3 (CO), 150.6 (CN), 89.2, 88.9 (cp), 57.7, 50.7 [*C*H(CH_3)$_2$], 34.2 S(CH_3), 25.5, 24.5, 20.2, 19.8 [CH(*C*H_3)$_2$]. IR(CH_2Cl_2, cm^{-1}): 2070 (CN) and 1835 (CO). FAB mass spectrum: *m/z* 541, M^+.

Complex **3d** was obtained by addition of 1 equivalent KCN to $[Mo_2(cp)_2(CO)_2\{\mu\text{-}S(Me)Ph\}(\mu\text{-}SPh)][BF_4]$ prepared as follows. To a solution of $[Mo_2(cp)_2(CO)_2(\mu\text{-}SPh)_2]$ (0.22 g, 0.37 mmol) in MeCN (70 cm^3) was added $[OMe_3][BF_4]$ (0.54 g, 1 equivalent). After 4 h of stirring at room temperature the volume of the solution was reduced to 10 cm^3 and ether (*ca*. 20 cm^3) was added to precipitate the product. The solution was filtered and the product washed several times with ether and with pentane. Yield 60% (Found: C, 42.7; H, 3.5; S, 8.8. Calc. for $C_{25}H_{23}BF_4Mo_2O_2S_2$: C, 43.0; H, 3.3; S, 9.2%). Mass spectrum: the peak corresponding to the complex anion (*m/z* 611, M_a) was not observed; other peaks at *m/z*, 540 ($[M_a - 2CO - Me]^+$), 462 ($[M_a - 2CO - C_6H_6]^+$) and 386 ($[M_a - 2CO - Me - 2Ph]^+$). To a solution of $[Mo_2(cp)_2(CO)_2\{\mu\text{-}S(Me)Ph\}(\mu\text{-}SPh)][BF_4]$ (0.0824 g, 0.11 mmol) in MeCN (50 cm^3) was added KCN (0.077 g, 1 equivalent). An instant change from greenish brown to dark orange was observed. The solution was taken to dryness and the residue stirred with thf and filtered to remove $K[BF_4]$. The volume of the thf extract was reduced to 4 cm^3 and pentane (8 cm^3) was added. The solution was filtered and the solid washed several times with pentane. Yield *ca.* 60%. Mass spectrum: *m/z* 609, M^+; 540, $[M - CO - CN - Me]^+$; 463, $[M - CO - CN - Me - Ph]^+$ and 386, $[M - CO - CN - Me - 2Ph]^+$.

***trans*-$[Mo_2(cp)_2(CO)(CNMe)(\mu\text{-}SR)_2]$ (R = Ph or CF_3).** To a solution of *trans*,*syn*-$[Mo_2(cp)_2(CO)_2(\mu\text{-}SR)_2]$ (0.33 mmol) in MeCN (20 cm^3) was added 1 equivalent KCN in a minimum volume of water–MeCN (1:5). After 10 min of stirring at room temperature, 1 equivalent $[OMe_3][BF_4]$ was added. After the solvent was removed under vacuum, the isocyanide complex formed was extracted by ether (3 × 10 cm^3) and washed by cold pentane (2 × 5 cm^3). The two isomers of *trans*,*syn*-$[Mo_2(cp)_2(CO)(CNMe)(\mu\text{-}SCF_3)_2]$ were separated by column chromatography: the mixture of isomers was dissolved in the minimum volume of CH_2Cl_2 and **4b** (*syn* isomer, garnet-red solid) was eluted with CH_2Cl_2–hexane (1:3) and **4a** (*syn* isomer, brown-yellow solid) with CH_2Cl_2–hexane (3:7), yield 60%. **4b** (Found: C, 30.5; H, 2.2; N, 2.4. Calc. for $C_{15}H_{13}F_6Mo_2NOS_2$: C, 30.35; H, 2.2; N, 2.35%): mass spectrum: *m/z* 593, M^+; 578, $[M - Me]^+$; 524, $[M - CF_3]^+$ or $[M - CO - MeNC]^+$; 455, $[M - 2CF_3]^+$ or $[M - CO - MeNC - CF_3]^+$; 386, $[M - CO - MeNC - 2CF_3]^+$ and 321 $[M - CO - MeNC - 2CF_3 - cp]^+$. R = Ph, *syn* isomer: garnet-red solid, yield 60%.

A similar procedure was followed to obtain the *anti* isomer of *trans*-$[Mo_2(cp)_2(CO)(CNMe)(\mu\text{-}SCF_3)_2]$ from *trans*,*anti*-$[Mo_2(cp)_2(CO)_2(\mu\text{-}SCF_3)_2]$ as a green solid in 60% yield.

***trans*-$[Mo_2(cp)_2(CO)(CNBu^t)(\mu\text{-}SR)_2]$ (R = Pr^i, Ph or CF_3).** To a solution of *trans*-$[Mo_2(cp)_2(CO)_2(\mu\text{-}SR)_2]$ (R = Pr^i *syn*-**1b**, Ph *syn*-**1d**, CF_3 *syn*- and *anti*-**1e**) (0.1 g) in MeCN (20 cm^3) was added 1 equivalent Bu^tNC. An instant reaction was observed. The solvent was removed under vacuum and the residue washed twice with cold pentane (5 cm^3).

R = Pr^i, *syn* isomer: red solid, yield 80%; mass spectrum: *m/z* 583 (M^+), 541 ($[M - CMe_2]^+$), 455 ($[M - CO - Bu^t - Pr^i]^+$) and 386 ($[M - CO - CNBu^t - 2Pr^i]^+$). R = Ph, *syn* isomer: red solid, yield 85–90%; mass spectrum: *m/z* 651 (M^+), 623 ($[M - CO]^+$), 540 ($[M - CO - CNBu^t]^+$), 463 ($[M - CO - CNBu^t - Ph]^+$), 386 ($[M - CO - CNBu^t - 2Ph]^+$) and 321 ($[M - CO - CNBu^t - 2Ph - cp]^+$). R = CF_3, *syn* isomer: red solid, yield 85–90%; mass spectrum: *m/z* 635 (M^+), 566 ($[M - CF_3]^+$), 538 ($[M - CO - CF_3]^+$), 455 ($[M - CO - CNBu^t - CF_3]^+$), 412 ($[M - CO - Bu^t - 2CF_3]^+$) and 386 ($[M - CO - CNBu^t - 2CF_3]^+$). *Anti* isomer: green solid, yield 85–90%; mass spectrum: *m/z* 635 (M^+), 566 ($[M - CF_3]^+$), 538 ($[M - CO - CF_3]^+$), 455 ($[M - CO - CNBu^t - CF_3]^+$), 412 ($[M - CO - Bu^t - 2CF_3]^+$) and 386 ($[M - CO - CNBu^t - 2CF_3]^+$).

Crystallography

Crystal data. $C_{15}H_{13}F_6Mo_2NOS_2$ **4b**, M = 593.3, monoclinic, space group $P2_1/n$ (equivalent to no. 14), a = 15.436(2), b = 8.895(1), c = 14.470(1) Å, β = 92.325(9)°, U = 1985.0(4) $Å^3$, Z = 4, D_c = 1.985 g cm^{-3}, $F(000)$ = 1152, μ(Mo-Kα) = 14.9 cm^{-1}, T = 293 K, λ(Mo-Kα) = 0.710 69 Å.

Crystals are deep red plates, obtained by recrystallization from pentane at −10 °C. One, *ca.* 0.10 × 0.43 × 0.83 mm, was mounted on a glass fibre and, after preliminary photographic examination, transferred to an Enraf-Nonius CAD4 diffractometer (with monochromated radiation) for determination of accurate cell parameters (from the settings of 25 reflections, θ = 10–11°, each centred in four orientations) and for measurement of diffraction intensities (3497 unique reflections to θ_{max} = 25°; of these 2627 were 'observed' with $I > 2\sigma_I$).

During processing: corrections were applied for Lorentz-polarization effects, absorption (by semi-empirical ψ-scan methods) and to eliminate negative net intensities (by Bayesian statistical methods). No crystal deterioration was observed. The structure was determined by the heavy-atom method using the SHELX 76 program[20] and refined on F by full-matrix least-squares methods. Hydrogen atoms on the cp rings were included in idealized positions, those in the methyl group were located in difference maps and refined with geometrical constraints; the isotropic thermal parameters of all were refined freely. The non-hydrogen atoms were allowed anisotropic thermal parameters. Refinement to convergence was rapid, with R = 0.056 and R_g = 0.076[20] for all 3497 reflections, weighted $w = (\sigma_{F^2} + 0.00375F^2)^{-1}$. In the final difference map the highest peaks (to *ca.* 1.0 e $Å^{-3}$) were all close to the molybdenum atoms.

Scattering factors for neutral atoms were taken from ref. 21. Computer programs used in this analysis have been noted above or in Table 4 of ref. 22, and were run on a DEC-MicroVAX 3600 machine in the Nitrogen Fixation Laboratory.

Atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/508.

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