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Reactions of di- and poly-nuclear complexes 13 [*]. Synthesis, structure and fluxional behaviour of hydrido- and thiolato- or selenato-bridged complexes $[Mo_2Cp_2(\mu\text{-}H)(\mu\text{-}ER)(CO)_4]$ ($E = S$, $R = Me$, ^tBu, Bz, or Ph; $E = Se$, $R = Ph$)

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Abstract

Oxidative addition of thiols or selenoles across the Mo_2 centre of $[Mo_2Cp_2(CO)_4]$ gives complexes with bridging thiolate or selenate and hydride ligands $[Mo_2Cp_2(\mu\text{-}H)(\mu\text{-}ER)(CO)_4]$ ($E = S$, $R = Me$ (**4**), ^tBu (**5**), Bz (**6**), Ph (**7**); $E = Se$, $R = Ph$ (**8**)). The complex **4** is also formed on reaction of $[Mo_2Cp_2(\mu\text{-}SMe)_2(CO)_4]$ with vanadocene $[VCp_2]$ with the possible involvement of a thioaldehyde, hydride derivative of the vanadocene. Crystals of **4** are monoclinic, space group *C*2/*c*, with $a = 17.225$ (1), $b = 8.418$ (1) $c = 22.960$ (2) Å, $\beta = 90.346$ (5)°, $R = 0.023$ for 4213 observed reflections. In the solid state, molecules of **4** contain a planar $Mo_2(\mu\text{-}H)(\mu\text{-}S)$ core and the Cp ligands are *cis* with respect to the Mo–Mo bond, the two $CpMo(CO)_2$ units being related by an approximate plane of symmetry which contains the bridging H and S donor atoms and which is normal to the Mo–Mo bond. The fluxional nature of complexes **4–8** in solution is shown from variable-temperature ^1H and ^{13}C NMR spectra to arise from *cis–trans* isomerisation.

Keywords: Molybdenum; Bridging thiolate; Hydride ligands; Fluxional behavior; Crystal structure

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1. Introduction

Transition metal–sulfur cluster complexes are useful models for the active sites of natural enzymes [2] and for heterogeneous catalysis at metal surfaces [3]. In addition, they are active as homogeneous catalysts in hydrodesulfurization (HDS) and CO-hydrogenation reactions [4]. The discovery that some important biological systems may contain M/M′/S cores, such as the Mo/Fe/S core in nitrogenase, has stimulated the study of heteronuclear transition-metal sulfido clusters. We have reported the preparation of several sulfido–molybdenum–cobalt clusters and their use as models [5], and we now describe an attempt to prepare an analogous series of molybdenum–vanadium clusters using the molybdenum–thiolato complex $[Mo_2Cp_2(\mu\text{-}SMe)_2(CO)_4]$ **1** and $[VCp_2]$ **2** as synthons. Although **1** and **2** proved to be poor synthons for clusters containing the Mo/V/S core, their reaction produced a new thiolato, hydrido-bridged complex $[Mo_2Cp_2(\mu\text{-}H)(\mu\text{-}SMe)(CO)_4]$ **4**. Such hydrido-bridged organometallic compounds are attractive species, effective both in synthesis and catalysis [6]. A variety of μ-hydrido transition metal dimers, in which the two metals are also bridged by phosphido [7e,8] or halido groups, have been reported, but the number of dinuclear thiolato, hydrido-bridged complexes is rather limited. Indeed, the only known examples of this type are the diiridium anion $[\{Ir_2H(CH_3)(CO)_2(PR_3)_2\}(\mu\text{-}H)(\mu\text{-}S^tBu)_2]^-$ [9], the diiron cation $[\{Fe_2(CO)_4(PR_3)_2\}(\mu\text{-}H)(\mu\text{-}SMe_2)]^+$ [10], and the tungsten derivatives $[\{W_2Cl_6\}(\mu\text{-}H)(\mu\text{-}SMe_2)_2]^-$ [11] and $[\{W_2(^5\eta\text{-}C_5H_4R)_2\ Cl_4\ (\mu\text{-}H)(\mu\text{-}SR')]$ ($R = {}^iPr$ or Me; $R' = $ Me, Et, Ph, ^iPr, or ^tBu) [8d].

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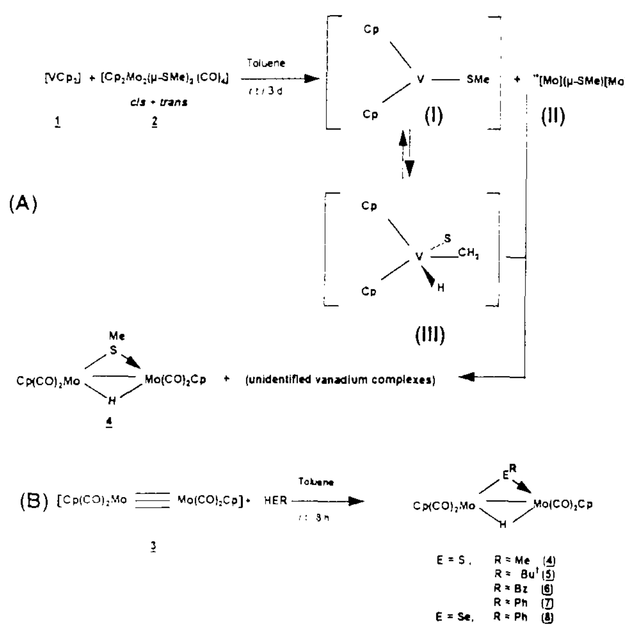
This paper describes the synthesis and the structural characterisation of a new series of thiolato or selenato, hydrido-bridged molybdenum complexes [$Mo_2Cp_2(\mu$-H)(μ-ER)$(CO)_4$] (E = S, R = Me, ^{t}Bu, Bz or Ph; E = Se, R = Ph), and some aspects of their fluxional behaviour.

2. Results and discussion

2.1. Synthesis and spectroscopic characterisation of [$Mo_2Cp_2(\mu$-H)(μ-SR)$(CO)_4$]

In an attempt to synthesise mixed vanadium and molybdenum clusters we stirred a toluene solution of [$Mo_2Cp_2(\mu$-SMe$)_2(CO)_4$] **1** with vanadocene [VCp_2] **2** for several days. Instead of the expected heterometallic complex a dinuclear molybdenum compound formulated as **4** was formed (Scheme 1, Eq. (A)). The reaction (A) may proceed initially via the thioalkylation of [VCp_2] to yield [VCp_2(SMe)] (I) and the unsaturated monothiolato-complex '[Mo](μ-SMe)[Mo]' (II), followed by (i) the isomerisation of the vanadium compound (I) to form a thioaldehyde derivative (III) [12], and by (ii) hydride migration from (III) to (II), generating the saturated μ-hydrido complex **4**. This would imply that (III) is a key intermediate in the hydrogenation reaction that produces **4**. Evidence consistent with this reaction pathway is presented below.



Scheme 1.

Treatment of vanadocene with [$Mo_2Cp_2(\mu$-SPh$)_2(CO)_4$] did not give the related complex [$Mo_2Cp_2(\mu$-H)(μ-SPh$)_2(CO)_4$] **7**. This may be explained by the inability of [Cp_2VSPh] to isomerise to a thioaldehyde hydride analogous to III by β-H elimination. Reaction (A) was conducted in anhydrous conditions, but the solvent (toluene) could be an alternative source of

Table 1
NMR chemical shifts (δ) at low temperature for complexes [a]

Complexes	^{1}H	^{13}C [b]
4a (62%) [c]	4.56 (s, 5H, Cp); 4.46 (s, 5H, Cp); 2.15 (s, 3H, SMe); −11.19 (s, 1H, Mo–H)	92.21; 92.19 (C_5H_5)
		247.88, 247.54, 245.21, 243.53, 243.16, 241.03(CO)
4b (38%)	4.34 (s, 10H, Cp); 2.76 (s, 9H, SMe); −11.71 (s, 1H, Mo–H)	91.14 (C_5H_5)
5a (25%)	4.68 (s, 5H, Cp); 4.62 (s, 5H, Cp); 1.37 (s, 9H, S^{t}Bu); −11.71 (s, 1H, Mo–H)	92.49, 91.29 (C_5H_5); 49.40 (SC–$CH_3)_3$); 33.19 (SC($CH_3)_3$)
5b (75%)	4.38 (s, 10H, Cp); 1.49 (s, 9H, S^{t}Bu); −11.59 (s, 1H, Mo–H)	248.88, 242.11(CO); 91.56 (C_5H_5); 49.03(SC($CH_3)_3$); 32.65 (SC($CH_3)_3$)
6a (75%)	4.59 (s, 5H, Cp); 4.57 (s, 5H, Cp); 3.98 (S, 2H, SCH_2Ph); −11.39 (s, 1H, Mo–H)	92.22, 91.88 (C_5H_5)
		248.14, 247.65, 244.43, 243.79, 243.28, 241.23 (CO)
6b (25%)	40 (s, 10H, Cp); 4.29 (s, 2H, SCH_2Ph); −11.71 (s, 1H, Mo–H)	91.17(C_5H_5)
7a (33%)	5.32 (s, 5H, Cp); 5.05 (s, 5H, Cp); −10.77 (s, 1H, Mo–H)	245.31, 243.76, 242.59, 242.00 (CO); 142.88, 132.32, 127.94, 127.93 (SC_6H_5); 93.0, 92.52 (C_5H_5)
7b (67%)	5.29 (s, 10H, Cp); −11.27 (s, 1H, Mo–H)	245.51, 240.17 (CO); 141.00, 132.50, 127.59, 127.41 (SC_6H_5); 91.42 (C_5H_5)
8a (67%)	5.32 (s, 5H, Cp); 5.02 (s, 5H, Cp); −10.79 (s, 1H, Mo–H)	92.42, 90.32 (C_5H_5) 244.98, 244.80, 242.31, 239.70 (CO)
8a (33%)	5.2 (s, 10H, Cp); −11.62 (s, 1H, Mo–H)	91.72 (C_5H_5)

[a] Chemical Shifts (δ) in ppm measured in toluene-d_8 at 193 K for **4–6**, and in $CDCl_3$ at 223 K for **7** and **8**.
[b] Hydrogen-1 decoupled.
[c] Relative percentages of **a** and **b** given in parentheses.

hydride ligand [7t]. However, this is not the case here because no formation of **4** was observed when a toluene solution of $[Mo_2Cp_2(\mu\text{-}SMe)_2(CO)_4]$ **1** was stirred for several days at room temperature. Evidently the presence of vanadocene and of an SR group with β-H is necessary for the formation of **4**.

The variable yield (10–50%) obtained for **4** in reaction (A) (Scheme 1) led us to devise a more straightforward synthesis: we treated $[Mo_2Cp_2(CO)_4]$ with thiols HSR (R = Me, ^{t}Bu, Ph, of Bz) and a selenole (HSePh) in toluene with stirring at room temperature for several days. The major product (Scheme 1, Eq. (B)) was the expected complex $[Mo_2Cp_2(\mu\text{-}H)(\mu\text{-}ER)(CO)_4]$ (E = S, R = Me (**4**), ^{t}Bu (**5**), Bz (**6**), or Ph (**7**) and E = Se, R = Ph (**8**)) which was separated by chromatography from the dinuclear species $[Mo_2Cp_2(\mu\text{-}SR)_2(CO)_4]$ and $[Mo_2Cp_2(\mu\text{-}SR)_2(CO)_2]$ which were also formed in very low yields. Complexes **4**–**8** are obtained by an oxidative addition of HSR or HSePh, across the Mo_2 centre of **3** by a mechanism proposed previously by Curtis et al. [8a] for reactions of halides HX (X = Cl or Br) with $[Mo_2Cp_2(CO)_4]$. The attempted reaction of $[Mo_2(\eta^5\text{-}C_5Me_5)_2(CO)_4]$ with thiols did not afford the related complexes $[Mo_2(\eta^5\text{-}C_5Me_5)_2(\mu\text{-}H)(\mu\text{-}SR)(CO)_4]$; this illustrates the important differences in the steric and electronic effects of C_5H_5 and C_5Me_5 where reactions with bimetallic complexes are concerned.

NMR (^{1}H, ^{13}C) spectrometry showed that complexes **4**–**8** were isolated as a mixture of two isomers. These were inseparable by conventional chromatographic techniques and were obtained in the same ratio from several preparations, strongly suggesting that at room temperature they are in equilibrium. Their NMR spectra (Table 1) revealed that at low temperature the two isomers do not interconvert. Their ^{1}H NMR spectra in the cyclopentadienyl region displayed two different patterns: one consists of two signals of equal intensity, the other of a single signal, consistent with the presence of a *trans* isomer (**a**) with inequivalent cyclopentadienyl rings and a *cis*-isomer (**b**) with equivalent rings, consistent with ^{1}H NMR patterns predicted for *trans* and *cis* isomers when the ring 'Mo_2EH' is planar (Fig. 1), as has been determined crystallographically for *cis*-$[Mo_2Cp_2(\mu\text{-}H)(\mu\text{-}SMe)(CO)_4]$ **4b** (see below).

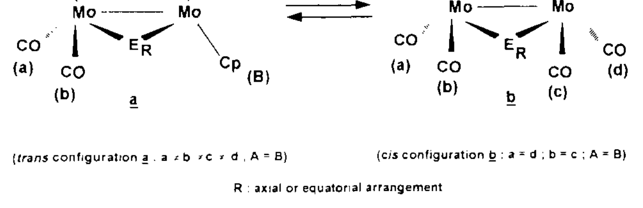


Fig. 1. Possible isomers for $[Mo_2Cp_2(\mu\text{-}H)(\mu\text{-}ER)(CO)_4]$.

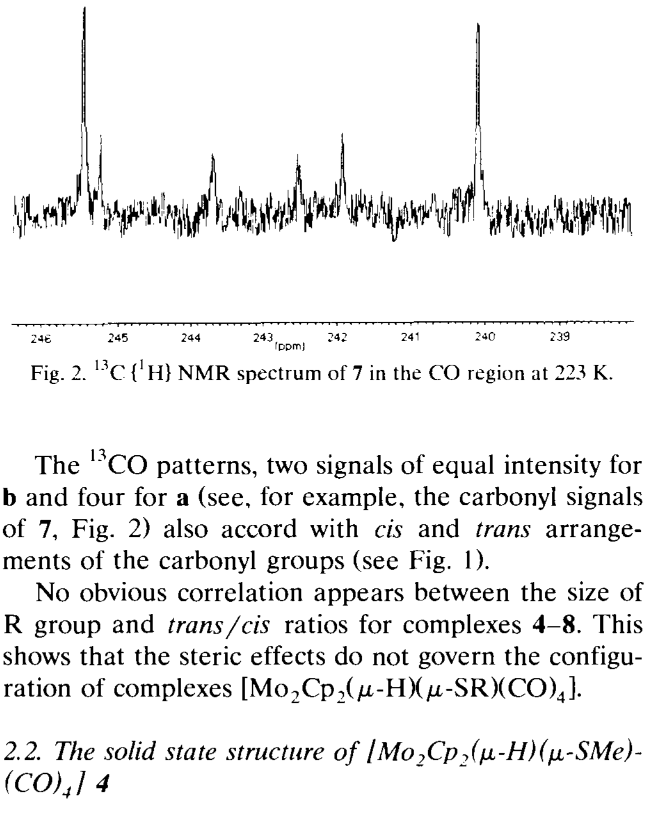


Fig. 2. $^{13}C\{^1H\}$ NMR spectrum of **7** in the CO region at 223 K.

The ^{13}CO patterns, two signals of equal intensity for **b** and four for **a** (see, for example, the carbonyl signals of **7**, Fig. 2) also accord with *cis* and *trans* arrangements of the carbonyl groups (see Fig. 1).

No obvious correlation appears between the size of R group and *trans/cis* ratios for complexes **4**–**8**. This shows that the steric effects do not govern the configuration of complexes $[Mo_2Cp_2(\mu\text{-}H)(\mu\text{-}SR)(CO)_4]$.

2.2. The solid state structure of $[Mo_2Cp_2(\mu\text{-}H)(\mu\text{-}SMe)(CO)_4]$ 4

X-ray analysis of **4** (Table 2, Fig. 3) reveals that the molecule contains two nearly identical $CpMo(CO)_2$ units that are linked through a bridging $\mu\text{-}SCH_3$ group and by a three-centre two-electron Mo–H–Mo bond [Mo–Mo = 3.237(1) Å] so that each Mo atom attains an 18-electron configuration. The $Mo_2(\mu\text{-}H)(\mu\text{-}S)$ unit is planar to within experimental error [H–Mo(1)–Mo(2)–S = −176(2)°], the bridging H and S atoms are each equidistant from the Mo atoms but the Mo–H–Mo angle [123(2)°] is much more obtuse than the Mo–S–Mo angle [84.0(1)°]. The molecule has an approximate plane of symmetry which is normal to the Mo–Mo vector and passes through the bridging H and S atoms so that the Cp(1)–Mo(1)–Mo(2)–Cp(2), C(1)–Mo(1)–Mo(2)–C(4) and C(2)–Mo(1)–Mo(2)–C(3) torsion angles [−3.4(1)°, −3.7(2)° and −4.9(1)°] are nearly zero [Cp(1) and Cp(2) are the centroids of rings C(R1)–C(R5) and C(R6)–C(R10) respectively]. Thus, in the solid, molecules of **4** deviate only insignificantly from the idealised *cis* configuration shown in Scheme 2 and Fig. 1. The magnitudes of the Cp(1)– and Cp(2)–Mo–Mo–S torsion angles [−97° and 94°] are appreciably greater than those of the Cp(1)– and Cp(2)–Mo–Mo–H angles [78° and −82°], presumably reflecting the different steric bulks of the bridging ligands. If the Mo–Mo bond is disregarded, each Mo atom has a four-legged piano-stool coordination with the S–Mo–C(1) and –C(4) angles [83.4(1)° and 84.1(1)°] some 10–13° larger than the H–Mo–C(2) and –C(3) angles [73.4(8)° and 70.7(8)°]. The thiolato-methyl group lies on the car-

Table 2
Selected bond lengths (Å) and angles (°) in compound **4**

Bond lengths			
Mo(1)–Mo(2)	3.237(1)	Mo(1)–S	2.416(1)
Mo(1)–C(1)	1.956(3)	Mo(1)–C(2)	1.956(3)
Mo(1)–C(R1)	2.304(3)	Mo(1)–C(R2)	2.301(3)
Mo(1)–C(R3)	2.338(3)	Mo(1)–C(R4)	2.383(3)
Mo(1)–C(R5)	2.361(3)	Mo(1)–H	1.851(26)
Mo(2)–S	2.420(1)	Mo(2)–C(3)	1.949(3)
Mo(2)–C(4)	1.952(3)	Mo(2)–C(R6)	2.376(3)
Mo(2)–C(R7)	2.317(3)	Mo(2)–C(R8)	2.277(3)
Mo(2)–C(R9)	2.292(3)	Mo(2)–C(R10)	2.361(3)
Mo(2)–H	1.829(26)	S–C(5)	1.811(3)
O(1)–C(1)	1.148(4)	O(2)–C(2)	1.147(3)
O(3)–C(3)	1.151(4)	O(4)–C(4)	1.149(3)
Bond angles			
Mo(2)–Mo(1)–S	48.0(1)	Mo(2)–Mo(1)–C(1)	111.8(1)
Mo(2)–Mo(1)–C(2)	90.9(1)	Mo(2)–Mo(1)–H	28.2(8)
S–Mo(1)–C(1)	83.4(1)	S–Mo(1)–C(2)	121.5(1)
S–Mo(1)–H	76.2(8)	C(1)–Mo(1)–C(2)	76.0(2)
C(1)–Mo(1)–H	125.8(9)	C(2)–Mo(1)–H	73.4(8)
Mo(1)–Mo(2)–S	47.9(1)	Mo(1)–Mo(2)–C(3)	90.3(1)
Mo(1)–Mo(2)–C(4)	109.7(1)	Mo(1)–Mo(2)–H	28.6(8)
S–Mo(2)–C(3)	124.0(1)	S–Mo(2)–C(4)	84.1(1)
S–Mo(2)–H	76.4(8)	C(3)–Mo(2)–C(4)	77.2(2)
C(3)–Mo(2)–H	70.7(8)	C(4)–Mo(2)–H	122.4(9)
Mo(1)–S–Mo(2)	84.0(1)	Mo(1)–S–C(5)	116.4(1)
Mo(2)–S–C(5)	115.1(1)	Mo(1)–H–Mo(2)	123.2(15)
Mo(2)–Mo(1)–Cp(1)	120.1	S–Mo(1)–Cp(1)	121.4
C(1)–Mo(1)–Cp(1)	126.1	C(2)–Mo(1)–Cp(1)	114.8
H–Mo(1)–Cp(1)	107.2	Mo(1)–Mo(2)–Cp(2)	132.7
S–Mo(2)–Cp(2)	117.2	C(3)–Mo(2)–Cp(2)	118.8
C(4)–Mo(2)–Cp(2)	112.5	H–Mo(2)–Cp(2)	124.7

Cp(1), Cp(2) are the centroids of rings C(R1)–C(R5) and C(R6)–C(R10) respectively.

bonyl side of the $Mo_2(\mu\text{-}H)(\mu\text{-}S)$ plane with C(5) nearly eclipsing C(1) relative to S–Mo(1) and C(4) relative to S–Mo(2) [respective torsion angles −12.3(2)° and 7.0(2)°]. Bond lengths in **4** appear unexceptional [13].

The *cis*-configuration adopted by **4** [14] contrasts with the *trans* configuration found in the phosphido and arsenido complexes $[Mo_2Cp_2(\mu\text{-}H)(\mu\text{-}ER_2)(CO)_4]$, $ER_2 = PMe_2$ [15 (X-ray), 16 (neutron)], P^tBu_2 [17], $AsMe_2$ [17], and in $[Mo_2Cp_2(CO)_2(\mu\text{-}H)\{\mu\text{-}n\text{-}C_6H_4\text{-}(PPh)(PPhH)\}]$ [17]. Like **4**, these complexes all have nearly planar and symmetrical $Mo_2(\mu\text{-}H)(\mu\text{-}E)$ bridging units, the Mo–Mo distances in the phosphido complexes of 3.247(1)–3.282(1) Å are similar to the value in **4** and the bridging Mo–P–Mo angles of 81–86° compare well with the Mo–S–Mo angle in **4**. Finally, the Mo–H distances and Mo–H–Mo angle in **4** are similar to the neutron diffraction values of 1.851(4) Å and 1.869(4) Å and 122.9(2)° for the PMe_2 complex [16]. It would appear reasonable to conclude that corresponding bond lengths in *cis* and *trans* isomers of species such as **4** are unlikely to be widely different.

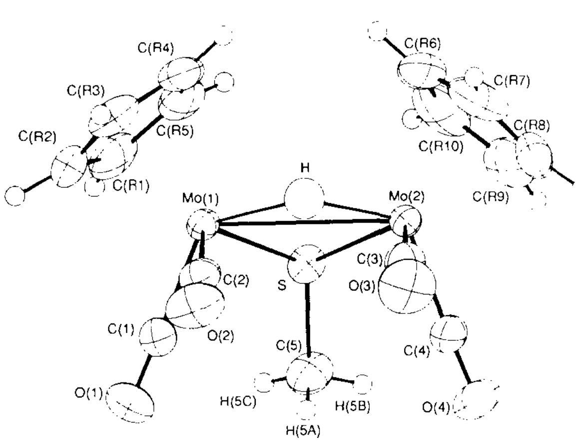
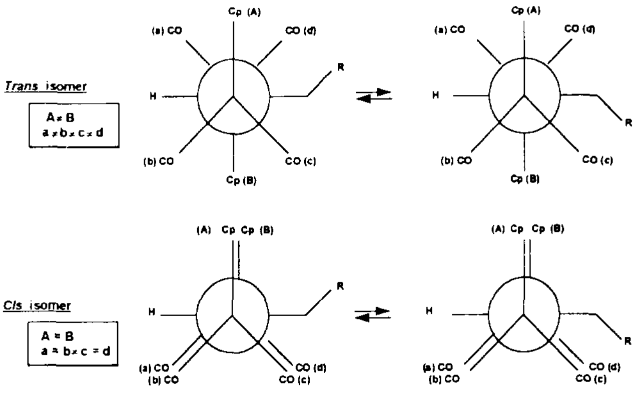


Fig. 3. A view of the molecule $[Mo_2Cp_2(\mu\text{-}H)(\mu\text{-}SMe)(CO)_4]$ **4** showing 50% probability ellipsoids, except for Cp and methyl hydrogen atoms, which are represented by spheres of arbitrary radius.



Scheme 2.

2.3. Dynamic NMR studies

The line shapes in variable-temperature ^1H NMR spectra of complexes **4–8** are temperature dependent and clearly indicate averaging of the low-temperature resonances with increasing temperature, implying that fluxional processes are operative in solution. The ^1H NMR spectrum of **4** in the Cp and hydride region between 193 and 353 K is presented in Fig. 4 as an example. At 193 K there are two Cp group signals of equal intensity at 4.56 ppm and 4.46 ppm, which correspond to isomer **a**, and one at 4.34 ppm corresponding to the equivalent Cp groups of isomer **b**. From their relative intensities, the ratio of **a**:**b** is 1.6:1. This is confirmed by the observation of two singlets at −11.19 ppm and −11.71 ppm with the same relative intensities because of the hydride of each isomer. On warming, broadening and then coalescence of Cp and hydride, signals occur until at 353 K the spectrum comprises singlets at 4.77 ppm and −11.28 ppm, respectively. All the line-shape changes throughout the temperature range were found to be completely reversible. Experiments using a wide range of concentrations of the complexes were conducted to confirm that these fluxional processes are intramolecular.

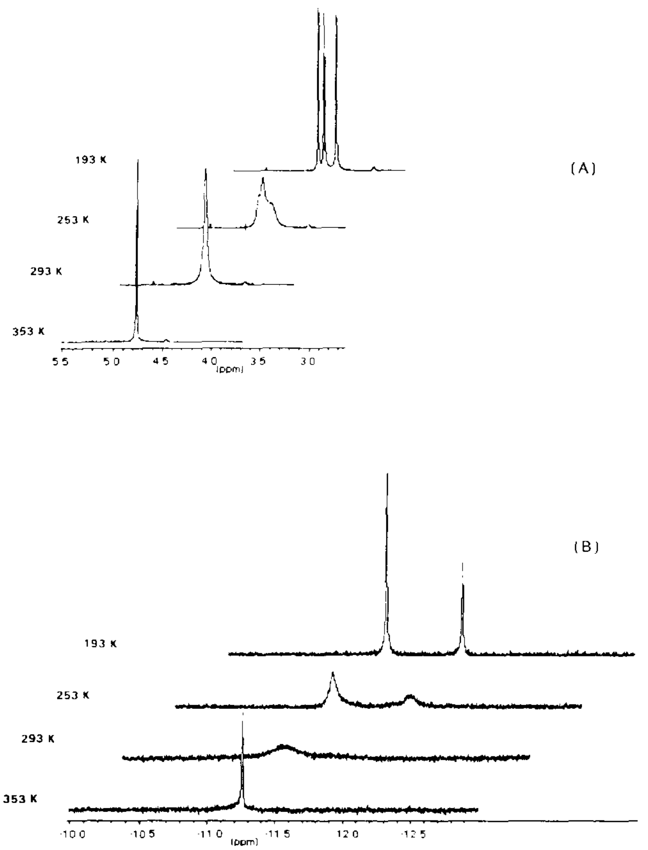


Fig. 4. Variable-temperature ^1H NMR spectra (in toluene-d_8) of **4** in the cyclopentadienyl (A) and hydride (B) regions.

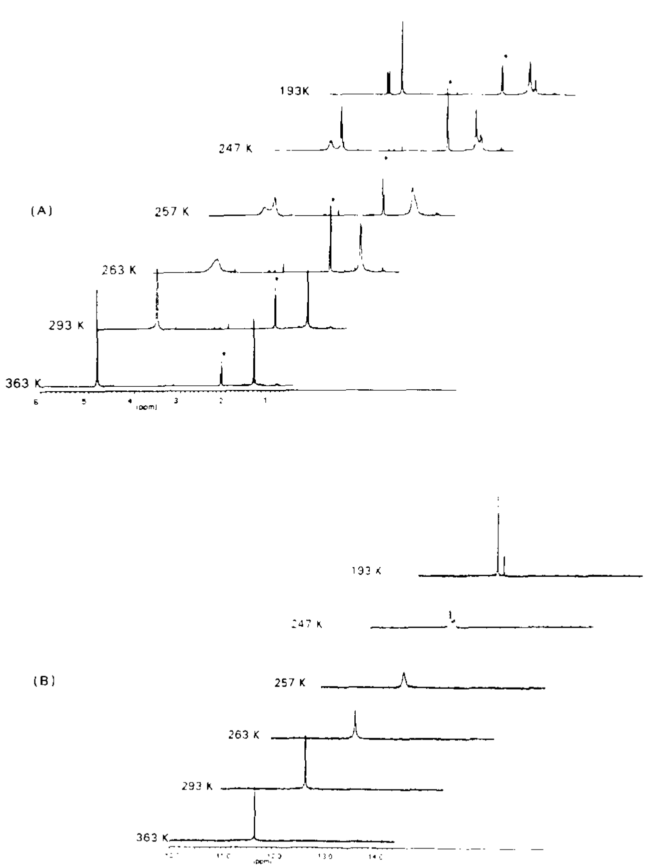


Fig. 5. Variable-temperature ^1H NMR spectra (in toluene-d_8) of **5** in the cyclopentadienyl and S^{t}Bu (A) and in the hydride region (B). *Resonance of the solvent.

Similar behaviour was observed for the other complexes **5–8**. The ^1H NMR spectrum of **5** as a function of temperature is displayed in Fig. 5. The activation barriers of the observed dynamic processes are estimated from the chemical shift differences $\Delta\nu$ [18] and from the coalescence temperatures of the Cp, or Me, or hydride signals in the ^1H NMR spectra. Data are summarized in Table 3.

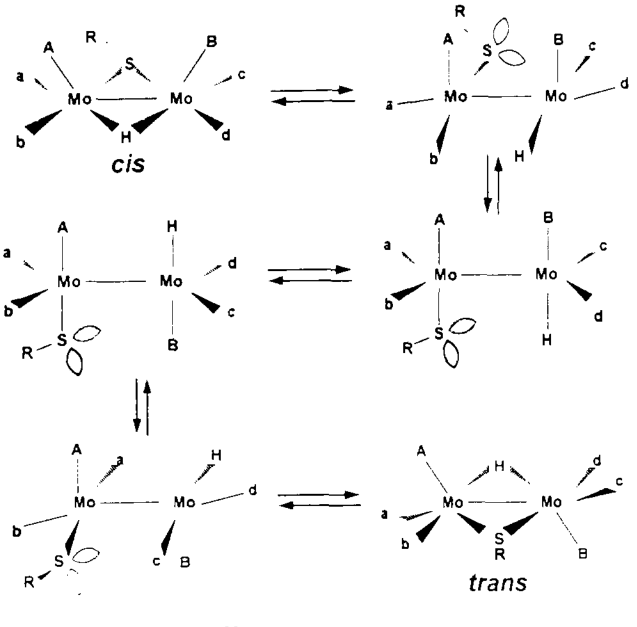
The values of the energy barriers associated with site exchange are low (50–64 kJ mol^{-1}, see Table 3). They are of the order expected for inversion at sulphur or selenium, as observed in many other dinuclear complexes, such as in *trans* $[Mo_2Cp_2(\mu\text{-SMe})_2(CO)_4]$ [19]. $[Ru_2Cp_2(\mu\text{-EPh})_2(CO)_2]$ (E = S or Se) [20], $[Mo_2(\eta^2\text{-}C_7H_7)(\mu\text{-S}^tBu)_3(CO)_2(PR_3)]$ [21], and very recently in $[W_2(\eta^5\text{-}C_3H_4R)Cl_4(\mu\text{-H})(\mu\text{-SR})]$ [8d]. However our data (see Table 1, Figs. 4 and 5) are inconsistent with such a process. Indeed, a *cis* axial ⇌ *cis* equatorial and a *trans* axial ⇌ *trans* equatorial interconversions would imply the presence of only two signals for cyclopentadienyl groups in the ^1H NMR spectra at low temperatures, with four signals for CO groups in the ^{13}C NMR

Table 3
Dynamic ^1H NMR data

Compounds	Resonance	T_c/K [a]	$\Delta\nu$ [b] Hz	ΔP [c]	$\Delta G^*_{a\to b}$ [d] kJ mol^{-1}	$\Delta G^*_{b\to a}$ [d] kJ mol^{-1}
4	C_5H_5	257	51	0.24	53.6	52.6
5	$SC(CH_3)$	256	37.5	0.50	53.0	55.4
6	C_5H_5	247	54	0.50	52.6	50.3
7	Mo–*H*	265	148	0.31	52.0	53.5
8	C_5H_5	296	24	0.34	64.4	62.8

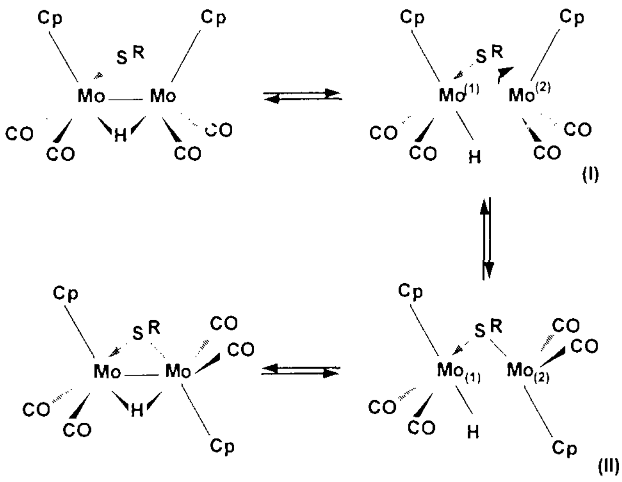
[a] Coalescence temperature.
[b] Frequency difference between resonances of exchanging groups in low-temperature limit.
[c] Difference in fractional proportion of the sites; the total population is taken as unity.
[d] Highest error limit: ±1 kJ mol^{-1}.

spectra (see Scheme 2). The fluxionality of analogous μ-phosphido complexes $[Mo_2Cp_2(\mu\text{-H})(\mu\text{-PRPh})(CO)_4]$ (R = H or Ph) [7n,7o] and $[MoMnCp(\mu\text{-H})(\mu\text{-PPh}_2)(CO)_6]$ [7j,22] has been attributed to the interconversion of two *trans* enantiomers via a trigonal intermediate, consistent with the results of Faller and Anderson [23]. Recently Curtis *et al.* [7a] have proposed a mechanism for the isomerisation of the μ-phosphido compound $[Mo_2Cp_2(\mu\text{-PHPh})_2(CO)_4]$ including an inversion of configuration at the P atom via square or/and trigonal bipyramidal low-energy intermediates (CO groups in the equatorial positions). In all these proposed mechanisms [7j,7n,7o,22] complexes preserve a *trans* structure. X-ray analysis of **4b** has shown that the two cyclopentadienyl groups are *cis* with respect to the Mo–Mo axis, implying that for complexes **4–8** a *cis* form is involved in the isomerisation process. Therefore we attribute the fluxional process observed in the variable temperature NMR spectra to a *cis*(**b**) → *trans*(**a**) interconversion, which has been widely discussed, for instance, for μ-carbonyl complexes $[Fe_2Cp_2(CO)_4(\mu\text{-CO})]$ [24] and $[Fe_2Cp_2(\mu\text{-CO})(\mu\text{-GeMe})(CO)_2]$ [25]. For di-μ compounds $[Mo_2Cp_2(\mu\text{-ER})_2(CO)_2]$ (M = Fe or Ru; E = S or Se) [26] and $[Mo_2Cp_2(\mu\text{-SR})_2(CO)_4]$ [19], the barrier of the *cis–trans* interconversion must be relatively high compared with that of the earlier μ-carbonyl complexes, because the process does not occur on the NMR timescale.



A, B = Cp ; a, b, c, d = CO

Scheme 3. Possible mechanism for *cis/trans* interconversion of complexes **4–8**.



Scheme 4.

One possible mechanism for the isomerisation of **4–8** is shown in Scheme 3. It proceeds via the breaking of Mo–S and Mo–H bonds, followed by the internal rotation of the non-bridged intermediates, and then by the reformation of the hydride and thiolato bridges. This mechanism involves the classical SP–TBP–SP interconversion of the square pyramidal (SP) and trigonal bipyramidal (TBP) intermediates in their low-energy states. However, the fluxional process shown in Scheme 3 does not account for the lack of the contribution from both the steric and electronic demands of R to $\Delta G^{\neq}$. The replacement of methyl group by bulkier groups (^{t}Bu, Ph) in the complexes studied here induces only very slight changes in $\Delta G^{\neq}$ (Table 3). This sharply contrasts with the decrease of about 10 kJ mol^{-1} and 15 kJ mol^{-1} observed for analogous complexes $[W_2Cp'_2Cl_4(\mu\text{-H})(\mu\text{-SR})]$ [8d] when R = Me is substituted by R = Et or ^{i}Pr. The barrier determined for the fluxional process seems too low for a mechanism which involves many bond breakings. The alternative fluxional process for $[Mo_2Cp_2(\mu\text{-H})(\mu\text{-SR})(CO)_4]$ **4–8** shown in Scheme 4 is more likely to account for the observed trends in $\Delta G^{\neq}$ with the steric bulk of R. This involves only the breaking of the Mo(2)–H bond and then rotation of the CpMo(2)$(CO)_2$ moiety about the Mo(2)–S vector. The higher energy barrier calculated for the selenato-bridged complex **8** supports this proposal. The orbital overlap between Mo(2) and Se atoms is greater than that between Mo(2) and S atoms, making the barrier to rotation of the CpMo(2)$(CO)_2$ moiety around the Mo(2)–S vector lower than that around the Mo(2)–Se axis.

3. Experimental section

3.1. General procedures

The reactions were performed under either dinitrogen or argon using standard Schlenk techniques, and solvents were deoxygenated and dried by standard methods. Literature methods were used for the preparation of $[Mo_2Cp_2(CO)_4]$ ($Cp' = C_5H_5$ or C_5Me_5) [27], $[Mo_2Cp_2(\mu\text{-SMe})_2(CO)_4]$ [28], and $[VCp_2]$ [29].

IR spectra were obtained with a Perkin-Elmer 1430 spectrophotometer in dichloromethane solutions in the ν(CO) region. NMR spectra were recorded on a Bruker AC300 spectrophotometer. Peak positions are relative to tetramethylsilane as an internal reference. The mass spectra were measured on a GC/MS Helwett-Packard 5595C. Chemical analyses were performed by the Centre de Microanalyses du CNRS, Vernaison.

3.2. *Synthesis of* $[Mo_2Cp_2(\mu\text{-}H)(\mu\text{-}ER)(CO)_4]$

3.2.1. *Method A: Reaction of* $[Mo_2Cp_2(\mu\text{-SMe})_2(CO)_4]$ *2 with* $[VCp_2]$

Complex **2** (1.8 g, 3.4 mmol) was dissolved in toluene (30 ml), and the toluene solution containing $[VCp_2]$ (0.6 g, 3.4 mmol) was added. The reaction mixture was stirred at room temperature for 3 d. The solution changed from green-brown to yellow-brown during this time. The solvent was removed under high vacuum, and the residue, after being dissolved in the minimum of CH_2Cl_2, was adsorbed onto silica and added to the top of a chromatography column. Elution with hexane: CH_2Cl_2 (4:1) afforded a red band yielding complex **4**. The solid was washed with pentane (yield: 10–50%). Traces of $[Mo_2Cp_2(\mu\text{-SMe})_2(CO)_2]$ [28] were also formed in this reaction.

3.2.2. *Method B: Reaction of* $[Mo_2Cp_2(CO)_4]$ *3 with HER*

In a typical reaction, a solution of complex **3** (1 g, 2.3 mmol) and thiol or selenol (ca. 4.6 mmol) was stirred at room temperature (when $ER = S^tBu$, the solution must be heated at 60°C) for 8 h. The solvent was removed under high vacuum, and the residue, after being dissolved in the minimum of CH_2Cl_2, was chromatographed on silica gel. Elution with CH_2Cl_2: hexane (1:4) gave complexes **4**–**8**, which were washed with pentane.

4 (red solid; yield: 42%), Anal. Found: C, 36.9, H; 3.2. $C_{15}H_{14}Mo_2O_4S$ Calc.: C, 37.3; H, 2.9%. Mass spectrum: m/z 482 (M^+). IR(CH_2Cl_2): ν(CO) 1980s, 1940s, 1880s cm^{-1}.

5 (brown solid; yield: 21%). Anal. Found: C, 41.8; H, 3.9. $C_{18}H_{20}Mo_2O_4S$. Calc.: C, 41.2; H, 3.8%. Mass spectrum: m/z 524 (M^+). IR (CH_2Cl_2): ν(CO) 1970s, 1930m, 1870s, cm^{-1}.

6 (brown solid; yield: 20%). Anal. Found: C, 45.2; H, 3.4. $C_{21}H_{18}Mo_2O_4S$ Calc.: C, 45.2, H, 3.2%. Mass spectrum: m/z 558 (M^+). IR (CH_2Cl_2): ν(CO) 1980s, 1940s, 1875s cm^{-1}.

7 (brown solid; yield: 50%). Anal. Found:C, 44.3; H, 2·7. $C_{20}H_{16}Mo_2O_4S$ Calc.: C, 44.1; H, 2.9%. Mass spectrum: m/z 544 (M^+). IR(CH_2Cl_2): ν(CO) 1980s, 1945s, 1880s cm^{-1}.

8 (brown solid: yield: 42%). Anal. Found:C, 40.6; H, 2.6%, $C_{20}H_{16}Mo_2O_4S$ Calc.: C, 40.6; H, 2.7%. Mass spectrum: m/z 591 (M^+). IR (CH_2Cl_2): ν(CO) 1980m, 1940s, 1875s cm^{-1}.

3.3. *Temperature-dependent NMR spectroscopy*

The energies of activation in Table 3 were calculated according to the procedure given by Shanan-Atidi and Bar-Eli [18]. The variable-temperature ^1H NMR study allowed the determination of T_c the coalescence temperature. At this temperature, the observed chemical shift was found to be close to the weighted-average chemical shifts obtained from the slow-exchange spectrum. Through the use of the relative populations of exchanging ligands and the coalescence temperature, the activation energy for intramolecular ligand scrambling was calculated [18,30].

3.4. *Crystal structure analysis of* $[Mo_2Cp_2(\mu\text{-}H)(\mu\text{-}SMe)(CO)_4]$ *4*

All measurements were made at 22°C on an Enraf-Nonius CAD4 diffractometer using graphite-monochromatised Mo Kα radiation, $\lambda = 0.71073$ Å. The crystal was a burgundy-coloured plate $0.27 \times 0.27 \times 0.13$ mm.

3.4.1. *Crystal data*

$C_{15}H_{14}Mo_2SO_4$, $M = 482.22$, monoclinic, space group $C2/c$, $a = 17.225(1)$ Å, $b = 8.418(1)$ Å, $c = 22.960(2)$ Å, $\beta = 90.346(5)°$, $V = 3329.2(4)$ Å^3, $Z = 8$, $D_{calc} = 1.924$ g cm^{-3}, $\mu(Mo\text{-}K\alpha) = 16.1$ cm^{-1}.

3.4.2. *Measurements*

Cell dimensions are based on the setting angles of 23 reflections with $11.4 < \theta(Mo\ K\alpha) < 14.7°$. The intensities of 9653 reflections with $1 < \theta(Mo\ K\alpha) > 30°$, $0 \leq h \leq 24$, $\overline{11} \leq k \leq \overline{11}$ and $\overline{32} \leq l \leq 32$ were measured from $\omega/2\theta$ scans and were corrected empirically for absorption (correction factors 0.93–1.05 on F) [31]. Merging yielded 4551, unique intensities ($R_{int} = 0.033$). Eight reflections were rejected because duplicate intensity estimations were inconsistent and further calculations proceeded with 4213 unique intensities for which $I > 3\sigma(I)$.

3.4.3. *Structure analysis*

All atoms were located by Patterson and Fourier methods. In the final full-matrix least-squares calculations on F with $w^{-1} = \sigma^2(F)$, anisotropic U_{ij} values were refined for non-H atoms (Table 4). The positional and isotropic U parameters of the bridging H atoms were also adjusted. Other H atoms rode on their

Table 4
Fractional coordinates and equivalent isotropic displacement parameters (Å^2) for **4**

Atom	x	y	z	U
Mo(1)	−0.13491(1)	−0.08239(2)	−0.36163(1)	0.028
Mo(2)	−0.31938(1)	−0.10657(2)	−0.38795(1)	0.029
S	−0.24574(3)	0.03767(6)	−0.31506(2)	0.035
O(1)	−0.09191(13)	−0.19208(31)	−0.23646(9)	0.072
O(2)	−0.11546(13)	−0.44773(22)	−0.37151(9)	0.063
O(3)	−0.30556(14)	−0.46846(22)	−0.41039(10)	0.070
O(4)	−0.40485(12)	−0.25382(29)	−0.28248(9)	0.070
C(1)	−0.10918(14)	−0.15012(32)	−0.28232(11)	0.046
C(2)	−0.12424(14)	−0.31309(27)	−0.36793(10)	0.040
C(3)	−0.30952(14)	−0.33408(29)	−0.40172(11)	0.043
C(4)	−0.37197(13)	−0.19858(29)	−0.32087(10)	0.044
C(5)	−0.26368(16)	−0.02117(33)	−0.24048(10)	0.052
C(R1)	−0.05785(17)	0.14132(35)	−0.36148(13)	0.058
C(R2)	−0.01089(14)	0.00915(38)	−0.37720(12)	0.057
C(R3)	−0.03782(17)	−0.04583(33)	−0.43107(12)	0.055
C(R4)	−0.09913(17)	0.05073(37)	−0.44904(11)	0.056
C(R5)	−0.11193(16)	0.16539(31)	−0.40648(14)	0.055
C(R6)	−0.32077(19)	0.05947(44)	−0.47165(15)	0.070
C(R7)	−0.36765(25)	−0.07007(42)	−0.48141(13)	0.077
C(R8)	−0.42910(19)	−0.06353(51)	−0.44150(19)	0.084
C(R9)	−0.41805(23)	0.06910(53)	−0.40676(19)	0.087
C(R10)	−0.35137(24)	0.14538(36)	−0.42634(18)	0.079
H	−0.2185(15)	−0.1531(30)	−0.4055(11)	0.045(7)

For the bridging H atom U is the isotropic displacement parameter and for other atoms $U = \frac{1}{3}\Sigma_{i=1}^{3}\Sigma_{j=1}^{3}U_{ij}a_i^*a_j^*(\vec{a}_i, \vec{a}_j)$.

parent C atoms with C–H = 0.96 Å and $U(\mathrm{H}) = 1.2U_{\mathrm{eq}}(\mathrm{C})$; the orientation of the methyl group was initially obtained from a difference synthesis. Refinement of 204 parameters, including an isotropic extinction parameter $r^* = 110(15)$, converged ($\Delta/\sigma < 0.01$) at $R = 0.023$, $R\mathrm{w} = 0.029$, $S = 1.8$, with function values in the final difference synthesis in the range ± 0.6 e Å^{-3}. All calculations were performed on a VAX 4000/60 computer with the GX package [32]. Scattering factors and anomalous dispersion correction were taken from Ref. [33].

Tables of fractional atomic coordinates, isotropic and anisotropic displacement parameters, and a complete bond length and angle listing for **4** are available from the Cambridge Crystallgoraphic Data Centre.

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