

Reactions of dinuclear and polynuclear complexes. Part 18ⁱ Substitution reactions of a μ -chloro or a μ -thiolato ligand in the dinuclear cyclopentadienyl molybdenum(III) complex

$[\text{Cp}_2\text{Mo}_2(\mu\text{-Cl})(\mu\text{-SMe})_3]$: crystal structure of
 $[\text{Cp}_2\text{Mo}_2(\mu\text{-SCH}_2\text{CH}_2\text{SH})(\mu\text{-SMe})_3] \cdot 0.5\text{CH}_2\text{Cl}_2$

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Abstract

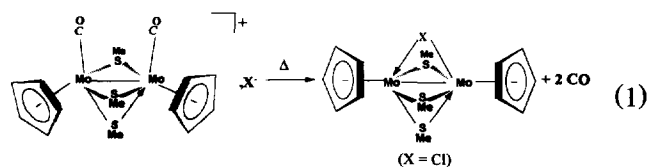
Thermal reaction of the chloro-bridged complex $[\text{Cp}_2\text{Mo}_2(\mu\text{-Cl})(\mu\text{-SMe})_3]$ **1** with the dithiols $\text{HS}(\text{CH}_2)_n\text{SH}$ ($n = 2$ or 3) affords the quadruply thio-bridged complexes $[\text{Cp}_2\text{Mo}_2(\mu\text{-S}(\text{CH}_2)_n\text{SH})(\mu\text{-SMe})_3]$ where $n = 2$ (**2**) or 3 (**3**). **2** has been shown by X-ray diffraction to contain the μ - η^1 -dithiolate ligand $^-\text{S}(\text{CH}_2)_2\text{SH}$ which bridges an Mo–Mo single bond whose length is 2.606(1) Å. The substitution reaction of the chloro bridge in **1** also occurs with phenylphosphine, H_2PPh , giving the μ -phosphido compound $[\text{Cp}_2\text{Mo}_2(\mu\text{-HPPh})(\mu\text{-SMe})_3]$ **4**. In contrast with diphenylphosphine, HPPH_2 , the thiolate ligand *trans* to the chloro bridge is replaced by a PPh_2 group, giving the new μ -chloro complex $[\text{Cp}_2\text{Mo}_2(\mu\text{-Cl})(\mu\text{-PPh}_2)(\mu\text{-SMe})_2]$ **5**. All new products have been characterized by spectroscopic analyses. © 1997 Elsevier Science S.A.

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1. Introduction

Cyclopentadienyl complexes $[\text{Cp}_2\text{Mo}_2(\mu\text{-X})_4]^{n+}$, where $n = 0$ or 1 , in which dimolybdenum(III/III) or -(III/IV) units are linked by four bridging groups have been widely described [2,3]. Current interest in these systems relates to the insertion and reaction of bridging halide groups. Thus, Rakowski-Dubois and coworkers recently reported that the $\mu\text{-SMe}_2$ ligand in the dimolybdenum(III) complex $[\text{Cp}_2\text{Mo}_2(\text{S}_2\text{CH}_2)(\mu\text{-SMe})(\mu\text{-SMe}_2)]^+$ is thermally labile and that it can be replaced by halide to give the μ -halo derivative

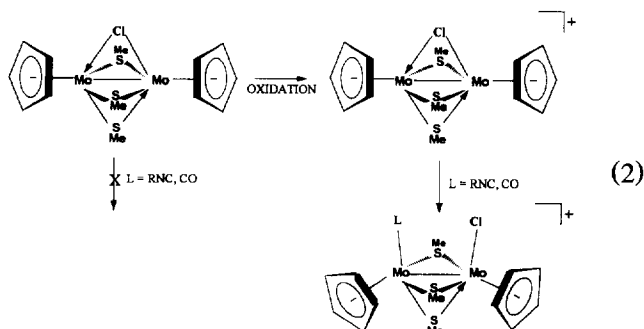
$[\text{Cp}_2\text{Mo}_2(\text{S}_2\text{CH}_2)(\mu\text{-SMe})(\mu\text{-X})]$ [4]. Several years ago we reported a synthesis (Eq. (1)) of the related hetero-bridged compounds $[\text{Cp}_2\text{Mo}_2(\mu\text{-X})(\mu\text{-SMe})_3]$ where $\text{X} = \text{Cl}$ (**1**) or Br [5].



More recently we studied the electrochemical oxidation of **1** and found that removal of one electron to give the mixed valence Mo(III)/Mo(IV) compound $[\text{Cp}_2\text{Mo}_2(\mu\text{-Cl})(\mu\text{-SMe})_3]^+$ (Eq. (2)) activates the chloro bridge to nucleophilic attack [6].

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ⁱ See Ref. [1] for part 17.



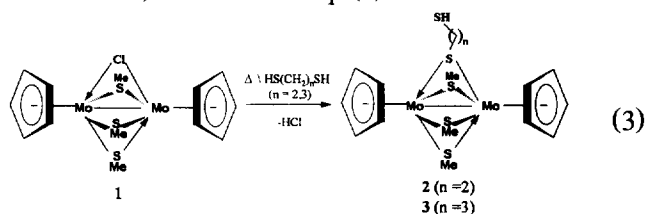
The stability of the dinuclear tris-thiolato-bridged structure in these reactions contrasts with the ready cleavage of an $M_2(\mu\text{-Cl})$ core [7] or $M\text{-Cl}$ bonds [8]. This suggested to us that the dinuclear $\text{Mo}_2(\mu\text{-Cl})(\mu\text{-SMe})_3$ unit could be used to activate various substrates by replacement of the chloro-bridge and that quadruply-bridged molybdenum systems could thereby be synthesized.

Accordingly, we now report reactions of the molybdenum(III) complex $[\text{Cp}_2\text{Mo}_2(\mu\text{-Cl})(\mu\text{-SMe})_3]$ **1** with nucleophilic dithiols, $\text{HS}(\text{CH}_2)_n\text{SH}$ ($n = 2, 3$), and phosphines, HPPH_2 and H_2PPh , which demonstrate the ability of **1** to generate new quadruply-bridged compounds, the dinuclear structure being maintained by three or two thiolate groups.

2. Results and discussion

2.1. Synthesis and spectroscopic characterization of μ -ethanedithiolate ($n = 2$) and μ -propanedithiolate ($n = 3$) derivatives $[\text{Cp}_2\text{Mo}_2\{\mu\text{-S}(\text{CH}_2)_n\text{SH}\}(\mu\text{-SMe})_3]$ **2** ($n = 2$), **3** ($n = 3$)

Reaction of **1** with an excess of dithiol was carried out in refluxing THF. Only one product was formed in the reaction, as shown in Eq. (3).



The μ -ethanedithiolato **2** and μ -propanedithiolato **3** compounds have been characterized by spectroscopic analyses (Table 1). The IR spectra, in KBr pellets, display $\nu(\text{SH})$ bands at 2180 cm^{-1} for **2** and 1975 cm^{-1} for **3**. ^1H NMR spectra exhibit resonances for two equivalent cyclopentadienyl rings and for three inequivalent bridging thiolato ligands, confirming that the integrity of the $\text{Cp}_2\text{Mo}_2(\mu\text{-SMe})_3$ core is maintained. The ^1H NMR patterns of the alkanedithiolato ligands, consisting of two multiplets for CH_2 groups and a

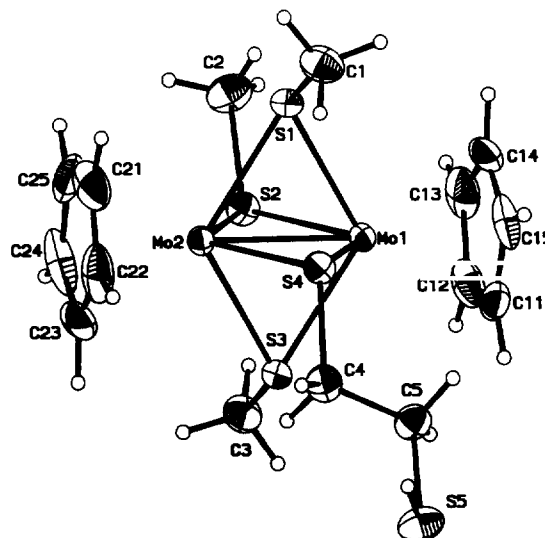


Fig. 1. A view of a molecule of $[\text{Cp}_2\text{Mo}_2\{\mu\text{-S}(\text{CH}_2)_2\text{SH}\}(\mu\text{-SMe})_3]$ **2**. 50% probability ellipsoids are displayed, except for hydrogen atoms which are shown as spheres of arbitrary radius. For clarity the disorder of the bridging sulphur atoms is not displayed.

triplet at about 1 ppm for SH, are characteristic. However, the mode of coordination of the μ -dithiolato bridges, $\mu\text{-}\eta^1\text{-S}(\text{CH}_2)_n\text{SH}$ or $\mu\text{-}\eta^2\text{-S}(\text{CH}_2)_n\text{SH}$, could not be ascertained from the spectroscopic data and was eventually determined by means of a single-crystal X-ray diffraction study of **2**.

2.2. The solid state structure of $[\text{Cp}_2\text{Mo}_2\{\mu\text{-S}(\text{CH}_2)_2\text{SH}\}(\mu\text{-SMe})_3]$ **2**

Complex **2** (Fig. 1) belongs to a well characterized group of structures which contain a $\text{Cp}_2\text{Mo}_2(\mu\text{-S})_4$ residue where Cp can be a substituted or unsubstituted cyclopentadienyl ring and the bridging sulphur atom may come inter alia from such ligands as S^{2-} , MeS^- , Me_2S , $\text{CH}_2\text{S}_2^{2-}$, $^-\text{SCH}=\text{CHS}^-$ or $^-\text{SCHMeCH}_2\text{S}^-$ [4,9]. In general ligands with two sulphur atoms bond in a $\mu\text{-}\eta^2$ -mode, with both S atoms in bridging roles. The few exceptions contain S–S bonds (e.g. S_2Ph [10]) with only one sulphur atom attached to the metal. The pendant role of S5 in **2** is therefore slightly unusual, and, given the stability of $[\text{CpMo}(\mu\text{-SCHMeCH}_2\text{S})_2]$ [11], there seems no compelling structural reason why **2** should not form $[\text{Cp}_2\text{Mo}_2\{\mu\text{-S}(\text{CH}_2)_2\text{S}\}(\mu\text{-SMe})_2]$ through loss of MeSH. Distances and angles in **2** (Table 2) are consistent with the proposed structure: the Mo–Mo distance is virtually identical to the mean of $2.603\text{ \AA}$ for 21 such bonds in $\text{Cp}_2\text{Mo}_2(\mu\text{-S})_4$ species; the 21 individual values fall in a narrow range ($2.573\text{--}2.628\text{ \AA}$).² The Mo–S distances in **2** vary little, the S

² The Cambridge Structural Database (October, 1996 version) was surveyed with the programs QUEST and VISTA mounted at the Daresbury National Laboratory, Warrington, UK. See also Ref. [12].

Table 1
Selected spectroscopic data for complexes 2–5

Complex		^1H NMR ^a	^{13}C NMR ^{a,b}	^{31}P NMR ^{a,c}
$[\text{Cp}_2\text{Mo}_2(\mu\text{-SMe})_3(\mu\text{-S}(\text{CH}_2)_2\text{SH})]$	2	5.15 (s, 10H, C_5H_5), 2.36 (m, 2H, $\text{S}(\text{CH}_2)_2\text{SH}$), 2.17 (m, 2H, $\text{S}(\text{CH}_2)_2\text{SH}$), 1.61 (s, 3H, SCH_3), 1.56 (s, 3H, SCH_3), 1.55 (s, 3H, SCH_3) 1.34 (t, 1H, SH , $^3J = 7.8\text{ Hz}$)		
$[\text{Cp}_2\text{Mo}_2(\mu\text{-SMe})_3(\mu\text{-S}(\text{CH}_2)_3\text{SH})]$	3	5.19 (s, 10H, C_5H_5), 2.19 (m, 4H, $\text{S}(\text{CH}_2)_3\text{SH}$), 1.60 (s, 3H, SCH_3), 1.59 (s, 3H, SCH_3), 1.57 (s, 3H, SCH_3), 1.43 (m, 2H, $\text{S}(\text{CH}_2)_3\text{SH}$) 1.07 (t, 1H, SH , $^3J = 7.2\text{ Hz}$)		
$[\text{Cp}_2\text{Mo}_2(\mu\text{-SMe})_3(\mu\text{-HPPH})]$	4a	7.5–7.16 (m, 5H, PC_6H_5), 5.35 (s, 10H, C_5H_5) 4.88 (d, $^1J_{\text{P-H}} = 369\text{ Hz}$, 1H, PH) 1.70 (d, $J_{\text{P-H}} = 2.5\text{ Hz}$, 3H, SCH_3) 1.53 (d, $J_{\text{P-H}} = 1.3\text{ Hz}$, 3H, SCH_3) 1.52 (s, 3H, SCH_3)	{135.48 (d, $J_{\text{P-C}} = 38\text{ Hz}$), 134.80 (d, $J_{\text{P-C}} = 8\text{ Hz}$), 127.53 (d, $J_{\text{P-C}} = 2.8\text{ Hz}$), 127.17 (d, $J_{\text{P-C}} = 9.5\text{ Hz}$), C_6H_5 }, 88.83 (s, C_5H_5), 13.24 (d, $J_{\text{P-C}} = 19.9\text{ Hz}$, SCH_3), 9.70 (d, $J_{\text{P-C}} = 19.6\text{ Hz}$, SCH_3), 6.45 (s, SCH_3).	22.5 (d, $^1J_{\text{P-H}} = 369\text{ Hz}$)
	4b	7.5–7.16 (m, 5H, PC_6H_5) 5.44 (d, $^1J_{\text{P-H}} = 375.5\text{ Hz}$, 1H, PH) 5.37 (s, 10H, C_5H_5) 1.73 (d, $J_{\text{P-H}} = 0.9\text{ Hz}$, 3H, SCH_3) 1.63 (d, $J_{\text{P-H}} = 1.0\text{ Hz}$, 3H, SCH_3) 1.50 (s, 3H, SCH_3)		80.2 (d, $^1J_{\text{P-H}} = 375.5\text{ Hz}$)
$[\text{Cp}_2\text{Mo}_2(\mu\text{-SMe})_3(\mu\text{-PPh}_2)]$	5	7.15 (m, 10H, PC_6H_5), 5.43 (s, 10H, C_5H_5) 1.61 (d, $J_{\text{P-H}} = 1.0\text{ Hz}$, 6H, SCH_3)	{141.91 (d, $J_{\text{P-C}} = 39\text{ Hz}$), 134.64 (d, $J_{\text{P-C}} = 7.7\text{ Hz}$), 127.53 (d, $J_{\text{P-C}} = 2.5\text{ Hz}$), 126.89 (d, $J_{\text{P-C}} = 9.7\text{ Hz}$), C_6H_5 }, 90.36 (s, C_5H_5), 13.46 (d, $J_{\text{P-C}} = 15.3\text{ Hz}$, SCH_3)	120.3 (s)

^a Chemical shifts δ ppm measured at 293 K in C_6D_6 for 2–3, in CDCl_3 for 4–5.

^b Hydrogen-1 decoupled.

^c Without hydrogen-1 decoupling.

Table 2
Selected bond lengths (Å) and angles (deg)

Mo(1)–C(11)	2.266(4)	Mo(1)–C(12)	2.271(4)
Mo(1)–C(13)	2.300(4)	Mo(1)–C(14)	2.313(4)
Mo(1)–C(15)	2.293(4)	Mo(1)–S(1)	2.465(2)
Mo(1)–S(2)	2.450(2)	Mo(1)–S(3)	2.457(2)
Mo(1)–S(4)	2.476(2)	Mo(2)–C(21)	2.276(5)
Mo(2)–C(22)	2.308(4)	Mo(2)–C(23)	2.300(4)
Mo(2)–C(24)	2.262(4)	Mo(2)–C(25)	2.248(5)
Mo(1)–Mo(2)	2.606(1)	Mo(2)–S(1)	2.466(2)
Mo(2)–S(2)	2.454(2)	Mo(2)–S(3)	2.462(2)
Mo(2)–S(4)	2.458(2)	S(1)–C(1)	1.827(6)
S(2)–C(2)	1.827(6)	S(3)–C(3)	1.837(5)
S(4)–C(4)	1.844(5)	S(5)–C(5)	1.822(5)
C(4)–C(5)	1.486(7)	C(11)–C(15)	1.374(3)
C(21)–C(22)	1.360(3)		
S(2)–Mo(1)–S(3)	74.1(1)	S(2)–Mo(1)–S(1)	73.8(1)
S(3)–Mo(1)–S(1)	116.2(1)	S(2)–Mo(1)–S(4)	115.7(1)
S(3)–Mo(1)–S(4)	73.7(1)	S(1)–Mo(1)–S(4)	73.2(1)
S(2)–Mo(2)–S(4)	116.3(1)	S(2)–Mo(2)–S(3)	73.9(1)
S(4)–Mo(2)–S(3)	73.9(1)	S(2)–Mo(2)–S(1)	73.7(1)
S(4)–Mo(2)–S(1)	73.5(1)	S(3)–Mo(2)–S(1)	116.0(1)
C(1)–S(1)–Mo(1)	115.0(2)	C(1)–S(1)–Mo(2)	116.9(2)
Mo(1)–S(1)–Mo(2)	63.8(1)	C(2)–S(2)–Mo(1)	115.8(2)
C(2)–S(2)–Mo(2)	115.5(2)	Mo(1)–S(2)–Mo(2)	64.2(1)
C(3)–S(3)–Mo(1)	116.3(2)	C(3)–S(3)–Mo(2)	114.7(2)
Mo(1)–S(3)–Mo(2)	64.0(1)	C(4)–S(4)–Mo(2)	113.5(2)
C(4)–S(4)–Mo(1)	118.9(2)	Mo(2)–S(4)–Mo(1)	63.8(1)
C(5)–C(4)–S(4)	113.1(4)	C(4)–C(5)–S(5)	112.5(4)

atoms being equidistant from the Mo atoms they bridge, and agree with an average Mo–S length of 2.454 Å derived from a database survey of $\text{Mo}_2(\mu\text{-SMe})_4$ complexes.³

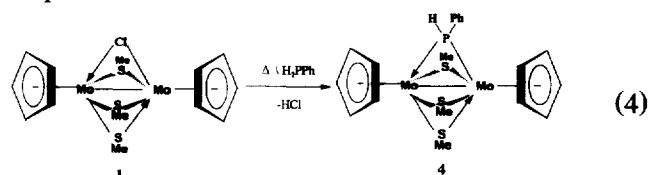
All four bridging S atoms are disordered (Fig. 2). Roughly one molecule in eight packs so the sulphur atoms lie in the alternative S1*–S4* sites. This disorder leaves the methyl carbon positions unaltered, so far as can be seen. Interestingly, in 1970 Connolly and Dahl [3] reported a similar disorder in $[\text{Cp}_2\text{Mo}_2(\mu\text{-SMe})_4]$, the first molecule of this group to be structurally examined.

2.3. Reaction of 1 with primary phosphine, H_2PPh , and secondary phosphine, HPPh_2

The facile substitution of the chloro bridge in 1 by dithiolate ligands, with cleavage of an S–H bond and of the Mo–Cl–Mo bridge followed by release of HCl, led us to try to extend this reaction to the phosphorus-donor ligands phenylphosphine, H_2PPh , and diphenylphosphine, HPPh_2 . These reactions were conducted in the presence of excess phosphine under reflux in THF.

When H_2PPh was used, the substitution of the chloro bridge proceeded with elimination of HCl in a fashion

resembling that of the reaction with alkanedithiols (Eq. (4)).



However, the product, 4, was isolated as a mixture of two isomers (**4a**–**4b**) which were separated by column chromatography. The ^1H NMR spectrum of each isomer displays a doublet, at 4.88 ppm [$^1J(^{31}\text{P}-^1\text{H}) = 369.0\text{ Hz}$] for **4a** and at 5.44 ppm [$^1J(^{31}\text{P}-^1\text{H}) = 375.5\text{ Hz}$] for **4b**, which can be assigned to the P–H group. A single resonance for the two equivalent cyclopentadienyl rings at about 5.3 ppm and three peaks, two doublets [$J(^{31}\text{P}-^1\text{H}) = 1.3\text{ Hz}$ and 2.5 Hz for **4a**; $J(^{31}\text{P}-^1\text{H}) \approx 1\text{ Hz}$ for **4b**] and a single resonance, in the SMe region indicate that the $\text{Mo}_2(\mu\text{-SMe})_3$ core is retained (Table 1). The ^{13}C NMR pattern of **4a** confirms this structure and shows, in the SMe region, two doublets [$J(^{31}\text{P}-^{13}\text{C}) = 19.9\text{ Hz}$ and 19.6 Hz] and a singlet. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectra exhibit one signal at 22.5 for **4a** and 80.2 ppm for **4b**. In the ^1H -coupled spectra these signals appear as doublets with $^1J(^{31}\text{P}-^1\text{H}) = 369.0\text{ Hz}$ (**4a**) and 375.5 Hz (**4b**). The infrared spectra show bands at ca. 2340 cm^{-1} attributed to the $\nu(\text{PH})$ absorption. The large difference in ^{31}P NMR chemical shift between **4a** and **4b** suggests that the Mo–P bond order in **4a** is greater than that in **4b** [13]. The Mo–Mo distances in the two isomers are unlikely to differ greatly in view of the presence of one

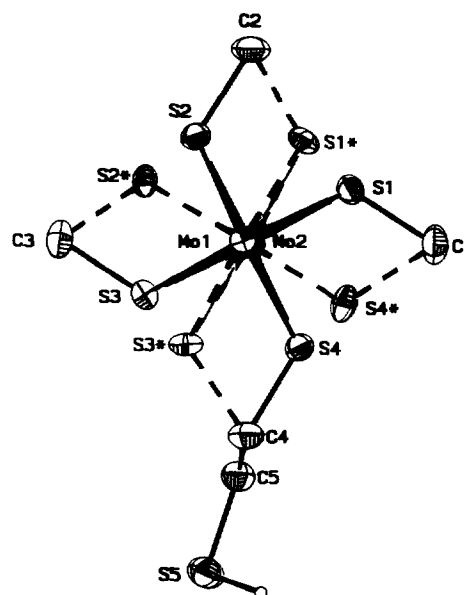
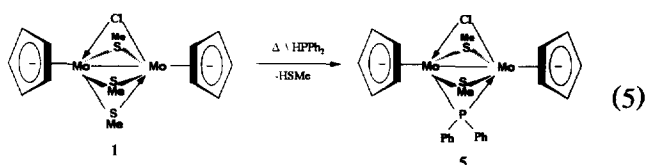


Fig. 2. The disorder of the bridging sulphur atoms in 2. The molecule is viewed along the Mo–Mo vector and hydrogen atoms and Cp rings are omitted. About one molecule in eight adopts the alternative orientation defined by S1*–S4*.

³ See footnote 2.

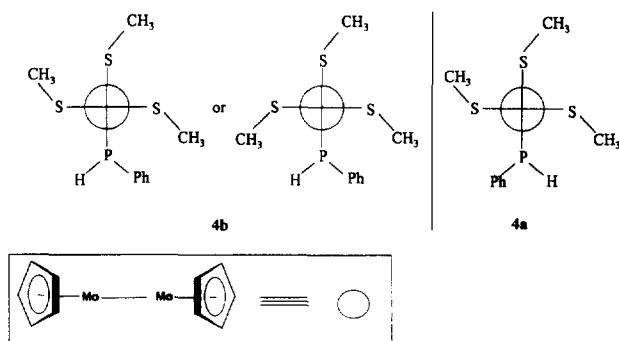
PPh₃ and three SMe bridges, so that longer Mo–P bonds in **4b** are probably accompanied by a more acute Mo–P–Mo angle. Presumably these effects arise from greater steric repulsions between the HPPh phenyl group and a methyl substituent of one of the bridging thiolates in **4b**. In the ¹H NMR spectra the chemical shifts of the hydrogen atoms of the PH groups, 4.88 ppm for **4a**, 5.44 ppm for **4b**, are in accordance with this assumption. Proposed structures for **4a** and **4b** which conform with these observations are shown in Scheme 1.

The reaction of **1** with diphenylphosphine follows a different course from that of the corresponding reaction with H₂PPh (Eq. (5)): in the presence of excess HPPh₂ the complex [Cp₂Mo₂(μ-Cl)(μ-SMe)₃] **1** is completely transformed into [Cp₂Mo₂(μ-Cl)(μ-PPh₂)(μ-SMe)₂] (**5**).

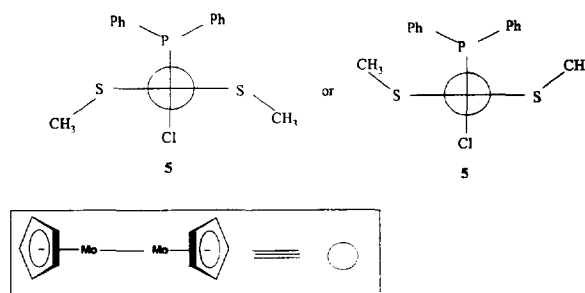


Spectroscopic data and elemental analyses indicate the substitution of one thiolato bridge by a phosphido group. The ¹H NMR spectrum of **5** exhibits one peak at 5.43 ppm, which is attributed to two equivalent cyclopentadienyl rings, and a doublet at 1.61 ppm [$J(^{31}\text{P}-^1\text{H}) = 1.0 \text{ Hz}$] due to two equivalent SMe bridges. Resonances due to two phenyl groups are observed at about 7.15 ppm. The ¹³C NMR spectrum of **5** confirms the ¹H NMR assignment (see Table 1). A ¹³C{³¹P} NMR experiment indicates that the thiolato bridges are equivalent. The ³¹P spectra with or without ¹H decoupling, show a single resonance at 120.3 ppm. Moreover, elemental analyses indicate the presence of one Cl atom in the molecule. The equivalence of the thiolato groups indicates that the SMe bridge *trans* to the chloro bridge in **1** is replaced by PPh₂ and suggests a *syn* orientation of the methyl groups as shown in Scheme 2.

The mechanism of formation of **5** remains unclear. The retention of the bridging chlorine atom is surprising



Scheme 1.



Scheme 2.

in the light of the other substitution reactions of **1**, even when allowance is made for the greater steric bulk of PPh₂ compared with PPhH or S(CH₂)_nSH. It is apparent that further theoretical and modelling studies are necessary in order to understand and rationalize fully the reactions of [Cp₂Mo₂(μ-Cl)(μ-SMe)₃] **1**.

In conclusion, we have described the synthesis from the dinuclear precursor [Cp₂Mo₂(μ-Cl)(μ-SMe)₃] of complexes possessing mixed bridge systems and their structural and spectroscopic characterization. Complexes **4** and **5** are two examples of new quadruply-bridged systems in which there are two or three types of different bridging group: SMe and HPPh for **4**, SMe, Cl and PPh₂ for **5**. Experiments with nitrogenous and oxygenated reagents are under way to extend the scope of these chloro or thiolato bridge substitution reactions.

3. Experimental section

3.1. General procedures

The reactions were performed under nitrogen using standard Schlenk techniques, and solvents were deoxygenated and dried by standard methods.

IR spectra were obtained with a Perkin–Elmer 1430, and NMR spectra were recorded on a Bruker AC300 spectrophotometer. Shifts are relative to tetramethylsilane as an internal reference for ¹H and ¹³C, and to H₃PO₄ for ³¹P. The mass spectra were measured on GC/MS Hewlett-Packard 5595C. Chemical analyses were performed by the Centre de Microanalyses du CNRS, Vernaion. Literature methods were used for preparation of [Cp₂Mo₂(μ-Cl)(μ-SMe)₃] [**5**].

3.2. General procedure for the preparation of [Cp₂Mo₂(μ-Y)(μ-SMe)₃] (Y = S(CH₂)₂SH **2**, S(CH₂)₃SH **3**, HPPh **4**) and [Cp₂Mo₂(μ-Cl)(μ-PPh₂)(μ-SMe)₂] **5**

In a typical experiment, a mixture of [Cp₂Mo₂(μ-Cl)(μ-SMe)₃] (200 mg, 0.4 mmol) and alkanedithiol HS(CH₂)_nSH [2 ml, 24 mmol (*n* = 2), 20 mmol (*n* = 3)] or phosphine (HPPh₂: 1.4 ml, 8 mmol, H₂PPh: 100 μl,

0.9 mmol) was heated in refluxing THF (30 ml) for 2–4 h [$\text{HS}(\text{CH}_2)_n\text{SH}$ or H_2PPh] or for 72 h (HPPH_2). The solution changed from green to orange-brown during this time. The solvent was then removed under vacuum and the residue, after being dissolved in the minimum of CH_2Cl_2 , was chromatographed on a silica gel column. Elution with hexane:dichloromethane (1:1) gave an orange band yielding 2–5. Complexes 2–5 were washed with pentane.

2: brown solid; yield, 80%. Anal. Found: C, 32.0; H, 4.3. $\text{C}_{15}\text{H}_{24}\text{Mo}_2\text{S}_5$. Calc.: C, 32.4; H, 4.4. MS: m/z 556 (M^+).

3: brown solid; yield, 80%.

4: brown solid; yield, 60%. Anal. Found: C, 40.6; H, 4.3; P, 6.3. $\text{C}_{19}\text{H}_{25}\text{Mo}_2\text{PS}_3$. Calc.: C, 39.9; H, 4.4; P, 5.4.

5: brown solid; yield, 80%. Anal. Found: C, 45.9; H, 4.1; Cl, 6.8; P, 5.0. $\text{C}_{24}\text{H}_{26}\text{ClMo}_2\text{PS}_2$. Calc. C, 45.8; H, 4.1; Cl, 5.6; P, 4.9.

3.3. Crystal structure of $[\text{Cp}_2\text{Mo}_2(\mu\text{-S}(\text{CH}_2)_2\text{SH})(\mu\text{-SMe})_3] \cdot 0.5 \text{CH}_2\text{Cl}_2$, 2 · CH_2Cl_2 (2:1)

Measurements were made at 20 °C on an Enraf–Nonius CAD4 diffractometer with graphite-monochromatized $\text{Mo K}\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$, using a crystal of dimensions $0.15 \times 0.08 \times 0.02 \text{ mm}^3$.

Crystal data: $\text{C}_{15}\text{H}_{24}\text{Mo}_2\text{S}_5 \cdot 0.5\text{CH}_2\text{Cl}_2$, $M = 599.03$, monoclinic, space group $P2_1/n$, $a = 8.0607(10)$, $b = 8.9654(10)$, $c = 29.956(2) \text{ \AA}$, $\beta = 92.066(6)^\circ$, $V = 2163.4(4) \text{ \AA}^3$, $Z = 4$, $D_c = 1.839 \text{ g cm}^{-3}$, $\mu(\text{Mo K}\alpha) = 1.762 \text{ mm}^{-1}$.

Cell dimensions are based on the setting angles of 25 reflections with $10.4 < \theta(\text{Mo K}\alpha) < 20.8^\circ$. The intensities of 5063 reflections with $2.4 < \theta(\text{Mo K}\alpha) < 27^\circ$, $0 \leq h \leq 10$, $-11 \leq k \leq 0$ and $-38 \leq l \leq 38$ were estimated from ω – 2θ scans and corrected for L_p effects, and for absorption using experimental ψ -scans (empirical transmission factors 0.660–0.689 [14]). Averaging gave 4724 unique reflections ($R_{\text{int}} = 0.015$); of these 435 with $I < 0$ were excluded from refinement calculations and 3720 were deemed observed [$I > 2\sigma(I)$]. The structure was solved by Patterson [15] and Fourier methods and refined to convergence ($\Delta/\sigma < 0.04$ for 243 parameters, Table 3) on F^2 with $w = [\sigma^2(F^2) + (0.0282P)^2 + 9.8P]^{-1}$ where $P = (F_{\text{obs}}^2 + 2F_{\text{calc}}^2)/3$. Final agreement indices were $R[I > 2\sigma(I)] = 0.034$ and $wR_2(\text{all data}) = 0.181$ and in the final difference map $|\Delta\rho| < 0.75 \text{ e \AA}^{-3}$. Anisotropic U^{ij} were refined for all non-hydrogen atoms. The Cp rings (C11–C15 and C21–C25) were refined as variable metric rigid groups with riding H atoms [$\text{C–H} = 0.93 \text{ \AA}$; $U(\text{H}) = 1.2U_{\text{eq}}(\text{C})$]. One orientation parameter was refined for each methyl group [$\text{C–H} = 0.96 \text{ \AA}$; $U(\text{H}) = 1.5U_{\text{eq}}(\text{C})$]. H(5) was observed in a difference map; the refined S(5)–H(5) length is $1.22(8) \text{ \AA}$. C4 and C5 H atoms rode on their parent

Table 3

Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$)

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq}
Mo(1)	1926(1)	162(1)	1497(1)	32(1)
Mo(2)	326(1)	2144(1)	1013(1)	32(1)
S(1)	3338(2)	2333(2)	1178(1)	41(1)
S(1 [*])	3165(13)	1442(13)	869(4)	46(3)
S(2)	1577(2)	–76(2)	684(1)	41(1)
S(2 [*])	244(15)	–532(12)	804(4)	46(5)
S(3)	–1079(2)	–16(2)	1338(1)	39(1)
S(3 [*])	–1009(15)	807(14)	1634(4)	46(3)
S(4)	682(2)	2413(2)	1827(1)	40(1)
S(4 [*])	1909(17)	2781(14)	1703(5)	53(3)
S(5)	–2868(2)	1432(2)	2887(1)	69(1)
C(1)	4022(7)	3748(7)	1583(2)	64(2)
C(2)	3435(8)	263(7)	367(2)	66(2)
C(3)	–1764(7)	–1445(7)	933(2)	59(2)
C(4)	–1272(6)	2226(7)	2124(2)	51(1)
C(5)	–1110(7)	1254(6)	2525(2)	52(1)
C(11)	2060(6)	–1442(5)	2081(2)	63(2)
C(12)	2318(6)	–2255(5)	1701(2)	68(2)
C(13)	3784(6)	–1785(6)	1527(2)	83(2)
C(14)	4433(5)	–682(6)	1800(2)	88(3)
C(15)	3367(7)	–470(5)	2143(2)	73(2)
C(21)	60(7)	4524(5)	756(2)	85(3)
C(22)	–1379(8)	4210(7)	960(2)	83(2)
C(23)	–2152(6)	3083(7)	731(2)	88(3)
C(24)	–1193(9)	2701(6)	385(2)	95(3)
C(25)	175(7)	3592(7)	400(2)	83(2)
Cl(1S)	141(5)	1062(4)	4644(1)	162(1)
C(1S)	–708(18)	344(21)	5106(7)	102(6)

U_{eq} is defined as one-third of the trace of the orthogonalized U^{ij} tensor.

carbon atoms [$\text{C–H} = 0.97 \text{ \AA}$; $U(\text{H}) = 1.2U_{\text{eq}}(\text{C})$]. The site occupancy factor for S1–S4 is 0.888(2). The alternative S1^{*}–S4^{*} sites have occupancies of 0.112(2). The CH_2Cl_2 solvate molecule is disordered over a symmetry centre with Cl(1S) and C(1S) having occupancies of 0.5; the H atoms attached to C(1S) were not included in the calculations. Scattering factors and anomalous dispersion corrections were those incorporated in the least-squares refinement program SHELXL-93 [16] and the GX package [17] was used for other calculations.

4. Supplementary material

Tables of atomic parameters, a complete geometry listing, and observed and calculated structure factors are available from the authors. The structure will be deposited in the Cambridge Structural Database.

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References

- [1] S. Poder-Guillou, P. Schollhammer, F.Y. Pétillon, J. Talarmin, K.W. Muir, P. Baguley, *Inorg. Chim. Acta* in press.
- [2] (a) E. Hey-Hawkins, K. Fromm, *Polyhedron* 15 (1995) 2027. (b) J.H. Shin, G. Parkin, *Polyhedron* 15 (1994) 1489. (c) E. Hey-Hawkins, K. Fromm, *Z. Anorg. Allg. Chem.* 619 (1993) 261. (d) C. Saadeh, S.B. Colbran, D.C. Craig, A.D. Rae, *Organometallics* 12 (1993) 133. (e) H. Adams, N.A. Bayley, A. Bisson, M.J. Morris, *J. Organomet. Chem.* 444 (1993) C34. (f) C.R. Koval, L.L. Lopez, B.B. Kaul, S. Renshaw, K. Green, M. Rakowski Dubois, *Organometallics* 14 (1995) 3440. (g) J. Allshouse, B.B. Kaul, M. Rakowski Dubois, *Organometallics* 13 (1994) 28 and references cited therein. (h) D.L. Dubois, W.K. Miller, M. Rakowski Dubois, *J. Am. Chem. Soc.* 103 (1981) 3429. (i) P.D. Grebenik, M.L.H. Green, A. Izquierdo, V.S.B. Mtetwa, K. Prout, *J. Chem. Soc. Dalton Trans.* (1987) 9. (j) R. Poli, *J. Coord. Chem.* 29 (1993) 121. (k) J.U. Desai, J.C. Gordon, H.B. Kraatz, V.T. Lee, B.E. Owens-Waltermire, R. Poli, A.L. Rheingold, C.B. White, *Inorg. Chem.* 33 (1994) 3752. (m) H.B. Kraatz, R. Poli, *J. Organomet. Chem.* 475 (1994) 167. (n) J.U. Desai, J.C. Gordon, H.B. Kraatz, B.E. Owens-Waltermire, R. Poli, A.L. Rheingold, *Angew. Chem. Int. Ed. Engl.* 32 (1993) 1486. (n) J.C. Green, M.L.H. Green, P. Mountford, M.J. Parkington, *J. Chem. Soc. Dalton Trans.* (1990) 3407.
- [3] N.G. Connelly, L.F. Dahl, *J. Am. Chem. Soc.* 92 (1970) 7470.
- [4] D.S. Tucker, S. Dietz, K.G. Parker, V. Carperos, J. Gabay, B. Noll, M. Rakowski Dubois, C.F. Campana, *Organometallics* 14 (1995) 4325.
- [5] M.B. Gomez de Lima, J.E. Guerschais, R. Mercier, F.Y. Pétillon, *Organometallics* 5 (1986) 1952.
- [6] F. Barrière, Y. Le Mest, F.Y. Pétillon, S. Poder-Guillou, P. Schollhammer, J. Talarmin, *J. Chem. Soc. Dalton Trans.* (1996) 3967.
- [7] (a) E. Berkovich, J. Blum, H. Schumann, *J. Organomet. Chem.* 469 (1994) 111. (b) H. Werner, B. Klingert, A.L. Rheingold, *Organometallics* 7 (1988) 911.
- [8] R. Poli, *Chem. Rev.* 91 (1991) 509.
- [9] (a) M. McKenna, L.L. Wright, D.J. Miller, L. Tanner, R.C. Haltiwanger, M.R. Dubois, *J. Am. Chem. Soc.*, 105 (1983) 5329, (b) W.K. Miller, R.C. Haltiwanger, M.C. VanDerveer, M.R. Dubois, *Inorg. Chem.* 22 (1983) 2973. L.L. Lopez, J. Gabay, R.C. Haltiwanger, K. Green, J. Allshouse, C. Casewit, M.R. Dubois, *Organometallics* 12 (1993) 4764 and references cited therein.
- [10] H. Brunner, R. Grassl, J. Wachter, B. Nuber, M.L. Ziegler, *J. Organomet. Chem.* 427 (1992) 57.
- [11] M.R. Dubois, R.C. Haltiwanger, D.J. Miller, G. Glatzmaier, *J. Am. Chem. Soc.* 101 (1979) 5245.
- [12] *International Tables for Crystallography*, vol. C, International Union of Crystallography, Kluwer, Dordrecht, 1992, pp. 714–778.
- [13] (a) P.E. Garrou, *Chem. Rev.* 81 (1981) 229. (b) J.L. Petersen, R.P. Stewart Jr., *Inorg. Chem.* 19 (1980) 186.
- [14] A.C.T. North, D.C. Philips, F.S. Mathews, *Acta Crystallogr. Sect. A*: 24 (1968) 351.
- [15] G.M. Sheldrick, *SHELXS*. A Program for the Solution of Crystal Structures, University of Göttingen, Germany, 1985; *Acta Crystallogr. Sect. A*: 45 (1990) 467.
- [16] G.M. Sheldrick, *SHELXL93*. A Program for the Refinement of Crystal Structures, University of Göttingen, Germany, 1993.
- [17] P.R. Mallinson, K.W. Muir, *J. Appl. Crystallogr.* 18 (1985) 51. L.J. Farrugia, *GX PC Version*, University of Glasgow, 1996.