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Unexpected formation of the novel mixed μ-oxo, μ-sulfido, bis(μ-thiolato) compound $[Mo(IV)_2Cp_2(\mu\text{-}O)(\mu\text{-}S)(\mu\text{-}SMe)_2]$

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Abstract

A novel example of C–S bond cleavage in a dimolybdenum derivative leads to the formation of the quadruply bridged compound $[Mo(IV)_2Cp_2(\mu\text{-}O)(\mu\text{-}S)(\mu\text{-}SMe)_2]$. This μ-oxo species is formed by reaction of the chloro-bridged complex $[Mo(III)_2Cp_2(\mu\text{-}Cl)(\mu\text{-}SMe)_3]$ with PhCCLi and subsequent hydration at the dimolybdenum site. The Mo–Mo bond length of 2.4900(3) Å in $[Mo_2Cp_2(\mu\text{-}O)(\mu\text{-}S)(\mu\text{-}SMe)_2]$ is unusually short. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Mo(IV) complexes; Dinuclear complexes; Oxo and sulfido bridges; C–S cleavage; Mo–Mo bonding

1. Introduction

Binuclear organometallic complexes may either contain metal–metal bonds or act as Lewis acids and they continue to attract interest for both these reasons [1–4]. Thus, we have elaborated various dimolybdenum(III) complexes in which access to the central bimetallic $\{Mo_2Cp_2(\mu\text{-}SMe)_3\}^+$ core depends on whether CO, Cl or MeCN is chosen as the additional protecting group (Scheme 1) [5]. Loss of the carbonyl ligands in $[Mo_2Cp_2(CO)_2(\mu\text{-}SMe)_3]Cl$ (**1**) on drastic heating gives rise to the reactive complex $[Mo_2Cp_2(\mu\text{-}Cl)(\mu\text{-}SMe)_3]$ (**2**). The bridging chloro ligand in **2** can be displaced by various molecules under mild conditions [5]. However, we now report that reaction of **2** with PhCCLi does not lead to substitution of chloride by acetylide; instead, the μ-oxo, μ-sulfido compound $[Mo_2Cp_2(\mu\text{-}O)(\mu\text{-}S)(\mu\text{-}SMe)_2]$ (**4**) is unexpectedly obtained. The affinity of the molybdenum atom for oxygen is well known, and when it has access to oxygen or water it readily forms oxo-compounds. However, the mechanisms of these reactions are poorly understood. Moreover, the products they give rise to, are often intractable; even when the products can be isolated and characterized, they are usually obtained only in moderate yields that are hard to reproduce. Nevertheless, such compounds may possess original structures and promising reactivity.

The dimolybdenum(IV) complex **4** belongs to a much studied group of $CpMo(\mu\text{-}X)_4MoCp$ complexes, $Cp = \eta^5\text{-}C_5H_5$ or its derivatives, [6–19] in which two CpMo units are joined by four bridging ligands whose donor atoms belong to Group 16. In the vast majority of these complexes the bridging ligands are either thiolate (or disulfide), SR^-, or sulfide, S^{2-}, though in a few known cases these sulfur-donor ligands have been replaced by their Se [8,9,11] or Te [12] analogues. However, **4** contains, to the best of our knowledge, the first example of an oxo-bridge in this group of complexes. The reaction giving rise to **4** also involves an interesting example of C–S bond cleavage in a dimolybdenum complex.

2. Results and discussion

Complex **4** was the only tractable product obtained within 24 h on thermolysis of a mixture of **2** and

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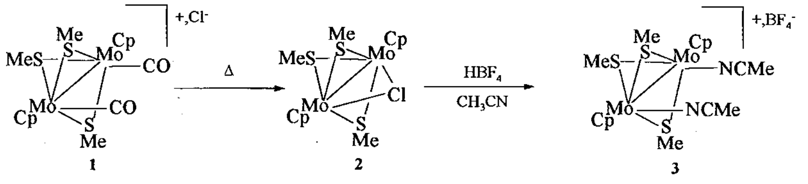


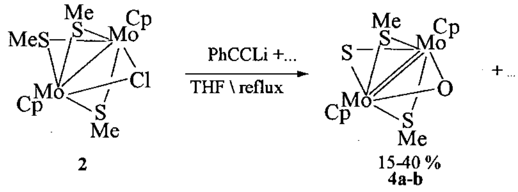
Scheme 1.

PhCCLi under reflux in THF (Scheme 2). When the reflux was performed under an inert atmosphere, **2** did not appear to react, suggesting that its transformation into **4** requires oxygen. Chromatography of the crude product on a silica gel column with dichloromethane–acetone mixtures as eluents afforded a green fraction containing **4** in yields of up to 40%. The yield of **4** did not alter when the **2**:PhCCLi mole ratio was decreased or increased. Elemental analyses of **4** were consistent with the formula $C_{12}H_{16}Mo_2OS_3$. Its ^{1}H-NMR spectrum in $CDCl_3$ showed that a methyl group was lost during the reaction and indicated that **4** was formed as a mixture of two isomers (**4a**/**4b** ratio: 7/3) that were not separable by column chromatography. Each isomer displayed one resonance at low field (at about 6.5 ppm) for the two cyclopentadienyl groups, which suggests a symmetrical geometry and an increase of the oxidation state of the molybdenum atoms relative to that found for **2**. A single resonance at 1.21 ppm and two peaks at about 1.1 ppm were assigned to the SMe bridges; they suggest that the isomerism arises from differing orientations of the methyl groups: syn in **4a** and anti in **4b**.

An X-ray diffraction study of green crystals of **4** obtained from diethyl ether confirmed these conclusions (Fig. 1). Thus, **4** contains an $Mo_2(\mu\text{-}O)(\mu\text{-}S)(\mu\text{-}SMe)_2$ core in which each of the four bridging atoms is equidistant from Mo1 and Mo2. The near-planar Mo_2S3O1 and Mo_2S1S2 units are normal [dihedral angle 89.9(3)°] to one another. The Cp–Mo–Mo–Cp linkage is close to linear. The thiolato sulfur atoms, S1 and S2, are trans and their associated methyl groups are syn with respect to the Mo–Mo vector. The geometry around each metal atom can be described as a $CpMoS_3O$ four-legged piano stool, distorted by the intrusion of a μ-oxo group.

The Mo–Mo distance of 2.4900(3) Å in **4** is short compared with the values in other quadruply bridged $CpMo(\mu\text{-}X)_4MoCp$ complexes (Table 1). We attribute this to the small size of the oxo ligand rather than to the Mo–Mo bond order of two that is required by electron counting rules. For complexes with four bridging sulfur atoms the slight variation observed in the Mo–Mo distances is not related to the order of the Mo–Mo bond (Table 1); thus, the Type 1 $[Cp_2Mo_2(SR)_4]$ species containing Mo(III)–Mo(III) single bonds and the Type 2 $[Cp_2Mo_2(SR)_2(S)_2]$ complexes with Mo(IV)–Mo(IV) double bonds show virtually the same small range of Mo–Mo distances. Slightly longer Mo–Mo distances are found in cationic complexes, whether they have Mo(IV)–Mo(IV) double bonds (Type 3) or single bonds like the paramagnetic Type 4 species. Slightly longer bonds are also found where Se or Te replaces S, but only a few complexes of this type have been characterised. This conclusion is consistent with earlier discussions of related halo-bridged complexes [22–25], where it was concluded that the "Mo–Mo distance is substantially insensitive to the occupation of the δ orbital and depends mostly on the size of the bridging atoms" [22].

In **4** the μ-Mo–O(oxo) [both 1.963(2) Å], μ-Mo–SMe [2.465(1)–2.481(1) Å] and μ-Mo–S(sulfido) [2.364(1)–2.367(1) Å] distances all lie toward the upper ends of



Scheme 2.

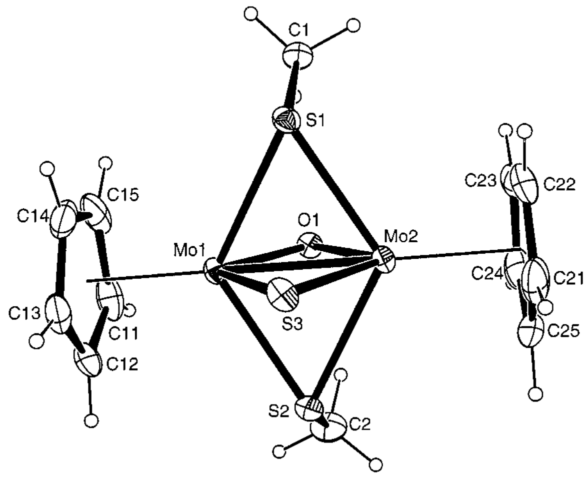


Fig. 1. Molecular structure of $[Mo_2Cp_2(\mu\text{-}O)(\mu\text{-}S)(\mu\text{-}SMe)_2]$ **4a**. Selected bond lengths (Å) and angles (°): Mo(1)–Mo(2) 2.4900(3), Mo(1)–O(1) 1.963(2), Mo(2)–O(1) 1.963(2), Mo(1)–S(1) 2.4810(7), Mo(1)–S(2) 2.4650(8), Mo(1)–S(3) 2.3669(8), Mo(2)–S(1) 2.4742(8), Mo(2)–S(2) 2.4713(8), Mo(2)–S(3) 2.3637(8), Mo(2)–S(1)–Mo(1) 60.33(2), Mo(1)–S(2)–Mo(2) 60.59(2), Mo(2)–S(3)–Mo(1) 63.52(2), Mo(2)–O(1)–Mo(1) 78.72(7).

Table 1
A summary of Mo–Mo distances in CpMo(μ-X)$_4$ MoCp complexes [a]

Type [b]	Compound	Configuration	Mean (Å)	Range (Å)	Refs.
1	$[Cp_2Mo_2(SR)_4]$	d^3–d^3 $\sigma^2\delta^{*2}\delta^2$	2.593	2.576–2.605	[15,16]
2	$[Cp_2Mo_2(SR)_2(S)_2]$	d^2–d^2 $\sigma^2\delta^{*2}$	2.588	2.573–2.600	[6,7,14,17]
3	$[Cp_2Mo_2(SR)_3(S)]^+$	d^2–d^2 $\sigma^2\delta^{*2}$	2.611	2.599–2.628	[18]
4	$[Cp_2Mo_2(SR)_4]^+$	d^3–d^2 $\sigma^2\delta^{*2}\delta^1$	2.618	2.599–2.635	[15,19]
	Overall **1**–**4**		2.604	2.573–2.635	
	$[Cp_2Mo_2(Se_2)(SPh)_2]$	d^3–d^3 $\sigma^2\delta^{*2}\delta^2$	2.661		[11]
	$[Cp_2Mo_2(SeR)_2(Se)_2]$	d^2–d^2 $\sigma^2\delta^{*2}$	2.647	2.640–2.654	[8,9]
	$[Cp_2Mo_2(S)(Te)(SPh)_2]$	d^2–d^2 $\sigma^2\delta^{*2}$	2.626		[12]

[a] Cp is used here for any cyclopentadienyl ring, irrespective of the degree of substitution.

[b] See text.

their respective ranges. For example, the μ-Mo–O(oxo) distances in $[Cp_2Mo_2Br_2(\mu\text{-}O)(\mu\text{-}Br)(\mu\text{-}SMe)]$ are 1.907(6)–1.914(7) Å [20]. For the complexes included in Table 1 one finds that for μ-Mo–X distances the respective ranges are: X = S 2.29–2.36 Å, X = Se 2.46–2.51 Å, X = Te 2.70 Å; for μ-Mo-XR distances the ranges are: X = S 2.42–2.49 Å and X = Se 2.57–2.61 Å. Typically, the Mo–X distances are 0.10–0.12 Å shorter than the corresponding Mo–XR distances. The Mo–X distances roughly follow the trends in covalent radii of X: O, 0.68; S, 1.02; Se, 1.22; Te, 1.47 Å. Note that though the smaller size of O leads to a short Mo–Mo bond in **4** the greater size of Se and Te has only a very limited effect in increasing the Mo–Mo distances (Table 1).

The formation of **4** is presumably a result of the hydrolysis of the μ-chloro site in **2**. A subsequent deprotonation-with-oxidation step [26] and a regiospecific demethylation of a single thiolate bridge [13,21] are required to form the μ-oxo and the μ-sulfido groups. An aqueous solution of $[Mo_2Cp_2(\mu\text{-}SMe)_3(\mu\text{-}Cl)](BF_4)$ (**2**$^+$) was quantitatively converted into the oxo derivative $[Mo_2Cp_2(\mu\text{-}SMe)_3(\mu\text{-}O)](BF_4)$ (**5**) [27], which could be a good candidate as intermediate in the formation of **4**. On reacting **5** with LiCCPh in refluxing tetrahydrofuran, only moderate yields of **4** were obtained. Therefore, this experiment does not ascertain firmly that **5** is the expected intermediate.

3. Experimental

3.1. General

The usual procedures for handling reactive organometallic reagents were followed. The solvents were purified as described previously [28]. Literature methods were used for the preparation of $[Mo_2Cp_2(\mu\text{-}Cl)(\mu\text{-}SMe)_3]$ [29] and LiCCPh [30]. ^{1}H-NMR spectra were recorded on a Brucker AC 300 spectrophotometer; shifts are relative to tetramethylsilane as an internal reference. Chemical analyses were performed by the ‘Centre de Microanalyses du CNRS’, Vernaison.

3.2. Synthesis of 4

To a THF solution (30 ml) of $[Mo_2Cp_2(\mu\text{-}Cl)(\mu\text{-}SMe)_3]$ (**2**) (0.2 g, 0.4 mmol) were added two equivalents of PhCCLi in THF (10 ml). The mixture was heated with stirring at 65°C for 24 h. The resulting brownish green solution was then evaporated and chromatographied on a silica gel column. Elution with CH_2Cl_2–acetone (1:1) gave a green band, which yielded complex **4**. After washing with cold pentane (2 × 5 ml) compound **4** was obtained as a green powder (37–74 mg, 15–40% yields). Anal. Found: C, 31.2; H, 3.5. Calc. for $C_{12}H_{16}Mo_2OS_3$: C, 31.0; H, 3.4%. ^{1}H-NMR (300.0 MHz, CDCl$_3$, room temperature, δ): **4a** (70%); 6.48 (s, 10H, C_5H_5), 1.21 (s, 6H, SCH_3); **4b** (30%); 6.50 (s, 10H, C_5H_5), 1.12 (s, 3H, SCH_3), 1.05 (s, 3H, SCH_3).

3.3. Structure analysis of 4a

4a, $C_{12}H_{16}Mo_2OS_3$, is monoclinic, space group $C2/c$, $a = 16.525(1)$, $b = 12.690(2)$, $c = 15.389(1)$ Å, $\beta = 108.03(1)°$, $V = 3068.6(4)$ Å^3, $Z = 8$, $T = 293(2)$ K, $R(F) = 0.036$, $wR(F^2) = 0.078$ for all 4437 independent reflections with $5.5 < \theta(\text{Mo–K}_\alpha) < 30°$, $|\Delta\rho| < 0.91$ e$^-$ Å^{-3} [31].

4. Supplementary material

Crystallographic information files (CIF files) for **4a** have been deposited with the Cambridge Structural Database. The deposition number is CCDC 154010.

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