

Reactions of dinuclear and polynuclear complexes

XV [☆]. Reinvestigation of the reaction between $[\text{CpMo}(\text{CO})_3\text{H}]$, allyl chloride and dimethyl disulfide: Crystal structure of $[(\text{C}_5\text{H}_5)\text{Mo}(\text{CO})(\mu\text{-SMe})_3\text{Mo}(\text{CO})_2(\mu\text{-SMe})\text{Mo}(\text{CO})_2(\text{C}_5\text{H}_5)]$

Sylvie Poder-Guillou ^a, Philippe Schollhammer ^a, François Y. Pétilion ^{a,*}, Jean Talarmin ^a, Susan E. Girdwood ^b, Kenneth W. Muir ^{b,*}

^a *Unité de Recherche associée au CNRS 322, Chimie, Electrochimie Moléculaires et Chimie Analytique, Faculté des Sciences, Université de Bretagne Occidentale, BP 809, 29285 Brest-Cédex, France*

^b *Department of Chemistry, University of Glasgow, Glasgow G 12 8QQ, UK*

Received 20 April 1995

Abstract

The thermal reaction of $[\text{C}_5\text{H}_5\text{Mo}(\text{CO})_3\text{H}]$ with dimethyl disulfide and allyl chloride has been reinvestigated. In addition to the expected cationic species $[(\text{C}_5\text{H}_5)_2\text{Mo}_2(\mu\text{-SMe})_3(\text{CO})_2]\text{Cl}$ (**1**), the new trinuclear complex $[(\text{C}_5\text{H}_5)\text{Mo}(\text{CO})(\mu\text{-SMe})_3\text{Mo}(\text{CO})_2(\mu\text{-SMe})\text{Mo}(\text{CO})_2(\text{C}_5\text{H}_5)]$ (**2**) was obtained. An X-ray diffraction study showed that **2** contains a $(\text{C}_5\text{H}_5)(\text{CO})\text{Mo}(\mu\text{-SMe})_3\text{Mo}(\text{CO})_2$ core in which the triply bridged Mo–Mo bond is of normal length (2.800(1) Å). This core is linked to the $\text{C}_5\text{H}_5\text{Mo}(\text{CO})_2\text{SMe}$ unit via its sulfur atom and through an unusually weak Mo–Mo bond of 3.115(2) Å, the Mo–Mo–Mo angle being 144.5(1)°.

Keywords: Molybdenum; Allyl halide; Bridging thiolate; Trinuclear complex; Crystal structure; Cyclopentadienyl

1. Introduction

Recently we reported the unexpected formation of the dinuclear molybdenum(III) carbonyl sulfido complex $[\text{Cp}_2^*\text{Mo}_2(\text{CO})_2(\mu\text{-SMe})_2(\mu\text{-S})]$ ($\text{Cp}^* = \text{C}_5\text{Me}_5$) in the reaction of $[\text{Cp}^*\text{Mo}(\text{CO})_2]_2$ with MeSSMe , which proceeded by the dealkylation of the SMe bridge of a dinuclear intermediate $[(\text{Cp}_2^*\text{Mo}_2(\text{CO})_2(\mu\text{-SMe})_3)^+]$. The corresponding reaction does not occur with $[\text{CpMo}(\text{CO})_2]_2$ [1]. This surprising result led us to reinvestigate the reactions of $[\text{Cp}'\text{Mo}(\text{CO})_3]_2$ and $[\text{Cp}'\text{Mo}(\text{CO})_3\text{H}]$ ($\text{Cp}' = \text{C}_5\text{H}_5$ or C_5Me_5 [2]) with dialkyl disulfide REER (ER = SMe, SPh or St–Bu) in the presence of allyl halide $\text{C}_3\text{H}_5\text{X}$ (X = Cl or Br). In the case of the cyclopentadienyl complex $[\text{CpMo}(\text{CO})_3\text{H}]$ this reaction is known to give the tris (thiolato) bridged dimolybdenum(III) complex $[\text{Cp}_2\text{Mo}_2(\text{CO})_2(\mu\text{-SMe})_3]\text{X}$ (X = Cl (**1**) or Br) with a high yield [3]. We

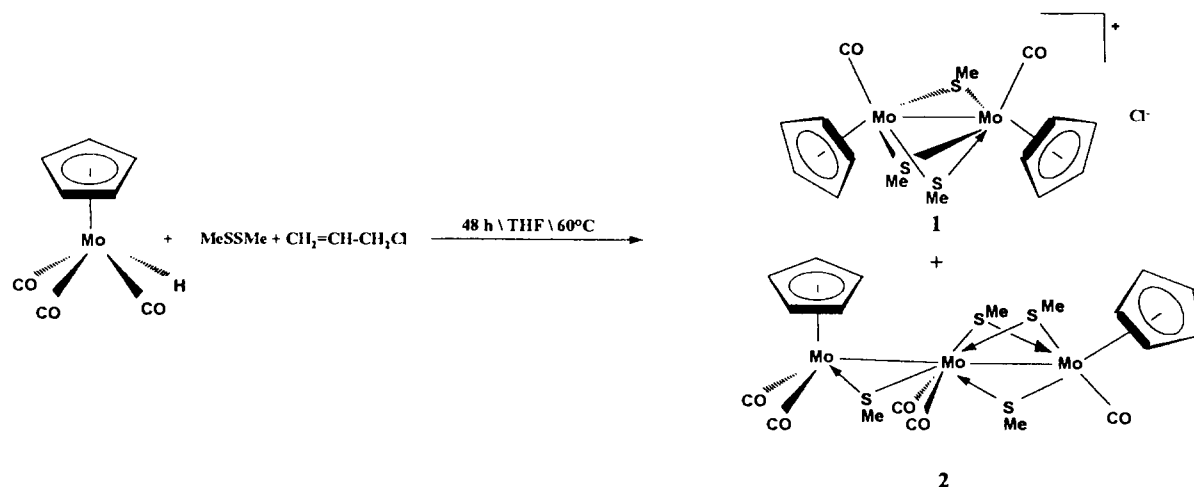
now show that the products depend markedly upon the experimental conditions and describe the formation and the structural characterization of the new trinuclear complex $[(\text{C}_5\text{H}_5)\text{Mo}(\text{CO})(\mu\text{-SMe})_3\text{Mo}(\text{CO})_2(\mu\text{-SMe})\text{Mo}(\text{CO})_2(\text{C}_5\text{H}_5)]$ (**2**).

2. Results

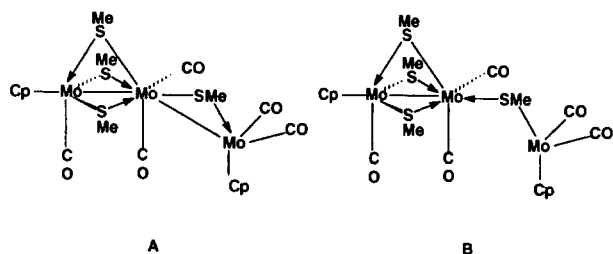
The reaction of $[\text{CpMo}(\text{CO})_3\text{H}]$ with dimethyl disulfide in the presence of allyl chloride, in tetrahydrofuran (THF) under vacuum at 60°C for 48 h, gave rise, as expected, to a red–orange suspension of $[\text{Cp}_2\text{Mo}_2(\text{CO})_2(\mu\text{-SMe})_3]\text{Cl}$ (**1**) (45% yield) [3]. Chromatography of the filtrate afforded the new coproduct $[(\text{C}_5\text{H}_5)\text{Mo}(\text{CO})(\mu\text{-SMe})_3\text{Mo}(\text{CO})_2(\mu\text{-SMe})\text{Mo}(\text{CO})_2(\text{C}_5\text{H}_5)]$ (**2**) (15–25% yield). This product is not observed when the reaction time is shorter (24 h) (Scheme 1). Complex **2** was characterized by spectroscopic analyses (see Section 3). Its ¹H NMR spectrum exhibits resonances for two different cyclopentadienyl rings and for four inequivalent bridging thiolato ligands. The ¹³C spectrum

[☆] For Part XIV, see [1].

* Corresponding authors.



Scheme 1.



displays five carbonyl peaks, and elemental analyses accord with the presence of three molybdenum atoms (see Section 3). These conclusions are fully compatible with the results of a single-crystal X-ray diffraction study of **2**.

Molecules of **2** contain three chemically inequivalent molybdenum atoms arranged so that the central Mo(1)–

Mo(2)–Mo(3) angle is $144.5(1)^\circ$ (Fig. 1). Selected bond lengths and angles are shown in Table 1. The Mo(2)–Mo(3) bond, which is of normal length ($2.800(1) \text{ \AA}$), is bridged by three SMe groups. The geometry of the Mo(2)–(μ -SMe)₃–Mo(3) core is such that the plane through Mo(2) and Mo(3) normal to the nearly coplanar bridging unit defined by Mo(2), Mo(3), S(3) and S(4) ($Mo(2)–S(3)–Mo(3)–S(4) = -10.9(1)^\circ$) passes close to S(2), and to the carbonyl carbon atoms C(21) and C(31), the C(21) and C(31) carbonyl groups being nearly eclipsed when viewed along the Mo(2)–Mo(3) vector ($C(21)–Mo(2)–Mo(3)–C(31) = -8.0(4)^\circ$). A Cp ring π bonded to Mo(3) completes its coordination, which may be described as a slightly distorted four-legged piano stool with S(3) and S(4) mutually *trans*, supplemented by the bond to Mo(2). The rather irregular eightfold coordination of Mo(2) involves all four bridging thiolate groups, two CO ligands and links to

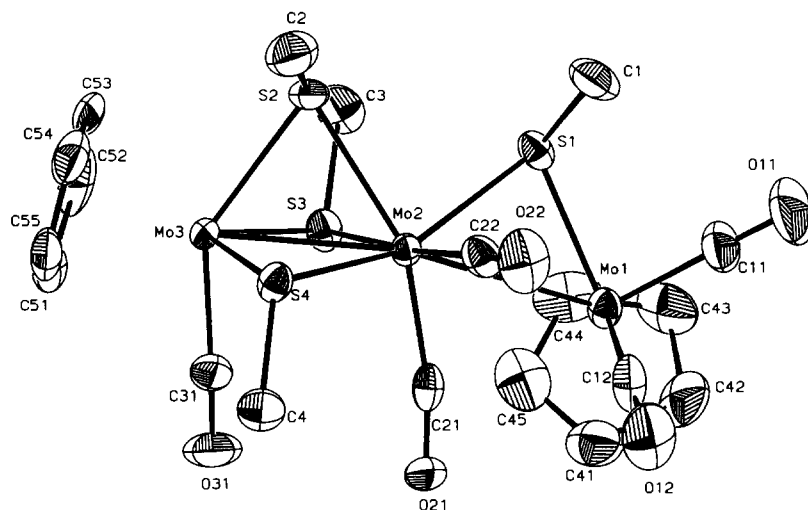


Fig. 1. The molecular structure of $[(C_5H_5)Mo(CO)(\mu-SMe)_3Mo(CO)_2(\mu-SMe)Mo(CO)_2(C_5H_5)]$ (**2**). 50% probability ellipsoids are shown and hydrogen atoms are omitted.

Mo(1) and Mo(3); Mo(1) is roughly *trans* to S(4) and carbonyl C(22) to S(3) (Table 1). Mo(2), S(1) and carbonyls C(11) and C(12) define the base of a second four-legged piano stool centred on Mo(1).

The Mo(1)–Mo(2) distance of 3.115(1) Å is sufficiently long to call in question the existence of a direct bond between these atoms. Electron-counting rules suggest both **A**, with two Mo–Mo bonds and 18-electron configurations at all three metal atoms, and **B**, with one Mo–Mo bond and a 16-electron configuration at Mo(1), as plausible structures. A survey of the Cambridge Structural Database [4] reveals 58 entries for the

Mo₂(μ-SR) fragment (R = alkyl), in which the mean Mo–Mo and Mo–S distances are 2.77 and 2.47 Å, the longest Mo–Mo bond length being 2.97 Å. Longer S-bridged Mo–Mo distances appear to have been reported only in association with a three-centre two-electron bridging hydride, e.g. 3.237(1) Å in [Cp₂Mo₂(μ-H)(μ-SMe)(CO)₄] [5]. However, the Mo(1)–S(1)–Mo(2) angle (80.4(1)°) is only 10–12° greater than the corresponding angles at S(2)–S(4), whereas in [W(CO)₅(μ-SMe)W(CO)₃Cp], in which there is no direct W–W bond, there is a very much larger W–S–W angle of 119.7(1)° [6]. The closest parallel that we have

Table 1
Selected bond lengths (Å) and angles (°)

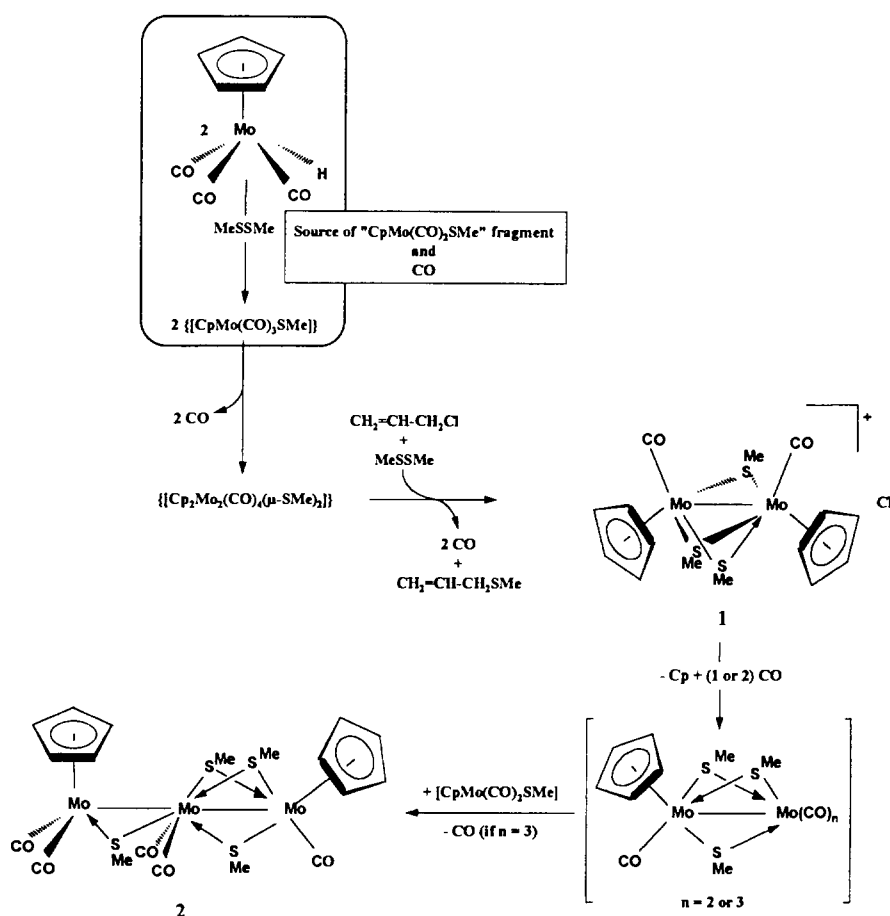
Bond lengths			
Mo(1)–Mo(2)	3.115(2)	Mo(1)–S(1)	2.402(3)
Mo(1)–C(11)	1.936(12)	Mo(1)–C(12)	1.942(11)
Mo(1)–C(41)	2.304(13)	Mo(1)–C(42)	2.269(13)
Mo(1)–C(43)	2.279(13)	Mo(1)–C(44)	2.354(12)
Mo(1)–C(45)	2.358(11)	Mo(2)–Mo(3)	2.800(1)
Mo(2)–S(1)	2.426(3)	Mo(2)–S(2)	2.521(3)
Mo(2)–S(3)	2.526(3)	Mo(2)–S(4)	2.486(3)
Mo(2)–C(21)	1.956(9)	Mo(2)–C(22)	2.019(10)
Mo(3)–S(2)	2.486(3)	Mo(3)–S(3)	2.440(3)
Mo(3)–S(4)	2.417(3)	Mo(3)–C(31)	2.012(10)
Mo(3)–C(51)	2.269(10)	Mo(3)–C(52)	2.280(11)
Mo(3)–C(53)	2.314(11)	Mo(3)–C(54)	2.368(13)
Mo(3)–C(55)	2.326(12)	S(1)–C(1)	1.813(12)
S(2)–C(2)	1.790(12)	S(3)–C(3)	1.826(10)
S(4)–C(4)	1.829(10)		
Bond angles			
Mo(2)–Mo(1)–S(1)	50.2(1)	Mo(2)–Mo(1)–C(11)	117.4(4)
Mo(2)–Mo(1)–C(12)	87.3(3)	S(1)–Mo(1)–C(11)	82.5(4)
S(1)–Mo(1)–C(12)	115.7(4)	C(11)–Mo(1)–C(12)	78.8(5)
Mo(1)–Mo(2)–Mo(3)	144.5(1)	Mo(1)–Mo(2)–S(1)	49.5(1)
Mo(1)–Mo(2)–S(2)	135.7(1)	Mo(1)–Mo(2)–S(3)	92.6(1)
Mo(1)–Mo(2)–S(4)	148.9(1)	Mo(1)–Mo(2)–C(21)	64.1(3)
Mo(1)–Mo(2)–C(22)	84.0(3)	Mo(3)–Mo(2)–S(1)	128.1(1)
Mo(3)–Mo(2)–S(2)	55.4(1)	Mo(3)–Mo(2)–S(3)	54.3(1)
Mo(3)–Mo(2)–S(4)	54.0(1)	Mo(3)–Mo(2)–C(21)	101.9(3)
Mo(3)–Mo(2)–C(22)	130.0(3)	S(1)–Mo(2)–S(2)	86.7(1)
S(1)–Mo(2)–S(3)	85.6(1)	S(1)–Mo(2)–S(4)	152.4(1)
S(1)–Mo(2)–C(21)	113.4(3)	S(1)–Mo(2)–C(22)	88.8(3)
S(2)–Mo(2)–S(3)	76.0(1)	S(2)–Mo(2)–S(4)	73.7(1)
S(2)–Mo(2)–C(21)	157.1(3)	S(2)–Mo(2)–C(22)	103.4(3)
S(3)–Mo(2)–S(4)	107.4(1)	S(3)–Mo(2)–C(21)	93.9(3)
S(3)–Mo(2)–C(22)	174.4(3)	S(4)–Mo(2)–C(21)	90.4(3)
S(4)–Mo(2)–C(22)	77.5(3)	C(21)–Mo(2)–C(22)	88.6(4)
Mo(2)–Mo(3)–S(2)	56.6(1)	Mo(2)–Mo(3)–S(3)	57.1(1)
Mo(2)–Mo(3)–S(4)	56.3(1)	Mo(2)–Mo(3)–C(31)	85.8(3)
S(2)–Mo(3)–S(3)	78.1(1)	S(2)–Mo(3)–S(4)	75.5(1)
S(2)–Mo(3)–C(31)	142.2(3)	S(3)–Mo(3)–S(4)	112.5(1)
S(3)–Mo(3)–C(31)	77.9(3)	S(4)–Mo(3)–C(31)	87.4(3)
Mo(1)–S(1)–Mo(2)	80.4(1)	Mo(1)–S(1)–C(1)	115.4(4)
Mo(2)–S(1)–C(1)	111.1(4)	Mo(2)–S(2)–Mo(3)	68.0(1)
Mo(2)–S(2)–C(2)	114.9(4)	Mo(3)–S(2)–C(2)	114.9(4)
Mo(2)–S(3)–Mo(3)	68.6(1)	Mo(2)–S(3)–C(3)	113.5(4)
Mo(3)–S(3)–C(3)	113.1(4)	Mo(2)–S(4)–Mo(3)	69.6(1)
Mo(2)–S(4)–C(4)	113.4(4)	Mo(3)–S(4)–C(4)	114.2(4)
Mo(1)–C(11)–O(12)	177.2(11)	Mo(1)–C(12)–O(12)	172.5(10)
Mo(2)–C(21)–O(21)	168.8(8)	Mo(2)–C(22)–O(22)	179.1(9)
Mo(3)–C(31)–O(31)	176.3(9)		

found to the Mo(1)–Mo(2) bond in **2** is provided by $[\text{W}(\text{CO})_5(\mu\text{-SMe})\text{Mo}(\text{CO})_2\text{Cp}]$, in which the stereochemistry, in particular the acute Mo–S–W angle of $79.4(1)^\circ$, suggests that the W–Mo distance of $3.131(1)$ Å represents a direct metal–metal bond [6]. In **2** a CO weakly semibridges the Mo(1)–Mo(2) bond (Mo(1) . . . C(21), 2.87 Å; Mo(1)–Mo(2)–C(21), $64.1(3)^\circ$; Mo(2)–C(21)–O(21), $169(1)^\circ$), a feature also present in $[\text{W}(\text{CO})_5(\mu\text{-SMe})\text{Mo}(\text{CO})_2\text{Cp}]$. The structural evidence thus favours **A** rather than **B** as a description of **2**.

All four Mo₂S bridges in **2** are asymmetrical and the Mo–S distances show a significant variation, from $2.402(3)$ to $2.521(3)$ Å. This probably reflects a number of factors, one being the metal coordination number, since Mo(2)–S(1) is greater than Mo(1)–S(1) and, across the Mo(2)–Mo(3) bond, Mo(2)–S is greater than Mo(3)–S. Other bond lengths are in accord with standard values [7].

Although the mechanism of formation of the trinuclear complex **2** remains unclear, that **1** is an intermediate in the process is strongly suggested by the fact that when the reaction was conducted at 60°C for 1 day, **1** was obtained with a high yield (80%) whereas, if the

heating was prolonged for a further 24 h, **2** was formed and the yields of **1** fell dramatically (45%). We note (Scheme 2) that the formation of **1** involves the liberation of CO and generation of a mononuclear $\{\text{CpMo}(\text{CO})_2\text{SMe}\}$ fragment which dimerizes to give **1** after further reaction with MeSSMe and allyl chloride. Subsequent thermolysis of the cationic product $[\text{Cp}_2\text{Mo}_2(\text{CO})_2(\mu\text{-SMe})_3]\text{Cl}$ (**1**), with replacement of a cyclopentadienyl ligand by one or two CO groups liberated in the earlier stages of the reaction, gives the key intermediate $\{\text{CpMo}(\text{CO})(\mu\text{-SMe})_3\text{Mo}(\text{CO})_n\}$ ($n = 2$ or 3); reaction of this intermediate with a $\{\text{CpMo}(\text{CO})_2\text{SMe}\}$ fragment generated in the first stage gives the product **2** after further loss of CO. A similar mechanism has been proposed by Schulze and Ziegler [8] to account for the formation of $[(\text{C}_7\text{H}_7)\text{W}(\mu\text{-ER})_3\text{W}(\text{CO})(\mu\text{-ER})_2\text{W}(\text{CO})_4]$ from $[(\text{C}_7\text{H}_7)\text{W}(\text{CO})_2\text{ER}]$. We exclude the dinuclear complex $[\text{CpMo}(\text{CO})_2(\mu\text{-SMe})_2]$ as an intermediate in the formation of **2**, since it has been shown that its thermolysis in THF in the presence of $[\text{CpMo}(\text{CO})(\mu\text{-SMe})_3\text{Mo}(\text{CO})_3]$ [9], or under CO in the presence of $[\text{Cp}_2\text{Mo}_2(\text{CO})_2(\mu\text{-SMe})_3]\text{Cl}$ does not yield **2**. We also recently found that the pentamethylcyclopentadienyl analogues of the complexes $[\text{CpMo}(\text{CO})(\mu\text{-$



Scheme 2.

$\text{SMe}_3\text{Mo}(\text{CO})_3$] and **2** can be isolated from the reaction of $[\text{Cp}^*\text{Mo}(\text{CO})_2]_2$ with dimethyl disulfide [1]. In this case, their formation could arise from the presence of the intermediate $\{[\text{Cp}_2^*\text{Mo}_2(\text{CO})_2(\mu\text{-SMe})_3]^+\}$, which has also been invoked to account for the formation of the sulfido product $[\text{Cp}_2^*\text{Mo}_2(\text{CO})_2(\mu\text{-SMe})_2(\mu\text{-S})]$.

3. Experimental details

The reactions were performed under a nitrogen or an argon atmosphere using standard Schlenk techniques. Solvents were deoxygenated and dried by standard methods. The $[\text{CpMo}(\text{CO})_3\text{H}]$ was made as previously described [10]. IR spectra were recorded on a Perkin-Elmer 1430 spectrophotometer, and NMR spectra on a Bruker AC300 spectrophotometer. Shifts are relative to tetramethylsilane as an internal reference. Chemical analyses were performed by the Centre de microanalyses du CNRS, Vernaison.

A mixture of $[\text{CpMo}(\text{CO})_3\text{H}]$ (2g, 8 mmol), dimethyl disulfide (8 ml, 88 mmol) and allyl chloride (2 ml, 25 mmol) in THF (30 ml) was heated under vacuum at

60°C for 48 h. Filtration of the cooled mixture gave the cationic red–orange complex $[\text{Cp}_2\text{Mo}_2(\text{CO})_2(\mu\text{-SMe})_3]\text{Cl}$ (**1**). The solvent was removed from the filtrate under vacuum to yield a brown residue which was chromatographed on silica gel. Elution with hexane: CH_2Cl_2 (80:20) gave some traces of the complex $[\text{CpMo}(\text{CO})_3]_2$ and also yielded **2**. The products were washed with pentane.

2 (green solid, yield, 15–25%): Anal. Found: C, 30.0; H, 3.0; S, 16.6. $\text{C}_{19}\text{H}_{22}\text{Mo}_3\text{O}_5\text{S}_4$ Calc.: C, 30.5; H, 2.9; S, 17.1%. IR (KBr pellet): $\nu(\text{CO})$ 1990, 1960, 1905, 1835, 1805 cm^{-1} . ^1H NMR (CD_2Cl_2): δ 5.53 (s, 5H, C_5H_5), 5.23 (s, 5H, C_5H_5), 2.69 (s, 3H, S- CH_3), 2.42 (s, 3H, S- CH_3), 1.69 (s, 3H, S- CH_3), 1.47 (s, 3H, S- CH_3) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2): δ 248.13, 243.30, 236.30, 233.06, 219.40 (CO); 94.12, 91.63 (C_5H_5); 29.22, 23.93, 10.04, 8.64 (S- CH_3) ppm.

3.1. Crystal structure of $[(\text{C}_5\text{H}_5)\text{Mo}(\text{CO})(\mu\text{-SMe})_3\text{Mo}(\text{CO})_2(\mu\text{-SMe})\text{Mo}(\text{CO})_2(\text{C}_5\text{H}_5)]$ (**2**)

All measurements were made at 22°C on an Enraf–Nonius CAD4 diffractometer using graphite-monochro-

Table 2

Fractional atomic coordinates and isotropic temperature factors with standard deviations in the least significant digits in parentheses (for anisotropic atoms, the equivalent isotropic temperature factors are shown)

	x	y	z	U (\AA^2)
Mo(1)	0.01636(10)	0.19240(5)	0.44000(4)	0.029
Mo(2)	0.10175(9)	0.15929(4)	0.29264(3)	0.020
Mo(3)	-0.02185(9)	0.10288(5)	0.17052(3)	0.022
S(1)	0.1579(3)	0.0705(1)	0.3901(1)	0.028
S(2)	0.2140(3)	0.0314(1)	0.2269(1)	0.031
S(3)	-0.1401(3)	0.0581(1)	0.2754(1)	0.029
S(4)	0.1757(3)	0.2207(1)	0.1831(1)	0.029
O(11)	0.2906(13)	0.1778(6)	0.5442(4)	0.090
O(12)	0.1664(12)	0.3805(5)	0.4301(4)	0.069
O(21)	-0.1123(9)	0.3287(4)	0.3097(3)	0.044
O(22)	0.4130(9)	0.2750(5)	0.3255(4)	0.056
O(31)	-0.2975(10)	0.2431(5)	0.1900(4)	0.059
C(1)	0.3745(13)	0.0655(7)	0.4074(6)	0.050
C(2)	0.4070(13)	0.0520(7)	0.1897(6)	0.053
C(3)	-0.0987(14)	-0.0576(6)	0.2964(5)	0.049
C(4)	0.0939(13)	0.3319(6)	0.1682(5)	0.042
C(11)	0.1914(14)	0.1832(7)	0.5042(5)	0.050
C(12)	0.1188(13)	0.3080(7)	0.4311(4)	0.043
C(21)	-0.0319(11)	0.2639(6)	0.3104(4)	0.028
C(22)	0.3010(12)	0.2326(6)	0.3140(5)	0.032
C(31)	-0.1953(12)	0.1954(6)	0.1834(5)	0.034
C(41)	-0.2385(16)	0.2527(8)	0.4546(6)	0.057
C(42)	-0.1774(17)	0.2253(8)	0.5152(5)	0.062
C(43)	-0.1617(16)	0.1327(8)	0.5132(6)	0.061
C(44)	-0.2161(14)	0.1026(8)	0.4519(7)	0.059
C(45)	-0.2635(13)	0.1772(9)	0.4157(6)	0.059
C(51)	-0.0578(14)	0.1147(7)	0.0598(5)	0.042
C(52)	0.0657(13)	0.0525(8)	0.0709(5)	0.046
C(53)	-0.0087(17)	-0.0193(7)	0.1016(5)	0.054
C(54)	-0.1750(17)	-0.0034(8)	0.1103(5)	0.057
C(55)	-0.2033(15)	0.0803(8)	0.0834(6)	0.058

mated Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$). The crystal was a burgandy-coloured plate $0.29 \times 0.10 \times 0.04 \text{ mm}$.

3.2. Crystal data

$\text{C}_{19}\text{H}_{22}\text{Mo}_3\text{O}_5\text{S}_4$; $M = 746.46$; monoclinic; space group, $P2_1/n$; $a = 8.217(4)$, $b = 15.060(6)$ and $c = 20.275(3) \text{ \AA}$; $\beta = 90.52(2)^\circ$; $V = 2509(2) \text{ \AA}^3$; $Z = 4$; $D_{\text{calc}} = 1.976 \text{ g cm}^{-3}$, $\mu = 1.79 \text{ mm}^{-1}$.

3.3. Measurements

Cell dimensions are based on the setting angles of 25 reflections with $19^\circ \leq \theta(\text{Mo K}\alpha) \leq 24^\circ$. The intensities of 5833 reflections with $\theta(\text{Mo K}\alpha) \leq 27^\circ$, $0 \leq h \leq 10$, $0 \leq k \leq 19$, $-25 \leq l \leq 25$ were measured from ω -2 θ scans and were corrected empirically for absorption (correction factors on $F = 0.80$ – 1.20) [11]. Merging yielded 5454 unique intensities ($R_{\text{int}} = 0.039$) and further calculations proceeded with 3535 unique reflections for which $I > 3\sigma(I)$.

3.4. Structure analysis

The structure was solved by the heavy-atom method and refined by the full-matrix least-squares method on F with $w = 1/\sigma^2(F)$ (Table 2). Anisotropic U_{ij} values were used for all non-H atoms. H atoms rode on parent C atoms with the constraints $\text{C-H} = 0.96 \text{ \AA}$ and $U(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. The orientations of the four methyl groups were obtained from a difference synthesis. Refinement of 281 parameters, including an isotropic extinction parameter $r^* = 3.7(8) \times 10^{-3}$, converged ($\Delta/\sigma < 0.16$) at $R = 0.039$, $R_w = 0.043$, $S = 1.6$ with $|\Delta\rho| < 1.2 \text{ electrons \AA}^{-3}$. Calculations were performed on a VAX 4000/60 computer using the GX package [12]. Scattering factors and anomalous dispersion corrections were taken from [13]. Atom coordinates are shown in Table

2. A table of thermal parameters and complete lists of bond lengths and angles have been deposited with the Cambridge Crystallographic Data Centre.

Acknowledgments

We thank EPSRC, Glasgow University and the University of Brest for support.

References

- [1] P. Schollhammer, F.Y. Pétilion, R. Pichon, S. Poder-Guillou, J. Talarmin, K.W. Muir and Lj. Manojlović-Muir, *Organometallics*, **14** (1995) 2277.
- [2] S. Poder-Guillou, P. Schollhammer, F.Y. Pétilion, J. Talarmin and K.W. Muir, in preparation.
- [3] M.B. Gomes de Lima, J.E. Guerschais, R. Mercier and F.Y. Pétilion, *Organometallics*, **5** (1986) 1952.
- [4] F.H. Allen, S. Bellard, M.D. Brice, B.A. Cartwright, A. Doubleday, H. Higgs, T. Hummelink, B.G. Hummelink-Peters, O. Kennard, W.D.S. Motherwell, J.R. Rodgers and D.G. Watson, *Acta Crystallogr., Sect. B*, **35** (1979) 2331.
- [5] P. Schollhammer, F.Y. Pétilion, R. Pichon, S. Poder-Guillou, J. Talarmin, K.W. Muir and S.E. Girdwood, *J. Organomet. Chem.*, **486** (1995) 183.
- [6] J.E. Guerschais, J.L. Le Quéré, F.Y. Pétilion, Lj. Manojlović-Muir, K.W. Muir and D.W.A. Sharp, *J. Chem. Soc. Dalton Trans.*, (1982) 283.
- [7] A.G. Orpen, L. Brammer, F.H. Allen, O. Kennard, D.G. Watson and R. Taylor, in *International Tables for Crystallography*, Volume C, International Union of Crystallography, 1992.
- [8] W. Schulze and M.L. Ziegler, *Z. Anorg. Allg. Chem.*, **481** (1981) 78.
- [9] F.Y. Pétilion, J.L. Le Quéré, J. Roué, J.E. Guerschais and D.W.A. Sharp, *J. Organomet. Chem.*, **204** (1980) 207.
- [10] S.A. Keppie and M.F. Lappert, *J. Chem. Soc. A*, (1971) 3216.
- [11] N. Walker and D. Stuart, *Acta Crystallogr., Sect. A*, **39** (1983) 158.
- [12] P.R. Mallinson and K.W. Muir, *J. Appl. Crystallogr.*, **18** (1985) 51.
- [13] *International Tables for X-ray Crystallography*, Vol. IV, Kynoch, Birmingham, 1974, Tables 2.1B and 2.3.1.