DALTON
FULL PAPER

Wraparound ligands: addition of activated alkynes to sulfur- and thiolate-bridged dimolybdenum complexes derived from trithiocarbonates

Harry Adams, Christopher Allott, Matthew N. Bancroft and Michael J. Morris *

Department of Chemistry, University of Sheffield, Sheffield, UK S3 7HF

Received 14th July 2000, Accepted 18th October 2000
First published as an Advance Article on the web 20th November 2000

The complex $[Mo_2(\mu\text{-}S)(\mu\text{-}SCH_2CH_2SCCR{=}CR)Cp_2]$ **1** (R = CO_2Me, Cp = $\eta\text{-}C_5H_5$) reacted with dimethyl acetylenedicarboxylate (DMAD, RC≡CR, R = CO_2Me) to afford two isomeric compounds, $[Mo_2(\mu\text{-}SCR{=}CRSCH_2CH_2SCCR{=}CR)Cp_2]$ **3** and $[Mo_2\{\mu\text{-}SCH_2CH_2SCCR{=}CRCR{=}CRS\}Cp_2]$ **4**. In the first of these the DMAD has added between the μ-S ligand and the bridging thiolate, whereas in the second it has added between the μ-S ligand and the dimetallaallyl unit. Complex **4** was successfully structurally characterised, but crystallisation of **3** led unexpectedly to the oxidation product $[Mo_2\{\mu\text{-}SCR{=}CRS({=}O)CH_2CH_2S({=}O)_2CCR{=}CR\}Cp_2]$ **5**. Reaction of **1** with methyl propiolate (RC≡CH, R = CO_2Me) afforded $[Mo_2(\mu\text{-}SCH{=}CRSCH_2CH_2SCCR{=}CR)Cp_2]$ **6**, a product analogous to **3**, regiospecifically. The complexes $[Mo_2(\mu\text{-}S)(\mu\text{-}SCH_2CH_2CH_2SCCR{=}CR)Cp_2]$ **7** and $[Mo_2(\mu\text{-}S)(\mu\text{-}SMe)\{\mu\text{-}CRC(SMe)CR\}Cp_2]$ **9** both incorporated DMAD in a similar manner to give $[Mo_2(\mu\text{-}SCR{=}CRSCH_2CH_2CH_2SCCR{=}CR)Cp_2]$ **8** and $[Mo_2\{\mu\text{-}CRC(SMe)CR\}(\mu\text{-}SCR{=}CRSMe)Cp_2]$ **10** respectively. The crystal structures of **5**, **6** and **10** have also been determined.

Introduction

The chemistry of molybdenum complexes with sulfur ligands is relevant both to heterogeneous catalysis (particularly in the hydrodesulfurisation of fossil fuels) and to biochemical systems such as the molybdenum cofactor (Moco) in molybdoenzymes.[1] Recent crystal structure determinations of molybdenum and tungsten enzymes have confirmed that the metal is bonded to a pterin fragment through a dithiolene linkage,[2] and several subsequent papers have described attempts to model this co-ordination environment in complexes such as $[MO(dithiolene)_2]^{2-}$ (M = Mo or W).[3] One established way to construct the dithiolene ligand in simple mono- and di-nuclear compounds is through the reaction of alkynes with terminal sulfido ligands.[4] Hence the reactivity patterns of sulfido groups, and other sulfur ligands, towards alkynes are worthy of further investigation.

We recently described the unusual reactions of the dimolybdenum alkyne complex $[Mo_2(\mu\text{-}RC_2R)(CO)_4Cp_2]$ (R = CO_2Me, Cp = $\eta\text{-}C_5H_5$) with various sulfur heterocycles such as ethylene trithiocarbonate (1,3-dithiolane-2-thione), propylene trithiocarbonate (1,3-dithiane-2-thione), and 4,5-bis(carbomethoxy)-1,3-dithiole-2-thione. As shown in Scheme 1, these proceeded by oxidative decarbonylation of the metal centre, cleavage of the C=S bond to give a μ-sulfido group, ring opening of the heterocycle and coupling to the alkyne to give a hybrid thiolate–dimetallaallyl ligand.[5] In the case of simple acyclic trithiocarbonates such as dimethyl trithiocarbonate a similar product was obtained, though with the additional novel feature that the C(SMe) group had effectively become inserted into the alkyne rather than occupying a terminal position in the dimetallaallyl unit.[6] These products form the starting point for the further reactions described in this paper.

During our characterisation of these products we noticed that in the mass spectra of the cyclic derivatives loss of the backbone of the original heterocycle was a prominent process. Thus for example in the spectrum of $[Mo_2(\mu\text{-}S)(\mu\text{-}SCH_2CH_2SCCR{=}CR)Cp_2]$ **1** a loss of 28 mass units from the molecular ion was observed, whereas in $[Mo_2(\mu\text{-}S)\{\mu\text{-}SCR{=}CRSCCR{=}CR\}Cp_2]$ **2** a loss of 142 (*i.e.* RC≡CR) was seen. In the hope of inducing a similar extrusion of this portion of the molecule in solution, we examined the thermal reaction of **1** towards dimethyl acetylenedicarboxylate (DMAD, $MeO_2CC{\equiv}CCO_2Me$) as this might be expected to form **2**. Such a reaction would parallel the synthesis of 4,5-bis(carbomethoxy)-1,3-dithiole-2-thione by reaction of ethylene trithiocarbonate with DMAD.[7] In fact however we discovered that complexes of this type undergo simple addition reactions with activated alkynes to give new compounds containing extended ligand systems which encircle the dimolybdenum unit.

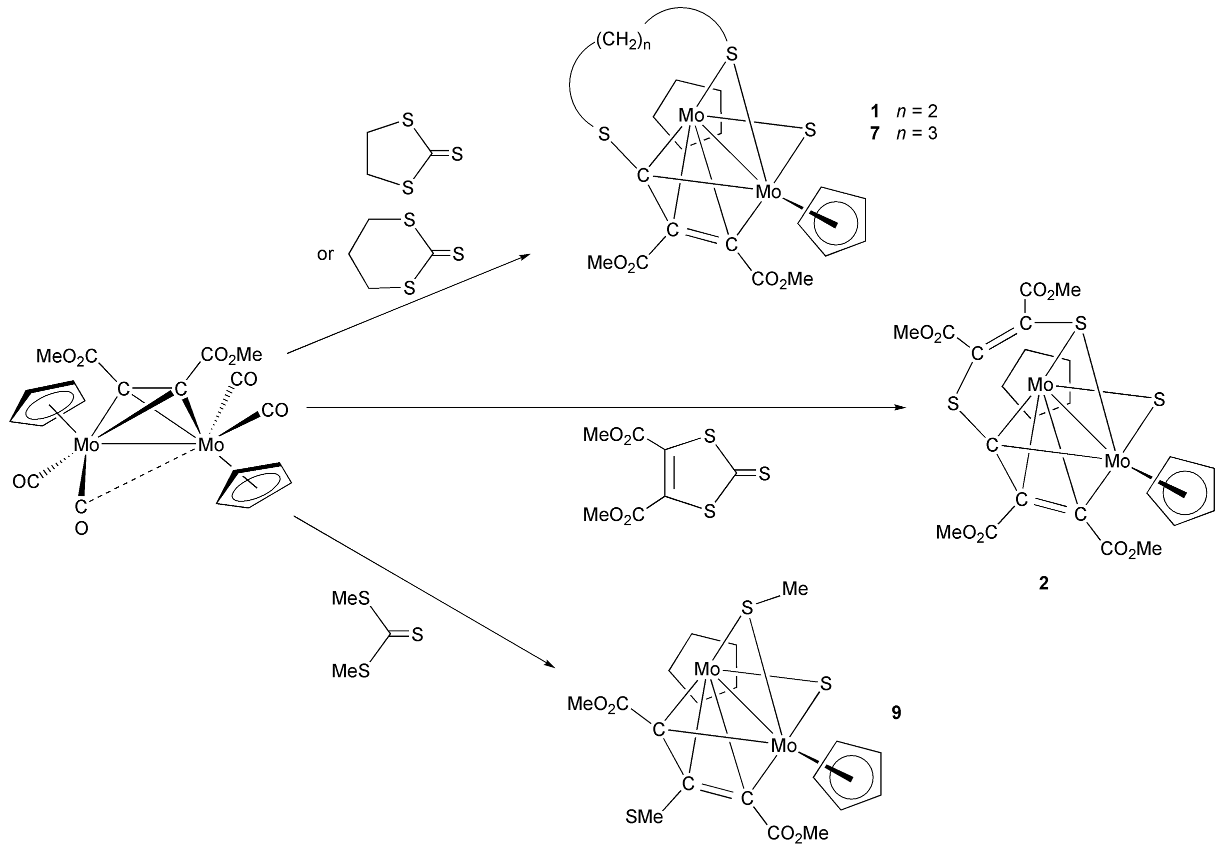
Results and discussion

Reactions of complex 1 with alkynes

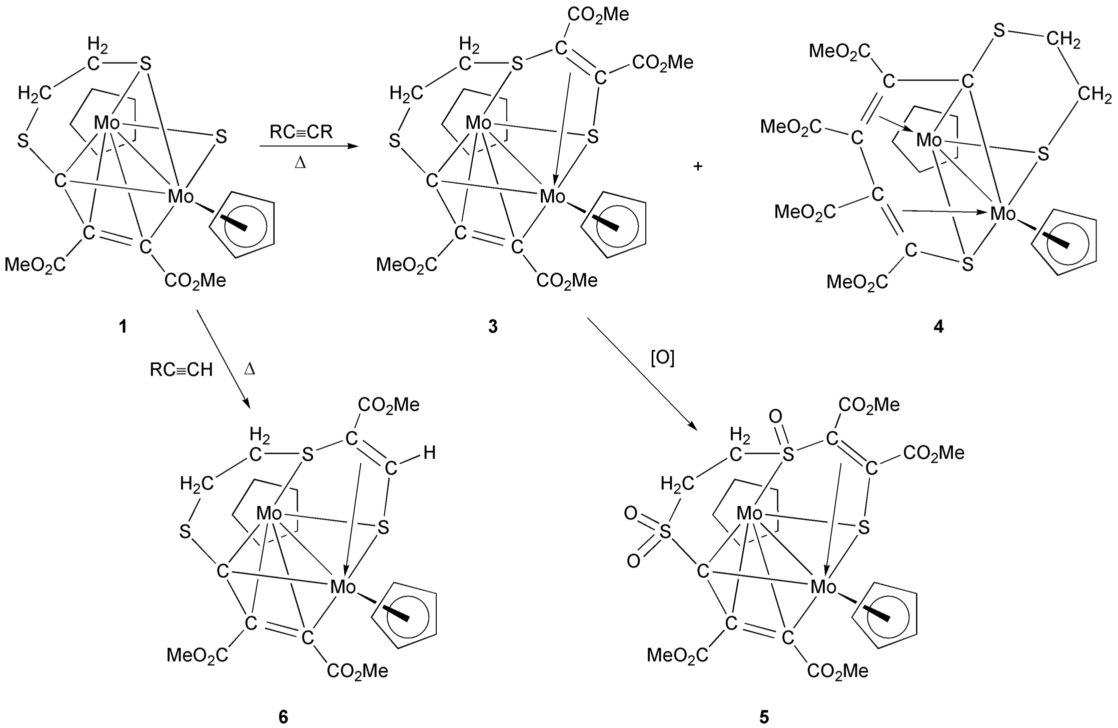
Complex **1** did not react with DMAD at room temperature in toluene, but on heating the solution to reflux complete consumption of the starting material occurred over a period of 9 h to afford two products: brown **3** (70%) and red **4** (23%), which were separated by column chromatography (Scheme 2). Elemental analysis and mass spectrometry indicated that the compounds were isomers formed by addition of one DMAD molecule to **1**. Both mass spectra exhibit molecular ions, but that of **3** shows sequential losses of C_2H_4 and DMAD, whereas that of **4** shows only loss of C_2H_4. The ^1H NMR spectra of the two compounds were also very similar, each showing two Cp resonances, four methyl peaks and four complex multiplets corresponding to the inequivalent protons of the C_2H_4 unit. The most significant difference between the two complexes was observed in the ^{13}C NMR spectrum, particularly in the five carbons directly bound to Mo, *i.e.* those forming the original dimetallaallyl unit and those of the added alkyne. For **3** these five signals appeared at δ 130.5, 101.3, 89.2, 84.0 and 49.1, whereas for **4** they occurred at δ 133.9, 120.4, 99.0, 69.8 and 64.8, thus clearly indicating a difference in the bonding mode of the DMAD.

Crystals of complex **4** were grown by diffusion of light petroleum into a dichloromethane solution; the structure is illustrated in Fig. 1, with selected bond lengths and angles

DOI: 10.1039/b005700m



Scheme 1 Synthesis of the starting materials used in this work.[5] All reactions carried out in refluxing toluene.



Scheme 2 Reactions of complex **1** with alkynes. R = CO_2Me.

collected in Table 1. The two molybdenum atoms are joined by a bond of 2.7677(8) Å, which is longer than the 2.5825(7) Å observed in **2** (the structure of **1** has not been determined, hence **2** is the closest comparison available).[5] A single Mo–Mo bond suffices for each molybdenum to attain an 18-electron configuration, in contrast to the formal double bond required in **2**, hence the lengthening of this distance. This bond is bridged by a μ-$SCH_2CH_2SCCR{=}CRCR{=}CRS$ ligand formed by linking of the incoming DMAD with the bridging sulfido group and the dimetallaallyl ligand, thus creating a ten-atom chain which wraps around the centre of the molecule. This ligand can be regarded as formally tetra-anionic (through the two terminal S atoms and the central carbon), with the result that the Mo atoms are therefore Mo^{III} and have undergone a formal reduction from the molybdenum(IV) starting material. Within the new ligand, the added DMAD interacts only with Mo(2) whereas the initial $C_2(CO_2Me)_2$ group, bonded through C(11) and C(12), interacts with Mo(1). The original quadruply

Table 1 Selected bond lengths (Å) and angles (°) for complex **4**

Mo(1)–C(12)	2.215(5)	Mo(1)–C(13)	2.227(5)
Mo(1)–C(11)	2.268(5)	Mo(1)–S(3)	2.4267(15)
Mo(1)–S(1)	2.433(2)	Mo(1)–Mo(2)	2.7677(8)
Mo(2)–C(13)	2.167(5)	Mo(2)–C(20)	2.185(6)
Mo(2)–C(21)	2.282(5)	Mo(2)–S(3)	2.4043(15)
Mo(2)–S(1)	2.450(2)	S(1)–C(15)	1.834(7)
S(2)–C(14)	1.785(7)	S(2)–C(13)	1.785(6)
S(3)–C(20)	1.766(5)	C(11)–C(12)	1.434(7)
C(11)–C(21)	1.515(7)	C(12)–C(13)	1.414(7)
C(14)–C(15)	1.496(10)	C(20)–C(21)	1.423(7)
C(12)–Mo(1)–C(13)	37.1(2)	C(12)–Mo(1)–C(11)	37.3(2)
C(13)–Mo(1)–C(11)	63.8(2)	C(12)–Mo(1)–S(3)	112.41(15)
C(13)–Mo(1)–S(3)	103.21(14)	C(11)–Mo(1)–S(3)	82.57(13)
C(12)–Mo(1)–S(1)	112.40(14)	C(13)–Mo(1)–S(1)	75.27(14)
C(11)–Mo(1)–S(1)	127.10(13)	S(3)–Mo(1)–S(1)	75.52(5)
C(13)–Mo(2)–C(20)	108.5(2)	C(13)–Mo(2)–C(21)	76.0(2)
C(20)–Mo(2)–C(21)	37.1(2)	C(13)–Mo(2)–S(3)	105.82(14)
C(20)–Mo(2)–S(3)	44.95(14)	C(21)–Mo(2)–S(3)	71.01(13)
C(13)–Mo(2)–S(1)	75.97(15)	C(20)–Mo(2)–S(1)	120.01(14)
C(21)–Mo(2)–S(1)	127.84(14)	S(3)–Mo(2)–S(1)	75.61(6)
Mo(1)–S(1)–Mo(2)	69.06(4)	C(20)–S(3)–Mo(2)	60.9(2)
C(20)–S(3)–Mo(1)	99.4(2)	Mo(2)–S(3)–Mo(1)	69.91(4)
C(12)–C(11)–C(21)	114.7(4)	C(13)–C(12)–C(11)	112.9(5)
C(13)–C(12)–C(16)	122.3(5)	C(12)–C(13)–Mo(2)	116.1(4)
Mo(2)–C(13)–Mo(1)	78.1(2)	C(21)–C(20)–S(3)	116.9(4)
C(20)–C(21)–C(11)	121.3(4)		

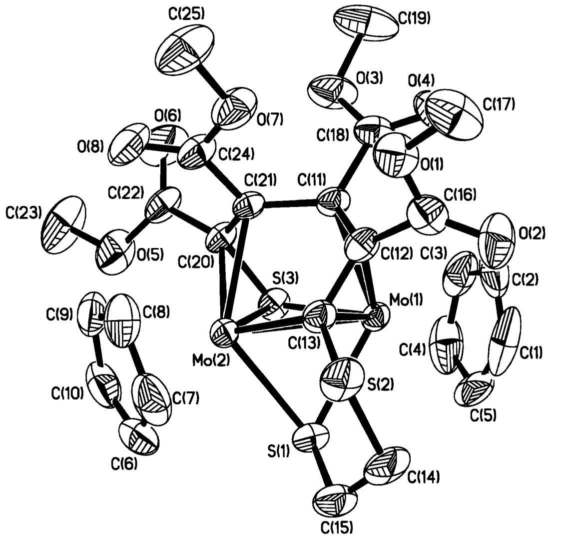


Fig. 1 Molecular structure of [Mo_2{μ-$SCH_2CH_2SCCR{=}CRCR{=}CRS$}$Cp_2$] **4** in the crystal showing the atomic numbering scheme.

Table 2 Selected bond lengths (Å) and angles (°) for complex **5**

Mo(1)–C(11)	2.153(14)	Mo(1)–C(13)	2.232(13)
Mo(1)–C(12)	2.299(13)	Mo(1)–S(3)	2.407(4)
Mo(1)–S(1)	2.408(4)	Mo(1)–Mo(2)	2.727(2)
Mo(2)–C(13)	2.135(13)	Mo(2)–C(21)	2.161(13)
Mo(2)–C(11)	2.177(14)	Mo(2)–C(20)	2.331(14)
Mo(2)–S(3)	2.376(4)	S(1)–O(11)	1.451(13)
S(1)–C(20)	1.77(2)	S(1)–C(15)	1.84(2)
S(2)–O(10)	1.439(12)	S(2)–O(9)	1.452(12)
S(2)–C(14)	1.74(2)	S(2)–C(13)	1.752(14)
S(3)–C(21)	1.82(2)	C(11)–C(12)	1.47(2)
C(12)–C(13)	1.42(2)	C(14)–C(15)	1.51(2)
C(20)–C(21)	1.43(2)		
C(11)–Mo(1)–C(13)	61.6(5)	C(11)–Mo(1)–C(12)	38.3(5)
C(13)–Mo(1)–C(12)	36.4(5)	C(11)–Mo(1)–S(3)	76.2(4)
C(13)–Mo(1)–S(3)	104.4(3)	C(12)–Mo(1)–S(3)	110.3(4)
C(11)–Mo(1)–S(1)	128.3(4)	C(13)–Mo(1)–S(1)	80.3(4)
C(12)–Mo(1)–S(1)	116.6(3)	S(3)–Mo(1)–S(1)	81.60(13)
C(13)–Mo(2)–C(21)	119.6(5)	C(13)–Mo(2)–C(11)	62.8(5)
C(21)–Mo(2)–C(11)	122.4(6)	C(13)–Mo(2)–C(20)	88.8(5)
C(21)–Mo(2)–C(20)	37.0(5)	C(11)–Mo(2)–C(20)	128.2(5)
C(13)–Mo(2)–S(3)	108.6(4)	C(21)–Mo(2)–S(3)	47.0(4)
C(11)–Mo(2)–S(3)	76.4(4)	C(20)–Mo(2)–S(3)	73.3(4)
C(20)–S(1)–C(15)	102.9(8)	C(20)–S(1)–Mo(1)	98.3(5)
C(15)–S(1)–Mo(1)	113.3(6)	O(10)–S(2)–O(9)	115.2(8)
C(14)–S(2)–C(13)	104.5(7)	C(21)–S(3)–Mo(2)	60.3(4)
C(21)–S(3)–Mo(1)	101.2(5)	Mo(2)–S(3)–Mo(1)	69.52(10)
C(12)–C(11)–Mo(1)	76.3(8)	C(12)–C(11)–Mo(2)	93.9(9)
Mo(1)–C(11)–Mo(2)	78.1(5)	C(13)–C(12)–C(11)	102.4(11)
C(13)–C(12)–Mo(1)	69.3(7)	C(11)–C(12)–Mo(1)	65.4(8)
C(12)–C(13)–S(2)	120.6(10)	C(12)–C(13)–Mo(2)	97.3(9)
S(2)–C(13)–Mo(2)	136.6(8)	C(12)–C(13)–Mo(1)	74.4(8)
S(2)–C(13)–Mo(1)	130.0(7)	Mo(2)–C(13)–Mo(1)	77.3(4)
C(21)–C(20)–S(1)	113.4(12)	C(21)–C(20)–Mo(2)	65.1(7)
S(1)–C(20)–Mo(2)	103.2(7)	C(20)–C(21)–S(3)	119.0(12)
C(20)–C(21)–Mo(2)	78.0(8)	S(3)–C(21)–Mo(2)	72.7(5)

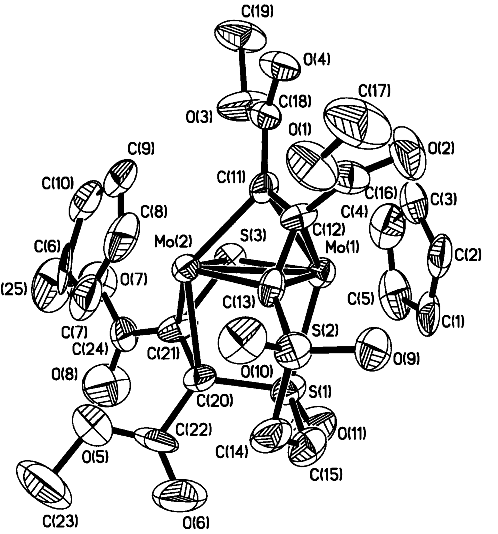


Fig. 2 Molecular structure of [Mo_2{μ-$SCR{=}CRS({=}O)CH_2CH_2S({=}O)_2CCR{=}CR$}$Cp_2$] **5** in the crystal showing the atomic numbering scheme.

bridged structure in **1** has been disrupted to some extent, though the three remaining bridging atoms S(1), S(3) and C(13) retain their orthogonal positioning. Moreover the two carbons which lie closest to the fourth orthogonal position, C(11) and C(21), are almost coplanar with Mo(1), Mo(2) and S(1) (the mean deviation for a plane formed by these five atoms is 0.1069 Å), and this plane is at an angle of 83.8° to that consisting of Mo(1), Mo(2), S(3) and C(13) (the mean deviation of this plane is 0.0322 Å).

After many attempts a crystal suitable for X-ray diffraction was grown from a solution of complex **3** in dichloromethane and dibutyl ether. However solving the structure revealed that oxidation of the compound had occurred during crystallisation (presumably as a result of the presence of peroxides in the ether). The crystal studied proved to be of [Mo_2{μ-$SCR{=}CRS({=}O)CH_2CH_2S({=}O)_2CCR{=}CR$}$Cp_2$] **5** in which three additional oxygen atoms have been incorporated, one at S(1) and two at S(2) (see Scheme 2, Fig. 2 and Table 2). Comparisons of bond lengths must be treated with some caution as the *R* factor for this structure is rather high. However we believe that the overall structure of the molecule reflects that of **3**, *i.e.* the manner of linkage of the DMAD does not change on oxidation (a view confirmed by the results described below) and it is only lone pairs on the sulfur atoms which are unused in bonding to Mo that become oxidised. The Mo(1)–Mo(2) bond of 2.727(2) Å is once more longer than that in **2**. This bond is again bridged by a single ligand, but in this case the DMAD molecule has joined the μ-S ligand to the sulfur of the original thiolate bridge, and is π-bound to Mo(2). The dimetallaallyl unit remains intact, with C(11) and C(13) symmetrically bonded to both Mo atoms and C(12) bonded only to Mo(1). The hybrid ligand can again be regarded as formally

Table 3 Selected bond lengths (Å) and angles (°) for complex **6**

Mo(1)–C(13)	2.149(7)	Mo(1)–C(11)	2.154(8)
Mo(1)–C(12)	2.331(7)	Mo(1)–S(1)	2.352(2)
Mo(1)–S(3)	2.705(2)	Mo(1)–Mo(2)	2.7245(14)
Mo(2)–C(11)	2.111(8)	Mo(2)–C(21)	2.263(7)
Mo(2)–C(20)	2.311(8)	Mo(2)–S(3)	2.376(2)
Mo(2)–C(13)	2.383(7)	S(1)–C(20)	1.850(8)
S(1)–C(15)	1.863(8)	S(2)–C(14)	1.786(10)
S(2)–C(13)	1.800(7)	S(3)–C(21)	1.617(9)
C(11)–C(12)	1.554(10)	C(12)–C(13)	1.361(10)
C(14)–C(15)	1.483(14)	C(20)–C(21)	1.494(10)
C(13)–Mo(1)–C(11)	61.7(3)	C(13)–Mo(1)–C(12)	35.1(3)
C(11)–Mo(1)–C(12)	40.3(3)	C(13)–Mo(1)–S(1)	87.8(2)
C(11)–Mo(1)–S(1)	130.3(2)	C(12)–Mo(1)–S(1)	122.8(2)
C(13)–Mo(1)–S(3)	108.9(2)	C(11)–Mo(1)–S(3)	75.6(2)
C(12)–Mo(1)–S(3)	113.0(2)	S(1)–Mo(1)–S(3)	79.45(8)
S(1)–Mo(1)–Mo(2)	81.26(7)	C(11)–Mo(2)–C(21)	123.9(3)
C(11)–Mo(2)–C(20)	126.2(3)	C(21)–Mo(2)–C(20)	38.1(3)
C(11)–Mo(2)–S(3)	84.0(2)	C(21)–Mo(2)–S(3)	40.7(2)
C(20)–Mo(2)–S(3)	67.0(2)	C(11)–Mo(2)–C(13)	58.4(3)
C(21)–Mo(2)–C(13)	124.3(3)	C(20)–Mo(2)–C(13)	91.5(3)
S(3)–Mo(2)–C(13)	112.7(2)	C(20)–S(1)–C(15)	112.6(4)
C(20)–S(1)–Mo(1)	94.1(3)	C(15)–S(1)–Mo(1)	105.4(3)
C(14)–S(2)–C(13)	91.5(4)	C(21)–S(3)–Mo(2)	65.9(3)
C(21)–S(3)–Mo(1)	103.4(3)	Mo(2)–S(3)–Mo(1)	64.48(6)
Mo(2)–C(11)–Mo(1)	79.4(3)	C(13)–C(12)–C(11)	98.1(6)
C(12)–C(13)–S(2)	114.6(5)	Mo(1)–C(13)–Mo(2)	73.7(2)
C(21)–C(20)–S(1)	123.5(5)	S(1)–C(20)–Mo(2)	105.2(4)
C(20)–C(21)–S(3)	112.5(6)		

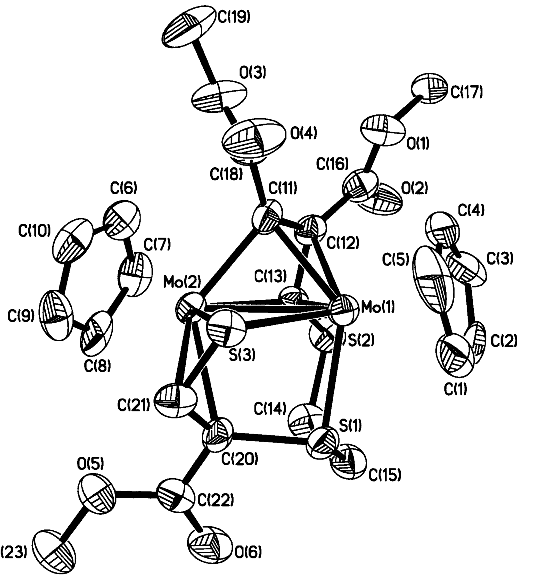


Fig. 3 Molecular structure of [Mo_2(μ-SCH=CRSCH$_2$CH$_2$SCCR=CR}Cp_2] **6** in the crystal showing the atomic numbering scheme.

tetra-anionic, and the Mo atoms as Mo^{III}. No further spectroscopic characterisation was carried out on **5** since only a few crystals were obtained, and no attempt was made to reproduce its synthesis.

In order to confirm the structure of complex **3** further, we sought to prepare an analogous complex through the reaction of **1** with methyl propiolate (RC≡CH). The reaction was slower (3 d in refluxing toluene) but a single red product **6** was isolated in 50% yield. Its mass spectrum showed a molecular ion which confirmed the addition of one methyl propiolate to **1**, and also showed ions due to sequential loss of C_2H_4 and methyl propiolate. The ^{1}H NMR spectrum showed two inequivalent Cp ligands, three methyl groups, a single resonance integrating as one proton at δ 4.71, and the four multiplets of the CH$_2$-CH$_2$ group. Moreover the pattern of signals in the ^{13}C NMR spectrum closely resembles that of **3**, with peaks at δ 130.3, 98.1, 88.1, 83.2 (CH) and 46.4 due to the carbons of the alkyne and the dimetallaallyl fragment. Only one isomer was observed, implying that addition of the alkyne is regiospecific.

Crystals of complex **6** were grown by diffusion of light petroleum into a concentrated dichloromethane solution. The structure is shown in Fig. 3 with selected bond lengths and angles given in Table 3. The Mo–Mo bond, 2.7245(14) Å, is of a very similar length to that in the oxidised complex **5**, and is again bridged by a ten atom chain in which the methyl propiolate links the original μ-S and μ-thiolate ligands, with the CH terminus of the alkyne joined to the former. Again the quadruply bridged orthogonal structure is largely maintained: atoms Mo(1), Mo(2), C(13) and S(3) lie in a plane (mean deviation 0.0304 Å) which intersects at an angle of 101.7° with the plane formed by Mo(1), Mo(2), C(11), C(20) and S(1) (mean deviation 0.1164 Å). As in the structure of **5**, sulfur atom S(1) is bonded only to Mo(1); hence we believe that the structure of **5** does give an accurate picture of the ligand in **3** if the sulfur oxidation is disregarded.

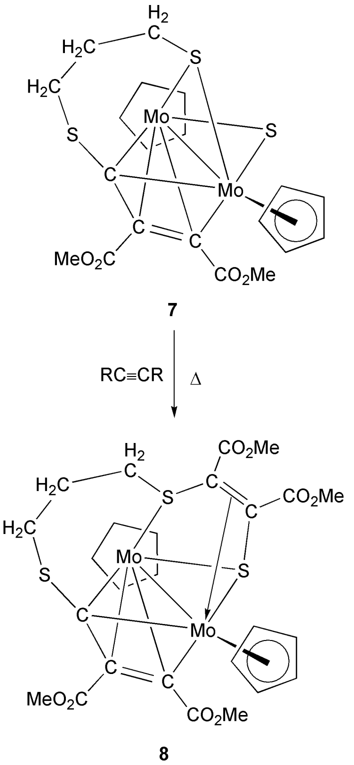
The reaction of complex **1** with 3-hexyne failed to give any tractable products, and we therefore concluded that, as in many other reactions of this type which presumably involve initial attack of the sulfur lone pair on the alkyne, activated alkynes such as DMAD and methyl propiolate are more prone to react.

Reactions of complexes 2, 7 and 9 with alkynes

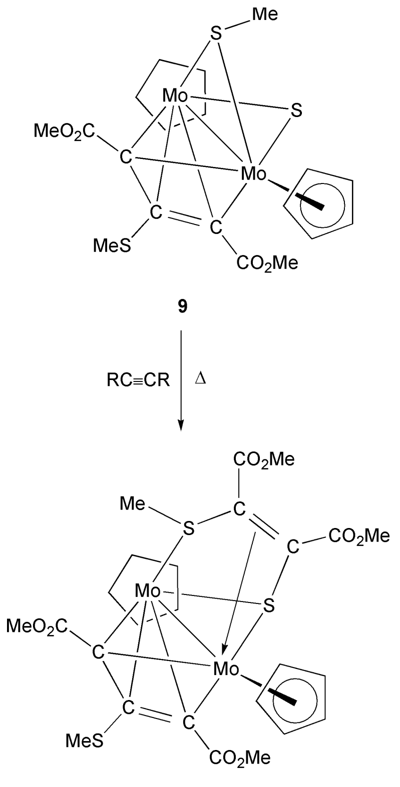
Given the results obtained with complex **1**, we next examined the reaction of **2** with alkynes. Surprisingly however, after 4.5 h reflux in toluene with an excess of DMAD, the complex was recovered largely unchanged. One possible reason for this lack of reaction might be the degree of ring strain imposed in the product. In the crystal structures of **3**, **5** and **6** the torsion angles for the C–S bonds in the SCH$_2$CH$_2$S fragment lie between 63 and 78° which would be impossible for an unsaturated spacer group to attain. If the flexibility of this linking group is important, a more promising candidate for reaction would be the related complex **7**, which has an extra CH$_2$ group compared to **1**.

Treatment of complex **7** with DMAD in refluxing toluene indeed proved successful, giving a single product **8** in only 1.5 h compared to the 10 h required for **1** (Scheme 3). The characterising data of **8** are closely related to those of **3** and **6** in that its mass spectrum showed a molecular ion with losses of C_3H_6 and DMAD, and its ^{13}C NMR spectrum the expected pattern of peaks for the five carbons bound to Mo, at δ 146.7, 106.6, 82.6, 82.3 and 56.4. The same mode of linking of the alkyne was again confirmed by a crystal structure determination, but the *R* factor of this structure was unacceptably high (*R*1 = 0.1461) (possibly due to the presence of a superlattice in the crystal); thus while it confirmed the atom connectivity shown, we do not report the full structural details here.

If the reactivity of the starting materials is governed by the flexibility of the linking group, then complex **9**, derived from dimethyl trithiocarbonate and containing no spacer group, might also be expected to react rapidly. In fact, however, although **9** did react with DMAD to give a single red product **10** in 89% yield (Scheme 4), completion of the process required 23 h. Its mass spectrum confirmed the addition of one alkyne molecule, though the spectrum was more complex than those of the previously described products. Some of the peaks in the ^{1}H and ^{13}C NMR spectra of **10** in CDCl$_3$ are very broad at room temperature, but at low temperature (190 K) the ^{13}C spectrum was sufficiently sharp to distinguish a pattern of signals similar to that of **3**, **6** and **8**, with the five carbons bound to molybdenum appearing at δ 121.6, 114.9, 84.0, 82.4 and 49.4. The ^{1}H NMR spectrum remains broad at low temperature, and we are inclined to attribute this to partial oxidation to paramagnetic species by solvent impurities rather than a fluxional process involving sulfur inversion. A carefully purified sample



Scheme 3 Reaction of complex **7** with DMAD. R = CO_2Me.



Scheme 4 Reaction of complex **9** with DMAD. R = CO_2Me.

in acetone-d_6 did not show the same broadening, though of course the polarity of the solvent may also have an influence.

We therefore formulated the product as [Mo_2{μ-CRC(SMe)-CR}(μ-SCRCRSMe)Cp_2] and this was again confirmed by structure determination. The structure is shown in Fig. 4, with selected bond lengths and angles given in Table 4. The two molybdenum atoms are joined by a bond of 2.7201(6) Å, which can be compared with the 2.5605(10) Å in the starting complex **9**. The dimetallaallyl fragment originally present is retained.

Table 4 Selected bond lengths (Å) and angles (°) for complex **10**

Mo(1)–C(11)	2.193(5)	Mo(1)–C(12)	2.216(5)
Mo(1)–C(13)	2.321(5)	Mo(1)–S(3)	2.4081(13)
Mo(1)–S(1)	2.4674(14)	Mo(1)–Mo(2)	2.7201(6)
Mo(2)–C(11)	2.153(5)	Mo(2)–C(12)	2.155(5)
Mo(2)–C(21)	2.167(5)	Mo(2)–C(20)	2.290(5)
Mo(2)–S(3)	2.3893(13)	S(1)–C(20)	1.768(5)
S(1)–C(15)	1.814(5)	S(3)–C(21)	1.780(5)
C(11)–C(13)	1.440(7)	C(12)–C(13)	1.431(8)
C(20)–C(21)	1.440(7)		
C(11)–Mo(1)–C(12)	61.45(19)	C(11)–Mo(1)–C(13)	37.08(18)
C(12)–Mo(1)–C(13)	36.69(19)	C(11)–Mo(1)–S(3)	76.89(14)
C(12)–Mo(1)–S(3)	105.49(13)	C(13)–Mo(1)–S(3)	110.15(13)
C(11)–Mo(1)–S(1)	127.89(15)	C(12)–Mo(1)–S(1)	78.85(14)
C(13)–Mo(1)–S(1)	115.49(14)	S(3)–Mo(1)–S(1)	83.38(4)
S(1)–Mo(1)–Mo(2)	78.56(3)	C(11)–Mo(2)–C(12)	63.1(2)
C(11)–Mo(2)–C(21)	122.82(19)	C(12)–Mo(2)–C(21)	118.83(19)
C(11)–Mo(2)–C(20)	128.10(19)	C(12)–Mo(2)–C(20)	87.31(18)
C(21)–Mo(2)–C(20)	37.56(18)	C(11)–Mo(2)–S(3)	78.04(14)
C(12)–Mo(2)–S(3)	108.15(14)	C(21)–Mo(2)–S(3)	45.66(13)
C(20)–Mo(2)–S(3)	72.01(13)	C(20)–S(1)–Mo(1)	92.99(18)
C(21)–S(3)–Mo(2)	60.56(16)	C(21)–S(3)–Mo(1)	101.38(17)
Mo(2)–S(3)–Mo(1)	69.08(4)	Mo(2)–C(11)–Mo(1)	77.50(17)
Mo(2)–C(12)–Mo(1)	76.96(16)	C(12)–C(13)–C(11)	103.3(4)
C(21)–C(20)–S(1)	118.9(4)	C(20)–C(21)–S(3)	117.1(4)

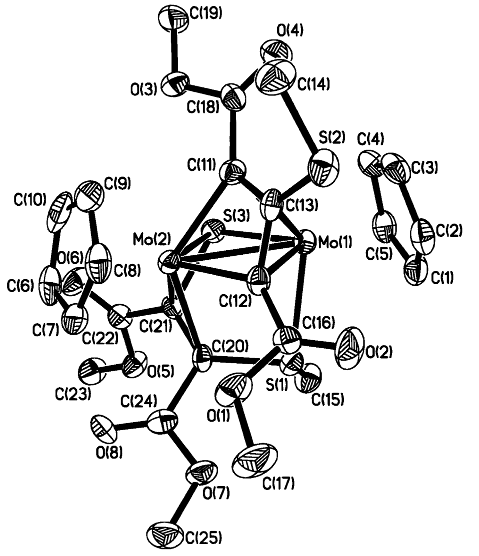


Fig. 4 Molecular structure of [Mo_2{μ-CRC(SMe)CR}(μ-SCR=CRS-Me)Cp_2] **10** in the crystal showing the atomic numbering scheme.

In the structure of **9** two crystallographically independent molecules were found, one of which had the central carbon equidistant from the two Mo atoms while in the other it was displaced towards one Mo and not bonded to the other. The latter situation seems to be more common as it was also seen in the structure of **2** and related complexes.[5] It is also the case in **10**, with the central carbon C(13) bonded only to Mo(1) [Mo(1)–C(13) 2.321(5) Å] and out of range of Mo(2) [the non-bonding Mo(2)–C(13) distance is 2.687 Å]. In complexes **1**, **2** and **9** we proposed that the Cp ligands were rendered equivalent in solution by a fluxional process involving the central carbon flipping rapidly from one Mo to the other. In **10** (and the other complexes reported in this paper) the Cp ligands are already inequivalent and consequently there is no way of knowing whether a similar fluxionality is occurring.

The second bridging ligand is the hybrid thioether–thiolate group, SCR=CRSMe, in which S(3) is bonded almost symmetrically to both molybdenums, but S(1), bearing the methyl group, is bonded only to Mo(1). The result is a five-membered chelate ring somewhat reminiscent of a methylated dithiolene ligand, and indeed Rakowski Dubois and co-workers reported a similar ligand in $[Mo_2(\mu\text{-}SCH_2S)(\mu\text{-}SCH{=}CHSMe)Cp_2]^+$, prepared by methylation of $[Mo_2(\mu\text{-}SCH_2S)(\mu\text{-}SCH{=}CHS)Cp_2]$. The analogous $[Mo_2(\mu\text{-}SCH_2S)(\mu\text{-}SCH{=}CHSBu^t)Cp_2]^+$ was also prepared by reaction of acetylene with $[Mo_2(\mu\text{-}S)(\mu\text{-}SCH_2S)(\mu\text{-}SBu^t)Cp_2]^+$ which constitutes a further example of the addition of an alkyne between a bridging sulfido group and a bridging thiolate ligand.[8]

Treatment of complex **2** with elemental sulfur has been shown to produce the terminal dithiolene complexes $[Mo_2(S)(\mu\text{-}S)_2(SCR{=}CRS)Cp_2]$, with the remaining DMAD is released in the form of a 1,2-dithiole-3-thione. We therefore briefly examined the reactions of **3** and **4** with sulfur in the hope of isolating larger sulfur heterocycles. In the event, however, both complexes were recovered unchanged after heating with sulfur in toluene for 4.5 and 3 h respectively.

Conclusion

The sulfur ligands in complexes such as **1**, **7** and **9** are sufficiently reactive to undergo addition of activated alkynes to afford new long chain hybrid ligands containing coordinated thiolate and thioether functionalities, and with retention of the dimetallaallyl unit. Only in the case of **1** an alternative mode of addition, linking the bridging sulfur with the dimetallaallyl group, is also observed, leading to isolation of **4** in low yield. Complex **2** is unreactive towards alkynes, possibly because of the unsaturated nature of the linking group between the sulfur and the dimetallaallyl unit.

Experimental

General experimental techniques were as described in a recent paper from this laboratory.[9] Infrared spectra were recorded in CH_2Cl_2 solution on a Perkin-Elmer 1600 FT-IR machine, ^1H and ^{13}C spectra in $CDCl_3$ solution on a Bruker AC250 machine with automated sample-changer or an AMX400 spectrometer. The $^{13}C\text{-}\{^1H\}$ NMR spectra were routinely recorded using an attached proton test technique (JMOD pulse sequence). Chemical shifts are given on the δ scale relative to $SiMe_4$ (δ 0.0) for ^1H and ^{13}C; coupling constants are given in Hz. Mass spectra were recorded on a Fisons/BG Prospec 3000 instrument operating in fast atom bombardment mode with *m*-nitrobenzyl alcohol as matrix. Elemental analyses were carried out by the Microanalytical Service of the Department of Chemistry. Light petroleum refers to the fraction boiling in the range 60–80 °C. The starting complexes were prepared as described previously.[5]

Syntheses

Complexes $[Mo_2(\mu\text{-}SCR{=}CRSCH_2CH_2SCCR{=}CR\}Cp_2]$ 3 and $[Mo_2\{\mu\text{-}SCH_2CH_2SCCR{=}CRCR{=}CRS\}Cp_2]$ 4. A solution of complex **1** (200 mg, 0.33 mmol) and DMAD (45 µl, 0.37 mmol, 1.1 equivalents) in toluene (50 cm^3) was heated to reflux for 4 hours. After this time TLC monitoring showed the presence of starting material, and a further portion of DMAD (45 µl, 0.37 mmol) was added and reflux resumed for 3 hours. When again TLC showed the presence of starting material a third portion of DMAD (45 µl, 0.37 mmol, 1.1 eq.) was added and reflux continued for 3 hours. TLC now showed only a trace of starting material. The solvent was removed by rotary evaporation and the solid residue absorbed onto silica prior to column chromatography. A brown band of **3** was eluted in CH_2Cl_2–acetone (16 : 1) (172 mg, 0.23 mmol, 70%) followed by a red band of **4**, eluted in a 9 : 1 mixture of the same solvents (57 mg, 0.077 mmol, 23%). Data for **3**: mp 102–120 °C (decomp.); ^1H NMR δ 5.30, 4.88 (both s, 5 H, Cp), 3.76, 3.68, 3.66, 3.61 (all s, 3 H, Me), 3.57, 3.29, 2.94, 1.79 (all m, 1 H, SCH_2CH_2S); ^{13}C NMR δ 177.2, 173.5, 170.7, 164.2 (all CO_2Me), 130.5, 101.3 (both Mo–C), 97.6, 91.9 (both Cp), 89.2, 84.0 (both Mo–C), 52.7, 52.3, 52.0, 51.5 (all Me), 49.1 (Mo–C), 27.6, 24.5 (both SCH_2CH_2S) (Found: C, 40.05; H, 3.59; S, 13.17. Calc. for $C_{25}H_{26}Mo_2O_8S_3$: C, 40.44; H, 3.53; S, 12.95%); MS *m*/*z* 742 (M^+), 713 ($M^+ - C_2H_4$) and 573 ($M^+ - C_2H_4$ and DMAD). Data for **4**: mp >250 °C; ^1H NMR δ 5.33, 5.11 (both s, 5 H, Cp), 3.79, 3.75, 3.65, 3.58 (all s, 3H, Me), 3.17, 2.88, 2.34, 1.46 (all m, 1 H, SCH_2CH_2S); ^{13}C NMR δ 173.0, 172.8, 169.5, 168.4 (all CO_2Me), 133.9, 120.4 (both Mo–C), 100.9 (Cp), 99.0 (Mo–C), 93.1 (Cp), 69.8, 64.8 (both Mo–C), 53.0, 52.6, 51.8, 51.5 (all Me), 41.6, 30.0 (both SCH_2CH_2S) (Found: C, 39.40; H, 3.40; Cl, 4.53; S, 12.18. Calc. for $C_{25}H_{26}Mo_2O_8S_3\cdot 0.5CH_2Cl_2$: C, 38.97; H, 3.44; Cl, 4.52; S, 12.23%); MS: *m*/*z* 743 (M^+) and 713 ($M^+ - C_2H_4$).

$[Mo_2(\mu\text{-}SCH{=}CRSCH_2CH_2SCCR{=}CR\}Cp_2]$ 6. A solution of complex **1** (400 mg, 0.67 mmol) and methyl propiolate (180 µl, 2.02 mmol, 3.0 equivalents) in toluene (50 cm^3) was heated to reflux for 24 hours. After this time TLC showed that a large quantity of starting material remained, so a further portion of methyl propiolate (180 µl, 2.02 mmol) was added and reflux continued for 24 hours. Again TLC showed the presence of starting material, and so a third portion of methyl propiolate (180 µl, 2.02 mmol) was added and reflux continued for 24 hours. After this time no starting material could be seen on the TLC plate. Solvent was removed by rotary evaporation and the solid residue adsorbed onto silica prior to column chromatography. Elution with CH_2Cl_2–acetone (19 : 1) gave a red band of product **6** (230 mg, 0.34 mmol, 50%). mp 222–230 °C (decomp.). ^1H NMR: δ 5.12, 4.80 (both s, 5 H, Cp), 4.71 (s, 1 H, CH), 3.79 (m, 1 H of SCH_2CH_2S), 3.73, 3.65, 3.58 (all s, 3 H, Me), 3.42, 2.96, 1.70 (all m, 1 H, SCH_2CH_2S). ^{13}C NMR: δ 177.5, 177.3, 164.6 (all CO_2Me), 130.3, 98.1 (both Mo–C), 94.4, 91.3 (both Cp), 88.1 (Mo–C), 83.2 (Mo–CH), 52.0, 51.7, 51.3 (all Me), 46.4 (Mo–C), 28.4, 25.0 (both SCH_2CH_2S) (Found: C, 40.28; H, 3.55; S, 14.25. Calc. for $C_{23}H_{24}Mo_2O_6S_3$: C, 40.36; H, 3.53; S, 14.05%). MS: *m*/*z* 684 (M^+), 657 ($M^+ - C_2H_4$) and 572 ($M^+ - C_2H_4$ and $HC{\equiv}CCO_2Me$).

$[Mo_2(\mu\text{-}SCR{=}CRSCH_2CH_2CH_2SCCR{=}CR\}Cp_2]$ 8. A solution of complex **7** (593 mg, 0.97 mmol) and DMAD (120 µl, 0.98 mmol, 1.01 equivalents) in toluene (50 cm^3) was heated to reflux for 90 minutes. The solvent was removed by rotary evaporation and the solid residue absorbed onto silica prior to column chromatography. A brown band of **8** was eluted as the only product with 16 : 1 CH_2Cl_2–acetone (498 mg, 0.66 mmol, 68%). mp 160 °C. ^1H NMR: δ 5.37, 4.87 (both s, 5 H, Cp), 3.78, 3.72, 3.67, 3.61 (all s, 3 H, Me), 3.42 (m, 2 H of $SCH_2CH_2CH_2S$), 3.18 (ddd, *J* = 14.7, 11.0, 5.8, 1 H of $SCH_2CH_2CH_2S$), 3.03 (ddd, *J* = 14.7, 7.0, 3.1 Hz, 1 H of $SCH_2CH_2CH_2S$), 2.39 (m, 1 H of $SCH_2CH_2CH_2S$) and 2.02 (m, 1 H of $SCH_2CH_2CH_2S$). ^{13}C NMR: δ 177.2, 174.0, 170.4, 165.0 (all CO_2Me), 146.7, 106.6 (both Mo–C), 97.7, 91.8 (both Cp), 82.6, 82.3, 56.4 (all Mo–C), 52.6 (2 Me), 52.0, 51.4 (both Me), 39.4, 35.7, 32.0 (all $SCH_2CH_2CH_2S$) (Found: C, 39.63; H, 3.61; S, 12.29. Calc. for $C_{26}H_{28}Mo_2O_8S_3\cdot 0.5CH_2Cl_2$: C, 39.83; H, 3.65; S, 12.03%). MS: *m*/*z* 756 (M^+), 714 ($M^+ - C_3H_6$) and 574 ($M^+ - C_3H_6$ and DMAD).

$[Mo_2\{\mu\text{-}CRC(SMe)CR\}(\mu\text{-}SCR{=}CRSMe)Cp_2]$ 10. A solution of complex **9** (317 mg, 0.53 mmol) and DMAD (65 µl, 0.53 mmol, 1.0 equivalents) in toluene (50 cm^3) was heated to reflux for 1.5 hours. After this time TLC showed that a large quantity of starting material remained. A further portion of DMAD (130 µl, 1.06 mmol, 2.0 equivalents) was therefore added and reflux resumed for 23 hours. After removal of the solvent the residue was chromatographed. A green band of unchanged **9** was eluted with CH_2Cl_2–acetone (19 : 1) (11 mg, 3.5% recovery). A red band of product **10** was eluted in an 8 : 1 mixture of the same solvents (350 mg, 0.47 mmol, 89%). mp 226 °C. ^1H NMR (CD_2Cl_2, 298 K): δ 5.27 (s, 5 H, Cp), 4.80 (br s, 5 H, Cp), 3.67, 3.62, 3.60, 3.53 (all s, 3 H, CO_2Me), 2.28, 1.81 (both s, 3 H, SMe). ^1H NMR (CD_3COCD_3, 298 K):

Table 5 Summary of crystallographic data for complexes **4**–**6** and **10**

	4	**5**	**6**	**10**
Empirical formula	$C_{25}H_{26}Mo_2O_8S_3$	$C_{25}H_{26}Mo_2O_{11}S_3$	$C_{23}H_{24}Mo_2O_6S_3$	$C_{25}H_{28}Mo_2O_8S_3$
Formula weight	742.52	790.52	684.48	744.53
T/K	293(2)	293(2)	293(2)	150(2)
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/n$
a/Å	10.132(2)	14.069(3)	8.637(6)	9.9813(5)
b/Å	18.609(4)	15.140(3)	30.228(2)	16.7621(9)
c/Å	14.999(3)	16.208(3)	9.5010(10)	16.0913(9)
β/°	108.04(3)	97.21(3)	92.77(6)	90.7700(10)
V/Å^3	2689.0(9)	3425.1(12)	2477.6(17)	2692.0(2)
Z	4	4	4	4
μ/mm^{-1}	1.214	0.964	1.303	1.213
Reflections collected	5111	7606	4797	11814
Independent reflections	3962 [R(int) = 0.1309]	6002 [R(int) = 0.0948]	3845 [R(int) = 0.1325]	3867 [R(int) = 0.0614]
Final $R1$, $wR2$ [$I > 2\sigma(I)$]	0.0472, 0.1293	0.1112, 0.2999	0.0519, 0.1312	0.0451, 0.1071
(all data)	0.0523, 0.1346	0.1715, 0.4402	0.0672, 0.1906	0.0565, 0.1161

δ 5.31 (s, 5 H, Cp), 4.89 (s, 5 H, Cp), 3.67, 3.63, 3.62, 3.51 (all s, 3 H, CO_2Me), 2.30, 1.88 (both s, 3 H, SMe). ^{13}C NMR (CD_2Cl_2, 190 K): δ 177.0, 176.1 (both CO_2Me), 170.7 (br s, 2 CO_2Me), 121.6, 114.9 (both Mo–C), 96.7 (br s, Cp), 92.8 (Cp), 84.0 (Mo–C), 82.4 (br s, Mo–C), 52.7, 51.9, 51.5, 51.3 (all CO_2Me), 49.4 (br s, Mo–C), 29.2 (br s, SMe) and 14.5 (SMe) (Found: C, 40.24; H, 3.70; S, 12.95. Calc. for $C_{25}H_{28}Mo_2O_8S_3$: C, 40.33; H, 3.79; S, 12.92%). MS: m/z 744 (M^+), 729 ($M^+ - Me$), 712 ($M^+ - 2Me$) and 697 ($M^+ - SMe$).

Crystal structure determinations of complexes 4, 5, 6 and 10

Crystal data for complexes **4**, **5**, **6** and **10** are summarised in Table 5. General procedures for data collection and structure solution were as described in recent papers, using a Siemens P4 diffractometer for **4**, **5** and **6** and a Bruker Smart CCD area detector with Oxford Cryosystems low temperature system for **10**.[9,10] Complex scattering factors were taken from the program package SHELXL 93[11] as implemented on a Viglen 486dx computer.

CCDC reference number 186/2243.

See http://www.rsc.org/suppdata/dt/b0/b005700m/ for crystallographic files in .cif format.

Acknowledgements

We thank the EPSRC for the award of a studentship (to M. N. B.).

References

1 *ACS Symp. Ser.*, 1996, **653**; J. Wachter, *Angew. Chem., Int. Ed. Engl.*, 1989, **28**, 1613.

2 R. Hille, *Chem. Rev.*, 1996, **96**, 2757; M. K. Johnson, D. C. Rees and M. W. W. Adams, *Chem. Rev.*, 1996, **96**, 2817.

3 J. Yadav, S. K. Das and S. Sarkar, *J. Am. Chem. Soc.*, 1997, **119**, 4315; E. S. Davies, R. L. Beddoes, D. Collison, A. Dinsmore, A. Docrat, J. A. Joule, C. R. Wilson and C. D. Garner, *J. Chem. Soc., Dalton Trans.*, 1997, 3985; E. S. Davies, G. M. Aston, R. L. Beddoes, D. Collison, A. Dinsmore, A. Docrat, J. A. Joule, C. R. Wilson and C. D. Garner, *J. Chem. Soc., Dalton Trans.*, 1998, 3647; C. A. Goddard and R. H. Holm, *Inorg. Chem.*, 1999, **38**, 5389; B. S. Lim, J. P. Donahue and R. H. Holm, *Inorg. Chem.*, 2000, **39**, 263.

4 D. Coucouvanis, A. Hadjikyriacou, M. Draganjac, M. G. Kanatzidis and O. Ileperuma, *Polyhedron*, 1986, **5**, 349; T. R. Halbert, W.-H. Pan and E. I. Stiefel, *J. Am. Chem. Soc.*, 1983, **105**, 5476; J. T. Goodman, S. Inomata and T. B. Rauchfuss, *J. Am. Chem. Soc.*, 1996, **118**, 11674; M. Rakowski Dubois, B. R. Jagirdar, S. Dietz and B. C. Noll, *Organometallics*, 1997, **16**, 294; S. Kuwata, M. Andou, K. Hashizume, Y. Mizobe and M. Hidai, *Organometallics*, 1998, **17**, 3429.

5 H. Adams, M. N. Bancroft and M. J. Morris, *Chem. Commun.*, 1997, 1445; H. Adams, C. Allott, M. N. Bancroft and M. J. Morris, *J. Chem. Soc., Dalton Trans.*, 2000, 4145.

6 H. Adams, C. Allott, M. N. Bancroft and M. J. Morris, *J. Chem. Soc., Dalton Trans.*, 1998, 2607.

7 B. R. O'Connor and F. N. Jones, *J. Org. Chem.*, 1970, **35**, 2002.

8 J. Birnbaum, R. C. Haltiwanger, P. Bernatis, C. Teachout, K. Parker and M. Rakowski Dubois, *Organometallics*, 1991, **10**, 1779.

9 H. Adams, L. J. Gill and M. J. Morris, *Organometallics*, 1996, **15**, 464.

10 H. Adams, A. Biebricher, S. R. Gay, T. Hamilton, P. E. McHugh, M. J. Morris and M. J. Mays, *J. Chem. Soc., Dalton Trans.*, 2000, 2983.

11 G. M. Sheldrick, SHELXL 93, An integrated system for solving and refining crystal structures from diffraction data, University of Göttingen, 1993.