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Deconstruction of cyclic and acyclic trithiocarbonates by C–S and C=S bond cleavage during oxidative decarbonylation of dimolybdenum alkyne complexes †

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

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

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The dimolybdenum alkyne complex $[Mo_2(\mu\text{-}R^1C{\equiv}CR^2)(CO)_4Cp_2]$ **1** (Cp = η-C_5H_5; $R^1 = R^2 = CO_2Me$) reacted with the 1,3-dithiole-2-thiones $S{=}CS_2C_2R_2$ (R = CO_2Me, SMe, or SCOPh) to afford the new compounds $[Mo_2(\mu\text{-}S)(\mu\text{-}SCR{=}CRSCCR^1{=}CR^2)Cp_2]$ by a complicated process involving cleavage of the C=S bond to give a μ-sulfido ligand, ring opening of the heterocycle and coupling with the alkyne to afford a hybrid thiolate-dimetalla-allyl ligand. One of these products ($R = R^1 = R^2 = CO_2Me$) has been structurally characterised. The alkyne complexes **2** ($R^1 = R^2 = CO_2Et$) and **3** ($R^1 = R^2 = Ph$) furnished analogous products on treatment with $S{=}CS_2C_2(CO_2Me)_2$ whereas **4**, the dimolybdenum complex of the unsymmetrical alkyne $PhC{\equiv}CCO_2Et$, gave two regioisomers, both of which have also been structurally characterised. Related complexes $[Mo_2(\mu\text{-}S)\{\mu\text{-}S(CH_2)_nSCC(CO_2Me){=}C(CO_2Me)\}Cp_2]$ were formed from **1** and ethylene or propylene trithiocarbonate, $S{=}CS_2(CH_2)_n$ (n = 2 or 3). In contrast, the reaction of **1** with acyclic dialkyl trithiocarbonates $S{=}C(SR)_2$ afforded complexes containing sulfido (μ-S), thiolate (μ-SR) and CSR units, but surprisingly the last of these occupies the central position in the dimetalla-allyl ligand rather than the terminus. The crystal structure of one of these compounds, $[Mo_2(\mu\text{-}S)(\mu\text{-}SMe)\{\mu\text{-}C(CO_2Me)C(SMe)\text{-}C(CO_2Me)\}Cp_2]$, has been determined. Based on these observations, a possible mechanism for the reaction is suggested.

Introduction

The chemistry of transition metal complexes with sulfur ligands is of continuing importance because of its relevance both to heterogeneous catalysis (particularly in the hydrodesulfurisation of fossil fuels) and to biochemical systems such as the molybdenum cofactor (Moco) in molybdoenzymes.[1] Dinuclear cyclopentadienyl molybdenum complexes with sulfur and/or thiolate ligands have been investigated extensively over the past 20 years,[2] and complexes such as $[Mo_2(\mu\text{-}S)_2(\mu\text{-}SH)_2Cp_2]$ and $[Mo_2(\mu\text{-}S)_2(\mu\text{-}S_2CH_2)Cp_2]$ have been shown to display a wide-ranging reactivity which includes C–S bond making and breaking, dihydrogen activation, and the catalytic reduction of SO_2 to sulfur and water.[3] Moreover mixed-metal clusters derived from these species can effect the stoichiometric homogeneous desulfurisation of organic compounds[4] and have been shown to be precursors of effective hydrodesulfurisation catalysts when supported on alumina and treated with H_2S.[5]

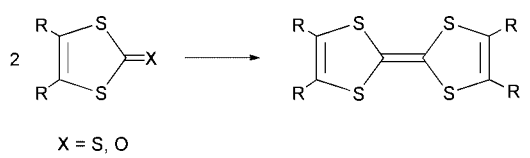
During our recent investigations of the dimolybdenum alkyne complexes $[Mo_2(\mu\text{-}R^1C{\equiv}CR^2)(CO)_4Cp_2]$ (R^1, R^2 = alkyl, aryl, CO_2Me, *etc.*) we examined their reactions with thiols, RSH. In several cases C–S bond cleavage accompanied by oxidative decarbonylation was observed, providing convenient routes to higher oxidation state compounds containing sulfido ligands, including the known species $[Mo_2(\mu\text{-}S)_2(\mu\text{-}SR)_2Cp_2]$ but also novel complexes such as $[Mo_2(\mu\text{-}S)_2(\mu\text{-}MeO_2CCH{=}CHCO_2Me)Cp_2]$ and $[Mo_2(\mu\text{-}S)(\mu\text{-}SPr^i)_2(\mu\text{-}C_2Ph_2)Cp_2]$.[6,7] As a result, we were prompted to discover whether the same systems would be able to cleave C=S double bonds. This paper reports the results obtained with various cyclic and acyclic trithiocarbonates, and amplifies the accounts given in two preliminary communications.[8]

† Electronic supplementary information (ESI) available: elemental analysis data. See http://www.rsc.org/suppdata/dt/b0/b004293p/

Results and discussion

Desulfurisation and ring opening of 1,3-dithiole-2-thiones

Previous work has shown that the outcomes of reactions involving the dimolybdenum alkyne complexes $[Mo_2(\mu\text{-}R^1C_2R^2)(CO)_4Cp_2]$ often depend on the identity of the substituents R^1 and R^2. In this work we concentrated mainly on $[Mo_2(\mu\text{-}MeO_2CC_2CO_2Me)(CO)_4Cp_2]$ **1**, containing the strongly bound electron-deficient alkyne dimethyl acetylenedicarboxylate (DMAD). The initial sulfur-containing substrates chosen were 1,3-dithiole-2-thiones. These compounds are of considerable importance as they undergo reductive coupling by cleavage of the C=S bond to form tetrathiafulvalenes (TTFs), a process usually carried out with $P(OEt)_3$ but also known to be promoted by some transition metal complexes (Scheme 1).[9,10]



Scheme 1 Desulfurisation of 1,3-dithiole-2-thiones to form tetrathiafulvalenes (TTFs).

Despite this, their organometallic chemistry has rarely been explored previously. Part of our motivation for this choice was the possibility that the dimolybdenum complex might abstract sulfur from the heterocycles, leading to the corresponding TTF; in the event, while cleavage of the C=S bond was achieved, subsequent reactions took a more unexpected course.

Reaction of complex **1** with 1 equivalent of thione **5** in refluxing toluene resulted in gradual formation of a single green product **8**, which was isolated by column chromatography in 64% yield after a total reaction time of 6 h (Scheme 2). The compound is air-stable in the solid state and in solution, and

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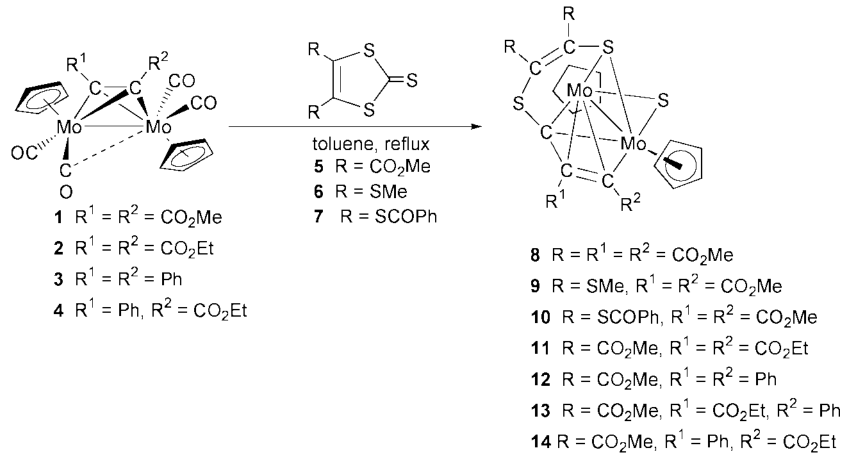


Scheme 2 Reactions of the dimolybdenum alkyne complexes with 1,3-dithiole-2-thiones.

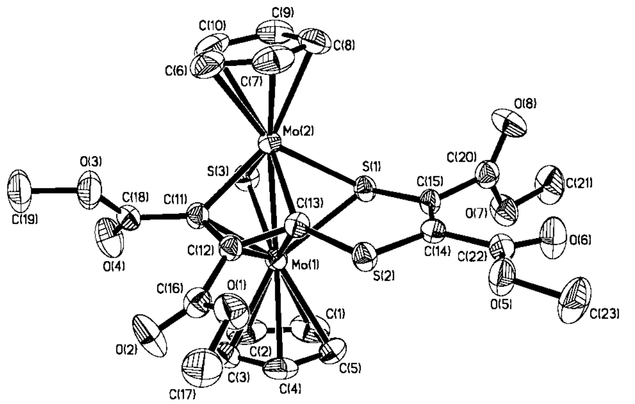


Fig. 1 Molecular structure of $[Mo_2(\mu\text{-}S)\{\mu\text{-}SC(CO_2Me){=}C(CO_2Me)\text{-}SCC(CO_2Me){=}C(CO_2Me)\}Cp_2]$ **8** in the crystal showing the atomic numbering scheme.

soluble in polar solvents such as CH_2Cl_2, but not in saturated hydrocarbons. Its IR spectrum confirmed complete loss of all the carbonyl ligands, and mass spectral and analytical data indicated retention of the alkyne ligand and incorporation of one molecule of heterocycle. The ^1H NMR spectrum accordingly showed equivalent Cp ligands and four inequivalent CO_2Me groups (two of which were coincidentally equivalent in the room temperature spectrum). In addition to these features, the ^{13}C NMR spectrum contained five peaks, two at approximately δ 135 and three around δ 110, which could be assigned to the remaining carbons of the thione and the alkyne.

The molecular structure of complex **8** as determined by X-ray diffraction is shown in Fig. 1, with important bond lengths and angles collected in Table 1; this structure was reported in our preliminary paper,[8] but for ease of comparison we reiterate the main points here. The two molybdenum atoms are joined by a short bond [2.5825(7)Å], which from electron counting considerations could be regarded as a double bond, assuming that the 18-electron rule is obeyed in a compound which is formally of Mo^{IV}. Cleavage of the C=S bond of the thione has produced the bridging sulfido ligand S(3). The remaining bridging positions are occupied by a new ligand originating from ring opening of the remaining portion of the heterocycle and coupling to the alkyne, forming a seven atom chain which is co-ordinated as a bridging thiolate through S(1) and as a bridging dimetalla-allyl unit through carbons C(11), C(12) and C(13) (the original thione carbon). In the light of this structure, we can assign the two ^{13}C NMR peaks at δ 134.5 and 132.6 to the unco-ordinated CR=CR group derived from the thione, and the three peaks at approximately δ 110 to the three carbons of the dimetalla-allyl unit.

The atoms Mo(1), Mo(2), S(1) and C(11) form a plane which intersects at an angle of 90°, within experimental error, with a second plane formed by Mo(1), Mo(2), S(3) and C(13). This arrangement is reminiscent of that found in other quadruply bridged molybdenum(IV) complexes such as $[Mo_2(\mu\text{-}S)_2(\mu\text{-}SMe)_2Cp_2]$[11] and $[Mo_2(\mu\text{-}S)_2(\mu\text{-}SPr^i)(\mu\text{-}PPh_2)Cp_2]$,[12] and can be regarded as two base-sharing four-legged piano stool units. This compound, together with the others described in this paper, are the first in which carbon atoms form part of this quadruply bridged motif, though examples are also known in which nitrogen or halide ligands accompany three sulfur donors.[13]

Table 1 Selected bond lengths [Å] and angles [°] for complex **8**

Mo(1)–C(11)	2.176(5)	Mo(1)–C(13)	2.223(5)
Mo(1)–S(3)	2.3434(15)	Mo(1)–C(12)	2.360(5)
Mo(1)–S(1)	2.4594(14)	Mo(1)–Mo(2)	2.5825(7)
Mo(2)–C(11)	2.162(5)	Mo(2)–C(13)	2.200(5)
Mo(2)–S(3)	2.3246(15)	Mo(2)–S(1)	2.4715(15)
S(1)–C(15)	1.769(5)	S(2)–C(14)	1.737(5)
S(2)–C(13)	1.739(5)	C(11)–C(12)	1.416(7)
C(12)–C(13)	1.415(7)	C(14)–C(15)	1.349(7)
C(11)–Mo(1)–C(13)	61.6(2)	C(11)–Mo(1)–S(3)	76.52(14)
C(13)–Mo(1)–S(3)	109.89(13)	C(11)–Mo(1)–C(12)	36.1(2)
C(13)–Mo(1)–C(12)	35.8(2)	S(3)–Mo(1)–C(12)	109.68(13)
C(11)–Mo(1)–S(1)	111.45(14)	C(13)–Mo(1)–S(1)	74.14(14)
S(3)–Mo(1)–S(1)	72.65(5)	C(12)–Mo(1)–S(1)	108.03(13)
C(11)–Mo(1)–Mo(2)	53.23(14)	C(13)–Mo(1)–Mo(2)	53.86(13)
S(3)–Mo(1)–Mo(2)	56.07(4)	C(12)–Mo(1)–Mo(2)	65.77(12)
S(1)–Mo(1)–Mo(2)	58.65(4)	C(11)–Mo(2)–C(13)	62.2(2)
C(11)–Mo(2)–S(3)	77.18(15)	C(13)–Mo(2)–S(3)	111.42(13)
C(11)–Mo(2)–S(1)	111.47(14)	C(13)–Mo(2)–S(1)	74.28(14)
S(3)–Mo(2)–S(1)	72.74(5)	C(11)–Mo(2)–Mo(1)	53.70(13)
C(13)–Mo(2)–Mo(1)	54.69(13)	S(3)–Mo(2)–Mo(1)	56.76(4)
S(1)–Mo(2)–Mo(1)	58.19(4)	C(15)–S(1)–Mo(1)	114.1(2)
C(15)–S(1)–Mo(2)	113.4(2)	Mo(1)–S(1)–Mo(2)	63.16(4)
C(14)–S(2)–C(13)	103.8(2)	Mo(2)–S(3)–Mo(1)	67.18(4)
C(12)–C(11)–Mo(2)	95.2(3)	C(12)–C(11)–Mo(1)	79.1(3)
Mo(2)–C(11)–Mo(1)	73.1(2)	C(13)–C(12)–C(11)	105.4(4)
C(13)–C(12)–Mo(1)	66.8(3)	C(11)–C(12)–Mo(1)	64.8(3)
C(12)–C(13)–S(2)	123.2(4)	C(12)–C(13)–Mo(2)	93.6(3)
S(2)–C(13)–Mo(2)	141.6(3)	C(12)–C(13)–Mo(1)	77.4(3)
S(2)–C(13)–Mo(1)	123.0(3)	Mo(2)–C(13)–Mo(1)	71.45(15)
C(15)–C(14)–S(2)	127.2(4)	C(14)–C(15)–S(1)	129.7(4)

In the ^1H NMR spectrum of complex **8** the two cyclopentadienyl ligands are equivalent, even at low temperature (218 K). This is clearly not the case in the solid-state structure as the central carbon of the dimetalla-allyl unit, C(12), is displaced towards Mo(1) [Mo(1)–C(12) 2.360(5), Mo(2)···C(12) non-bonding distance 2.690 Å]. We therefore postulate that in solution a rapid fluxional process occurs in which the σ, π-co-ordination modes of this ligand are interchanged, which would merely require C(12) to flip between the two metal atoms. Further support for this idea is provided by the crystal structure of **17**, discussed below. Moreover the three previously recorded

Table 2 Comparison of ^{13}C NMR data for the dimetalla-allyl ligands in complexes **8** and **11**–**14**. The numbering system used is that of the crystal structures

Compound	R^1	R^2	δ C(11)	δ C(12)	δ C(13)
8	CO_2Me	CO_2Me	112.9	111.4	108.4
11	CO_2Et	CO_2Et	113.9	111.1	108.3
12	Ph	Ph	132.1	128.9	106.3
13	CO_2Et	Ph	132.7	108.7	106.6
14	Ph	CO_2Et	113.4	129.8	105.1

examples in which a similar C_3R_3 ligand bridges a CpMo–MoCp bond, notwithstanding the fact that all form part of larger nuclearity clusters, all display the same phenomenon: solution equivalence of the Cp ligands, but asymmetric co-ordination of the dimetalla-allyl in the solid state.[14] This militates against the situation being merely due to crystal packing forces.

Generality of the reaction. Substituted 1,3-dithiole-2-thiones in which the 4 and 5 positions are occupied by thiolate groups are readily available by alkylation or acylation of the $C_3S_5^{2-}$ dianion (dmit), which can be made by sodium reduction of CS_2 in DMF and stabilised as $[NEt_4]_2[Zn(dmit)_2]$.[9] We therefore examined the reactions of heterocycles **6** (R = SMe) and **7** (R = SCOPh), prepared in this way, with **1**. Analogous products **9** and **10** were formed in crystallised yields of 44 and 54% respectively.[8] Their characterising data are unremarkable in the light of the structure of **8**. One interesting feature however is that all three compounds display FAB mass spectra consisting of an envelope of peaks corresponding to the molecular ion and a second which corresponds to the loss of C_2R_2, *i.e.* the original thione backbone. Solution thermolysis of the compounds does not effect this transformation.

It appears that all three sulfur atoms of the trithiocarbonate group are required for successful reaction as other related heterocycles containing O or NPr^i in place of S did not give any tractable products.[8] The effect of changing the alkyne ligand was also explored. Complexes **2** ($R^1 = R^2 = CO_2Et$) and **3** ($R^1 = R^2 = Ph$) both reacted successfully with heterocycle **5** to give compounds **11** (69%) and **12**[8] (20%) respectively. Complex **4**, containing the unsymmetrical alkyne $PhC\equiv CCO_2Et$, also reacted to give two isomeric products **13** and **14** in which the thione is coupled to the CCO_2Et or the CPh terminus of the alkyne respectively. The fact that these products are formed in roughly equal amounts shows that there is little regioselectivity in the coupling process in this case. Reactions of **5** with complexes containing less strongly bound alkynes such as acetylene or but-2-yne led only to decomposition.

Complexes **11**–**14** were characterised by their spectroscopic data and also by X-ray crystallography in the case of the isomers **13** and **14** in order to confirm the substitution pattern of the dimetalla-allyl ligand. One notable feature here is that replacement of an ester substituent on the dimetalla-allyl ligand by Ph causes a downfield shift of 20–30 ppm in the ^{13}C NMR spectrum for that carbon atom, which in conjunction with the X-ray data allows us to assign the peaks unambiguously (Table 2). In each case the original thione carbon C(13) is assigned as that occurring at highest field. As with **8**–**10**, the compounds all show ready loss of the $C_2(CO_2Me)_2$ unit from the hybrid ligand in their mass spectra.

The molecular structures of complexes **13** and **14** are shown in Figs. 2 and 3. For ease of comparison selected bond lengths and angles are collected in Table 3; the same numbering scheme is used for both structures. Both molecules contain the same gross features found in **8**: short Mo–Mo bond, and a quadruply bridged structure with three positions occupied by the hybrid ligand and the other by the symmetrically bridging sulfido ligand. In complex **13** the thione carbon is linked to the alkyne carbon which bears the CO_2Et substituent whereas in **14** it is joined to the CPh group. It is also noticeable that in both isomers the unsymmetrical co-ordination of the dimetalla-allyl fragment is observed: C(12) is bonded to Mo(1) [distances of 2.382(4) and 2.454(5) Å for **13** and **14** respectively] but is much further away from Mo(2) (non-bonding distances of 2.678 and 2.658 Å respectively).

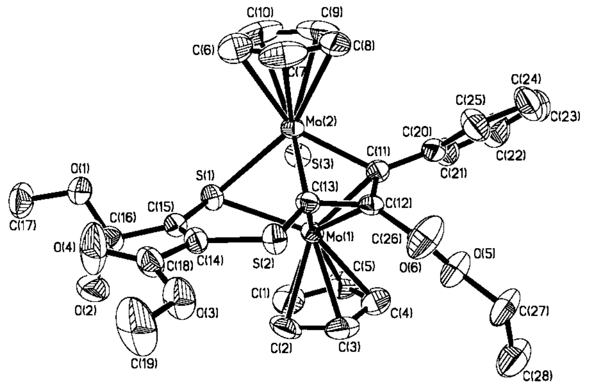


Fig. 2 Molecular structure of $[Mo_2(\mu\text{-}S)\{\mu\text{-}SC(CO_2Me)=C(CO_2Me)SCC(CO_2Et)=C(Ph)\}Cp_2]$ **13**.

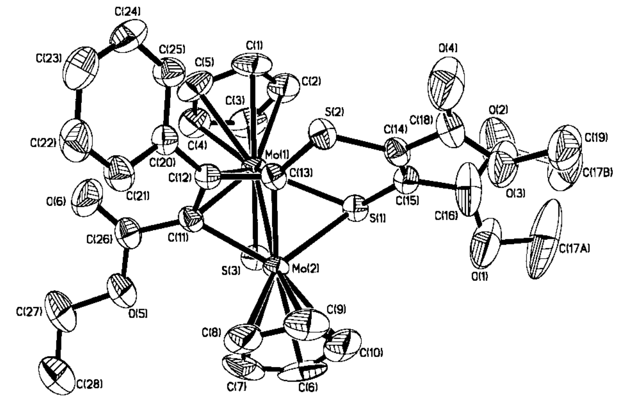
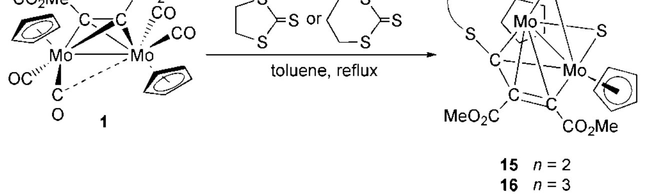


Fig. 3 Molecular structure of $[Mo_2(\mu\text{-}S)\{\mu\text{-}SC(CO_2Me)=C(CO_2Me)SCC(Ph)=C(CO_2Et)\}Cp_2]$ **14**.

We also investigated whether cyclic trithiocarbonates with saturated backbones could be tolerated in the reaction. To this end, compound **1** was treated with ethylene trithiocarbonate and propylene trithiocarbonate (1,3-dithiane-2-thione) under similar conditions (Scheme 3). These reactions were noticeably slower than those involving **5**, typically taking 16 h to reach completion, but each gave a single green product, **15** and **16** respectively, in reasonable yield (55%). The characterising data for these compounds are similar to those of **8**: in the ^1H and ^{13}C NMR spectra one observes equivalent Cp ligands, inequivalent CO_2Me groups, and signals due to two or three CH_2 units, the protons of which are all inequivalent. In the ^{13}C NMR spectrum three signals are found for the dimetalla-allyl unit in the expected positions.



Scheme 3 Reactions of complex **1** with saturated cyclic trithiocarbonates.

Table 3 Selected bond lengths [Å] and angles [°] for complexes **13** and **14**

	13	**14**
Mo(1)–C(11)	2.188(4)	2.191(5)
Mo(1)–C(13)	2.242(4)	2.202(5)
Mo(1)–S(3)	2.326(2)	2.334(2)
Mo(1)–C(12)	2.382(4)	2.454(5)
Mo(1)–S(1)	2.4814(12)	2.4812(15)
Mo(1)–Mo(2)	2.5770(6)	2.5700(7)
Mo(2)–C(13)	2.154(5)	2.183(5)
Mo(2)–C(11)	2.187(4)	2.141(5)
Mo(2)–S(3)	2.3092(12)	2.3158(15)
Mo(2)–S(1)	2.4819(12)	2.4535(14)
S(1)–C(15)	1.754(5)	1.773(6)
S(2)–C(13)	1.717(4)	1.728(5)
S(2)–C(14)	1.745(5)	1.743(6)
C(11)–C(12)	1.411(7)	1.417(7)
C(12)–C(13)	1.427(6)	1.408(7)
C(14)–C(15)	1.331(7)	1.336(8)
C(11)–Mo(1)–C(13)	61.3(2)	60.9(2)
C(11)–Mo(1)–S(3)	77.56(14)	77.6(2)
C(13)–Mo(1)–S(3)	108.45(12)	109.89(14)
C(11)–Mo(1)–C(12)	35.7(2)	34.9(2)
C(13)–Mo(1)–C(12)	35.78(14)	34.7(2)
S(3)–Mo(1)–C(12)	109.67(11)	108.95(12)
C(11)–Mo(1)–S(1)	111.96(11)	110.14(14)
C(13)–Mo(1)–S(1)	72.25(11)	72.66(14)
S(3)–Mo(1)–S(1)	73.24(4)	72.66(5)
C(12)–Mo(1)–S(1)	106.58(10)	105.04(12)
C(11)–Mo(1)–Mo(2)	53.89(11)	52.73(14)
C(13)–Mo(1)–Mo(2)	52.54(11)	53.78(14)
S(3)–Mo(1)–Mo(2)	55.92(3)	56.11(4)
C(12)–Mo(1)–Mo(2)	65.24(11)	63.83(12)
S(1)–Mo(1)–Mo(2)	58.73(3)	58.09(3)
C(13)–Mo(2)–C(11)	62.7(2)	61.9(2)
C(13)–Mo(2)–S(3)	112.23(12)	111.24(13)
C(11)–Mo(2)–S(3)	77.94(13)	78.93(15)
C(13)–Mo(2)–S(1)	73.66(11)	73.53(13)
C(11)–Mo(2)–S(1)	111.99(12)	112.93(13)
S(3)–Mo(2)–S(1)	73.51(4)	73.48(5)
C(13)–Mo(2)–Mo(1)	55.71(11)	54.47(13)
C(11)–Mo(2)–Mo(1)	53.94(11)	54.50(13)
S(3)–Mo(2)–Mo(1)	56.53(4)	56.77(4)
S(1)–Mo(2)–Mo(1)	58.71(3)	59.14(4)
C(15)–S(1)–Mo(1)	114.4(2)	118.1(2)
C(15)–S(1)–Mo(2)	113.0(2)	108.6(2)
Mo(1)–S(1)–Mo(2)	62.56(3)	62.77(4)
C(13)–S(2)–C(14)	102.5(2)	102.6(3)
Mo(2)–S(3)–Mo(1)	67.55(4)	67.11(4)
C(12)–C(11)–Mo(2)	93.7(3)	94.5(3)
C(12)–C(11)–Mo(1)	79.7(3)	82.8(3)
Mo(2)–C(11)–Mo(1)	72.17(13)	72.8(2)
C(11)–C(12)–C(13)	105.4(4)	103.9(4)
C(11)–C(12)–Mo(1)	64.7(2)	62.3(3)
C(13)–C(12)–Mo(1)	66.7(2)	62.8(3)
C(12)–C(13)–S(2)	121.7(4)	122.6(4)
C(12)–C(13)–Mo(2)	94.7(3)	93.0(3)
S(2)–C(13)–Mo(2)	139.4(2)	135.3(3)
C(12)–C(13)–Mo(1)	77.5(3)	82.5(3)
S(2)–C(13)–Mo(1)	129.5(2)	133.2(3)
Mo(2)–C(13)–Mo(1)	71.75(14)	71.8(2)
C(15)–C(14)–S(2)	126.7(4)	126.2(4)
C(14)–C(15)–S(1)	131.2(4)	131.0(4)

Reactions with acyclic trithiocarbonates. Since compounds of type **15** and **16** can be formed, with an aliphatic chain linking the two sulfurs of the trithiocarbonate, the next logical step was to investigate simple aliphatic trithiocarbonates, in which the linking group is removed altogether. Thus reactions of complex **1** with three representative trithiocarbonates $S{=}C(SR)_2$ (R = Me, Pr^i or Bu) were undertaken (Scheme 4). The reaction times were longer still (48–77 h) and the resulting yields lower (25–45%), but again single green products **17**–**19** could be isolated either as crystalline solids or, in the case of **19**, an oil.[8] The ^{1}H and ^{13}C NMR spectra again show the equivalent Cp ligands,

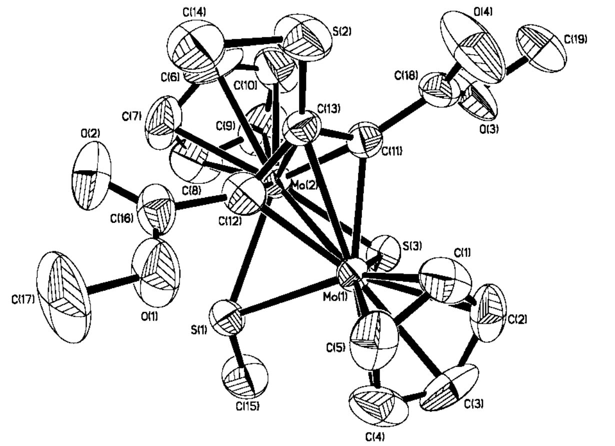
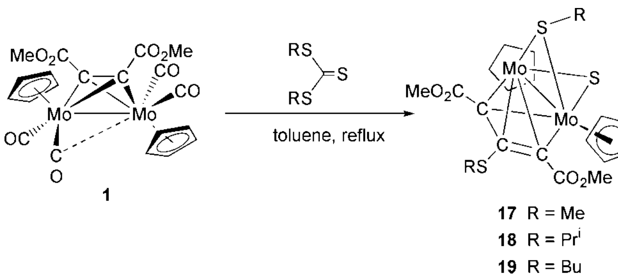


Fig. 4 Molecular structure of $[Mo_2(\mu\text{-}S)\{\mu\text{-}SMe\}\{\mu\text{-}C(CO_2Me)\text{-}C(SMe){=}C(CO_2Me)\}Cp_2]$ **17**. Only molecule 1 of the two independent molecules in the unit cell is shown.



Scheme 4 Reactions of complex **1** with acyclic trithiocarbonates.

and the inequivalence both of the ester functionalities and of the substituents R. However a significant difference was observed in the ^{13}C NMR signals attributed to the dimetalla-allyl unit. In the spectrum of **17** these occur at δ 141.2, 102.7 and 98.0, which, when compared to the values in Table 2, show that one peak is shifted downfield and the other two slightly upfield, such that one of them now appears at a lower chemical shift than for the Cp ligands.

Determination of the structure of complex **17** revealed an unexpected feature which accounts for this change. The crystal contains two independent molecules in the unit cell. One is shown in Fig. 4, and selected bond lengths and angles for both are given in Table 4. The only significant difference between them lies in the position of C(13), which is discussed further below, until which we confine our attention to the illustrated molecule 1. The Mo–Mo bond of 2.5605(10) Å is slightly shorter than that in **8**, **13** and **14**, and is bridged symmetrically by sulfido ligand S(3) and the methanethiolate sulfur S(1). The methyl substituent on this sulfur is directed away from the dimetalla-allyl group, whereas in the other structures the linking group constrains the thiolate substituent in the direction of the dimetalla-allyl.

The dimetalla-allyl ligand provides the unexpected feature. By analogy with the other compounds discussed, we had expected the C(SMe) unit derived from the trithiocarbonate to occupy the terminal position within this ligand, *i.e.* a C(SMe)-C(CO$_2$Me)C(CO$_2$Me) arrangement. Instead it occupies the *central* position in a C(CO$_2$Me)C(SMe)C(CO$_2$Me) unit. The numbering scheme adopted for the dimetalla-allyl ligand is consistent with those used previously in that the alkyne carbons are designated as C(11) and C(12) and that derived from the thione as C(13); in this case, therefore, C(13) is the *central* atom of this ligand. Since the two terminal carbons C(11) and C(12) are in very similar environments (rendered inequivalent only by the presence of the bridging thiolate substituent), we assign the two higher-field ^{13}C NMR signals to these, and the low field signal to the central C(SMe) group.

Table 4 Selected bond lengths [Å] and angles [°] for the two independent molecules of complex **17**

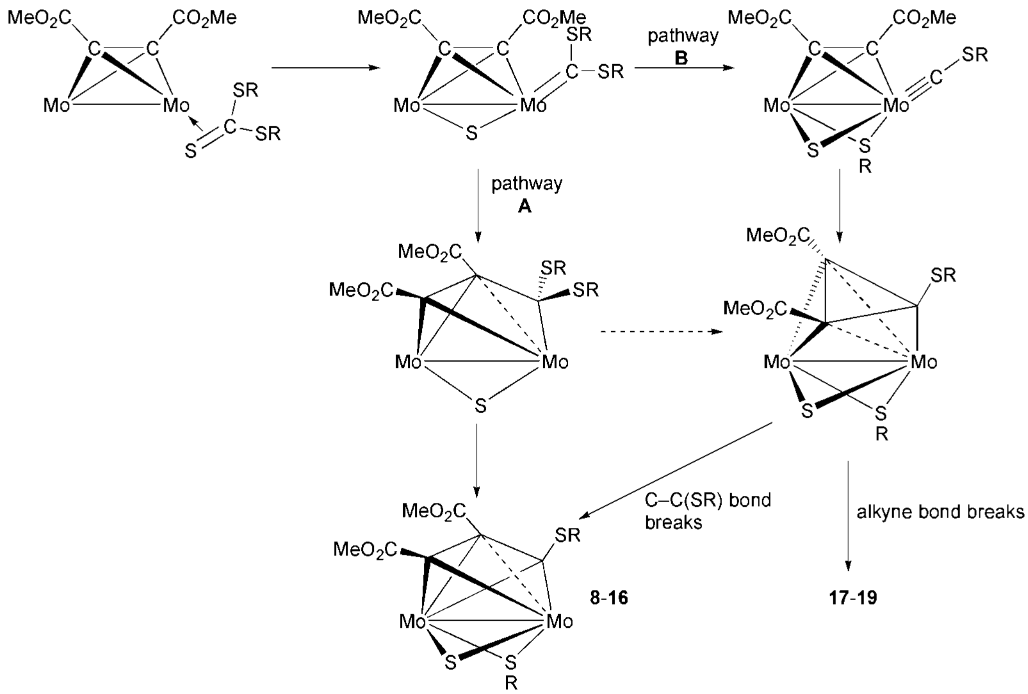
Mo(1)–C(11)	2.173(5)	Mo(1)–C(12)	2.204(6)
Mo(1)–S(3)	2.3177(15)	Mo(1)–S(1)	2.476(2)
Mo(1)–Mo(2)	2.5605(10)	Mo(1)–C(13)	2.564(5)
Mo(2)–C(11)	2.152(5)	Mo(2)–C(12)	2.203(6)
Mo(2)–S(3)	2.322(2)	Mo(2)–S(1)	2.466(2)
Mo(2)–C(13)	2.594(6)	S(2)–C(13)	1.749(6)
C(11)–C(13)	1.429(7)	C(12)–C(13)	1.393(8)
Mo(1A)–C(11A)	2.184(6)	Mo(1A)–C(12A)	2.199(6)
Mo(1A)–S(3A)	2.328(2)	Mo(1A)–S(1A)	2.465(2)
Mo(1A)–C(13A)	2.509(6)	Mo(1A)–Mo(2A)	2.5596(8)
Mo(2A)–C(11A)	2.149(5)	Mo(2A)–C(12A)	2.198(5)
Mo(2A)–S(3A)	2.314(2)	Mo(2A)–S(1A)	2.469(2)
S(2A)–C(13A)	1.758(6)	C(11A)–C(13A)	1.426(8)
C(12A)–C(13A)	1.405(7)		
C(11)–Mo(1)–C(12)	61.2(2)	C(11)–Mo(1)–S(3)	76.96(15)
C(12)–Mo(1)–S(3)	111.0(2)	C(11)–Mo(1)–S(1)	110.03(15)
C(12)–Mo(1)–S(1)	68.5(2)	S(3)–Mo(1)–S(1)	79.45(5)
C(11)–Mo(1)–Mo(2)	53.33(15)	C(12)–Mo(1)–Mo(2)	54.5(2)
S(3)–Mo(1)–Mo(2)	56.60(4)	S(1)–Mo(1)–Mo(2)	58.59(4)
C(11)–Mo(1)–C(13)	33.9(2)	C(12)–Mo(1)–C(13)	32.9(2)
S(3)–Mo(1)–C(13)	106.11(13)	S(1)–Mo(1)–C(13)	98.80(13)
Mo(2)–Mo(1)–C(13)	60.82(12)	C(11)–Mo(2)–C(12)	61.5(2)
C(11)–Mo(2)–S(3)	77.26(15)	C(12)–Mo(2)–S(3)	110.8(2)
C(6)–Mo(2)–S(3)	143.7(3)	C(7)–Mo(2)–S(3)	147.6(3)
C(11)–Mo(2)–S(1)	111.2(2)	C(12)–Mo(2)–S(1)	68.7(2)
S(3)–Mo(2)–S(1)	79.59(5)	C(11)–Mo(2)–Mo(1)	54.08(15)
C(12)–Mo(2)–Mo(1)	54.5(2)	S(3)–Mo(2)–Mo(1)	56.42(4)
S(1)–Mo(2)–Mo(1)	59.00(4)	C(11)–Mo(2)–C(13)	33.4(2)
C(12)–Mo(2)–C(13)	32.5(2)	S(3)–Mo(2)–C(13)	105.02(12)
S(1)–Mo(2)–C(13)	98.28(12)	Mo(1)–Mo(2)–C(13)	59.66(12)
Mo(2)–S(1)–Mo(1)	62.41(4)	Mo(1)–S(3)–Mo(2)	66.98(4)
C(13)–C(11)–Mo(2)	90.5(3)	C(13)–C(11)–Mo(1)	88.2(3)
Mo(2)–C(11)–Mo(1)	72.6(2)	C(13)–C(12)–Mo(2)	89.4(4)
C(13)–C(12)–Mo(1)	88.0(4)	Mo(2)–C(12)–Mo(1)	71.1(2)
C(12)–C(13)–C(11)	104.2(5)	Mo(1)–C(13)–Mo(2)	59.51(12)
C(11A)–Mo(1A)–C(12A)	61.1(2)	C(11A)–Mo(1A)–S(3A)	76.4(2)
C(12A)–Mo(1A)–S(3A)	110.58(15)	C(11A)–Mo(1A)–S(1A)	110.27(15)
C(12A)–Mo(1A)–S(1A)	69.15(15)	S(3A)–Mo(1A)–S(1A)	79.07(6)
C(11A)–Mo(1A)–C(13A)	34.5(2)	C(12A)–Mo(1A)–C(13A)	33.9(2)
S(3A)–Mo(1A)–C(13A)	107.22(13)	S(1A)–Mo(1A)–C(13A)	101.11(13)
C(11A)–Mo(1A)–Mo(2A)	53.17(15)	C(12A)–Mo(1A)–Mo(2A)	54.37(14)
S(3A)–Mo(1A)–Mo(2A)	56.28(5)	S(1A)–Mo(1A)–Mo(2A)	58.81(4)
C(13A)–Mo(1A)–Mo(2A)	62.90(12)	C(11A)–Mo(2A)–C(12A)	61.6(2)
C(11A)–Mo(2A)–S(3A)	77.4(2)	C(12A)–Mo(2A)–S(3A)	111.1(2)
C(11A)–Mo(2A)–S(1A)	111.4(2)	C(12A)–Mo(2A)–S(1A)	69.11(15)
S(3A)–Mo(2A)–S(1A)	79.26(6)	C(11A)–Mo(2A)–Mo(1A)	54.4(2)
C(12A)–Mo(2A)–Mo(1A)	54.41(15)	S(3A)–Mo(2A)–Mo(1A)	56.79(5)
S(1A)–Mo(2A)–Mo(1A)	58.69(4)	Mo(1A)–S(1A)–Mo(2A)	62.50(4)
Mo(2A)–S(3A)–Mo(1A)	66.93(5)	C(13A)–C(11A)–Mo(2A)	93.2(4)
C(13A)–C(11A)–Mo(1A)	85.3(3)	Mo(2A)–C(11A)–Mo(1A)	72.4(2)
C(13A)–C(12A)–Mo(2A)	91.8(4)	C(13A)–C(12A)–Mo(1A)	85.3(3)
Mo(2A)–C(12A)–Mo(1A)	71.2(2)	C(12A)–C(13A)–C(11A)	103.7(5)

The position of C(13) in the two independent molecules is worthy of further comment. In molecule 1, shown in the figure, C(13) is approximately equidistant from both molybdenum atoms [Mo(1)–C(13) 2.564(5), Mo(2)–C(13) 2.594(6) Å], whereas in the second molecule the situation is comparable to that found in the other structures discussed earlier, with one shorter bond and one longer, non-bonding distance [Mo(1A)–C(13A) 2.509(6), Mo(2A)···C(13A) 2.645 Å]. The energy difference between these two positions is evidently very small, since in this case the presence of two distinct molecules in the crystal is presumably due to crystal packing; therefore the flipping of the central carbon of the dimetalla-allyl ligand to render the two Cp ligands equivalent in the NMR spectra is clearly a viable fluxional process.

It is interesting that in the reactions of dialkyl trithiocarbonates, dithioesters and related compounds with $[Mo_2(CO)_4Cp_2]$, described by Alper *et al.*,[15] and with $[Fe_2(CO)_9]$, studied by Patin and co-workers, cleavage of the C–S bond was often observed whereas complete cleavage of the C=S bond could not be achieved.[16] In contrast, reaction of ethylene trithiocarbonate with $[Fe_2(CO)_9]$ did result in the isolation of a compound containing a dithiocarbene ligand.[17]

Mechanistic considerations. Given that the reactions leading to complexes **8**–**19** involve cleavage of C=S and C–S bonds as well as C–C bond formation, it is remarkable that single products are isolated in relatively good yields. No intermediates were observed when monitoring the reactions by TLC. Presumably, as in other reactions of **1**, the initial step involves thermal dissociation of a CO ligand. Co-ordination of the thione could then occur either through the thione sulfur or more likely in a side-on manner through the C=S bond. We have additional evidence elsewhere that such a co-ordination mode is possible.[18]

Our initial theory for the mechanism of formation of complex **8** involved cleavage of the C=S bond to give an intermediate dithiolium carbene species (Scheme 5, pathway A). Literature precedent for this is provided by the reaction of the parent 1,3-dithiole-2-thione with $[Fe_2(CO)_9]$ which afforded $[Fe_3(\mu_3\text{-}S)_2(CO)_8(=CS_2C_2H_2)]$ containing a dithiocarbene ligand formed by cleavage of the C=S bond; the proposed mechanism



Scheme 5 Possible mechanism of formation of the new complexes. The Cp and carbonyl ligands have been omitted for clarity.

involved initial desulfurisation of the thione to give $[Fe_3(\mu_3\text{-}S)_2(CO)_9]$, which trapped the free carbene by CO substitution.[19] Free dithiolium carbenes are thought to be relatively stable due to their pseudo-aromatic nature, and were implicated by Hartzler in reactions of activated alkynes with CS_2.[20] They can also be formed at metal centres by treatment of CS_2 complexes with alkynes.[21] In the present case, coupling of the carbene with the alkyne ligand and ring opening by cleavage of one of the C–S bonds would give the observed product.

We were however forced to reconsider this mechanism by the structure determination of complex **17** as it cannot account for the apparent insertion of the C(SR) unit into the alkyne. A viable alternative is shown as pathway B of Scheme 5. After formation of the dithiocarbene, cleavage of the C–S bond occurs to give a thiocarbyne ligand, which undergoes coupling with the alkyne ligand to give a three-membered ring. Cleavage of the original alkyne C–C bond would then give rise to products of type **17**–**19**. Obviously in the case of the acyclic trithiocarbonates this is completely regioselective as no isomers were observed containing a chain with the C(SR) group at a terminal carbon. This mechanism could also account for the formation of products **8**–**16** from the cyclic trithiocarbonates by cleavage of one of the other C–C bonds: insertion of the thione carbon into the centre of the alkyne cannot occur because it is anchored to the thiolate bridge through the spacer group [CR=CR or $(CH_2)_n$].

In support of this proposal, by far the most common literature route to dimetalla-allyl complexes is though coupling of an alkyne with a carbyne (alkylidyne) ligand, with a rather smaller number arising through ring opening of cyclopropenes. Moreover, similar three-membered ring intermediates have been proposed for other cases where a CR unit apparently inserts into the centre of an alkyne. For example, the reaction of $[WFe_2(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_8Cp]$ with C_2Ph_2 gave two dinuclear dimetalla-allyl complexes, one of which contained a rearranged μ-CPhC(C_6H_4Me-4)CPh chain,[22] and interconversion of two dimetalla-allyl isomers was observed in $[W_2(\mu\text{-}CSiMe_3)(\mu\text{-}CMeCMeCSiMe_3)(CH_2SiMe_3)_4]$, which was found to undergo a fluxional process in which the substituents of the bridging ligand changed places, *i.e.* $CMeCMeCSiMe_3$ was in equilibrium with $CMeC(SiMe_3)CMe$.[23] Further examples involving dimetalla-allyl ligands are known on trinuclear metal centres.[24]

Conclusion

The reactions of the molybdenum alkyne complexes $[Mo_2(\mu\text{-}R^1C{\equiv}CR^2)(CO)_4Cp_2]$ with cyclic and acyclic trithiocarbonates provide convenient routes to quadruply bridged molybdenum(IV) dimers containing, for the first time, mixed sulfur–carbon ligation. This is another example of how our oxidative decarbonylation strategy involving C–S or C=S bond cleavage can lead from low-valent carbonyl precursors to higher oxidation state Mo/S species which are inaccessible from starting materials such as $[Mo_2(\mu\text{-}S)_2(\mu\text{-}SH)_2Cp_2]$. The present case also involves C–C bond forming processes, and constitutes one of the simplest routes available to complexes containing dimetalla-allyl ligands, which will allow us to explore their reactivity in more detail in future work.

Experimental

General experimental techniques were as described in recent papers from this laboratory.[25] Infrared spectra were recorded in CH_2Cl_2 solution on a Perkin-Elmer 1600 FT-IR machine using 0.5 mm NaCl cells, ^{1}H and ^{13}C NMR spectra in $CDCl_3$ solution on a Bruker AC250 machine with automated sample-changer or an AMX400 spectrometer. Chemical shifts are given on the δ scale relative to $SiMe_4$ (δ 0.0). The ^{13}C-{^{1}H} NMR spectra were routinely recorded using an attached proton test technique (JMOD pulse sequence). 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. Satisfactory analytical data have been obtained for all new complexes and have been deposited as Electronic Supplementary Information.

The alkyne complexes **1**–**4** were prepared by a slight modification of the literature method.[26] The heterocycles **5**,[27] **6** and **7**[28] were prepared by literature methods, as were 1,3-dithiane-2-thione[29] and the dialkyl trithiocarbonates.[30,31] Ethylene trithiocarbonate was obtained commercially.

Syntheses

$[Mo_2(\mu\text{-}S)\{\mu\text{-}SC(CO_2Me){=}C(CO_2Me)SCC(CO_2Me){=}C(CO_2Me)\}Cp_2]$ 8. A solution of $[Mo_2(\mu\text{-}MeO_2CC_2CO_2Me)(CO)_4Cp_2]$

1 (783 mg, 1.36 mmol) and 4,5-bis(methoxycarbonyl)-1,3-dithiole-2-thione **5** (340 mg, 1.36 mmol) in toluene (150 cm^3) was heated to reflux for 6 h, with the reaction progress monitored by TLC. The solvent was removed by rotary evaporation and the solid residue absorbed onto silica prior to column chromatography. The green product was eluted in CH_2Cl_2–acetone (50 : 1). Recrystallisation from dichloromethane and light petroleum yielded dark green-black crystals (618 mg, 64%). Crystals suitable for X-ray diffraction were grown by diffusion of a strong CH_2Cl_2 solution into light petroleum. mp 200–203 °C. ^1H NMR (−55 °C): δ 5.75 (s, 10 H, Cp), 3.89, 3.88, 3.87, 3.60 (all s, 3 H, Me). ^{13}C NMR: δ 174.4, 168.5, 164.1, 161.5 (all CO$_2$Me), 134.5, 132.6 (CCO$_2$Me), 112.9, 111.4, 108.4 (2 CCO$_2$Me + μ-C of dimetalla-allyl), 99.8 (Cp), 53.3, 53.2, 52.8, 52.2 (all Me). MS: *m*/*z* 715 (M^+) and 572 (M^+ − DMAD).

[Mo$_2$(μ-S){μ-SC(SMe)=C(SMe)SCC(CO$_2$Me)=C(CO$_2$Me)}-Cp$_2$] 9. A solution of complex **1** (0.50 g, 0.87 mmol) and 4,5-bis(methylsulfanyl)-1,3-dithiole-2-thione (0.20 g, 0.88 mmol) in toluene (150 cm^3) was heated to reflux for 7 h. Subsequent column chromatography gave a green band of **9** (0.265 g, 44%), eluted in CH_2Cl_2–acetone (100 : 1). mp 200–202 °C. ^1H NMR: δ 5.78 (s, 10 H, Cp), 3.85, 3.58 (both s, 3 H, CO$_2$Me), 2.52, 2.48 (both s, 3 H, SMe). ^{13}C NMR: δ 174.0, 161.7 (CO$_2$Me), 137.0, 124.3 (CSMe), 110.7, 110.4, 109.9 (2 CCO$_2$Me + μ-C), 99.7 (Cp), 52.6, 52.0 (CO$_2$*Me*), 20.2, 19.8 (SMe). MS: *m*/*z* 691 (M^+) and 572 [M^+ − C_2(SMe)$_2$].

[Mo$_2$(μ-S){μ-SC(SCOPh)=C(SCOPh)SCC(CO$_2$Me)=C(CO$_2$-Me)}Cp$_2$] 10. Prepared as above from complex **1** (1.00 g, 1.74 mmol) and 4,5-bis(benzoylsulfanyl)-1,3-dithiole-2-thione (0.720 g, 1.77 mmol) in refluxing toluene (150 cm^3) over 6 h. Column chromatography gave **10** (0.813 g, 54%) as a green band, eluted with CH_2Cl_2–acetone (50 : 1). mp 168–170 °C. ^1H NMR: δ 7.96–7.37 (m, 10 H, Ph), 5.94 (s, 10 H, Cp), 3.85, 3.60 (both s, 3 H, CO$_2$Me). ^{13}C NMR: δ 189.3, 188.1 (COPh), 173.8, 161.5 (CO$_2$Me), 136.4 (C_{ipso}), 136.2 (CSCOPh), 135.9 (C_{ipso}), 134.1–127.6 (Ph), 125.4 (CSCOPh), 112.0, 110.7, 110.2 (2 CCO$_2$Me + μ-C), 100.2 (Cp), 52.7, 52.1 (Me). MS: *m*/*z* 871 (M^+) and 573 [M^+ − C_2(SCOPh)$_2$].

[Mo$_2$(μ-S){μ-SC(CO$_2$Me)=C(CO$_2$Me)SCC(CO$_2$Et)=C(CO$_2$-Et)}Cp$_2$] 11. A solution of complex **2** (1.00 g, 1.66 mmol) and compound **5** (0.423 g, 1.69 mmol, 1.02 equivalents) in toluene (150 cm^3) was heated to reflux for 6.5 h. The solvent was removed and the residue chromatographed. A green band of product was eluted in CH_2Cl_2–acetone (30 : 1). Recrystallisation from dichloromethane and light petroleum yielded dark green-black needles (0.849 g, 1.14 mmol, 69%). mp 182 °C. ^1H NMR: δ 5.73 (s, 10 H, Cp), 4.32, 4.03 (both, q, *J* = 7.1, CH$_2$), 3.86, 3.85 (both s, 3 H, CO$_2$Me), 1.35, 1.20 (both t, *J* = 7.1 Hz, Me of Et). ^{13}C NMR: δ 172.7, 168.5, 164.3, 161.0 (2 CO$_2$Me + 2 CO$_2$Et), 134.8, 132.2 (CCO$_2$Me), 113.9, 111.1, 108.3 (2 CCO$_2$Et + μ-C of dimetalla-allyl), 99.8 (Cp), 62.0, 60.5 (CH$_2$), 53.3, 53.2 (CO$_2$*Me*), 14.5, 14.3 (Me of Et). MS: *m*/*z* 743 (M^+) and 600 (M^+ − DMAD).

[Mo$_2$(μ-S){μ-SC(CO$_2$Me)=C(CO$_2$Me)SCCPh=CPh}Cp$_2$] 12. This compound was prepared as above from [Mo$_2$(μ-C$_2$-Ph$_2$)(CO)$_4$Cp$_2$] (0.5 g, 0.67 mmol) and **5** (0.204 g, 0.81 mmol) in refluxing toluene (150 cm^3) over 6 h. Column chromatography gave a green zone (0.126 g, 20%), eluted in CH_2Cl_2. mp 230–231 °C. ^1H NMR: δ 7.40–6.60 (m, 10 H, Ph), 5.60 (s, 10 H, Cp), 3.89, 3.89 (both s, 3 H, Me). ^{13}C NMR: δ 168.5, 164.8 (CO$_2$Me), 148.0 (C_{ipso}), 133.9 (CCO$_2$Me), 132.7 (CPh), 132.1 (CCO$_2$Me), 129.4–124.5 (m, Ph), 122.9 (CPh), 106.3 (μ-C), 99.4 (Cp) and 53.2 (coincident Me). MS: *m*/*z* 751 (M^+) and 608 (M^+ − DMAD).

[Mo$_2$(μ-S){μ-SC(CO$_2$Me)=C(CO$_2$Me)SCC(CO$_2$Et)=CPh}-Cp$_2$] 13 and [Mo$_2$(μ-S){μ-SC(CO$_2$Me)=C(CO$_2$Me)SCCPh=C(CO$_2$Et)}Cp$_2$] 14. A solution of [Mo$_2$(μ-PhC$_2$CO$_2$Et)(CO)$_4$-Cp$_2$] (1.00 g, 1.64 mmol) and compound **5** (0.42 g, 1.66 mmol) in toluene (50 cm^3) was heated to reflux for 5 h. The solvent was removed and the solid residue chromatographed. A green band consisting of a mixture of products **13** and **14** (0.61 g, 0.81 mmol, 49% crude yield) was eluted in CH_2Cl_2–acetone (50 : 1). Careful rechromatography yielded a green band of **13** (0.22 g, 0.29 mmol, 18%) eluted in a 200 : 1 mixture of the same solvents followed by a second green band of **14** (0.28 g, 0.38 mmol, 23%) eluted in a 50 : 1 mixture. Crystals of both isomers suitable for X-ray diffraction were grown by diffusion of a dichloromethane solution into light petroleum. Data for **13**: mp 194–196 °C; ^1H NMR: δ 7.19–6.75 (m, 5 H, Ph), 5.60 (s, 10 H, Cp), 4.21 (q, *J* = 7.2, 2 H, CH$_2$), 3.88, 3.88 (both s, 3 H, CO$_2$Me) and 1.16 (t, *J* = 7.2 Hz, 3 H, Me of Et); ^{13}C NMR: δ 168.7, 164.6, 161.6 (2 CO$_2$Me + CO$_2$Et), 148.0 (C_{ipso}), 134.9, 132.9 (CCO$_2$Me), 132.7 (CPh), 129.4–124.9 (m, Ph), 108.7, 106.6 (CCO$_2$Et + μ-C), 61.6 (CH$_2$), 53.3, 53.2 (CO$_2$*Me*) and 14.2 (Me of Et); MS: *m*/*z* 747 (M^+) and 604 (M^+ − DMAD). Data for **14**: mp 226–227 °C; ^1H NMR: δ 7.53–7.42 (m, Ph), 5.71 (s, 10 H, Cp), 3.96 (q, *J* = 7.1, 2 H, CH$_2$), 3.87, 3.86 (both s, 3 H, CO$_2$Me) and 1.08 (t, *J* = 7.1 Hz, 3 H, Me of Et); ^{13}C NMR: δ 173.6, 168.5, 164.6 (2 CO$_2$Me + CO$_2$Et), 133.9, 131.5 (CCO$_2$Me), 130.0–128.8 (m, Ph), 129.8 (C_{ipso} + CPh), 113.4, 105.1 (CCO$_2$Et + μ-C), 99.4 (Cp), 60.3 (CH$_2$), 53.3, 53.2 (CO$_2$*Me*), 14.3 (Me of Et); MS: *m*/*z* 747 (M^+) and 604 (M^+ − DMAD).

[Mo$_2$(μ-S){μ-SCH$_2$CH$_2$SCC(CO$_2$Me)=C(CO$_2$Me)}Cp$_2$] 15. A solution of complex **1** (1.00 g, 1.74 mmol) and ethylene trithiocarbonate (260 mg, 1.91 mmol) in toluene (150 cm^3) was heated to reflux for 16 h. After removal of the solvent, chromatography of the residue gave a single green zone consisting of **15**, which was eluted with CH_2Cl_2–acetone (16 : 1). Recrystallisation from dichloromethane and light petroleum gave pure **15** (0.603 g, 57%) as dark green mildly air-sensitive needles. mp 172–173 °C. ^1H NMR: δ 6.03 (s, 10 H, Cp), 3.75, 3.48 (both s, 3 H, Me), 2.71, 2.29 (both m, 2 H, CH$_2$). ^{13}C NMR: δ 174.5, 162.3 (CO$_2$Me), 123.1, 111.4, 104.6 (2 CCO$_2$-Me + μ-C), 99.7 (Cp), 52.2, 51.7 (Me), 35.9, 29.8 (CH$_2$). MS: *m*/*z* 601 (M^+) and 573 (M^+ − C_2H_4).

[Mo$_2$(μ-S){μ-SCH$_2$CH$_2$CH$_2$SCC(CO$_2$Me)=C(CO$_2$Me)}Cp$_2$] 16. In a similar manner to the above, reaction of complex **1** (1.00 g, 1.74 mmol) with 1,3-dithiane-2-thione (262 mg, 1.74 mmol) in refluxing toluene (150 cm^3) for 17 h gave a green band of **16** on elution of the chromatography column with CH_2Cl_2–acetone (30 : 1). Yield 0.59 g, 55%. mp 183–185 °C. ^1H NMR: δ 6.02 (s, 10 H, Cp), 3.77, 3.48 (both s, 3 H, Me), 2.84–2.77 (m, 4 H, 2 CH$_2$) and 1.82 (m, 2 H, CH$_2$). ^{13}C NMR: δ 174.5, 163.2 (CO$_2$Me), 129.8, 121.4, 102.9 (2 CCO$_2$Me + μ-C), 99.7 (Cp), 52.3, 51.7 (Me), 37.0, 32.5, 31.2 (CH$_2$). MS: *m*/*z* 615 (M^+) and 573 [M^+ − C_3H_6].

[Mo$_2$(μ-S)(μ-SMe){μ-C(CO$_2$Me)C(SMe)C(CO$_2$Me)}Cp$_2$] 17. A solution of complex **1** (1.50 g, 2.59 mmol) and dimethyl trithiocarbonate (0.37 g, 2.67 mmol) in toluene (100 cm^3) was heated to reflux for 48 h. After removal of the solvent, the residue was absorbed onto silica and chromatographed. Elution with CH_2Cl_2–acetone (40 : 1) produced a green band of product **17** (0.69 mmol, 44%). Recrystallisation from dichloromethane and diethyl ether yielded dark green-black blocks suitable for X-ray diffraction. mp 184–200 °C (decomp.). ^1H NMR: δ 5.94 (s, 10 H, Cp), 3.67, 3.53 (both s, 3 H, CO$_2$Me), 2.18, 1.97 (both s, 3 H, SMe). ^{13}C NMR: δ 176.5, 175.5 (CO$_2$Me), 141.2 (CSMe), 102.7 (CCO$_2$Me), 99.6 (Cp), 98.0 (CCO$_2$Me), 52.8, 52.2 (CO$_2$Me), 46.3 (μ-SMe) and 13.7 (SMe). MS: *m*/*z* 603 (M^+), 587 (M^+ − Me), 572 (M^+ − 2 Me), 555 (M^+ − SMe) and 541 (M^+ − SMe and Me).

Table 5 Summary of crystallographic data for complexes **8**, **13**, **14** and **17**

	8	**13**	**14**	**17**
Empirical formula	$C_{23}H_{22}Mo_2O_8S_3$	$C_{28}H_{26}Mo_2O_6S_3$	$C_{28}H_{26}Mo_2O_6S_3$	$C_{19}H_{22}Mo_2O_4S_3$
Formula weight	714.47	746.55	746.55	602.43
T/K	293(2)	293(2)	293(2)	293(2)
Crystal system	Monoclinic	Orthorhombic	Triclinic	Monoclinic
Space group	$P2_1/c$	$P2_12_12_1$	$P\bar{1}$	$P2_1/n$
a/Å	17.994(4)	8.728(4)	10.051(2)	10.086(3)
b/Å	8.4820(10)	17.574(4)	12.137(4)	13.077(3)
c/Å	16.713(4)	18.489(4)	12.260(3)	33.601(7)
a/°			78.15(2)	
β/°	98.97(3)		77.210(10)	95.00(2)
γ/°			87.97(2)	
V/Å^3	2519.6(9)	2836.0(16)	1427.3(7)	4414.9(19)
Z	4	4	2	8
μ/mm^{-1}	1.291	1.147	1.139	1.442
Reflections collected	5513	3654	9417	10070
Independent reflections	4384 [R(int) = 0.0427]	3446 [R(int) = 0.0440]	7983 [R(int) = 0.1478]	7770 [R(int) = 0.0331]
Final $R1$, $wR2$ indices [$I > 2\sigma(I)$]	0.0393, 0.1014	0.0290, 0.0758	0.0773, 0.1964	0.0406, 0.0797
(all data)	0.0580, 0.1625	0.0300, 0.0768	0.0983, 0.2891	0.0671, 0.0913

[Mo_2(μ-S)(μ-SPr^i){μ-C(CO_2Me)C(SPr^i)C(CO_2Me)}Cp_2] 18. In a similar manner to the above, complex **1** (1.00 g, 1.74) and diisopropyl trithiocarbonate (342 mg, 1.76 mmol) reacted in refluxing toluene (150 cm^3) over 47 h to give complex **18** (0.37 g, 32%), isolated by column chromatography in CH_2Cl_2–acetone (60 : 1). Recrystallisation from cyclohexane gave dark green plates. mp 132–133 °C. ^{1}H NMR: δ 5.92 (s, 10 H, Cp), 3.66 (s, 3 H, CO_2Me), 3.52 (spt, J = 6.5, 1 H, CH), 3.49 (s, 3 H, CO_2Me), 1.19 (d, J = 6.5, 6 H, CH*Me*$_2$), 1.09 (d, J = 6.7, 6 H, CH*Me*$_2$) and 0.49 (spt, J = 6.7 Hz, 1 H, CH). ^{13}C NMR: δ 175.3, 174.8 (*C*O_2Me), 140.9 (CSPr^i), 103.1 (*C*CO_2Me), 99.2 (Cp), 98.1 (*C*CO_2Me), 69.3 (CH), 52.1, 51.6 (CO_2*Me*), 34.5 (CH), 28.4, 23.8 (Me). MS: m/z 659 (M^+), 615 ($M^+ -$ Pr^i), 585 ($M^+ -$ SPr^i), 573 ($M^+ -$ 2 Pr^i) and 540 ($M^+ -$ SPr^i and Pr^i).

[Mo_2(μ-S)(μ-SBu){μ-C(CO_2Me)C(SBu)C(CO_2Me)}Cp_2] 19. In an analogous fashion, a solution of complex **1** (0.50 g, 0.87 mmol) and dibutyl trithiocarbonate (0.20 g, 0.90 mmol) in toluene (150 cm^3) was heated to reflux for 77 h. Column chromatography, eluting with CH_2Cl_2–light petroleum (19 : 1), gave a green band, which, on removal of solvent, produced complex **19** as a green oil (153 mg, 26%). ^{1}H NMR: δ 5.92 (s, 10 H, Cp), 3.66, 3.52 (both s, 3 H, CO_2Me), 2.70 (t, J = 7.3, 2 H, CH_2), 1.81 (t, J = 7.6, 2 H, CH_2), 1.55–1.08 (m, 8 H, CH_2), 0.88, 0.78 (both t, J = 7.2 Hz, 3 H, Me). ^{13}C NMR: δ 175.3, 174.9 (*C*O_2Me), 140.8 (CSBu), 102.9 (*C*CO_2Me), 99.2 (Cp), 98.7 (*C*CO_2Me), 63.5 (CH_2), 52.0, 51.5 (CO_2*Me*), 37.7, 31.2, 29.7, 21.9, 21.8 (CH_2), 13.7, 13.6 (Me). MS: m/z 688 (M^+), 629 ($M^+ -$ Bu), 597 ($M^+ -$ SBu), 572 ($M^+ -$ 2 Bu) and 541 ($M^+ -$ SBu and Bu).

Crystal structure determinations of complexes 8, 13, 14 and 17

The crystal data for the four structures are collected in Table 5. General procedures were as described previously.[25] In the structure of **14** atom C(17) was found to be disordered and refined with equal occupancy over two sites. Complex scattering factors were taken from the program package SHELXL 93 [32] as implemented on the Viglen 486dx computer.

CCDC reference number 186/2206.

See http://www.rsc.org/suppdata/dt/b0/b004293p/ for crystallographic files in .cif format.

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