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# Bridge to terminal migration and ring closure in a dimolybdenum metallacyclopentadiene complex

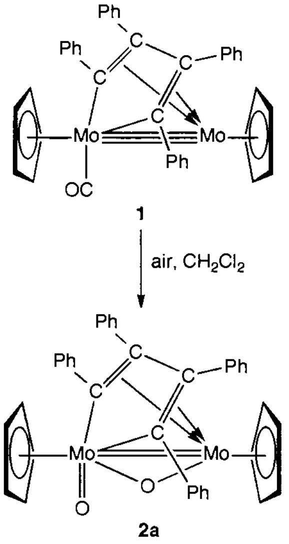
**Harry Adams, Louise J. Gill and Michael J. Morris** *[,†]

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

The dinuclear complex [$Mo_2(O)(\mu\text{-}O)(\mu\text{-}C_4Ph_4)(\eta\text{-}C_5H_5)_2$] **2a** reacted with PhNCO in refluxing toluene to give [$Mo_2(O)(\mu\text{-}NPh)(\mu\text{-}C_4Ph_4)(\eta\text{-}C_5H_5)_2$] **3a**. A crystal structure determination of the $\eta\text{-}C_5H_4Me$ analogue **3b** revealed that the bridging $C_4Ph_4$ ligand displays an unprecedented bonding mode in which one terminus bridges the two metal atoms whereas the other is bonded to only one molybdenum in the manner of a terminal alkylidene. Owing to the similarity of the $^{13}C$ NMR spectra of **2a** and **3a**, we now propose that this bonding mode is also present in the former, and that the ligand rearrangement occurs during the air oxidation of the metallacyclopentadiene complex [$Mo_2(CO)(\mu\text{-}C_4Ph_4)(\eta\text{-}C_5H_5)_2$] **1** to form **2a**. The reaction of **2a** with $Pr^iSH$ afforded an analogous sulfido complex, [$Mo_2(S)(\mu\text{-}O)(\mu\text{-}C_4Ph_4)(\eta\text{-}C_5H_5)_2$] **4a**. A second product of this reaction was identical to that formed by treatment of **2** with elemental sulfur and had the formula [$Mo_2(O)(\mu\text{-}O)(\mu\text{-}S)(\eta\text{-}C_4Ph_4)(\eta\text{-}C_5H_5)_2$] **5a**. The crystal structure of the analogous complex [$Mo_2(O)(\mu\text{-}O)(\mu\text{-}S)(\eta\text{-}C_4tol_4)(\eta\text{-}C_5H_4Me)_2$] **5d** was determined, and confirmed that the $C_4R_4$ ligand had closed up into an $\eta^4$-cyclobutadiene ring. This sequence of reactions therefore represents the gradual migration of the bridging metallacyclopentadiene unit partially (in **2** or **3**) or wholly (in **5**) onto one molybdenum atom, a process believed to be sterically driven.

Conventionally organometallic chemistry is considered to deal with metals in low oxidation states. In recent years however a much wider spectrum of compounds has become available in which organic ligands are bonded to higher oxidation state metals with π-donor ligands such as oxo or imido.[1] These can serve as useful models for oxidation catalysts or for organometallic species adsorbed on oxide surfaces. Several studies have concerned themselves with the difference in reactivity between closely related, or indeed juxtaposed, low- and high-oxidation state metal fragments.[2] The most common method for the synthesis of organometallic oxo complexes is the simple exposure of carbonyl complexes to atmospheric oxygen, but a variety of other oxidizing agents have been used, including NO gas,[3] hydrogen peroxide,[4] and recently $Me_3NO$ in combination with air.[5]

Some years ago, in their classic study of alkyne oligomerisation at dinuclear metal centres, Knox, Stone and co-workers reported the synthesis of [$Mo_2(CO)(\mu\text{-}C_4Ph_4)(\eta\text{-}C_5H_5)_2$] **1**, which contains two diphenylacetylene molecules linked in the form of a metallacyclopentadiene ring.[6] Although the crystal structure of this complex was not determined, its spectroscopic data were very similar to those of the Cr analogue, which was structurally characterised. Oxidation of this air-sensitive green compound by atmospheric oxygen gave a brown product which was formulated as [$Mo_2(O)(\mu\text{-}O)(\mu\text{-}C_4Ph_4)(\eta\text{-}C_5H_5)_2$] **2a** (Scheme 1). As a continuation of our recent work on alkyne scission in molybdenum–ruthenium clusters,[7] we have recently used both **1** and **2** in the construction of mixed-metal clusters. Treatment of **1** with [$Co_2(CO)_8$] afforded the butterfly cluster [$Co_2Mo_2(\mu_3\text{-}CPh)_2(\mu_4\text{-}C_2Ph_2)(CO)_4(\eta\text{-}C_5H_5)_2$], in which the organic ligand was cleaved into three fragments (an alkyne and two alkylidynes, *i.e.* 2 + 1 + 1 carbons),[8] whereas reaction of **2a** with [$Ru_3(CO)_{12}$] gave the unusual bow-tie cluster [$Mo_2Ru_3(\mu_3\text{-}O)_2(\mu_3\text{-}CPh)(\mu\text{-}C_3Ph_3)(CO)_8(\eta\text{-}C_5H_5)_2$], in which two organic fragments (a dimetallaallyl and an alkylidyne, *i.e.* 3 + 1 carbons) are formed.[9] Here we report some further reaction chemistry which has revealed a possible reason for the differing reactivity of the two complexes, namely the unique coordination mode adopted by the μ-$C_4Ph_4$ ligand in **2a** and its derivatives.



**Scheme 1** Synthesis of **2a** showing the structure previously proposed by Stone[6]

## Results and Discussion

### Reaction of 2 with phenyl isocyanate

Although initially we saw no reason to doubt the structure of **2a** proposed by Stone,[6] close examination of its spectroscopic data did reveal one puzzling inconsistency. The $^{13}C$ NMR spectrum of **1** contains peaks at δ 200.0 and 106.7 assigned to the pairwise equivalent μ-CPh and CPh carbons respectively, with the former occurring at lower field due to their bridging carbene character. In **2a**, the corresponding peaks are at δ 242.8, 197.9, 90.9 and 84.7, *i.e.* there is an unexplained shift of nearly 45 ppm in one of the signals assigned to the bridging CPh carbons. All four carbon atoms of the chain are now different, but this could easily be the case in the postulated structure. Attempts to grow crystals of **2a** or its analogues containing $\eta\text{-}C_5H_4Me$ ligands (**2b**), *p*-tolyl substituents on the alkyne (**2c**), or both (**2d**) were

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† E-Mail: M.Morris@sheffield.ac.uk

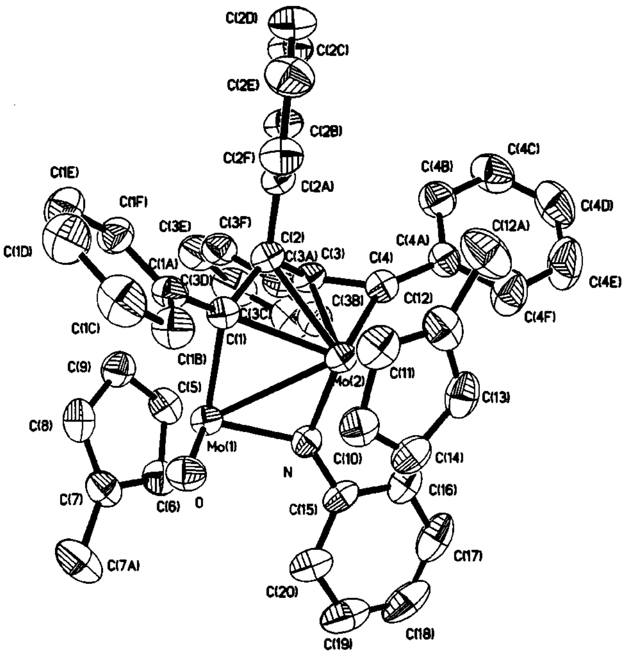


**Fig. 1** Molecular structure of complex **3b** in the crystal, showing the atom numbering scheme

**Table 1** Selected bond lengths (Å) and angles (°) for **3b**·THF

| | | | |
|---|---|---|---|
| Mo(1)–O | 1.703(3) | Mo(1)–N | 1.941(3) |
| Mo(1)–C(1) | 2.138(4) | Mo(1)–Mo(2) | 2.7654(8) |
| Mo(2)–C(4) | 1.997(4) | Mo(2)–N | 2.008(4) |
| Mo(2)–C(3) | 2.245(4) | Mo(2)–C(1) | 2.262(4) |
| Mo(2)–C(2) | 2.274(4) | N–C(15) | 1.405(5) |
| C(1)–C(2) | 1.419(6) | C(2)–C(3) | 1.488(5) |
| C(3)–C(4) | 1.398(6) | | |
| O–Mo(1)–N | 106.0(2) | O–Mo(1)–C(1) | 100.8(2) |
| N–Mo(1)–C(1) | 98.3(2) | O–Mo(1)–Mo(2) | 101.35(11) |
| N–Mo(1)–Mo(2) | 46.55(10) | C(1)–Mo(1)–Mo(2) | 53.10(11) |
| C(4)–Mo(2)–N | 106.7(2) | C(4)–Mo(2)–C(3) | 37.9(2) |
| N–Mo(2)–C(3) | 93.3(2) | C(4)–Mo(2)–C(1) | 101.7(2) |
| N–Mo(2)–C(1) | 92.42(14) | C(3)–Mo(2)–C(1) | 66.85(14) |
| C(4)–Mo(2)–C(2) | 66.7(2) | N–Mo(2)–C(2) | 111.36(14) |
| C(3)–Mo(2)–C(2) | 38.45(13) | C(1)–Mo(2)–C(2) | 36.5(2) |
| C(4)–Mo(2)–Mo(1) | 119.51(12) | N–Mo(2)–Mo(1) | 44.58(10) |
| C(3)–Mo(2)–Mo(1) | 84.82(11) | C(1)–Mo(2)–Mo(1) | 49.07(11) |
| C(2)–Mo(2)–Mo(1) | 77.99(11) | C(15)–N–Mo(1) | 135.7(3) |
| C(15)–N–Mo(2) | 134.6(3) | Mo(1)–N–Mo(2) | 88.87(14) |
| C(2)–C(1)–Mo(1) | 126.6(3) | C(2)–C(1)–Mo(2) | 72.2(2) |
| Mo(1)–C(1)–Mo(2) | 77.83(13) | C(1)–C(2)–C(3) | 117.3(4) |
| C(1)–C(2)–Mo(2) | 71.3(2) | C(3)–C(2)–Mo(2) | 69.7(2) |
| C(4)–C(3)–C(2) | 109.7(3) | C(4)–C(3)–Mo(2) | 61.4(2) |
| C(2)–C(3)–Mo(2) | 71.8(2) | C(3)–C(4)–Mo(2) | 80.7(3) |

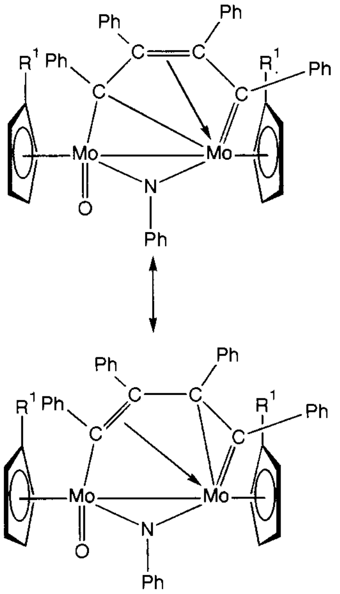


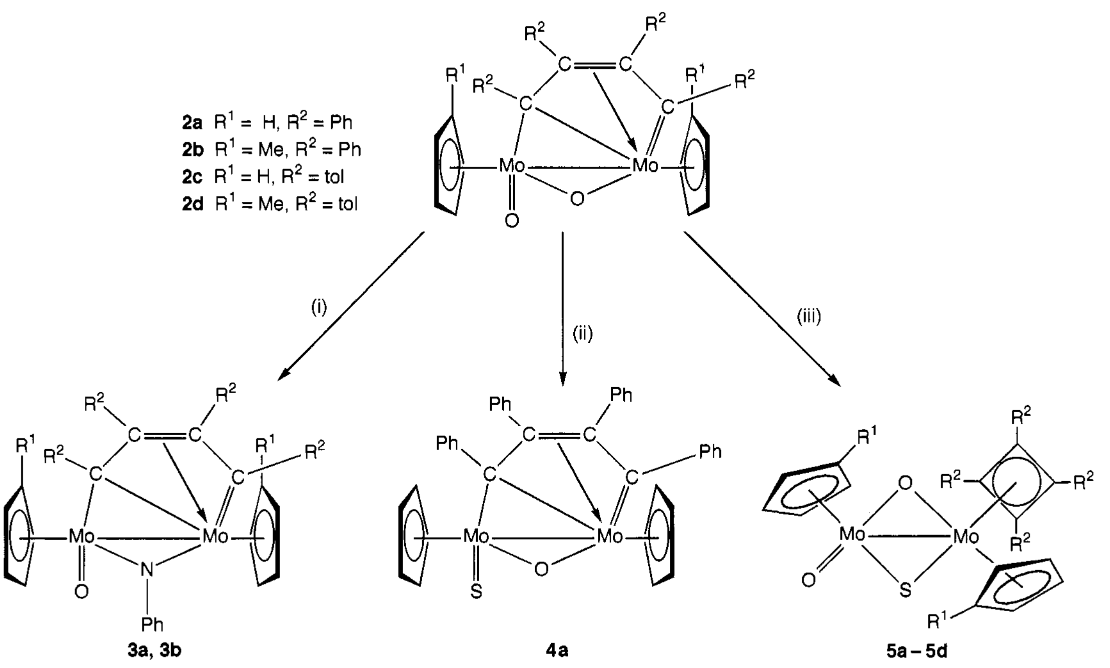
**Fig. 2** Two interpretations of the structure of **3**

all unsuccessful. We therefore examined some of the chemistry of **2a** in an effort to resolve this question.

One of the common reactions that molybdenum oxo complexes undergo is that with organic isocyanates RNCO, which results in the elimination of $CO_2$ and replacement of the oxo group by the isoelectronic imido ligand.[10] Treatment of **2a** with PhNCO (5 equivalents, refluxing toluene, 3 h) gave a single orange-red product, **3a** (64% yield), in which, according to the spectroscopic data, one oxo ligand had been replaced by an imido group. It was not possible to replace both oxo ligands by imido groups even on extended reaction. The solid-state IR spectrum of **3a** shows peaks at 1267 $cm^{-1}$ due to the bridging imido ligand and 886 $cm^{-1}$ which can be assigned to a terminal Mo=O group, compared to a similar peak at 915 $cm^{-1}$ in **2a**. The spectrum also contains strong absorptions due to the C–H out of plane vibrations of the cyclopentadienyl and phenyl groups at 810, 761 and 701 $cm^{-1}$, which are present in all the compounds discussed here. The $^{13}C$ NMR spectrum of **3a** contains four peaks at δ 235.8, 195.8, 91.9 and 83.8 which are assigned to the $C_4$ chain; these values are very close to those observed for **2a** (see above) and it is therefore reasonable to propose that the co-ordination of this unit was not affected by the oxo–imido replacement. In order to obtain crystals suitable for an X-ray diffraction study, the η-$C_5H_4Me$ analogue **3b** was prepared; its $^{13}C$ NMR shifts are virtually identical to those of **3a**.

The structure of **3b** is shown in Fig. 1, with important bond lengths and angles given in Table 1. As expected, the molecule contains a dimolybdenum core with a Mo–Mo bond of length 2.7654(8) Å. This bond is bridged somewhat asymmetrically by the phenylimido ligand [Mo(1)–N 1.941(3), Mo(2)–N 2.008(4) Å]. The remaining oxo ligand is in a terminal position on Mo(1) with a typical Mo=O bond length of 1.703(3) Å. The main point of interest, however, lies in the unprecedented bonding mode adopted by the organic fragment. The four-carbon chain is folded in a zigzag fashion reminiscent of *trans*-buta-1,3-diene (as opposed to the original metallocyclopentadiene in which it is reminiscent of *cis*-buta-1,3-diene); the C(2)–C(3)–C(4) angle of 109.7(3)° is slightly less than the C(1)–C(2)–C(3) angle of 117.3(4)°. Carbon C(1) bridges the two metal atoms asymmetrically, with bond lengths of Mo(1)–C(1) 2.138(4) and Mo(2)–C(1) 2.262(4) Å. Carbons C(2) and C(3) are bonded only to Mo(2) with bond lengths of 2.274(4) and 2.245(4) Å respectively. Remarkably, carbon atom C(4) is also bonded only to Mo(2), in effect as a terminal alkylidene, with the Mo(2)–C(4) bond length of 1.997(4) Å being considerably shorter than the bonds to the other three carbons of the ligand. By way of comparison, the Mo=C bond length in the recently reported complex $[Mo_2(OCH_2Bu^t)_6(\mu\text{-}S)(=CPh_2)(PMe_3)]$, which contains a terminal diphenylcarbene ligand, is 1.951(10) Å.[11]

An alternative description of the bonding in **3b** could be visualised as shown in Fig. 2. Carbon atoms C(1) and C(2) can be considered as a μ-vinyl group of the type found in many dinuclear complexes, being σ-bound to Mo(1) and π-bound to Mo(2).[12] Carbon atoms C(3) and C(4) might then be considered as an $\eta^2$-vinyl group bound to Mo(2). This is a much rarer mode of co-ordination, but has been observed in a number of mononuclear complexes, particularly of Group 6 metals.[13] The $^{13}C$ chemical shift of the α-carbon usually occurs at around δ 250 and the crystal structures of several such molecules show that the $\eta^2$-vinyl ligand typically has a Mo=C bond length of approximately 1.95 Å and a Mo–$C_\beta$ bond length of approximately 2.3 Å, comparable to those in **3b**. The C–C bond lengths



Scheme 2 Synthesis of new complexes from **2**. (i) PhNCO, toluene, reflux, 3 h, 64%; (ii) Pr$^i$SH, toluene, reflux, 3.5 h, 22%; (iii) $S_8$, toluene, reflux, 6 h, 23–79%

of the $C_4$ chain in **3b** support this interpretation to some extent in that the C(2)–C(3) bond is longer [1.488(5) Å] than the C(1)–C(2) bond of 1.419(6) Å. The C(3)–C(4) bond length of 1.398(6) Å is slightly shorter than that in most $\eta^2$-vinyl species, where the $C_\alpha$–$C_\beta$ distance is typically well over 1.4 Å.

Two bonding modes have been observed previously for the $\mu$-$C_4R_4$ ligand in dinuclear systems: the common 'flyover' type, first recognised in diiron species (the so-called ferroles)[14] and also present in **1**; and the much rarer variety in which the four carbon atoms are coplanar and lie perpendicular to the metal–metal bond, as observed only in $[Mo_2Cl_2(\mu\text{-}C_4Ph_4)(\eta\text{-}C_5H_5)_2]$[15] and in $[W_2Cl_4(\mu\text{-}C_4Me_4)(\eta\text{-}C_5H_4R)_2]$ (R = Me or Pr$^i$).[16] A third variant in which the ligand bridges three metals in a triosmium cluster has also been described.[17] It is clear that in order to reach the unusual bonding situation in **3b**, all that needs to happen is the breaking of the Mo(1)–C(4) bond originally present in **1**. It therefore represents a case in which one of the bridging carbon atoms of a flyover complex, which can be considered as a $\mu$-alkylidene, has migrated to a terminal position on one metal atom. Bridge-to-terminal alkylidene migration has been observed in a dimolybdenum system during the formation of $[(\eta\text{-}C_5H_5)Mo(CO)_3Mo(=CR_2)(N_2CR_2)(\eta\text{-}C_5H_5)]$ (R = *p*-tolyl) from $[Mo_2(CO)_4(\mu\text{-}CR_2)(\eta\text{-}C_5H_5)_2]$ and $N_2CR_2$, and was accompanied by a similar downfield displacement of the $^{13}C$ NMR signal. The $^{13}C$ NMR shift of the bridging alkylidene was δ 177, which moved to δ 292.6 for the terminal alkylidene in the product. The Mo=$CR_2$ bond length in the product was 1.98(1) Å.[18]

As mentioned above, the spectroscopic data, particularly the $^{13}C$ NMR spectra, of the imido complexes **3** are very similar to those of the oxo complexes **2**. We therefore propose that the $C_4R_4$ ligand is bonded in the same way in **2** as in **3**, and that the breaking of the Mo–μ-C bond occurs during the oxidation of **1** to **2**. The change in bonding mode may be caused by the oxidation of the metals, but another possibility is that it is sterically driven: crowding in **1** is evidently quite severe as shown by the presence of only one CO ligand. Muetterties and Slater have reported a similar compound. $[Mo_2(CO)(\mu\text{-}C_4Et_4)(\eta\text{-}C_5H_5)_2]$, which is evidently less crowded as it reacts with 1 atm (101 325 Pa) of CO to give $[Mo_2(CO)_3(\mu\text{-}C_4Et_4)(\eta\text{-}C_5H_5)_2]$, whereas **1** does not react with CO under these conditions.[19] In the case of **1** it appears that the introduction of an additional bridging ligand is sufficient to cause the four-carbon chain to migrate partially to one molybdenum atom. This is supported by the reaction of **2** with sulfur (see below). It is also notable that the bulkier **2d** failed to react with PhNCO to give an analogous imido complex.

## Reaction of 2 with Pr$^i$SH

Recent work in this laboratory has demonstrated that the dealkylation of thiols to form sulfido ligands can be observed in alkyne-bridged and phosphido-bridged dimolybdenum complexes.[20] So it proved again in the reaction of **2a** with an excess of Pr$^i$SH (Scheme 2). Two products were formed, the sulfido–oxo species $[Mo_2(S)(\mu\text{-}O)(\mu\text{-}C_4Ph_4)(\eta\text{-}C_5H_5)_2]$ **4a** and $[Mo_2(O)(\mu\text{-}O)(\mu\text{-}S)(\eta\text{-}C_4Ph_4)(\eta\text{-}C_5H_5)_2]$ **5a**; the latter is discussed below. Repetition of the reaction using Bu$^t$SH in place of Pr$^i$SH only gave reduced yields of the same two products, again possibly for steric reasons.

The $^1H$ NMR spectrum of **4a** showed only two in equivalent $\eta$-$C_5H_5$ ligands and phenyl protons, while mass spectral and analytical data indicated loss of one oxo ligand with incorporation of one sulfur atom. The $^{13}C$ NMR spectrum contained peaks for the CPh carbons at δ 261.6, 189.0, 90.4 and 85.3, clearly showing that the co-ordination of the $C_4Ph_4$ fragment is the same as in **2** and **3**. The IR spectrum of **4a** contained no clear peaks in the region associated with Mo=O absorptions, and on this basis we propose an analogous structure with a μ-O ligand and a terminal sulfido group; however this is somewhat uncertain as no peaks could be definitely assigned to Mo(μ-O)-Mo or Mo=S groups. The fate of the Pr$^i$ group, and indeed of the displaced oxo ligand, is unknown. Replacement of a terminal oxo ligand by a sulfido group has previously been observed in related dimeric systems.[21]

## Reaction of 2 with sulfur

Since the reaction of **2a** with Pr$^i$SH gave complexes with sulfido ligands, a logical step was treatment of **2** with elemental sulfur in the hope of preparing the same compounds in better yield. However in the event no trace of **4a** was formed; instead the reaction produced $[Mo_2(O)(\mu\text{-}O)(\mu\text{-}S)(\eta\text{-}C_4Ph_4)(\eta\text{-}C_5H_5)_2]$ **5a** as the major product (79%), identical to the second compound isolated from the Pr$^i$SH reaction. Minor products included an organic compound thought to be tetraphenylthiophene, and a small amount of an unidentified green complex which may possibly have the formula $[Mo_2O_2S_2(C_4Ph_4)(\eta\text{-}C_5H_5)_2]$. It is

**Table 2** Selected bond lengths (Å) and angles (°) for **5d**·$0.5C_5H_{12}$

| | | | |
|---|---|---|---|
| Mo(1)–O(1) | 2.062(3) | Mo(1)–C(2) | 2.245(4) |
| Mo(1)–C(3) | 2.258(5) | Mo(1)–C(1) | 2.294(4) |
| Mo(1)–C(4) | 2.401(4) | Mo(1)–S(1) | 2.4070(14) |
| Mo(1)–Mo(2) | 2.8129(9) | Mo(2)–O(2) | 1.712(4) |
| Mo(2)–O(1) | 1.887(3) | Mo(2)–S(1) | 2.2896(14) |
| C(1)–C(4) | 1.443(6) | C(1)–C(2) | 1.469(6) |
| C(2)–C(3) | 1.485(6) | C(3)–C(4) | 1.465(6) |
| O(1)–Mo(1)–S(1) | 91.86(10) | O(1)–Mo(1)–Mo(2) | 42.12(10) |
| S(1)–Mo(1)–Mo(2) | 51.31(4) | O(2)–Mo(2)–O(1) | 107.5(2) |
| O(2)–Mo(2)–S(1) | 106.75(14) | O(1)–Mo(2)–S(1) | 100.45(10) |
| O(2)–Mo(2)–Mo(1) | 106.12(14) | O(1)–Mo(2)–Mo(1) | 47.15(10) |
| S(1)–Mo(2)–Mo(1) | 55.15(4) | Mo(2)–S(1)–Mo(1) | 73.54(4) |
| Mo(2)–O(1)–Mo(1) | 90.73(13) | C(4)–C(1)–C(2) | 89.8(3) |
| C(1)–C(2)–C(3) | 89.8(3) | C(4)–C(3)–C(2) | 88.4(3) |
| C(1)–C(4)–C(3) | 91.6(3) | | |

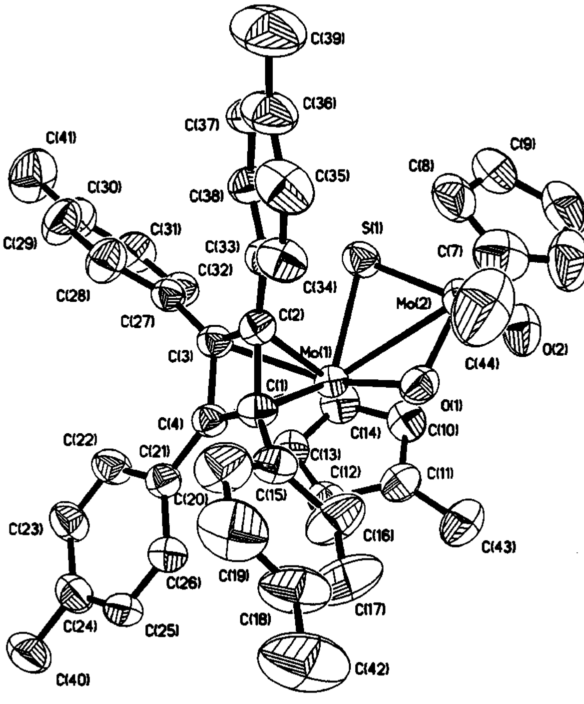
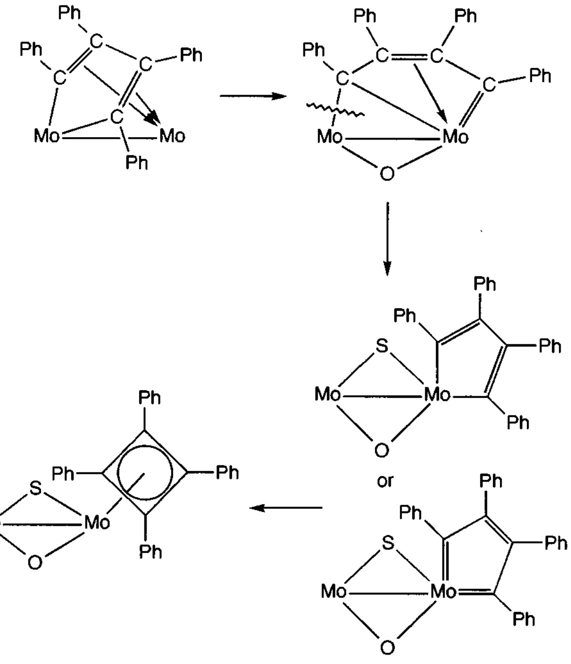


**Fig. 3** Molecular structure of complex **5d** in the crystal, showing the atom numbering scheme

interesting to note that the reaction of the ferrole complex $[Fe_2(\mu\text{-}C_4Ph_4)(CO)_6]$ with elemental sulfur resulted in elimination of the metallacycle in the form of tetraphenylthiophene in 80% yield.[14]

Examination of the $^1H$ and $^{13}C$ NMR spectra of **5a** immediately indicated that the co-ordination of the organic ligand was much more symmetrical, as the four phenyl groups were all in equivalent environments; moreover the $^{13}C$ NMR resonances due to the terminal and bridging carbene carbons were no longer present and the signal for the CPh groups now appeared as a single peak at δ 96.6. Analytical and mass spectral data revealed that both oxo ligands were still present and that one sulfur atom had been added. The solid-state IR spectrum contained a peak due to Mo=O at 889 $cm^{-1}$. Unfortunately **5a** steadfastly refused to crystallise and so the analogous compounds **5b**, **5c**, and **5d** were prepared, all of which exhibited similar spectroscopic characteristics. After many attempts, suitable crystals for X-ray study were obtained from **5d**, containing both $\eta\text{-}C_5H_4Me$ ligands and *p*-tolyl substituents on the alkyne.

A perspective view of **5d** is shown in Fig. 3, with selected bond lengths and angles given in Table 2. The complex is based on a dimolybdenum core with a Mo–Mo bond length of 2.8129(9) Å, slightly longer than in **3b**. This bond is asymmetrically bridged by an oxo ligand and a sulfido ligand, both of which lie closer to Mo(2). The central portion of the molecule is not quite planar; the angle between the $Mo_2(\mu\text{-}S)$ and $Mo_2(\mu\text{-}O)$ planes is 161.3°. A second oxo ligand is terminally bonded to Mo(2) with a bond length very similar to that in **3b**. The methylcyclopentadienyl ligands are disposed in a *trans* arrangement with respect to each other.



**Scheme 3** Possible pathway for the conversion of **1** into **5**

The major point of interest again concerns the $C_4R_4$ moiety, which has now closed up into a $\eta^4$-cyclobutadiene ligand bonded to Mo(1). Angles and lengths within this ring are typical for $\eta\text{-}C_4Ph_4$ ligands, and the phenyl substituents are arranged in a staggered manner with alternate rings being almost perpendicular to the cyclobutadiene: the torsion angles between the phenyl ring planes and the $C_4$ ring plane are 82.0, 15.4, 75.8 and 25.8° for the rings attached to C(1)–C(4) respectively. As observed previously in complexes containing both cyclobutadiene and $\eta\text{-}C_5H_5$ ligands, the average M–C distance for the cyclobutadiene ring (2.299 Å) is less than that for the $C_5H_5$ ligand (2.383 Å).[22] In terms of oxidation state, if the cyclobutadiene is regarded as $C_4Ph_4^{2-}$, both Mo atoms are $Mo^V$; indeed the structure bears some resemblance to that of the dithiolene complex $[Mo_2(S)(\mu\text{-}S)_2(SCH{=}CHS)(\eta\text{-}C_5H_5)_2]$.[23] It should be noted that cyclobutadiene ligands are relatively rare in metal–metal bonded dinuclear complexes, the most closely related example being $[Mo_2(CO)_3(\mu\text{-}C_2Ph_2)(\eta\text{-}C_4Ph_4CO)(\eta\text{-}C_4Ph_4)]$.[24]

Considering as a whole the transformation from **1** to **2** to **5**, if the organic ligand is regarded as $C_4R_4^{2-}$ throughout, this sequence represents the gradual oxidation of the dinuclear centre from $Mo^{II}_2$ in **1** to $Mo^{IV}_2$ in **2** and then $Mo^V_2$ in **5**, though assigning oxidation states to the individual metals within these is sometimes more problematical. Whereas complex **2** represents the partial migration of the original metallacyclopentadiene ligand to one metal atom, this process is carried to completion in **5**. We can speculate that the course of events may be as shown in Scheme 3.

Introduction of a further ligand, the sulfur atom, into **2** forces the remaining bridging carbon to migrate to the same molybdenum which already bears the carbene, giving a terminal metallacyclopentadiene ligand which could then undergo reductive elimination to form the cyclobutadiene. It is also possible that the initial species formed by migration of the carbon atom possesses a bis(carbene) structure, *i.e.* a metallacyclopentatriene ring. Examples of these have been isolated and structurally characterised at mononuclear Mo, Nb and Ru centres, and on co-ordination of an additional ligand have been observed to change to the more usual metallacyclopentadiene ring.[25] Examples of the closure of both types of ring into cyclobutadienes at mononuclear centres are known.

## Conclusion

Oxidation of $[Mo_2(CO)(\mu\text{-}C_4Ph_4)(\eta\text{-}C_5H_5)_2]$ causes partial migration of the metallacyclopentadiene ligand to one molybdenum atom, resulting in a novel co-ordination mode for this ligand in $[Mo_2(O)(\mu\text{-}O)(\mu\text{-}C_4Ph_4)(\eta\text{-}C_5H_5)_2]$ **2a** and its imido derivative $[Mo_2(O)(\mu\text{-}NPh)(\mu\text{-}C_4Ph_4)(\eta\text{-}C_5H_5)_2]$ **3a**. Further oxidation with elemental sulfur causes cyclisation of the organic ligand to give the cyclobutadiene complex $[Mo_2(O)(\mu\text{-}O)(\mu\text{-}S)(\eta\text{-}C_4Ph_4)(\eta\text{-}C_5H_5)_2]$ **5a**. Although the combination of two alkynes to produce cyclobutadienes is a very common process, especially in mononuclear complexes, the chemistry described here represents the first time that this has been observed in a stepwise fashion at a dinuclear metal centre. It is clear that changing the ligand environment from low valent carbonyls to high valent oxo, imido or sulfido groups has a profound effect on the structure and reactivity of organic ligands which are present.

## Experimental

General experimental techniques were as described in recent papers from this laboratory.[26,27] Infrared spectra were recorded as KBr discs on a Perkin-Elmer 1600 FT-IR machine. Proton and $^{13}C$ NMR spectra were obtained 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 $SiMe_4 = 0.0$. The $^{13}C\text{-}\{^1H\}$ 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. Di-*p*-tolylacetylene was prepared by appropriate modification of the literature method for $C_2Ph_2$.[28] The complexes $[Mo_2(CO)_6(\eta\text{-}C_5H_5)_2]$ and $[Mo_2(CO)_6(\eta\text{-}C_5H_4Me)_2]$ were synthesized by the literature procedures.[29,30] The synthesis and spectroscopic data of **2a** have already been described by us;[9] the reaction can be carried out as a one-pot procedure from $[Mo_2(CO)_6(\eta\text{-}C_5H_5)_2]$ in yields of up to 85% as described below for **2b**.

### Preparations

**$[Mo_2(O)(\mu\text{-}O)(\mu\text{-}C_4Ph_4)(\eta\text{-}C_5H_4Me)_2]$ 2b.** A solution of $[Mo_2(CO)_6(\eta\text{-}C_5H_4Me)_2]$ (3 g, 5.79 mmol) and $C_2Ph_2$ (2.92 g, 16.4 mmol) in octane (150 $cm^3$) was heated to reflux for 22 h. The solvent was removed *in vacuo* and the resultant green solid redissolved in dichloromethane (100 $cm^3$) and stirred vigorously in air for 2 h. Purification by chromatography gave a small amount of $C_2Ph_2$ followed by a maroon band of $[Mo_2(\mu\text{-}C_2Ph_2)(CO)_4(\eta\text{-}C_5H_4Me)_2]$ (372.7 mg, 0.58 mmol, 10%) eluted in $CH_2Cl_2$. The major product, crude **2b**, was eluted as an orange-brown band in acetone–$CH_2Cl_2$ (1 : 9). After rechromatography the yield of pure **2b** was 1.789 g, 42%. M.p. 157 °C (decomp.) $^1H$ NMR: δ 7.67–6.74 (m, 20 H, Ph), 6.15 (dt, $J = 7$ and 1, 1 H, $C_5H_4Me$), 5.85 (q, $J = 2$, 1 H, $C_5H_4Me$), 5.62 (m, $J = 2$, 2 H, $C_5H_4Me$), 4.99 (q, $J = 3$, 1 H, $C_5H_4Me$), 4.74 (q, $J = 2$, 1 H, $C_5H_4Me$), 3.75 (q, $J = 3$, 1 H, $C_5H_4Me$), 3.59 (q, $J = 3$ Hz, 1 H, $C_5H_4Me$), 1.91 (s, 6 H, coincident Me). $^{13}C$ NMR: δ 241.0 (Mo=C), 197.8 (μ-C), 151.2, 145.3, 144.4, 138.5 ($C_{ipso}$), 130.7–125.4 (m, Ph), 122.6 (CMe), 107.9, 105.2, 103.8, 103.3, 99.2, 97.7, 96.7, 93.3 ($C_5H_4Me$), 89.2, 84.7 (CPh), 14.1, 13.3 (Me) (Found: C, 64.80; H, 5.13. Calc. for $C_{40}H_{34}Mo_2O_2$: C, 65.04; H, 4.64%). MS: *m*/*z* 739 ($M + H^+$).

The complexes $[Mo_2(O)(\mu\text{-}O)(\mu\text{-}C_4tol_4)(\eta\text{-}C_5H_5)_2]$ **2c** and $[Mo_2(O)(\mu\text{-}O)(\mu\text{-}C_4tol_4)(\eta\text{-}C_5H_4Me)_2]$ **2d** were prepared in an analogous manner in 59 and 33% yields respectively.

**2c** M.p. 146 °C (decomp.). $^1H$ NMR: δ 7.59–6.61 (m, 15 H, tol), 6.01 (m, 1 H, tol), 5.64 (s, 5 H, $C_5H_5$), 5.18 (s, 5 H, $C_5H_5$), 2.37, 2.30, 2.18, 2.17 (all s, 3 H, Me). $^{13}C$ NMR: δ 242.9 (Mo=C), 197.7 (μ-C), 148.3, 142.7, 142.3, 137.4, 137.0, 135.6, 135.1, 135.0 ($C_{ipso}$ and CMe), 130.7–127.6 (m, tol), 106.7, 99.3 ($C_5H_5$), 90.9, 84.8 (Ctol), 21.4, 21.2, 21.1, 21.0 (Me) (Found: C, 65.53; H, 5.15. Calc. for $C_{42}H_{38}Mo_2O_2$: C, 65.80; H, 4.96%). MS: *m*/*z* 767 ($M + H^+$).

**2d** M.p. 174 °C (decomp.). $^1H$ NMR: δ 7.55–6.47 (m, 16 H, tol), 6.03 (m, 1 H, $C_5H_4Me$), 5.82 (m, 1 H, $C_5H_4Me$), 5.60 (m, 2 H, $C_5H_4Me$), 4.94 (m, 1 H, $C_5H_4Me$), 4.65 (m, 1 H, $C_5H_4Me$), 3.81 (m, 1 H, $C_5H_4Me$), 3.53 (m, 1 H, $C_5H_4Me$), 2.48, 2.30 (s, 3 H, Me), 2.15 (s, 6 H, coincident Me), 1.94, 1.87 (s, 3 H, Me of $C_5H_4Me$). $^{13}C$ NMR: δ 240.8 (Mo=C), 197.3 (μ-C), 148.4, 142.8, 141.8, 137.1, 136.7, 135.6, 135.4, 134.8 ($C_{ipso}$ and CMe of tol), 130.6–127.5 (m, tol), 122.4 (CMe of $C_5H_4Me$), 107.5, 105.3, 103.8, 103.3, 99.0, 97.5, 96.5, 92.9 ($C_5H_4Me$), 89.1, 84.7 (Ctol), 21.4, 21.2, 21.1, 21.0 (Me of tol), 13.4, 12.5 (Me of $C_5H_4Me$) (Found: C, 65.58; H, 5.39. Calc. for $C_{44}H_{42}Mo_2O_2$: C, 66.50; H, 5.29%). MS: *m*/*z* 795 ($M + H^+$).

**$[Mo_2(O)(\mu\text{-}NPh)(\mu\text{-}C_4Ph_4)(\eta\text{-}C_5H_5)_2]$ 3a.** A solution of **2a** (1 g, 1.41 mmol) in toluene (150 $cm^3$) was treated with PhNCO (0.765 $cm^3$, 7.04 mmol) and heated to reflux for 3 h, by which time TLC monitoring indicated the presence of one product. After removal of the solvent the mixture was absorbed onto silica gel and chromatographed to give three faint orange-yellow bands eluted in light petroleum–$CH_2Cl_2$ (1 : 1), followed by a large orange-red zone of **3a** (706.5 mg, 63.9%) eluted in $CH_2Cl_2$. M.p. 170–172 °C. IR 886 $cm^{-1}$ (Mo=O). $^1H$ NMR: δ 7.73–6.92 (m, 25 H, Ph), 5.45 (s, 5 H, $C_5H_5$), 4.97 (s, 5 H, $C_5H_5$). $^{13}C$ NMR: δ 235.8 (Mo=C), 195.8 (μ-C), 167.9 ($C_{ipso}$ of NPh), 151.7, 145.7, 144.0, 138.2 ($C_{ipso}$), 130.9–120.7 (m, Ph), 105.9 ($C_5H_5$), 98.7 ($C_5H_5$), 91.9 (CPh), 83.8 (CPh) (Found: C, 67.62; H, 4.83; N, 1.67. Calc. for $C_{44}H_{35}Mo_2NO$: C, 67.26; H, 4.46; N, 1.78%). MS: *m*/*z* 785 ($M^+$).

**$[Mo_2(O)(\mu\text{-}NPh)(\mu\text{-}C_4Ph_4)(\eta\text{-}C_5H_4Me)_2]$ 3b.** Prepared in the same manner as **3a** above, again in 64% yield. M.p. 156–158 °C. $^1H$ NMR: δ 7.77–6.65 (m, 25 H, Ph), 6.07 (m, 2 H, $C_5H_4Me$), 5.79 (m, 1 H, $C_5H_4Me$), 5.70 (m, 1 H, $C_5H_4Me$), 5.53 (m, 1 H, $C_5H_4Me$), 4.30 (m, 1 H, $C_5H_4Me$), 3.23 (t, 2 H, $C_5H_4Me$), 1.85 (s, 6 H, coincident Me). $^{13}C$ NMR: δ 235.2 (Mo=C), 195.9 (μ-C), 166.8 ($C_{ipso}$ of NPh), 152.0, 145.4, 143.7, 138.6 ($C_{ipso}$), 130.9–124.2 (m, Ph), 126.3, 117.0 (CMe), 107.2, 106.1, 103.2, 102.0, 101.0, 99.6, 94.8, 94.3 ($C_5H_4Me$), 90.5, 82.7 (CPh), 13.2, 12.5 (Me) (Found: C, 67.76; H, 5.37; N, 1.58. Calc. for $C_{46}H_{39}Mo_2NO\cdot C_4H_8O$: C, 67.80; H, 5.31; N, 1.58%). MS: *m*/*z* 814 ($M + H^+$).

**$[Mo_2(S)(\mu\text{-}O)(\mu\text{-}C_4Ph_4)(\eta\text{-}C_5H_5)_2]$ 4a.** A solution of **2a** (275 mg, 0.387 mmol) and $Pr^iSH$ (0.179 $cm^3$, 1.94 mmol) in toluene (150 $cm^3$) was heated to reflux for 3.5 h with TLC monitoring. Separation of the products by column chromatography gave four very faint bands followed by an orange band of $[Mo_2(S)(\mu\text{-}O)(\mu\text{-}C_4Ph_4)(\eta\text{-}C_5H_5)_2]$ **4a** (62 mg, 22%), eluted with $CH_2Cl_2$–light petroleum (7 : 3). M.p. 220–222 °C. $^1H$ NMR: δ 7.64–6.68 (m, 19 H, Ph), 5.80 (d, 1 H, Ph), 5.45 (s, 5 H, $C_5H_5$), 5.03 (s, 5 H, $C_5H_5$). $^{13}C$ NMR: δ 261.6 (Mo=C), 189.0 (μ-C), 151.7, 146.0, 145.5, 135.5 ($C_{ipso}$), 132.2–125.3 (m, Ph), 104.8, 97.1 ($C_5H_5$), 90.4, 85.3 (CPh) (Found: C, 62.98; H, 4.31; S, 4.38. Calc. for $C_{38}H_{30}Mo_2OS$: C, 62.81; H, 4.13; S, 4.41%). MS: *m*/*z* 728 ($M + 2H^+$). Finally a band of **5a** (43.3 mg, 15%) was eluted with acetone–$CH_2Cl_2$ (1 : 9).

**$[Mo_2(O)(\mu\text{-}O)(\mu\text{-}S)(\eta\text{-}C_4Ph_4)(\eta\text{-}C_5H_5)_2]$ 5a.** A solution of **2a** (300 mg, 0.423 mmol) and sulfur (68 mg, 0.26 mmol) in toluene

(150 cm$^3$) was heated to reflux for 6 h. The solvent was then removed and the residue absorbed onto silica for chromatography. Several very minor bands were removed in $CH_2Cl_2$–light petroleum (3 : 1), including one pink organic compound (possibly tetraphenylthiophene) and one unidentified green complex [$^1$H NMR: δ 7.47–7.05 (m, 20 H), 6.05, 5.53 (s, 5 H, $C_5H_5$). MS: *m*/*z* 771], which were not investigated further. Elution with acetone–$CH_2Cl_2$ (1 : 9) produced a small black band (discarded) followed by the orange product, **5a** (247.9 mg, 79%). M.p. 124 °C (decomp.). IR 889 cm$^{-1}$ (Mo=O). $^1$H NMR: δ 7.31–7.15 (m, 20 H, Ph), 5.40 (s, 5 H, $C_5H_5$), 5.24 (s, 5 H, $C_5H_5$). $^{13}$C NMR: δ 134.2 ($C_{ipso}$), 130.4, 128.1, 127.5 (Ph), 107.1, 102.0 ($C_5H_5$), 96.6 ($C_4Ph_4$) (Found: C, 61.44; H, 4.21; S, 4.29. Calc. for $C_{38}H_{30}Mo_2O_2S$: C, 61.46; H, 4.04; S, 4.31%). MS: *m*/*z* 743 ($M + H^+$).

The compounds [$Mo_2(O)(\mu\text{-}O)(\mu\text{-}S)(\eta\text{-}C_4Ph_4)(\eta\text{-}C_5H_4Me)_2$] **5b**, [$Mo_2(O)(\mu\text{-}O)(\mu\text{-}S)(\eta\text{-}C_4tol_4)(\eta\text{-}C_5H_5)_2$] **5c** and [$Mo_2(O)(\mu\text{-}O)(\mu\text{-}S)(\eta\text{-}C_4tol_4)(\eta\text{-}C_5H_4Me)_2$] **5d** were synthesized as for **5a** above in yields of 34, 42 and 23% respectively.

**5b** M.p. 203 °C (decomp.). $^1$H NMR: δ 7.27–7.13 (m, 20 H, Ph), 6.07, 5.75, 5.46, 5.24, 4.91, 4.48, 4.21, 3.42 (all m, 1 H, $C_5H_4Me$), 2.19, 1.71 (s, 3 H, Me). $^{13}$C NMR: δ 134.6 ($C_{ipso}$), 131.2 (CMe), 130.3, 128.0, 127.3 (Ph), 125.5 (CMe), 107.8, 104.9, 103.7, 102.4, 101.3, 101.1, 97.0, 93.6 ($C_5H_4Me$), 94.1 ($C_4Ph_4$), 19.9, 12.0 (Me) (Found: C, 61.91; H, 4.39; S, 4.18. Calc. for $C_{40}H_{34}Mo_2O_2S$: C, 62.34; H, 4.42; S, 4.16%). MS: *m*/*z* 771 ($M + H^+$).

**5c** M.p. 198 °C (decomp.). $^1$H NMR: δ 7.13, 7.02 (both d, 8 H, tol), 5.41 (s, 5 H, $C_5H_5$), 5.21 (s, 5 H, $C_5H_5$), 2.32 (s, 12 H, Me). $^{13}$C NMR: δ 137.2 (CMe), 131.4 ($C_{ipso}$), 130.2, 128.8 (tol), 107.1, 101.9 ($C_5H_5$), 96.9 ($C_4tol_4$), 21.2 (Me). MS: *m*/*z* 798 ($M^+$).

**5d** M.p. 207 °C (decomp.). $^1$H NMR: δ 7.08 (m, 16 H, tol), 6.07, 5.77, 5.41, 5.18, 4.86, 4.45, 4.18, 3.40 (all q, 1 H, $C_5H_4Me$), 2.32 (s, 12 H, Me of tol), 1.69, 1.48 (s, 3 H, Me of $C_5H_4Me$). $^{13}$C NMR: δ 136.9 (CMe of tol), 131.8 ($C_{ipso}$), 131.2 (CMe of $C_5H_4Me$), 130.2, 128.7 (tol), 124.9 (CMe of $C_5H_4Me$), 107.9, 104.8, 103.5, 102.4, 101.2, 100.6, 97.1, 93.7 ($C_5H_4Me$), 95.7 ($C_4tol_4$), 21.2 (Me of tol), 13.9, 12.0 (Me of $C_5H_4Me$). MS: *m*/*z* 827 ($M + H^+$).

Despite many attempts (at least seven in each case, including the crystals used for the X-ray study) we were unable to obtain correct analytical data for complexes **5c** and **5d**; the results for C were always 1–5% lower than expected, although the results for H and S were within the expected range. We have no explanation for this, though one possibility would be the formation of molybdenum carbide during sample combustion.

### Crystal structure determinations of 3b·THF and 5d·0.5$C_5H_{12}$

The crystal data for the two structures are summarised in Table 3. Three-dimensional, room temperature X-ray data were collected on a Siemens P4 diffractometer by the ω-scan method. Of the reflections measured, all of which were corrected for Lorentz and polarisation effects but not for absorption, those independent reflections which exceeded the significance level $|F|/\sigma(|F|) > 4.0$ were used in the refinement. The structures were solved by direct methods and refined by full-matrix least-squares methods on $F^2$. Hydrogen atoms were included in calculated positions and refined in riding mode. Refinement converged at the final *R* values shown with allowance for the thermal anisotropy of all non-hydrogen atoms. The structure of **3b** contains a THF molecule, and in the structure of **5d** a molecule of pentane was located with C(3S) being sited on the position 0.5, 0.0, 0.0; this made the positioning of the hydrogen atoms on C(3S) difficult but the model refined seemed to be the best fit. Weighting schemes $w = 1/[\sigma^2(F_o^2) + (0.0685P)^2 + 1.3291P]$ (for **3b**) and $w = 1/[\sigma^2(F_o^2) + (0.0724P)^2 + 2.3205P]$ (for **5d**), where $P = (F_o^2 + 2F_c^2)/3$ were used in the latter stages of refinement. Complex scattering factors were taken from the program package SHELXL 93[31] as implemented on the Viglen 486dx computer.

CCDC reference number 186/1041.

**Table 3** Summary of crystallographic data for complexes **3b**·THF and **5d**·0.5$C_5H_{12}$

| | **3b**·THF | **5d**·0.5$C_5H_{12}$ |
|---|---|---|
| | $C_{50}H_{47}Mo_2NO_2$ | $C_{46.5}H_{48}Mo_2O_2S$ |
| *M* | 885.77 | 862.79 |
| *a*/Å | 11.796(3) | 10.955(3) |
| *b*/Å | 14.217(5) | 11.906(2) |
| *c*/Å | 14.292(3) | 16.280(2) |
| α/° | 89.42(2) | 85.660(10) |
| β/° | 67.540(10) | 80.06(2) |
| γ/° | 67.90(2) | 77.42(2) |
| *U*/Å$^3$ | 2027.1(10) | 2038.7(7) |
| $D_c$/Mg m$^{-3}$ | 1.451 | 1.406 |
| μ/mm$^{-1}$ | 0.660 | 0.703 |
| *F*(000) | 908 | 886 |
| Crystal size/mm | 0.66 × 0.34 × 0.30 | 0.73 × 0.32 × 0.32 |
| θ Range for data collection/° | 2.00–25.02 | 1.76–25.00 |
| Index ranges | $-1 \leqslant h \leqslant 14$,<br>$-15 \leqslant k \leqslant 16$,<br>$-16 \leqslant l \leqslant 16$ | $-1 \leqslant h \leqslant 13$,<br>$-13 \leqslant k \leqslant 14$,<br>$-19 \leqslant l \leqslant 19$ |
| Reflections collected | 8214 | 8398 |
| Independent reflections ($R_{int}$) | 7080 (0.0440) | 7165 (0.0218) |
| Data, restraints, parameters | 7080, 0, 491 | 7164, 0, 451 |
| Goodness-of-fit on $F^2$ | 1.026 | 1.031 |
| Final *R* indices [$I > 2\sigma(I)$], *R*1, *wR*2 | 0.0444, 0.1124 | 0.0471, 0.1229 |
| Final *R* indices (all data), *R*1, *wR*2 | 0.0603, 0.1235 | 0.0634, 0.1358 |
| Largest difference peak, hole/e Å$^{-3}$ | 0.747, −0.598 | 0.702, −1.054 |

Details in common: $T = 293(2)$ K; Mo-Kα radiation (λ = 0.710 73 Å); triclinic; space group $P\bar{1}$ ($C_i^1$ no. 2); $Z = 2$; refinement method full-matrix least squares on $F^2$.

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