

Dimolybdenum complexes with sulfide and thiolate ligands as precursors to mixed-metal clusters: crystal structure of $[\text{Mo}_2\text{Ru}_2(\mu_3\text{-S})_2(\mu\text{-SPr}^i)_2(\text{CO})_4(\eta\text{-C}_5\text{H}_5)_2]$

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The reaction of $[\text{Mo}_2(\text{CO})_4(\mu\text{-C}_2\text{Me}_2)(\eta\text{-C}_5\text{H}_5)_2]$ **1** with thiols, RSH, in boiling toluene provides a useful new route to the known compounds $[\text{Mo}_2(\mu\text{-S})_2(\mu\text{-SR})_2(\eta\text{-C}_5\text{H}_5)_2]$ (R = Et **2a** or Prⁱ **2b**) in 40–45% yield. Both compounds exist as two isomers which were separated by chromatography for R = Et. The sulfur ligands in these complexes are formed by dealkylation of the thiols at the dimolybdenum centre. Reaction of **2** with $[\text{Ru}_3(\text{CO})_{12}]$ in refluxing tetrahydrofuran produced high yields of the mixed-metal clusters $[\text{Mo}_2\text{Ru}_2(\mu_3\text{-S})_2(\mu\text{-SR})_2(\text{CO})_4(\eta\text{-C}_5\text{H}_5)_2]$ **3**; the crystal structure of the Prⁱ-substituted complex **3b** has been determined. The cluster consists of a tetrahedral metal core with both Mo₂Ru faces capped by triply bridging sulfides. One of the thiolate ligands still bridges the molybdenum–molybdenum edge, but the other has migrated to the ruthenium–ruthenium edge.

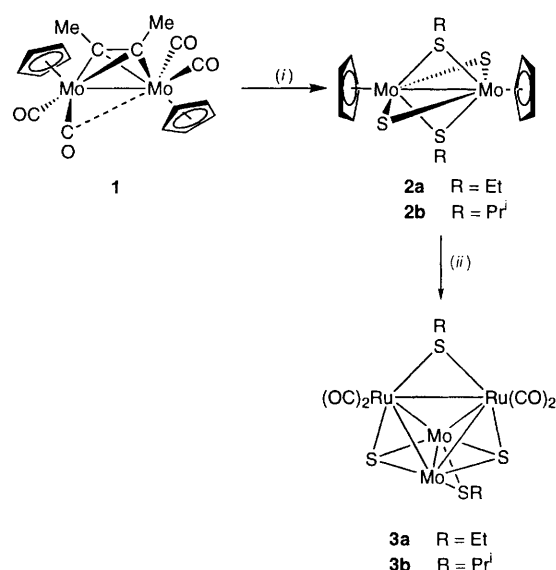
Metal complexes with sulfur-based ligand environments are of interest because of their relevance to biochemical catalysis by metalloenzymes and heterogeneous catalysis by metal sulfide surfaces.¹ Hydrodesulfurisation (the removal of sulfur-containing impurities from fossil fuels) is an important industrial process which in the future will have to operate with increased efficiency due to the unavoidable use of crude oil with a higher sulfur content coupled with ever more stringent environmental protection requirements for lower levels of sulfur emissions.² Since the early 1980s, many of the processes thought to occur on the catalyst surface during hydrodesulfurisation, such as C–S bond cleavage and activation of H₂, have been modelled on discrete dinuclear cyclopentadienylmolybdenum complexes.³ More recently, several groups have demonstrated that the ring opening of thiophenes occurs relatively easily on platinum metals such as Rh, Ir, Ru and Pt.⁴ We therefore sought to prepare mixed-metal complexes which might combine both types of activity with the view, ultimately, of obtaining new single-source hydrodesulfurisation catalysts (either homo- or hetero-geneous) which can deal efficiently with such difficult substrates. In this paper we describe an improved new route to known dimolybdenum complexes with sulfur and thiolate ligands and demonstrate that they act as precursors for the high-yield synthesis of mixed-metal molybdenum–ruthenium clusters.

Results and Discussion

Dimolybdenum complexes

We have investigated the reactions of thiols with the transversely bound alkyne complexes $[\text{Mo}_2(\text{CO})_4(\mu\text{-alkyne})(\eta\text{-C}_5\text{H}_5)_2]$ and shown that the outcome depends strongly on the identity of the alkyne as well as the thiol. For the present we concentrate on the reactions of the but-2-yne complex $[\text{Mo}_2(\text{CO})_4(\mu\text{-C}_2\text{Me}_2)(\eta\text{-C}_5\text{H}_5)_2]$ **1**; further results dealing with other alkyne complexes have recently been communicated and will be reported in full elsewhere.⁵

The chemistry performed is shown in Scheme 1. Treatment of complex **1** with an excess of EtSH or PrⁱSH (5–10 equivalents) in refluxing toluene overnight results in displacement of the alkyne and formation of $[\text{Mo}_2(\mu\text{-S})_2(\mu\text{-SR})_2(\eta\text{-C}_5\text{H}_5)_2]$ **2a**, **2b** in yields of around 40% in both cases. These air-stable purple compounds can be purified by column chromatography; both



Scheme 1 Synthesis of the dimolybdenum complexes and clusters: (i) RSH (5–10 equivalents), toluene, reflux, 16–20 h; (ii) $[\text{Ru}_3(\text{CO})_{12}]$ (1 equivalent), tetrahydrofuran, reflux, 2 h. The C₅H₅ ligands have been omitted from **3** for clarity

exist as two isomers which were separated in the case of **2a** but not for **2b**. In their ¹H NMR spectra both complexes display the characteristic low-field shifts of the C₅H₅ ligands (at approximately δ 6.5) previously observed in related quadruply bridged complexes, as well as appropriate signals for R (see Experimental section). The presence of two isomers is caused by the *syn* or *anti* orientation of the substituents on the thiolate ligands.

Compounds of type **2**, including those made here, have previously been prepared by thiol-exchange reactions of $[\text{Mo}_2(\mu\text{-S})_2(\mu\text{-SH})_2(\eta\text{-C}_5\text{H}_5)_2]$ with RSH under an atmosphere of H₂; our spectroscopic data agree entirely with those reported.⁶ The yields of the thiol-exchange reaction are however rather variable depending on R, and the synthesis of the starting hydrogen sulfide complex requires reduction of polymeric $[\{\text{Mo}_2\text{S}_x(\eta\text{-C}_5\text{H}_5)_2\}_n]$, with H₂ (in an autoclave) or LiBHET₃.^{7,8} Curtis and Williams⁹ reported that oxidation of

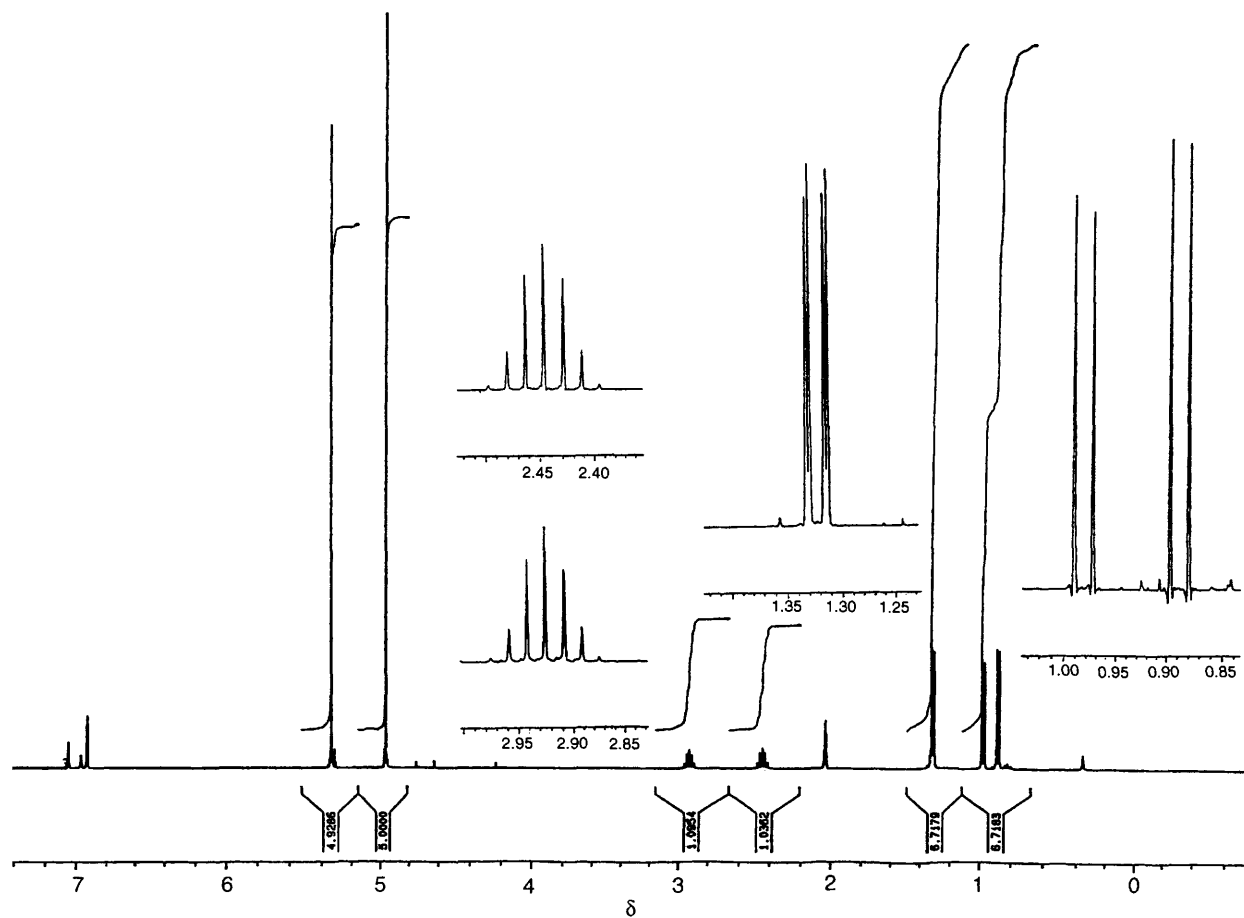


Fig. 1 Proton NMR spectrum of complex **3b** in $[^2\text{H}_8]$ toluene at 298 K, with expansions of the peaks due to the protons of the Pr^i groups. The peaks at δ 2.05 and around 7 are due to the solvent

$[\text{Mo}_2(\mu\text{-SMe})_2(\text{CO})_2(\eta\text{-C}_5\text{H}_5)_2]$ with S_8 gives $[\text{Mo}_2(\mu\text{-S})_2(\mu\text{-SMe})_2(\eta\text{-C}_5\text{H}_5)_2]$, but this reaction does not appear to have been extended to other thiols. Since alkyne complex **1** is readily available in 75–80% yield from $[\text{Mo}_2(\text{CO})_6(\eta\text{-C}_5\text{H}_5)_2]$, our synthesis of **2** represents a convenient alternative to the two earlier procedures. However it should be noted that attempts to carry out the reaction as a one-pot synthesis directly from $[\text{Mo}_2(\text{CO})_6(\eta\text{-C}_5\text{H}_5)_2]$ were largely unsuccessful, giving much reduced overall yields; we attribute this to unwanted side reactions between the thiols and the excess of but-2-yne remaining in the solution.

It is noteworthy that no dealkylation to sulfide ligands occurs in the thermal reaction of $[\text{Mo}_2(\text{CO})_6(\eta\text{-C}_5\text{H}_5)_2]$ or $[\text{Mo}_2(\text{CO})_4(\eta\text{-C}_5\text{H}_5)_2]$ with thiols or disulfides,¹⁰ though recently $[\text{Mo}_2(\mu\text{-S})(\mu\text{-SMe})_2(\text{CO})_2(\eta\text{-C}_5\text{Me}_5)_2]$ was isolated from the reaction of $[\text{Mo}_2(\text{CO})_4(\eta\text{-C}_5\text{Me}_5)_2]$ with S_2Me_2 .¹¹ We have previously shown that $[\text{Mo}_2(\text{CO})_4(\eta\text{-H})(\mu\text{-PPh}_2)(\eta\text{-C}_5\text{H}_5)_2]$ reacts with thiols to produce $[\text{Mo}_2(\mu\text{-S})_2(\mu\text{-SR})(\mu\text{-PPh}_2)(\eta\text{-C}_5\text{H}_5)_2]$, a reaction in which C–S bond cleavage does occur,¹² and its observation again in the preparation of **2** suggests that thiol dealkylation at dimolybdenum centres may be more common than previously supposed.

Molybdenum–ruthenium clusters

Dinuclear complexes with sulfur or thiolate ligands are common building blocks for the construction of larger clusters due to the ability of lone pairs on these ligands to co-ordinate to additional metal fragments.¹³ Previous work has shown that bimetallic Mo–Co, Mo–Fe and Mo–Ni clusters with $\mu_3\text{-S}$ ligands can be obtained by the reaction of suitable dimolybdenum complexes, particularly $[\text{Mo}_2(\mu\text{-SMe})_2(\text{CO})_2(\eta\text{-C}_5\text{H}_5)_2]$ and $[\text{Mo}_2(\mu\text{-S})_2(\mu\text{-SH})_2(\eta\text{-C}_5\text{H}_4\text{Me})_2]$, with metal

carbonyls.^{8,9,14} Moreover, some of these mixed-metal clusters will abstract sulfur from organosulfur compounds, including thiophene,¹⁵ and can be adsorbed on alumina and treated with H_2S to produce supported mixed sulfides which display activity similar to that of conventional hydrodesulfurisation catalysts.¹⁶ Until now, however, no examples of molybdenum–ruthenium clusters have been prepared by this route. Indeed the only examples of Mo–Ru–S clusters are $[\text{Mo}_2\text{Ru}(\mu_3\text{-S})(\text{CO})_7(\eta\text{-C}_5\text{H}_5)_2]$ and related complexes, prepared by metal exchange from $[\text{Ru}_3(\mu_3\text{-S})(\text{CO})_{10}]$ and $[\text{Mo}_2(\text{CO})_4(\eta\text{-C}_5\text{H}_5)_2]$.¹⁷ We therefore examined the reactivity of the dimolybdenum complexes towards ruthenium carbonyl as part of our current interest in mixed-metal Mo–Ru systems.¹⁸

The reactions of complex **2a** or **2b** with 1 equivalent of $[\text{Ru}_3(\text{CO})_{12}]$ under reflux for 2 h each gave one red-brown major product **3a**, **3b**. In the case of **2a** each individual isomer was found to react separately with $[\text{Ru}_3(\text{CO})_{12}]$ to give the same product **3a** as a single isomer with no difference in yield. The product clusters were initially identified by their spectroscopic data. The presence of $\text{Ru}(\text{CO})_x$ units in **3a** and **3b** was immediately apparent from the IR spectra, and their molecular formulae were readily deduced from the mass spectra, both of which show molecular ion envelopes centred on m/z 824 and 852 respectively. The NMR spectra provided more subtle information. In the ^1H NMR spectrum of **3b** (Fig. 1) it is clear that the thiolate ligands have been retained, and not only are the two Pr^i groups inequivalent, but so are the methyl groups of each one; decoupling experiments established that the methyl peaks at δ 1.4 are associated with the CH septet at δ 2.88. The two $\eta\text{-C}_5\text{H}_5$ ligands (and hence the two Mo atoms) are also different. Similar inequivalences are observed in the ^{13}C NMR spectrum, with the addition that four peaks due to the four CO ligands are observed, showing that the two ruthenium atoms

Table 1 Selected bond lengths (Å) and angles (°) with estimated standard deviations (e.s.d.s) for cluster **3b**

Mo(1)–Mo(2)	2.651(2)	Mo(1)–Ru(1a)	2.856(2)
Mo(1)–Ru(2a)	2.869(2)	Mo(1)–S(1)	2.391(3)
Mo(1)–S(2)	2.386(3)	Mo(1)–S(4)	2.536(3)
Mo(2)–Ru(1a)	2.928(2)	Mo(2)–Ru(2a)	2.952(2)
Mo(2)–S(1)	2.401(3)	Mo(2)–S(2)	2.409(3)
Mo(2)–S(4)	2.533(3)	Ru(1a)–Ru(2a)	2.682(2)
Ru(1a)–S(2)	2.328(3)	Ru(1a)–S(3)	2.358(3)
Ru(1a)–C(3)	1.877(9)	Ru(1a)–C(4)	1.929(15)
Ru(2a)–S(1)	2.334(3)	Ru(2a)–S(3)	2.351(3)
Ru(2a)–C(1)	1.914(10)	Ru(2a)–C(2)	1.908(10)
S(3)–C(15)	1.864(10)	S(4)–C(18)	1.882(12)
O(1)–C(1)	1.166(13)	O(2)–C(2)	1.162(13)
O(3)–C(3)	1.166(12)	O(4)–C(4)	1.131(20)
C(15)–C(16)	1.544(16)	C(15)–C(17)	1.523(17)
C(18)–C(19)	1.513(16)	C(18)–C(20)	1.512(15)
Mo(2)–Mo(1)–Ru(1a)	64.1(1)	Mo(2)–Mo(1)–Ru(2a)	64.5(1)
Ru(1a)–Mo(1)–Ru(2a)	55.9(1)	Mo(1)–Mo(2)–Ru(1a)	61.3(1)
Mo(1)–Mo(2)–Ru(2a)	61.3(1)	Ru(1a)–Mo(2)–Ru(2a)	54.3(1)
Mo(1)–Ru(1a)–Mo(2)	54.5(1)	Mo(1)–Ru(1a)–Ru(2a)	62.3(1)
Mo(2)–Ru(1a)–Ru(2a)	63.3(1)	Mo(1)–Ru(2a)–Mo(2)	54.2(1)
Mo(1)–Ru(2a)–Ru(1a)	61.8(1)	Mo(2)–Ru(2a)–Ru(1a)	62.4(1)
Mo(1)–S(1)–Mo(2)	67.2(1)	Mo(1)–S(1)–Ru(2a)	74.8(1)
Mo(2)–S(1)–Ru(2a)	77.1(1)	Mo(1)–S(2)–Mo(2)	67.1(1)
Mo(1)–S(2)–Ru(1a)	74.6(1)	Mo(2)–S(2)–Ru(1a)	76.3(1)
Ru(1a)–S(3)–Ru(2a)	69.4(1)	Mo(1)–S(4)–Mo(2)	63.1(1)
Ru(2a)–C(1)–O(1)	176.9(10)	Ru(2a)–C(2)–O(2)	178.4(9)
Ru(1a)–C(3)–O(3)	178.0(11)	Ru(1a)–C(4)–O(4)	178.3(11)

are also in different environments. The spectra of **3a** were very similar, implying that the two clusters have the same overall structure; the inequivalence of the methyl groups in **3b** is mirrored in the diastereotopic nature of the ethyl protons in **3a**.

The structure of cluster **3b** has been determined by X-ray crystallography; the molecular geometry is shown in Fig. 2, with selected bond lengths and angles collected in Table 1. The molecule consists of a core of two molybdenum atoms and two ruthenium atoms arranged in a tetrahedron, with the two Mo₂Ru faces capped by triply bridging sulfide ligands. The two homometallic bonds are symmetrically bridged by the SPrⁱ ligands and are both rather short [Mo–Mo 2.651(2) Å, Ru–Ru 2.862(2) Å]. The Mo–Ru bonds involving Mo(1) are shorter than those involving Mo(2) [Mo(1)–Ru(1a) 2.856(2), Mo(1)–Ru(2a) 2.869(2) Å whereas Mo(2)–Ru(1a) 2.928(2) and Mo(2)–Ru(2a) 2.952(2) Å] but all these distances are comparable to those found in other Mo–Ru clusters.^{17,18} The Mo–S bonds to the bridging thiolate ligand (average 2.535 Å) are rather longer than those to the μ₃-S ligands (average 2.397 Å), whereas the corresponding distances for Ru are more similar (average 2.355 and 2.331 Å respectively).

The co-ordination sphere around each molybdenum atom is completed by a cyclopentadienyl ring and that around each ruthenium by two terminal carbonyl ligands; the structural features of these are unremarkable. The two C₅H₅ rings lie almost parallel: the angle of inclination is 5.9°.

Examination of the solid-state structure of complex **3b** explains the asymmetry observed in the solution NMR spectra. Clearly the sulfur atoms of the thiolate ligands do not undergo inversion at room temperature, and the fixed orientation of their substituents is sufficient to render the two Mo atoms and the two Ru atoms inequivalent. It is interesting that inversion of the SPrⁱ ligand on the Ru–Ru edge would render the C₅H₅ ligands and the methyl groups of the other SPrⁱ equivalent, whereas fluxionality of the thiolate on the Mo–Mo edge would lead to pairwise equivalence of the CO ligands and the methyls of the other SPrⁱ. Inversion at both sulfur atoms would lead to equivalence of all of the CO ligands, and mobility of the SPrⁱ groups over the cluster would lead to averaging of the two Prⁱ environments. This seemed to provide a good opportunity

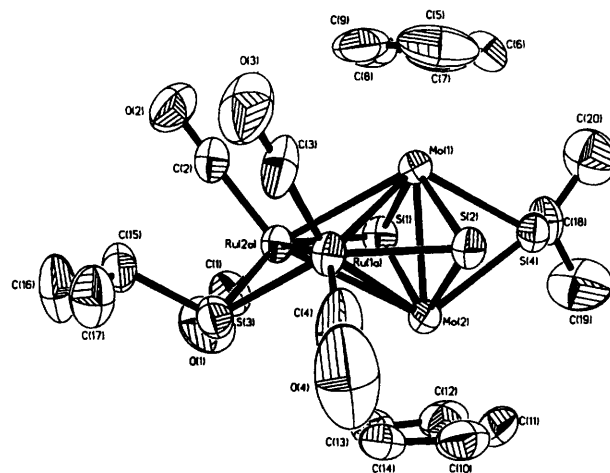


Fig. 2 Molecular structure of complex **3b** in the crystal, showing the atom numbering scheme

to obtain directly comparable values for the inversion of SPrⁱ ligands on Mo–Mo and Ru–Ru edges in the same complex, but unfortunately the ¹H NMR spectrum of **3b** at 90 °C in [²H₈]toluene is unchanged from that at 25 °C, showing that there is a large barrier to sulfur inversion in both ligands.

It should be noted that [Mo₂(μ-S)₂(μ-SMe)₂(η-C₅H₅)₂] is reported to react with [Co₂(CO)₈] to give sulfido clusters analogous to those obtained from [Mo₂(μ-S)₂(μ-SH)₂(η-C₅H₄Me)₂], *i.e.* dealkylation of the thiolate ligands occurs during the cluster-building reaction.⁹ In the present reaction both of the thiolate ligands are retained, though one of them migrates across the face of the cluster to the Ru–Ru edge. It is not yet apparent why this difference in reactivity exists, and clearly a greater understanding of the factors affecting C–S bond cleavage in such systems is worth pursuing.

Experimental

General experimental techniques and instrumentation were as described in recent papers from this Laboratory.^{18,19} Except

where otherwise stated, the ^1H and ^{13}C NMR spectra were recorded in CDCl_3 solution, with chemical shifts given on the δ scale relative to SiMe_4 (0.0 ppm). Light petroleum refers to that fraction boiling between 60 and 80 °C. The complex $[\text{Mo}_2(\text{CO})_6(\eta\text{-C}_5\text{H}_5)_2]$ was prepared by a literature method.²⁰ The alkyne complex **1** was prepared by a slight modification of the literature procedure; we find that improved yields (75–80%) are obtained by allowing the reaction between $[\text{Mo}_2(\text{CO})_4(\eta\text{-C}_5\text{H}_5)_2]$ and but-2-yne to stir overnight rather than the 2 h previously recommended.²¹

Syntheses

$[\text{Mo}_2(\mu\text{-S})_2(\mu\text{-SEt})_2(\eta\text{-C}_5\text{H}_5)_2]$ 2a. The complex $[\text{Mo}_2(\text{CO})_4(\mu\text{-C}_2\text{Me}_2)(\eta\text{-C}_5\text{H}_5)_2]$ (1.0 g, 2.05 mmol) was dissolved in toluene (125 cm³) and 5 equivalents of EtSH (0.7 cm³, 10.25 mmol) were added. The solution was then heated to reflux for 16 h, causing a change to purple. After removal of the solvent *in vacuo* and adsorption of the residue onto a small amount of silica, the products were separated on a column. A weak red band of unchanged **1** was followed by two purple bands; the first was eluted with light petroleum–dichloromethane (1:1) and the second with a 1:3 mixture of the same solvents. These were identified as the major (260 mg, 0.51 mmol) and minor (120 mg, 0.24 mmol) isomers of $[\text{Mo}_2(\mu\text{-S})_2(\mu\text{-SEt})_2(\eta\text{-C}_5\text{H}_5)_2]$, combined yield 36.5%. A third, unidentified, purple band (50 mg) was also eluted. Major isomer: ^1H NMR δ 6.49 (s, 10 H, C₅H₅), 1.47 (q, $J = 8$, 4 H, CH₂) and 0.62 (t, $J = 8$ Hz, 6 H, CH₃); mass spectrum m/z 508 (M^+). Minor isomer: ^1H NMR δ 6.44 (s, 10 H, C₅H₅), 1.49 (q, $J = 8$, 4 H, CH₂) and 0.66 (t, $J = 8$ Hz, 6 H, CH₃); mass spectrum m/z 508 (M^+).

$[\text{Mo}_2(\mu\text{-S})_2(\mu\text{-SPr}^i)(\eta\text{-C}_5\text{H}_5)_2]$ 2b. The complex $[\text{Mo}_2(\text{CO})_4(\mu\text{-C}_2\text{Me}_2)(\eta\text{-C}_5\text{H}_5)_2]$ (2.12 g, 4.35 mmol) was treated with 10 equivalents of PrⁱSH (4.0 cm³, 43.5 mmol) in refluxing toluene (150 cm³) for 20 h. The solvent was removed *in vacuo*, and the residue chromatographed. Elution with light petroleum–CH₂Cl₂ (4:1) removed a small amount of unreacted **1**, and elution with a 1:1 mixture of the same solvents produced a purple band containing both isomers of $[\text{Mo}_2(\mu\text{-S})_2(\mu\text{-SPr}^i)(\eta\text{-C}_5\text{H}_5)_2]$ (1.0205 g, 43.8%). Several minor bands were eluted with CH₂Cl₂ but none could be identified. The top of the column remained stained bright orange; Soxhlet extraction with methanol produced an orange solution but no tractable product could be isolated from it. Major isomer: ^1H NMR δ 6.44 (s, 10 H, C₅H₅), 1.71 (spt, $J = 7$, 2 H, CH) and 0.69 (d, $J = 7$ Hz, 12 H, Me). Minor isomer: ^1H NMR δ 6.51 (s, 10 H, C₅H₅), 1.98 (spt, $J = 7$, 2 H, CH) and 0.68 (d, $J = 7$ Hz, 12 H, Me). Mass spectrum: m/z 536 (M^+).

$[\text{Mo}_2\text{Ru}_2(\mu_3\text{-S})_2(\mu\text{-SEt})_2(\text{CO})_4(\eta\text{-C}_5\text{H}_5)_2]$ 3a. The major isomer of complex **2a** (150 mg, 0.30 mmol) and $[\text{Ru}_3(\text{CO})_{12}]$ (190 mg, 0.30 mmol) were dissolved in tetrahydrofuran (100 cm³) and heated to reflux. Over a period of 2 h the solution changed from dark red to brown and TLC monitoring showed the disappearance of the starting materials. The solvent was removed and the residue chromatographed. A faint orange band was eluted with light petroleum and identified as $[\text{Ru}_3(\text{CO})_{12}]$, and then the product, cluster **3a**, was eluted with light petroleum–CH₂Cl₂ (4:1) as a brown band. Yield 200 mg, 82%. The compound was recrystallised from heptane; three separate recrystallisations gave identical analytical results and heptane peaks were observed in the ^1H NMR spectrum of the recrystallised material. M.p. >250 °C. IR (C₆H₁₂) 2005, 1993 and 1937 cm⁻¹. NMR: ^1H , δ 5.67 (s, 5 H, C₅H₅), 5.24 (s, 5 H, C₅H₅), 3.03 (q, $J = 7$, 2 H, CH₂), 2.31 (m, 2 H, CH₂), 1.37 (t, $J = 7$, 3 H, CH₃) and 1.16 (t, $J = 7$ Hz, 3 H, CH₃); ^{13}C , δ 206.0, 204.9, 201.6, 200.2 (all s, CO), 97.6, 89.4 (both s, C₅H₅), 57.2 (s, CH₂), 34.8 (s, CH₂), 18.1 (s, CH₃) and 17.8 (s, CH₃)

(Found: C, 28.05; H, 2.75. Calc. for C₁₈H₂₀Mo₂O₄Ru₂S₄·0.25C₇H₁₆: C, 28.00; H, 2.85%). Mass spectrum: m/z 824 (M^+), 794, 768, 738, 711, 680 and 653.

$[\text{Mo}_2\text{Ru}_2(\mu_3\text{-S})_2(\mu\text{-SPr}^i)(\text{CO})_4(\eta\text{-C}_5\text{H}_5)_2]$ 3b. A solution of $[\text{Mo}_2(\mu\text{-S})_2(\mu\text{-SPr}^i)(\eta\text{-C}_5\text{H}_5)_2]$ (0.8219 g, 1.53 mmol) and $[\text{Ru}_3(\text{CO})_{12}]$ (0.99 g, 1.55 mmol) in tetrahydrofuran (125 cm³) was heated to reflux for 2.25 h. On chromatography as above a small amount of $[\text{Ru}_3(\text{CO})_{12}]$ was eluted with light petroleum followed by a dark orange-grey band of cluster **3b** (0.97 g, 74%) which was eluted with light petroleum–CH₂Cl₂ (5:1). M.p. 242 °C. IR (C₆H₁₂) 2004, 1992 and 1936 cm⁻¹. NMR: ^1H , δ 5.75 (s, 5 H, C₅H₅), 5.28 (s, 5 H, C₅H₅), 2.88 (spt, $J = 7$, 1 H, CH), 2.72 (spt, $J = 7$, 1 H, CH), 1.45 (d, $J = 7$, 3 H, Me), 1.43 (d, $J = 7$, 3 H, Me), 1.27 (d, $J = 7$, 3 H, Me) and 1.20 (d, $J = 7$ Hz, 3 H, Me); ^{13}C , δ 206.1, 204.8, 202.2, 200.1 (all s, CO), 97.6, 89.2 (both s, C₅H₅), 61.2, 43.7 (both s, CH), 27.6, 26.0 (both s, Me) and 25.5 (s, 2 Me coincident) (Found: C, 28.55; H, 2.90. Calc. for C₂₀H₂₄Mo₂O₄Ru₂S₄: C, 28.25; H, 2.80%). Mass spectrum: m/z 852 (M^+), 824, 796, 767 and 654.

Crystallography

Crystal data. C₂₀H₂₄Mo₂O₄Ru₂S₄ **3b**. $M = 850.67$, crystallises from chloroform–light petroleum as deep red-brown blocks, crystal dimensions 0.50 × 0.30 × 0.20 mm, monoclinic, space group $P2_1/n$ (a non-standard setting of $P2_1/c$ C_{2h}, no. 13), $a = 15.370(11)$, $b = 10.744(8)$, $c = 17.372(11)$ Å, $\beta = 104.08(5)^\circ$, $U = 2782(3)$ Å³, $Z = 4$, $D_c = 2.030$ g cm⁻³, Mo–K α radiation ($\lambda = 0.710$ 69 Å), $\mu(\text{Mo–K}\alpha) = 22.19$ cm⁻¹, $F(000) = 1647.53$.

Three-dimensional, room-temperature X-ray data were collected in the range $3.5 < 2\theta < 45^\circ$ on a Nicolet R3 diffractometer by the ω -scan method. The 3089 independent reflections (of 4053 measured) for which $|F|/\sigma(|F|) > 3.0$ were corrected for Lorentz and polarisation effects, but not for absorption. The structure was solved by direct methods and refined by blocked-cascade least-squares methods on F . Hydrogen atoms were included in calculated positions and refined in riding mode. Refinement converged at a final $R = 0.0489$ ($R' = 0.0503$, 289 parameters, mean and maximum δ/σ 0.001, 0.010), with allowance for the thermal anisotropy of all non-hydrogen atoms. Minimum and maximum final electron density -1.18 and 0.93 e Å⁻³. A weighting scheme $w^{-1} = [\sigma^2(F) + 0.00094F^2]$ was used in the latter stages of refinement. Complex scattering factors were taken from the program package SHELXTL²² as implemented on a Data General DG30 computer.

Atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/84.

Acknowledgements

We thank the SERC (now the EPSRC) for studentships (to S. R. G. and L. J. G.) and Johnson Matthey plc for a generous loan of ruthenium trichloride. We also thank Dr. B. F. Taylor for assistance in recording the NMR spectra.

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Received 13th February 1996; Paper 6/01060A