Phosphido-bridged dimolybdenum complexes with sulfide and thiolate ligands as precursors to mixed-metal clusters

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Abstract

Treatment of [Mo$_2$(μ-H)(μ-PPh$_2$)(CO)$_4$(η-C$_5$H$_5$)$_2$] with an excess of a thiol, RSH, in refluxing toluene produced the novel quadruply-bridged compounds [Mo$_2$(μ-S)$_2$(μ-SR)(μ-PPh$_2$)(η-C$_5$H$_5$)$_2$] (7a, R = Et; 7b, R = Pr^i; 7c, R = Bu^t; 7d, R = p-C$_6$H$_4$Me; 7e R = C$_{12}$H$_{25}$) in moderate to good yield. The sulfur ligands in the product are formed by dealkylation of the thiol at the dimolybdenum centre. The reaction is proposed to proceed via the unstable intermediate species [Mo$_2$(μ-SR)(μ-PPh$_2$)(CO)$_2$(η-C$_5$H$_5$)$_2$], which could not be isolated in a pure form. Reaction of 7a–d with [Ru$_3$(CO)$_{12}$] in refluxing tetrahydrofuran (thf) produced good yields of the mixed-metal clusters [Mo$_2$Ru$_2$(μ_3-S)$_2$(μ-SR)(μ-PPh$_2$)(CO)$_4$(η-C$_5$H$_5$)$_2$] 9; the X-ray crystal structure of the Et-substituted complex 9a has been determined. The cluster consists of a tetrahedral metal core with both Mo$_2$Ru faces capped by triply bridging sulfides. The phosphido group bridges the Mo–Mo bond, whereas the thiolate ligand has migrated to the Ru–Ru edge. © 1997 Elsevier Science S.A.

1. Introduction

Molybdenum complexes with sulfur-based ligands have been extensively studied for a number of years, and display an extremely rich and varied reaction chemistry [1]. Interest in such compounds stems both from their occurrence in biochemical systems such as nitrogenase, and from their relevance to important industrial processes, particularly hydrodesulfurisation, which employs a heterogeneous molybdenum–cobalt sulfide catalyst [2]. Dinuclear molybdenum complexes have been shown to act as models for some of the processes which occur on the catalyst surface [3], and a mixed-metal cluster derived from a dimolybdenum precursor, the unsaturated species [Co$_2$Mo$_2$(μ-S)$_2$(μ_4-S)(CO)$_4$(η-C$_5$H$_4$Me)$_2$], has been shown to be capable of removing sulfur from a range of organic substrates in solution [4]; moreover this and similar clusters have given rise to active hydrodesulfurisation catalysts after deposition on suitable supports and treatment with H$_2$S [5]. Recently the homogeneous hydrodesulfurisation of benzothiophene has been achieved in a dinuclear heterobimetallic

(RhW) complex, by way of an intermediate with a bridging thiolate ligand [6].

1

2
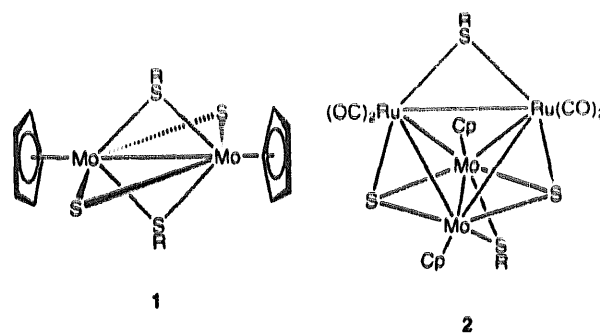
We recently reported an improved route to the quadruply bridged compounds [Mo$_2$(μ-S)$_2$(μ-SR)$_2$(η-C$_5$H$_5$)$_2$] (1a, R = Et; 1b, R = Pr^i), and their subsequent reaction with [Ru$_3$(CO)$_{12}$] to give the tetrahedral mixed metal clusters [Mo$_2$Ru$_2$(μ_3-S)$_2$(μ-SR)$_2$(CO)$_4$(η-C$_5$H$_5$)$_2$] 2 [7]. In the products, one of the thiolate ligands has migrated from the Mo–Mo bond to the Ru–Ru edge. We have previously communicated the synthesis of the related complexes [Mo$_2$(μ-S)$_2$(μ-SR)(μ-PPh$_2$)(η-C$_5$H$_5$)$_2$], in which one of the thiolate bridges in 1 is replaced by a phosphido group [8]. Prompted by the findings above, we were interested in

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discovering whether similar mixed-metal clusters could be synthesized from these, and if so, whether it would be the thiolate ligand or the phosphido bridge which would migrate over the cluster framework. Here we present full details of the synthesis of the dimolybdenum precursors with improved yields, and the results of their reactions with ruthenium carbonyl.
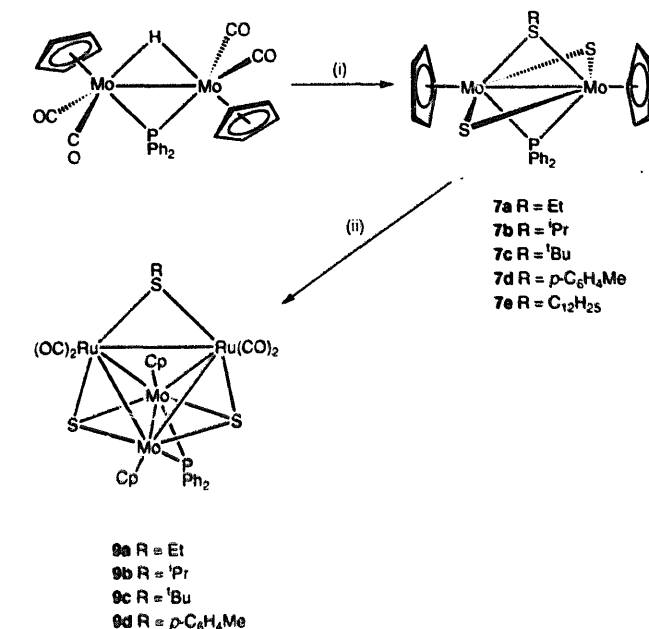
2. Results and discussion

2.1. Dimolybdenum complexes

We initially investigated the reaction of [Mo₂(μ-H)(μ-PPh₂)(CO)₄(η-C₅H₅)₂] 3 with thiols in the expectation that it would provide a route to the mixed ligand species [Mo₂(μ-SR)(μ-PPh₂)(CO)₂(η-C₅H₅)₂] 4. Complex 3 is known to react with further PPh₂H to give the bis-phosphido complex [Mo₂(μ-PPh₂)₂(CO)₂(η-C₅H₅)₂] 5, which can also be prepared by the reaction of [Mo₂(CO)₆(η-C₅H₅)₂] with P₂Ph₄ [9]. Moreover the bis-thiolato complexes [Mo₂(μ-SR)₂(CO)₂(η-C₅H₅)₂] 6 are also known to be accessible through a similar reaction of [Mo₂(CO)₆(η-C₅H₅)₂] with RSSR [10]. The synthesis of a mixed-ligand species therefore seemed an achievable goal.

3
4   X = PPh₂, Y = SR
5   X = Y = PPh₂
6   X = Y = SR
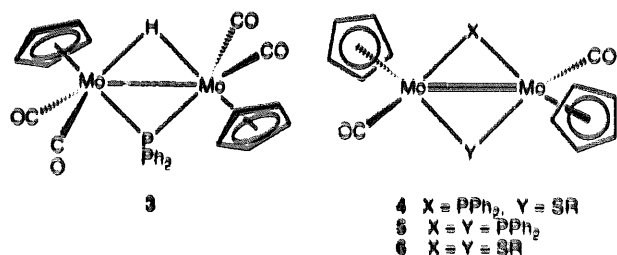
In the event, complex 3 reacted only rather slowly with thiols in refluxing toluene, and in each case two products, the first green and the second purple, were formed. We believe that the green compounds are indeed [Mo₂(μ-SR)(μ-PPh₂)(CO)₂(η-C₅H₅)₂] 4a–e, but it has proved impossible to characterise them owing to their instability. Whereas the bis-thiolato complexes 6 are air-stable and the bis-phosphido complex 5 decomposes only very slowly in air to give a mixture of the isolable oxo species cis and trans-[Mo₂(O)(μ-PPh₂)₂(CO)(η-C₅H₅)₂], the mixed-ligand analogues decompose to largely insoluble red-brown materials even on standing under argon or in a vacuum. However, the solution IR spectra of 4 are very similar to those of 5 and 6 (which are also green in colour) and the few spectroscopic data we were able to obtain are all consistent with this formulation.

The purple products were characterised as the quadruply-bridged Mo(IV) complexes [Mo₂(μ-S)₂(μ-

7a R = Et
7b R = ⁱPr
7c R = ᵗBu
7d R = p-C₆H₄Me
7e R = C₁₂H₂₅

9a R = Et
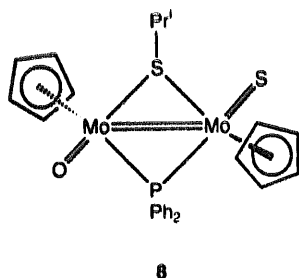9b R = ⁱPr
9c R = ᵗBu
9d R = p-C₆H₄Me

Scheme 1. Synthesis of the dimolybdenum complexes and tetranuclear clusters. Reagents and conditions: (i) RSH, 5 equiv., toluene, reflux, 48 h, then more RSH or S₈ (see text); (ii) [Ru₃(CO)₁₂], thf, reflux, 1 h.

SR)(μ-PPh₂)(η-C₅H₅)₂] 7a–e (see Scheme 1). The IR spectra confirmed the loss of all the carbonyl ligands, while the ¹H-NMR spectra showed signals for phenyl rings, η-C₅H₅ ligands and the R group in appropriate integral ratios (see Section 3). The low field shift of the cyclopentadienyl protons (around δ 6.4) is characteristic for quadruply-bridged structures of this type. Sulfur inversion at the bridging thiolate ligand must be slow on the NMR timescale, as shown by the observation of two doublets for the ipso carbon atoms of the PPh₂ group in the ¹³C-NMR spectra. This is also the case in [Mo₂(μ-S)₂(μ-SR)₂(η-C₅H₅)₂], allowing the existence of two separable isomers depending on the syn or anti orientation of the R groups [11]. Very small signals due to the bis-thiolate complexes 1 could be discerned in the NMR spectra of 7, implying that a ligand exchange process involving loss of the phosphido group occurs to a small extent during the reaction. Complex 1e is separable from 7e by chromatography, whereas 1a–d can be removed by recrystallisation.

Complex 7e was prepared from the involatile dodecane-1-thiol in order to determine the fate of the alkyl group during desulfurisation. Gas chromatography analysis of the liquid remaining after removal of the solvent showed that the main product was dodecane, with only trace amounts of dodec-1-ene (by comparison with authentic samples). A control reaction confirmed that the thiol itself was unchanged after heating under similar conditions. It therefore appears that, as in the related systems studied by Curtis [12], dealkylation occurs by

C–S bond homolysis with the resulting alkyl radical scavenging a hydrogen atom from the solvent.

In our original communication the yields of **7** were described as rather low, typically 15%. To obtain synthetically useful quantities we have now modified the reaction conditions to give better yields. After a reaction time of 48 h, the reaction mixture consists of green **4** and purple **7**. Addition of further thiol at this stage and continued refluxing results in the gradual disappearance of **4** and production of increased amounts of **7**, implying that (as expected) the former is an intermediate in the formation of the latter. In order to confirm this, the green product obtained from a synthesis of **7b** was separated chromatographically and heated with a further excess of thiol. This did indeed result in the formation of **7b**, but a second product was also isolated and tentatively identified as [Mo₂O(S)(μ-SPrⁱ)(μ-PPh₂)(η-C₅H₅)₂] **8**. We attribute this to the presence of an oxidation product, presumably [Mo₂O(μ-SPrⁱ)(μ-PPh₂)(CO)(η-C₅H₅)₂] by analogy with those derived from **5**, in the starting sample of **4b**. The characterisation of **8** is based on its IR spectrum (no carbonyl absorptions, but a clear Mo=O absorption at 891 cm⁻¹), mass spectrum and ¹H- and ³¹P-NMR spectra. Thus, in the ¹H-NMR spectrum the C₅H₅ ligands are inequivalent, and their chemical shift values (δ 5.16 and 5.49) suggest that the compound is not a quadruply-bridged species like **7**; the two methyl groups of the μ-SPrⁱ ligand are also inequivalent. The ³¹P-NMR spectrum confirmed the presence of the phosphido bridge, but again its different chemical shift (176.3 ppm) is indicative of a structure unlike that of **7**. We therefore propose the structure shown in which one molybdenum bears a terminal oxo ligand, and the other a terminal sulfido group; this formulation is backed up by the mass spectrum, which shows an appropriate molecular ion.

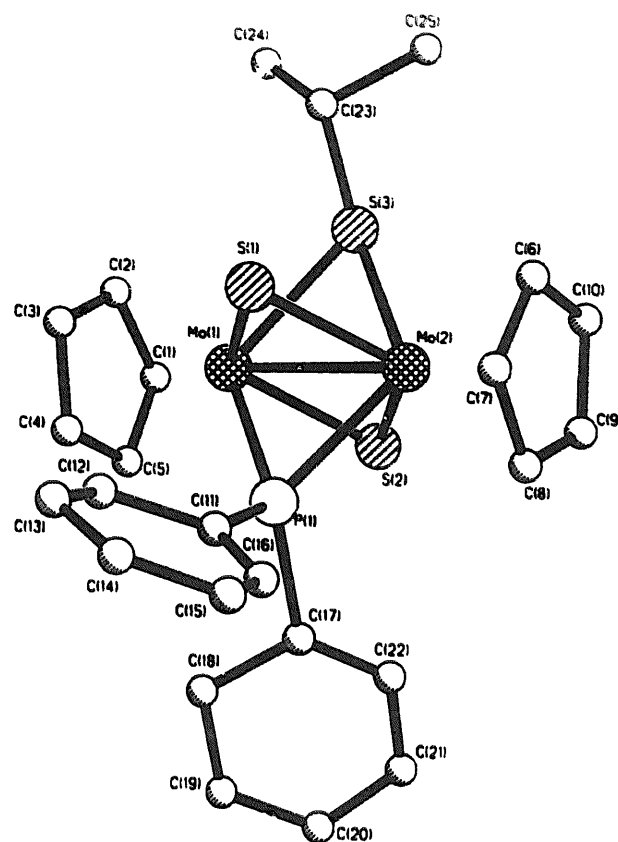
Fig. 1. Molecular structure of complex **7b** in the crystal.

sumably due to the bulky Buⁱ group hindering the approach of further thiol molecules. However addition of elemental sulfur successfully caused the rapid conversion of **4c** to **7c** on warming, though even then, the isolated yield was only 24%. An attempt to carry out the reaction as a general one-pot process by treatment of **3** with an appropriate amount of sulfur and an excess of PrⁱSH gave only a disappointing yield (17%) of **7b**, probably due to the fact that **3** itself reacts with sulfur to give low yields of a complex which we believe to be [Mo₂(μ-S)₂(μ-SH)(μ-PPh₂)(η-C₅H₅)₂] [13]. Thus the optimum procedure for the preparation of **7** consists of heating complex **3** with the appropriate thiol for 48 h, followed by addition of either more thiol or in the case of R = Buⁱ, elemental sulfur.

The X-ray crystal structure of complex **7b** (R = Prⁱ) has been determined and was reported briefly in our preliminary communication [8]; a diagram of the structure is shown in Fig. 1, with selected bond lengths and angles collected in Table 1. The Mo–Mo bond of length 2.623(2) Å is spanned symmetrically by the four bridging ligands, with the Mo₂(μ-S)₂ and Mo₂SP planes virtually perpendicular to each other (see below). One further point of interest in relation to the current work is that the Mo–P bonds to the phosphido bridge (2.409 and 2.400 Å) are slightly shorter than the Mo–S bonds of the bridging thiolate group, which are 2.498 and

In most cases the strategy of adding more thiol during the reaction raised the yield of **7** considerably, to 39–66% depending on R. In the case of R = Buⁱ, however, after 48 h reaction time the reaction mixture was green (due to **4c**) and only a small amount of **7c** was present (a yield of 6% was obtained by work-up at this point). Addition of more BuⁱSH and continued heating did not change this product distribution, pre-

Table 1
Selected bond lengths (Å) and angles (°) for complex 7b

Mo(1)-Mo(2)	2.623(2)	Mo(1)-S(1)	2.352(2)
Mo(1)-S(2)	2.368(3)	Mo(1)-S(3)	2.498(3)
Mo(1)-P(1)	2.409(4)	Mo(2)-S(1)	2.323(2)
Mo(2)-S(2)	2.359(3)	Mo(2)-S(3)	2.485(4)
Mo(2)-P(1)	2.400(3)	S(3)-C(23)	1.683(8)
S(3)-C(23A)	1.683(10)	P(1)-C(11)	1.763(6)
P(1)-C(17)	1.902(6)		
Mo(1)-S(2)-Mo(2)	67.4(1)	Mo(1)-S(1)-Mo(2)	68.2(1)
Mo(1)-S(3)-Mo(2)	63.5(1)	Mo(1)-P(1)-Mo(2)	66.1(1)

2.485 Å. Overall the structure is very similar to that previously determined for [Mo$_2$(μ-S)$_2$(μ-SMe)$_2$(η-C$_5$H$_4$Me)$_2$] [11].

2.2. Molybdenum–ruthenium clusters

On heating a solution of 7a–d with one equivalent of [Ru$_3$(CO)$_{12}$] in refluxing thf (the same conditions as employed for the synthesis of 2), the dimolybdenum complex was rapidly consumed and the new mixed-metal clusters [Mo$_2$Ru$_2$(μ_3-S)$_2$(μ-SR)(μ-
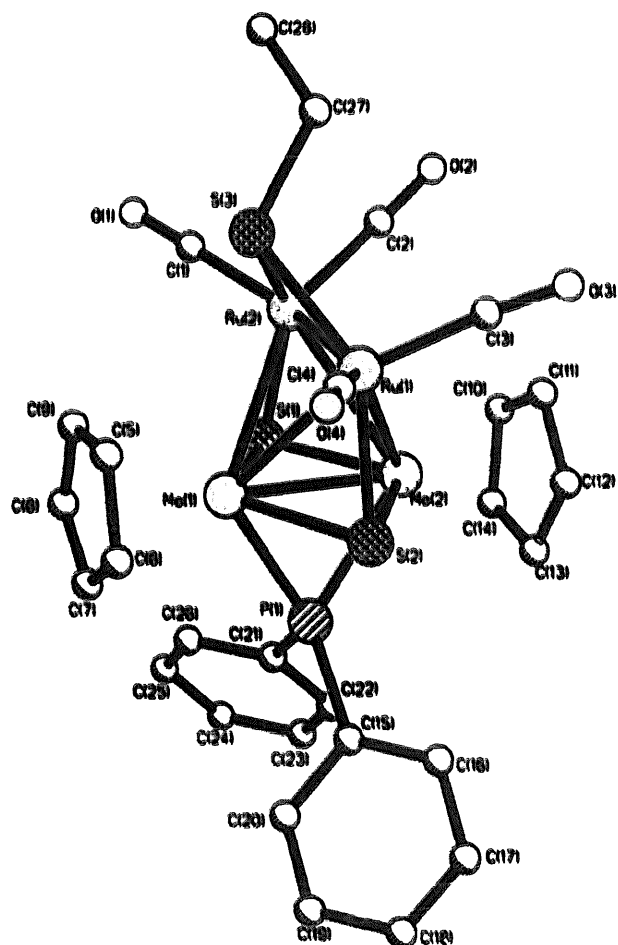

Fig. 2. Molecular structure of complex 9a·CH$_2$Cl$_2$ in the crystal.

Table 2
Selected bond lengths (Å) for complex 9a·0.33CH$_2$Cl$_2$

Mo(1)-S(2)	2.380(2)	Mo(1)-S(1)	2.381(2)
Mo(1)-P(1)	2.444(2)	Mo(1)-Mo(2)	2.6749(9)
Mo(1)-Ru(1)	2.8864(10)	Mo(1)-Ru(2)	2.8964(9)
Mo(2)-S(1)	2.365(2)	Mo(2)-S(2)	2.367(2)
Mo(2)-P(1)	2.463(2)	Mo(2)-Ru(2)	2.8132(9)
Mo(2)-Ru(1)	2.8458(9)	Ru(1)-C(3)	1.878(10)
Ru(1)-C(4)	1.906(9)	Ru(1)-S(2)	2.298(2)
Ru(1)-S(3)	2.332(2)	Ru(1)-Ru(2)	2.6533(9)
Ru(2)-C(2)	1.882(9)	Ru(2)-C(1)	1.921(9)
Ru(2)-S(1)	2.311(2)	Ru(2)-S(3)	2.323(2)
P(1)-C(21)	1.825(7)	P(1)-C(15)	1.840(7)
S(3)-C(27)	1.817(10)	O(1)-C(1)	1.130(10)
O(2)-C(2)	1.154(10)	O(3)-C(3)	1.145(10)
O(4)-C(4)	1.143(10)	C(27)-C(28)	1.494(14)

PPh$_2$)(CO)$_4$(η-C$_5$H$_5$)$_2$] 9a–d were formed in good yield. If the small amount of 1 present as an impurity in 7 is not removed previously, the analogous bis-thiolate clusters 2 are formed as low-yield by-products, but these are easily separated from 9 during chromatography.

The IR spectra of 9 closely resemble those of the analogous clusters 2, showing in the main three sharp bands in the ν(CO) region; for 9c the lowest frequency band is split into two. The incorporation of two Ru(CO)$_2$ units was also indicated by the mass spectra, which displayed molecular ion envelopes accompanied by peaks due to the loss of four carbonyl ligands, and by elemental analysis. The structure of the products was deduced from their ^{1}H-NMR spectra, which showed two inequivalent η-C$_5$H$_5$ ligands as well as signals for the phenyl rings and for R. Because of the presence of a symmetrical μ-PPh$_2$ group as opposed to a second thiolate ligand, the clusters contain a mirror plane, demonstrated by the observation of only one peak due to the ipso carbons of the phenyl rings in the ^{13}C-NMR spectra; the fact that the two Mo atoms are inequivalent whereas the two ruthenium atoms are equivalent therefore proves that it is the thiolate ligand which has migrated to the Ru–Ru edge whereas the μ-PPh$_2$ group

Table 3
Selected bond angles (°) for complex 9a·0.33CH$_2$Cl$_2$

| Mo(2)-Mo(1)-Ru(1)	61.42(2)	Mo(2)-Mo(1)-Ru(2)	60.50(2)
Ru(1)-Mo(1)-Ru(2)	54.62(2)	Mo(1)-Mo(2)-Ru(2)	63.65(2)
Mo(1)-Mo(2)-Ru(1)	62.95(2)	Ru(2)-Mo(2)-Ru(1)	55.92(2)
Ru(2)-Ru(1)-Mo(2)	61.42(2)	Ru(2)-Ru(1)-Mo(1)	62.88(2)
Mo(2)-Ru(1)-Mo(1)	55.63(2)	Ru(1)-Ru(2)-Mo(2)	62.66(2)
Ru(1)-Ru(2)-Mo(1)	62.50(2)	Mo(2)-Ru(2)-Mo(1)	55.85(2)
Mo(1)-P(1)-Mo(2)	66.07(5)	Ru(2)-S(1)-Mo(2)	73.96(6)
Ru(2)-S(1)-Mo(1)	76.22(6)	Mo(2)-S(1)-Mo(1)	68.61(5)
Ru(1)-S(2)-Mo(2)	75.16(6)	Ru(1)-S(2)-Mo(1)	76.18(6)
Mo(2)-S(2)-Mo(1)	68.59(5)	Ru(2)-S(3)-Ru(1)	69.49(6)
O(1)-C(1)-Ru(2)	178.6(9)	O(2)-C(2)-Ru(2)	178.2(8)
O(3)-C(3)-Ru(1)	174.7(8)	O(4)-C(4)-Ru(1)	176.1(8)
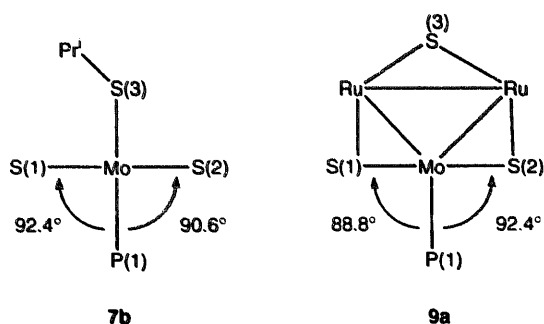
Fig. 3. Comparison of interplane angles in complexes **7b** and **9a**, viewed down the Mo–Mo bond.

has remained bonded to the Mo–Mo edge. Clearly inversion at the sulfur atom is again slow on the NMR timescale, and this remains the case at elevated temperatures: the ^{1}H-NMR spectrum of **9a** in toluene-d_8 was unchanged at 372 K.

Confirmation of the structure was obtained through a single crystal X-ray diffraction study of complex **9a** (R = Et), which unusually crystallises in the highly symmetrical hexagonal space group. The result is shown in Fig. 2, with selected bond lengths and angles collected in Tables 2 and 3, respectively. As expected, the molecule contains a tetrahedral cluster in which the two Mo$_2$Ru faces are capped by triply-bridging sulfide ligands, with the μ-SEt ligand bridging between the two ruthenium atoms and the μ-PPh$_2$ group between the two molybdenums. As observed in **2b**, the homometallic bonds (Mo–Mo 2.6749(9), Ru–Ru 2.6533(9) Å) are rather short compared to the Mo–Ru bonds; of the latter, those involving Mo(2) are significantly shorter than those involving Mo(1). The average bond lengths to the μ_3-S ligands (av. Mo–S 2.373, av. Ru–S 2.305 Å) are both slightly shorter than in **2b**, where the corresponding values were 2.397 and 2.331 Å. The μ-SEt and μ-PPh$_2$ ligands bridge their respective edges virtually symmetrically. The complex has a total of 60 valence electrons as expected for a tetrahedral cluster.

A comparison of the structures of **7b** and **9a** viewed down the Mo–Mo bond is shown in Fig. 3, emphasising the way in which the Mo(1)–Mo(2)–S(1)–S(2)–P(1) portion of the molecule remains unperturbed by the addition of the ruthenium fragments. The angles shown are those between the planes Mo(1)–Mo(2)–S(1), Mo(1)–Mo(2)–S(2) and Mo(1)–Mo(2)–P(1) (the numbering system is the same in both compounds).

From the successful formation of **9** in good yields (albeit slightly lower than those of **2**), we can conclude that replacing one bridging thiolate group in [Mo$_2$(μ-S)$_2$(μ-SR)$_2$(η-C$_5$H$_5$)$_2$] by a phosphido ligand does not appreciably hinder the cluster building reaction. This suggests that the approach of the ruthenium carbonyl fragments occurs at the opposite side of the molecule to the phosphido group. As with the analogous clusters **2**, no evidence was found for the dealkylation of the

thiolate ligand to form sulfide ligands, a process previously observed in the reaction of [Mo$_2$(μ-S)$_2$(μ-SMe)$_2$(η-C$_5$H$_5$)$_2$] with cobalt carbonyl [14]. As expected, the thiolate ligand migrates to the Ru–Ru edge in preference to the more strongly bound phosphido group. We are currently exploring possible routes to the bis(phosphido) complex [Mo$_2$(μ-S)$_2$(μ-PPh$_2$)$_2$(η-C$_5$H$_5$)$_2$] in order to discover whether a cluster can still be formed in the absence of any thiolate ligands, and if so whether one phosphido group can be encouraged to migrate to the Ru–Ru edge.

3. Experimental

General experimental techniques were as detailed in recent papers from this laboratory [15]. Infra-red spectra were recorded in CH$_2$Cl$_2$ or cyclohexane solution on a Perkin–Elmer 1600 FT–IR machine using 0.5 mm NaCl cells. ^{1}H-, ^{13}C- and ^{31}P-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$_4$ or H$_3$PO$_4$ = 0.0 ppm. The ^{13}C(^{1}H)-NMR spectra were 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 3-nitrobenzyl alcohol as matrix. Gas chromatography analyses were carried out on a Perkin–Elmer 8420 capillary GC machine fitted with a Chrompack CPSIL5 column (30 m × 0.32 mm i.d.) with H$_2$ as the carrier gas. Elemental analyses were carried out by the Microanalytical Service of the Department of Chemistry. The complex [Mo$_2$(μ-H)(μ-PPh$_2$)(CO)$_4$(η-C$_5$H$_5$)$_2$] was prepared by an adaptation of the literature method [16] in which a toluene solution of one equivalent of PPh$_2$H was added slowly from a dropping funnel to a refluxing toluene solution of [Mo$_2$(CO)$_6$(η-C$_5$H$_5$)$_2$]. This method gives good yields (typically 65%) and minimises the formation of the green bis-phosphido complex [Mo$_2$(μ-PPh$_2$)$_2$(CO)$_2$(η-C$_5$H$_5$)$_2$].

3.1. Preparation of [Mo$_2$(μ-S)$_2$(μ-SEt)(μ-PPh$_2$)(η-C$_5$H$_5$)$_2$] 7a

A solution of [Mo$_2$(μ-H)(μ-PPh$_2$)(CO)$_4$(η-C$_5$H$_5$)$_2$] (1.5 g, 2.42 mmol) and EtSH (1.0 cm^3, 13.5 mmol) in toluene (150 cm^3) was heated to reflux for 48 h. At this point further EtSH (0.53 cm^3) was added and heating continued for a further 48 h. After the solvent was removed in vacuo, the residue was absorbed on a small amount of silica and loaded onto a chromatography column. Elution with a 1:1 mixture of CH$_2$Cl$_2$ and light petroleum gave a purple band of **7a** (880 mg, 1.39 mmol, 57.5%).

M.p. 258°C. ^{1}H-NMR δ 7.12–6.80 (m, 10H, Ph), 6.40 (s, 10H, η-C$_5$H$_5$), 1.60 (q, J = 8, 2H, CH$_2$), 0.75 (t, J = 8, 3H, Me); ^{13}C-NMR 142.9 (d, J = 33, C$_{ipso}$), 141.3 (d, J = 28, C$_{ipso}$), 134.4–126.8 (m, Ph), 96.2 (s, η-C$_5$H$_5$), 25.6 (s, CH$_2$), 18.0 (s, Me); ^{31}P-NMR 28.2 ppm. Found: C, 42.13; H, 3.75; S, 13.99. Calcd. for C$_{24}$H$_{25}$Mo$_2$PS$_3$ · CH$_2$Cl$_2$: C, 41.84; H, 3.76; S, 13.39%. Mass spectrum m/z 633 (M$^+$).

3.2. Preparation of [Mo$_2$(μ-S)$_2$(μ-SPr^i)(μ-PPh$_2$)(η-C$_5$H$_5$)$_2$] 7b

A solution of [Mo$_2$(μ-H)(μ-PPh$_2$)(CO)$_4$(η-C$_5$H$_5$)$_2$] (1.5 g, 2.42 mmol) and 5 equivalents of Pr^{i}SH (1.1 cm^3, 11.87 mmol) in toluene (150 cm^3) was heated to reflux with TLC monitoring. After 46 h the orange band of starting material had disappeared and two products, one green and one purple, were evident. On column chromatography a 3:7 mixture of CH$_2$Cl$_2$ and light petroleum was used to elute the green band (320 mg), followed by a 1:1 mixture of the same solvents to elute the purple one. The green band was tentatively identified as [Mo$_2$(μ-SPr^i)(μ-PPh$_2$)(CO)$_2$(η-C$_5$H$_5$)$_2$] 4b on the basis of its IR spectrum (1890 sh, 1855 s cm^{-1}); it changed to a partly insoluble red material on standing under vacuum or in an inert atmosphere. The purple product was identified as [Mo$_2$(μ-S)$_2$(μ-SPr^i)(μ-PPh$_2$)(η-C$_5$H$_5$)$_2$] 7b (583 mg, 37.3%).

M.p. 259°C. ^{1}H-NMR δ 7.05–6.80 (m, 10H, Ph), 6.40 (s, 10H, η-C$_5$H$_5$), 2.05 (septet, J = 7, 1H, CH), 0.80 (d, J = 7, 6H, Me); ^{13}C-NMR 143.0 (d, J = 34, C$_{ipso}$), 141.4 (d, J = 28, C$_{ipso}$), 134.5–126.8 (m, Ph), 96.2 (s, η-C$_5$H$_5$), 33.4 (s, CH), 26.4 (s, Me); ^{31}P-NMR 27.2 ppm. Found: C, 45.90; H, 4.12. Calcd. for C$_{25}$H$_{27}$Mo$_2$PS$_3$: C, 46.44; H, 4.18%. Mass spectrum m/z 648 (M$^+$).

3.3. Preparation of [Mo$_2$(μ-S)$_2$(μ-SBu^t)(μ-PPh$_2$)(η-C$_5$H$_5$)$_2$] 7c

A solution of [Mo$_2^t$ μ-H)(μ-PPh$_2$)(CO)$_4$(η-C$_5$H$_5$)$_2$] (1.5 g, 2.42 mmol) and 5.5 equivalents of Bu^{t}SH (1.5 cm^3, 13.3 mmol) in toluene (150 cm^3) was heated to reflux for 48 h, at which point the mixture was green and only a small amount of purple product was visible on TLC. Addition of more Bu^{t}SH (1.0 cm^3) and heating for a further 24 h did not appear to cause any further change, and so elemental sulfur (155 mg, 0.6 mmol, i.e. one equivalent of S per Mo atom) was added and the solution was refluxed for 20 min, causing a rapid change to purple. Column chromatography gave 380 mg (23.8%) of purple 7c, eluted with a 1:1 mixture of CH$_2$Cl$_2$ and light petroleum.

M.p. 236°C. ^{1}H-NMR δ 7.10–6.75 (m, 10H, Ph), 6.40 (s, 10H, η-C$_5$H$_5$), 0.97 (s, 9H, Me); ^{13}C-NMR 143.5 (d, J = 35, C$_{ipso}$), 141.0 (d, J = 28, C$_{ipso}$),

134.6–126.8 (m, Ph), 76.6 (s, η-C$_5$H$_5$), 45.8 (s, CMe$_3$), 36.7 (Me); ^{31}P-NMR 30.1 ppm. Found: C, 43.66; H, 4.04; S, 13.33. Calcd. for C$_{26}$H$_{29}$Mo$_2$PS$_3$ · CH$_2$Cl$_2$: C, 43.50; H, 4.19; S, 12.90%. Mass spectrum m/z 660 (M$^+$).

3.4. Preparation of [Mo$_2$(μ-S)$_2$(μ-SC$_6$H$_4$Me)(μ-PPh$_2$)(η-C$_5$H$_5$)$_2$] 7d

Proceeding as above, the reaction between [Mo$_2$(μ-H)(μ-PPh$_2$)(CO)$_4$(η-C$_5$H$_5$)] (1.08 g, 1.74 mmol) and p-thiocresol (1.1 g, 8.87 mmol) was carried out in refluxing toluene for 48 h. A further 0.54 g of p-thiocresol was then added and heating was continued for a further 18 h. Column chromatography produced a small amount of an unstable green complex 4d, which was eluted with a 3:7 mixture of CH$_2$Cl$_2$ and light petroleum. The purple complex [Mo$_2$(μ-S)$_2$(μ-SC$_6$H$_4$Me)(μ-PPh$_2$)(η-C$_5$H$_5$)$_2$] 7d (0.471 g, 0.68 mmol, 38.9%) was eluted with a 1:1 mixture of the same solvents.

M.p. 292°C. ^{1}H-NMR δ 7.02–6.71 (m, 14H, Ph and C$_6$H$_4$Me), 6.41 (s, 10H, η-C$_5$H$_5$), 2.18 (s, 3H, Me); ^{13}C-NMR 142.8 (d, J = 35, PC$_{ipso}$), 141.2 (d, J = 27, PC$_{ipso}$), 135.6 (C$_{ipso}$), 134.3–126.7 (m, Ph and C$_6$H$_4$Me), 96.8 (s, η-C$_5$H$_5$), 20.8 (s, Me); ^{31}P-NMR 38.1 ppm. Found: C, 46.74; H, 3.74; S, 13.43. Calcd. for C$_{29}$H$_{27}$Mo$_2$PS$_3$ · CH$_2$Cl$_2$: C, 46.22; H, 3.75; S, 12.34%. Mass spectrum m/z 695 (M$^+$)

3.5. Preparation of [Mo$_2$(μ-S)$_2$(μ-SC$_{12}$H$_{25}$)(μ-PPh$_2$)(η-C$_5$H$_5$)$_2$] 7e

A solution of complex 3 (1.5 g, 2.42 mmol) and dodecyl thiol (2.9 cm^3, 11.5 mmol) in toluene (150 cm^3) was heated to reflux for 44 h with TLC monitoring. An additional 1.5 cm^3 of thiol was added and reflux was continued for a further 24 h. On column chromatography as above, elution with a 1:1 mixture of CH$_2$Cl$_2$ and light petroleum produced a purple band of complex 7e (1.24 g, 1.61 mmol, 66.4%) which yielded a slightly waxy solid. Recrystallisation from CH$_2$Cl$_2$ and light petroleum produced a crystalline solid.

M.p. 154°C. ^{1}H-NMR δ 7.10–6.77 (m, 10H, Ph), 6.37 (s, 10H, η-C$_5$H$_5$), 1.60–0.85 (m, 25H, C$_{12}$H$_{25}$); ^{13}C-NMR 142.9 (d, J = 33, C$_{ipso}$), 141.3 (d, J = 28, C$_{ipso}$), 134.4–126.8 (m, Ph), 96.2 (s, η-C$_5$H$_5$), 33.3–22.7 (m, CH$_2$), 14.2 (s, Me); ^{31}P-NMR 29.1 ppm. Found: C, 51.52; H, 5.72; S, 12.21. Calcd. for C$_{34}$H$_{45}$Mo$_2$PS$_3$ · 0.5CH$_2$Cl$_2$: C, 51.56; H, 5.65; S, 11.79%. Mass spectrum m/z 773 (M$^+$).

In a separate experiment, a solution of 3 (940 mg) and C$_{12}$H$_{25}$SH (2 cm^3) in toluene (150 cm^3) was heated to reflux for 72 h. The volume was reduced in vacuo at room temperature to just a few cm^3; the remaining volatile fractions were then distilled out of the reaction

mixture under reduced pressure (~ 10 mmHg). Two distillate fractions were collected, the first at 70°C and the second at 130°C. Both fractions were analysed by gas chromatography; the first consisted of dodecane and dodec-1-ene in a ratio of approximately 40:1, and the second consisted of the same two components in a 20:1 ratio together with excess dodecane-1-thiol. Column chromatography of the reaction mixture as above gave 7e (464 mg, 40%). In a control experiment, GC analysis of the commercial thiol used showed the presence of trace quantities of dodecane and dodec-1-ene; the same amounts were detected after the thiol was heated to reflux in toluene for 65 h, thus confirming that it remained unchanged under the conditions of the original reaction.

3.6. Reaction of 4b with further Pr^{i}SH

A solution of 3 (1.5 g, 2.42 mmol) and Pr^{i}SH (1.1 cm^3, 11.87 mmol) was heated to reflux in toluene for 46 h. The components of the mixture were then separated by chromatography as above to give 320 mg of green-brown 4b and 583 mg (37.3%) of 7b. The 4b produced was the redissolved in toluene (150 cm^3) and a further 1 cm^3 of Pr^{i}SH was added; the solution was then heated to reflux for 24 h. Chromatography as before produced a purple zone of 7b (82 mg), eluted with a 3:7 mixture of CH$_2$Cl$_2$ and light petroleum. Further elution with a 1:1 mixture of the same solvents gave a brown band containing complex 8 (178 mg). IR (KBr) 891 cm^{-1} (Mo=O); ^{1}H-NMR: 8.42–7.13 (m, 10H, Ph), 5.49 (s, 5H, η-C$_5$H$_5$), 5.16 (s, 5H, η-C$_5$H$_5$), 2.85 (spt, J = 7, 1H, CH), 1.61 (d, J = 7, 3H, Me), 0.81 (d, J = 7, 3H, Me); ^{31}P-NMR 176.3 ppm. Mass spectrum m/z 630 (M$^+$).

3.7. Preparation of [Mo$_2$Ru$_2$(μ$_3$-S)$_2$(μ-SEt)(μ-PPh$_2$)(CO)$_4$(η-C$_5$H$_5$)$_2$] 9a

A solution of [Mo$_2$(μ-S)$_2$(μ-SEt)(μ-PPh$_2$)(η-C$_5$H$_5$)$_2$] (237 mg, 0.38 mmol) and [Ru$_3$(CO)$_{12}$] (240 mg, 0.38 mmol) in thf (150 cm^3) was heated to reflux for 1 h. After the solvent was removed under vacuum, the residue was chromatographed. Elution with light petroleum removed a yellow band of [Ru$_3$(CO)$_{12}$] (120 mg, 50% recovery). Elution with a 1:4 mixture of CH$_2$Cl$_2$ and light petroleum produced red-brown 9a (182 mg, 0.19 mmol, 50.6%)

M.p. dec. > 250°C; IR (C$_6$H$_{12}$) ν(CO) 2000 m, 1988 s, 1934 s cm^{-1}; ^{1}H-NMR: δ 7.47–7.20 (m, 10H, Ph), 5.65 (s, 5H, η-C$_5$H$_5$), 5.27 (s, 5H, η-C$_5$H$_5$), 3.21 (q, 2H, J = 7, CH$_2$), 1.50 (t, J = 7, 3H, Me); ^{13}C-NMR: 206.4, 201.9 (both s, CO), 141.1 (d, J = 33, C$_{ipso}$), 96.2, 88.2 (both s, η-C$_5$H$_5$), 53.9 (s, CH$_2$), 17.8 (s, Me); ^{31}P-NMR: −0.82 ppm. Found: C, 35.26; H, 2.73; S, 10.13. Calcd. for C$_{28}$H$_{25}$Mo$_2$O$_4$PRuS$_3$ · 0.33CH$_2$Cl$_2$: C, 34.89; H, 2.63; S, 9.85%. Mass spec-

trum m/z 948, 920, 890, 861, 836 (M$^+$ -nCO, n = 0–4).

3.8. Preparation of [Mo$_2$Ru$_2$(μ$_3$-S)$_2$(μ-SPr^i)(μ-PPh$_2$)(CO)$_4$(η-C$_5$H$_5$)$_2$] 9b

A solution of [Mo$_2$(μ-S)$_2$(μ-SPr^i)(μ-PPh$_2$)(η-C$_5$H$_5$)$_2$] (570 mg, 0.88 mmol) and [Ru$_3$(CO)$_{12}$] (563 mg, 0.84 mmol) in thf (150 cm^3) was heated to reflux for 1 h. Chromatography as above gave a yellow band of [Ru$_3$(CO)$_{12}$] (237 mg, 42% recovery), followed by a golden-brown band eluted with a mixture of CH$_2$Cl$_2$/light petroleum (1:6) and identified as [Mo$_2$Ru$_2$(μ$_3$-S)$_2$(μ-SPr^i)$_2$(CO)$_4$(η-C$_5$H$_5$)$_2$] 2b (59 mg) by its ^{1}H-NMR spectrum (presumably arising from a small impurity of 1b in the sample of 7b used). The red-brown major product was eluted with a 1:4 mixture of the same solvents and identified as 9b (521 mg, 0.54 mmol, 61.5%).

M.p. dec. 230°C; IR (C$_6$H$_{12}$) ν(CO) 1999 m, 1988 s, 1933 s cm^{-1}; ^{1}H-NMR: δ 7.45–7.20 (m, 10H, Ph), 5.65 (s, 5H, η-C$_5$H$_5$), 5.27 (s, 5H, η-C$_5$H$_5$), 2.97 (spt, J = 7, 1H, CH) and 1.52 (d, J = 7, 6H, Me); ^{13}C-NMR 206.5, 202.1 (both s, CO), 141.2 (d, J = 34, C$_{ipso}$), 134.9–127.5 (m, Ph), 96.2, 88.1 (both s, η-C$_5$H$_5$), 62.5 (s, CH) and 25.5 (s, Me); ^{31}P-NMR −0.6 ppm. Found: C, 35.53; H, 2.80; S, 9.46. Calcd. for C$_{29}$H$_{27}$Mo$_2$O$_4$PRu$_2$S$_3$ · 0.5CH$_2$Cl$_2$: C, 35.31; H, 2.79; S, 9.58%. Mass spectrum m/z 962, 934, 905, 878, 847 (M$^+$ -nCO, n = 0–4).

3.9. Preparation of [Mo$_2$Ru$_2$(μ$_3$-S)$_2$(μ-SBu^t)(μ-PPh$_2$)(CO)$_4$(η-C$_5$H$_5$)$_2$] 9c

Proceeding as above, a solution of complex 7c (120 mg, 0.18 mmol) and [Ru$_3$(CO)$_{12}$] (118 mg, 0.18 mmol) in thf (150 cm^3) was heated to reflux for 1 h. On chromatography, the desired product 9c (95 mg, 0.097 mmol, 54%) was eluted as a red-brown zone in a 1:4 mixture of CH$_2$Cl$_2$ and light petroleum after the initial yellow band of recovered [Ru$_3$(CO)$_{12}$].

M.p. dec. > 250°C; IR (C$_6$H$_{12}$) ν(CO) 1999 m, 1988 s, 1930 s cm^{-1}; ^{1}H-NMR δ 7.47–7.20 (m, 10H, Ph), 5.65 (s, 5H, η-C$_5$H$_5$), 5.30 (s, 5H, η-C$_5$H$_5$), 1.50 (s, 9H, Me); ^{13}C-NMR: 206.6, 204.7 (both s, CO), 141.3 (d, J = 34, C$_{ipso}$), 135.0–127.5 (m, Ph), 96.7, 88.6 (both s, η-C$_5$H$_5$), 54.7 (CMe$_3$), 31.8 (Me). ^{31}P-NMR 0.46 ppm. Found: C, 36.57; H, 2.84; S, 9.95. Calcd. for C$_{30}$H$_{29}$Mo$_2$O$_4$PRu$_2$S$_3$: C, 36.96; H, 2.98; S, 9.86%. Mass spectrum m/z 975, 947, 919, 892, 863 (M$^+$ -nCO, n = 0–4)

3.10. Preparation of [Mo$_2$Ru$_2$(μ$_3$-S)$_2$(μ-SC$_6$H$_4$Me)(μ-PPh$_2$)(CO)$_4$(η-C$_5$H$_5$)$_2$] 9d

A solution of complex 7d (265 mg, 0.38 mmol) and [Ru$_3$(CO)$_{12}$] (244 mg, 0.38 mmol) in thf (150 cm^3) was

heated to reflux for 1 h. Chromatography as above gave $[Ru_3(CO)_{12}]$ (114 mg, 46% recovery) followed by a golden brown band of $[Mo_2Ru_2(\mu_3\text{-}S)_2(\mu\text{-}SC_6H_4Me)_2(CO)_4(\eta\text{-}C_5H_5)_2]$ (40 mg). Elution with a 1:4 mixture of CH_2Cl_2 and light petroleum produced red-brown 9d (284 mg, 74%).

M.p. dec. > 250°C. IR (C_6H_{12}) $\nu(CO)$ 2001 m, 1990 s, 1942 m, 1935 m cm^{-1}; ^{1}H-NMR δ 7.60–7.15 (m, 14H, Ph and C_6H_4Me), 5.67 (s, 5H, η-C_5H_5), 5.37 (s, 5H, η-C_5H_5), 2.37 (s, 3H, Me); ^{13}C-NMR 206.9, 202.1 (both s, CO), 149.9 (s, C_{ipso} of SC_6H_4Me), 141.1 (d, J = 34, C_{ipso} of PPh_2), 137.1–127.6 (m, Ph and

Table 4

Atom coordinates ($\times 10^4$) and temperature factors ($\text{Å}^2 \times 10^3$) for complex 7b; U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor

Atom	x	y	z	U_{eq}
Mo(1)	6904(1)	4220(1)	1246	29(1)
Mo(2)	6138(1)	3135(1)	441(1)	28(1)
S(1)	5923(1)	4635(1)	186(1)	35(1)
S(2)	7150(2)	2690(2)	1472(2)	30(1)
S(3)	5471(2)	3695(3)	1820(2)	48(1)
P(1)	7488(2)	3696(3)	−120(2)	30(1)
C(1)	7556(4)	4462(3)	2455(3)	48(3)
C(2)	6908(4)	5159(3)	2319(3)	61(4)
C(3)	7140(4)	5626(3)	1512(3)	37(3)
C(4)	7932(4)	5218(3)	1149(3)	40(3)
C(5)	8188(4)	4499(3)	1732(3)	33(3)
C(6)	4910(5)	2763(5)	−179(6)	38(4)
C(7)	5582(5)	2886(5)	−855(6)	46(5)
C(8)	6266(5)	2227(5)	−715(6)	32(3)
C(9)	6016(5)	1697(5)	48(6)	33(3)
C(10)	5179(5)	2028(5)	379(6)	32(3)
C(1A)	7422(12)	5626(10)	1273(11)	37(3)
C(2A)	8171(12)	5024(10)	1270(11)	37(3)
C(3A)	8072(12)	4424(10)	2014(11)	37(3)
C(4A)	7262(12)	4654(10)	2478(11)	37(3)
C(5A)	6861(12)	5397(10)	2020(11)	37(3)
C(6A)	6291(10)	1974(13)	−480(15)	32(3)
C(7A)	5699(10)	1679(13)	215(15)	32(3)
C(8A)	4960(10)	2292(13)	255(15)	32(3)
C(9A)	5095(10)	2966(13)	−415(15)	32(3)
C(10A)	5917(10)	2770(13)	−869(15)	32(3)
C(11)	7564(3)	4295(3)	−1143(4)	31(2)
C(12)	7585(4)	5234(4)	−1205(4)	53(3)
C(13)	7492(5)	5703(5)	−2056(4)	71(3)
C(14)	7502(8)	5268(10)	−2761(8)	80(6)
C(15)	7515(4)	4396(4)	−2693(4)	43(2)
C(16)	7554(4)	4002(4)	−1921(4)	40(2)
C(17)	8539(3)	2959(4)	−129(4)	35(2)
C(18)	9284(4)	3445(4)	−144(4)	40(2)
C(19)	10090(4)	2887(5)	−135(4)	59(3)
C(20)	10115(8)	2012(6)	−143(7)	47(4)
C(21)	9335(4)	1647(4)	−172(4)	51(2)
C(22)	8589(4)	2112(3)	−120(4)	40(2)
C(23)	4597(4)	4413(5)	1961(6)	53(1)
C(24)	4571(4)	4803(5)	2840(6)	53(1)
C(25)	3828(4)	3853(5)	1971(6)	53(1)
C(23A)	5413(9)	2932(7)	2665(6)	53(1)
C(24A)	5497(9)	3271(7)	3551(6)	53(1)
C(25A)	4680(9)	2317(7)	2756(6)	53(1)

Table 5

Crystal data and structure refinement for complex 9a·0.33CH_2Cl_2

Identification code	mnb502
Empirical formula	$C_{28.33}H_{25.67}Cl_{0.67}Mo_2O_4PRu_2S_3$
Formula weight	974.96
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Trigonal
Space group	P$\bar{3}$
Unit cell dimensions	a = 24.229(3) Å α = 90°
	b = 24.229(3) Å β = 90°
	c = 10.091(2) Å γ = 120°
Volume	5130.2(14) Å^3
Z	6
Density (calculated)	1.893 Mg/m^3
Absorption coefficient	1.896 mm^{-1}
F(000)	2844
Crystal size	0.55×0.32×0.22 mm
θ range for data collection	1.94 to 22.49°
Index ranges	$-1 < h < 25$, $-26 < k < 1$, $-1 < l$ < 10
Reflections collected	5837
Independent reflections	4374 (R_{int} = 0.0247)
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	4374/0/367
Goodness-of-fit on F^2	1.062
Final R indices $[I > 2\sigma(I)]$	$R1$ = 0.0376, w$R2$ = 0.0975
R indices (all data)	$R1$ = 0.0485, w$R2$ = 0.1039
Largest diff. peak and hole	1.144 and −1.224 eÅ^{-3}

C_6H_4Me), 96.5, 88.4 (both s, η-C_5H_5), 21.2 (s, Me); ^{31}P-NMR −0.74 ppm. Found: C, 37.12; H, 2.60; S, 8.34. Calcd. for $C_{31}H_{27}Mo_2O_4PRu_2S_3 \cdot CH_2Cl_2$: C, 37.29; H, 2.65; S, 8.77%. Mass spectrum m/z 1010, 981, 926, 898 (M$^+$ −nCO, n = 0, 1, 3, 4)

3.11. Crystal structure determination of complex 7b

Crystal data for $[Mo_2(\mu\text{-}S)_2(\mu\text{-}S^iPr)(\mu\text{-}PPh_2)(\eta$-$C_5H_5)_2]$, $C_{25}H_{27}Mo_2PS_3$; M = 946.53; crystallises from dichloromethane/petroleum ether as purple, elongated blocks; crystal dimensions 0.85 × 0.30 × 0.25 mm. Trigonal (rhombohedral setting), a = 15.524(9) Å, α = 84.55(5)°, U = 3694(4) Å^3; D_c = 1.744 g cm^{-3}. Z = 6. Space group R3c (C$_{3v}^6$, No. 161). Mo K$_\alpha$ radiation (λ = 0.71069 Å), μ(Mo Kα) = 13.16 cm^{-1}, F(000) = 1943.34.

Three-dimensional, room temperature X-ray data were collected in the range $3.5 < 2\theta < 45°$ on a Nicolet R3 4-circle diffractometer by the ω-scan method. The 2267 independent reflections (of 10165 collected in a monoclinic cell, approximately 3388 independent measured) for which $|F|/\sigma$ ($|F|) > 3.0$ were corrected for Lorentz and polarisation effects, and for absorption by analysis of 9 azimuthal scans (minimum and maximum transmission coefficients 0.263 and 0.289). The structure was solved by Patterson and Fourier techniques and refined by blocked cascade least squares methods. Both

cyclopentadienyl ligands were found to be rotationally disordered with occupancies 0.77:0.23 and 0.81:0.19. In each case, after occupancy and orientational optimization, the lower occupancy fragment was fixed in position. The isopropyl group was also found to be disordered 0.50: 0.50 in two orientations on the bridging sulfur atom: after optimization, each fragment was refined with constrained geometry. Hydrogen atoms were included in calculated positions, with isotropic thermal parameters related to those of the supporting atom, and refined in riding mode. Refinement converged at a final R 0.0271 (R_w 0.0266, 252 parameters, mean and maximum shift/e.s.d. 0.038 and 0.186), with allowance for the thermal anisotropy of all non-hydrogen atoms, with

the exception of those of the isopropyl fragments and the lower occupancy cyclopentadienyl ligands, which were given group isotropic thermal parameters and fixed isotropic thermal parameters respectively. A final difference electron density synthesis showed minimum and maximum values of -0.52 and $+0.68$ eÅ^{-3}. Complex scattering factors were taken from the program package SHELXTL [17] as implemented on the Data General DG30 computer, which was used for structure solution and refinement. A weighting scheme $w^{-1} = [\sigma^2(F) + 0.00034(F)^2]$ was used in the latter stages of the refinement. Table 4 lists the atomic positional parameters with estimated standard deviations.

3.12. Crystal structure determination of complex 9a

The crystal data for 9a · 0.33 CH$_2$Cl$_2$ and details of the structure refinement are collected in Table 5: atomic coordinates and equivalent isotropic displacement parameters are given in Table 6. Three-dimensional, room temperature X-ray data were collected on a Siemens P4 diffractometer by the ω-scan method. Of the 5837 reflections measured, all of which were corrected for Lorentz and polarisation effects (but not for absorption), 3665 independent reflections exceeded the significance level $|F|/\sigma(|F|) > 4.0$. The structure was solved by direct methods and refined by full matrix least-squares on F^2. Hydrogen atoms were included in calculated positions and refined in riding mode. Refinement converged at a final $R = 0.0376$ (w$R2 = 0.1039$ for all 4374 unique data, 367 parameters, mean and maximum δ/σ 0.000, 0.000), with allowance for the thermal anisotropy of all non-hydrogen atoms. A weighting scheme $w = 1/[\sigma2(F_o^2) + (0.0484P)2 + 14.605P]$ where $P = (F_o^2 + 2F_c^2)/3$ was used in the latter stages of refinement. Complex scattering factors were taken from the program package SHELXL93 [18] as implemented on the Viglen 486dx computer.

Full listings of bond lengths and angles, anisotropic thermal parameters and hydrogen atom positional parameters have been deposited with the Cambridge Crystallographic Data Centre. Structure factor tables are available from the authors.

References

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Table 6
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters (Å$^2 \times 10^3$) for 9a·0.33CH$_2$Cl$_2$; U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor

	x	y	z	U_{eq}
Mo(1)	3729(1)	1525(1)	6476(1)	39(1)
Mo(2)	4207(1)	1071(1)	4670(1)	36(1)
Ru(1)	4006(1)	2081(1)	3860(1)	43(1)
Ru(2)	3003(1)	921(1)	4106(1)	39(1)
P(1)	4435(1)	1113(1)	7058(2)	40(1)
S(1)	3239(1)	438(1)	5815(2)	41(1)
S(2)	4731(1)	2142(1)	5404(2)	45(1)
S(3)	2948(1)	1827(1)	3590(2)	53(1)
O(1)	1595(4)	135(4)	4837(9)	106(3)
O(2)	2827(4)	369(3)	1336(7)	88(2)
O(3)	4583(4)	2268(4)	1129(6)	93(2)
O(4)	4573(4)	3512(3)	4235(9)	108(3)
C(1)	2114(4)	428(4)	4551(9)	61(2)
C(2)	2893(4)	570(4)	2397(9)	55(2)
C(3)	4336(4)	2185(4)	2136(9)	60(2)
C(4)	4343(4)	2975(4)	4068(9)	61(2)
C(5)	3382(7)	2242(6)	6991(11)	84(4)
C(6)	3869(6)	2344(7)	7888(18)	128(7)
C(7)	3602(8)	1769(10)	8617(11)	113(5)
C(8)	3021(7)	1363(6)	8194(12)	90(4)
C(9)	2880(5)	1647(6)	7207(10)	74(3)
C(10)	4082(4)	284(5)	3119(11)	69(3)
C(11)	4399(6)	851(6)	2480(9)	71(3)
C(12)	4987(5)	1210(5)	3117(13)	89(4)
C(13)	5016(5)	848(6)	4155(11)	77(3)
C(14)	4446(5)	276(5)	4178(10)	71(3)
C(15)	5244(3)	1610(3)	7721(7)	42(2)
C(16)	5795(4)	1906(4)	6961(9)	64(2)
C(17)	6395(4)	2264(4)	7555(11)	71(3)
C(18)	6448(4)	2319(4)	8885(10)	69(3)
C(19)	5907(4)	2034(4)	9655(9)	67(3)
C(20)	5315(4)	1684(4)	9083(8)	55(2)
C(21)	4171(3)	392(3)	8042(7)	40(2)
C(22)	4539(4)	102(4)	8078(8)	54(2)
C(23)	4358(5)	−436(4)	8880(9)	65(2)
C(24)	3818(5)	−680(4)	9648(8)	63(2)
C(25)	3450(4)	−388(4)	9616(9)	59(2)
C(26)	3627(4)	137(4)	8835(8)	52(2)
C(27)	2758(5)	1848(5)	1856(10)	76(3)
C(28)	2059(6)	1462(7)	1593(13)	123(5)
Cl(1)	6018(5)	3259(5)	3242(11)	240(4)
C(1X)	6667	3333	4116(53)	328(28)

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