Phosphorus–Sulfur Bond Cleavage at a Mixed-metal Centre; Reaction of $[(OC)_3Co(\mu\text{-}PhCCH)Mo(CO)_2(\eta^5\text{-}C_5H_5)]$ with $PPh_2(SPh)$†

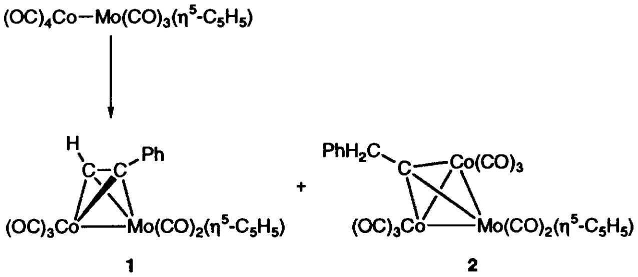
Scott L. Ingham,[a] **Martin J. Mays,***[,a] **Paul R. Raithby,**[a] **Gregory A. Solan,**[a]
Bharat V. Sundavadra,[a] **Gráinne Conole***[,b] **and Margarlith Kessler**[b]
[a] *University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, UK*
[b] *School of Chemistry, University of North London, Holloway Road, London N7 8DB, UK*

The bimetallic cobalt–molybdenum complex $[(OC)_4CoMo(CO)_3(\eta^5\text{-}C_5H_5)]$ reacted with phenylacetylene in benzene to give the bimetallic alkyne-bridged complex $[(OC)_3Co(\mu\text{-}PhCCH)Mo(CO)_2(\eta^5\text{-}C_5H_5)]$ **1** as the major product and the trimetallic alkylidyne-capped complex $[Co_2Mo(\mu_3\text{-}CCH_2Ph)(CO)_8(\eta^5\text{-}C_5H_5)]$ **2** as the minor product. Reaction of **1** with $PPh_2(SPh)$ resulted in substitution of a carbonyl group on the cobalt atom to give $[\{(PhS)Ph_2P\}(OC)_2Co(\mu\text{-}PhCCH)Mo(CO)_2(\eta^5\text{-}C_5H_5)]$ **3**. Thermolysis of **3** in refluxing toluene afforded, as the major product, the complex $[(\eta^5\text{-}C_5H_5)(OC)Mo(\mu\text{-}PPh_2CH{=}CPh)(\mu\text{-}SPh)Co(CO)_2]$ **4**, in which the unsymmetrical alkyne in **3** has been incorporated into a four-membered metallacycle, $\overline{Mo\text{–}PPh_2\text{–}CH\text{–}CPh}$, such that the phenyl substituent is positioned on the carbon atom remote from the phosphide group. The related complex $[(\eta^5\text{-}C_5H_5)(OC)Mo(\mu\text{-}PPh_2CH{=}CPh)(\mu\text{-}SPh)Co(CO)(PPh_3)]$ **5**, in which one of the carbonyl groups on the cobalt atom in **4** has been substituted by a triphenylphosphine ligand, has also been isolated as a minor product from this reaction. Conversion of **4** into **5** has been achieved separately by reaction of **4** with PPh_3. Similarly, reaction of $PPh_2(SPh)$ with **4** yields a related compound $[(\eta^5\text{-}C_5H_5)(OC)Mo(\mu\text{-}PPh_2CH{=}CPh)(\mu\text{-}SPh)Co(CO)\{PPh_2(SPh)\}]$ **6**, in which the same carbonyl group on the cobalt atom has been substituted by $PPh_2(SPh)$. Single-crystal X-ray diffraction studies have been performed on complexes **2**, **4** and **6**.

Molybdenum and cobalt sulfide species supported on alumina have been used as industrial catalysts in the hydrodesulfurisation process.[1] The mechanism by which the reaction occurs has been the subject of much interest and organometallic compounds have been studied as model systems.[2] Our interest in the organometallic chemistry of dicobalt and dimolybdenum compounds[3] has previously led us to investigate the reaction of the mixed-metal complex $[(OC)_3Co\{\mu\text{-}C_2(CO_2Me)_2\}Mo(CO)_2(\eta^5\text{-}C_5H_5)]$ with the thiophosphine $PPh_2(SPh)$ which proceeds *via* P–S bond cleavage to give $[(\eta^5\text{-}C_5H_5)(OC)Mo\{\mu\text{-}PPh_2C(CO_2Me){=}CCO_2Me\}(\mu\text{-}SPh)Co(CO)_2]$.[4] On the basis of spectroscopic evidence it was proposed that the four-membered metallacyclic ring present in this thiolato-bridged complex incorporates the molybdenum rather than the cobalt atom, even though in the related phosphido-bridged complex $[(OC)_2Co\{\mu\text{-}PPh_2C(CO_2Me){=}CCO_2Me\}(\mu\text{-}PPh_2)Mo(CO)(\eta^5\text{-}C_5H_5)]$ the metallacyclic ring incorporates the cobalt rather than the molybdenum atom. However, X-ray evidence for the structure of this thiolato complex could not be obtained. We now present structural evidence on two related thiolato-bridged complexes prepared from the reaction of the unsymmetrically alkyne-bridged complex $[(OC)_3Co(\mu\text{-}PhCCH)Mo(CO)_2(\eta^5\text{-}C_5H_5)]$ **1** with $PPh_2(SPh)$. The reactions of the major product from this reaction, $[(\eta^5\text{-}C_5H_5)(OC)Mo(\mu\text{-}PPh_2CH{=}CPh)(\mu\text{-}SPh)Co(CO)_2]$, with PPh_3 and $PPh_2(SPh)$ have also been investigated.

Results and Discussion

(*a*) *Synthesis of* $[(OC)_3Co(\mu\text{-}PhCCH)Mo(CO)_2(\eta^5\text{-}C_5H_5)]$ **1**.—Heating $[(OC)_4CoMo(CO)_3(\eta^5\text{-}C_5H_5)]$ with $PhC{\equiv}CH$ in benzene for 1 h at 343 K affords, after chromatographic work-up, the orange crystalline solid $[(OC)_3Co(\mu\text{-}PhCCH)Mo(CO)_2(\eta^5\text{-}C_5H_5)]$ **1** and the green crystalline complex $[Co_2Mo(\mu_3\text{-}CCH_2Ph)(CO)_8(\eta^5\text{-}C_5H_5)]$ **2** as the major (61%) and minor (12%) products respectively (Scheme 1). Complexes **1** and **2** have been characterised on the basis of their spectroscopic properties (see Table 1 and Experimental section) and, in the case of **2**, by a single-crystal X-ray diffraction study.



Scheme 1 Products from the thermolytic reaction of $[(OC)_4CoMo(CO)_3(\eta^5\text{-}C_5H_5)]$ with $PhC{\equiv}CH$ in benzene

The molecular structure of complex **2** is shown in Fig. 1. Selected bond distances and angles are listed in Table 2. Owing to the presence of two independent molecules A and B within the same unit cell of **2** the average values of the most relevant structural parameters will be used throughout the following discussion; bond lengths and angles are listed separately for the two molecules A and B in Table 2. The molecules are identical except for the position of the cyclopentadienyl ring.

The structure consists of a Co_2Mo triangle of metal atoms [Co(1)–Co(2) 2.486(2), Mo–Co(2) 2.673(2), Mo–Co(1) 2.680(2) Å], capped by a triply bridging phenylethylidyne ligand. Each

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.

Table 1 Infrared, ^{1}H and ^{31}P NMR data for the new complexes

Compound	$\tilde{\nu}$(CO)[a]/cm^{-1}	^{1}H NMR (δ)[b]	^{31}P NMR (δ)[c]
1	2050m, 2010vs, 1992s, 1986s, 1950w	7.7–6.9 (m, 5 H, Ph), 5.80 (s, 1 H, μ-PhCC*H*), 5.40 (s, 5 H, C_5H_5)	No phosphorus
2	2071s, 2031vs, 2017vs, 2002 (sh), 1964w	7.7–6.9 (m, 5 H, Ph), 5.31 (s, 5 H, C_5H_5), 5.01 (s, 2 H, μ-CC*H*$_2$Ph)	No phosphorus
3	2019w, 2011w, 1975s, 1953 (sh)	7.7–6.9 (m, 20 H, Ph), 4.91 (s, 5 H, C_5H_5), 4.32 [d, ^3J(HP) 6.1, 1 H, PhCC*H*]	−47.8 (s, br, $CoPPh_2SPh$)
4	2007s, 1963 (sh)[d]	7.7–6.9 (m, 20 H, Ph), 4.42 [d, ^2J(HP) 2.0, 5 H, C_5H_5], 4.31 [d, ^2J(HP) 6.4, 1 H, Ph_2PC*H*CPh]	−156.9 (s, Ph_2PCHCPh)
5	1943s, 1897w[d]	7.7–6.9 (m, 35 H, Ph), 4.81 (s, 5 H, C_5H_5), 3.10 [dd, ^2J(HP) 15.2, ^3J(HP) 7.1, Ph_2PC*H*CPh]	−80.3 (s, $CoPPh_3$), −157.5 (s, Ph_2PCHCPh)
6	1948s, 1904w	7.7–6.9 (m, 35 H, Ph), 4.80 (s, 5 H, C_5H_5), 2.88 [dd, ^2J(HP) 13.5, ^3J(HP) 4.7, Ph_2PC*H*CPh]	−40.3 (s, $CoPPh_2SPh$), −151.1 (s, Ph_2PCHCPh)

[a] Recorded in hexane solution. [b] Chemical shifts in ppm relative to $SiMe_4$ (0.0 ppm), coupling constants in Hz, in $CDCl_3$ at 293 K. [c] Chemical shifts in ppm relative to external $P(OMe)_3$ (0.0 ppm) (upfield shifts negative), {^{1}H}-gated decoupled, measured in $CDCl_3$ at 293 K. [d] Recorded in CH_2Cl_2 solution.

Table 2 Selected bond lengths (Å) and angles (°) for $[Co_2Mo(\mu_3\text{-}CCH_2Ph)(CO)_8(\eta^5\text{-}C_5H_5)]$ **2** in the two independent molecules A and B

Mo–C(01)	2.090(5)	2.094(5)
Mo–Co(2)	2.662(2)	2.683(2)
Mo–Co(1)	2.700(2)	2.659(2)
Co(1)–C(01)	1.941(5)	1.934(5)
Co(2)–C(01)	1.933(5)	1.935(5)
Co(1)–Co(2)	2.489(2)	2.482(2)
C(01)–C(02)	1.520(6)	1.516(7)
range Mo–C(C_5H_5)	2.309(6)–2.380(6)	2.299(6)–2.383(6)
range Co–C(CO)	1.772(7)–1.815(7)	1.777(6)–1.797(6)
range Mo–C(CO)	1.963(6), 2.008(6)	1.997(6), 1.999(6)
Co(2)–Mo–Co(1)	55.31(4)	55.36(4)
Co(1)–Co(2)–Mo	63.13(4)	61.84(4)
Co(1)–C(01)–Mo	84.0(2)	82.5(2)
Co(2)–C(01)–Mo	82.8(2)	83.4(2)
C(03)–C(02)–C(01)	115.7(4)	118.5(4)

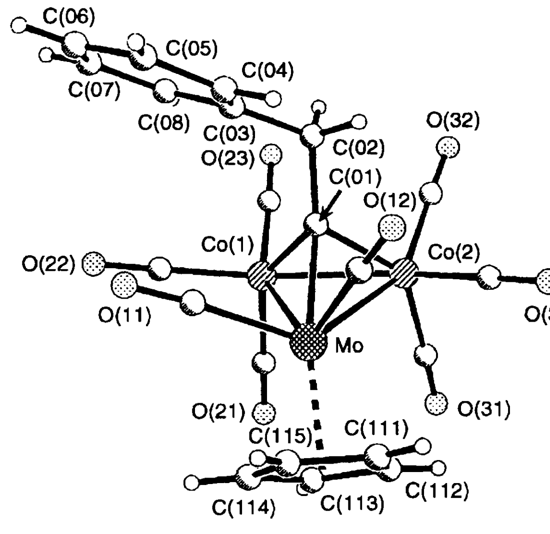


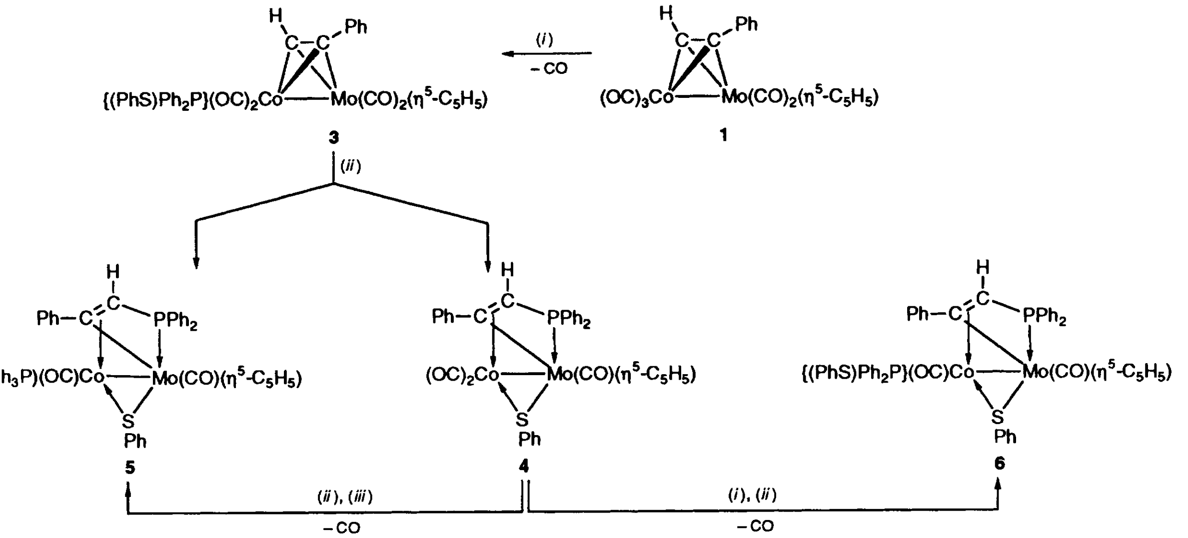
Fig. 1 Molecular structure of $[Co_2Mo(\mu_3\text{-}CCH_2Ph)(CO)_8(\eta^5\text{-}C_5H_5)]$ **2** including the atom numbering scheme (molecule A)

cobalt atom is bonded to three terminal carbonyl groups. The molybdenum atom is bonded to two carbonyl groups and η^5 to a cyclopentadienyl ligand which lies below the plane of the metal atoms (*i.e.* distal to the capping group). Within experimental error the apical carbon atom is situated equidistant from the two cobalt atoms [Co(1)–C(01) 1.938(5), Co(2)–C(01) 1.934(5) Å]. These distances are identical to those reported in the related structure $[Co_2Mo(\mu_3\text{-}CPh)(CO)_8(\eta^5\text{-}C_5H_5)]$.[5] The plane of the phenyl ring in complex **2** is bent towards the plane of the trimetallic core [C(03)–C(02)–C(01) 117.1(4)°].

Mathieu and co-workers[6] have reported the preparation of a series of alkyne-bridged Co–Mo complexes related to **1** by a similar method. Their reactions were, however, performed in refluxing hexane whereas in this work refluxing benzene was employed. This difference is presumably responsible for the additional formation of the alkylidyne complex **2** in our study and indeed the synthesis of **1** using the conditions employed by Mathieu and co-workers did not afford the trinuclear complex **2**. Other trinuclear Co–Co–Mo alkylidyne-capped complexes are known but have not been prepared by this method,[5,7] even though carbon-capped tricobalt complexes are accessible *via* the same route.[8]

(*b*) *Reaction of Complex* **1** *with* $PPh_2(SPh)$.—Reaction of $[(OC)_3Co(\mu\text{-}PhCCH)Mo(CO)_2(\eta^5\text{-}C_5H_5)]$ **1** with $PPh_2(SPh)$ at 323 K for 5 h in toluene gives, in addition to unreacted starting material, the complex $[\{(PhS)Ph_2P\}(OC)_2Co(\mu\text{-}PhCCH)Mo(CO)_2(\eta^5\text{-}C_5H_5)]$ **3** in 60% yield (Scheme 2). The spectroscopic properties of **3** are similar to those of other Co–Mo alkyne-bridged complexes, monosubstituted by a phosphine ligand at the cobalt centre.[4] The ^{13}C-{^{1}H} NMR spectrum at 293 K shows four separate resonances for the terminal carbonyl groups, two in the MoCO region (δ 229.2, 231.6) and two in the CoCO region (δ 206.6, 204.2). For the related complex $[(HPh_2P)(OC)_2Co\{\mu\text{-}(Me_3Si)CCH\}Mo(CO)_2(\eta^5\text{-}C_5H_5)]$, which also contains an unsymmetrical alkyne, a similar pattern of four terminal resonances was observed.[4] This pattern is compatible with non-fluxionality or with a trigonal twist of the terminal ligands at one or both of the metal centres.[3a,4]

(*c*) *Thermolysis of Complex* **3**.—The thermolysis of complex **3** at 384 K in toluene gives $[(\eta^5\text{-}C_5H_5)(OC)Mo(\mu\text{-}PPh_2CH{=}CPh)(\mu\text{-}SPh)Co(CO)_2]$ **4** and $[(\eta^5\text{-}C_5H_5)(OC)Mo(\mu\text{-}PPh_2\text{-}CH{=}CPh)(\mu\text{-}SPh)Co(CO)(PPh_3)]$ **5** in 50 and 8% yields respectively (Scheme 2). Complexes **4** and **5** have been characterised spectroscopically (see Table 1 and Experimental section) and, in the case of **4**, additionally by an X-ray diffraction study. In a separate experiment **5** has been prepared directly from **4** under the same reaction conditions as employed in the thermolysis of **3** (see below), which suggests that complex **5** is formed from **4** in the thermolysis of **3** as a result of the decomposition of $PPh_2(SPh)$ to PPh_3. In accord with this suggestion the reaction of $[Co_2(CO)_8]$ with $PPh_2(SPh)$ leads to the formation of complexes of formula $[Co_3(\mu_3\text{-}S)(\mu\text{-}PPh_2)(CO)_{7-x}(PPh_3)_x]$ (x = 0–2).[9] Although a cobalt–molybdenum complex with a bridging thiolate and a bridging metallacyclic



Scheme 2 Products derived from the reaction of $[(OC)_3Co(\mu\text{-}PhCCH)Mo(CO)_2(\eta^5\text{-}C_5H_5)]$ **1** with $PPh_2(SPh)$. (*i*) $PPh_2(SPh)$; (*ii*) heat; (*iii*) PPh_3

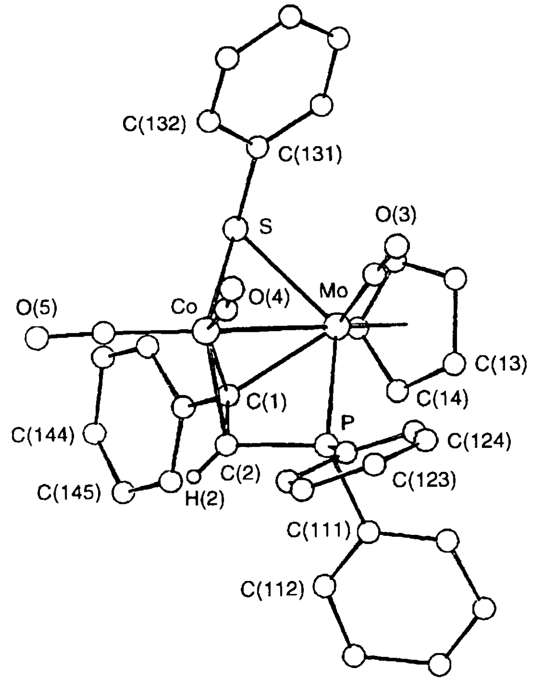


Fig. 2 Molecular structure of $[(\eta^5\text{-}C_5H_5)(OC)Mo(\mu\text{-}PPh_2CH{=}CPh)(\mu\text{-}SPh)Co(CO)_2]$ **4** including the atom numbering scheme

ligand closely related to **4** has been synthesised previously,[4] it was not structurally characterised and a single-crystal X-ray diffraction analysis of **4** has therefore been undertaken.

The molecular structure of complex **4** is illustrated in Fig. 2; Table 3 lists selected bond distances and angles. The cobalt–molybdenum bond is bridged by a $PPh_2CH{=}CPh$ fragment which forms a four-membered metallacyclic ring with the molybdenum atom, Mo–P–C=C. The Co–Mo bond length [2.631(1) Å] lies within the range reported for single Co–Mo bonds in related heteronuclear Co–Mo systems containing bridging organic ligands, and a single bond allows both the metals to satisfy the eighteen-electron rule.[5–8] The vinyl fragment of the metallacyclic ring π-bonds to the cobalt atom [Co–C(1) 1.927(5) and Co–C(2) 2.037(5) Å] as well as bonding to the molybdenum atom *via* C(1) [Mo–C(1) 2.208(5) Å]. The β-carbon of the vinyl group is bonded to the diphenylphosphide group [P–C(2) 1.753(5) Å], which completes the four-membered metallacycle Mo–C=C–P by σ-bonding to the molybdenum atom [Mo–P 2.438(1) Å]. This bonding arrangement has been obtained previously either by the insertion of alkynes into phosphido-bridged complexes or by the insertion of PPh_2 fragments into one of the M–C bonds of an alkyne-bridged complex.[10] Interestingly, in the related cobalt–molybdenum system $[(OC)_2Co\{\mu\text{-}PPh_2C(CO_2Me){=}CCO_2Me\}(\mu\text{-}PPh_2)Mo(CO)(\eta^5\text{-}C_5H_5)]$ the metallacycle incorporates the cobalt rather than the molybdenum atom; nevertheless the essential features of the M–P–C=C system in the two compounds are the same, with the C(1)=C(2) double bond lying approximately perpendicular relative to the M–M bond.[4]

Table 3 Selected bond lengths (Å) and angles (°) for $[(\eta^5\text{-}C_5H_5)(OC)Mo(\mu\text{-}PPh_2CH{=}CPh)(\mu\text{-}SPh)Co(CO)_2]$ **4**

Co–Mo	2.631(1)	Mo–C(1)	2.208(5)
Co–S	2.229(1)	P–C(2)	1.753(5)
Co–C(1)	1.927(5)	C(1)–C(2)	1.430(7)
Co–C(2)	2.037(5)	Co–C(4)	1.792(6)
Mo–S	2.454(1)	Co–C(5)	1.749(6)
Mo–P	2.438(1)	Mo–C(3)	2.007(6)

Mo–C(C_5H_5)	2.271(7)–2.372(6)
P–C(Ph)	1.801(3), 1.826(3)
S–C(Ph)	1.768(3)
C–O(CO)	1.127(7)–1.145(8)
C(1)–C(Ph)	1.497(6)
M–C(CO)	1.749(6)–2.007(6)
Mo–S–Co	68.2(1)
C(131)–S–Co	112.5(1)
C(131)–S–Mo	113.7(1)
C(2)–P–Mo	86.0(2)
Mo–C(1)–Co	78.7(2)
C(2)–C(1)–Co	73.0(3)
C(141)–C(1)–C(2)	123.4(4)
C(141)–C(1)–Mo	129.1(3)
C(141)–C(1)–Co	129.5(3)
C(2)–C(1)–Mo	103.8(3)
C(1)–C(2)–Co	64.8(3)
C(1)–C(2)–P	101.1(4)
P–C(2)–Co	99.1(2)
M–C–O(CO)	177.0(5)–178.0(5)

The vinyl fragment of the bridging metallacyclic ring in complex **4** is orientated such that only the isomeric form with the phenyl group on C(1) (the carbon atom bonded to both Co and Mo) is obtained. The alternative configuration with the phenyl group attached to C(2) (bonded only to Co) does not occur.

The cobalt–molybdenum bond in complex **4** is also asymmetrically bridged by a thiolate group [Co–S 2.229(1) and Mo–S 2.454(1) Å], with the sulfur atom formally donating two electrons to the cobalt atom and one to the molybdenum; this asymmetry is consistent with the smaller radius of the cobalt atom. The thiolate group has a bite angle of 68.2(1)°, larger than the value of 66.6(1)° found in the related dicobalt complex $[Co_2\{\mu\text{-}PPh_2CHCHC(O)\}(\mu\text{-}SPh)(CO)_2\{P(OMe)_3\}_2]$.[11] The cobalt atom is also bonded to two terminal carbonyl groups, whereas the molybdenum only bonds to one (all three are essentially linear). The molybdenum co-ordination sphere is completed by an η^5-cyclopentadienyl group with essentially identical bonding parameters to those reported for related structures.[3c,10c]

The spectroscopic properties of complex **4** are in agreement with the solid-state structure being maintained in solution. In the $^{31}P\text{-}\{^1H\}$ NMR spectrum a singlet resonance at δ −156.9 is assigned, by comparison with related complexes,[4] to the phosphorus atom that forms part of a four-membered P–C=C–Mo metallacyclic ring. The ^1H NMR shows, in addition to phenyl resonances, doublet resonances at δ 4.42 [^2J(HP) 2.0] and 4.31 [^2J(HP) 6.4 Hz] with relative integrals of 5:1 which are assigned respectively to cyclopentadienyl and PPh_2C*H*CPh protons.

It is noteworthy that complexes **4** and **5** both contain a four-membered, $PPh_2CH{=}CPh{-}Mo$ metallacycle, π-co-ordinated *via* the C=C double bond to cobalt. No complexes incorporating either a cobalt atom or the SPh group into the metallacyclic ring were obtained. A similar preference for a molybdenum–phosphorus metallacycle was observed in the thermolysis of $[\{(PhS)Ph_2P\}(OC)_2Co\{\mu\text{-}C_2(CO_2Me)_2\}Mo(CO)_2(\eta^5\text{-}C_5H_5)]$ which gives $[(\eta^5\text{-}C_5H_5)(OC)Mo\{\mu\text{-}PPh_2C(CO_2Me){=}CCO_2Me\}(\mu\text{-}SPh)Co(CO)_2]$.[4] In addition, the location of the vinyl group within the metallacycle is regiospecific, with the phenyl substituent positioned on the carbon atom remote from the phosphide group. In the thermolysis of $[Co_2(\mu\text{-}PhCCH)(CO)_5(P_2Ph_4)]$, which gives $[Co_2\{\mu\text{-}PPh_2CH{=}CPhC(O)\}(\mu\text{-}PPh_2)(CO)_4]$, a similar preference is observed for the more bulky substituent to be positioned on the carbon atom remote from the phosphide group.[3a]

(*d*) *Reaction of Complex* **4** *with* PPh_3 *or* $PPh_2(SPh)$.—Reaction of $[(\eta^5\text{-}C_5H_5)(OC)Mo(\mu\text{-}PPh_2CH{=}CPh)(\mu\text{-}SPh)Co(CO)_2]$ **4** with PPh_3 or $PPh_2(SPh)$ at 384 K in toluene gives respectively the complexes $[(\eta^5\text{-}C_5H_5)(OC)Mo(\mu\text{-}PPh_2CH{=}CPh)(\mu\text{-}SPh)Co(CO)(PPh_3)]$ **5** and $[(\eta^5\text{-}C_5H_5)(OC)Mo(\mu\text{-}PPh_2CH{=}CPh)(\mu\text{-}SPh)Co(CO)\{PPh_2(SPh)\}]$ **6** in yields of 60% in each case (Scheme 2). Complexes **5** and **6** have been characterised spectroscopically (see Table 1 and Experimental section) and in addition for **6** by single-crystal X-ray diffraction.

The molecular structure of complex **6** is shown in Fig. 3. Table 4 lists selected bond distances and angles. It is evident that the structure is very closely related to that of complex **4**, differing mainly in the replacement of one of the carbonyl ligands attached to the cobalt atom in **4** by a terminal $PPh_2(SPh)$ group. Other essential features of compound **6** are analogous to those described for **4**.

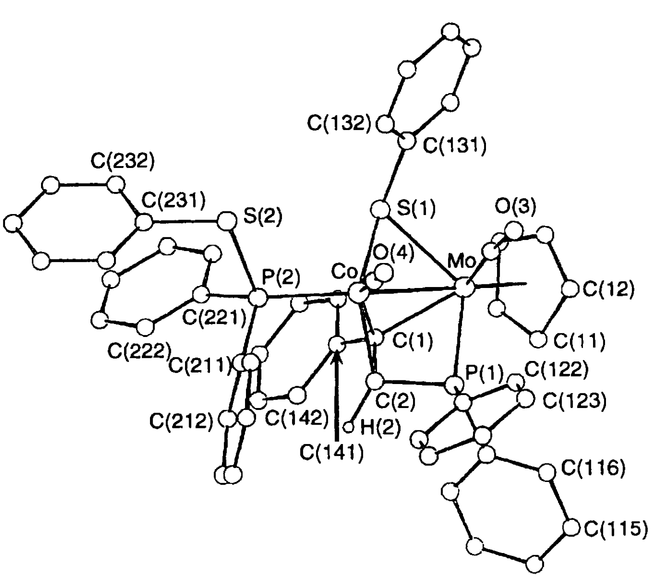


Fig. 3 Molecular structure of $[(\eta^5\text{-}C_5H_5)(OC)Mo(\mu\text{-}PPh_2CH{=}CPh)(\mu\text{-}SPh)Co(CO)\{PPh_2(SPh)\}]$ **6** including the atom numbering scheme

Table 4 Selected bond lengths (Å) and angles (°) for $[(\eta^5\text{-}C_5H_5)(OC)Mo(\mu\text{-}PPh_2CH{=}CPh)(\mu\text{-}SPh)Co(CO)\{PPh_2(SPh)\}]$ **6**

Co–Mo	2.607(5)	P(1)–C(2)	1.750(3)
Co–S(1)	2.233(8)	C(1)–C(2)	1.460(4)
Co–C(1)	1.970(3)	Co–C(4)	1.700(3)
Co–C(2)	2.040(3)	Mo–C(3)	1.990(3)
Mo–S(1)	2.460(9)	Co–P(2)	2.174(9)
Mo–P(1)	2.437(8)	S(2)–P(2)	2.129(11)
Mo–C(1)	2.220(3)		
Mo–C(C_5H_5)	2.290(4)–2.350(3)		
P(1)–C(Ph)	1.782(22)–1.808(19)		
S(1)–C(Ph)	1.785(16)		
C–O(CO)	1.130(4)–1.180(4)		
C(1)–C(Ph)	1.450(4)		
M–C(CO)	1.700(3), 1.990(3)		
P(2)–C(Ph)	1.756(24), 1.784(17)		
S(2)–C(Ph)	1.775(21)		
Mo–S(1)–Co	67.3(2)		
C(131)–S(1)–Co	117.6(8)		
C(131)–S(1)–Mo	110.1(7)		
C(2)–P(1)–Mo	85.3(9)		
Mo–C(1)–Co	76.7(9)		
C(2)–C(1)–Co	71.0(2)		
C(141)–C(1)–C(2)	124.0(2)		
C(141)–C(1)–Mo	132.0(2)		
C(141)–C(1)–Co	130.0(2)		
C(2)–C(1)–Mo	101.0(2)		
C(1)–C(2)–Co	66.0(1)		
C(1)–C(2)–P(1)	103.0(2)		
P(1)–C(2)–Co	99.0(1)		
C(211)–P(2)–Co	108.0(8)		
C(221)–P(2)–Co	125.5(8)		
M–C–O	170.0(3), 179.0(3)		

The Co–Mo bond length in complex **6** [2.607(5) Å] lies within the range reported for related di- and tri-nuclear Co–Mo systems,[4,7,8] and is very similar to that in **4** reported here. As in compound **4** the molybdenum atom is incorporated into a four-membered ring Mo–P–C=C, the unsaturated C–C bond of which is η^2 bonded to the cobalt atom. This π bond to the cobalt atom is unsymmetrical and the metal–carbon bond lengths [Co–C(1) 1.970(3) and Co–C(2) 2.040(3) Å] are similar in value (within experimental error) to those observed in **4**. The σ bond to the molybdenum atom [Mo–C(1) 2.220(3) Å] is also similar to the value of 2.208(5) Å observed in **4**. The vinyl carbon–carbon bond lengths in both **4** and **6** [C(1)–C(2) 1.430(7) **4** and 1.460(4) Å **6**] are comparable to the value of 1.474(11) Å reported for the C=C double bond in the related complex $[(OC)_2Co\{\mu\text{-}PPh_2C(CO_2Me){=}CCO_2Me\}(\mu\text{-}PPh_2)Mo(CO)(\eta^5\text{-}C_5H_5)]$.[4] The β-carbon atom of the vinyl group in **6** bonds to the diphenylphosphide group [P(1)–C(2) 1.750(3) Å], and the four-membered metallacycle Mo–C=C–P is completed by co-ordination of this group to the Mo atom [Mo–P(1) 2.437(8) Å]. Both the cobalt and molybdenum atoms are bonded to essentially linear carbonyl groups. The co-ordination sphere of the molybdenum atom is completed by an η^5-bonded cyclopentadienyl group with molybdenum–cyclopentadienyl distances and angles similar to those in related structures. The third carbonyl group found in **4**, which lies *trans* to the Co–Mo bond vector, is replaced by a bulky $PPh_2(SPh)$ group in **6** [Co–P(2) 2.174(9), P–C(Ph) 1.770 (average), P(2)–S(2) 2.129(11), S(2)–C(231) 1.775(21) Å], a feature which may be mainly due to steric factors. As in compound **4**, the bridging thiolate ligand bonds unsymmetrically to the two metal atoms [Co–S(1) 2.233(8) and Mo–S(1) 2.460(9) Å], with a bite angle of 67.3(2)°.

The spectroscopic properties (see Table 1 and Experimental section) of complexes **5** and **6** are consistent with the solid-state structure for **6** being maintained in solution for both complexes. In the $^{31}P-\{^1H\}$ NMR spectrum of **6** two singlet resonances are observed at δ −40.3 and −151.1. The more downfield signal is assigned to the $PPh_2(SPh)$ phosphorus atom and the more upfield signal, by comparison with **4**, to the phosphorus atom which forms part of the four-membered metallacycle. The ^1H NMR spectrum shows, in addition to phenyl resonances, a signal at δ 2.88 corresponding to the PPh_2CHCPh proton, which takes the form of a doublet of doublets with $^2J(HP)$ 13.5 and $^3J(HP)$ 4.7 Hz. The smaller coupling of 4.7 Hz is assigned, by comparison with that of **4**, to a two-bond coupling to the phosphido-phosphorus atom while the larger coupling of 13.5 Hz is assigned to a three-bond coupling to the $PPh_2(SPh)$ phosphorus atom. The spectroscopic data for **5** can be similarly assigned.

Experimental

All reactions were carried out under a nitrogen atmosphere using standard Schlenk techniques. Solvents were distilled under nitrogen from appropriate drying agents and degassed prior to use. Ultraviolet irradiation was carried out in a glass photolysis vessel using a Hanovia 125 W medium-pressure immersion lamp in a water-cooled quartz inner tube. Preparative thin-layer chromatography (TLC) was carried out on commercial Merck plates with a 0.25 mm layer of silica, or on 1 mm silica plates prepared at the University Chemical Laboratory, Cambridge. Column chromatography was performed on Kieselgel 60 (70–230 or 230–400 mesh). Products are given in order of decreasing R_f values.

The instrumentation used to obtain spectroscopic data has been described previously.[12] Unless otherwise stated all reagents were obtained from commercial suppliers and used without further purification. The compound $PPh_2(SPh)$ was prepared by the literature method.[13]

(*i*) *Synthesis of* $[(OC)_3Co(\mu\text{-}PhCCH)Mo(CO)_2(\eta^5\text{-}C_5H_5)]$ **1** *and* $[Co_2Mo(\mu_3\text{-}CCH_2Ph)(CO)_8(\eta^5\text{-}C_5H_5)]$ **2**.—To a solution containing $[Mo_2(CO)_6(\eta^5\text{-}C_5H_5)_2]$ (0.990 g, 2.00 mmol) in benzene (120 cm^3) was added $[Co_2(CO)_8]$ (0.760 g, 2.22 mmol). Under vigorous stirring the solution was purged with a steady stream of CO and then irradiated at 293 K for 4 h to give $[(OC)_4CoMo(CO)_3(\eta^5\text{-}C_5H_5)]$.[6] The reaction mixture was then cannulated into a round-bottomed flask containing $PhC{\equiv}CH$ (0.24 cm^3, 2.22 mmol) and heated at 343 K for 2 h. The solvent was removed under reduced pressure and the residue dissolved in the minimum volume of CH_2Cl_2 and loaded onto the top of a chromatography column. Elution with hexane gave red $[Co_2(\mu\text{-}PhCCH)(CO)_6]$ (0.180 g, 21%), followed by orange-red crystalline $[(OC)_3Co(\mu\text{-}PhCCH)Mo(CO)_2(\eta^5\text{-}C_5H_5)]$ **1** (0.630 g, 61%). Further elution gave green crystalline $[Co_2Mo(\mu_3\text{-}CCH_2Ph)(CO)_8(\eta^5\text{-}C_5H_5)]$ **2** (0.160 g, 12%). Complex **1** (Found: C, 46.8; H, 2.4. $C_{18}H_{11}CoMoO_5$ requires C, 46.8; H, 2.4%): fast atom bombardment (FAB) mass spectrum, *m*/*z* 462 (M^+) and (M^+ − *n*CO) (*n* = 0–5); $^{13}C\{^1H$ composite pulse decoupled) NMR ($CDCl_3$), δ 225.6 (s, MoCO), 225.4 (s, MoCO), 203.9 (s, CoCO), 136–128 (m, Ph), 93.3 (s, μ-*C*HCPh), 91.2 (s, C_5H_5) and 74.2 (s, μ-CH*C*Ph). Complex **2** (Found: C, 41.5; H, 2.0. $C_{21}H_{12}Co_2MoO_8$ requires C, 41.5; H, 2.0%): FAB mass spectrum, *m*/*z* 606 (M^+) and (M^+ − *n*CO) (*n* = 0–8); $^{13}C(^1H$ composite pulse decoupled) NMR ($CDCl_3$), δ 288.0 (s, *C*CH$_2$Ph), 206.6 (s, br, MoCO, CoCO), 135–128 (m, Ph), 90.3 (s, C_5H_5) and 63.2 (s, C*C*H$_2$Ph).

(*ii*) *Reaction of Complex* **1** *with* $PPh_2(SPh)$.—Complex **1** (0.630 g, 1.36 mmol) was dissolved in toluene (75 cm^3) and $PPh_2(SPh)$ (0.400 g, 1.36 mmol) added. After the solution had been heated to 333 K for 5 h the solvent was removed under reduced pressure. The residue was redissolved in the minimum volume of hexane and loaded onto the top of a chromatography column. Elution with hexane–CH_2Cl_2 (3:2) gave a trace of unreacted **1** and orange-red $[\{(PhS)Ph_2P\}(OC)_2Co(\mu\text{-}PhCCH)Mo(CO)_2(\eta^5\text{-}C_5H_5)]$ **3** (0.590 g, 60%). FAB mass spectrum: *m*/*z* 700 (M^+ − CO) and (M^+ − *n*CO) (*n* = 0–4). $^{13}C(^1H$ composite pulse decoupled) NMR ($CDCl_3$), δ 231.6 (s, MoCO), 229.2 (s, MoCO), 206.6 (s, br, CoCO), 204.2 (s, br, CoCO), 139–128 (m, Ph), 91.6 (s, C_5H_5), 91.2 (s, μ-*C*HCPh) and 71.9 (s, μ-CH*C*Ph).

(*iii*) *Thermolysis of Complex* **3**.—Complex **3** (0.500 g, 0.69 mmol) was dissolved in toluene (50 cm^3) and the solution heated to reflux for 5 h. The solvent was removed under reduced pressure and the residue dissolved in the minimum volume of CH_2Cl_2 and applied to the base of TLC plates. Elution with hexane–CH_2Cl_2 (1:1) gave orange crystalline $[(\eta^5\text{-}C_5H_5)(OC)Mo(\mu\text{-}PPh_2CH{=}CPh)(\mu\text{-}SPh)Co(CO)_2]$ **4** (0.240 g, 50%) followed by $[(\eta^5\text{-}C_5H_5)(OC)Mo(\mu\text{-}PPh_2CH{=}CPh)(\mu\text{-}SPh)Co(CO)(PPh_3)]$ **5** (0.051 g, 8%). Complex **4** (Found: C, 58.2; H, 3.7. $C_{34}H_{26}CoMoO_3PS$ requires C, 58.2; H, 3.7%). FAB mass spectrum: *m*/*z* 700 (M^+) and (M^+ − *n*CO) (*n* = 0–3); $^{13}C(^1H$ composite pulse decoupled) NMR ($CDCl_3$), δ 236.5 [d, ^2J(PC) 12, MoCO], 208.6 (s, br, CoCO), 205.2 (s, br, CoCO), 140–128 (m, Ph), 116.2 [d, ^2J(CP) 19, μ-PPh$_2$CH=*C*Ph], 91.1 (s, C_5H_5) and 31.4 [d, ^1J(CP) 40 Hz, μ-PPh$_2$*C*H=CPh]. Complex **5**: FAB mass spectrum, *m*/*z* 934 (M^+) and (M^+ − *n*CO) (*n* = 0–2).

(*iv*) *Reaction of Complex* **4** *with* PPh_3.—Complex **4** (0.050 g, 0.07 mmol) was dissolved in toluene (30 cm^3) and triphenylphosphine (0.020 g, 0.07 mmol) added. The solution was refluxed for 30 min, cooled to room temperature and the solvent removed under reduced pressure. The residue was dissolved in the minimum volume of CH_2Cl_2 and applied to the base of TLC plates. Elution with hexane–CH_2Cl_2 (4:1) gave a trace of unreacted **4** and orange-red crystalline **5** (0.040 g, 60%).

(*v*) *Reaction of Complex* **4** *with* $PPh_2(SPh)$.—Complex **4** (0.050 g, 0.07 mmol) was dissolved in toluene (30 cm^3) and $PPh_2(SPh)$ (0.021 g, 0.07 mmol) added. The solution was refluxed for 30 min, cooled to room temperature and the solvent removed under reduced pressure. The residue was dissolved in the minimum volume of CH_2Cl_2 and applied to the base of TLC plates. Elution with hexane–CH_2Cl_2 (4:1) gave a trace of unreacted **4** and orange-red crystalline $[(\eta^5\text{-}C_5H_5)(OC)Mo(\mu\text{-}PPh_2CH{=}CPh)(\mu\text{-}SPh)Co(CO)\{PPh_2(SPh)\}]$ **6** (0.041 g, 60%). FAB mass spectrum, *m*/*z* 966 (M^+) and (M^+ − *n*CO) (*n* = 0–2).

(*vi*) *Crystal Structure Determinations*.—*Crystal data*. $C_{21}H_{12}Co_2MoO_8$ **2**, *M* = 606.11, monoclinic, space group $P2_1/c$, $a = 15.986(5)$, $b = 14.567(7)$, $c = 18.949(6)$ Å, $\beta = 100.86(3)°$, $U = 4334(3)$ Å^3, $D_c = 1.858$ g cm^{-3}, $Z = 8$, $F(000) = 2384$. A brown crystal of size 0.25 × 0.28 × 0.42 mm, μ(Mo-Kα) = 2.128 mm^{-1}, was used in the data collection.

$C_{34}H_{26}CoMoO_3PS$ **4**, *M* = 700.10, monoclinic, space group $C2/c$, $a = 13.976(3)$, $b = 16.118(4)$, $c = 26.531(5)$ Å, $\beta = 96.14(2)°$, $U = 5942.23$ Å^3, $D_c = 1.57$ g cm^{-3}, $Z = 8$, $F(000) = 2832$. An orange crystal of size 0.38 × 0.38 × 0.53 mm, μ(Mo-Kα) = 8.65 cm^{-1}, was used.

$C_{51}H_{41}CoMoO_2P_2S_2$ **6**, *M* = 966.27, monoclinic, space

Table 5 Fractional atomic coordinates for $[Co_2Mo(\mu_3\text{-}CCH_2Ph)(CO)_8(\eta^5\text{-}C_5H_5)]$ **2**

Atom	*X/a*	*Y/b*	*Z/c*	Atom	*X/a*	*Y/b*	*Z/c*
Mo(1)	0.053 55(3)	0.152 81(3)	0.743 49(2)	Mo(2)	0.590 71(3)	0.178 75(3)	0.689 41(2)
Co(1)	0.129 04(4)	0.239 00(4)	0.865 04(3)	Co(3)	0.595 65(4)	0.310 94(5)	0.593 48(3)
Co(2)	0.203 34(4)	0.105 83(5)	0.822 27(4)	Co(4)	0.456 71(4)	0.233 79(5)	0.591 08(4)
C(01)	0.093 3(3)	0.112 0(3)	0.850 3(2)	C(1)	0.564 4(3)	0.183 4(3)	0.577 0(3)
C(02)	0.063 9(3)	0.047 7(3)	0.903 9(3)	C(2)	0.573 8(3)	0.122 8(4)	0.513 9(3)
C(03)	−0.024 5(3)	0.066 0(3)	0.919 0(2)	C(3)	0.661 9(3)	0.094 4(3)	0.505 4(2)
C(04)	−0.093 1(3)	0.014 2(4)	0.887 1(3)	C(4)	0.696 5(4)	0.011 6(4)	0.530 9(3)
C(05)	−0.173 5(3)	0.030 1(4)	0.902 4(3)	C(5)	0.777 6(5)	−0.012 5(5)	0.520 7(4)
C(06)	−0.185 6(4)	0.097 8(4)	0.948 3(3)	C(6)	0.823 2(4)	0.043 8(6)	0.485 5(4)
C(07)	−0.117 5(4)	0.149 8(4)	0.981 4(3)	C(7)	0.789 4(4)	0.124 6(5)	0.458 8(4)
C(08)	−0.372 2(3)	0.132 9(4)	0.967 4(3)	C(8)	0.709 0(4)	0.149 9(4)	0.469 3(3)
C(111)	0.045 3(4)	0.120 4(4)	0.622 1(3)	C(211)	0.532 4(4)	0.162 8(4)	0.791 2(3)
C(112)	0.119 7(4)	0.169 3(5)	0.641 7(3)	C(212)	0.534 8(4)	0.256 7(4)	0.779 5(3)
C(113)	0.098 7(4)	0.256 0(5)	0.661 8(3)	C(213)	0.620 1(4)	0.283 7(4)	0.787 4(3)
C(114)	0.010 2(4)	0.260 9(4)	0.654 5(3)	C(214)	0.669 5(4)	0.205 7(5)	0.804 8(3)
C(115)	−0.023 4(4)	0.176 4(4)	0.629 0(3)	C(215)	0.615 3(4)	0.131 1(4)	0.807 2(3)
O(11)	−0.114 7(2)	0.216 1(3)	0.791 5(2)	O(41)	0.772 7(3)	0.110 5(3)	0.674 2(2)
O(12)	−0.011 6(3)	−0.047 8(3)	0.744 0(2)	O(42)	0.538 7(3)	−0.025 1(3)	0.653 7(3)
O(21)	0.216 1(3)	0.385 5(3)	0.799 7(3)	O(51)	0.571 8(3)	0.468 5(3)	0.684 4(2)
O(22)	−0.006 4(3)	0.353 4(3)	0.901 1(2)	O(52)	0.780 8(3)	0.315 5(3)	0.614 7(2)
O(23)	0.213 5(3)	0.220 8(3)	1.015 2(2)	O(53)	0.544 8(4)	0.394 9(4)	0.452 4(2)
O(31)	0.322 0(3)	0.219 1(4)	0.758 3(3)	O(61)	0.375 6(3)	0.388 1(4)	0.651 3(3)
O(32)	0.307 4(3)	0.042 3(3)	0.957 4(2)	O(62)	0.381 7(3)	0.235 3(4)	0.437 7(2)
O(33)	0.201 9(3)	−0.060 0(3)	0.736 2(3)	O(63)	0.354 5(3)	0.087 5(4)	0.637 4(3)
C(11)	−0.053 0(3)	0.191 6(4)	0.776 9(3)	C(41)	0.705 6(4)	0.136 4(4)	0.675 9(3)
C(12)	0.012 8(4)	0.025 9(4)	0.745 1(3)	C(42)	0.556 8(4)	0.050 3(4)	0.665 4(3)
C(21)	0.181 8(4)	0.328 7(4)	0.823 5(3)	C(51)	0.580 6(3)	0.406 9(4)	0.649 4(3)
C(22)	0.043 7(3)	0.306 2(4)	0.884 8(3)	C(52)	0.708 6(4)	0.312 8(4)	0.605 3(3)
C(23)	0.182 7(3)	0.228 1(4)	0.956 1(3)	C(53)	0.565 2(4)	0.360 4(4)	0.506 1(3)
C(31)	0.277 1(3)	0.174 6(4)	0.782 5(3)	C(61)	0.407 5(4)	0.328 3(5)	0.628 7(3)
C(32)	0.266 7(3)	0.067 2(4)	0.905 9(3)	C(62)	0.410 7(4)	0.236 9(5)	0.497 3(4)
C(33)	0.201 6(4)	0.004 7(5)	0.770 1(3)	C(63)	0.394 8(4)	0.143 5(5)	0.619 2(3)

Table 6 Fractional atomic coordinates for $[(\eta^5\text{-}C_5H_5)(OC)Mo(\mu\text{-}PPh_2CH{=}CPh)(\mu\text{-}SPh)Co(CO)_2]$ **4**

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Co	0.190 16(5)	0.107 08(4)	0.159 95(3)	C(124)	0.416 3(2)	0.412 5(1)	0.166 6(1)
Mo	0.260 80(3)	0.069 83(3)	0.074 73(2)	C(125)	0.417 2(2)	0.382 8(1)	0.117 2(1)
P	0.383 82(9)	0.133 47(8)	0.134 57(5)	C(126)	0.406 5(2)	0.298 1(1)	0.107 4(1)
S	0.095 95(9)	0.049 66(8)	0.096 29(5)	C(131)	0.012 1(2)	0.120 8(2)	0.066 1(1)
C(1)	0.277 8(3)	0.016 9(3)	0.151 9(2)	C(132)	−0.043 0(2)	0.170 4(2)	0.095 0(1)
C(2)	0.330 7(3)	0.079 1(3)	0.181 6(2)	C(133)	−0.109 7(2)	0.226 0(2)	0.071 1(1)
C(3)	0.215 3(4)	0.184 9(3)	0.055 8(2)	C(134)	−0.121 2(2)	0.232 0(2)	0.018 4(1)
O(3)	0.190 5(3)	0.249 1(2)	0.043 8(2)	C(135)	−0.066 0(2)	0.182 4(2)	−0.010 5(1)
C(4)	0.167 7(4)	0.216 5(4)	0.160 0(2)	C(136)	0.000 6(2)	0.126 8(2)	0.013 4(1)
O(4)	0.149 7(4)	0.285 1(3)	0.160 9(2)	C(141)	0.272 3(3)	−0.071 8(2)	0.168 1(1)
C(5)	0.140 2(4)	0.078 8(4)	0.215 2(2)	C(142)	0.188 5(3)	−0.118 2(2)	0.156 5(1)
O(5)	0.110 5(4)	0.060 7(4)	0.252 2(2)	C(143)	0.186 1(3)	−0.201 4(2)	0.170 7(1)
C(111)	0.509 2(2)	0.101 7(2)	0.134 5(1)	C(144)	0.267 4(3)	−0.238 3(2)	0.196 5(1)
C(112)	0.550 7(2)	0.047 1(2)	0.171 4(1)	C(145)	0.351 2(3)	−0.191 9(2)	0.208 0(1)
C(113)	0.645 7(2)	0.021 2(2)	0.170 3(1)	C(146)	0.353 6(3)	−0.108 6(2)	0.193 8(1)
C(114)	0.699 2(2)	0.049 9(2)	0.132 4(1)	C(11)	0.225 5(4)	−0.014 2(3)	0.002 8(2)
C(115)	0.657 8(2)	0.104 5(2)	0.095 5(1)	C(12)	0.283 6(4)	−0.058 7(4)	0.040 7(2)
C(116)	0.562 8(2)	0.130 4(2)	0.096 6(1)	C(13)	0.368 9(5)	0.053 5(4)	0.015 1(3)
C(121)	0.394 8(2)	0.243 1(1)	0.146 9(1)	C(14)	0.373 9(5)	−0.016 6(4)	0.048 5(3)
C(122)	0.393 8(2)	0.272 8(1)	0.196 2(1)	C(15)	0.277 2(4)	0.054 7(4)	−0.012 9(2)
C(123)	0.404 6(2)	0.357 5(1)	0.206 0(1)				

group $P2_1/n$, a = 16.894(4), b = 12.353(3), c = 21.230(5) Å, β = 104.33(2)°, U = 4292.76 Å^3, D_c = 1.49 g cm^{-3}, Z = 4, $F(000)$ = 1976. An orange crystal of size 0.15 × 0.23 × 0.14 mm, μ(Mo-Kα) = 6.87 cm^{-1}, was used.

Data collection. Data for crystal **2** were collected on a Nicolet R3mV diffractometer using monochromated Mo-Kα radiation and ω–2θ scan mode to a maximum value for 2θ of 45°, while those for crystals **4** and **6** were collected on a Philips PW 1100 instrument in the range θ 3–25° with a scan width of 0.90° for **4** and 0.80° for **6**, using a technique described previously.[14] Equivalent reflections were merged to give 4419 data for **2** with $F_{obs} > 4\sigma(F_{obs})$ and 4336 data for **4** and 1590 for **6** with $I/\sigma(I) > 3.0$. Absorption corrections were applied to the data in each case after initial refinement with isotropic thermal parameters for all atoms.[15]

Structure solution and refinement. Complex **2**. Structure solution was by a combination of direct methods and Fourier techniques.[16,17] Anisotropic thermal motion was assumed for all non-hydrogen atoms. Full-matrix least-squares refinement on F_{obs}^2 for all data (except those marked as systematically

Table 7 Fractional atomic coordinates for $[(\eta^5\text{-}C_5H_5)(OC)Mo(\mu\text{-}PPh_2CH{=}CPh)(\mu\text{-}SPh)Co(CO)\{PPh_2(SPh)\}]$ **6**

Atom	*x*	*y*	*z*
Co	0.0754(2)	−0.3261(3)	−0.1880(2)
Mo	0.1322(2)	−0.1329(2)	−0.1538(1)
S(1)	0.1270(5)	−0.2889(7)	−0.0829(4)
S(2)	0.0630(5)	−0.6057(6)	−0.1577(4)
P(1)	0.0752(5)	−0.1410(7)	−0.2710(4)
P(2)	−0.0053(5)	−0.4651(7)	−0.1954(4)
O(3)	0.2931(13)	−0.2264(19)	−0.1769(11)
O(4)	0.1893(14)	−0.4372(18)	−0.2463(11)
C(1)	0.0063(16)	−0.1993(21)	−0.1842(13)
C(2)	0.0007(16)	−0.2250(22)	−0.2524(13)
C(3)	0.2319(19)	−0.2021(23)	−0.1695(13)
C(4)	0.1430(18)	−0.3911(24)	−0.2223(14)
C(111)	0.1155(12)	−0.2008(16)	−0.3327(8)
C(112)	0.1951(12)	−0.1753(16)	−0.3351(8)
C(113)	0.2265(12)	−0.2155(16)	−0.3854(8)
C(114)	0.1782(12)	−0.2812(16)	−0.4333(8)
C(115)	0.0985(12)	−0.3067(16)	−0.4308(8)
C(116)	0.0672(12)	−0.2664(16)	−0.3806(8)
C(121)	0.0258(12)	−0.0218(14)	−0.3121(9)
C(122)	−0.0578(12)	−0.0068(14)	−0.3195(9)
C(123)	−0.0968(12)	0.0832(14)	−0.3531(9)
C(124)	−0.0521(12)	0.1582(14)	−0.3794(9)
C(125)	0.0315(12)	0.1432(14)	−0.3720(9)
C(126)	0.0705(12)	0.0532(14)	−0.3384(9)
C(131)	0.2281(9)	−0.3353(14)	−0.0463(9)
C(132)	0.2581(9)	−0.4324(14)	−0.0647(9)
C(133)	0.3373(9)	−0.4658(14)	−0.0347(9)
C(134)	0.3866(9)	−0.4021(14)	0.0138(9)
C(135)	0.3566(9)	−0.3050(14)	0.0322(9)
C(136)	0.2774(9)	−0.2716(14)	0.0022(9)
C(141)	−0.0641(11)	−0.1877(17)	−0.1567(10)
C(142)	−0.1430(11)	−0.2010(17)	−0.1958(10)
C(143)	−0.2099(11)	−0.1947(17)	−0.1685(10)
C(144)	−0.1979(11)	−0.1752(17)	−0.1020(10)
C(145)	−0.1190(11)	−0.1619(17)	−0.0630(10)
C(146)	−0.0521(11)	−0.1681(17)	−0.0903(10)
C(211)	−0.0456(12)	−0.4942(16)	−0.2795(7)
C(212)	−0.1201(12)	−0.4470(16)	−0.3103(7)
C(213)	−0.1487(12)	−0.4533(16)	−0.3777(7)
C(214)	−0.1027(12)	−0.5069(16)	−0.4144(7)
C(215)	−0.0282(12)	−0.5541(16)	−0.3836(7)
C(216)	0.0004(12)	−0.5478(16)	−0.3161(7)
C(221)	−0.0844(11)	−0.4790(18)	−0.1557(10)
C(222)	−0.1567(11)	−0.5338(18)	−0.1839(10)
C(223)	−0.2153(11)	−0.5495(18)	−0.1486(10)
C(224)	−0.2017(11)	−0.5103(18)	−0.0852(10)
C(225)	−0.1294(11)	−0.4554(18)	−0.0570(10)
C(226)	−0.0708(11)	−0.4398(18)	−0.0923(10)
C(231)	−0.0099(11)	−0.7059(15)	−0.1515(11)
C(232)	−0.0286(11)	−0.7189(15)	−0.0915(11)
C(233)	−0.0873(11)	−0.7944(15)	−0.0847(11)
C(234)	−0.1273(11)	−0.8568(15)	−0.1377(11)
C(235)	−0.1087(11)	−0.8438(15)	−0.1977(11)
C(236)	−0.0499(11)	−0.7684(15)	−0.2046(11)
C(11)	0.1180(21)	0.0554(27)	−0.1692(17)
C(12)	0.2063(19)	0.0297(26)	−0.1459(17)
C(13)	0.2185(25)	−0.0158(34)	−0.0865(21)
C(14)	0.1461(22)	−0.0222(29)	−0.0637(17)
C(15)	0.0838(21)	0.0245(28)	−0.1164(17)

absent) and 582 parameters converged to $R_1 = 0.031[F > 4\sigma(F)]$ and $R_2 = 0.075$ (all data), $(\Delta/\sigma)_{max} = 0.001$, goodness of fit = 1.11. The function minimised was $\Sigma w(F_{obs}{}^2 - F_{calc}{}^2)^2$, $w = 1/[\sigma^2(F_{obs}{}^2) + (0.0331P)^2 + 1.5239P]$ where $P = (F_{obs}{}^2 + 2F_{calc}{}^2)/3$ and σ was obtained from counting statistics. A final electron-density Fourier-difference synthesis revealed maximum and minimum residual peaks of 0.63 and −0.30 e Å^{-3}.

Complexes **4** *and* **6**. The coordinates of the metal atoms in both structures were deduced from Patterson syntheses and the remaining non-hydrogen atoms located from subsequent Fourier-difference syntheses.[18] The hydrogen atom, H(2), attached to C(2) in **4** was located in a Fourier-difference synthesis calculated using data with sin $\theta < 0.35$, but the equivalent hydrogen atom in **6** could not be located directly and was therefore included in a geometrically idealised position and constrained to 'ride' on C(2); the atomic fractional coordinates of H(2) in **4** were not refined. For both **4** and **6** the remaining phenyl hydrogen atoms were included in geometrically idealised positions and constrained to 'ride' on the relevant carbon atoms, with all hydrogen atoms given a fixed thermal parameter of 0.08 Å^2. The metal atoms and the atoms of the carbonyl ligands were assigned anisotropic thermal parameters in the final cycles of full-matrix refinement, in which weights of $w = 1/\sigma^2(F_o)$ were assigned to the individual reflections. Refinement converged at $R_1 = 0.047$ and $R_2 = 0.052$ for **4** and $R_1 = 0.088$ and $R_2 = 0.089$ for **6**. Poor diffraction by the only crystal of **6** available accounts for the relatively high *R* factors and poor estimated standard deviations (e.s.d.s) observed, nonetheless the main features of the structure were well established. Fractional atomic coordinates for the non-hydrogen atoms are listed in Tables 5, 6 and 7 respectively.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters, and remaining bond lengths and angles.

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