Synthesis and Reactions with Alkynes of Complexes containing Both Phosphorus and Sulfur Bridging Ligands: Crystal and Molecular Structures of $[Mn_2(\mu\text{-}PPh_2)(\mu\text{-}SPh)(CO)_8]$, $[Co_3(\mu_3\text{-}S)(\mu\text{-}PPh_2)(CO)_6(PPh_3)]$ and $[Co_3(\mu_3\text{-}S)(\mu\text{-}PPh_2CHCPh)(CO)_6(PPh_3)]$ *

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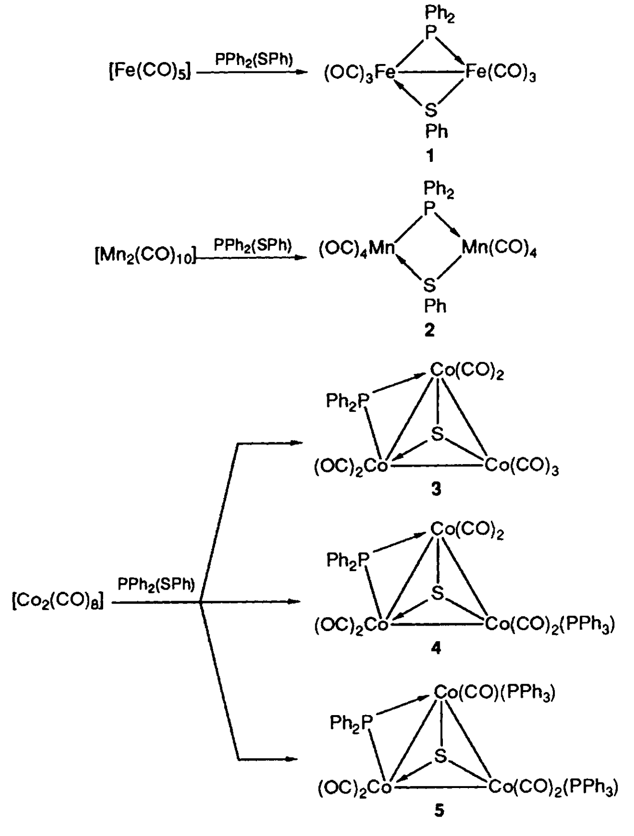
The metal carbonyls $[Mn_2(CO)_{10}]$ and $[Co_2(CO)_8]$ react with the ligand $PPh_2(SPh)$ to give respectively the binuclear complex $[Mn_2(\mu\text{-}PPh_2)(\mu\text{-}SPh)(CO)_8]$ **2** and a combination of trinuclear complexes $[Co_3(\mu_3\text{-}S)(\mu\text{-}PPh_2)(CO)_7]$ **3**, $[Co_3(\mu_3\text{-}S)(\mu\text{-}PPh_2)(CO)_6(PPh_3)]$ **4** and $[Co_3(\mu_3\text{-}S)(\mu\text{-}PPh_2)(CO)_5(PPh_3)_2]$ **5** in a yield ratio which depends on the reaction conditions. Complex **4** reacts thermally with $PhC{\equiv}CH$ which inserts regiospecifically into the phosphido-bridge to generate $[Co_3(\mu_3\text{-}S)(\mu\text{-}PPh_2CHCPh)(CO)_6(PPh_3)]$ **6**. A similar regiospecific insertion of alkyne to give the complex $[Fe_2\{\mu\text{-}PPh_2CHC(CH_2OH)\}(\mu\text{-}SPh)(CO)_6]$ **7** takes place when $[Fe_2(\mu\text{-}PPh_2)(\mu\text{-}SPh)(CO)_6]$ **1** is treated with $HOCH_2C{\equiv}CH$ under photolytic conditions. In contrast neither thermal nor photolytic reactions of **2** with alkynes could be induced. The crystal structures of **2**, **4** and **6** have been determined.

The thermolytic reaction of metal carbonyls with diphosphanes (P_2R_4) (R = alkyl or aryl) was one of the earliest and has proved to be one of the most successful methods of preparing complexes containing bridging phosphido groups.[1] The relative ease of cleavage of the P–P bond in P_2R_4 coupled with the ability of a diphosphane to substitute carbonyl ligands allows the smooth formation of bis(phosphido)-bridged complexes.[1–6] A similar methodology can be envisaged for the preparation from the thiophosphine $PPh_2(SPh)$ and metal carbonyls of complexes containing both a diphenylphosphido ($\mu\text{-}PPh_2$) and a thiolato (μ-SPh) bridge. However, the reaction of $[Fe(CO)_5]$ with $PPh_2(SPh)$ to give $[Fe_2(\mu\text{-}PPh_2)(\mu\text{-}SPh)(CO)_6]$ **1** provides, to our knowledge, the only example of a phosphido-thiolato-bridged complex which has been prepared in this way.[3]

There are now many examples of the insertion of alkynes and other unsaturated organic molecules into one of the metal–phosphorus bonds of a bridging phosphido group.[7–16] Insertion reactions involving bridging RS groups have, however, been less well studied and it seemed of interest to determine from a study of complexes containing both a thiolato and a bridging phosphido group whether the former or the latter would undergo insertion the more readily. Accordingly we have attempted the synthesis of other complexes containing both $\mu\text{-}PPh_2$ and μ-SPh ligands by treating $[Mn_2(CO)_{10}]$ and $[Co_2(CO)_8]$ with $PPh_2(SPh)$. The reaction of the manganese complex with $PPh_2(SPh)$ is analogous to its reaction with P_2Ph_4[1] and leads to the expected product, $[Mn_2(\mu\text{-}PPh_2)(\mu\text{-}SPh)(CO)_8]$ **2**, but dicobalt octacarbonyl reacts in a more complex manner to yield a combination of $[Co_3(\mu_3\text{-}S)(\mu\text{-}PPh_2)(CO)_7]$ **3**, $[Co_3(\mu_3\text{-}S)(\mu\text{-}PPh_2)(CO)_6(PPh_3)]$ **4** and $[Co_3(\mu_3\text{-}S)(\mu\text{-}PPh_2)(CO)_5(PPh_3)_2]$ **5** in a yield ratio which depends on the reaction conditions employed (Scheme 1). The reactions of **1**, **2** and **4** with alkynes have been studied (Scheme 2) and the crystal structure of one of the products of the reaction of **4** with $PhC{\equiv}CH$, $[Co_3(\mu_3\text{-}S)(\mu\text{-}PPh_2CHCPh)(CO)_6(PPh_3)]$ **6**, is reported (Fig. 3).



Scheme 1 Products from the reactions of $[Fe(CO)_5]$, $[Mn_2(CO)_{10}]$ and $[Co_2(CO)_8]$ with $PPh_2(SPh)$

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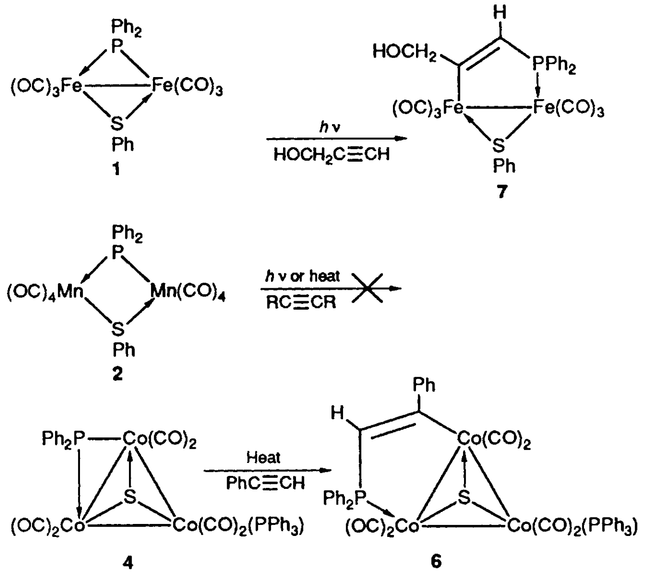
* *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.

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

Complex	ν(CO)[a]/cm^{-1}	^{31}P NMR (δ)[b]
2 $[Mn_2(\mu\text{-}PPh_2)(\mu\text{-}SPh)(CO)_8]$	2066m, 2007vs, 1988m	−162.8 (s, μ-PPh$_2$)
3 $[Co_3(\mu_3\text{-}S)(\mu\text{-}PPh_2)(CO)_7]$	2076m, 2033s, 2014m	71.9 (s, μ-PPh$_2$)
4 $[Co_3(\mu_3\text{-}S)(\mu\text{-}PPh_2)(CO)_6(PPh_3)]$	2046w, 2015s, 1995m	60.0 (s, μ-PPh$_2$), −94.8 (s, PPh$_3$)
5 $[Co_3(\mu_3\text{-}S)(\mu\text{-}PPh_2)(CO)_5(PPh_3)_2]$	2029s, 1982s, 1972s, 1942w	25.8 (s, μ-PPh$_2$), −86.3 (s, PPh$_3$), −94.3 (s, PPh$_3$)
6 $[Co_3(\mu_3\text{-}S)(\mu\text{-}PPh_2CHCPh)(CO)_6(PPh_3)]$	2051m, 2024s, 2004m, 1965w, 1933vw	−92.8 (s, PPh$_3$), −123.9 (s, μ-PPh$_2$CHCPh)
7 $[Fe_2\{\mu\text{-}PPh_2CHC(CH_2OH)\}(\mu\text{-}SPh)(CO)_6]$	2066m, 2025s, 2003s, 1981m, 1964m	−87.3 [s, μ-PPh$_2$CHC(CH$_2$OH)]

[a] Infrared spectra recorded in hexane solution unless otherwise indicated. [b] Chemical shifts are given relative to P(OMe)$_3$ with upfield shifts negative.



Scheme 2 Products from the reactions of complexes **1**, **2** and **4** with alkynes

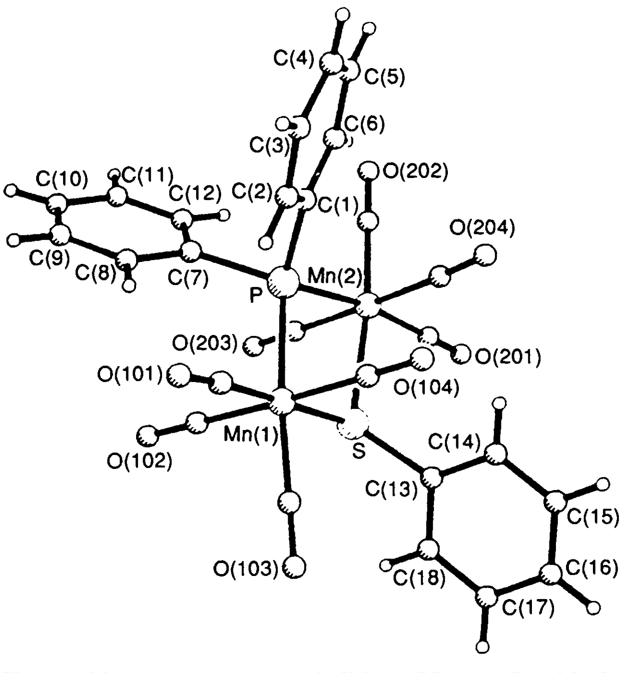


Fig. 1 Molecular structure of $[Mn_2(\mu\text{-}PPh_2)(\mu\text{-}SPh)(CO)_8]$ **2** including the atom numbering scheme

Table 2 Selected bond distances (Å) and angles (°) for complex **2**

Mn(1)–P	2.398(2)	Mn(2)–C(204)	1.869(9)
Mn(1)–S	2.393(2)	Mn(2)–C(203)	1.853(8)
Mn(1)–C(104)	1.838(9)	Mn(2)–C(202)	1.812(8)
Mn(1)–C(103)	1.828(7)	Mn(2)–C(201)	1.838(9)
Mn(1)–C(102)	1.870(8)	P–C(1)	1.853(7)
Mn(1)–C(101)	1.785(8)	P–C(7)	1.852(7)
Mn(2)–P	2.390(2)	S–C(13)	1.798(7)
Mn(2)–S	2.401(2)		
C–O(carbonyl)	1.127(11)–1.147(10)		
S–Mn(1)–P	79.0(1)	Mn(2)–P–C(7)	116.3(2)
S–Mn(2)–P	79.0(1)	Mn(2)–S–C(13)	119.1(3)
Mn(1)–P–Mn(2)	100.4(1)	Mn(1)–P–C(1)	115.7(2)
Mn(1)–S–Mn(2)	100.2(1)	Mn(1)–P–C(7)	113.7(2)
Mn(2)–P–C(1)	114.6(3)	Mn(1)–S–C(13)	109.7(2)

Results and Discussion

(*a*) *Reaction of* $[Mn_2(CO)_{10}]$ *with* PPh$_2$(SPh).—Reaction of $[Mn_2(CO)_{10}]$ with PPh$_2$(SPh) at 423 K in toluene gives the complex $[Mn_2(\mu\text{-}PPh_2)(\mu\text{-}SPh)(CO)_8]$ **2** in 49% yield. Complex **2** has been characterised spectroscopically (see Table 1 and Experimental section) and by a single-crystal X-ray diffraction study. The molecular structure is illustrated in Fig. 1. Table 2 lists selected bond lengths and angles and atomic coordinates are given in Table 5. The structure consists of discrete dinuclear molecules with no unusually short intermolecular contacts.

The two manganese atoms in complex **2** are bridged by a PPh$_2$ ligand and a SPh ligand. Both Mn(1) and Mn(2) are additionally ligated by four terminal CO groups, two equatorial and two axial, completing an approximately octahedral arrangement around each metal centre. The Mn–C$_{ax}$ bond distances are slightly longer than the Mn–C$_{eq}$ bond distances [1.869(9)–1.838(9) *vs.* 1.838(9)–1.785(8) Å]. The Mn$_2$PS core adopts an 'open book' structure in which the Mn(1)–Mn(2) bond is the hinge with an angle of 166.3° between the Mn(1)–Mn(2)–P and the Mn(1)–Mn(2)–S planes. In the related phosphidothiolato-bridged complex $[Mn_2(\mu\text{-}SPh)\{\mu\text{-}PMe(SPh)\}(CO)_8]$[17] the manganese–sulfur bond distances are comparable with those in complex **2** [2.414(2), 2.409(2) *vs.* 2.393(2), 2.401(2) Å (**2**)]. Complex **2**, however, possesses a μ-PPh$_2$ ligand in place of the μ-PMe(SPh) group and this appears to have a significant lengthening effect on the manganese–phosphorus bond distances [2.398(2), 2.390(2) (**2**) *vs.* 2.335(2), 2.336(2) Å] suggesting that the bonds to the μ-PPh$_2$ ligand are the weaker. The phenyl groups on the phosphorus atom in **2** are electron withdrawing relative to the methyl and phenylthio groups on the phosphorus in $[Mn_2(\mu\text{-}SPh)\{\mu\text{-}PMe(SPh)\}(CO)_8]$, and this is presumably responsible for the reduction in the co-ordinating ability of the phosphido-phosphorus atom. Similar manganese–phosphorus bond distances to those for **2** are observed in the bis(diphenylphosphido) complex $[Mn_2(\mu\text{-}PPh_2)_2(CO)_8]$.[18] The Mn(1)–P–Mn(2) and Mn(1)–S–Mn(2) angles associated with the bridging groups in **2** are very similar, averaging 100.3° compared with the 101.2° for the Mn–P–Mn angles in $[Mn_2(\mu\text{-}PPh_2)_2(CO)_8]$, and are in the range associated with the absence of any significant interaction between the metal

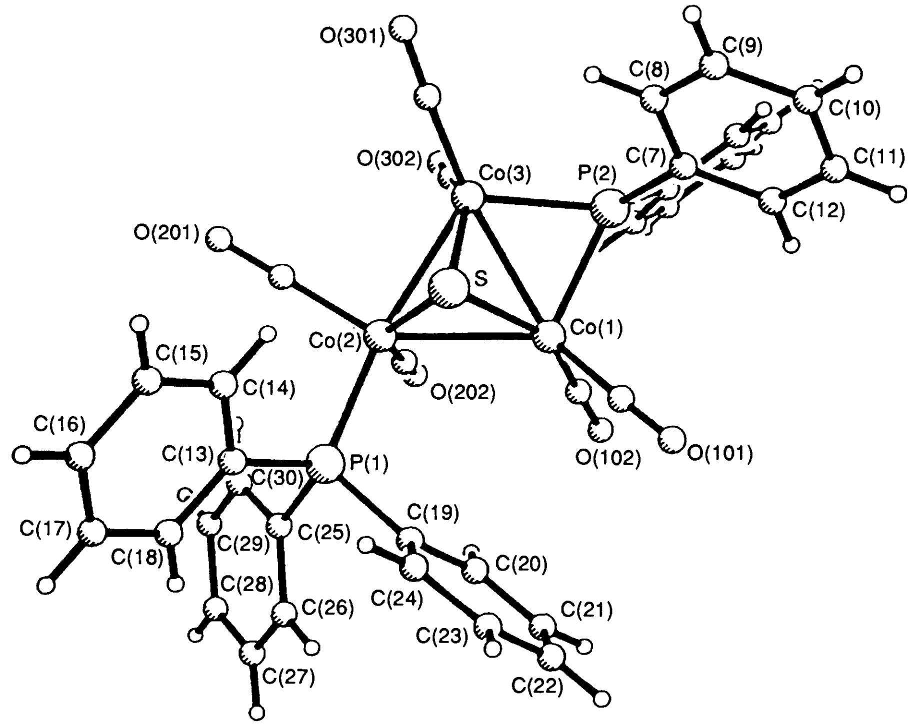


Fig. 2 Molecular structure of $[Co_3(\mu_3\text{-}S)(\mu\text{-}PPh_2)(CO)_6(PPh_3)]$ **4** including the atom numbering scheme

Table 3 Selected bond distances (Å) and angles (°) for complex **4**

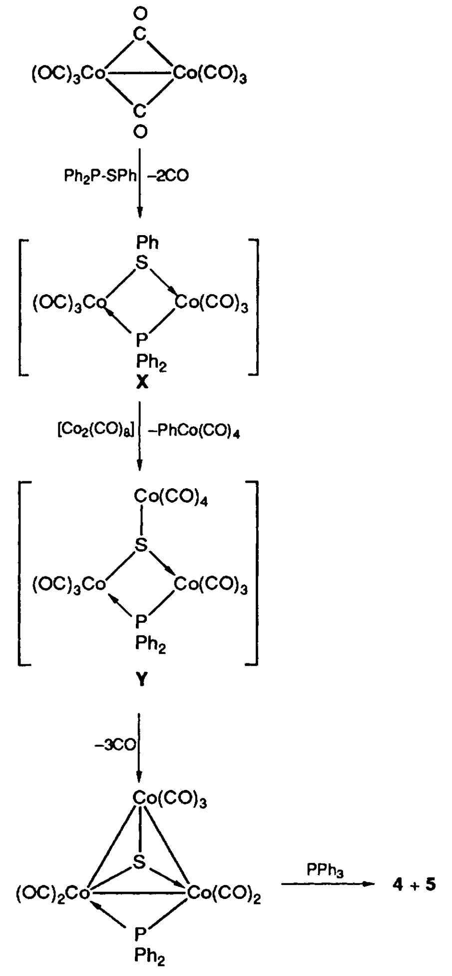
S–Co(1)	2.172(2)	P(1)–Co(2)	2.225(2)
S–Co(2)	2.153(2)	Co(1)–Co(2)	2.598(2)
S–Co(3)	2.183(2)	Co(1)–Co(3)	2.496(2)
P(2)–Co(3)	2.178(2)	Co(2)–Co(3)	2.536(2)
P(2)–Co(1)	2.200(2)		
Co–C(carbonyl)	1.763(6)–1.787(7)		
C–O(carbonyl)	1.130(7)–1.141(7)		
P–C(phenyl)	1.816(5)–1.831(5)		
Co(1)–P(2)–Co(3)	69.5(1)	P(1)–Co(2)–S	101.2(1)
Co(1)–Co(3)–P(2)	55.7(1)	Co(1)–Co(2)–P(1)	108.0(1)
Co(3)–Co(2)–P(2)	54.8(1)	Co(3)–Co(2)–P(1)	155.9(1)
Co(1)–S–Co(3)	69.9(1)	Co(1)–Co(2)–Co(3)	58.1(1)
Co(1)–S–Co(2)	73.9(1)	Co(1)–Co(3)–Co(2)	62.2(1)
Co(2)–S–Co(3)	71.6(1)	Co(2)–Co(1)–Co(3)	59.7(1)

centres.[19] The Mn ··· Mn non-bonded distance is 3.678 Å and that for P ··· S is 3.048 Å.

(*b*) *Reaction of* $[Co_2(CO)_8]$ *with* $PPh_2(SPh)$.—A large variety of sulfur-capped polynuclear cobalt complexes have been prepared from the reactions of dicobalt octacarbonyl with either elemental sulfur or sulfur-containing molecules [*e.g.* R_2S, RSH, H_2S, $R^1OC(S)SR^2$, $R^1C(S)SR^2$, $R^1C(S)NR^2$ (R,R^1,R^2 = H, alkyl or aryl)].[20–26] Similarly, the reaction of $[Co_2(CO)_8]$ with $PPh_2(SPh)$ in CH_2Cl_2 solution at room temperature gives the trimetallic species $[Co_3(\mu_3\text{-}S)(\mu\text{-}PPh_2)(CO)_7]$ **3** and $[Co_3(\mu_3\text{-}S)(\mu\text{-}PPh_2)(CO)_6(PPh_3)]$ **4** in 41 and 15% yield respectively. The same reaction performed in refluxing toluene solution purged with CO gives the complexes **4** and $[Co_3(\mu_3\text{-}S)(\mu\text{-}PPh_2)(CO)_5(PPh_3)_2]$ **5** in 40 and 10% yield respectively but no trace of **3**. All the above complexes **3**–**5** have been characterised spectroscopically (see Table 1 and Experimental section). Crystals of **4** suitable for X-ray determination were obtained by slow evaporation of a dichloromethane–hexane solution of the complex. The molecular structure of **4** is shown in Fig. 2 and selected bond lengths and angles are listed in Table 3. Table 6 gives the atomic coordinates.

An apical sulfur atom is linked to three metal atoms with Co(1) and Co(3) bridged equatorially by one phosphido group. Each cobalt atom is ligated by two carbonyl groups and Co(2) is, in addition, ligated by one triphenylphosphine molecule. The ligand-bridged Co(1)–Co(3) bond at 2.496(2) Å is the shortest of the three metal–metal bonds [Co(1)–Co(2) 2.598(2), Co(3)–Co(2) 2.536(2) Å]. The two Co–P bonds to the bridging phosphido group are unequal in length [Co(3)–P(2) 2.178(2), Co(1)–P(2) 2.200(2) Å] perhaps reflecting the inequivalence of Co(3) and Co(1) resulting from the presence of the PPh_3 ligand on Co(2). A similar rationale can explain the unequal length of Co(3)–S [2.183(2) Å] and Co(1)–S [2.172(2) Å]. The fact that Co(2)–S [2.153(2) Å] is the shortest cobalt–sulfur bond is perhaps a consequence of an unfavourable interaction between the phosphido-phenyl group and the apical sulfur.

The precise mechanism for the reaction of $[Co_2(CO)_8]$ with $PPh_2(SPh)$ to give the trinuclear complexes **3**–**5** is unclear but radical processes are almost certainly involved. A possible route is outlined in Scheme 3. In the first step $[Co_2(CO)_8]$ reacts with $Ph_2P\text{–}SPh$, with the loss of two CO groups, to form a binuclear intermediate $[Co_2(\mu\text{-}PPh_2)(\mu\text{-}SPh)(CO)_6]$ **X** with a structure which lacks a metal–metal bond and resembles that of complex **2**. A corresponding bis(phosphido)-bridged binuclear complex, $[Co_2(\mu\text{-}PPh_2)_2(CO)_6]$, is relatively stable, although it rearranges readily to the trimeric species $[Co_3(\mu\text{-}PPh_2)_3(CO)_6]$.[27] The cleavage of the Ph–S bond involved in the formation of intermediate **Y** from **X** is seen also in the formation of paramagnetic $[Co_3(\mu_3\text{-}S)(CO)_9]$ from the reaction of PhSH with $[Co_2(CO)_8]$.[22] The loss of three carbonyl groups from **Y** with concomitant metal–metal bond formation would then produce complex **3**. The triphenylphosphine involved in the formation of the substituted complexes **4** and **5** must be generated by a radical process from $PPh_2(SPh)$. Interestingly the ligand $PPh_2(SPh)$ has been reported as being thermally unstable isomerising readily to the phosphine sulfide $Ph_3P{=}S$.[28] However, reaction of $Ph_3P{=}S$ with $[Co_2(CO)_8]$ under the same conditions as for $PPh_2(SPh)$ afforded only decomposition products. The ability of $[Co_2(CO)_8]$ to react with $PPh_2(SPh)$ under milder conditions than those needed to bring about reaction of $[Mn_2(CO)_{10}]$ may be correlated with the greater ease of fragmentation of $[Co_2(CO)_8]$ into monomeric $[Co(CO)_4]^{\bullet}$ species.[29] The fact that $[Mn_2(\mu\text{-}PPh_2)(\mu\text{-}SPh)(CO)_8]$ **2**



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Scheme 3 Possible pathways for the formation of the trinuclear complex $[Co_3(\mu_3\text{-}S)(\mu\text{-}PPh_2)(CO)_7]$ **3** and of complexes **4** and **5**

Table 4 Selected bond distances (Å) and angles (°) for complex **6**

S–Co(1)	2.141(4)	C(2)–Co(1)	1.987(18)
S–Co(2)	2.185(5)	Co(2)–P(2)	2.186(5)
S–Co(3)	2.165(5)	Co(1)–Co(2)	2.569(3)
Co(3)–P(1)	2.195(6)	Co(1)–Co(3)	2.511(3)
P(1)–C(1)	1.750(15)	Co(2)–Co(3)	2.500(3)
C(1)–C(2)	1.364(23)	C(2)–C(3)	1.478(22)
Co–C(carbonyl)	1.693(22)–1.776(16)		
C–O(carbonyl)	1.107(21)–1.181(25)		
P–C(phenyl)	1.813(15)–1.838(20)		
Co(1)–C(2)–C(1)	122.0(12)	Co(2)–S–Co(3)	70.1(2)
C(2)–C(1)–P(1)	121.8(14)	Co(1)–Co(2)–P(2)	137.0(2)
C(1)–P(1)–Co(3)	110.0(6)	Co(3)–Co(2)–P(2)	137.8(1)
P(1)–Co(3)–Co(1)	90.4(1)	Co(1)–Co(2)–Co(3)	59.4(1)
Co(3)–Co(1)–C(2)	95.4(4)	Co(1)–Co(3)–Co(2)	61.7(1)
Co(1)–S–Co(3)	71.3(1)	Co(2)–Co(1)–Co(3)	58.9(1)
Co(1)–S–Co(2)	72.8(2)		

is the only product of the reaction of $PPh_2(SPh)$ with the manganese complex, even under more severe conditions, suggests that a different and perhaps non-radical mechanism is involved in this case. In the light of these results it was of interest to determine whether the reaction of **2** with $[Co_2(CO)_8]$ would give one or more sulfur-capped heterotrinuclear complexes related to **3**–**5**. The results of this experiment were, however, inconclusive as only starting material and decomposition products could be isolated.

(*c*) *Reaction of* $[Co_3(\mu_3\text{-}S)(\mu\text{-}PPh_2)(CO)_6(PPh_3)]$ **4** *with* PhC≡CH.—Reaction of $[Co_3(\mu_3\text{-}S)(\mu\text{-}PPh_2)(CO)_6(PPh_3)]$ **4** with PhC≡CH at 363 K gave the alkyne-inserted complex $[Co_3(\mu_3\text{-}S)(\mu\text{-}PPh_2CHCPh)(CO)_6(PPh_3)]$ **6** and the bis(triphenylphosphine) substituted complex $[Co_3(\mu_3\text{-}S)(\mu\text{-}PPh_2)(CO)_5(PPh_3)_2]$ **5** in 41 and 11% yields respectively. Complex **6** has been characterised spectroscopically (see Table 1 and Experimental section). Slow evaporation of a tetrahydrofuran (thf)–hexane solution gave crystals suitable for a single-crystal X-ray determination. The molecular structure of **6** is shown in Fig. 3 and selected bond distances and angles are listed in Table 4 with the atomic coordinates given in Table 7.

As is the case with the molecular structure of complex **4**, the molecular geometry of the tricobalt–sulfur pyramid in **6** resembles those of previously reported examples.[20–26] The ligand $PPh_2CH{=}CPh$ bridges Co(1) and Co(3), with the two metal atoms being ligated respectively by C(2) and P(1). The five-membered dimetallacyclic ring so formed is almost planar (maximum deviation from plane 0.046 Å) with a dihedral angle of 16.7° relative to the plane of the metal triangle and 97° relative to the Co(1)–S–Co(3) plane. Each cobalt atom, as in **4**, is ligated by two carbonyl groups and Co(2) is bonded additionally to one triphenylphosphine molecule. The effect of the inserted PhCCH unit on the Co_3S pyramid in **6** as compared to that in $[Co_3(\mu_3\text{-}S)(\mu\text{-}PPh_2)(CO)_6(PPh_3)]$ **4** is to lengthen the ligand-bridged Co(1)–Co(3) bond by 0.015 Å and shorten both the Co(1)–Co(2) and Co(3)–Co(2) distances by 0.029 and 0.036 Å respectively. These changes increase the Co(1)–Co(2)–Co(3) angle by 1.3°. The position of the apical sulfur with respect to the metal triangle is also altered, with a lengthening of Co(2)–S by 0.032 Å and a shortening of Co(1)–S and Co(3)–S by 0.031 and 0.018 Å respectively. It may be that the $\mu\text{-}PPh_2CH{=}CPh$ ligand in **6** interacts less strongly with the apical sulfur than the $\mu\text{-}PPh_2$ group in **4**, and that the movement of the sulfur atom towards the Co(1)–Co(3) edge and away from Co(2) takes place partly for this reason and perhaps partly also because the interaction of the sulfur atom with the PPh_3 ligand on Co(2) is thereby reduced.

The ^1H NMR spectrum of complex **6** shows, in addition to phenyl resonances, a doublet of doublets centred at δ 6.30 with $^2J(PH)$ 16.0 Hz and $^5J(PH)$ 4.4 Hz due to the $PPh_2C\mathit{H}CPh$ proton. This five-bond coupling constant is unusually high but could be a consequence of the high degree of conjugation in the system. In the $^{13}C\text{-}\{^1H\}$ NMR two doublet signals are seen for the vinyl carbons of the $\mu\text{-}PPh_2CH{=}CPh$ ligand. One resonance at δ 155.6 is assigned to the carbon atom adjacent to phosphorus with $J(PC)$ 28 Hz. The other signal at δ 181.0 is assigned to the β-carbon with $J(PC)$ 40 Hz. Two singlet signals are observed in the $^{31}P\text{-}\{^1H\}$ NMR at δ −92.8 and −123.9, assigned respectively to the PPh_3 and the PPh_2 phosphorus atoms.

(*d*) *Reaction of* $[Fe_2(\mu\text{-}PPh_2)(\mu\text{-}SPh)(CO)_6]$ **1** *with* HOCH$_2$C≡CH.—The photolytic reaction of $[Fe_2(\mu\text{-}PPh_2)(\mu\text{-}SPh)(CO)_6]$ **1** with HOCH$_2$C≡CH in benzene gives $[Fe_2\{\mu\text{-}PPh_2CHC(CH_2OH)\}(\mu\text{-}SPh)(CO)_6]$ **7** in good yield (*ca.* 73%). The structure of complex **7** is assigned on the basis of its spectroscopic properties (see Table 1 and Experimental section) and a comparison of these properties with those of **6** (Scheme 2).

The ^1H NMR spectrum of complex **7** shows a doublet of triplets at δ 6.47 with $^2J(PH)$ 16.3 Hz and $^4J(HH)$ 1.6 Hz due to the $PPh_2C\mathit{H}C(CH_2OH)$ proton. A multiplet peak at δ 4.66 is assigned to the $PPh_2CHC(C\mathit{H}_2OH)$ protons. Selective decoupling experiments showed that the complexity of this latter peak results from the overlapping of signals due to the inequivalent coupled CH_aH_b protons.[30] A 1:3:1 triplet peak centred at δ 1.93 is assigned to the alcoholic $PPh_2CHC(CH_2O\mathit{H})$ proton. In the $^{13}C\text{-}\{^1H\}$ NMR spectrum recorded at 293 K six distinct carbonyl resonances are observed indicating the absence of any fluxional process at this temperature. Four of these resonances take the form of doublets, of which the three doublets having the larger coupling constant are assigned to

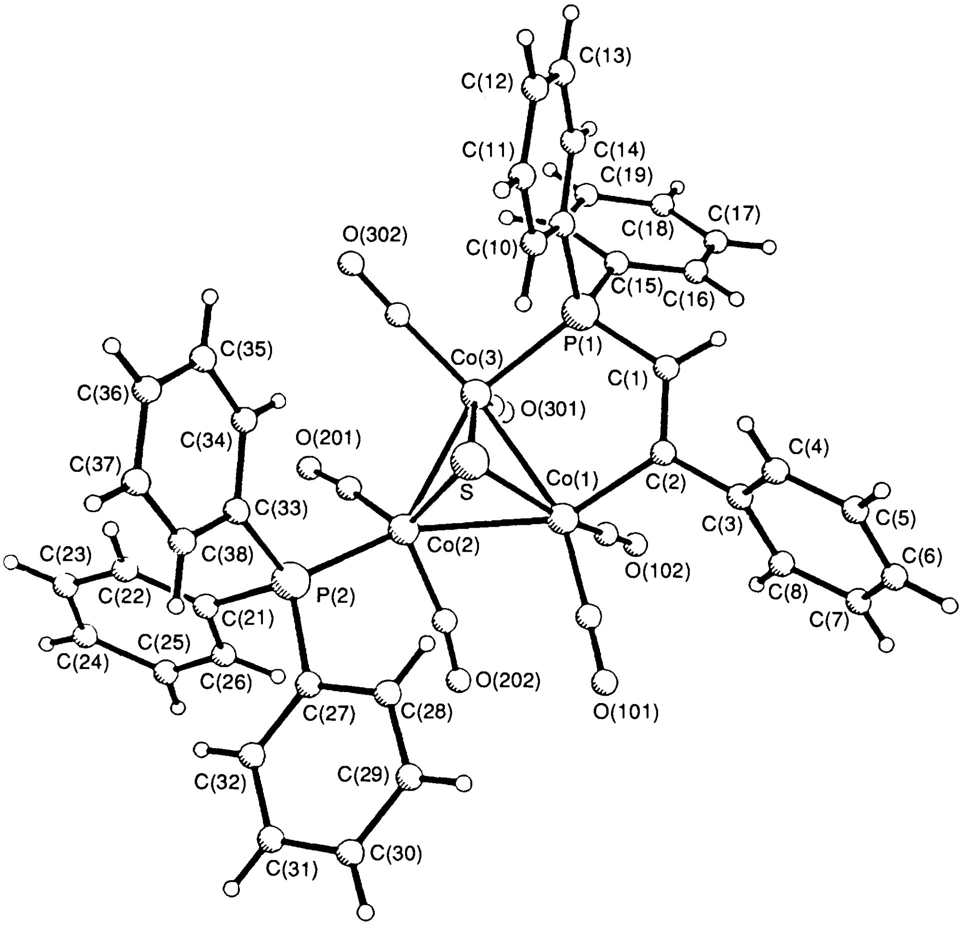
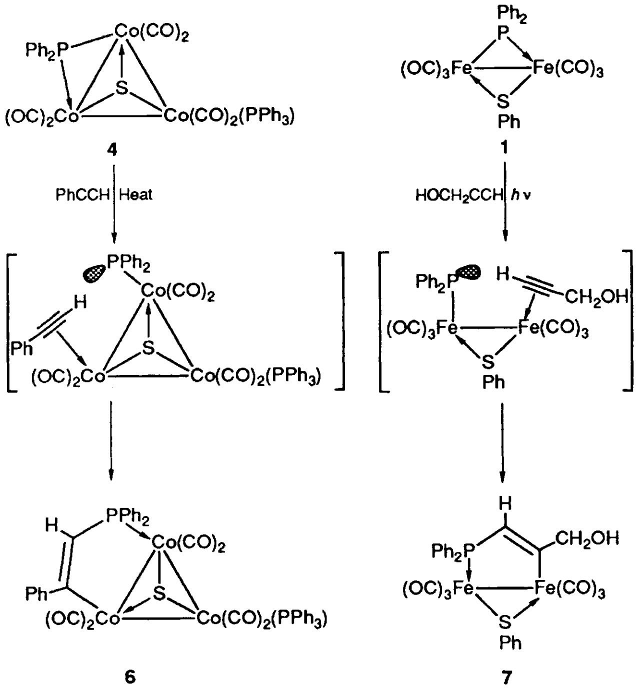


Fig. 3 Molecular structure of $[Co_3(\mu_3\text{-}S)(\mu\text{-}\eta^2\text{-}PPh_2CHCPh)(CO)_6(PPh_3)]$ **6** including the atom numbering scheme



Scheme 4 Possible mechanism for the regiospecific insertions of alkynes into the μ-PPh_2 bridges of complexes **4** and **1**

carbonyls coupled through two bonds to phosphorus [^2J(PC) 25–41 Hz]. The other doublet [^3J(PC) 11 Hz] and the two singlet signals are assigned to those carbonyls ligated to the Fe atom not co-ordinated by phosphorus. The vinyl group carbon atom adjacent to phosphorus gives a doublet centred at δ 121.5 [^1J(PC) 68 Hz] and the β-carbon a doublet at δ 201.0 [^2J(PC) 32 Hz]. The $^{31}P\text{-}\{^1H\}$ NMR spectrum shows a single resonance at δ −87.3 which is assigned to the phosphorus atom of the Fe–C=C–P–Fe dimetallacycle.

The detailed mechanisms for the reaction of $[Co_3(\mu_3\text{-}S)(\mu\text{-}PPh_2)(CO)_6(PPh_3)]$ **4** with PhC≡CH to give **6** and for the reaction of $[Fe_2(\mu\text{-}PPh_2)(\mu\text{-}SPh)(CO)_6]$ **1** with $HOCH_2C{\equiv}CH$ to give **7** are uncertain but the similar nature of the products obtained in each case suggest they are related. Scheme 4 outlines one possible pathway for each system. Since there is no loss of CO during the transformations the first step could involve alkyne co-ordination made possible by a three-electron donating phosphido-bridge opening to give a terminal phosphide ligand acting as a one-electron donor. This requires either heating (**4**) or photolysis (**1**). The pendant phosphides then presumably attack at the less-hindered end of the co-ordinated alkynes in each case to yield regiospecifically the complexes **6** and **7**. Such nucleophilic attack of a terminal phosphide on an alkyne has also been proposed as the first step in the reaction of the mononuclear phosphide complex $[M(\eta^5\text{-}C_5H_5)(CO)_x(PPh_2)]$ (M = Fe, x = 2; M = Mo or W, x = 3) to give $[M(\eta^5\text{-}C_5H_5)(CO)_{x-1}\{PPh_2CRCR'C(O)\}]$ (R = H or CO_2Me, R′ = CO_2Me).[31] A photolytically induced phosphido-bridge opening similar to that shown for $[Fe_2(\mu\text{-}PPh_2)(\mu\text{-}SPh)(CO)_6]$ **1** in Scheme 4 has been postulated as a possible first step in the regiospecific reaction of $[Co_2(\mu\text{-}PPh_2)_2(CO)_6]$ with alkynes, RC≡CH, which gives $[Co_2\{\mu\text{-}PPh_2CHCRC(O)\}(\mu\text{-}PPh_2)(CO)_4]$.[32] The regiospecificity observed for the insertion of alkynes into the phosphido bridges of **1** and **4** is, as mentioned above, attributed to the sterically unfavourable

Table 5 Fractional atomic coordinates (× 10^4) for complex **2**

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Mn(1)	7 402(1)	495(1)	4 117(1)	O(204)	7 666(3)	−1 783(7)	2 650(2)
Mn(2)	7 239(1)	−2 972(1)	3 591(1)	C(1)	6 272(3)	−234(8)	3 016(3)
P	6 616(1)	−926(2)	3 634(1)	C(2)	6 219(4)	1 173(9)	2 937(3)
S	7 949(1)	−1 664(2)	4 183(1)	C(3)	5 911(4)	1 651(10)	2 492(3)
C(101)	6 978(3)	2 087(8)	4 070(3)	C(4)	5 676(4)	799(11)	2 107(3)
O(101)	6 740(3)	3 145(6)	4 060(3)	C(5)	5 725(5)	−568(12)	2 177(3)
C(102)	7 020(3)	−10(8)	4 690(3)	C(6)	6 027(4)	−1 086(9)	2 636(3)
O(102)	6 789(3)	−259(7)	5 042(2)	C(7)	5 832(3)	−1 089(7)	3 907(2)
C(103)	8 087(3)	1 268(7)	4 513(3)	C(8)	5 554(3)	53(7)	4 113(3)
O(103)	8 511(3)	1 749(6)	4 761(2)	C(9)	4 962(4)	−37(9)	4 300(3)
C(104)	7 759(4)	919(8)	3 537(3)	C(10)	4 638(4)	−1 241(8)	4 305(3)
O(104)	7 966(3)	1 222(7)	3 176(3)	C(11)	4 891(3)	−2 370(8)	4 106(3)
C(201)	7 827(4)	−4 391(9)	3 626(3)	C(12)	5 494(3)	−2 304(7)	3 912(3)
O(201)	8 160(3)	−5 331(7)	3 662(3)	C(13)	8 792(3)	−1 446(7)	4 080(3)
C(202)	6 645(4)	−4 016(8)	3 213(3)	C(14)	9 010(4)	−1 224(9)	3 623(3)
O(202)	6 275(3)	−4 710(7)	2 982(3)	C(15)	9 664(4)	−1 037(10)	3 589(4)
C(203)	6 920(3)	−3 589(7)	4 170(3)	C(16)	10 114(4)	−1 085(9)	4 013(5)
O(203)	6 731(3)	−4 007(6)	4 523(2)	C(17)	9 905(4)	−1 285(9)	4 464(4)
C(204)	7 520(4)	−2 219(8)	3 011(3)	C(18)	9 247(4)	−1 501(9)	4 507(3)

Table 6 Fractional atomic coordinates (× 10^4) for complex **4**

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Co(1)	2 090(1)	6 462(1)	3 044(1)	C(19)	−1 677(5)	3 459(4)	2 742(3)
Co(2)	1 044(1)	4 683(1)	1 722(1)	C(20)	−737(6)	3 439(5)	3 345(3)
Co(3)	2 880(1)	7 018(1)	1 879(1)	C(21)	−1 086(8)	3 726(6)	4 068(3)
P(1)	−1 135(1)	3 125(1)	1 800(1)	C(22)	−2 345(9)	4 037(7)	4 200(4)
P(2)	3 876(1)	8 324(1)	3 031(1)	C(23)	−3 266(9)	4 078(8)	3 608(4)
S	508(1)	6 417(1)	2 115(1)	C(24)	−2 961(7)	3 788(6)	2 871(4)
C(1)	5 900(5)	8 745(5)	3 415(3)	C(25)	−1 046(5)	1 497(4)	1 634(3)
C(2)	6 441(6)	7 716(5)	3 295(3)	C(26)	−1 801(6)	631(5)	2 014(3)
C(3)	7 977(6)	7 960(6)	3 526(3)	C(27)	−1 655(8)	−580(5)	1 884(3)
C(4)	9 015(7)	9 228(6)	3 882(4)	C(28)	−796(7)	−947(5)	1 378(3)
C(5)	8 505(6)	10 259(5)	4 007(3)	C(29)	−24(7)	−100(5)	983(3)
C(6)	6 942(6)	10 026(5)	3 772(3)	C(30)	−162(7)	1 100(5)	1 112(3)
C(7)	3 501(5)	9 814(4)	3 428(3)	C(101)	1 152(6)	6 877(5)	3 812(3)
C(8)	2 971(8)	10 402(6)	2 961(4)	C(102)	3 112(6)	5 728(5)	3 499(3)
C(9)	2 632(9)	11 488(7)	3 270(5)	O(101)	613(6)	7 173(5)	4 324(2)
C(10)	2 845(8)	12 040(6)	4 039(4)	O(102)	3 687(6)	5 273(5)	3 846(3)
C(11)	3 341(7)	11 471(6)	4 508(3)	C(201)	901(7)	4 254(5)	715(3)
C(12)	3 678(6)	10 351(5)	4 204(3)	C(202)	2 451(6)	4 047(5)	1 964(3)
C(13)	−2 878(6)	2 827(5)	1 153(3)	O(201)	870(6)	3 974(5)	75(2)
C(14)	−2 950(6)	3 807(5)	859(3)	O(202)	3 350(5)	3 628(4)	2 077(3)
C(15)	−4 286(7)	3 602(6)	384(3)	C(301)	2 731(7)	7 876(5)	1 218(3)
C(16)	−5 535(7)	2 435(6)	198(3)	C(302)	4 446(6)	6 548(5)	1 612(3)
C(17)	−5 479(7)	1 469(6)	486(4)	O(301)	2 659(6)	8 450(5)	812(3)
C(18)	−4 162(6)	1 654(6)	963(3)	O(302)	5 457(5)	6 276(4)	1 423(3)

interaction of the phosphido-phenyl groups with the R substituent on the alkyne. In the reaction of [$Ru_3(\mu\text{-}H)(\mu\text{-}PPh_2)_3(CO)_7$] with PhC≡CPh, insertion of the symmetrically substituted alkyne into the phosphido-bridge also occurs, but in this case with concomitant cleavage of a P–Ph bond to give the phosphinidene complex [$Ru_3(\mu\text{-}PPh_2)_2\{\mu_3\text{-}PhPC(Ph)=C(Ph)\}(CO)_6$].[9]

The bridging ligands in complexes **6** and **7** of general formula $PPh_2CH=CR$, obtained respectively from the reactions of complexes **4** and **1** with PhC≡CH and $HOCH_2C≡CH$, adopt a different mode of bonding from that reported in structurally characterised complexes containing related ligands.[6–8,30] Thus the product from the reaction of [$(\eta^5\text{-}C_5H_5)Ni(\mu\text{-}PPh_2)(\mu\text{-}CO)Fe(CO)_3$] with PhC≡CPh, [$(OC)_3Fe(\mu\text{-}PPh_2CPh=CPh)Ni(\eta^5\text{-}C_5H_5)$], represents the typical bonding arrangement adopted, where a four-membered metallacycle is π-co-ordinated to the second metal.[7] Werner and Zolk[10b] have on the basis of spectroscopic evidence, however, formulated the complex [$Co_2\{\mu\text{-}PMe_2C(CO_2Me)C(CO_2Me)\}(\mu\text{-}PMe_2)(\eta^5\text{-}C_5H_5)_2$] as containing a similar five-membered dimetallacycle to that in **6** and **7**.

It was not possible to induce the reaction of [$Mn_2(\mu\text{-}PPh_2)(\mu\text{-}SPh)(CO)_8$] **2** with alkynes either thermally or photolytically. The related bis(phosphido)-bridged complex [$Mn_2(\mu\text{-}PPh_2)_2(CO)_8$] does react photolytically with alkynes to give alkyne-inserted products but in low yields.[16] It would appear that the thiolato-bridge in **2** has an inhibiting effect on its reactivity.

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 125W 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.

Table 7 Fractional atomic coordinates (× 10^4) for complex **6**

Atom	*x*	*y*	*z*
Co(1)	1988(2)	2844(2)	1259(1)
Co(2)	1998(2)	3225(2)	2690(1)
Co(3)	3104(2)	4678(2)	2130(1)
S	3580(4)	2917(4)	2281(2)
P(1)	4088(4)	5038(4)	1291(2)
P(2)	2417(4)	2284(3)	3718(2)
C(101)	1463(16)	1335(19)	1019(9)
O(101)	1141(12)	349(13)	879(7)
C(102)	712(19)	3451(16)	661(11)
O(102)	−125(13)	3819(12)	249(8)
C(201)	1746(15)	4490(20)	3149(10)
O(201)	1487(10)	5313(11)	3487(7)
C(202)	477(16)	2566(16)	2157(9)
O(202)	−526(11)	2166(11)	1920(7)
C(301)	1870(17)	5527(16)	1803(10)
O(301)	1078(12)	6110(11)	1597(7)
C(302)	4196(18)	5623(16)	2955(11)
O(302)	4883(14)	6218(14)	3436(8)
C(1)	3723(15)	3880(13)	526(9)
C(2)	2899(14)	2942(15)	484(9)
C(3)	2736(15)	1970(13)	−149(10)
C(4)	3749(16)	1452(14)	−247(9)
C(5)	3625(17)	580(15)	−861(11)
C(6)	2429(18)	219(16)	−1388(12)
C(7)	1441(18)	673(17)	−1297(10)
C(8)	1559(16)	1532(15)	−675(9)
C(9)	5788(15)	5218(15)	1676(9)
C(10)	6348(15)	4339(15)	2026(11)
C(11)	7631(18)	4357(18)	2291(11)
C(12)	8328(17)	5361(22)	2235(11)
C(13)	7798(19)	6224(19)	1908(12)
C(14)	6506(15)	6182(15)	1639(10)
C(15)	3684(14)	6355(16)	845(10)
C(16)	3185(15)	6334(19)	30(10)
C(17)	2813(17)	7303(22)	−280(11)
C(18)	2874(16)	8338(22)	184(13)
C(19)	3364(19)	8401(17)	993(14)
C(20)	3767(17)	7398(18)	1332(11)
C(21)	1621(16)	2786(16)	4417(10)
C(22)	2259(19)	3258(15)	5184(11)
C(23)	1676(21)	3672(16)	5690(12)
C(24)	431(25)	3656(19)	5444(13)
C(25)	−262(22)	3196(18)	4654(14)
C(26)	352(17)	2828(16)	4159(11)
C(27)	1934(14)	724(13)	3511(10)
C(28)	2214(17)	82(16)	2882(10)
C(29)	1840(17)	−1122(16)	2672(11)
C(30)	1160(16)	−1711(16)	3092(12)
C(31)	926(16)	−1074(16)	3729(12)
C(32)	1313(16)	133(16)	3936(11)
C(33)	4046(14)	2394(14)	4330(9)
C(34)	4800(15)	3432(15)	4340(10)
C(35)	6041(15)	3581(16)	4796(10)
C(36)	6494(18)	2728(18)	5261(11)
C(37)	5748(19)	1729(17)	5261(11)
C(38)	4524(16)	1586(15)	4803(10)
O(1)	7487(25)	1102(22)	3273(16)
C(51)	7810(46)	129(41)	3641(30)
C(52)	6694(46)	−791(41)	3319(30)
C(53)	5718(47)	−189(41)	3096(31)
C(54)	6254(37)	1072(33)	3075(24)

Table 8 Crystallographic data and structure parameters for the complexes **2**, **4** and **6**

Complex	**2**	**4**	**6**
Formula	$C_{26}H_{15}Mn_2O_8PS$	$C_{36}H_{25}Co_3O_6P_2S$	$C_{46}H_{31}Co_3O_{6.5}P_2S$
M	628.3	824.4	958.5
Crystal symmetry	Monoclinic	Triclinic	Triclinic
Space group	*C*2/*c*	$P\bar{1}$	$P\bar{1}$
a/Å	20.569(9)	9.306(3)	11.398(2)
b/Å	9.799(3)	11.376(6)	11.554(2)
c/Å	26.773(9)	18.567(9)	18.024(4)
α/°		105.41(4)	95.73(3)
β/°	96.53(3)	93.69(3)	107.89(3)
γ/°		110.33(3)	94.04(3)
U/Å^3	5361(3)	1750(1)	2235(1)
Z	8	2	2
D_c/g cm^{-3}	1.557	1.564	1.424
F(000)	2528	832	972
Crystal dimensions (mm)	0.32 × 0.41 × 0.39	0.16 × 0.40 × 0.60	0.32 × 0.28 × 0.38
μ(Mo-Kα)/mm^{-1}	1.127	1.594	1.266
Total no. reflections	4027	6823	5307
No. unique data [$F > 4\sigma(F)$]	2727	4635	3271
R	0.048	0.041	0.095
R′	0.087	0.058	0.129
Goodness of fit	1.38	1.13	1.83
Weighting scheme, w^{-1}	$\sigma^2(F) + 0.0030F^2$	$\sigma^2(F) + 0.0015F^2$	$\sigma^2(F) + 0.0040F^2$

The instrumentation used to obtain spectroscopic data has been described previously.[33] 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.[3]

Reactions.—$[Mn_2(CO)_{10}]$ *with* $PPh_2(SPh)$. The complex $[Mn_2(CO)_{10}]$ (1.0 g, 2.56 mmol) along with $PPh_2(SPh)$ (0.76 g, 2.60 mmol) were dissolved in toluene (50 cm^3) and added to a Carius tube fitted with a stopcock. The reaction vessel was then sealed and heated to 150 °C for 3 h. After removal of the solvent on the rotary evaporator, the residue was redissolved in the minimum of CH_2Cl_2 and applied to the base of preparative TLC plates. Elution with hexane–CH_2Cl_2 (1 : 1) gave the yellow crystalline complex $[Mn_2(\mu\text{-}PPh_2)(\mu\text{-}SPh)(CO)_8]$ **2** (0.79 g, 49%) and traces of unidentified products. Complex **2** (Found: C, 49.6; H, 2.6. $C_{26}H_{15}Mn_2O_8PS$ requires C, 49.7; H, 2.7%): FAB mass spectrum, *m*/*z* 628 (M^+) and $M^+ - n$CO (*n* = 1–8); ^{1}H NMR ($CDCl_3$), δ 7.9–7.1 (m, 15 H, Ph).

$[Co_2(CO)_8]$ *with* $PPh_2(SPh)$. (*a*) The complex $[Co_2(CO)_8]$ (0.30 g, 0.88 mmol) and $PPh_2(SPh)$ (0.26 g, 0.88 mmol) were dissolved in CH_2Cl_2 (40 cm^3) and stirred at room temperature for 21 h. After concentration of the solvent on the rotary evaporator the dark brown solution was adsorbed onto silica.

The silica was pumped dry and added to the top of a chromatography column. Elution with hexane–CH_2Cl_2 (4:1) gave brown crystalline [$Co_3(\mu_3\text{-}S)(\mu\text{-}PPh_2)(CO)_7$] **3** (0.21 g, 41%), followed by green-brown crystalline [$Co_3(\mu_3\text{-}S)(\mu\text{-}PPh_2)(CO)_6(PPh_3)$] **4** (0.11 g, 15%) and unidentified decomposition products. Complex **3**: FAB mass spectrum, *m/z* 590 (M^+) and $M^+ - n$CO (n = 1–7); ^{1}H NMR ($CDCl_3$), δ 7.9–7.1 (m, 10 H, Ph). Complex **4** (Found: C, 52.5; H, 3.1; P, 7.5. $C_{36}H_{25}Co_3O_6P_2S$ requires C, 52.4; H, 3.0; P, 7.5%): FAB mass spectrum, *m/z* 824 (M^+) and $M^+ - n$CO (n = 1–6); ^{1}H NMR ($CDCl_3$), δ 8.0–7.1 (m, 25 H, Ph).

(*b*) The complex [$Co_2(CO)_8$] (0.50 g, 1.46 mmol) and $PPh_2(SPh)$ (0.50 g, 1.70 mmol) were dissolved in a CO-purged solution of toluene (40 cm^3). The solution was refluxed for 0.5 h. After removal of the solvent on the rotary evaporator, column chromatographic separation, eluting with hexane–CH_2Cl_2 (7:3), gave green-brown crystalline [$Co_3(\mu_3\text{-}S)(\mu\text{-}PPh_2)(CO)_6(PPh_3)$] **4** (0.53 g, 44%) and green crystalline [$Co_3(\mu_3\text{-}S)(\mu\text{-}PPh_2)(CO)_5(PPh_3)_2$] **5** (0.11 g, 7%) along with unidentified decomposition products. Complex **5**: FAB mass spectrum, *m/z* 1058 (M^+) and $M^+ - n$CO (n = 1–5); ^{1}H NMR ($CDCl_3$), δ 8.0–7.1 (m, 40 H, Ph).

[$Co_3(\mu_3\text{-}S)(\mu\text{-}PPh_2)(CO)_6(PPh_3)$] **4** *with* PhCCH. The complex [$Co_3(\mu_3\text{-}S)(\mu\text{-}PPh_2)(CO)_6(PPh_3)$] **4** (0.50 g, 0.61 mmol) was dissolved in a CO-purged solution of toluene (50 cm^3) and a five-fold excess of PhCCH was added. The solution was heated at 363 K for 3.5 h. After removal of the solvent on the rotary evaporator the residue was dissolved in the minimum quantity of CH_2Cl_2 and adsorbed onto silica. The silica was pumped dry and added to the top of a chromatography column. Elution with hexane–CH_2Cl_2 (7:3) gave unreacted **4** (0.11 g), followed by red crystalline [$Co_3(\mu_3\text{-}S)(\mu\text{-}PPh_2CHCPh)(CO)_6(PPh_3)$] **6** (0.23 g, 41%) and green [$Co_3(\mu_3\text{-}S)(\mu\text{-}PPh_2)(CO)_5(PPh_3)_2$] **5** (0.07 g, 11%). Complex **6**: FAB mass spectrum, *m/z* 926 (M^+) and $M^+ - n$CO (n = 1–6); NMR, ^{1}H (CD_2Cl_2), δ 7.7–7.0 (m, 40 H, Ph) and 6.30 [dd, ^2J(PH) 16.0, J(PH) 4.4, 1 H, $PPh_2C\mathit{H}CPh$]; ^{13}C ($CDCl_3$, ^{1}H composite pulse decoupled), δ 211–208 (m, 6CO), 181.0 [d, J(PC) 40, $PPh_2CH\mathit{C}Ph$], 155.6 [d, J(PC) 28 Hz, $PPh_2\mathit{C}HCPh$)] and 138–124 (m, Ph).

[$Fe_2(\mu\text{-}PPh_2)(\mu\text{-}SPh)(CO)_6$] **1** *with* $HOCH_2CCH$. To a solution of [$Fe_2(\mu\text{-}PPh_2)(\mu\text{-}SPh)(CO)_6$] **1** (0.30 g, 0.52 mmol) in benzene (120 cm^3) a five-fold excess of $HOCH_2CCH$ was added. Irradiation of the solution at room temperature for 21 h resulted in a colour change from bright to dark orange. After removal of the benzene on a rotary evaporator the residue was redissolved in the minimum quantity of CH_2Cl_2 and adsorbed onto silica. The silica was pumped dry and added to the top of a chromatography column. Elution with hexane–ethyl acetate (4:1) gave unreacted **1** (0.024 g) and orange crystalline [$Fe_2\{\mu\text{-}PPh_2CHC(CH_2OH)\}(\mu\text{-}SPh)(CO)_6$] **7** (0.24 g, 73%) as the only product. Complex **7** (Found: C, 51.9; H, 3.2. $C_{27}H_{19}Fe_2O_7PS$ requires C, 51.5; H, 3.0%): FAB mass spectrum, *m/z* 630 (M^+) and $M^+ - n$CO (n = 1–6). NMR ($CDCl_3$), ^{1}H, δ 7.9–7.2 (m, 15 H, Ph), 6.47 [dt, ^2J(PH) 16.3, ^4J(HH) 1.6, 1 H, $PPh_2C\mathit{H}C(CH_2OH)$], 4.66 [m, 2 H, $PPh_2CHC(C\mathit{H}_2OH)$] and 1.93 [t, ^3J(HH) 5.9, 1 H, $PPh_2CHC(CH_2O\mathit{H})$]; ^{13}C (^{1}H composite pulse decoupled), δ 214.6 (s, 1CO), 213.5 [d, J(PC) 25, 1CO], 211.2 (s, 1CO), 208.8 [d, J(PC) 30, 1CO], 207.8 [d, J(PC) 41, 1CO], 206.8 [d, J(PC) 10.9, 1CO], 201.0 [d, J(PC) 32, $PPh_2CH\mathit{C}(CH_2OH)$], 145–127 (m, Ph), 121.5 [d, J(PC) 68, $PPh_2\mathit{C}HC(CH_2OH)$] and 74.3 [d, J(PC) 26 Hz, $PPh_2CHC(\mathit{C}H_2OH)$].

Crystal Structure Analyses of Complexes **2**, **4** *and* **6**.—Intensity data for compounds **2** and **4** were collected on a Siemens R3m/V diffractometer and on a Stoe four-circle diffractometer for compound **6**, with graphite-monochromated Mo-Kα radiation (λ = 0.710 73 Å) in all cases. Three check reflections were monitored periodically throughout data collection and showed no significant variations. All intensity data were corrected for Lorentz polarisation effects, and absorption corrections by the ψ-scan method were also applied. Crystal data and structure parameters are given in Table 8. Calculations were carried out on a Viglen VigIV/25 computer using the SHELXTL PLUS package.[34]

Structures were solved by a combination of direct methods and Fourier difference techniques, and refined by full-matrix least-squares analysis. In all complexes non-hydrogen atoms were refined anisotropically, but in compound **6** C(3), C(6) and the thf atoms were refined isotropically. The hydrogen atoms were placed in idealised positions and allowed to ride on the relevant carbon atoms (C–H 0.960 Å). Final atomic coordinates for the three structures are presented in Tables 5–7.

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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