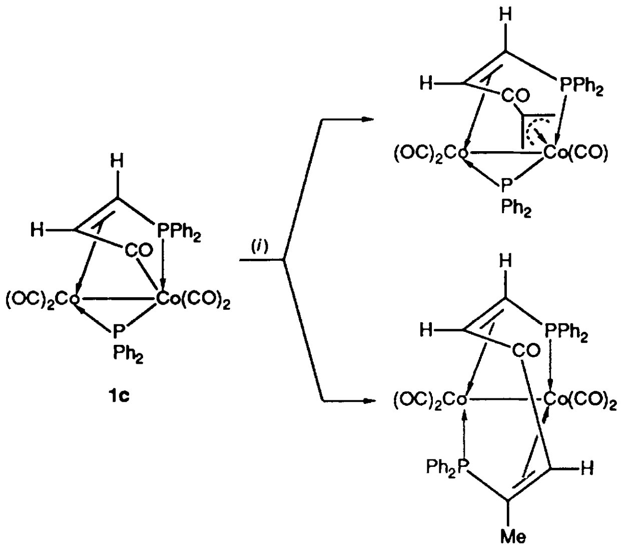
Reaction of CS_2 with a Ligand-bridged Dicobalt Complex: Crystal and Molecular Structures of $[Co_2\{\mu\text{-}PPh_2CHC(SiMe_3)C(O)CS\}(\mu\text{-}PPh_2S)(CO)_3]$ and $[Co_2(\mu\text{-}PPh_2CHCPhCS)(\mu\text{-}PPh_2S)(CO)_3]$†

Avelino Martín, Martin J. Mays,* Paul R. Raithby and Gregory A. Solan
University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, UK

Thermolysis of $[Co_2\{\mu\text{-}PPh_2CHCRC(O)\}(\mu\text{-}PPh_2)(CO)_4]$ (R = $SiMe_3$ **1a** or Ph **1b**) in CS_2 affords the complexes $[Co_2\{\mu\text{-}PPh_2CHCRC(O)CS\}(\mu\text{-}PPh_2S)(CO)_3]$ (R = $SiMe_3$ **2a** or Ph **2b**) in *ca.* 40–50% yield. In the case of **1b** a complex with the formula $[Co_2(\mu\text{-}PPh_2CHCPhCS)(\mu\text{-}PPh_2S)(CO)_3]$ **3b** was also isolated in *ca.* 8% yield. X-Ray diffraction studies on complexes **2a** and **3b** reveal in both cases that cleavage of a carbon–sulfur bond in a CS_2 molecule and insertion of the resulting CS and S fragments into respectively Co–C and Co–P bonds have occurred. In each case also the carbon–carbon double bond of the metallacyclic bridging ligand in **1a** and **1b** has been displaced from its co-ordination to cobalt. The reactions of **2a** and **2b** with organophosphites and isocyanides lead to monosubstituted products.

There is a growing list of examples of chemical reactions of bi- and poly-nuclear transition-metal complexes in which μ-phosphido (μ-PR_2) groups participate,[1–12] even though these groups were originally proposed as inert bridging ligands for stabilising such complexes.[13] In two recent papers we have reported the reactions of some diphenylphosphido-bridged binuclear cobalt complexes with allene in which a μ-PPh_2 group participates, namely (1) the insertion of one molecule of allene into a cobalt–phosphorus bond in the complex $[Co_2(\mu\text{-}PPh_2)_2(CO)_6]$ to give $[Co_2(\mu\text{-}PPh_2C_3H_4)(\mu\text{-}PPh_2)(CO)_4]$[14] and (2) the reaction of allene with the complex $[Co_2\{\mu\text{-}PPh_2CHCHC(O)\}(\mu\text{-}PPh_2)(CO)_4]$ **1c** which gives, in addition to $[Co_2\{\mu\text{-}PPh_2CHCHC(O)C_3H_4\}(\mu\text{-}PPh_2)(CO)_3]$, the complex $[Co_2\{\mu\text{-}PPh_2CHCHC(O)CHCMePPh_2\}(CO)_4]$ (Scheme 1).[15]

Carbon disulfide can be regarded as a heteroallene and in this paper the reactions of two complexes of the type $[Co_2\{\mu\text{-}PPh_2CHCRC(O)\}(\mu\text{-}PPh_2)(CO)_4]$ (R = $SiMe_3$ **1a** or Ph **1b**) with CS_2 are explored. The fragmentation of CS_2 in this reaction is followed by insertion of CS and S groups into respectively Co–C and Co–P bonds to give the complexes $[Co_2\{\mu\text{-}PPh_2CHCRC(O)CS\}(\mu\text{-}PPh_2S)(CO)_3]$ (R = $SiMe_3$ **2a** or Ph **2b**) and $[Co_2(\mu\text{-}PPh_2CHCPhCS)(\mu\text{-}PPh_2S)(CO)_3]$ **3b** in moderate yield (Scheme 2). The reactions of **2a** and **2b** with certain nucleophiles have also been examined.



Scheme 1 Products from the reaction of $[Co_2\{\mu\text{-}PPh_2CHCHC(O)\}(\mu\text{-}PPh_2)(CO)_4]$ **1c** with allene. (*i*) $H_2C{=}C{=}CH_2$, heat

Results and Discussion

(*a*) *Reaction of* $[Co_2\{\mu\text{-}PPh_2CHCRC(O)\}(\mu\text{-}PPh_2)(CO)_4]$ (R = SiMe **1a** or Ph **1b**) *with* CS_2.—Reaction of $[Co_2\{\mu\text{-}PPh_2CHCRC(O)\}(\mu\text{-}PPh_2)(CO)_4]$ (R = $SiMe_3$ **1a** or Ph **1b**) with CS_2 at 343 K for 48 h affords the complexes $[Co_2\{\mu\text{-}PPh_2CHCRC(O)CS\}(\mu\text{-}PPh_2S)(CO)_3]$ (R = $SiMe_3$ **2a** or Ph **2b**) in moderate yield (40–50%). The reaction of **1b** leads in addition to a second product, $[Co_2(\mu\text{-}PPh_2CHCPhCS)(\mu\text{-}PPh_2S)(CO)_3]$ **3b**, in lower yield (8%) (Scheme 2). The three complexes **2a**, **2b** and **3b** have been characterised spectroscopically (see Table 1 and Experimental section) and the molecular structures of **2a** and **3b** have, in addition, been determined by single-crystal X-ray diffraction studies. The structures of **2a** and **3b** are illustrated in Figs. 1 and 2 respectively. Tables 2 and 3 list selected bond distances and angles for **2a** and **3b**; atomic coordinates are given in Tables 4 and 5 respectively.

Crystals of complex **2a** suitable for an X-ray diffraction study were obtained by slow evaporation of a pentane solution at 273 K. The complex is chiral as is the precursor $[Co_2\{\mu\text{-}PPh_2CHC(SiMe_3)C(O)\}(\mu\text{-}PPh_2)(CO)_4]$ **1a**. Since crystallisation occurs in a centrosymmetric space group a racemic mixture of both enantiomers is present in the crystals. The structure reveals a $(OC)_2Co{-}Co(CO)$ skeleton with two different ligands bridging the two cobalt atoms. One of these is a Ph_2PS group in which P(1) bonds to Co(2) and S(2) to Co(1). The other is a bridging thioacyl group, μ-RCS [R = $C(O)C(SiMe_3)CHPPh_2$], which is located with the C–S bond vector perpendicular to the Co–Co bond with both S(1) and C(28) atoms bonded to each Co atom. The R group of the thioacyl bridge, $C(O)C(SiMe_3)CHPPh_2$, additionally co-ordinates to

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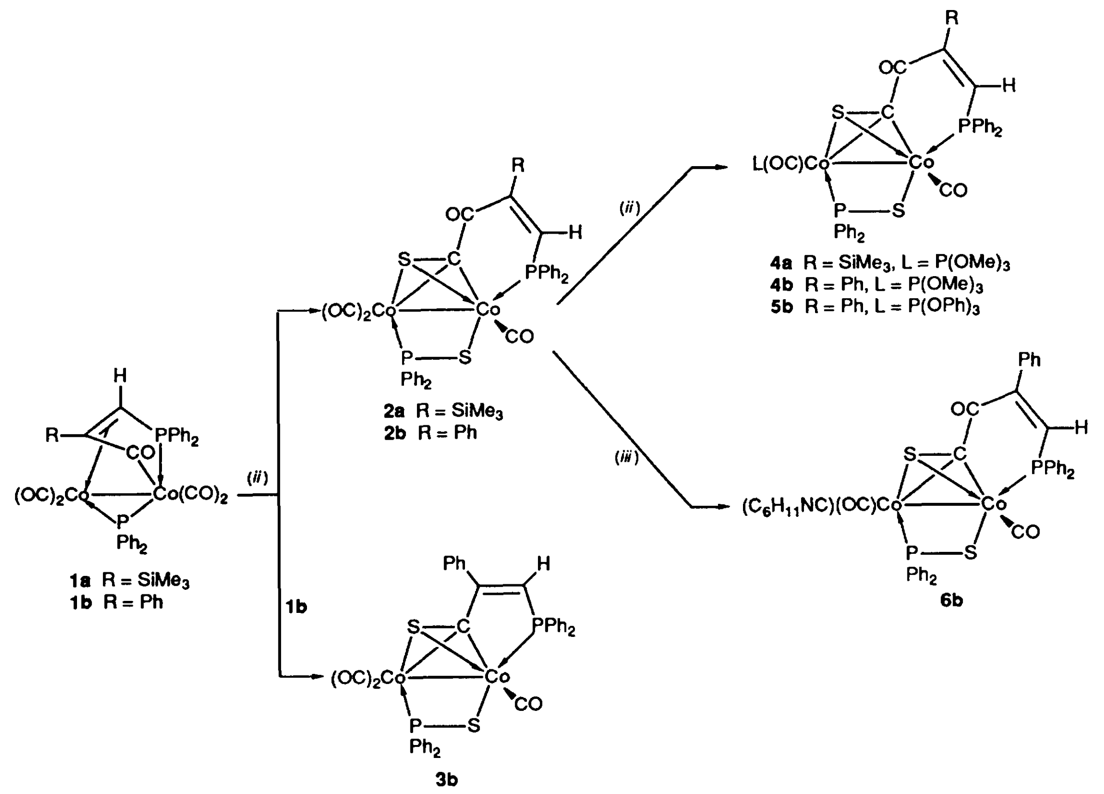
† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.



Scheme 2 Products derived from the reactions of $[Co_2\{\mu\text{-}PPh_2CHCRC(O)\}(\mu\text{-}PPh_2)(CO)_4]$ (R = $SiMe_3$ **1a** or Ph **1b**) with CS_2. (*i*) CS_2; (*ii*) L; (*iii*) $C_6H_{11}NC$

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

Compound	$\nu(CO)^a/cm^{-1}$	^1H NMR $(\delta)^b$	^{31}P NMR $(\delta)^c$
2a	2047s, 2005vs, 1989 (sh), 1615w	7.8–7.3 (m, 20 H, Ph), 6.70 [d, $^2J(PH)$ 5.0, 1 H, $PPh_2CHC(SiMe_3)C(O)CS$], 0.26 (s, 9 H, $SiMe_3$)	−92.9 [s, μ-$PPh_2CHC(SiMe_3)C(O)CS$], −101.4 (s, μ-PPh_2S)
2b	2049s, 2007s, 1995 (sh), 1626w	7.7–7.3 (m, 25 H, Ph), 6.71 [s, 1 H, $PPh_2CHCPhC(O)CS$]	−100.3 [s, μ-$PPh_2CHCPhC(O)CS$], −101.1 (s, μ-PPh_2S)
3b	2038s, 1993s, 1985 (sh)	7.7–6.8 (m, 26 H, Ph and $PPh_2CHCPhCS$)	−76.0 and −86.5 (s, μ-$PPh_2CHCPhCS$ and μ-PPh_2S)
4a	2030vs, 1987s, 1607m	7.6–7.2 (m, 20 H, Ph), 6.73 [dd, $^2J(PH)$ 4.9, $^5J(P'H)$ 3.3, 1 H, $PPh_2CHC(SiMe_3)C(O)CS$], 3.23 [d, $^3J(PH)$ 10.5, 9 H, $P(OMe)_3$], 0.24 (s, 9 H, $SiMe_3$)	17.5 [s, $P(OMe)_3$], −93.3 [s, μ-$PPh_2CHC(SiMe_3)C(O)CS$], −105.0 (s, μ-PPh_2S)
4b	2032s, 1989s, 1615w	7.9–7.2 (m, 25 H, Ph), 6.70 [d, $^5J(PH)$ 3.9, 1 H, $PPh_2CHCPhC(O)CS$], 3.30 [d, $^3J(PH)$ 10.4, 9 H, $P(OMe)_3$]	17.1 [s, $P(OMe)_3$], −100.5 [s, μ-$PPh_2CHCPhC(O)CS$], −103.9 (s, μ-PPh_2S)
5b	2036s, 1995s, 1625w	7.9–6.6 [m, 41 H, Ph and $PPh_2CHCPhC(O)CS$]	1.3 [s, $P(OPh)_3$], −101.4 [m, μ-PPh_2S and μ-$PPh_2CHCPhC(O)CS$]
6b	2033s, 1995m, 1628w $\nu(CN)$ 2128	7.8–7.2 (m, 25 H, Ph), 6.63 [s, 1 H, $PPh_2CHCPhC(O)CS$], 1.8–1.3 (m, 11 H, C_6H_{11})	−94.8 (s, μ-PPh_2S), −104.0 [s, μ-$PPh_2CHCPhC(O)CS$]

[a] Recorded in CH_2Cl_2 solution. [b] ^1H chemical shifts (δ) in ppm relative to $SiMe_4$ (0.0), coupling constants in Hz in $CDCl_3$ at 293 K. [c] ^{31}P chemical shifts (δ) in ppm relative to external $P(OMe)_3$ (0.0) (upfield shifts negative), $\{^1H\}$-gated decoupled, measured in $CDCl_3$ at 293 K

Co(1) *via* P(2) to complete a six-membered metallacyclic ring, Co(1)–P–C=C–C(O)–C(S), in which the S(1) atom is exocyclic to the ring.

The Co–Co distance [2.477(1) Å] in complex **2a** is shorter than in the five-membered ring complex $[Co_2\{\mu\text{-}PPh_2CHCPhC(O)\}(\mu\text{-}PPh_2)(CO)_4]$ **1b** [Co–Co 2.513(3) Å][16] but is comparable to that in related alkynehexacarbonyldicobalt derivatives.[17] The length of the C(28)–S(1) bond [1.723(5) Å] of the thioacyl group is at the lower end of the range observed for such bonds in complexes containing bridging thioacyl groups.[18–23] The relatively short C(28)–C(27) bond [1.445(7) Å] may indicate some multiple bond character. The six-membered metallacyclic ring, Co(1)–P–C=C–C(O)–C(S), adopts a puckered arrangement with the remaining bond distances C(27)–C(26) [1.496(7) Å], C(26)=C(25) [1.325(7) Å], C(25)–P(2) [1.823(5) Å] and P(2)–Co(1) [2.184(1) Å] falling within the normal ranges for these bonds in related complexes.[4,14,16]

The Co–P–S–Co ring is puckered, with S(2) sitting 0.671 Å out of the plane defined by the Co(1)Co(2)P(1) moiety. This contrasts with the almost planar configurations adopted by the corresponding M–P–S–M rings in the metal–metal bonded complexes $[Pt_2(\mu\text{-}SPEt_2)_2\{P(OPh)_3\}_2]$[24] and $[Pd_2(\mu\text{-}$

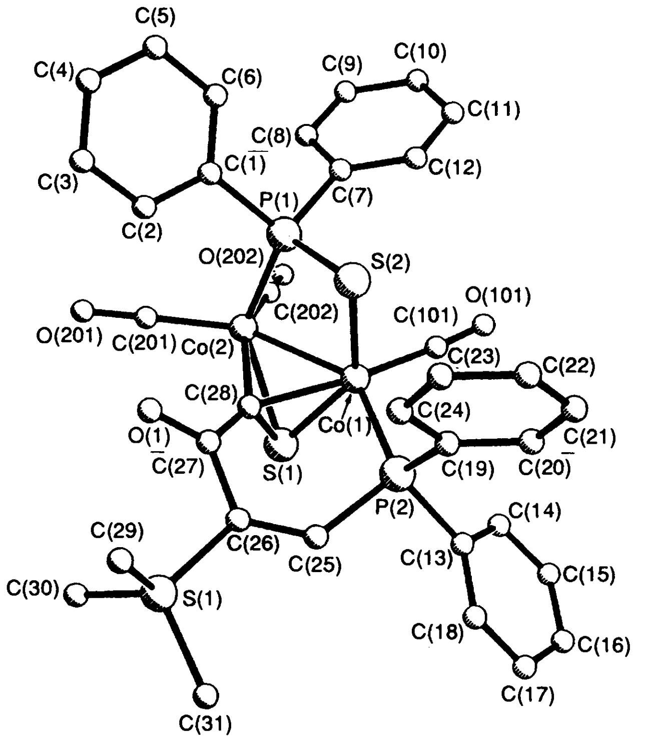


Fig. 1 Molecular structure of $[Co_2\{\mu\text{-}PPh_2CHC(SiMe_3)C(O)CS\}(\mu\text{-}PPh_2S)(CO)_3]$ **2a** including the atom numbering scheme. Hydrogen atoms have been omitted for clarity

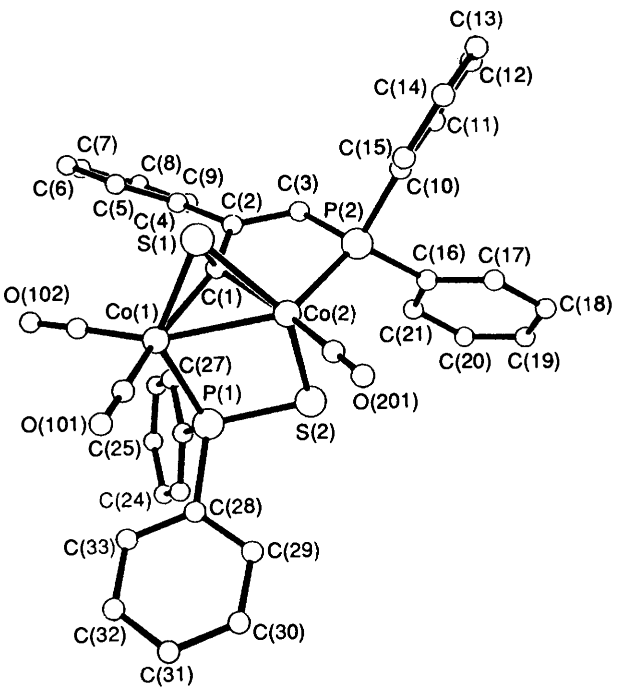


Fig. 2 Molecular structure of $[Co_2(\mu\text{-}PPh_2CHCPhCS)(\mu\text{-}PPh_2S)(CO)_3]$ **3b** including the atom numbering scheme. Hydrogen atoms have been omitted for clarity

$SPPh_2)_2(CNMe)_2]\cdot CHCl_3$.[25] The sulfur–phosphorus bond [2.024(2) Å] is shorter than that observed in related phosphine sulfides [2.066 Å],[26] slightly shorter than that in $[Pt_2(\mu\text{-}SPEt_2)_2\{P(OPh)_3\}_2]$ [2.046(3) Å] and comparable with that in $[Pd_2(\mu\text{-}SPPh_2)_2(CNMe)_2]\cdot CHCl_3$ (2.028 Å). The midpoints of the C(28)–S(1), Co(1)–Co(2) and P(1)–S(2) bonds form an angle of *ca.* 138°. This is similar to the situation for the alkynediphosphane-bridged complex $[Co_2\{\mu\text{-}C_2(CO_2Me)_2\}(\mu\text{-}P_2Ph_4)(CO)_4]$ where the corresponding angle for the midpoints of the alkyne C–C, Co–Co and P_2Ph_4 P–P bonds is *ca.* 130°.[16]

Table 2 Selected bond lengths (Å) and angles (°) for $[Co_2\{\mu\text{-}PPh_2CHC(SiMe_3)C(O)CS\}(\mu\text{-}PPh_2S)(CO)_3]$ **2a**

Co(1)–Co(2)	2.477(1)	Co(2)–C(201)	1.775(6)
Co(1)–P(2)	2.184(1)	Co(2)–C(202)	1.796(6)
Co(1)–S(1)	2.201(1)	Co(2)–C(28)	1.920(5)
Co(1)–S(2)	2.297(2)	P(1)–S(2)	2.024(2)
Co(1)–C(101)	1.786(6)	P(2)–C(25)	1.823(5)
Co(1)–C(28)	1.915(5)	S(1)–C(28)	1.723(5)
Co(2)–P(1)	2.207(1)	Si–C(26)	1.910(5)
Co(2)–S(1)	2.228(1)	O(1)–C(27)	1.228(7)
C–O(carbonyl)	1.132(7)–1.145(7)		
P–C(phenyl)	1.823(5)–1.840(5)		
Co(2)–Co(1)–P(2)	143.7(1)	P(1)–Co(2)–C(28)	96.7(1)
Co(2)–Co(1)–S(1)	56.5(1)	S(1)–Co(2)–C(28)	48.4(1)
P(2)–Co(1)–S(1)	99.1(1)	Co(2)–P(1)–S(2)	106.3(1)
Co(2)–Co(1)–S(2)	90.3(1)	Co(1)–S(1)–Co(2)	68.0(1)
P(2)–Co(1)–S(2)	97.6(1)	Co(1)–S(1)–C(28)	56.9(2)
S(1)–Co(1)–S(2)	140.8(1)	Co(2)–S(1)–C(28)	56.4(2)
Co(2)–Co(1)–C(28)	49.8(1)	Co(1)–S(2)–P(1)	82.3(1)
P(2)–Co(1)–C(28)	94.0(2)	Co(1)–C(28)–Co(2)	80.5(2)
S(1)–Co(1)–C(28)	48.9(1)	Co(1)–C(28)–S(1)	74.3(2)
S(2)–Co(1)–C(28)	94.8(1)	Co(2)–C(28)–S(1)	75.2(2)
Co(1)–Co(2)–P(1)	74.7(1)	Co(1)–C(28)–C(27)	127.4(4)
Co(1)–Co(2)–S(1)	55.5(1)	Co(2)–C(28)–C(27)	142.7(4)
P(1)–Co(2)–S(1)	130.0(1)	S(1)–C(28)–C(27)	131.2(4)
Co(1)–Co(2)–C(28)	49.7(1)		

Table 3 Selected bond lengths (Å) and angles (°) for $[Co_2(\mu\text{-}PPh_2CHCPhCS)(\mu\text{-}PPh_2S)(CO)_3]$ **3b**

Co(1)–Co(2)	2.506(2)	Co(2)–C(1)	1.900(9)
Co(1)–S(1)	2.515(3)	S(1)–C(1)	1.724(9)
Co(1)–P(1)	2.199(3)	S(2)–P(1)	2.022(4)
Co(1)–C(1)	1.921(9)	P(2)–C(3)	1.817(10)
Co(2)–S(1)	2.216(3)	C(1)–C(2)	1.481(14)
Co(2)–S(2)	2.305(3)	C(2)–C(3)	1.357(14)
Co(2)–P(2)	2.197(3)	C(2)–C(4)	1.490(13)
Co–C(carbonyl)	1.786(12)–1.809(13)		
C–O(carbonyl)	1.127(17)–1.145(14)		
P–C(phenyl)	1.816(8)–1.830(9)		
Co(2)–Co(1)–S(1)	55.6(1)	Co(1)–S(1)–C(1)	56.7(3)
Co(2)–Co(1)–P(1)	78.1(1)	Co(2)–S(1)–C(1)	56.0(3)
S(1)–Co(1)–P(1)	133.0(1)	Co(2)–S(2)–P(1)	86.5(1)
Co(2)–Co(1)–C(1)	48.6(3)	Co(1)–P(1)–S(2)	105.7(1)
S(1)–Co(1)–C(1)	48.6(3)	Co(2)–P(2)–C(3)	102.6(4)
P(1)–Co(1)–C(1)	96.1(3)	Co(1)–C(1)–Co(2)	82.0(4)
Co(1)–Co(2)–S(1)	55.5(1)	Co(1)–C(1)–S(1)	74.6(4)
Co(1)–Co(2)–S(2)	88.7(1)	Co(2)–C(1)–S(1)	75.2(3)
S(1)–Co(2)–S(2)	141.5(1)	Co(1)–C(1)–C(2)	147.6(6)
Co(1)–Co(2)–P(2)	131.8(1)	Co(2)–C(1)–C(2)	124.2(7)
S(1)–Co(2)–P(2)	102.1(1)	S(1)–C(1)–C(2)	126.7(6)
S(2)–Co(2)–P(2)	91.4(1)	C(1)–C(2)–C(3)	114.8(8)
Co(1)–Co(2)–C(1)	49.4(3)	C(1)–C(2)–C(4)	120.1(8)
S(1)–Co(2)–C(1)	48.8(3)	C(3)–C(2)–C(4)	125.1(9)
S(2)–Co(2)–C(1)	98.6(3)	P(2)–C(3)–C(2)	113.7(8)
P(2)–Co(2)–C(1)	83.1(3)	C(2)–C(4)–C(5)	119.3(9)
Co(1)–S(1)–Co(2)	68.9(1)		

The spectroscopic properties of complex **2a** are in accordance with the solid-state structure being maintained in solution, with a weak IR band at 1615 cm^{-1} assigned to ν(C=O) of the six-membered Co(1)–P–C=C–C(O)–C(S) metallacyclic ring. The ^1H NMR spectrum shows, in addition to phenyl resonances, a doublet at δ 6.70 with $^2J(PH)$ 5.0 Hz, assigned to the $PPh_2C\mathit{H}C(SiMe_3)C(O)CS$ proton and a singlet of relative intensity nine at δ 0.26, assigned to the $PPh_2CHC(Si\mathit{Me}_3)$-C(O)CS protons.

In the $^{31}P\text{-}\{^1H\}$ NMR spectrum of complex **2a** two singlet resonances are observed. The more downfield signal at δ −92.9 [relative to $P(OMe)_3$ (δ 0.0)] is tentatively assigned to the

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

Atom	*x*	*y*	*z*
Co(1)	7 342(6)	8 436(4)	78 912(3)
Co(2)	19 412(6)	14 438(4)	69 272(3)
P(1)	12 762(12)	23 703(7)	76 012(7)
P(2)	−8 745(12)	1 306(7)	80 966(7)
S(1)	15 234(12)	2 276(7)	69 828(7)
S(2)	−1 868(13)	19 662(8)	—81 528(8)
Si	−27 481(15)	−457(9)	58 596(8)
O(1)	−11 675(41)	13 963(23)	61 178(24)
C(101)	16 999(57)	7 772(31)	86 830(32)
O(101)	23 394(52)	7 663(28)	91 788(26)
C(201)	19 152(51)	18 166(30)	60 426(31)
O(201)	18 913(45)	20 539(28)	54 711(23)
C(202)	35 746(53)	14 906(29)	71 628(29)
O(202)	46 138(40)	14 866(25)	72 895(26)
C(1)	7 511(45)	32 226(28)	71 364(29)
C(2)	134(51)	31 509(32)	65 178(32)
C(3)	−4 016(56)	37 817(38)	61 544(36)
C(4)	−832(58)	44 651(38)	63 985(43)
C(5)	6 218(64)	45 445(34)	70 028(47)
C(6)	10 488(54)	39 193(31)	73 797(37)
C(7)	24 758(51)	27 181(28)	82 398(28)
C(8)	35 540(51)	30 382(30)	79 788(32)
C(9)	44 849(58)	32 818(34)	84 440(45)
C(10)	43 516(76)	32 088(38)	91 655(46)
C(11)	33 075(81)	28 982(41)	94 280(37)
C(12)	23 384(65)	26 578(34)	89 690(30)
C(13)	−6 272(48)	−7 927(29)	84 873(29)
C(14)	4 672(78)	−9 560(37)	88 446(47)
C(15)	6 534(91)	−16 483(41)	91 750(57)
C(16)	−2 351(76)	−21 604(36)	91 419(42)
C(17)	−12 783(72)	−20 393(39)	87 538(47)
C(18)	−14 883(62)	−13 524(37)	84 404(43)
C(19)	−20 831(45)	5 497(28)	86 427(26)
C(20)	−21 952(52)	3 907(34)	93 589(30)
C(21)	−30 391(60)	7 616(35)	97 757(32)
C(22)	−37 800(55)	13 083(35)	94 706(35)
C(23)	−36 688(56)	14 740(35)	87 699(38)
C(24)	−28 335(51)	11 051(31)	83 427(32)
C(25)	−17 433(48)	−963(29)	72 722(27)
C(26)	−16 614(45)	2 388(27)	66 399(27)
C(27)	−8 156(50)	8 886(28)	65 166(28)
C(28)	3 920(46)	9 047(26)	68 779(25)
C(29)	−40 322(72)	6 409(50)	57 853(49)
C(30)	−18 691(65)	−651(38)	50 271(33)
C(31)	−33 688(69)	−9 863(41)	60 459(39)

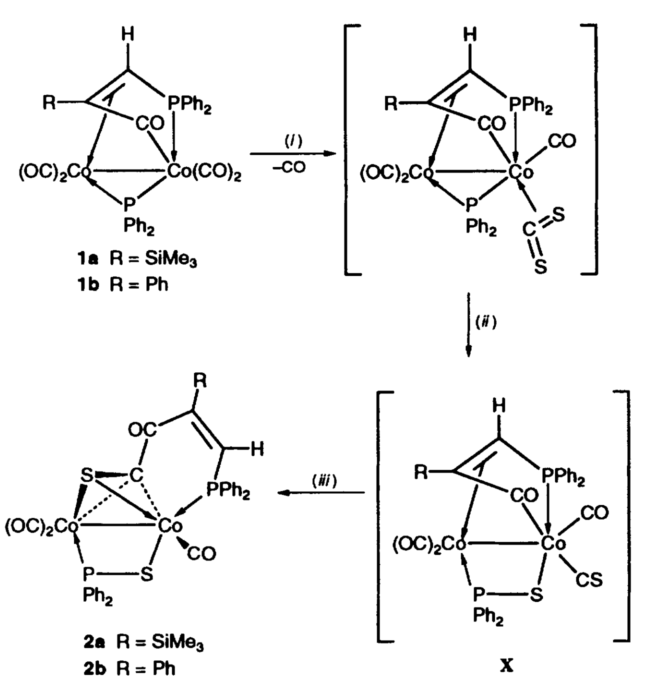
Table 5 Fractional atomic coordinates (× 10^4) for complex **3b**

Atom	*x*	*y*	*z*
Co(1)	1867(2)	2161(1)	1942(1)
Co(2)	916(2)	2976(1)	3132(1)
S(1)	3484(3)	2883(3)	2970(1)
S(2)	−1643(3)	2059(3)	2641(1)
P(1)	−759(3)	1674(2)	1685(1)
P(2)	790(3)	2180(2)	4094(1)
C(101)	2043(14)	3460(12)	1501(6)
O(101)	2188(12)	4279(8)	1233(5)
C(102)	2639(13)	959(11)	1335(6)
O(102)	3077(12)	162(9)	944(4)
C(201)	465(14)	4582(12)	3306(5)
O(201)	228(13)	5593(8)	3408(5)
C(1)	2087(10)	1595(8)	2835(4)
C(2)	2182(11)	527(8)	3197(5)
C(3)	1524(11)	667(9)	3823(5)
C(4)	2938(11)	−594(9)	2865(5)
C(5)	4276(12)	−443(10)	2529(5)
C(6)	4970(14)	−1489(11)	2215(6)
C(7)	4276(15)	−2639(12)	2216(7)
C(8)	2980(14)	−2823(12)	2558(6)
C(9)	2278(13)	−1759(10)	2880(6)
C(10)	1987(11)	2922(9)	4950(5)
C(11)	2120(12)	2333(10)	5534(5)
C(12)	2986(14)	2933(11)	6196(6)
C(13)	3710(14)	4105(11)	6269(7)
C(14)	3607(14)	4713(11)	5709(6)
C(15)	2732(12)	4100(10)	5044(6)
C(16)	−1166(11)	1833(9)	4383(5)
C(17)	−1689(13)	2682(11)	4918(6)
C(18)	−3204(15)	2455(12)	5136(7)
C(19)	−4158(14)	1404(11)	4767(6)
C(20)	−3686(13)	584(10)	4257(6)
C(21)	−2171(12)	775(9)	4043(5)
C(22)	−1473(11)	48(9)	1260(5)
C(23)	−2811(13)	−271(10)	761(5)
C(24)	−3345(15)	−1511(12)	459(7)
C(25)	−2552(15)	−2426(12)	684(7)
C(26)	−1263(14)	−2156(12)	1182(6)
C(27)	−700(14)	−893(11)	1480(6)
C(28)	−1737(11)	2551(9)	1070(5)
C(29)	−2817(12)	3398(10)	1295(6)
C(30)	−3485(14)	4052(12)	807(6)
C(31)	−3073(14)	3918(11)	119(6)
C(32)	−2026(14)	3083(11)	−96(7)
C(33)	−1347(12)	2403(10)	375(5)

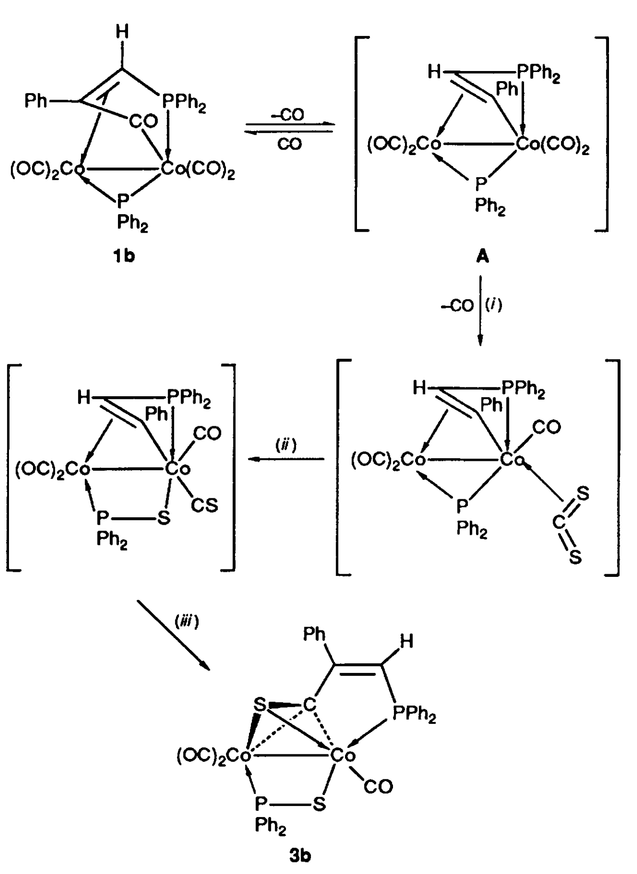
P$Ph_2CHC(SiMe_3)C(O)CS$ phosphorus atom; the corresponding resonance for $[Co_2\{\mu\text{-}PPh_2CHC(SiMe_3)C(O)\}(\mu\text{-}PPh_2)(CO)_4]$ **1a** occurs at δ −86.3.[15] The signal due to the bridging *P*Ph_2S ligand is observed at a slightly higher field, δ −101.4. In the $^{13}C\text{-}\{^1H\}$ NMR spectrum of **2a**, recorded at 293 K, a sharp doublet at δ 202.5 with a coupling constant of 18 Hz is ascribed to the carbon atom of the vinyl group remote from the phosphorus atom. The vinyl group carbon atom adjacent to the phosphorus atom gives rise to a doublet resonance at δ 139.5 with $^1J(PC)$ 26 Hz. A comparison of these vinyl ^{13}C NMR resonances with the corresponding resonances of the starting material **1a** (δ 77.8 and 46.5 respectively)[15] shows the dramatic effect the loss of the vinyl co-ordination to the metal has on the chemical shift. Three separate broad resonances are observed for the terminal carbonyl ligands, implying that the two carbonyl ligands on at least one of the cobalt atoms are non-fluxional at room temperature. A slightly sharper carbonyl resonance at higher field, δ 168.1, is assigned to the CO of the six-membered metallacyclic ring. A broad singlet resonance at δ 106.3 is assigned to the $PPh_2CHC(SiMe_3)C(O)$*C*(S) carbon. Complex **2b** is assigned an analogous structure to **2a** on the basis of spectroscopic data (see Table 1 and Experimental section).

A plausible route to the formation of complexes **2a** and **2b** is shown in Scheme 3. In the first step, displacement of a terminal carbonyl group in **1** allows the CS_2 group to become η^2-co-ordinated to the cobalt atom which is part of the five-membered metallacycle. Desulfurisation of the co-ordinated CS_2 group by the bridging phosphido ligand could then give intermediate **X** in which formation of a terminal CS ligand and a bridging PPh_2S ligand has occurred. In the final step, insertion of the terminal CS ligand into the Co–C(O)CR bond in **X** leads *via* displacement of the C–C double bond to complexes **2a** and **2b**.

The molecular structure of complex **3b** is shown in Fig. 2. Crystals suitable for an X-ray diffraction study were obtained by slow evaporation of a pentane solution at 273 K. In complex **3b**



Scheme 3 Possible route to the formation of $[Co_2\{\mu\text{-}PPh_2CHCRC(O)CS\}(\mu\text{-}PPh_2S)(CO)_3]$ (R = $SiMe_3$ **2a** or Ph **2b**). (*i*) CS_2; (*ii*) desulfurisation; (*iii*) insertion of CS



Scheme 4 Possible route to the formation of $[Co_2(\mu\text{-}PPh_2CHCPhCS)(\mu\text{-}PPh_2S)(CO)_3]$ **3b**. Key as in Scheme 3

the cobalt carbonyl skeleton $(OC)_2Co–Co(CO)$ is bridged, as in **2a**, by μ-Ph_2PS and μ-RCS groups. The R group on the thioacyl bridge in this case is $CPhCHPPh_2$, which co-ordinates to Co(2) *via* the PPh_2 group. The five-membered metallacycle Co(2)–PPh_2–CH=CPh–C(S) so formed adopts a distorted-planar arrangement with the PPh_2 fragment sitting 0.275 Å out of the plane defined by the Co(2)C(1)C(2)C(3) moiety. The C(1)–S(1) bond distance [1.724(9) Å] in the thioacyl group, μ-RCS, in which the C–S bond vector is again perpendicular to the Co–Co bond, is similar to that in **2a** [1.723(5) Å]. The C(1)–C(2) bond [1.481(14) Å] is significantly longer than that in **2a** [1.445(7) Å] at the 3σ level of their standard deviations. The absence of a C(O) group adjacent to C(2) in **3b** may explain this difference in bond lengths since the presence of a CO group may facilitate a certain degree of delocalisation. The Co–Co distance [2.506(2) Å] is also longer than that in **2a** [2.477(1) Å], falling in the mid-range of values observed for single Co–Co bond distances in similar compounds.[4,7,11,14–17] The bridging Ph_2PS ligand is puckered as in complex **2a**, the deviation from planarity in **3b** being less significant with S(2) sitting 0.274 Å out of the plane defined by the Co(1)Co(2)P(1) moiety, compared with 0.671 Å in **2a**.

The spectroscopic properties of complex **3b** are in accord with the solid-state structure being maintained in solution. Two singlet resonances are observed in the $^{31}P\text{-}\{^1H\}$ NMR spectrum at δ −76.0 and −86.5. The assignment of each signal to a particular phosphorus environment is, however, uncertain. Comparison of the corresponding data for complex **2b** {δ −100.3 and −101.1 [s, μ-$PPh_2CHCPhC(O)CS$ and μ-PPh_2S]}, shows the significant effect extrusion of the CO group from the metallacycle has on the ^{31}P chemical shift. In the $^{13}C\text{-}\{^1H\}$ NMR of **3b** at 293 K three distinct signals are observed in the terminal carbonyl region. The $PPh_2CH\mathit{C}PhCS$ carbon appears as a doublet [^2J(PC) 25 Hz at δ 166.1], as does the $PPh_2\mathit{C}HCPhCS$ carbon resonance [^1J(PC) 23 Hz at δ 136.3]. A broad signal observed at δ 123.6 is assigned to the $PPh_2CHCPh\mathit{C}(S)$ carbon.

The mechanism for the formation of complex **3b** is unclear. Scheme 4, however, outlines a possible route involving initial decarbonylation of complex **1b** to give intermediate **A**. Such a decarbonylation has been observed for the related complexes $[Co_2\{\mu\text{-}PPh_2CRCR'C(O)\}(\mu\text{-}PPh_2)(CO)_4]$ (R = R′ = Ph or CO_2Me) when they are left to stir in solution or, more rapidly, when they are refluxed in dichloromethane under a nitrogen atmosphere.[16] Displacement of a terminal CO group in **A** allows the CS_2 group to become η^2-co-ordinated to the cobalt atom which is part of the four-membered metallacycle. Desulfurisation of the co-ordinated CS_2 ligand by the bridging phosphido group followed by insertion of the resulting CS group into the Co–CPhCH bond leads to **3b**. It is not clear why the reaction of **1a** with CS_2 does not give a complex **3a** analogous to **3b**.

The formation of complexes **2a**, **2b** and **3b** corresponds to the intramolecular desulfurisation of a CS_2 ligand; a similar desulfurisation has been previously observed in the reactions of alkyl and aryl tertiary phosphines with a number of η^2-CS_2 complexes in which, in each case, one sulfur atom is extruded as a phosphine sulfide to give a thiocarbonyl-co-ordinated complex.[27] In the reaction of **1a** and **1b** with CS_2 the bridging-phosphido group presumably adopts a similar role to that played by the tertiary phosphines in these latter reactions.

Examples of bimetallic complexes containing perpendicularly bridged thioacyl groups (μ-RCS) are now relatively numerous and they can be prepared by a variety of synthetic routes.[18–23] Complexes **2a**, **2b** and **3b**, however, represent the first examples of such complexes being prepared by insertion into a metal–carbon bond of a CS fragment derived from the cleavage of a carbon–sulfur double bond of CS_2. In addition, the formation of a μ-Ph_2PS bridge represents a rare example of the insertion of a sulfur atom into a metal–phosphorus bond.[28]

(*b*) *Reaction of* $[Co_2\{\mu\text{-}PPh_2CHCRC(O)CS\}(\mu\text{-}PPh_2S)(CO)_3]$ (R = $SiMe_3$ **2a** *or* Ph **2b**) *with Organophosphites and Isocyanides*.—The reaction of organophosphites $[P(OR)_3]$ and isocyanides (RNC) with organo-bridged di-and tri-metallic systems can involve attack at one of the carbon atoms of the bridge or at one of the metal centres with concomitant ligand loss or rearrangement.[9,29–31] The reactions of complex **2b** with

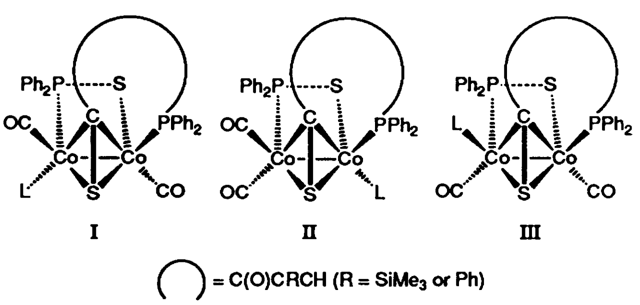


Fig. 3 Possible structures for the monosubstituted complexes **4a**, **4b**, **5b** and **6b** where L = $P(OMe)_3$, $P(OPh)_3$ or $C_6H_{11}NC$

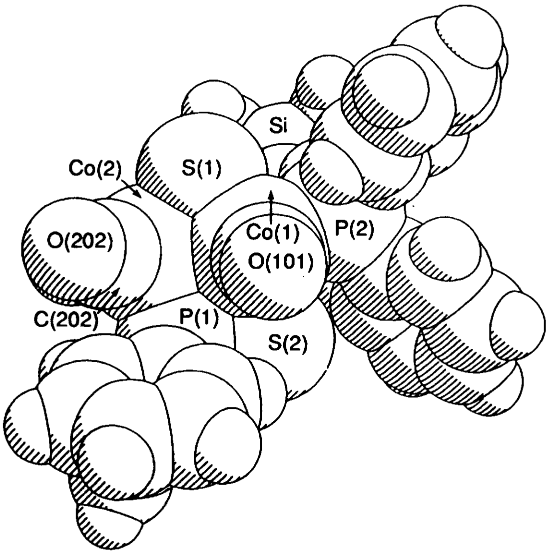


Fig. 4 Space-filling diagram of the molecular structure of complex **2a**

$P(OMe)_3$, $P(OPh)_3$ or $C_6H_{11}NC$ and of **2a** with $P(OMe)_3$ yield the monosubstituted products $[Co_2\{\mu\text{-}PPh_2CHCRC(O)CS\}(\mu\text{-}PPh_2S)(CO)_2L]$ [R = $SiMe_3$, L = $P(OMe)_3$ **4a**; R = Ph, L = $P(OMe)_3$ **4b**, $P(OPh)_3$ **5b** or CNC_6H_{11} **6b**]. All the complexes **4a**, **4b**, **5b** and **6b** have been characterised spectroscopically (see Table 1 and Experimental section) and their proposed structures are shown in Scheme 2. The observation of two bands in the terminal carbonyl region in the IR spectra of **4a**, **4b**, **5b** and **6b** is consistent with monosubstitution. This is supported for **6b** by the single IR ν(C=NR) band. Furthermore the expected two broad $^{13}C\text{-}\{^1H\}$ NMR resonances are observed in the carbonyl region for **4a**, **4b**, **5b** and **6b**. The FAB mass spectra of all the complexes display molecular ion peaks together with fragmentations corresponding to the loss of one and two carbonyl groups.

In view of the fact that complexes **2a** and **2b** are non-fluxional at room temperature, it is likely that **4a**, **4b**, **5b** and **6b**, for which three alternative structures can be drawn (Fig. 3), are also non-fluxional. Indeed, the ^1H NMR spectra recorded at 293 K are consistent with each complex being present in solution as a single isomer. Of the three structural possibilities shown in Fig. 3 one is unlikely on the basis of the NMR data. Thus the carbon atom of the bridging thioacyl group for **4a**, **4b** and **5b** shows a doublet in the $^{13}C\text{-}\{^1H\}$ NMR spectra due to coupling to the phosphorus of the substituent ligand, with couplings in the range 40–44 Hz. In complexes of the type $[Co_2(\mu\text{-}RC{\equiv}CR)(CO)_4(PR_3)_2]$, crystal structural evidence shows that the organophosphine groups occupy sites *cis* to the perpendicularly bridged alkyne.[32,33] The $^{13}C\text{-}\{^1H\}$ NMR spectra of such compounds show negligible values for $^2J(PC)_{cis}$, assuming that the solid-state structure is maintained in solution. The significant values of the $^2J(PC)$ couplings of **4a**, **4b** and **5b** suggest that the phosphite groups occupy sites *trans* to the bridging thioacyl group as in the structures **I** and **II** (Fig. 3).

In the ^1H NMR spectrum of complex **4a** the $PPh_2C\textit{H}C(SiMe_3)C(O)CS$ proton appears as a doublet of doublets. A splitting of 4.9 Hz is assigned as being due to coupling of the proton to the phosphorus atom which forms part of the six-membered metallacyclic ring. The other of 3.3 Hz must be due to coupling to the $P(OMe)_3$ substituent, since in **2a** there is no coupling of the corresponding proton to the $\mu\text{-}Ph_2PS$ phosphorus atom. For **4b** the corresponding signal appears as a doublet, with a coupling of 3.9 Hz to the $P(OMe)_3$ group but with negligible coupling to the metallacyclic phosphorus atom just as observed for **2b**. The couplings of 3.3 Hz for **4a** and 3.9 Hz for **4b** would, if structure **II** is the one adopted by these complexes, need to be consistent with a four-bond coupling or, for structure **I**, with a five-bond coupling. A four-bond coupling perhaps seems more likely although we recently reported a five-bond phosphorus–hydrogen coupling constant of 4.4 Hz for the complex $[Co_3(\mu_3\text{-}S)(\mu\text{-}PPh_2CH{=}CPh)(CO)_6(PPh_3)]$[12] and it is therefore not possible to distinguish with certainty between structures of type **I** and **II** on this basis. In the $^{31}P\text{-}\{^1H\}$ NMR spectrum the signals are too broad to detect the possible couplings which might have provided further information.

A structure of type **II** would result from the substitution by $P(OMe)_3$ of the single carbonyl ligand on the cobalt atom incorporated in the six-membered metallacyclic ring in complexes **2a** and **2b**, whereas a structure of type **I** results from substitution of one of the two carbonyl ligands on the other cobalt atom. This latter possibility seems electronically the more plausible. Fig. 4 shows a space-filling diagram of the molecular structure of **2a**. On steric grounds the substitution of a CO group by a bulky ligand [*e.g.* $P(OPh)_3$ **5b**] would appear more likely to occur at the site occupied by C(202)O(202) (structure **I**) rather than C(101)O(101) (structure **II**). Although the NMR data do not permit a distinction to be made between structures **I** and **II** for **4a** and **4b** (Fig. 3), both electronic and steric arguments therefore point towards a structure of type **I** being the more likely. The close similarity between the IR [ν(CO)] spectra of **5b** and **6b** and those of **4a** and **4b** suggests that all these four complexes have the same structure in solution.

Conclusion

The reactions of complexes **1a** and **1b** with the heteroallene CS_2 are quite different from that of $[Co_2\{\mu\text{-}PPh_2CHCHC(O)\}(\mu\text{-}PPh_2)(CO)_4]$ **1c** with allene itself (Scheme 1).[15] Most notably in the reactions with CS_2 the carbon–carbon double bond of the five-membered metallacycle in **1** has been displaced from its co-ordination to cobalt.

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. 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.[34] Unless otherwise stated all reagents were obtained from commercial suppliers and the compounds $[Co_2\{\mu\text{-}PPh_2CHCRC(O)\}(\mu\text{-}PPh_2)(CO)_4]$ (R = $SiMe_3$ **1a** or Ph **1b**) were prepared by the literature methods.[15,16]

Reaction of $[Co_2\{\mu\text{-}PPh_2CHCRC(O)\}(\mu\text{-}PPh_2)(CO)_4]$ (R = $SiMe_3$ **1a** *or* Ph **1b**) *with* CS_2.—(*a*) The complex $[Co_2\{\mu\text{-}$

Table 6 Crystallographic data and structure parameters for complexes **2a** and **3b**

	C$_{34}$H$_{30}$Co$_2$O$_4$P$_2$S$_2$Si **2a**	C$_{36}$H$_{26}$Co$_2$O$_3$P$_2$S$_2$ **3b**
M	774.6	750.5
Crystal symmetry	Monoclinic	Triclinic
Space group	$P2_1/n$ (no. 14)	$P1$ (no. 2)
a/Å	10.705(2)	8.381(3)
b/Å	17.921(2)	11.005(4)
c/Å	18.597(2)	19.063(6)
α/°		101.67(2)
β/°	91.19(2)	96.51(3)
γ/°		94.51(3)
U/Å^3	3567(2)	1701(1)
Z	4	2
D_c/g cm^{-3}	1.442	1.465
F(000)	1584	764
Crystal colour and habit	Dark brown prism	Black prism
Crystal dimensions (mm)	0.23 × 0.32 × 0.40	0.25 × 0.35 × 0.32
μ(Mo-Kα)/mm^{-1}	1.206	1.226
No. measured reflections	5449	4973
No. unique reflections	4657	4459
No. observed reflections	3760 [$F > 4\sigma(F)$]	2583 [$F > 5\sigma(F)$]
No. parameters refined	406	245
Largest and mean Δ/σ	0.003, 0.001	0.001, 0.000
R	0.046	0.061
R'	0.066	0.065
Goodness of fit	1.28	1.20
Weighting scheme, w^{-1}	$\sigma^2(F) + 0.0020F^2$	$\sigma^2(F) + 0.0010F^2$
Largest difference peak, hole/e Å^{-3}	0.40, −0.49	0.48, −0.40

PPh$_2$CHC(SiMe$_3$)C(O)}(μ-PPh$_2$)(CO)$_4$] **1a** (0.50 g, 0.689 mmol) was dissolved in CS$_2$ (50 cm^3) and sealed in a 100 cm^3 Roth autoclave. After stirring the solution at 343 K for 48 h the solvent was removed *in vacuo*, and the residue was dissolved in the minimum amount of CH$_2$Cl$_2$ and adsorbed onto silica. Column chromatographic separation, eluting with hexane–CH$_2$Cl$_2$ (4:6), gave [Co$_2${μ-PPh$_2$CHC(SiMe$_3$)C(O)CS}(μ-PPh$_2$S)(CO)$_3$] **2a** (0.272 g, 51%) as the only isolable product (Found: C, 52.5; H, 3.9; P, 7.8. C$_{34}$H$_{30}$Co$_2$O$_4$P$_2$S$_2$Si requires C, 52.7; H, 3.9; P, 8.0%). Fast atom bombardment (FAB) mass spectrum: *m/z* 774 (M^+) and $M^+ - n$CO (n = 0–3). NMR (CDCl$_3$): ^{13}C (^{1}H composite pulse decoupled), δ 202.5 [d, ^2J(PC) 18, PPh$_2$CH*C*(SiMe$_3$)C(O)CS], 202.1 (s, 1CO), 201.9 (s, 1CO), 196.5 (s, 1CO), 168.1 [s, PPh$_2$CHC(SiMe$_3$)*C*(O)CS], 142–128 (m, Ph), 139.5 [d, ^1J(PC) 26 Hz, PPh$_2$*C*HC(SiMe$_3$)C(O)CS], 106.3 [s, PPh$_2$CHC(SiMe$_3$)C(O)*C*S] and −0.9 [s, PPh$_2$CHC(Si*Me*$_3$)C(O)CS].

(*b*) The complex [Co$_2${μ-PPh$_2$CHCPhC(O)}(μ-PPh$_2$)(CO)$_4$] (0.50 g, 0.685 mmol) was dissolved in CS$_2$ (50 cm^3) and sealed in a 100 cm^3 Roth autoclave. After heating the solution to 343 K for 48 h the solvent was removed *in vacuo* and the residue dissolved in the minimum quantity of CH$_2$Cl$_2$, adsorbed onto silica and added to the top of a chromatography column. Elution with hexane–CH$_2$Cl$_2$ (1:1) gave brown crystalline [Co$_2$(μ-PPh$_2$CHCPhCS)(μ-PPh$_2$)(CO)$_3$] **3b** (0.041 g, 8%) and red-brown crystalline [Co$_2${μ-PPh$_2$CHCPhC(O)CS}(μ-PPh$_2$)(CO)$_3$] **2b** (0.230 g, 43%). Complex **3b** (Found: C, 57.4; H, 3.4; P, 7.9. C$_{36}$H$_{26}$Co$_2$O$_3$P$_2$S$_2$ requires C, 57.6; H, 3.5; P, 8.3%): FAB mass spectrum, *m/z* 750 (M^+) and $M^+ - n$CO (n = 0–3). NMR (CDCl$_3$): ^{13}C (^{1}H composite pulse decoupled), δ 203.1 (s, 1CO), 201.5 (s, 1CO), 194.3 (s, 1CO), 166.1 [d, ^2J(PC) 25, PPh$_2$CH*C*PhCS], 141–127 (m, Ph), 136.3 [d, ^1J(PC) 23 Hz, PPh$_2$*C*HCPhCS] and 123.6 (s, PPh$_2$CHCPh*C*S). Complex **2b** (Found: C, 56.9; H, 3.4; P, 7.9. C$_{37}$H$_{26}$Co$_2$O$_4$P$_2$S$_2$ requires C, 57.1; H, 3.4; P, 8.0%): FAB mass spectrum, *m/z* 778 (M^+) and $M^+ - n$CO (n = 0–4). NMR (CDCl$_3$): ^{13}C (^{1}H composite pulse decoupled), δ 202.7 (s, 1CO), 202.1 (s, 1CO), 200.7 [d, ^2J(PC) 10, PPh$_2$CH*C*PhC(O)CS], 196.8 (s, 1CO), 159.5 [s, PPh$_2$CHCPh*C*(O)CS], 142–128 (m, Ph), 137.7 [d, ^1J(PC) 14 Hz, PPh$_2$*C*HCPhC(O)CS] and 107.5 [s, PPh$_2$CHCPhC(O)*C*S].

Reaction of [Co$_2${μ-PPh$_2$CHCRC(O)CS}(μ-PPh$_2$S)(CO)$_3$] (R = SiMe$_3$ **2a** *or* Ph **2b**) *with* P(OMe)$_3$.—(*a*) The complex [Co$_2${μ-PPh$_2$CHC(SiMe$_3$)C(O)CS}(μ-PPh$_2$S}(CO)$_3$] **2a** (0.150 g, 0.194 mmol) was dissolved in toluene (35 cm^3) and P(OMe)$_3$ (0.024 cm^3, 0.194 mmol) added dropwise. After heating the solution at 353 K for 45 min the solvent was removed *in vacuo*. The dark brown residue was redissolved in the minimum quantity of CH$_2$Cl$_2$, adsorbed onto silica and chromatographically separated eluting with CH$_2$Cl$_2$ to give dark brown crystalline [Co{μ-PPh$_2$CHC(SiMe$_3$)C(O)CS}(μ-PPh$_2$S)(CO)$_2${P(OMe)$_3$}] **4a** (0.128 g, 76%) (Found: C, 49.2; H, 4.5; P, 10.2. C$_{36}$H$_{39}$Co$_2$O$_6$P$_3$S$_2$Si requires C, 49.6; H, 4.5; P, 10.7%). FAB mass spectrum, *m/z* 870 (M^+) and $M^+ - n$CO (n = 0–2). NMR (CDCl$_3$): ^{13}C (^{1}H composite pulse decoupled), δ 204.0 [d, ^2J(PC) 17, PPh$_2$CH*C*(SiMe$_3$)C(O)CS], 203.9 (s, 1CO), 194.5 (s, 1CO), 166.0 [s, PPh$_2$CHC(SiMe$_3$)*C*(O)CS], 143–127 (m, Ph), 142.2 [dd, ^1J(PC) 26, ^4J(PC) 13, PPh$_2$*C*HC(SiMe$_3$)C(O)CS], 101.8 [d, ^2J(PC) 41, PPh$_2$CHC(SiMe$_3$)C(O)*C*S], 51.4 [d, ^2J(PC) 4 Hz, P(OMe)$_3$] and −0.8 (s, SiMe$_3$).

(*b*) The complex [Co$_2${μ-PPh$_2$CHCPhC(O)CS}(μ-PPh$_2$S)(CO)$_3$] **2b** (0.150 g, 0.193 mmol) was dissolved in toluene (35 cm^3) and P(OMe)$_3$ (0.024 cm^3, 0.194 mmol) added dropwise. After heating the solution to 353 K for 45 min the solvent was removed *in vacuo* to give a dark brown residue. The residue was redissolved in CH$_2$Cl$_2$, adsorbed onto silica and added to the top of a chromatography column. Elution with CH$_2$Cl$_2$ gave the brown crystalline complex [Co$_2${μ-PPh$_2$CHCPhC(O)CS}(μ-PPh$_2$S)(CO)$_2${P(OMe)$_3$}] **4b** (0.150 g, 89%) (Found: C, 53.3; H, 3.9; P, 10.1. C$_{39}$H$_{35}$Co$_2$O$_6$P$_3$S$_2$ requires C, 53.6; H, 4.0; P, 10.6%). FAB mass spectrum, *m/z* 874 (M^+) and $M^+ - n$CO (n = 0–2). NMR (CDCl$_3$): ^{13}C (^{1}H composite pulse decoupled), δ 203.8 (s, 1CO), 202.1 [s, PPh$_2$CH*C*PhC(O)CS], 193.4 (s, 1CO), 158.4 [s, PPh$_2$CHCPh*C*(O)CS], 143–127 (m, Ph), 137.8 [s, br, PPh$_2$*C*HCPhC(O)CS], 103.1 [d, ^2J(PC) 44 Hz, PPh$_2$CHCPhC(O)*C*S] and 51.5 [s, P(OMe)$_3$].

Reaction of [Co$_2${μ-PPh$_2$CHCPhC(O)CS}(μ-PPh$_2$S)(CO)$_3$] **2b** *with* P(OPh)$_3$ *or* C$_6$H$_{11}$NC.—(*a*) The complex [Co$_2${μ-PPh$_2$CHCPhC(O)CS}(μ-PPh$_2$S)(CO)$_3$] **2b** (0.100 g, 0.129 mmol) was dissolved in toluene (30 cm^3) and P(OPh)$_3$ (0.020 cm^3, 0.129 mmol) added dropwise. After heating the solution to

358 K for 2 h the solvent was removed *in vacuo*. The residue was chromatographically separated, eluting with CH_2Cl_2, to give the red-brown crystalline complex $[Co_2\{\mu\text{-}PPh_2CHCPhC(O)CS\}(\mu\text{-}PPh_2S)(CO)_2\{P(OPh)_3\}]$ **5b** (0.108 g, 79%). FAB mass spectrum, *m*/*z* 1060 (M^+) and $M^+ - n$CO (n = 0–3). NMR ($CDCl_3$): ^{13}C (^1H composite pulse decoupled), δ 203.9 (s, 1CO), 200.5 [d, ^2J(PC) 11, $PPh_2CH\textit{C}PhC(O)CS$], 193.4 (s, 1CO), 157.0 [d, ^3J(PC) 8, $PPh_2CHCPh\textit{C}(O)CS$], 151.8 [d, ^2J(PC) 11, OC_{ipso}, Ph], 142–121 (m, Ph), 137.4 [dd, ^4J(PC) 25, ^1J(PC) 12, $PPh_2\textit{C}HCPhC(O)CS$] and 103.0 [d, ^2J(PC) 40 Hz, $PPh_2CHCPhC(O)\textit{C}S$].

(*b*) Complex **2b** (0.100 g, 0.129 mmol) was dissolved in toluene (30 cm^3) and $C_6H_{11}NC$ (0.014 cm^3, 0.129 mmol) added dropwise. After heating the solution to 338 K for 1 h the solvent was removed *in vacuo*. The remaining dark brown residue was redissolved in CH_2Cl_2 and applied to the base of TLC plates and eluted with CH_2Cl_2 to give a trace of $[Co_2\{\mu\text{-}PPh_2CHCPhC(O)CS\}(\mu\text{-}PPh_2S)(CO)_3]$ **2b** and red-brown crystalline $[Co_2\{\mu\text{-}PPh_2CHCPhC(O)CS\}(\mu\text{-}PPh_2S)(CO)_2(CNC_6H_{11})]$ **6b** (0.047 g, 43%). Complex **6b**: FAB mass spectrum, *m*/*z* 859 (M^+) and $M^+ - n$CO (n = 0–3). NMR ($CDCl_3$): ^{13}C (^1H composite pulse decoupled), δ 204.1 (s, 1CO), 203.4 [s, $PPh_2CH\textit{C}PhC(O)CS$], 196.0 (s, 1CO), 160.1 [s, $PPh_2CHCPh\textit{C}(O)CS$], 158.2 (s, $\textit{C}NC_6H_{11}$), 143–127 (m, Ph), 138.0 [d, ^1J(PC) 14, $PPh_2\textit{C}HCPhC(O)CS$], 107.0 [d, ^2J(PC) 40 Hz, $PPh_2CHCPhC(O)\textit{C}S$], 54.2 (s, $N\textit{C}HCH_2CH_2CH_2CH_2CH_2$), 32.7 (s, $NCH\textit{C}H_2CH_2CH_2CH_2\textit{C}H_2$), 25.0 (s, $NCHCH_2\textit{C}H_2CH_2\textit{C}H_2CH_2$) and 22.6 (s, $NCHCH_2CH_2\textit{C}H_2CH_2CH_2$).

Crystal-Structural Determinations on Complexes **2a** *and* **3b**.—Intensity data for compound **2a** was collected on a Stoe four-circle diffractometer and on a Siemens R3m/V diffractometer for compound **3b**, with graphite-monochromated Mo-Kα radiation (λ = 0.710 73 Å) in both 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 for both compounds. All the non-hydrogen atoms were assigned anisotropic thermal parameters. Hydrogen atoms were placed in idealised positions (C–H 0.96 Å) and allowed to ride on the relevant carbon atom. Weighting schemes were applied, and analysis of the variation of the sum of $w\Delta^2$ ($\Delta = F_o - F_c$) according to F_o and sin θ indicated that they were appropriate in each case. Crystal data and structure parameters are given in Table 6. Calculations were carried out on a Viglen VigIV/25 computer using the SHELXTL (PC version) package.[35]

Structures were solved by a combination of direct methods and Fourier difference techniques, and refined by full-matrix least-squares analysis.

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

Acknowledgements

We thank the SERC for financial support (to G. A. S.).

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Received 8*th February* 1993; *Paper* 3/00766I