A comparison of the reactions of PPh₂CH₂SR (R = Me, Ph) with alkyne-bridged dicobalt carbonyl complexes and with an iron dicobalt μ₃-thioxo carbonyl complex

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Abstract

The reactions of Ph_2PCH_2SR (R = Me, Ph) in toluene with the dicobalt complexes $[Co_2(\mu\text{-}R^1CCR^2)(CO)_6]$ ($R^1 = R^2 = CO_2Me$ and $R^1 = H$, $R^2 = CO_2Me$) give the monosubstituted complexes $[Co_2(\mu\text{-}R^1CCR^2)(CO)_5PPh_2CH_2SMe]$ **1** and $[Co_2(\mu\text{-}R^1CCR^2)(CO)_5PPh_2CH_2SPh]$ **2**. On heating **1** and **2** in toluene solution, loss of CO leads to the bridged species $[Co_2(\mu\text{-}R^1CCR^2)(\mu\text{-}PPh_2CH_2SMe)(CO)_4]$ **3** and $[Co_2(\mu\text{-}R^1CCR^2)(\mu\text{-}PPh_2CH_2SPh)(CO)_4]$ **4**. This transformation is readily reversed by treatment of **3** and **4** with CO, showing the Co–S bond in these complexes to be relatively weak. Similar reactions of Ph_2PCH_2SR (R = Me, Ph) with $[Co_2Fe(\mu_3\text{-}S)(CO)_9]$, however, give only the ligand bridged species $[Co_2Fe(\mu_3\text{-}S)(\mu\text{-}Ph_2PCH_2SR)(CO)_7]$ (R = Me **5** and R = Ph **6**). Treatment of **5** and **6** with CO causes cleavage of the Co–S bond but, in contrast to **3** and **4**, the ligand bridged species readily reform when the CO purge ceases. The structures of **3a** and **6** have been confirmed by single-crystal X-ray analysis.

Keywords: Cobalt; Carbonyl; Iron; Alkyne; Phosphine; Sulfur

1. Introduction

Reaction of the ligand Ph_2PSPh with alkyne bridged dicobalt carbonyl complexes leads to P–S bond cleavage and the formation of metallocyclic complexes with either Ph_2P or PhS fragments incorporated into the bridging organic ligand [1]. For comparative purposes we have now studied the reactions of the ligands Ph_2PCH_2SR (R = Me or Ph) [2] with alkyne bridged dicobalt carbonyl complexes and with $[Co_2Fe(\mu_3\text{-}S)(CO)_9]$ [3] to investigate whether P–C or S–C bonds can also be cleaved in these systems. Such cleavage of P–C [4] and S–C [5–8] bonds has been observed in studies of related dicobalt complexes. The reactions of the alkyne bridged dicobalt carbonyl complexes studied in this paper lead to new complexes in which the Ph_2PCH_2SR is coordinated through phosphorus to one of the cobalt atoms. Thermolysis of these complexes leads to CO loss and the formation of complexes in

which the Ph_2PCH_2SR ligand bridges the two metal centres but no P–C or S–C bond cleavage is observed. The loss of CO is readily reversed, with cleavage of the weak Co–S bond. The strength of Co–S bonds is clearly variable, however, since the reaction of $[Co_2Fe(\mu_3\text{-}S)(CO)_9]$ [3] with Ph_2PCH_2SR, which we have also studied, leads only to the complexes $[Co_2Fe(\mu_3\text{-}S)(\mu\text{-}Ph_2PCH_2SR)(CO)_7]$ in which the bidentate ligand bridges the two cobalt atoms. Treatment of these ligand bridged iron dicobalt complexes with CO does break the Co–S bond, but the resulting complexes readily reconvert to the bridged complexes on standing in solution in the absence of CO. The crystal structures of $[Co_2\{\mu\text{-}C_2(CO_2Me)_2\}(\mu\text{-}PPh_2CH_2SMe)(CO)_4]$ and $[Co_2Fe(\mu_3\text{-}S)(\mu\text{-}PPh_2CH_2SPh)(CO)_7]$ are presented.

2. Results and discussion

The complexes $[Co_2\{\mu\text{-}R^1CCR^2\}(CO)_5PPh_2CH_2SR]$ ($R^1 = R^2 = CO_2Me$, R = Me **1a**, R = Ph **2a**; $R^1 = H$, $R^2 = CO_2Me$, R = Me **1b**, R = Ph **2b**) are obtained in

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moderate yields from the reaction of $[Co_2\{\mu\text{-}R^1CCR^2\}(CO)_6]$ ($R^1 = R^2 = CO_2Me$ or $R^1 = H$, $R^2 = CO_2Me$) with PPh_2CH_2SR (R = Me or Ph) in toluene at 313 K (see Scheme 1).

The spectroscopic properties of **1a**, **1b**, **2a** and **2b** in solution (Table 1) are consistent with those found for analogous alkyne bridged dicobalt hexacarbonyl complexes monosubstituted at cobalt by other tertiary phosphines [9]. The ^1H NMR spectra all show a characteristic doublet resonance corresponding to the methylene group of the PPh_2CH_2SR ligand, with a coupling constant $^2J_{PH}$ of 4-6 Hz, in addition to the expected resonances for the other groups present. For **1b** and **2b**, the two protons of the methylene group are inequivalent (diastereoisotopic) and it is therefore somewhat surprising that a single doublet is still observed. Presumably, the reason is that the chemical shifts of the two methylene protons are coincident, thus rendering the expected *geminal* coupling invisible. The ^{31}P NMR spectrum of each of the complexes shows a single peak due to the phosphorus atom of the PPh_2CH_2SR ligand.

On heating **1a**, **1b**, **2a** and **2b** to 333 K in toluene, displacement of a CO group by the ligand sulphur atom occurs in each case to give the bridged complexes **3a**, **3b**, **4a** and **4b** in good yield (Scheme 1). This reaction is readily reversed by heating toluene solutions of **3a**, **3b**, **4a** and **4b** to 333 K whilst purging with CO gas.

The crystal structure of $[Co_2\{\mu\text{-}C_2(CO_2Me)_2\}(\mu\text{-}PPh_2CH_2SMe)(CO)_4]$ **3a** has been determined by an X-ray diffraction study. The molecular structure is shown in Fig. 1; selected bond lengths and angles are given in Table 2 and fractional atom coordinates in Table 3.

The structure of **3a** consists of two $Co(CO)_2$ units bridged by a dmad ligand (dmad = dimethylacetylene dicarboxylate) and the bidentate Ph_2PCH_2SMe ligand, with one unit being coordinated by P and the other by S. The structure of the complex can therefore be thought of as being derived from the structure of $[Co_2\{\mu\text{-}C_2(CO_2Me)_2\}(CO)_6]$ [10] by replacement of two pseudo-equatorial carbonyls, one on each cobalt, by an S and a P donor atom. The five-membered ring Co-Co-P-C-S is non-planar, being puckered so as to minimise ring strain. The cobalt to carbonyl-carbon distances are within the expected range (varying between 1.783(4) and 1.796(5) Å) and, in contrast to $[Co_2\{\mu\text{-}C_2(CO_2Me)_2\}(\mu\text{-}P_2Ph_4)(CO)_4]$ [11] and $[Co_2(\mu\text{-}PhCCPh)(\mu\text{-}Ph_2PCH_2PPh_2)(CO)_4]$ [12], in which the pseudo-equatorial carbonyls have significantly longer Co-C distances than those of the pseudo-axial carbonyls, the Co-C distances in **3a** are very uniform. Indeed, the average equatorial Co-C distance is 1.789(5) Å compared with 1.790(5) Å for the corresponding axial distances.

The Co-P bond length of 2.2210(13) Å is comparable with those found in $[Co_2\{\mu\text{-}C_2(CO_2Me)_2\}(\mu\text{-}P_2Ph_4)(CO)_4]$ (2.232(1) and 2.224(1) Å) [11], as is the Co-Co distance of 2.4656(8) Å (compared with 2.452(1)

Table 1
Infrared and proton NMR spectra for the new complexes

| Compound	$\nu(CO)$ (cm^{-1}) [a]	^1H NMR (δ in ppm)
1a $Co_2[\mu\text{-}C_2(CO_2Me)_2](CO)_5PPh_2CH_2SMe$	2082s, 2035s, 1990w	7.6-7.3 (m, 10H, Ph); 3.59 (s, 6H, CO$_2$Me); 3.46 (d, $^2J_{PH}$ 4.3 Hz, 2H, CH$_2$); 1.68 (d, $^4J_{PH}$ 1.08 Hz, 3H, SMe)
1b $Co_2(\mu\text{-}HCCCO_2Me)(CO)_5PPh_2CH_2SMe$	2074s, 2024s, 1979w	7.8-7.3 (m, 10H, Ph); 5.25 (d, $^3J_{PH}$ 2.8 Hz, 1H, CH); 3.61 (s, 3H, CO$_2$Me); 3.35 (d, $^2J_{PH}$ 5.1 Hz, 2H, CH$_2$); 1.79 (s, 3H, SMe)
2a $Co_2[\mu\text{-}C_2(CO_2Me)_2](CO)_5PPh_2CH_2SPh$	2083s, 2037s, 1991w	7.6-7.0 (m, 15H, Ph); 3.93 (d, $^2J_{PH}$ 5.1 Hz, 2H, CH$_2$); 3.56 (s, 6H, CO$_2$Me)
2b $Co_2(\mu\text{-}HCCCO_2Me)(CO)_5PPh_2CH_2SPh$	2075s, 2025s, 1979w	7.6-7.1 (m, 15H, Ph); 5.32 (d, $^3J_{PH}$ 2.9 Hz, 1H, CH); 3.80 (d, $^2J_{PH}$ 5.8 Hz, 2H, CH$_2$); 3.54 (s, 3H, CO$_2$Me)
3a $Co_2[\mu\text{-}C_2(CO_2Me)_2](\mu\text{-}PPh_2CH_2SMe)(CO)_4$	2049m, 2022s, 1994m	7.7-7.3 (m, 10H, Ph); 3.80 (s, 6H, CO$_2$Me); 3.58 (d, $^2J_{PH}$ 6.96 Hz, 2H, CH$_2$); 2.37 (br, 3H, SMe)
3b $Co_2(\mu\text{-}HCCCO_2Me)(\mu\text{-}PPh_2CH_2SMe)(CO)_4$	2039m, 2009s, 1997m	7.6-7.3 (m, 10H, Ph); 6.08 (s, 1H, CH); 3.76 (s, 3H, CO$_2$Me); 3.61 (dd, $^{gem}J_{HH}$ 11.7 Hz, $^2J_{PH}$ 6.4 Hz, 1H, CH$_2$); 3.50 (dd, $^{gem}J_{HH}$ 11.7 Hz, $^2J_{PH}$ 4.9 Hz, CH$_2$); 2.33 (s, 3H, SMe)
4a $Co_2[\mu\text{-}C_2(CO_2Me)_2](\mu\text{-}PPh_2CH_2SPh)(CO)_4$	2050m, 2024s, 1997m	7.7-7.0 (m, 15H, Ph); 3.91 (d, $^2J_{PH}$ 5 Hz, 2H, CH$_2$); 3.80 (s, 6H, CO$_2$Me)
4b $Co_2(\mu\text{-}HCCCO_2Me)(\mu\text{-}PPh_2CH_2SPh)(CO)_4$	2076m, 2041s, 2012m	7.7-7.2 (m, 15H, Ph); 6.14 (s, 1H, CH); 4.06 (dd, $^{gem}J_{HH}$ 11.2 Hz, $^2J_{PH}$ 6.3 Hz, 1H, CH$_2$); 4.02 (dd, $^{gem}J_{HH}$ 11.2 Hz, $^2J_{PH}$ 4.7 Hz, CH$_2$); 3.69 (s, 3H, CO$_2$Me)
5 $Co_2Fe(\mu_3\text{-}S)(\mu\text{-}PPh_2CH_2SMe)(CO)_7$	2055s, 2017vs, 2000s, 1946w	7.7-7.3 (m, 10H, Ph); 3.56 (br, 1H, CH$_2$); 3.42 (br, 1H, CH$_2$); 2.34 (s, 3H, Me)
6 $Co_2Fe(\mu_3\text{-}S)(\mu\text{-}PPh_2CH_2SPh)(CO)_7$	2055s, 2018vs, 1999s, 1946w	7.7-7.3 (m, 15H, Ph); 3.82 (dd, $^{gem}J_{HH}$ 11.5 Hz, $^2J_{PH}$ 6.6 Hz, CH$_2$); 3.71 (dd, $^{gem}J_{HH}$ 11.5 Hz, $^2J_{PH}$ 9.2 Hz, CH$_2$)
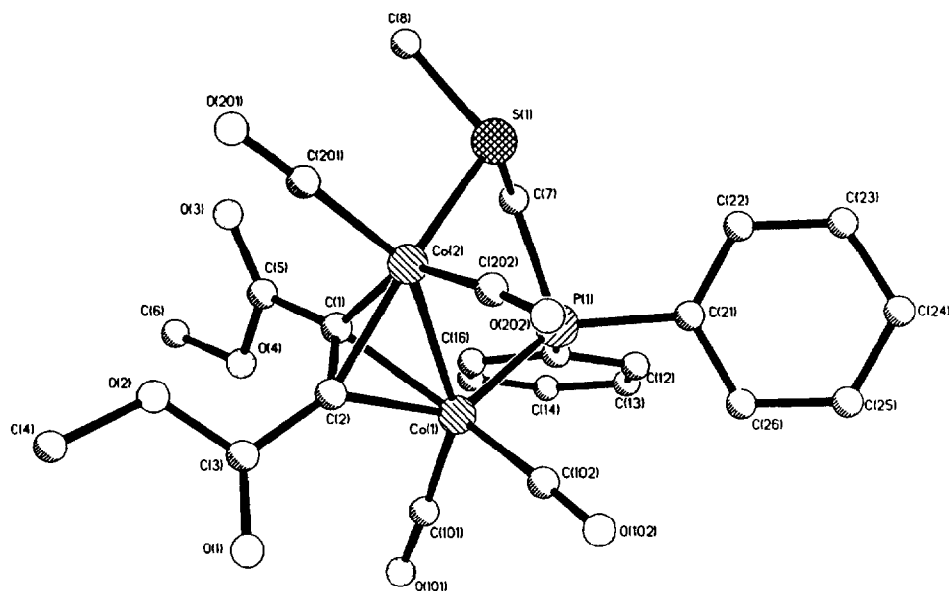
Fig. 1. The molecular structure of 3a; H-atoms have been omitted for clarity.

Table 2
Selected bond lengths and angles in complex [Co₂{μ-C₂(CO₂Me)₂}(PPh₂CH₂SMe)(CO)₄] 3a

Bond lengths (Å)			
Co(1)–C(101)	1.783(4)	S(1)–C(8)	1.805(4)
Co(1)–C(102)	1.786(4)	S(1)–C(7)	1.807(4)
Co(1)–C(2)	1.917(3)	P(1)–C(11)	1.825(4)
Co(1)–C(1)	1.962(3)	P(1)–C(21)	1.831(4)
Co(1)–P(1)	2.2210(13)	P(1)–C(7)	1.831(4)
Co(1)–Co(2)	2.4656(8)	C(1)–C(2)	1.362(5)
Co(2)–C(202)	1.792(5)	C(101)–O(101)	1.132(5)
Co(2)–C(201)	1.796(5)	C(102)–O(102)	1.139(5)
Co(2)–C(1)	1.928(3)	C(201)–O(201)	1.122(5)
Co(2)–C(2)	1.950(4)	C(202)–O(202)	1.135(5)
Co(2)–S(1)	2.2951(13)		

Bond angles (°)			
C(101)–Co(1)–C(102)	100.0(2)	C(1)–Co(2)–S(1)	99.50(11)
C(101)–Co(1)–C(2)	102.5(2)	C(2)–Co(2)–S(1)	138.55(11)
C(102)–Co(1)–C(2)	104.6(2)	C(202)–Co(2)–Co(1)	98.44(14)
C(101)–Co(1)–C(1)	102.5(2)	C(201)–Co(2)–Co(1)	149.99(14)
C(102)–Co(1)–C(1)	142.4(2)	C(1)–Co(2)–Co(1)	51.28(10)
C(2)–Co(1)–C(1)	41.1(2)	C(2)–Co(2)–Co(1)	49.79(10)
C(101)–Co(1)–P(1)	102.27(13)	S(1)–Co(2)–Co(1)	99.37(5)
C(102)–Co(1)–P(1)	104.48(1)	C(8)–S(1)–C(7)	98.7(2)
C(2)–Co(1)–P(1)	137.44(11)	C(8)–S(1)–Co(2)	109.5(2)
C(1)–Co(1)–P(1)	99.70(11)	C(7)–S(1)–Co(2)	105.06(13)
C(101)–Co(1)–Co(2)	150.58(12)	C(11)–P(1)–C(21)	103.9(2)
C(102)–Co(1)–Co(2)	99.42(13)	C(11)–P(1)–C(7)	99.7(2)
C(2)–Co(1)–Co(2)	50.98(11)	C(21)–P(1)–C(7)	104.9(2)
C(1)–Co(1)–Co(2)	50.05(10)	C(11)–P(1)–Co(1)	118.45(12)
P(1)–Co(1)–Co(2)	93.94(5)	C(21)–P(1)–Co(1)	117.98(12)
C(202)–Co(2)–C(201)	99.4(2)	C(7)–P(1)–Co(1)	109.71(13)
C(202)–Co(2)–C(1)	144.4(2)	C(2)–C(1)–Co(2)	70.3(2)
C(201)–Co(2)–C(1)	102.4(2)	C(2)–C(1)–Co(1)	67.7(2)
C(202)–Co(2)–C(2)	106.9(2)	Co(2)–C(1)–Co(1)	78.67(13)
C(201)–Co(2)–C(2)	101.6(2)	C(1)–C(2)–Co(1)	71.2(2)
C(1)–Co(2)–C(2)	41.1(2)	C(1)–C(2)–Co(2)	68.6(2)
C(202)–Co(2)–S(1)	104.3(2)	Co(1)–C(2)–Co(2)	79.23(14)
C(201)–Co(2)–S(1)	99.4(2)	S(1)–C(7)–P(1)	111.0(2)

Å in [Co$_2$(μ-C$_2$(CO$_2$Me)$_2$)(μ-P$_2$Ph$_4$)(CO)$_4$]). It is worth noting that the Co–S distance (2.2951(13) Å) is longer than the Co–P distance (2.2210(13) Å). This presumably reflects the greater strength of the Co–P bond arising from a combination of the better σ-donor ability and π-acceptor ability of phosphorus as compared with sulphur.

The spectroscopic properties of 3a, 3b, 4a and 4b (Table 1) are consistent with their having the same structure in solution as found for 3a in the solid state. Thus the ^{1}H NMR spectra show the CH$_2$ resonances of the ligand to be present either as doublets in the case of 3a and 4a or as the expected pair of double doublets for both 3b and 4b.

The complexes [Co$_2$Fe(μ_3-S)(μ-Ph$_2$PCH$_2$SR)- (CO)$_7$] (R = Me 5, R = Ph 6) were prepared in good yield from the reaction of [Co$_2$Fe(μ_3-S)(CO)$_9$] with the ligands Ph$_2$PCH$_2$SMe and Ph$_2$PCH$_2$SPh in toluene at 313 K (Scheme 1). The reactions were monitored by thin-layer chromatography and showed the initial forma-

tion of brown complexes, presumably [Co$_2$Fe(μ_3-S)(PPh$_2$CH$_2$SR)(CO)$_8$]. These complexes were not, however, isolable from solution, and upon removal of solvent converted to the green complexes 5 and 6. When complexes 5 and 6 were reacted with carbon monoxide, the same brown products were obtained but again they could not be isolated. This makes for an interesting comparison with the brown complex [Co$_2$Fe(μ_3-S)(PPh$_2$CH$_2$PPh$_2$)(CO)$_8$], which has been isolated and characterised by Aime et al. [13]. This complex forms in addition to the ligand bridged species [Co$_2$Fe(μ_3-S)(μ-PPh$_2$CH$_2$PPh$_2$)(CO)$_7$]. The fact that [Co$_2$Fe(μ_3-S)(PPh$_2$CH$_2$PPh$_2$)(CO)$_8$] is isolable, whereas [Co$_2$Fe(μ_3-S)(PPh$_2$CH$_2$SR)(CO)$_8$] is not, presumably reflects the fact that when the second donor atom is phosphorus there is significant steric hindrance to attack at cobalt because of the two attached phenyl rings. In contrast, in 5 and 6 the second donor atom, sulphur, is only attached to one group. There is therefore less steric hindrance and hence the carbonylation

Table 3

Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{Å}^2 \times 10^3$) for 3a

Atom	x	y	z	U_{eq}
Co(1)	2235(1)	2134(1)	2192(1)	35(1)
Co(2)	2216(1)	1715(1)	3749(1)	40(1)
S(1)	5202(1)	826(1)	3846(1)	45(1)
P(1)	5141(1)	1196(1)	1952(1)	36(1)
O(1)	−2431(4)	3891(3)	2807(2)	73(1)
O(2)	−1537(4)	4575(3)	3854(2)	67(1)
O(3)	3172(4)	4601(3)	3765(2)	65(1)
O(4)	2307(4)	5289(3)	2477(2)	59(1)
C(1)	2149(4)	3287(3)	3056(2)	34(1)
C(2)	589(5)	3073(3)	3064(2)	38(1)
C(3)	−1283(5)	3858(3)	3213(2)	39(1)
C(4)	−3307(6)	5392(5)	4106(3)	72(1)
C(5)	2590(4)	4435(3)	3160(2)	37(1)
C(6)	2739(8)	6434(5)	2539(4)	89(2)
C(101)	1729(5)	3228(4)	1268(3)	46(1)
O(101)	1346(5)	3952(3)	699(2)	77(1)
C(102)	1345(5)	943(4)	1977(2)	45(1)
O(102)	729(4)	195(3)	1872(2)	77(1)
C(201)	1513(6)	2276(4)	4795(3)	55(1)
O(201)	1037(5)	2645(4)	5442(2)	88(1)
C(202)	1466(6)	347(4)	3877(3)	58(1)
O(202)	872(6)	−456(4)	3925(3)	100(1)
C(7)	6212(5)	1357(4)	2854(2)	44(1)
C(8)	5846(6)	1706(4)	4554(3)	56(1)
C(11)	6333(5)	1907(3)	1091(2)	38(1)
C(12)	7541(5)	1195(4)	473(2)	48(1)
C(13)	8406(5)	1803(4)	−153(3)	56(1)
C(14)	8109(6)	3099(4)	−174(3)	58(1)
C(15)	6919(6)	3811(4)	424(3)	61(1)
C(16)	6009(6)	3229(4)	1054(3)	52(1)
C(21)	5998(5)	−537(3)	1794(2)	40(1)
C(22)	7309(5)	−1419(4)	2245(3)	53(1)
C(23)	7933(6)	−2715(4)	2080(3)	65(1)
C(24)	7258(6)	−3131(4)	1476(3)	65(1)
C(25)	5958(6)	−2270(4)	1027(3)	58(1)
C(26)	5318(5)	−969(4)	1188(3)	48(1)

U_{eq} is defined as one third of the trace of the orthogonalised U_{ij} tensor.

products of **5** and **6** revert readily to the bridged complexes.

The crystal structure of [Co$_2$Fe(μ_3-S)(μ-Ph$_2$PCH$_2$-SPh)(CO)$_7$] **6** has been determined by an X-ray diffraction study. The molecular structure is shown in Fig. 2; selected bond lengths and angles are given in Table 4 and fractional atom coordinates in Table 5.

The structure of **6** consists of a pseudo-tetrahedral core of atoms (2Co, Fe, S) and is analogous to the structure of [Co$_2$Fe(μ_3-S)(CO)$_9$] [14], with the formal replacement of two equatorial carbonyl groups, one on each cobalt atom, by a sulphur and a phosphorus atom.

As in **3a**, the five-membered ring is puckered. The Co–P distance is slightly shorter than in **3a**, as is the Co–S distance, although the Co–S distance remains longer than the Co–P distance.

The Co–Co distance in **6** is slightly shorter than in the parent complex [Co$_2$Fe(μ_3-S)(CO)$_9$] [14], presumably due to the constraints imposed by the five-membered Co–Co–P–C–S ring. The Co–Fe distances are also shorter, consistent with an overall increase in strength of the metal–metal bonds.

The spectroscopic properties of **5** and **6** in solution (Table 1) are consistent with their having the same structure in solution as that of **6** in the solid state. Thus the ^{1}H NMR spectrum of **6** shows a characteristic pair of double doublets between δ 3.5 and 4, each pair

having the same *geminal* HH coupling of 11.5 Hz but different $^2J_{PH}$ values (6.6 and 9.2 Hz). The ^{31}P NMR spectra of **5** and **6** each show a singlet resonance at ca. δ -100, as would be expected for a terminal phosphine. Previous workers [13] have shown that the bis-diphenylphosphinomethane bridged carbonylthiodicobaltiron complex is highly fluxional at room temperature. The ^{13}C NMR of **5** and **6** show that the results of Aime et al. also hold for the ligands Ph$_2$PCH$_2$SR (R = Me, Ph). Unlike other bis-substituted carbonylthiodicobaltiron complexes, those which are bridged do not undergo internuclear scrambling of carbonyls even at room temperature, although localised exchange does occur. In the ^{13}C NMR spectra of **5** and **6**, the iron bonded carbonyls exchange rapidly and so give rise to a single sharp signal, whilst the cobalt bonded carbonyls give rise to a broad resonance. The broadness of the latter can be attributed to the large quadrupolar moment of cobalt and makes it impossible to determine whether or not the carbonyls on the cobalt atoms are fluxional and undergo localised exchange either at each cobalt centre or between the two centres.

3. Conclusions

The reactions of the ligands Ph$_2$PCH$_2$SR with two different types of complex each containing a dicobalt
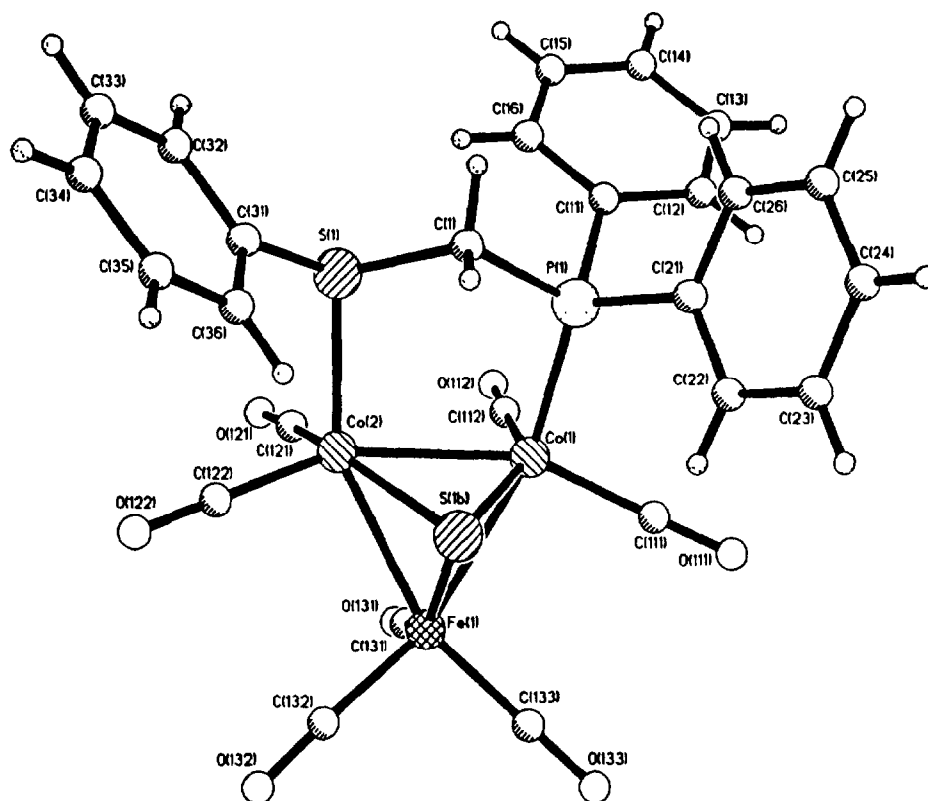

Fig. 2. The molecular structure of **6**; H-atoms have been omitted for clarity.

unit reveal that, although the ligand bridged products obtained in each case are similar, there are marked differences in stability relative to the corresponding products in which the ligand is monodentate. These differences can be attributed to the different pathways involved in the formation of the ligand bridged complexes. Thus in alkyne bridged dicobalt complexes, poorer π-acceptors tend to replace carbonyl groups in pseudo-axial sites [9], and therefore initial phosphine

substitution occurs pseudo-axially. For bidentate ligands, the subsequent formation of a bridged dicobalt complex requires pseudo-equatorial substitution at both Co atoms. The isomerisation from a pseudo-axial to a pseudo-equatorial configuration which is therefore necessary for the ligand to become bidentate is presumably energetically unfavourable and inhibits the formation of the bridged complex. In the case of $[Co_2Fe(\mu_3\text{-}S)(CO)_9]$, the available evidence indicates that initial

Table 4

Selected bond lengths and angles in complex $[Co_2Fe(\mu_3\text{-}S)(\mu\text{-}PPh_2CH_2SPh)(CO)_7]$ **6**

Bond lengths (Å)

Co(1)–C(112)	1.760(10)	Fe(1)–S(1B)	2.174(3)
Co(1)–C(111)	1.790(12)	S(1)–C(31)	1.779(9)
Co(1)–S(1B)	2.161(3)	S(1)–C(1)	1.808(9)
Co(1)–P(1)	2.207(3)	P(1)–C(21)	1.820(9)
Co(1)–Co(2)	2.518(2)	P(1)–C(11)	1.820(9)
Co(1)–Fe(1)	2.528(2)	P(1)–C(1)	1.832(8)
Co(2)–C(122)	1.770(12)	C(111)–O(111)	1.130(11)
Co(2)–C(121)	1.795(11)	C(112)–O(112)	1.146(11)
Co(2)–S(1B)	2.167(3)	C(121)–O(121)	1.137(11)
Co(2)–S(1)	2.278(3)	C(122)–O(122)	1.144(11)
Co(2)–Fe(1)	2.544(2)	C(131)–O(131)	1.147(13)
Fe(1)–C(133)	1.772(11)	C(132)–O(132)	1.128(13)
Fe(1)–C(132)	1.78(2)	C(133)–O(133)	1.133(12)
Fe(1)–C(131)	1.785(13)		

Bond angles (°)

C(112)–Co(1)–C(111)	100.2(4)	C(133)–Fe(1)–S(1B)	102.7(3)
C(112)–Co(1)–S(1B)	143.9(3)	C(132)–Fe(1)–S(1B)	105.6(4)
C(111)–Co(1)–S(1B)	107.8(3)	C(131)–Fe(1)–S(1B)	146.2(4)
C(112)–Co(1)–P(1)	100.1(3)	C(133)–Fe(1)–Co(1)	100.0(4)
C(111)–Co(1)–P(1)	100.7(3)	C(132)–Fe(1)–Co(1)	156.1(4)
S(1B)–Co(1)–P(1)	96.64(9)	C(131)–Fe(1)–Co(1)	96.1(4)
C(112)–Co(1)–Co(2)	91.6(3)	S(1B)–Fe(1)–Co(1)	54.10(8)
C(111)–Co(1)–Co(2)	156.5(3)	C(133)–Fe(1)–Co(2)	154.6(3)
S(1B)–Co(1)–Co(2)	54.52(7)	C(132)–Fe(1)–Co(2)	99.3(4)
P(1)–Co(1)–Co(2)	97.12(8)	C(131)–Fe(1)–Co(2)	99.4(3)
C(112)–Co(1)–Fe(1)	100.4(4)	S(1B)–Fe(1)–Co(2)	53.98(7)
C(111)–Co(1)–Fe(1)	97.1(3)	Co(1)–Fe(1)–Co(2)	59.52(5)
S(1B)–Co(1)–Fe(1)	54.55(7)	Co(1)–S(1B)–Co(2)	71.16(8)
P(1)–Co(1)–Fe(1)	149.91(8)	Co(1)–S(1B)–Fe(1)	71.35(9)
Co(2)–Co(1)–Fe(1)	60.56(5)	Co(2)–S(1B)–Fe(1)	71.78(8)
C(122)–Co(2)–C(121)	99.4(5)	C(31)–S(1)–C(1)	99.5(4)
C(122)–Co(2)–S(1B)	101.1(4)	C(31)–S(1)–Co(2)	113.4(3)
C(121)–Co(2)–S(1B)	147.1(3)	C(1)–S(1)–Co(2)	107.3(3)
C(122)–Co(2)–S(1)	100.2(3)	C(21)–P(1)–C(11)	104.1(4)
C(121)–Co(2)–S(1)	96.6(3)	C(21)–P(1)–C(1)	98.5(4)
S(1B)–Co(2)–S(1)	104.71(10)	C(11)–P(1)–C(1)	105.0(4)
C(122)–Co(2)–Co(1)	154.2(4)	C(21)–P(1)–Co(1)	120.1(3)
C(121)–Co(2)–Co(1)	99.8(3)	C(11)–P(1)–Co(1)	115.7(3)
S(1B)–Co(2)–Co(1)	54.32(7)	C(1)–P(1)–Co(1)	111.2(3)
S(1)–Co(2)–Co(1)	94.51(8)	S(1)–C(1)–P(1)	111.4(4)
C(122)–Co(2)–Fe(1)	100.8(4)	O(111)–C(111)–Co(1)	179.1(9)
C(121)–Co(2)–Fe(1)	96.7(3)	O(112)–C(112)–Co(1)	177.2(10)
S(1B)–Co(2)–Fe(1)	54.24(7)	O(121)–C(121)–Co(2)	176.1(9)
S(1)–Co(2)–Fe(1)	152.85(8)	O(122)–C(122)–Co(2)	178.7(9)
Co(1)–Co(2)–Fe(1)	59.92(5)	O(131)–C(131)–Fe(1)	178.7(10)
C(133)–Fe(1)–C(132)	96.8(5)	O(132)–C(132)–Fe(1)	177.0(12)
C(133)–Fe(1)–C(131)	97.6(5)	O(133)–C(133)–Fe(1)	178.2(11)
C(132)–Fe(1)–C(131)	98.4(6)		

phosphine substitution occurs equatorially at Co (not Fe) [13]. Thus the second step, involving coordination of the sulphur to the other Co atom to give **5** and **6**, does not require the energetically unfavourable isomerisation step needed in the corresponding reactions leading to **3** and **4**. It is most probably for this reason that a monosubstituted product involving the displacement of only one CO group cannot be isolated from the reaction of $[Co_2Fe(\mu_3\text{-S})(CO)_9]$ and Ph_2PCH_2SR, although the possibility that the metal–sulphur bond in the dicobalt complex is inherently weaker than in the trinuclear iron–dicobalt complex cannot be excluded.

4. Experimental

All reactions were carried out under an atmosphere of dry nitrogen, 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 1 mm silica plates prepared at the University Chemical Laboratory, Cambridge; products are presented in order of decreasing R_f values.

The instrumentation used to obtain spectroscopic data has been described previously [15]. Phosphorus-31 NMR chemical shifts are given relative to $P(OMe)_3$ with upfield shifts negative. All NMR spectra were recorded at 293 K. The compounds $[Co_2(\mu\text{-R}^1CCR^2)(CO)_6]$ ($R^1 = R^2 = CO_2Me$, or $R = H$, $R^2 = CO_2Me$) [9a,16,17], $[Co_2Fe(\mu_3\text{-S})(CO)_9]$ [18,19] and Ph_2PCH_2SR (R = Me or Ph) [2] were prepared by literature methods.

4.1. Reaction of $[Co_2\{\mu\text{-}C_2(CO_2Me)_2\}(CO)_6]$ with $MeSCH_2PPh_2$

To a solution of $[Co_2\{\mu\text{-}C_2(CO_2Me)_2\}(CO)_6]$ (0.377 g, 0.88 mmol) in toluene (30 cm^3) was added a solution

Table 5
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{Å}^2 \times 10^3$) for **6**

Atom	x	y	z	U_{eq}
Co(1)	1396(1)	2801(1)	3948(1)	44(1)
Co(2)	1066(1)	2116(1)	2797(1)	46(1)
Fe(1)	−171(2)	3495(1)	2923(1)	58(1)
S(1B)	2201(2)	3273(1)	3076(1)	48(1)
S(1)	2813(2)	1130(1)	3146(1)	45(1)
P(1)	3450(2)	2156(1)	4423(1)	41(1)
C(1)	4243(9)	1593(6)	3784(4)	49(2)
C(11)	3257(10)	1392(5)	5066(5)	48(2)
C(12)	3327(14)	1635(7)	5734(6)	85(4)
C(13)	3028(17)	1081(9)	6216(6)	111(5)
C(14)	2704(18)	271(9)	6037(9)	111(5)
C(15)	2619(15)	39(8)	5387(8)	100(4)
C(16)	2896(13)	590(7)	4890(6)	80(3)
C(21)	5084(9)	2743(6)	4809(4)	44(2)
C(22)	5184(11)	3568(6)	4645(5)	59(3)
C(23)	6472(12)	4008(7)	4880(5)	73(3)
C(24)	7680(11)	3601(9)	5271(6)	79(4)
C(25)	7585(12)	2789(9)	5433(6)	83(4)
C(26)	6287(11)	2363(7)	5195(5)	67(3)
C(31)	3879(9)	882(6)	2521(4)	46(2)
C(32)	4124(11)	66(6)	2390(5)	66(3)
C(33)	4955(13)	−142(8)	1932(6)	84(4)
C(34)	5536(13)	437(9)	1584(6)	81(4)
C(35)	5338(12)	1241(9)	1712(5)	78(3)
C(36)	4478(11)	1481(7)	2176(5)	63(3)
C(111)	1395(10)	3633(7)	4536(6)	61(3)
C(112)	70(11)	2149(6)	4198(5)	60(3)
C(121)	−517(12)	1483(7)	2833(5)	63(3)
C(122)	1005(10)	2098(7)	1907(6)	62(3)
C(131)	−1912(13)	3136(7)	3073(7)	86(4)
C(132)	−730(14)	3756(8)	2047(8)	94(4)
C(133)	−261(11)	4505(7)	3250(6)	71(3)
O(111)	1382(9)	4152(5)	4911(4)	91(3)
O(112)	−771(10)	1734(5)	4389(5)	109(3)
O(121)	−1533(8)	1079(5)	2817(4)	96(3)
O(122)	993(8)	2092(5)	1333(4)	79(2)
O(131)	−3037(10)	2920(6)	3174(6)	125(4)
O(132)	−1136(13)	3941(7)	1498(5)	139(4)
O(133)	−284(10)	5155(5)	3455(5)	116(3)

U_{eq} is defined as one third of the trace of the orthogonalised U_{ij} tensor.
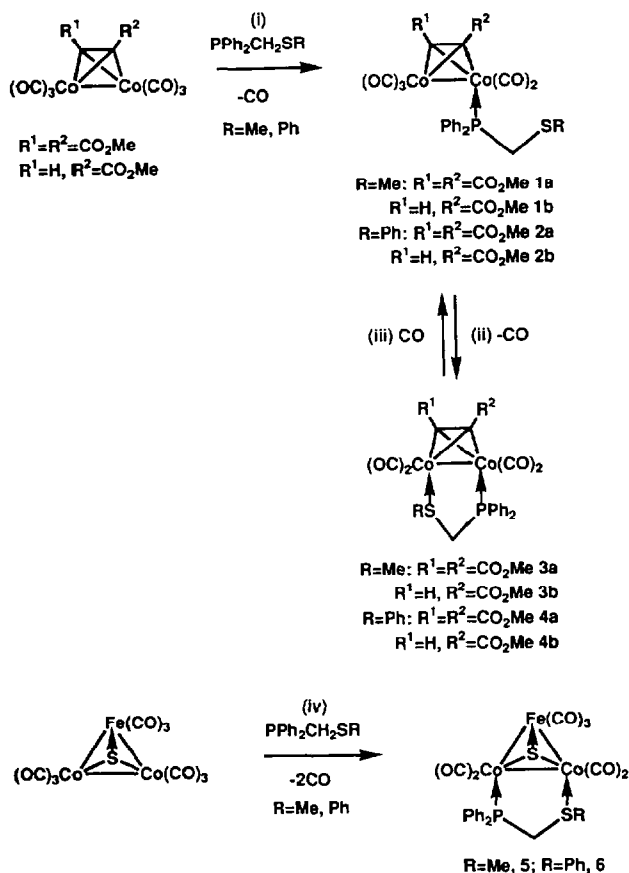
Scheme 1. Reagents and conditions for the formation of the new complexes. (i) PPh$_2$CH$_2$SR, toluene, 40°C; (ii) toluene, 60°C; (iii) CO, toluene, 60°C.

of MeSCH$_2$PPh$_2$ (0.217 g, 0.88 mmol) in toluene (20 cm^3). The solution was stirred at 313 K for 18 h and after removal of the solvent in vacuo, the mixture was purified using preparative TLC with hexane–ethyl acetate (4:1) as eluant. This gave red crystalline [Co$_2$(μ-C$_2$(CO$_2$Me)$_2$)(CO)$_5$(PPh$_2$CH$_2$SMe)] (1a) (0.246 g, 43%). 1a Anal. Found: C, 46.54; H, 3.18. C$_{25}$H$_{21}$O$_9$PSCo$_2$ Calc.: C, 46.46; H, 3.27%. MS 646 (M^+), M^+ − n(CO) (n = 1 to 5). ^{13}C NMR (CDCl$_3$ at 298 K): δ 203.1 (s, 2CO), 198.9 (s, 3CO), 170.6 (s, CO$_2$Me), 133–128 (m, Ph), 72.5 (s, CCO$_2$Me), 52.5 (s, CO$_2$Me), 34.0 (d, J(P–C) 17.2 Hz, CH$_2$), 18.2 (d, J(P–C) 2.52 Hz, SMe). ^{31}P NMR (CDCl$_3$ at 298 K): δ −94.9 (s, PPh$_2$CH$_2$SMe).

4.2. Reaction of [Co$_2$(μ-HCCCO$_2$Me)(CO)$_6$] with MeSCH$_2$PPh$_2$

To a solution of [Co$_2$(μ-HCCCO$_2$Me)(CO)$_6$] (0.090 g, 0.24 mmol) in toluene (20 cm^3) was added a solution of MeSCH$_2$PPh$_2$ (0.060 g, 0.24 mmol) in toluene (10 cm^3). The mixture was stirred at 313 K for 4 h. After removal of the solvent in vacuo, the resulting oil was purified using preparative TLC with hexane–ethyl acetate (4:1) as eluant. This gave red crystalline [Co$_2$(μ-

HCCCO$_2$Me)(CO)$_5$(PPh$_2$CH$_2$SMe)] (1b) (0.120 g, 85%). MS 588 (M^+), M^+ − n(CO) (n = 1 to 5). ^{13}C NMR (CDCl$_3$ at 298 K): δ 203.9 (s, 2CO), 200.1 (s, 3CO), 171.9 (s, CO$_2$Me), 135–128 (m, Ph), 73.1 (s, CCH), 71.2 (s, CCO$_2$Me), 52.4 (s, CO$_2$Me), 35.1 (d, J(P–C) 18.6 Hz, CH$_2$), 18.3 (d, J(P–C) 3.65 Hz, SMe). ^{31}P NMR (CDCl$_3$ at 298 K): δ −93.0 (s, PPh$_2$CH$_2$SMe).

4.3. Reaction of [Co$_2${ μ-C$_2$(CO$_2$Me)$_2$}(CO)$_6$] with PPh$_2$CH$_2$SPh

The complex [Co$_2${ μ-C$_2$(CO$_2$Me)$_2$}(CO)$_6$] (0.361 g, 0.84 mmol) and PPh$_2$CH$_2$SPh (0.260 g, 0.84 mmol) in toluene (30 cm^3) were used in an analogous procedure to 4.1 above. Preparative TLC using hexane–ethyl acetate (4:1) as eluant yielded red crystalline [Co$_2$(μ-C$_2$(CO$_2$Me)$_2$)(CO)$_5$(PPh$_2$CH$_2$SPh)] (2a) (0.484 g, 81%). 2a Anal. Found: C, 50.66; H, 3.20. C$_{30}$H$_{23}$O$_9$PSCo$_2$ Calc.: C, 50.86; H, 3.27%. MS 708 (M^+), M^+ − n(CO) (n = 1 to 5). ^{13}C NMR (CDCl$_3$ at 298 K): δ 208.5 (s, Co(CO)$_2$), 202.9 (s, Co(CO)$_3$), 170.6 (s, CO$_2$Me), 136–126 (m, Ph), 72.5 (s, CCO$_2$Me), 52.6 (s, CO$_2$Me) 33.5 (d, J(P–C) = 14.4, CH$_2$). ^{31}P NMR (CDCl$_3$ at 298 K): δ −95.8 (s, PPh$_2$CH$_2$SPh).

4.4. Reaction of [Co$_2$(μ-HCCCO$_2$Me)(CO)$_6$] with PPh$_2$CH$_2$SPh

The complex [Co$_2$(μ-HCCCO$_2$Me)(CO)$_6$] (0.250 g, 0.68 mmol) and PPh$_2$CH$_2$SPh (0.208 g, 0.68 mmol) in toluene (40 cm^3) were used in an analogous procedure to 4.2 above. Preparative TLC using hexane-ethyl acetate (5:1) as eluant yielded red crystalline [Co$_2$(μ-HCCCO$_2$Me)(CO)$_5$(PPh$_2$CH$_2$SPh)] (2b) (0.306 g, 58%). 2b Anal. Found: C, 51.63; H, 3.28. C$_{28}$H$_{21}$O$_7$PSCo$_2$ Calc.: C, 51.71; H, 3.25%. MS 650 (M^+), M^+ − n(CO) (n = 1 to 5). ^{13}C NMR (CDCl$_3$ at 298 K): δ 204.0 (s, 2CO), 200.2 (s, 3CO), 171.8 (s, CO$_2$Me), 136–126 (m, Ph), 73.0 (s, CCH), 71.3 (s, CCCO$_2$Me), 52.4 (s, CO$_2$Me), 34.9 (d, J(P–C) 15.9 Hz, CH$_2$). ^{31}P NMR (CDCl$_3$ at 298 K) δ −94.4 (s, PPh$_2$CH$_2$SPh).

4.5. Thermolysis of [Co$_2$(μ-C$_2$(CO$_2$Me)$_2$)(CO)$_5$(PPh$_2$CH$_2$SMe)] 1a

Complex 1a (0.196 g, 0.30 mmol) was dissolved in toluene (40 cm^3) and the solution heated at 333 K for 48 h. The solvent was removed in vacuo and purification with preparative TLC using hexane–ethyl acetate (3 : 2) as eluant gave [Co$_2${ μ-C$_2$(CO$_2$Me)$_2$}(μ-PPh$_2$CH$_2$SMe)(CO)$_4$] (3a) (0.152 g, 81%). 3a Anal. Found: C, 46.74; H, 3.35. C$_{24}$H$_{21}$O$_8$PSCo$_2$ Calc.: C, 46.62; H, 3.42%. MS 618 (M^+), M^+ − n(CO) (n = 1 to 4). ^{13}C NMR (CDCl$_3$ at 298 K): δ 200.8 (br, 4CO),

173.4 (s, CO_2Me), 135–128 (m, Ph), 52.4 (s, CO_2Me), 43.4 (d, J(P–C) 22.8 Hz, CH_2), 26.5 (s, SMe). ^{31}P NMR ($CDCl_3$ at 298 K): δ −94.9 (s, PPh_2CH_2SMe).

4.6. Thermolysis of $[Co_2(\mu\text{-}HCCCO_2Me)(CO)_5 (PPh_2CH_2SMe)]$ 1b

Complex 1b (0.120 g, 0.20 mmol) was dissolved in toluene (30 cm^3) and the solution heated at 333 K for 22 h. The solvent was removed in vacuo and purification with preparative TLC using hexane–ethyl acetate (4 : 1) as eluant gave [Co_2(μ-HCCCO$_2$Me)(μ-PPh$_2$CH$_2$SMe)(CO)$_4$] (3b) (0.059 g, 53%). 3b Anal. Found: C, 47.25; H, 3.45; P, 5.34. $C_{22}H_{19}O_6PSCo_2$ Calc.: C, 47.16; H, 3.42; P, 5.53%. MS 560 (M^+), $M^+ - n$(CO) ($n = 1$ to 4). ^{13}C NMR ($CDCl_3$ at 298 K): δ 201.0 (br, 4CO), 174.9 (s, CO_2Me), 135–128 (m, Ph), 52.2 (s, CO_2Me), 44.6 (d, J(P–C) 23.2 Hz, CH_2), 26.8 (s, SMe). ^{31}P NMR ($CDCl_3$ at 298 K): δ −94.2 (s, PPh_2CH_2Me).

4.7. Thermolysis of $[Co_2(\mu\text{-}C_2(CO_2Me)_2(CO)_5 (PPh_2CH_2SPh)]$ 2a

Complex 2a (0.484 g, 0.68 mmol) was dissolved in toluene (40 cm^3) and the solution heated at 333 K for 36 h. The solvent was removed in vacuo and purification with preparative TLC using hexane–ethyl acetate (3 : 1) as eluant gave [$Co_2\{\mu$-C$_2$(CO$_2$Me)$_2\}$(μ-PPh$_2$CH$_2$SPh)(CO)$_4$] (4a) (0.350 g, 75%). 4a Anal. Found: C, 51.10; H, 3.46. $C_{29}H_{23}O_8PSCo_2$ Calc.: C, 51.19; H, 3.41%. MS 680 (M^+), $M^+ - n$(CO) ($n = 1$ to 4). ^{13}C NMR ($CDCl_3$ at 298 K): δ 201.0 (br, 4CO), 173.5 (s, CO_2Me), 132–128 (m, Ph), 52.7 (s, CO_2Me), 44.9 (d, J(P–C) 22.9 Hz, CH_2). ^{31}P NMR ($CDCl_3$ at 298 K): δ −97.9 (s, PPh_2CH_2SPh).

4.8. Thermolysis of $[Co_2(\mu\text{-}HCCCO_2Me)(CO)_5 (PPh_2CH_2Ph)]$ 2b

Complex 2b (0.100 g, 0.154 mmol) was dissolved in toluene (20 cm^3) and the solution heated at 333 K for 18 h. The solvent was removed in vacuo and purification with preparative TLC using hexane–ethyl acetate (6 : 1) as eluant gave [Co_2(μ-HCCCO$_2$Me)(μ-PPh$_2$CH$_2$Ph)(CO)$_4$] (4b) (0.032 g, 33%). Anal. Found: C, 51.63; H, 3.28. $C_{27}H_{21}O_6PSCo_2$ Calc.: C, 51.71; H, 3.25%. MS 622 (M^+), $M^+ - n$(CO) ($n = 1$ to 4). ^{13}C NMR ($CDCl_3$ at 298 K): δ 203.0 (br, 4CO), 175.0 (s, CO_2Me), 138–127 (m, Ph), 52.2 (s, CO_2Me), 46.5 (d, J(P–C) 22.7 Hz, CH_2). ^{31}P NMR ($CDCl_3$ at 298 K): δ −97.7 (s, PPh_2CH_2SPh).

4.9. Carbonylation reactions of 3 and 4

A solution of 0.2 mmol of 3 or 4 in 30 cm^3 toluene was purged by a steady stream of carbon monoxide at

333 K for 4 h. The solvent was removed in vacuo and the resulting mixture purified by TLC using hexane–ethyl acetate mixtures (as in 4.5 to 4.8) as eluant. This gave complexes 1 and 2 respectively in 50–60% yield followed by a trace of 3 and 4 (unreacted starting material).

4.10. Reaction of $[Co_2Fe(\mu_3\text{-}S)(CO)_9]$ with $MeSCH_2PPh_2$

To a solution of [Co_2Fe(μ_3-S)(CO)$_9$] (0.150 g, 0.33 mmol) in toluene (30 cm^3) was added a solution of MeSCH$_2$PPh$_2$ (0.081 g, 0.33 mmol) in toluene (10 cm^3). The solution was stirred at 313 K for 1 h. After removal of the solvent in vacuo, the mixture was purified using preparative TLC with hexane–ethyl acetate (5 : 1) as eluant. This gave a trace of the brown starting complex and green/brown crystalline [Co_2Fe(μ_3-S)(μ-MeSCH$_2$PPh$_2$)(CO)$_7$] (5) (0.157 g, 74%). MS 648 (M^+), $M^+ - n$(CO) ($n = 1$ to 7). ^{13}C NMR ($CDCl_3$ at 298 K): δ 212.9 (s, 3FeCO), 199.5 (br, 4CoCO), 135–128 (m, Ph), 48.0 (d, J(P–C) 18.8 Hz, CH_2), 27.7 (s, SMe). ^{31}P NMR ($CDCl_3$ at 298 K): δ −103.3 (s, PPh_2CH_2SMe).

4.11. Reaction of $[Co_2Fe(\mu_3\text{-}S)(CO)_9]$ with $PhSCH_2PPh_2$

To a solution of [Co_2Fe(μ_3-S)(CO)$_9$] (0.146 g, 0.32 mmol) in toluene (30 cm^3) was added a solution of PhSCH$_2$PPh$_2$ (0.098 g, 0.32 mmol) in toluene (10 cm^3). The solution was stirred at 313 K for 1 h. After removal of the solvent in vacuo, the mixture was purified using preparative TLC with hexane–ethyl acetate (5 : 1) as eluant. This gave a trace of the brown starting complex and green crystalline [Co_2Fe(μ_3-S)(μ-PhSCH$_2$PPh$_2$)(CO)$_7$] (6) (0.179 g, 79%) as the sole isolable product. A brown product, presumably [Co_2Fe(μ_3-S)(PhSCH$_2$PPh$_2$)(CO)$_8$], could not be isolated, converting in solution to the green product [Co_2Fe(μ_3-S)(μ-PhSCH$_2$PPh$_2$)(CO)$_7$]. 6 Anal. Found: C, 43.97; H, 2.62. $C_{26}H_{17}O_7PS_2Co_2Fe$ Calc.: C, 43.97; H, 2.41%. MS 710 (M^+), $M^+ - n$(CO) ($n = 1$ to 7). ^{13}C NMR ($CDCl_3$ at 298 K): δ 212.8 (s, 3FeCO), 200 (br, 4CoCO), 134–128 (m, Ph), 49.4 (d, J(P–C) 16.6 Hz, CH_2). ^{31}P NMR ($CDCl_3$ at 298 K): δ −107.9 (s, PPh_2CH_2SPh).

4.12. Crystal data for 3a

$C_{24}H_{21}Co_2O_8PS$, $M = 618.30$, crystal size 0.45 × 0.41 × 0.34 mm^3, triclinic, space group $P\bar{1}$, $a = 8.106(2)$, $b = 11.029(2)$, $c = 15.918(3)$ Å, $\alpha = 83.07(3)$, $\beta = 82.25(3)$ $\gamma = 69.78(3)°$, $V = 1319.0(5)$ Å^3, $Z = 2$, $\rho_{calc} = 1.557$ Mg m^{-3}, $F(000) = 628$, $\lambda = 0.71073$ Å, $T = 293(2)$ K, μ(Mo Kα) = 1.022 mm^{-1}. Data were

collected on a Nicolet R3 diffractometer by $\omega/2\theta$ scans ($5.38° \leq 2\theta \leq 45.10°$), and corrected for absorption using psi-scan data (max/min transmission 0.415/0.322). Of a total of 3718 reflections collected, 3453 were unique. The structure was solved by direct methods (SHELXTL PLUS) and refined by full-matrix least-squares on F^2 (SHELXL-93; G.M. Sheldrick, Göttingen, 1993) to $R_1 = 0.0376$, $wR_2 = 0.0966[F > 4\sigma(F)]$ and $R_1 = 0.0468$, $wR_2 = 0.1067$ (all data). Where $R_1 = \Sigma ||F_o| - |F_c||/\Sigma |F_o|$, $R_2 = \sqrt{\{\Sigma w(F_o^2 - F_c^2)^2/\Sigma wF_o^4\}}$, $w = 1/[\sigma^2(F_o^2) + (xP)^2 + yP]$, $P = (F_o^2 + 2F_c^2)/3$.

4.13. Crystal data for 6

$C_{26}H_{17}Co_2FeO_7PS_2$, $M = 710.20$, crystal size $0.33 \times 0.30 \times 0.28$ mm^3, monoclinic, space group $P2_1/c$, $a = 9.202(2)$, $b = 16.228(3)$, $c = 19.988(4)$ Å, $\beta = 101.25(3)°$, $V = 2927.5(10)$ Å^3, $Z = 4$, $\rho_{calc} = 1.611$ Mg m^{-3}, $F(000) = 1424$, $\lambda = 0.71073$ Å, $T = 293(2)$ K, $\mu(\text{Mo K}\alpha) = 1.022$ mm^{-1}. Data were collected on a Siemens-Stoe AED diffractometer by θ/ω scans ($5.02° \leq 2\theta \leq 45°$). Of a total of 4101 reflections collected, 3841 were unique. The structure was solved by direct methods (SHELXTL PLUS) and refined by full-matrix least-squares on F^2 (SHELXL-93; G.M. Sheldrick, Göttingen, 1993) to $wR_1 = 0.0520$, $wR_2 = 0.1267[F > 4\sigma(F)]$ and $wR_1 = 0.1060$, $wR_2 = 0.1910$ (all data). Where $R_1 = \Sigma ||F_o| - |F_c||/\Sigma |F_o|$, $R_2 = \sqrt{\{\Sigma w(F_o^2 - F_c^2)^2/\Sigma wF_o^4\}}$, $w = 1/[\sigma^2(F_o^2) + (xP)^2 + yP]$, $P = (F_o^2 + 2F_c^2)/3$.

Acknowledgements

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