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Labile SR′C(O)CRCH-bridged dicobalt complexes; synthesis, structures and ^{13}CO labelling studies

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Abstract—Three alkyne-bridged dicobalt carbonyl complexes, $[Co_2(\mu\text{-RCCH})(CO)_6]$ (R = H **1a**, Me **1b**, CH_2OH **1c**) have been reacted with $Ph_2P(SPh)$ and with the new thiophosphine ligands, $Ph_2P(SR')$ (R′ = Bu^n, Bu^t), to give, initially, both mono-substituted $[Co_2(\mu\text{-RCCH})(CO)_5\{PPh_2(SR')\}]$ [(R′ = Ph; R = H **2a**, Me **2b**, CH_2OH **2c**), (R′ = Bu^n; R = H **3a**, Me **3b**, CH_2OH **3c**), (R′ = Bu^t; R = H **4a**, Me **4b**)] and bis-substituted $[Co_2(\mu\text{-RCCH})(CO)_4\{PPh_2(SPh)\}_2]$ [(R′ = Ph; R = H **5a**, Me **5b**, CH_2OH **5c**), (R′ = Bu^n; R = H **6a**, Me **6b**, CH_2OH **6c**), (R′ = Bu^t; R = H **7a**, Me **7b**)] products. Thermolysis of complexes **2**–**4** gives $[Co_2(\mu\text{-PPh}_2)\{\mu\text{-SR′C(O)CRCH}\}(CO)_4]$ [(R′ = Ph; R = H **8a**, Me **8b**, CH_2OH **8c**), (R′ = Bu^n; R = H **9a**, Me **9b**), (R′ = Bu^t; R = H **10a**, R = Me **10b**)] in which sulphur–phosphorus bond cleavage and sulphur–carbon bond formation at the dicobalt centre have occurred to generate SR′C(O)CRCH ligands incorporated into 5-membered ring metallacycles. The transformations are regiospecific with the bulky substituents (R = H) in all cases being located adjacent to the CO moiety of the metallacycle. Treatment of the complex $[Co_2(\mu\text{-PPh}_2)\{\mu\text{-SPhC(O)CHCH}\}(CO)_4]$ **8a** with ^{13}CO and monitoring of the reaction via ^{13}C-{^{1}H}-NMR spectroscopy reveals the formation of a selectively labelled species, $[Co_2(\mu\text{-PPh}_2)\{\mu\text{-SPh}^{13}\text{C(O)CHCH}\}(^{13}CO)_2(CO)_2]$, in which the ketonic bridging carbonyl signal has been enhanced, while only two of the four signals due to the terminal carbonyl groups have been similarly enhanced. The mechanistic implications of this labelling study are discussed and pathways postulated for the reversible fragmentation of the SR′C(O)CRCH-bridged dicobalt systems. Single crystal X-ray diffraction studies have been performed on $[Co_2(\mu\text{-HCCH})(CO)_4\{PPh_2(SBu^n)\}_2]$ **6a**, revealing axially substituted thiophosphine groups and on $[Co_2(\mu\text{-PPh}_2)\{\mu\text{-SBu}^n\text{C(O)CHCH}\}(CO)_4]$ **9a**, in which an almost planar Co–S–C–C=C metallacycle-coordinated to the other cobalt is observed.

Keywords: dicobalt; labile; metallacycle; thiolate; phosphide; regioselectivity; labelling.

INTRODUCTION

Bimetallic transition metal complexes in which the metal centres are spanned by linked alkyne and carbonyl groups [μ-C(O)CRCR] have been thoroughly studied and a number of different bonding modes have been reported [1–3]. A common observation with these complexes is of the ease with which the alkyne–CO link can be cleaved, often to generate alkyne-bridged bimetallic species [2]. Notably, in the case of $[Rh_2(\mu\text{-CO})\{\mu\text{-C(O)CPhC(C}_6F_5)\}(\eta^5\text{-C}_5Me_5)_2]$, an equilibrium exists in the solid and in solution, with the isomeric alkyne-bridged species $[Rh_2\{\mu\text{-CPhC(C}_6F_5)\}(CO)_2(\eta^5\text{-C}_5Me_5)_2]$ [3].

As a consequence of our studies on the reactions of alkyne-hexacarbonyldicobalt complexes with ligands capable of undergoing intra-ligand bond cleavage, we have prepared a series of dicobalt complexes involving the C(O)CRCR structural motif incorporated into more elaborate bridging systems [4–7]. For example, dicobalt complexes with bridging ligands which incorporate linked alkyne, carbonyl and phosphide groups can be prepared from the reaction of $[Co_2(\mu\text{-CRCR})$

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$(CO)_6$] **1** (R = H, alkyl, aryl or CO_2Me) with diphosphane, $Ph_2P(PPh_2)$, the ordering of the linked groups being influenced by the nature of the R groups [6]. As part of a preliminary communication, we reported that the reaction of $[Co_2(\mu\text{-HCCH})(CO)_6]$ **1a** with the thiophosphine, $Ph_2P(SPh)$, affords, as the sole product, $[Co_2(\mu\text{-}PPh_2)\{\mu\text{-SPhC(O)CHCH}\}(CO)_4]$ **8a**, in which the thiolate rather than the phosphide fragment is linked to the ketonic carbon of the C(O)CHCH moiety [7]. In order to examine the generality and regioselectivity of this reaction, we have sought to explore the role of the substituents on both the alkyne and on the thiolate group (Scheme 1). In addition, we describe the results of ^{13}CO labelling experiments undertaken in order to examine the rigidity of the bridging SRC(O)CRCR ligand in these dicobalt systems.

RESULTS AND DISCUSSION

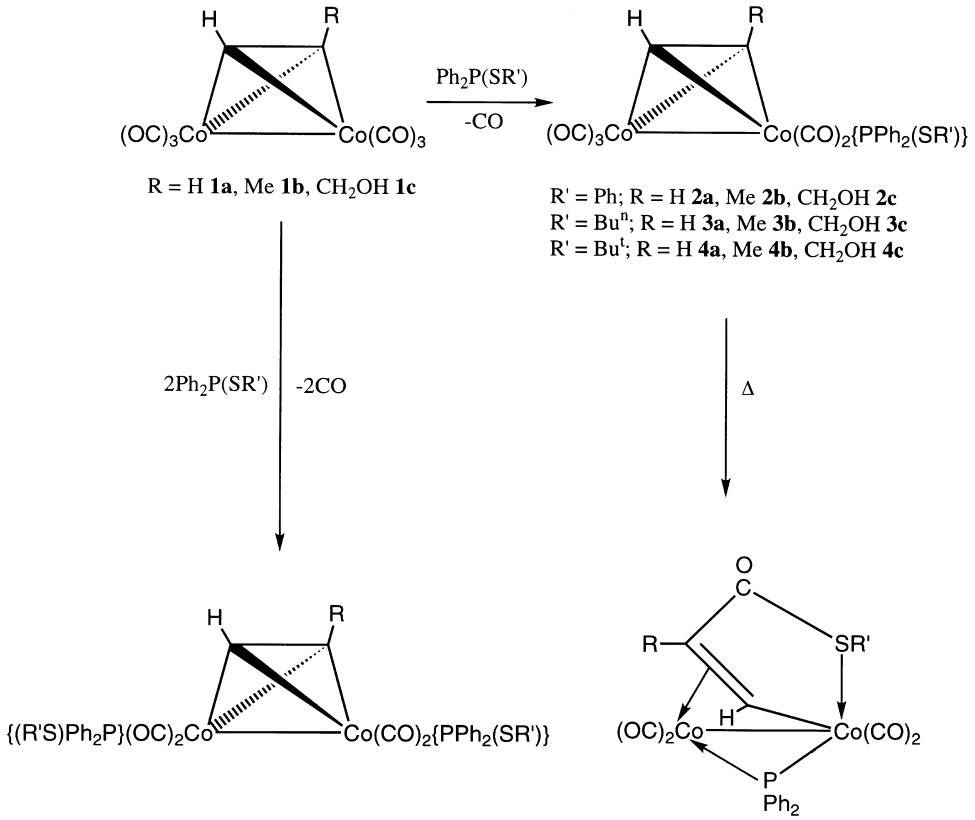
Preparation of $Ph_2P(SR')$ ($R' = Bu^n$, Bu^t)

Two new thiophosphine ligands, $Ph_2P(SBu^n)$ and $Ph_2P(SBu^t)$, have been prepared in high yield from the reactions of the corresponding sodium thiolates with chlorodiphenylphosphine in THF (see Experimental). The FAB mass spectra of the compounds show their molecular ion peaks while the $^{31}P\text{-}\{^1H\}$ NMR spectra display resonances for the respective diphenylphosphide phosphorus atoms.

Reactions of 1 *with* $Ph_2P(SR')$

The reactions of $[Co_2(\mu\text{-RCCH})(CO)_6]$ (R = H **1a**, Me **1b**, CH_2OH **1c**) with $Ph_2P(SR')$ ($R' = Ph$, Bu^t, Bu^n) in toluene at 293 K afford $[Co_2(\mu\text{-RCCH})(CO)_5\{PPh_2(SR')\}]$ [($R' = Ph$; R = H **2a**, Me **2b**, CH_2OH **2c**), ($R' = Bu^n$; R = H **3a**, Me **3b**, CH_2OH **3c**), ($R' = Bu^t$; R = H **4a**, Me **4b**)] and $[Co_2(\mu\text{-RCCH})(CO)_4\{PPh_2(SR')\}_2]$ [($R' = Ph$; R = H **5a**, Me **5b**, CH_2OH **5c**), ($R' = Bu^n$; R = H **6a**, Me **6b**, CH_2OH **6c**, ($R' = Bu^t$; R = H **7a**, Me **7b**)] (Scheme 1). All of the complexes have been characterised by mass spectrometry, IR, ^1H, ^{31}P and ^{13}C NMR spectroscopy (see Table 1 and Experimental). In addition, the structure of complex **6a** has been the subject of an X-ray diffraction study.

The spectroscopic properties of the mono-substituted species, **2**, **3** and **4**, in solution are consistent with those found for analogous alkyne bridged dicobalt pentacarbonyl complexes with other phosphine substituents [8]. The $^{31}P\text{-}\{^1H\}$ NMR spectrum in each



Scheme 1. Products from the reaction of **1** with $Ph_2P(SR')$.

Table 1. Infrared, ^{1}H and ^{31}P NMR data for complexes **2–10**

Compound	ν(CO) (cm^{-1})[a]	^{1}H NMR (δ)[b]	^{31}P NMR (δ)[c]
2a	2068s, 2018s, 1999m, 1978m	7.7–6.9[m, 15H, Ph], 5.00[s, br, 2H, C*H*]	−47.7[s, *P*Ph_2(SPh)]
2b	2065s, 2014vs, 2006vs, 1993m, 1975w	7.5–7.0[m, 15H, Ph], 5.10[s, br, 1H, C*H*], 1.93[s, 3H, Me]	−48.1[s, *P*Ph_2(SPh)]
2c	2025s, 2056s, 2025vs, 1999w	7.7–6.9[m, 15H, Ph], 5.19[dd, ^{3}J(PH) 4.5, 1H, C(CH_2OH)C*H*], 4.39[t, ^{3}J(HH) 6, 1H, C(CH_2O*H*)CH], 3.63[d, ^{3}J(HH) 6, 2H, C(CH_2OH)CH]	−49.9[s, PPh_2(SPh)]
3a	2068s, 2015s, 2010s, 1973m	7.8–7.2[m, 10H, Ph], 5.28[d, ^{3}J(PH) 2.9, 2H, C*H*CH], 2.55–0.7[m, 9H, Bu^n]	−59.9[s, *P*Ph_2(SBu^n)]
3b	2063s, 2011vs, 2005vs, 1992m, 1967w	7.9–7.2[m, 10H, Ph], 5.12[d, ^{3}J(PH) 3.4, 1H, C*H*], 2.41[s, 3H, Me], 2.8–0.7[m, 9H, Bu^n]	−60.6[s, *P*Ph_2(SBu^n)]
3c	2096s, 2056s, 2027vs, 2000w	not recorded	−61.0[s, *P*Ph_2(SBu^n)]
4a	2067s, 2016vs, 2009vs, 1973w	7.8–7.0[m, 10H, Ph], 5.24[d, ^{3}J(PH) 3.0, 2H, C*H*C*H*], 1.4[s, 9H, Bu^t]	−66.1[s, *P*Ph_2(SBu^t)]
4b	2064s, 2013vs, 2006vs, 1992m, 1967w	7.7–7.1[m, 10H, Ph], 5.16[d, ^{3}J(PH) 3.7, 1H, C*H*], 2.47[s, 3H, Me], 1.37[s, 9H, Bu^t]	−66.1[s, *P*Ph_2(SBu^t)]
5a	2032s, 1990sh, 1980s, 1957w,	7.7–7.0(m, 30H, Ph), 4.25[t, ^{3}J(PH) 3.2, 2H, C*H*], 4.34[dd, ^{3}J(PH) 5.1, 1H, C(O)C*H*CH]	−49.0[s, 2*P*PH_2(SPh)]
5b	2027s, 1977s, 1954w,	8.0–6.9[m, 3OH, Ph], 4.26[d, ^{3}J(PH) 3.1, 1H, C*H*], 1.33[s, 3H, Me]	−48.7[s, 2*P*PH_2(SPh)]
5c	2035s, 1986s	7.7–6.9[m, 30H, Ph], 4.36[dd, ^{3}J(PH) 4.1, ^{3}J(PH) 3.9, 1H, C(CH_2OH)C*H*], 3.92[m, 2H, C(CH_2OH)CH]	−50.6[s, 2*P*Ph_2(SPh)]
6a	2031s, 1988vs, 1978vs, 1954w	7.7–6.9[m, 20H, Ph], 4.59[t, ^{3}J(PH) 3.4, 2H, C*H*C*H*], 2.5–0.7[m, 9H, Bu^n]	−60.7[s, 2*P*PH_2(SBu^n)]
6b	2018s, 1974vs, 1954m	7.9–7.0[m, 20H, Ph], 4.49[s, br, C*H*], 2.13[m, 3H, Me], 2.8–0.7[m, 9H, Bu^n]	−60.3[s, 2*P*PH_2(SBu^n)]
6c	2095m, 2056vs, 2027vs	7.8–7.2[m, 20H, Ph], 4.59[dd, ^{3}J(PH) 4.1, ^{3}J(PH) 3.9, 1H, C(CH_2OH)C*H*], 3.92[m, 2H, C(CH_2OH)CH], 2.8–0.7 [m, 9H, Bu^n]	−62.5[s, 2*P*Ph_2(SBu^n)]
7a	2019s, 1997vs, 1977m	7.8–7.0[m, 20H, Ph], 4.60[s, br, 2H, C*H*C*H*], 1.37[s, 9H, Bu^t]	−66.1[s, 2*P*Ph_2(SBu^t)]
7b	2016s, 1992m, 1970m	not recorded	−66.3[s, 2*P*Ph_2(SBu^t)]
8a	2054m, 2018s, 2012sh, 1980m, 1722w	7.8–7.3[m, 15H, Ph], 6.25[dd, ^{3}J(PH) 19.5, ^{3}J(HH) 4.5, 1H, C(O)CHC*H*], 4.34[dd, ^{3}J(PH) 5.1, 1H, C(O)C*H*CH]	43.0[s, μ-*P*Ph_2]
8b	2052m, 2014s, 1977s, 1688w	7.8–7.3[m, Ph, 15H], 6.20[d, ^{3}J(PH) 19.4, 1H, C(O)MeC*H*], 1.80[d, ^{4}J(PH) 4.0, 3H, C(O)C*Me*CH]	50.8[s, br, μ-PPh_2]
8c	2056m, 2017s, 1979m, 1677w	8.1–7.1[m, Ph, 15H], 6.27[d, ^{3}J(PH) 19.3, 1H, C(O)C(CH_2OH)C*H*], 4.10[dd, ^{3}J(PH) 14.0, ^{3}J(HH) 6.8, 2H, CH_2O*H*], 2.53[t, ^{3}J(HH) 6.8, 1H, CH_2O*H*]	49.4[s, μ-*P*Ph_2]
9a	2049m, 2014s, 1972m, 1654w	7.8–7.3[m, 10H, Ph], 6.12[dd, ^{3}J(PH) 19.6, ^{3}J(HH) 4.4, 1H, C(O)CHC*H*] 4.32 [dd, ^{3}J(PH) 5.2, ^{3}J(HH) 4.4, 1H, C(O)C*H*CH], 2.8–0.7[m, 9H, Bu^n]	17.8[s, μ-*P*Ph_2]
9c	2052m, 2013s, 1967m, 1655w	7.9–7.2[m, 10H, Ph], 6.11[d, ^{3}J(PH) 19.1, 1H, C(O)C(CH_2OH)C*H*], 4.13[s, br, 2H, CH_2OH], 2.8–0.7[m, 9H, Bu^n]	12.8[s, μ-*P*Ph_2]
10a	2047m, 2017s, 1982s, 1714m	not recorded	21.2[s, μ-*P*Ph_2]
10b	2045m, 2016s, 1983m, 1713m	7.7–7.1[m, 10H, Ph], 6.07[d, ^{3}J(PH) 20.0, 1H, C(O)CMeC*H*], 1.74[d, ^{4}J(PH) 3.5, 3H, C(O)C*Me*CH], 1.27[s, 9H, Bu^t]	18.1[s, μ-*P*Ph_2]

[a] Recorded in *n*-hexane solution.

[b] ^{1}H chemical shifts (δ) in ppm relative to $SiMe_4$ (0.0 ppm), 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 ppm) (upfield shifts negative), $\{^{1}H\}$-gated decoupled, measured in $CDCL_3$ at 293 K.

case shows the presence of a terminal $Ph_2P(SPh)$ ligand as a broad singlet resonance, assignable to the phosphorus atom of the ligand bound directly to a quadrupolar ^{59}Co atom. In the ^{13}C-$\{^1H\}$ NMR spectra, two carbonyl resonances of intensity ratio 3:2 suggest that the three carbonyl ligands residing on the unsubstituted cobalt are fluxional at room temperature on the NMR timescale and that the carbonyl ligands on the phosphine-substituted cobalt are either fluxional or are both coordinated pseudo-equatorially with the $Ph_2P(SR')$ group in a pseudo-axial position. X-ray studies of other reported alkyne-bridged pentacarbonyl–phosphinedicobalt complexes do show a preference for the phosphine ligands to be coordinated pseudo-axially [8].

The molecular structure of the bis-substituted complex $[Co_2(\mu\text{-HCCH})(CO)_4\{PPh_2(SBu^n)\}_2]$ **6a** complex has been determined by a single crystal X-ray diffraction study. The structure is illustrated in Fig. 1; Table 2 lists selected bond distances and angles.

The Co–Co bond [2.457(1) Å] in **6a** is bridged by an acetylene unit which lies almost perpendicular to the cobalt–cobalt bond [C(1)–Co(1)–Co(2) 50.5(2), C(1)–Co(2)–Co(1) 50.9(2), C(2)–Co(1)–Co(2) 51.3(2), C(2)–Co(2)–Co(1) 50.6(2)°]. Each cobalt atom is further bonded by two carbonyl ligands and a thiophosphine ligand which bonds *via* the phosphorus atom to complete a distorted octahedral arrangement about both metal centres. The two thiophosphine groups are orientated in a "sawhorse" configuration about the cobalt–cobalt bond occupying pseudo-axial sites on each each metal centre [Co(1)–P(1) 2.175(2) Å, P(1)–Co(1)–Co(2) 150.70(5)°; Co(2)–P(2) 2.169(2) Å, P(2)–Co(2)–Co(1) 147.82(5)°]. The configuration of $[Co_2(\mu\text{-HCCH})(CO)_4\{PPh_2(SBu^n)\}_2]$ **6a** is similar to that observed for the related complexes $[Co_2(\mu\text{-PhCCH})(CO)_4\{PPh_2(SPh)\}_2]$ [9] and $[Co_2(\mu\text{-HCCH})(CO)_4(PMe_3)_2]$ [10] with the phosphorus-containing ligands occupying pseudo-axial sites despite the resulting greater steric interactions with the bridging alkynes.

The spectroscopic properties of **6a** and the other bis-substituted complexes, **5**–**7**, are similar to those reported for analogous bis-substituted triorgano–phosphine complexes [8, 11]. The ^{31}P-$\{^1H\}$ NMR spectrum, in each case, exhibits one broad signal due to the phosphorus atoms being equivalent and directly coordinated to quadrupolar ^{59}Co atoms. In the complexes containing a symmetrical alkyne bridge (**5a**, **6a**, **7a**), one terminal carbonyl resonance is observed in the ^{13}C-$\{^1H\}$ NMR spectra. However, in the ^{13}C-$\{^1H\}$ NMR spectra of complexes containing an unsymmetrical alkyne bridge (**5b**, **5c**, **6b**, **6c**, **7b**), two terminal peaks are observed implying, either that the CO groups on each substituted cobalt atom are non-fluxional on the NMR timescale at room temperature, or that there is a fluxional process which leaves the CO groups inequivalent, such as the trigonal twist process which has been suggested elsewhere for related complexes [6].

Syntheses and properties of $[Co_2(\mu\text{-}PPh_2)\{\mu\text{-}SR'C(O)CRCH\}(CO)_4]$ **8**–**10**

Syntheses. The thermolysis of $[Co_2(\mu\text{-RCCH})(CO)_5\{PPh_2(SR')\}]$ [(R′ = Ph; R = H **2a**, Me **2b**, CH_2OH **2c**), (R′ = Bu^n; R = H **3a**, Me **3b**), (R′ = Bu^t; R = H **4a**, Me **4b**)] in toluene at 313 K gives, in addition to the starting material, the complexes $[Co_2(\mu\text{-}PPh_2)\{\mu\text{-}SR'C(O)CRCH\}(CO)_4]$ [(R′ = Ph; R = H **8a**, Me **8b**, CH_2OH **8c**), (R′ = Bu^n; R = H **9a**, Me **9b**), (R′ = Bu^t; R = H **10a**, R = Me **10b**)] in moderate yields (Scheme 1). These complexes have been characterised by ^1H, ^{13}C, ^{31}P NMR and IR spectroscopy, and by mass spectrometry and micro-

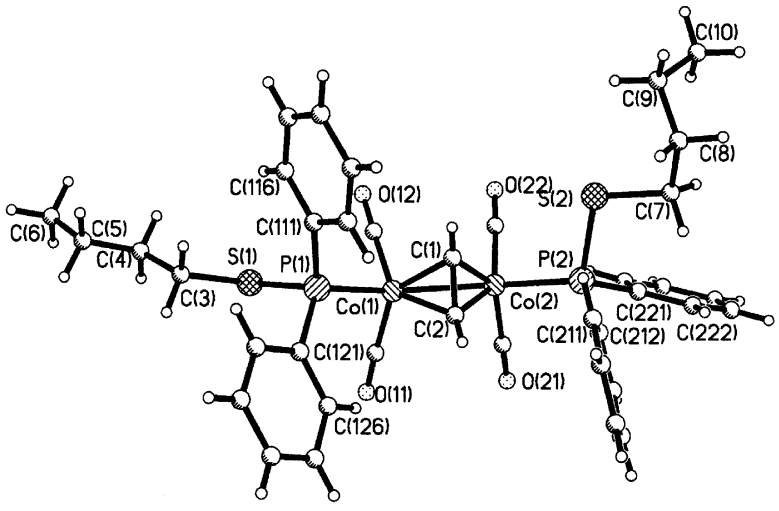


Fig. 1. Molecular structure of $[Co_2(\mu\text{-HCCH})(CO)_4\{PPh_2(SBu^n)\}_2]$ **6a** including the atom numbering scheme.

Table 2. Selected bond lengths (Å) and angles (°) for $[Co_2(\mu\text{-HCCH})(CO)_4\{PPh_2(SBu^n)\}_2]$ **6a**

Co(1)–Co(2)	2.457(1)	Co(1)–P(1)	2.175(2)
Co(2)–P(2)	2.169(2)	Co(1)–C(1)	1.946(6)
Co(1)–C(2)	1.939(6)	Co(2)–C(1)	1.934(6)
Co(2)–C(2)	1.959(6)	C(1)–C(2)	1.298(8)
P(1)–S(1)	2.072(2)	P(2)–S(2)	2.075(2)
S(1)–C(3)	1.809(6)	S(2)–C(7)	1.802(6)
Co(1)–C(11)	1.780(7)	Co(1)–C(12)	1.780(7)
Co(2)–C(21)	1.771(7)	Co(2)–C(22)	1.780(7)
Co(2)–C(1)–Co(1)	78.5(2)	Co(1)–C(2)–Co(2)	78.1(2)
C(2)–Co(1)–C(1)	39.0(2)	C(1)–Co(2)–C(2)	39.0(2)
C(1)–Co(1)–Co(2)	50.5(2)	C(2)–Co(1)–Co(2)	51.3(2)
C(1)–Co(2)–Co(1)	50.9(2)	C(2)–Co(2)–Co(1)	50.6(2)
P(1)–Co(1)–Co(2)	150.70(5)	P(2)–Co(2)–Co(1)	147.82(5)
S(1)–P(1)–Co(1)	105.21(8)	S(2)–P(2)–Co(2)	107.23(8)
	range: Co–C–O	177.4(6)–179.4(6)	

analysis. Complex **9a** has been the subject of a single crystal X-ray diffraction study.

Characterisation. The molecular structure of complex $[Co_2(\mu\text{-}PPh_2)\{\mu\text{-}SBu^nC(O)CHCH\}(CO)_4]$ **9a**, including the atom numbering scheme, is illustrated in Fig. 2. Table 3 lists selected bond distances and angles.

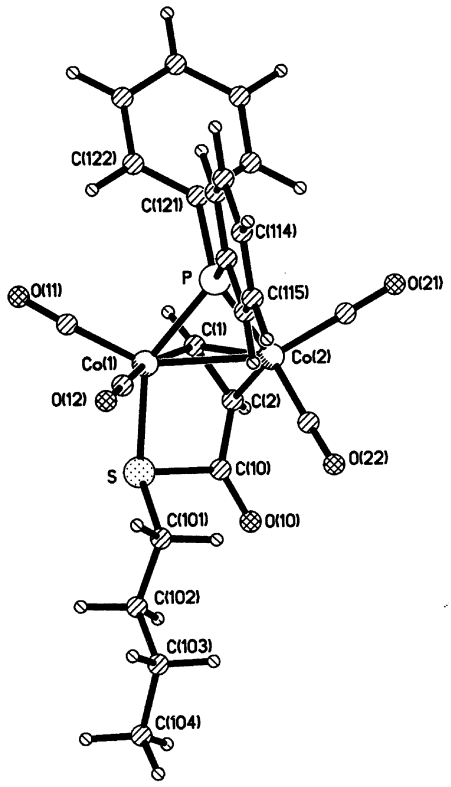


Fig. 2. Molecular structure of $[Co_2(\mu\text{-}PPh_2)\{\mu\text{-}SBu^n\text{-}C(O)CHCH\}(CO)_4]$ **9a** including the atom numbering scheme.

The single cobalt–cobalt bond [2.477(1) Å] is bridged by a diphenylphosphido group and the flyover ring [μ-$SBu^nC(O)CHCH$]. The latter is coordinated *via* S(1) and C(1) to Co(1) to form an almost planar [max. deviation from plane by C(1) 0.28 Å], five-membered metallacyclic ring [Co(1)–S–C(10)–C(2)=C(1)], in which the carbon–carbon double bond is π-coordinated to Co(2) *via* C(1) and C(2). The [μ-SBu^n-C(O)CHCH] ligand is attached to Co(1) such that S(1) and C(1) lie pseudo-*trans* and pseudo-*cis*, respectively, relative to the bridging phosphido group. The [μ-$SBu^nC(O)CHCH$] ligand is arranged in a similar manner to that of [μ-$PPh_2C(O)CHCH$] in $[Co_2(\mu\text{-}PPh_2)\{\mu\text{-}PPh_2C(O)CHCH\}(CO)_3(PPh_3)]$ [6] and shows very little structural deviation from the related complex, $[Co_2(\mu\text{-}PPh_2)\{\mu\text{-}SPhC(O)CHCH\}(CO)_4]$ **8a**, reported in an earlier communication [7]. The phosphido group bridges the two metal centres asymmetrically with Co(1)–P [2.202(2) Å] being considerably longer than Co(2)–P [2.136(2) Å]. This is presumably due to the better π-donation from Co(2) into the d-orbitals of the phosphorus [Co(2), zero oxidation state; Co(1), oxidation state II].

The spectroscopic properties of the metallacyclic ring complexes **8**–**10** are all very similar and, on this basis, can be considered to have related structures. In their IR spectra (in hexane), in addition to terminal ν_{CO} bands, weak bands at lower wavenumber (*region*: 1722–1653 cm^{-1}) corresponding to the presence of the inserted carbonyl in the [μ-SR′*C*(*O*)CRCH moiety] are observed.

The NMR spectra are particularly informative about the conformation of **8**–**10**. In the $^{31}P\text{-}\{^1H\}$ NMR spectra, one broad singlet resonance (*region*: 12.8–50.8 ppm), typical of a phosphido ligand bridging a single metal–metal bond [12] is observed for each complex. Similarly, in the ^1H NMR spectra, the orientation of the unsymmetrical olefinic moieties within the five-membered rings can be established unequivocally. When the olefinic moiety has only H sub-

Table 3. Selected bond lengths (Å) and angles (°) for $[Co_2(\mu\text{-}PPh_2)\{\mu\text{-}SBu^nC(O)CHCH\}(CO)_4]$ **9a**

Co(1)–Co(2)	2.477(1)	Co(1)–P	2.202(2)
Co(2)–P	2.136(2)	Co(1)–S	2.258(2)
S–C(10)	1.880(8)	C(10)–C(2)	1.436(10)
C(1)–C(2)	1.402(9)	Co(1)–C(1)	1.973(7)
Co(2)–C(1)	1.928(7)	Co(2)–C(2)	2.099(7)
Co(1)–C(11)	1.785(8)	Co(1)–C(12)	1.779(8)
Co(2)–C(21)	1.748(7)	Co(2)–C(22)	1.782(8)
Co(2)–C(1)–Co(1)	78.8(2)	Co(2)–P–Co(1)	69.6(1)
C(1)–C(2)–C(10)	120.7(7)	C(2)–C(1)–Co(1)	117.0(5)
C(10)–S–Co(1)	97.0(2)		
	range: Co–C–O	176.5(7)–177.6(7)	

stituents (**8a**, **9a**, **10a**) then, in addition to phosphido and thiolate group resonances, two signals both taking the form of double doublets and integrating as one proton each are seen. The downfield signal (*ca.* δ 6.2) is assigned to the [μ-SR′C(O)CHC*H*] protons, with the more upfield signal (*ca.* δ 4.3) being assigned to the [μ-SR′C(O)C*H*CH] protons. The spectra of the complexes containing an unsymmetrical olefinic fragment within the μ-SR′C(O)CRCH ligand [(R′ = Ph; R = Me **8b**, CH_2OH **8c**), (R′ = Bu^n; R = Me **9b**, CH_2OH **9c**), (R′ = Bu^t; R = Me **10b**)] display, in addition to the phosphido, thiolate and R′ group resonances, one further signal at *ca.* δ 6.2 taking the form of a doublet and integrating as one proton. The observation of only one olefinic hydrogen signal implies that the transformation is regiospecific, with the position of the signal indicating that the olefinic carbon to which the hydrogen is attached is σ-bonded to one of the cobalt atoms. It is noteworty that regiospecificity is not observed in the related thermolytic reaction of $[Co_2(\mu\text{-}CRCH)(CO)_6]$ (R = Me **1b**, CH_2OH **1c**) with $Ph_2P(PPh_2)$ in which an approximately 1:1 mixture of $[Co_2(\mu\text{-}PPh_2)\{\mu\text{-}PPh_2C(O)CRCH\}(CO)_4]$ and $[Co_2(\mu\text{-}PPh_2)\{\mu\text{-}PPh_2C(O)CHCR\}(CO)_4]$ is obtained, although in this instance these are not the major products of the reactions [6].

In the $^{13}C\text{-}\{^1H\}$ NMR spectra of complexes **8**–**10**, in addition to upfield peaks corresponding to the olefinic carbon atoms, clearly identifiable signals are observed at lower fields for the terminal carbonyl [*range*: δ 207.8–198.8] groups and for the C(O) moieties [*range*: δ 184.2–178.8] of the bridging ligands. In most cases, all four of the terminal CO groups give rise to distinct resonances, suggesting the carbonyl ligands are non-equivalent at room temperature.

^{13}CO *labelling studies*. The facility with which the C(O)–CRCR link can be cleaved in a number of bimetallic complexes [1, 2] has prompted us to examine the possibility of similar cleavage within the SR′C(O)CRCH ligand using complex **8a** as a representative example.

Figure 3(a) shows the carbonyl region of the $^{13}C\text{-}\{^1H\}$ NMR spectrum at room temperature of ^{13}CO enriched **8a** $[Co_2(\mu\text{-}PPh_2)\{\mu\text{-}SPh^{13}C(O)CHCH\}(^{13}CO)_4]$, prepared by the reaction of a ^{13}CO enriched sample of **1a** with $Ph_2P(SPh)$. The enrichment is non-selective and five signals are seen; the four more downfield broader signals [δ 206.4, 202.3, 201.8, 198.9] correspond to the carbonyl groups bound to the quadrupolar cobalt atoms, while the sharper singlet resonance at δ 184.2 is due to the C(O) group incorporated into the bridging ligand. In Fig. 3(b) the ^{13}CO spectrum of complex **8a**, enriched by treating **8a** with ^{13}CO at 293 K, is shown. Two significant points emerge from a study of this latter spectrum: (i) the observed ^{13}CO enrichment of the ketonic C(O) group shows that this group exchanges rapidly with ^{13}CO gas at room temperature and (ii) only two of the four terminal carbonyl groups exchange. Accordingly the complex may be formulated as $[Co_2(\mu\text{-}PPh_2)\{\mu\text{-}SPh^{13}C(O)CHCH\}(^{13}CO)_2(CO)_2]$.

The substitution by ^{13}CO gas of the ketonic carbonyl group in solution at room temperature implies that, remarkably under these mild conditions, **8a** readily and reversibly undergoes both olefin–carbonyl and sulphur–carbonyl bond cleavage since these are both necessary for the labelling process. Scheme 2 shows a series of equilibria, the existence of which could account for the labelling process. Although we were unable to detect in solution by NMR spectroscopy any of the postulated intermediate species **A**, **B** or **C**, related complexes containing the proposed or similar bridging ligands have been isolated and shown to undergo carbonylation and/or decarbonylation reactions. Thus, examples of the reversible coupling of alkynes with CO groups on bimetallic centres have been well documented [1, 2, 3] although rare in dicobalt chemistry [13]. Dixneuf *et al.* have demonstrated the reversible decarbonylation reaction of the phosphide-containing metallacyclic ring species $[RuCo(\mu\text{-}CO)\{\mu\text{-}PPh_2C(O)CRCR'\}(CO)_5]$ to give $[RuCo(\mu\text{-}CO)\{\mu\text{-}PPh_2CRCR'\}(CO)_5]$ [14] which presumably proceeds via a similar set of equilibria. It should be noted that intermediate species **C** is not required for ^{13}CO exchange to take place but stable complexes containing a PhSCRCR bridging ligand are known

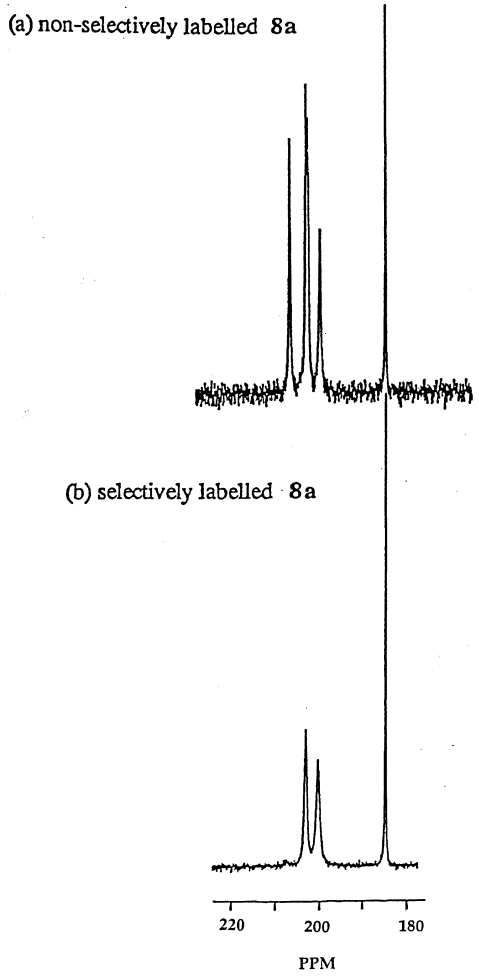


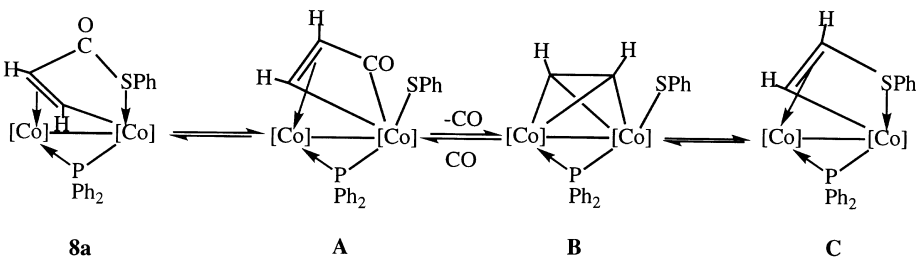
Fig. 3. Carbonyl regions of the ^{13}C-{^{1}H} NMR spectra of (a) non-selectivity labelled $[Co_2(\mu\text{-}PPh_2)\{\mu\text{-}SPH^{13}C(O)CHCH\}(^{13}CO)_4]$ **8a** and (b) selectively labelled $[Co_2(\mu\text{-}PPh_2)\{\mu\text{-}SPh^{13}C(O)CHCH\}(^{13}CO)_2(CO)_2]$ **8a**.

[15] and it seems likely that intermediate **B**, if it is formed, would be in equilibrium with a further intermediate of this type.

The other observation concerning the labelling, namely that only two of the four terminal carbonyl ligands in **8a** become labelled, is more difficult to explain and it is not clear which two are labelled. Two possible assigments are shown in Scheme 3; in (i) labelling of two carbonyl groups at one metal centre is proposed and in (ii) labelling has occurred at the axial sites of each metal centre. The observed spectra do not permit a distinction between these assignments. It is noteworthy, however, that substitution of carbonyl groups by phosphites or phosphines in complexes possessing the $(OC)_2Co\text{–}Co(CO)_2$ skeleton display a preference for sites axial to the metal–metal bond [4, 6, 7] and it may be that the ^{13}CO substitution favours only the axial sites.

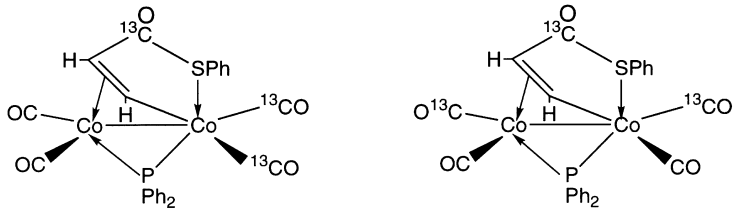
CONCLUSIONS

In all cases, the reactions of thiophosphines with alkyne–hexacarbonyldicobalt complexes proceed by initial coordination of the intact $Ph_2P(SR')$ ligand, followed by phosphorus–sulphur bond cleavage and subsequent coupling of the thiolate fragment with a coordinated CO and CRCH group on the dicobalt complex. The transformations are regiospecific, such that the bulky substituent on the olefinic group is positioned adjacent to the ketonic group. In no case does the generated phosphide fragment couple with the alkyne or the CO groups, instead preferring to adopt a bridging mode between the metal centres. This result may be contrasted with the corresponding reactions of related molybdenum–cobalt alkyne-bridged systems which react with $Ph_2P(SR')$ to give products in which the PPh_2 fragment is linked to the alkyne moiety while the thiolate fragment bridges the metal centres [15]. This difference may be kinetic or thermodynamic in origin but the ready rearrangement of the SPhC(O)CHCH-bridged complex to a $PPh_2CHCHC(O)$-bridged species on bis-phosphine substitution [7], suggests that any kinetic barriers are low. This suggestion is supported by the results from the ^{13}CO labelling of **8a**, which shows that the SR′C(O)CRCH ligand fragments readily and reversibly under mild conditions. In the absence of phosphines therefore, the preference for the SR′ group to be coupled to the organic moiety and for the Ph_2P



8a **A** **B** **C**

Scheme 2. A possible pathway to account for the ^{13}CO labelling of the ketonic carbonyl group in **8a**. Terminal carbonyl groups have been omitted for clarity.



Scheme 3. Two possible assignments for the selectively ^{13}CO labelled terminal carbonyl groups in **8a**.

group to bridge the two metal centres is probably thermodynamically determined.

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 mesh) 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 [17]. Unless otherwise stated, all reagents were obtained from commercial suppliers and the compounds $[Co_2(\mu\text{-}RCCH)(CO)_6]$ (R = H **1a**, Me **1b**, CH_2OH **1c**) and $Ph_2P(SPh)$ were prepared by literature methods [18, 19, 20].

Synthesis of the ligands $Ph_2P(SR')$ ($R' = Bu^n$ *or* Bu^t)

To a solution of NaH (2.00 g, 0.08 mol) in THF (200 cm^3), was added R′SH ($R' = Bu^n$ or Bu^t, 8.8 cm^3, 0.08 mol) and the solution was left to stir. After 2 h, Ph_2PCl (15.0 cm^3, 0.08 mol) was added and the mixture was stirred for a further 3 h. The solvent was removed under reduced pressure and the residue was dissolved in hot toluene and filtered. Removal of the toluene from the filtrate gave $Ph_2P(SBu^n)$ (20.20 g, 92%) as a clear liquid, while pure $Ph_2P(SBu^t)$ (20.03 g, 92%) could be obtained by recrystallisation of the residue from hexane. Compound $Ph_2P(SBu^n)$: fast atom bombardment (FAB) mass spectrum, m/z 274 (M^+). ^1H NMR: δ 2.80[m, 2H, CH_2-S], 1.69[m, 2H, CH_2CH$_2$S], 1.49[m, 2H, CH_2CH$_2$CH$_2$S] and 0.95[m, 3H, CH_3CH$_2$CH$_2$CH$_2$S]. ^{31}P-$\{^1H\}$ NMR: δ −113.0. ^{13}C-$\{^1H\}$ NMR: δ 142–128[m, Ph], 32.5[s, CH$_2$S], 32.3[s, CH$_2$CH$_2$S], 20.0[s, CH$_2$CH$_2$CH$_2$S] and 11.1[s, CH$_3$CH$_2$CH$_2$CH$_2$]. Compound $Ph_2P(SBu^t)$: FAB mass spectrum, m/z 274 (M^+). ^{31}P-$\{^1H\}$ NMR: δ −130.5.

Reactions of $[Co_2(\mu\text{-}CRCH)(CO)_6]$ **1** *with* $Ph_2P(SR')$

(i) To a solution of $[Co_2(\mu\text{-}HCCH)(CO)_6]$ **1a** (1.00 g, 3.21 mmol) in toluene (50 cm^3) was added $Ph_2P(SR')$ ($R' = Ph$, 0.944 g, 3.21 mmol; Bu^n, 0.881 g, 3.21 mmol; Bu^t, 0.881 g, 3.21 mmol) in toluene (50 cm^3). The solutions were stirred at 298 K for 24 h and, after removal of the solvent under reduced pressure, the mixtures were adsorbed onto a minimum amount of silica, added to the top of chromatography columns and purified by eluting with hexane–dichloromethane (10:1). This gave, in addition to a small amount of unreacted starting material, orange $[Co_2(\mu\text{-}CHCH)(CO)_5\{PPh_2(SR')\}]$ [$R' = Ph$ **2a** (1.149 g, 62%); $R' = Bu^n$ **3a** (1.075 g, 60%); $R' = Bu^t$ **4a** (1.038 g, 58%)] and orange crystalline $[Co_2(\mu\text{-}CHCH)(CO)_4\{PPh_2(SR')\}_2]$ [$R' = Ph$ **5a** (0.379 g, 14%); $R' = Bu^n$ **6a** (0.387 g, 15%); $R' = Bu^t$ **7a** (0.390 g, 15%)]. Complex **2a**: FAB mass spectrum, m/z 578 (M^+) and M^+-nCO (n = 1–5). ^{13}C NMR ($CDCl_3$, 293 K, ^1H composite pulse decoupled): δ 204.1(s, 2CO), 201.5(s, 3CO), 136–127(m, Ph) and 70.6(s, 2CH). Complex **5a**: FAB mass spectrum, m/z 844 (M^+) and M^+-nCO (n = 1–4). ^{13}C NMR ($CDCl_3$, 293 K, ^1H composite pulse decoupled): δ 206.0(s, 4CO), 136–128(m, Ph) and 70.9(s, 2CH). Complex **3a** (Found: C, 49.7; H, 3.8. $C_{23}H_{21}Co_2PSO_5$ requires C, 49.5; H, 3.8): FAB mass spectrum, m/z 558 (M^+) and (M^+-nCO) (n = 1–5). NMR ($CDCl_3$); ^{13}C(^1H composite pulse decoupled), δ 204.5[s, 2CoCO], 201.8[s, 3CoCO], 135–127[m, Ph], 70.7[s, CHCH], 32.4[s, CH_2], 31.7[s, CH_2], 21.7[s, CH_2] and 13.4[s, CH_3]. Complex **6a** (Found: C, 56.6; H, 5.0. $C_{38}H_{40}Co_2P_2S_2O_4$ requires C, 56.7; H, 5.0): FAB mass spectrum, m/z 804 (M^+) and (M^+-nCO) (n = 1–4). NMR ($CDCl_3$); ^{13}C(^1H composite pulse decoupled), δ 206.0[s, 4CoCO], 134–128[m, Ph], 70.7[s, CHCH], 32.5[s, CH_2], 32.0[s, CH_2], 22.7[s, CH_2] and 13.5[s, CH_3]. Complex **4a**: FAB mass spectrum, m/z 558 (M^+) and (M^+-nCO) (n = 1–5). NMR ($CDCl_3$); ^{13}C(^1H composite pulse decoupled), δ 205.0[s, 2CoCO], 201.9[s, 3CoCO], 137–127[m, Ph], 71.7[s, CHCH] and 32.6[s, Bu^t]. Complex **7a**: FAB mass spectrum, m/z 804 (M^+) and (M^+-nCO) (n = 1–4). NMR ($CDCl_3$); ^{13}C(^1H composite pulse decoupled), δ 206.1[s, 2CoCO], 205.9[s, 2CoCO], 135–127[m, Ph], 72.0[s, CHCH] and 32.5[s, Bu^t].

(ii) To a solution of $[Co_2(\mu\text{-MeCCH})(CO)_6]$ **1b** (1.00 g, 3.07 mmol) in toluene (50 cm^3) was added $Ph_2P(SR')$ (R′ = Ph, 0.902 g, 3.07 mmol; Bu^n, 0.841 g, 3.07 mmol; Bu^t, 0.841 g, 3.07 mmol) in toluene (50 cm^3). The solutions were stirred at 298 K for 24 h and after removal of the solvent under reduced pressure, the mixtures were adsorbed onto a minimum amount of silica, added to the top of chromatography columns and purified by eluting with hexane–dichloromethane (10:1). This gave, in addition to a small amount of unreacted starting material, orange $[Co_2(\mu\text{-CMeCH})(CO)_5\{PPh_2(SR')\}]$ [R′ = Ph **2b** (1.117 g, 63%); R′ = Bu^n **3b** (0.913 g, 52%); R′ = Bu^t **4b** (0.842 g, 48%)] and orange crystalline $[Co_2(\mu\text{-CMeCH})(CO)_4\{PPh_2(SR')\}_2]$ [R′ = Ph **5b** (0.342 g, 13%); R′ = Bu^n **6b** (0.352 g, 14%); R′ = Bu^t **7b** (0.251 g, 10%)]. Complex **2b** (Found: C, 52.8; H, 3.4; P, 5.3. $C_{26}H_{19}Co_2PSO_5$ requires C, 52.7; H, 3.2; P, 5.2): FAB mass spectrum, m/z 592 (M^+) and (M^+-nCO) (n = 1–5). NMR ($CDCl_3$); $^{13}C\{^1H$ composite pulse decoupled), δ 205.2[s, CoCO], 204.0[s, CoCO], 202.3[s, 3CO], 136–128[m, Ph], 89.8[s, *C*Me], 72.9[s, *C*H] and 19.4[s, Me]. Complex **5b**: FAB mass spectrum, m/z 858 (M^+) and (M^+-nCO) (n = 1–4). NMR ($CDCl_3$); $^{13}C\{^1H$ composite pulse decoupled), δ 206.2[s, 2CoCO], 205.9[s, 2CoCO], 136–127[m, Ph], 86.3[s, *C*Me], 72.5[s, *C*H] and 18.0[s, Me]. Complex **3b**: FAB mass spectrum, m/z 572 (M^+) and (M^+-nCO) (n = 1–5). NMR ($CDCl_3$); $^{13}C\{^1H$ composite pulse decoupled), δ 207.0[s, CoCO], 206.0[s, CoCO], 202.3[s, 3CoCO], 135–125[m, Ph], 88.8[s, *C*Me], 72.8[s, *C*H], 32.4[s, CH_2], 31.7[s, CH_2], 21.7[s, CH_2], 19.5[s, Me] and 13.4[s, CH_2CH_3]. Complex **5b**: FAB mass spectrum, m/z 818 (M^+) and (M^+-nCO) (n = 1–4). NMR ($CDCl_3$); $^{13}C\{^1H$ composite pulse decoupled), δ 206.0[s, 2CoCO], 205.9[s, 2CoCO], 136–128[m, Ph], 88.4[s, *C*Me], 72.1[s, *C*H], 32.3[s, CH_2], 31.9[s, CH_2], 21.8[s, CH_2], 18.1[s, Me] and 13.4[s, CH_2CH_3]. Complex **4b**: FAB mass spectrum, m/z 572 (M^+) and (M^+-nCO) (n = 1–5). NMR ($CDCl_3$); $^{13}C\{^1H$ composite pulse decoupled), δ 205.5[s, CoCO], 204.5[s, CoCO], 202.0[s, 3CoCO], 135–128[m, Ph], 89.0[s, *C*Me], 73.0[s, *C*H], 52.7[s, $C(CH_3)$], 32.6[s, $C(CH_3)_3$] and 19.3[s, Me]. Complex **7b**: FAB mass spectrum, m/z 818 (M^+) and (M^+-nCO) (n = 1–4).

(iii) To a solution of $[Co_2\{\mu\text{-}(CH_2OH)CCH\}(CO)_6]$ **1c** (1.00 g, 2.92 mmol) in toluene (50 cm^3) was added $Ph_2P(SR')$ (R′ = Ph, 0.860 g, 2.92 mmol; R′ = Bu^n, 0.801 g, 2.92 mmol) in toluene (50 cm^3). The solutions were stirred at 298 K for 24 h and after removal of the solvent under reduced pressure, the mixtures were adsorbed onto a minimum amount of silica, added to the top of chromatography columns and purified by eluting with hexane–ethylacetate (10:1). This gave, in addition to a small amount of unreacted starting material, orange $[Co_2\{\mu\text{-}(CH_2OH)CCH\}(CO)_5\{PPh_2(SR')\}]$ [R′ = Ph **2c** (1.134 g, 64%); R′ = Bu^n 3c (1.064 g, 62%)] and orange crystalline $[Co_2\{\mu\text{-}(CH_2OH)CCH\}(CO)_4\{PPh_2(SR')\}_2]$ [R′ = Ph **5c** (0.434 g, 17%); R′ = Bu^n **6c** (0.438 g, 18%)]. Complex **2c**: FAB mass spectrum, m/z 608 (M^+) and (M^+-nCO) (n = 1–5). NMR ($CDCl_3$); $^{13}C\{^1H$ composite pulse decoupled), Δ 205.7[s, br, 2CoCO], 205.1[s, 3CoCO], 135–128[m, Ph], 92.9[s, *C*(CH_2OH)CH], 70.1[s, C(CH_2OH)*C*H] and 62.8[s, C(*C*H_2OH)CH]. Complex **5c**: FAB mass spectrum, m/z 874 (M^+) and (M^+-nCO) (n = 1–4). NMR ($CDCl_3$); $^{13}C\{^1H$ composite pulse decoupled), δ 205.2[s, 2CoCO], 201.9[s, 2CoCO], 135–128[m, Ph], 91.2[s, *C*(CH_2OH)CH], 69.7[s, C(CH_2OH)*C*H] and 61.9[s, C(*C*H_2OH)CH]. Complex **3c**: FAB mass spectrum, m/z 588 (M^+) and (M^+-nCO) (n = 1–5). NMR ($CDCl_3$); $^{13}C\{^1H$ composite pulse decoupled), δ 206.0[s, CoCO], 203.5[s, CoCO], 201.0[s, 3CoCO], 134–128[m, Ph], 92.4[s, *C*(CH_2OH)CH], 70.8[s, C(CH_2OH)*C*H], 63.0[s, C(*C*H_2OH)CH], 32.4[s, CH_2], 31.7[s, CH_2], 21.7[s, CH_2] and 13.4[s, CH_3]. Complex **6c**: FAB mass spectrum, m/z 834 (M^+) and (M^+-nCO) (n = 1–4). NMR ($CDCl_3$); $^{13}C\{^1H$ composite pulse decoupled), δ 206.0[s, br, 4CoCO], 135–128[m, Ph], 92.0[s, *C*(CH_2OH)CH], 70.0[s, C(CH_2OH)*C*H], 62.9[s, C(*C*H_2OH)CH], 32.5[s, CH_2], 31.8[s, CH_2], 21.8[s, CH_2] and 13.4[s, CH_3].

Syntheses of $[Co_2(\mu\text{-}PPh_2)\{\mu\text{-SR′C(O)CRCH}\}(CO)_4]$ **8–10**

(i) Solutions of $[Co_2(\mu\text{-CHCH})(CO)_5\{PPh_2(SR')\}]$ (R′ = Ph **2a**, 0.289 g, 0.50 mmol; R′ = Bu^n **3a**, 0.300 g, 0.54 mmol; R′ = Bu^t **4a**, 0.300 g, 0.54 mmol) in toluene (50 cm^3) were thermolysed at 313 K for 5–8 h. After removal of the solvent under reduced pressure, the mixtures were purified using preparative TLC with hexane–dichloromethane (6:1) as eluent to give, in addition to a small amount of unreacted starting material, the red crystalline complexes $[Co_2(\mu\text{-}PPh_2)\{\mu\text{-SR′C(O)CHCH}\}(CO)_4]$ [R′ = Ph **8a** (0.173 g, 60%); R′ = Bu^n **9a** (0.168 g, 56%); R′ = Bu^t **10a** (0.159 g, 53%)]. Complex **8a** (Found: C, 51.6; H, 3.2; P, 5.5. $C_{25}H_{17}Co_2O_5PS$ requires C, 51.9; H, 3.0; P, 5.4): FAB mass spectrum, m/z 578 (M^+) and M^+-nCO (n = 1–5). ^{13}C NMR ($CDCl_3$, 293 K, ^1H composite pulse decoupled): δ 206.4(s, CO), 202.3(s, CO), 201.8(s, CO), 198.9(s, CO), 181.7[s, SPh*C*(O)CHCH], 142–128(m, Ph), 124.0[d, br, ^2J(PC) 30, SPhC(O)CH*C*H] and 63.1[s, br, SPhC(O)*C*HCH]. Complex **9a** (Found: C, 49.5; H, 3.8. $C_{23}H_{21}Co_2O_5PS$ requires C, 49.5; H, 3.8): FAB mass spectrum, m/z 558 (M^+) and M^+-nCO (n = 1–4). ^{13}C NMR ($CDCl_3$, 293 K, ^1H composite pulse decoupled): δ 206.6(s, CoCO), 202.9(s, CoCO), 202.0(s, CoCO), 199.0(s, CoCO), 184.2[s, SBu^nC(O)CHCH], 141–128(m, Ph), 124.0[d, ^2J(PC) 34, SBu^nC(O)CH*C*H], 62.7[s, SBu^n-C(O)*C*HCH], 29.7[s, CH_2], 29.4[s, CH_2], 21.9[s, CH_2] and 13.6[s, CH_3]. Complex **10a**: FAB mass spectrum, m/z 558 (M^+) and M^+-nCO (n = 1–4).

(ii) Solutions of $[Co_2(\mu\text{-CMeCH})(CO)_5\{PPh_2(SR')\}]$ (R′ = Ph **2b**, 0.289 g, 0.50 mmol; R′ = Bu^n **3b**, 0.300 g, 0.54 mmol; R′ = Bu^t **4b**, 0.300 g, 0.54 mmol) in toluene

($50\,cm^3$) were thermolysed at 313 K for 5–8 h. After removal of the solvent under reduced pressure, the mixtures were purified using preparative TLC with hexane–dichloromethane (6:1) as eluent to give, in addition to a small amount of unreacted starting material, the red crystalline complexes $[Co_2(\mu\text{-}PPh_2)\{\mu\text{-}SR'C(O)CMeCH\}(CO)_4]$ [R′ = Ph **8b** (0.173 g, 60%); R′ = Bu^n **9b** (0.168 g, 56%; R′ = Bu^t **10b** (0.159 g, 53%)]. Complex **8b** (Found: C, 52.4; H, 3.4; P, 5.4. $C_{26}H_{19}Co_2O_5PS$ requires C, 52.7; H, 3.2; P, 5.2): FAB mass spectrum, *m*/*z* 592 (M^+) and M^+-*n*CO (*n* = 1–5). ^{13}C NMR ($CDCl_3$, 293 K, ^{1}H composite pulse decoupled): δ 207.8(s, CoCO), 202.7(s, CoCO), 202.0(s, CoCO), 199.4(s, CoCO), 178.8[s, SPh*C*(O)CMeCH], 142–127[m, Ph and SPhC(O)C-Me*C*H], 78.9[s, br, SPhC(O)*C*MeCH] and 23.6[s, Me]. Complex **9b**: FAB mass spectrum, *m*/*z* 572 (M^+) and M^+-*n*CO (*n* = 1–4). ^{13}C NMR ($CDCl_3$, 293 K, ^{1}H composite pulse decoupled): δ 207.4(s, CoCO), 207.0(s, 2CoCO), 198.8(s, CoCO), 181.3[s, SBu^n-*C*(O)CMeCH], 141–128(m, Ph), 126.6[d, ^2J(PC) 33, SBu^{n}C(O)CMe*C*H], 70.6[s, SBu^{n}C(O)*C*MeCH], 29.7[s, CH_2], 29.4[s, CH_2], 21.9[s, SBu^{n}C(O)C*Me*CH], 21.7[s, CH_2] and 13.6[s, CH_3]. Complex **10b**: FAB mass spectrum, *m*/*z* 572 (M^+) and M^+-*n*CO (*n* = 1–4).

(iii) Solutions of $[Co_2\{\mu\text{-}(CH_2OH)CCH\}(CO)_5\{PPh_2(SR')\}]$ (R′ = Ph **2a**, 0.289 g, 0.50 mmol; R′ = Bu^n **3a**, 0.300 g, 0.54 mmol; R′ = Bu^t **4a**, 0.300 g, 0.54 mmol) in toluene ($50\,cm^3$) were thermolysed at 313 K for 5–8 h. After removal of the solvent under reduced pressure, the mixtures were purified using preparative TLC with hexane–dichloromethane (6:1) as eluent to give, in addition to a small amount of unreacted starting material, the red crystalline complexes $[Co_2(\mu\text{-}PPh_2)\{\mu\text{-}SR'C(O)C(CH_2OH)CH\}(CO)_4]$ [R′ = Ph **8c** (0.173 g, 60%); R′ = Bu^n **9c** (0.168 g, 56%)]. Complex **8c** (Found: C, 50.9; H, 3.4. $C_{26}H_{19}Co_2O_6PS$ requires C, 51.3; H, 3.1): FAB mass spectrum, *m*/*z* 608 (M^+) and M^+-*n*CO (*n* = 1–4). ^{13}C NMR ($CDCl_3$, 293 K, ^{1}H composite pulse decoupled): δ 206.5(s, CoCO), 201.8(s, 2CoCO), 198.9(s, CoCO), 180.5[s, SPh*C*(O)C(CH_2OH)CH], 142–128[m, Ph], 126.2[d, ^2J(PC) 33 SPhC(O)C-(CH_2OH)*C*H], 66.3[s, SPhC(O)C(*C*H_2OH)CH] and 63.4[s, SPhC(O)*C*(CH_2OH)CH]. Complex **9c**: FAB mass spectrum, *m*/*z* 588 (M^+) and M^+-*n*CO (*n* = 1–4). ^{13}C NMR ($CDCl_3$, 293 K, ^{1}H composite pulse decoupled): δ 207.0(s, CoCO), 204.0(s, CoCO), 202.0(s, CoCO), 200.0(s, CoCO), 183.3[s, SBu^n-*C*(O)C(CH_2OH)CH], 142–128(m, Ph), 128.3[d, ^2J(PC) 33, SBu^{n}C(O)C(CH_2OH)*C*H], 66.5[s, SBu^n-C(O)C(*C*H_2OH)CH], 64.9[s, SBu^{n}C(O)*C*(CH_2OH)CH], 29.7[s, CH_2], 29.0[s, CH_2], 21.9[s, CH_2] and 13.5[s, CH_3].

Isotopic labelling experiments

Isotopic enrichment of **1a**. Complex $[Co_2(\mu\text{-}HCCH)(CO)_6]$ **1a** (1.00 g, 3.21 mmol) was dissolved in toluene ($50\,cm^3$). The solution was degassed under reduced pressure, back-filled with an atmosphere of ^{13}CO and left to stir at 293 K for 24 h. The reaction mixture was filtered and the solvent removed under reduced pressure to give the isotopically labelled species $[Co_2(\mu\text{-}HCCH)(^{13}CO)_n(^{12}CO)_n]$ (*n* = 1–6). NMR evidence shows a degree of enrichment >90% had been achieved.

Preparation of non-selectively labelled **8a**. The non-selectively labelled complex $[Co_2(\mu\text{-}PPh_2)\{\mu\text{-}SPh^{13}C(O)CHCH\}(^{13}CO)_4]$ **8a** was prepared using the procedure outlined in parts (b) and (c) above, starting from an isotopically enriched sample of **1a**.

Preparation of selectively labelled **8a**. Complex $[Co_2(\mu\text{-}PPh_2)\{\mu\text{-}SPhC(O)CHCH\}(CO)_4]$ **8a** (0.200 g, 0.35 mmol) was dissolved in toluene ($50\,cm^3$). The solution was degassed under reduced pressure, back-filled with an atmosphere of ^{13}CO and left to stir at 293 K for 24 h. The reaction mixture was filtered and the solvent removed under reduced pressure to give the selectively labelled species $[Co_2(\mu\text{-}PPh_2)\{\mu\text{-}SPh^{13}C(O)CHCH\}(^{13}CO)_2(CO)_2]$. NMR evidence shows a degree of enrichment of the labelled carbonyl groups to be >90%.

Crystal structure analysis of complexes **6a** *and* **9a**

Crystal data for $[Co_2(\mu\text{-}HCCH)(CO)_4\{PPh_2(SBu^n)\}_2]$ **6a**. $C_{38}H_{40}Co_2O_4P_2S_2$, M = 804.62, triclinic, space group $P\bar{1}$ (no. 2), a = 10.634(2), b = 13.563(3), c = 13.864(3) Å, a = 74.16(2), b = 82.46(2), γ = 81.26(2)°, U = 1892.8(7) Å^3, D_c = 1.412 g cm^{-3}, Z = 2, μ(Mo–K_α) = 11.0 cm^{-1}, $F(000)$ = 832.

Data collection for **6a**. An orange crystal of size 0.06 × 0.46 × 0.48 mm was used in data collection. Intensity data were collected on a Siemens R3m/V diffractometer at 295 K, using ω-2θ scan mode with graphite monochromated Mo–K_α radiation (λ = 0.71073 Å). No significant drift was encountered during data collection. 13271 reflections ($-12 \le h \le 12$, $-15 \le k \le 15$, $-16 \le l \le 16$) were collected in the range θ 1.5–25.0° with a scan width of 1.20°, to give 6636 (R_{int} = 0.0640) independent reflections with $I/\sigma(I) > 2.0$.

Structure solution and refinement for **6a**. All intensity data were corrected for Lorentz polarisation effects, and absorption corrections by the ψ-scan method; minimum and maximum transmission factors 0.3161 and 0.3804. Computations were performed using the SHELTXL PLUS package [21]. The structure was solved by a combination of Patterson synthesis (Co atoms) and Fourier-difference techniques. The structure was refined by full matrix least squares with all atoms assigned anisotropic displacement parameters [22]. Hydrogen atoms were placed in idealised positions and allowed to ride on the relevant carbon atoms. Residual electron densisty found after all atoms had been assigned, was successfully attributed to disorder of the butyl fragment of one of the PPh_2(S-

Bu^n) ligands and this was included in the final refinement. In the final cycles of refinement, a weighting scheme of the form $\omega^{-1}=\sigma^2(F)+0.010F^2$ gave satisfactory agreement analysis. The refinement converged to $R=0.0553$, w$R=0.1088$ and a goodness of fit $=1.002$, with a final shift/esd of 0.019 and a residual electronic density of less than 1 e Å^{-3}.

Crystal data for $[Co_2(\mu\text{-}PPh_2)\{\mu\text{-}SBu^n C(O)CHCH\}(CO)_4]$ **9a**. $C_{23}H_{21}Co_2O_5PS$, $M=558.29$, orthorhombic, space group $P2_12_12_1$, $a=10.240(3)$, $b=10.612(4)$, $c=22.160(4)$ Å, $U=2408.1(6)$ Å^3, $D_c=1.540$ g cm^{-3}, $Z=4$, μ(Mo–K_a)$=10.6$ cm^{-1}, $F(000)=1136$.

Data collection for **9a**. A red crystal of size $0.25\times0.34\times0.29$ mm was used in data collection. Intensity data were collected on a 4 circle Philips diffractometer at 295 K, using ω-2θ scan modewith graphite monochromated Mo–K_α radiation ($\lambda=0.71073$ Å). No significant drift was encountered during data collection. 2438 reflections ($0\le h\le14$, $0\le k\le14$, $0\le l\le29$) were collected in the range θ 3–25°, with a scan width of 0.70°. Equivalent reflections were merged to give 1972 ($R_{int}=0.0644$) independent reflections with $I/\sigma(I)>3.0$.

Structure solution and refinement of **9a** [23]. The fractional coordinates of the metal atoms were obtained from a Patterson synthesis; remaining non-hydrogen atoms were located from subsequent Fourier-difference syntheses. The hydrogen atoms of this structure were included in geometrically idealised postions and constrained to ride on the relevant carbon atoms in calculated positions of C–H 1.080 Å with fixed thermal parameters of 0.08 Å^2, but were not refined. After initial refinement with isotropic thermal parameters for all atoms, empirical absorption correction were applied [24]. In the final stages of full matrix refinement the two metal atoms, the S and P atoms on the bridging ligands and the atoms of the CO groups were treated as anisotropically vibrating atoms. The final shift/esd was 0.032 and there was a residual electronic density of less than 1 e Å^{-3}. Refinement converged with reliability factors of $R=0.039$ and Rw$=0.042$ and with weights of $1/\sigma^2F_o$ assigned to individual reflections [23].

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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REFERENCES

1. (a) Checuti, M. J., Grant, B. E., Fanwick, P. E., *Organometallics*, 1995, **14**, 2937; (b) Checuti, M. J., Eigenbrot, C., Green, K. A., *Organometallics*, 1987, **6**, 2298; (c) Checuti, M. J., Grant, B. E., Fanwick, P. E., *Organometallics*, 1996, **15**, 4389; (d) Boag, N. M., Goodfellow, R. J., Green, M., Hessner, B., Howard, J. A. K., Stone, F. G. A., *J. Chem. Soc., Dalton Trans.*, 1983, 2585; (e) Gracey, B. P., Knox, S. A. R., Macpherson, K. A., Orpen, A. G., Stobart, S. R., *J. Chem. Soc., Dalton Trans.*, 1985, 1935; (f) Wong, A., Pawlick, R. V., Thomas, C. G., Leon, D. R., Liu, L.-K., *Organometallics*, 1991, **10**, 530; (g) Hogarth, G., Kayser, F., Knox, S. A. R., Morton, D. A. V., Orpen, A. G., Turner, M. L., *J. Chem. Soc., Chem. Commun.*, 1988, 358; (h) Fontaine, X. L. R., Jacobsen, G. B., Shaw, B. L., Thornton-Pett, M., *J. Chem. Soc., Dalton Trans.*, 1988, 741; (i) Dickson, R. S., Gatehouse, B. M., Nesbit, M. C., Pain, G. N., *J. Organomet. Chem.*, 1981, **215**, 97.
2. (a) Finnimore, S. R., Knox, S. A. R., Taylor, G. E., *J. Chem. Soc., Dalton Trans.*, 1982, 1783; (b) Dyke, A. F., Knox, S. A. R., Morris, M. J., Naish, P. J., *J. Chem. Soc., Dalton Trans.*, 1983, 1417.
3. Dickson, R. S., Evans, G. S. and Fallon, G. D., *Aust. J. Chem.*, 1985, **38,** 273.
4. (a) Martín, A., Mays, M. J., Raithby, P. R., Solan, G. A., *J. Chem. Soc., Dalton Trans.*, 1993, 1789; (b) Caffyn, A. J. M., Martín, A., Mays, M. J., Raithby, P. R., Solan, G. A., *J. Chem. Soc., Dalton Trans.*, 1994, 609.
5. Caffyn, A. J. M., Mays, M. J., Solan, G. A., Braga, D., Sabatino, P., Tiripicchio, A., Tiripicchio-Camellini, M., *Organometallics*, 1993, **12,** 1876.
6. (a) Caffyn, A. J. M., Braga, D., Sabatino, P., Conole, G., McPartlin, M., Powell, H. R., *J. Chem. Soc., Dalton Trans.*, 1991, 3103; (b) Caffyn, A. J. M., Mays, M. J., Solan, G. A., Conole, G., Tiripicchio, A., *J. Chem. Soc., Dalton Trans.*, 1993, 2345.
7. Edwards, A. J., Martín, A., Mays, M. J., Raithby, P. R. and Solan, G. A., *J. Chem. Soc., Chem. Commun.*, 1992, 1416.
8. (a) Bradley, D. H., Khan, M. A., Nicholas, K. M., *Organometallics*, 1989, **8**, 554; (b) Bradley, D. H., Khan, M. A., Nicholas, K. M., *Organometallics*, 1992, **11**, 2598; (c) Cragg, R. H., Jeffery, J. C., Went, M. J., *J. Chem. Soc., Dalton Trans.*, 1991, 137; (d) Caffyn, A. J. M., Mays, M. J., Conole, G., McPartlin, M., Powell, H. R., *J. Organomet., Chem.*, 1992, **436**, 83.
9. Solan, G. A., PhD Thesis. University of Cambridge, 1993.
10. Bonnet, J. J. and Mathieu, R., *Inorg. Chem.*, 1978, **17,** 1973.
11. Chia, L. S., Cullen, W. R., Franklin, M. and Manning, A. R., *Inorg, Chem.*, 1975, **14,** 2521.
12. Carty, A. J., *Adv. Chem. Ser.*, 1982, **196,** 163.
13. (a) Hermann, W. A., Bauer, C., Weichmann, J., *J. Organomet. Chem.*, 1983, **243**, C21; (b) Pályi, G., Varadi G., Márko, L., in *Stereochemistry of Organometallic and Inorganic Compounds*, vol. 1, ed. I. Bernal. Amsterdam, 1986, pp. 358–410.
14. Regragui, R., Dixneuf, P. H., Taylor, N. J., Carty, A. J., *Organometallics*, (a) 1984, **3**, 814; (b) 1990, **9**, 2234.
15. (a) Rumin, R., Guernou, K., Petillon, F. Y., Muir, K. W., *J. Chem. Soc., Dalton Trans.*, 1997, 1381; (b) Mays, M. J., Pateman, G. E., Solan, G. A., unpublished results.
16. (a) Martín, A., Mays, M. J., Raithby, P. R., Solan,

G. A., *J. Chem. Soc*., *Dalton Trans*., 1993, 1431; (b) Ingham, S. L., Mays, M. J., Raithby, P. R., Solan, G. A., Sundavadra, B. V., Conole, G., Kessler, M., *J. Chem. Soc*., *Dalton Trans*., 1994, 3607.
17. Caffyn, A. J. M., Mays, M. J. and Raithby, P. R., *J. Chem. Soc*., *Dalton Trans*., 1991, 2349.
18. Sternberg, H. W., Greenfield, H., Friedel, R. A., Wotiz, J., Markby, R. and Wender, I., *J. Am. Chem. Soc*., 1954, **76,** 1457.
19. Sternberg, H. W. and Greenfield, H., *J. Am. Chem. Soc*., 1956, **78,** 120.
20. Job, B. E., Mclean, R. A. N. and Thompson, D. T., *J. Chem. Soc*., *Chem. Commun*., 1966, 895.
21. SHELX PLUS program version 4.0. Siemens Analytical X-Ray Instruments, Madison, WI, 1990.
22. Cooper, M. K., Guerney, P. J. and McPartlin, M., *J. Chem. Soc*., *Dalton Trans*., 1982, 757.
23. Sheldrick, G. M., *SHELX* 76 *program for crystal structure determination*. University of Cambridge, 1976.
24. Walker, N. and Stuart, D., DIFABS program, *Acta Crystallogr*., 1968, **24,** 158 Sect A.