

Isomerisation and fragmentation of sulfur-containing organo-metallacycles on dicobalt centres induced by phosphorus donor ligands

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Treatment of the dibridged dicobalt complex $[\text{Co}_2(\mu\text{-PPh}_2)\{\mu\text{-}\eta^1(\text{S})\text{:}\eta^1(\text{C})\text{:}\eta^2(\text{C})\text{-SPHC(O)CR'CR}\}(\text{CO})_4]$ ($\text{R}' = \text{R} = \text{H}$ **1a**) with L, at ambient temperature, affords an inseparable mixture of two mono-substituted isomeric complexes of general formula $[\text{Co}_2(\mu\text{-PPh}_2)\{\mu\text{-}\eta^1(\text{S})\text{:}\eta^1(\text{C})\text{:}\eta^2(\text{C})\text{-SPHC(O)CHCH}\}(\text{CO})_3(\text{L})]$ [$\text{L} = \text{P(OMe)}_3$, **2a/3a**, PPhMe_2 **2b/3b**], differing only in the metal centre at which L is coordinated. When the reaction is performed with $[\text{Co}_2(\mu\text{-PPh}_2)\{\mu\text{-}\eta^1(\text{S})\text{:}\eta^1(\text{C})\text{:}\eta^2(\text{C})\text{-SPHC(O)CR'CR}\}(\text{CO})_4]$ [$\text{R}' = \text{Me}$, $\text{R} = \text{H}$ **1b**], in which R' and R are inequivalent, a similar mixture of inseparable isomers is isolated, $[\text{Co}_2(\mu\text{-PPh}_2)\{\mu\text{-}\eta^1(\text{S})\text{:}\eta^1(\text{C})\text{:}\eta^2(\text{C})\text{-SPHC(O)-CMeCH}\}(\text{CO})_3(\text{L})]$ [$\text{L} = \text{P(OMe)}_3$, **4a/5a**, PPhMe_2 **4b/5b**] and, in addition, a third separable isomer, $[\text{Co}_2(\mu\text{-PPh}_2)\{\mu\text{-}\eta^1(\text{S})\text{:}\eta^1(\text{C})\text{:}\eta^2(\text{C})\text{-SPHC(O)CHCMe}\}(\text{CO})_3(\text{L})]$ [$\text{L} = \text{P(OMe)}_3$, **6a**, PPhMe_2 **6b**], in which R' and R have interchanged. Addition of a further equivalent of L at elevated temperature to mixtures of **2/3** results in both carbonyl substitution and a rearrangement of the bridging ligand assembly to give $[\text{Co}_2(\mu\text{-SPh})\{\mu\text{-}\eta^1(\text{P})\text{:}\eta^1(\text{C})\text{:}\eta^2(\text{C})\text{-PPH}_2\text{CRCR'C(O)}\}(\text{CO})_2(\text{L})_2]$ [$\text{R}' = \text{R} = \text{H}$; $\text{L} = \text{P(OMe)}_3$, **7a**, PPhMe_2 **7b**] in high yield. A similar transformation is achieved on interaction of **4/5** and **6** with L leading to $[\text{Co}_2(\mu\text{-SPh})\{\mu\text{-}\eta^1(\text{P})\text{:}\eta^1(\text{C})\text{:}\eta^2(\text{C})\text{-PPH}_2\text{CRCR'C(O)}\}(\text{CO})_2(\text{L})_2]$ [$\text{R}' = \text{Me}$, $\text{R} = \text{H}$; $\text{L} = \text{P(OMe)}_3$, **8a**, PPhMe_2 **8b**] and, in addition, $[\text{Co}_2(\mu\text{-SPh})\{\mu\text{-}\eta^1(\text{P})\text{:}\eta^1(\text{C})\text{:}\eta^2(\text{C})\text{-PPH}_2\text{-CR'CR'C(O)}\}(\text{CO})_2(\text{L})_2]$ [$\text{R}' = \text{Me}$, $\text{R} = \text{H}$; $\text{L} = \text{P(OMe)}_3$, **9a**, PPhMe_2 **9b**], in which the positions of R' and R are reversed. Reaction of **2a/3a** with triphenylphosphine, gives the mixed phosphite–phosphine rearranged species $[\text{Co}_2(\mu\text{-SPh})\{\mu\text{-}\eta^1(\text{P})\text{:}\eta^1(\text{C})\text{:}\eta^2(\text{C})\text{-PPH}_2\text{CHCHC(O)}\}(\text{CO})_2\{\text{P(OMe)}_3\}(\text{PPh}_3)]$ **10** as the sole product. The facility of the bridging ligands in **1** to undergo a range of bond-breaking (C–S and C–C) and bond-forming (C–S, C–P and C–C) reactions induced by phosphorus donor ligand addition is discussed and pathways postulated. The single crystal X-ray structures of **2b**, **7a** and **10** are described.

1 Introduction

The cleavage of carbon–sulfur bonds mediated by transition metals occurs in a range of catalytic reactions,^{1–4} but has found prominence in the hydrodesulfurisation (HDS) process, in which it represents a key step during the removal of sulfur from organic compounds in petroleum feedstocks.^{5,6} A wide variety of transition metal complexes have been employed to model the supported HDS system (Co-/Mo-S species on Al_2O_3) and often sulfur-containing organometallacyclic ring species have been isolated and postulated as intermediates in the process.^{7–17} While many of these metallacyclic species are found in mono-nuclear complexes,^{7–13} a number are generated on two adjacent metal centres,^{14–17} a situation that has been suggested to model an edge of a MoS_2 crystallite in the commercial catalyst.¹⁸

As part of an on-going study of the chemistry of organo-transition metal complexes we have developed routes to species that contain heteroatoms incorporated into four-, five- or nine-membered organometallacycles.^{19–26} Recently we reported the synthesis of a family of dicobalt complexes of the type $[\text{Co}_2(\mu\text{-PPh}_2)\{\mu\text{-}\eta^1(\text{S})\text{:}\eta^1(\text{C})\text{:}\eta^2(\text{C})\text{-SRC(O)CR'CR}\}(\text{CO})_4]$ **1** and have shown that the almost planar five-membered Co–S–C–C=C metallacycle can undergo reversible fragmentation at room temperature on treatment with ^{13}CO gas.²⁷ Although the mechanism for this transformation is uncertain, a series of equilibria involving carbon–sulfur and carbon–carbon

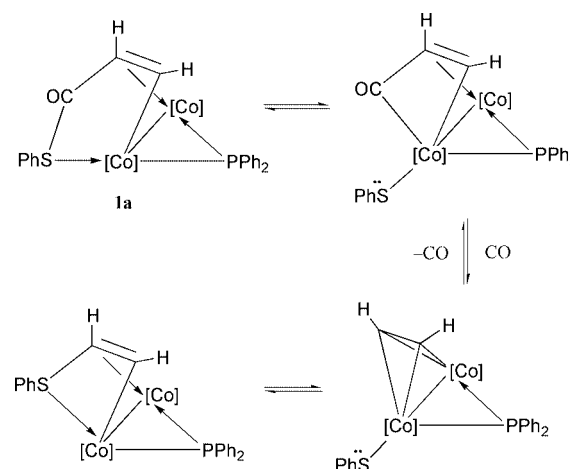
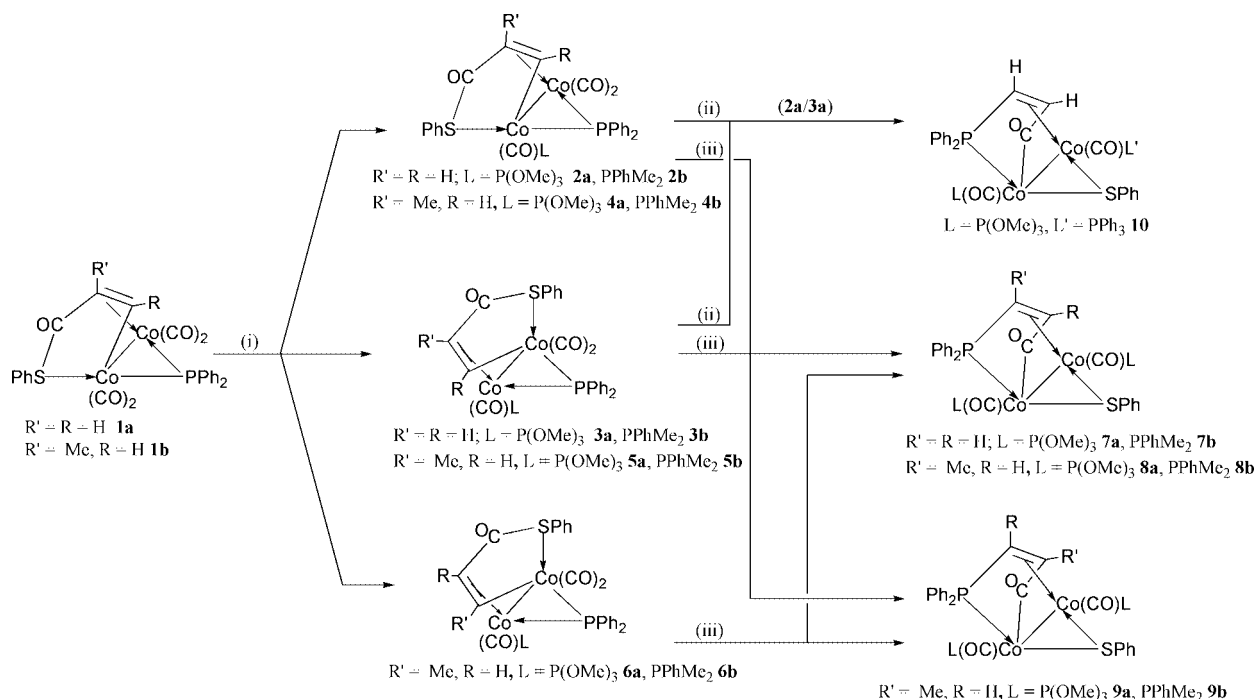


Fig. 1 Reversible fragmentation of **1a**.²³ $[\text{Co}] = \text{Co}(\text{CO})_2$.

bond-breaking and bond-forming reactions has been postulated (Fig. 1).

In this paper we describe the reactions of a number of monodentate phosphorus donor ligands (*viz.* organophosphites and -phosphines) with $[\text{Co}_2(\mu\text{-PPh}_2)\{\mu\text{-}\eta^1(\text{S})\text{:}\eta^1(\text{C})\text{:}\eta^2(\text{C})\text{-SPHC(O)CR'CR}\}(\text{CO})_4]$ ($\text{R}' = \text{R} = \text{H}$ **1a**; $\text{R}' =$



Scheme 1 Products from the reaction of **1** with **L**: Reagents and conditions: (i) **L**, 293 K, C_7H_8 , 4 h; (ii) **L'**, 383 K, C_7H_8 , 1 h; (iii) **L**, 383 K, C_7H_8 , 1 h.

Me, $R = H$ **1b**) which lead under mild conditions not only to carbonyl substitution, but also to reactions involving carbon–carbon and carbon–sulfur bond cleavage along with carbon–carbon, carbon–sulfur and carbon–phosphorus bond formation (see Scheme 1). A portion of this work has been the subject of a communication.²⁸

2 Results and discussion

2.1 Reaction of **1a** and **1b** with **L** at 293 K

The reactions of $[Co_2(\mu-PPh_2)\{\mu-\eta^1(S):\eta^1(C):\eta^2(C)-SPhC(O)-CR'CR\}(CO)_4]$ ($R' = R = H$ **1a**, $R' = Me$, $R = H$ **1b**) with a slight excess of **L** [$L = P(OMe)_3$, $PPhMe_2$] at 293 K in toluene for 4 h give the inseparable (by chromatography) isomeric purple complexes $[Co_2(\mu-PPh_2)\{\mu-\eta^1(S):\eta^1(C):\eta^2(C)-SPhC(O)-CR'CR\}(CO)_3(L)]$ [$R' = R = H$; $L = P(OMe)_3$ **2a/3a**, $PPhMe_2$ **2b/3b**], [$R' = Me$, $R = H$; $L = P(OMe)_3$ **4a/5a**, $PPhMe_2$ **4b/5b**] in ratios of between 3 : 2 and 2 : 1, respectively, as determined by an inspection of the relative intensities of the NMR signals from each isomer. When $R' = Me$, $R = H$, a third separable red complex $[Co_2(\mu-PPh_2)\{\mu-\eta^1(S):\eta^1(C):\eta^2(C)-SPhC(O)C(R)CR'\}-(CO)_3(L)]$ [$R' = Me$, $R = H$; $L = P(OMe)_3$ **6a**, $PPhMe_2$ **6b**] is also obtained. In general, all the reactions (Scheme 1) proceed with high combined yields. All the complexes have been characterised by 1H , ^{13}C , ^{31}P NMR and IR spectroscopy and by mass spectrometry and microanalysis (see Table 1 and Experimental section). In addition, complex **2b** has been the subject of a single crystal X-ray diffraction study.

Although **2b** forms part of an inseparable (by chromatography) isomeric mixture of complexes (**2b/3b**), crystallisation by slow evaporation of a CH_2Cl_2 –hexane solution at room temperature gave crystals of **2b** suitable for a single X-ray diffraction study. The molecular structure of complex **2b** including the atom numbering scheme is illustrated in Fig. 2. Selected bond distances and angles are displayed in Table 2.

The structure of **2b** consists of a singly-bonded dicobalt skeleton [$Co(1)-Co(2)$ 2.483(2) Å] bridged by PPh_2 and $SPhC(O)CHCH$ ligands and bound terminally by three carbonyl and one $PPhMe_2$ ligands. The $SPhC(O)CHCH$ ligand is σ -coordinated to $Co(1)$ via **S** and **C(1)** to form an almost planar [max. deviation from plane by $C(1) = 0.134$ Å] five-membered metallacyclic ring [$Co(1)-S-C(3)-C(2)=C(1)$] in

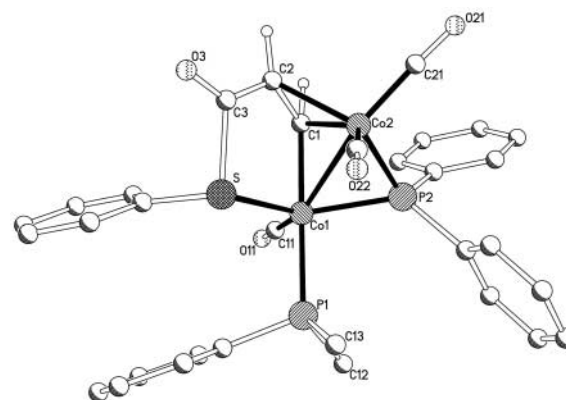


Fig. 2 Molecular structure of **2b** including the atom numbering scheme. All hydrogen atoms apart from **H1** and **H2** have been omitted for clarity.

which the carbon–carbon double bond is asymmetrically π -coordinated to $Co(2)$ via **C(1)** and **C(2)** [$Co(2)-C(1)$ 1.98(1), $Co(2)-C(2)$ 2.12(1) Å]. The PPh_2 ligand is asymmetrically bonded to $Co(1)$ and $Co(2)$ [$Co(1)-P(2)$ 2.182(4), $Co(2)-P(2)$ 2.135(4) Å] and its phosphorus atom lies pseudo-*trans* to both the **S** and **C(2)** atoms of the metallacycle [$P(2)-Co(1)-S$ 132.3(1), $P(2)-Co(2)-C(2)$ 122.8(4)°]. The terminal $PPhMe_2$ ligand is bound to $Co(1)$ and occupies a site *trans* to **C(1)** of the five-membered metallacycle [$C(1)-Co(1)-P(1)$ 173.8(4)°]. The distorted octahedral coordination environment at each metal is completed at $Co(1)$ by one terminal carbonyl ligand and at $Co(2)$ by two carbonyl groups.

The structure of **2b** can be compared with the structurally characterised unsubstituted complexes **1a**²⁸ and $[Co_2(\mu-PPh_2)\{\mu-\eta^1(S):\eta^1(C):\eta^2(C)-SPhC(O)CHCH\}(CO)_4]$ ²⁷ with no appreciable structural variation introduced on substitution of a carbonyl group by a phosphine.

The ^{31}P and 1H NMR spectra for the mixture of **2b/3b** both display two sets of signals in an approximately 2 : 1 ratio. In the ^{31}P NMR spectrum four broad signals are observed, two downfield (δ 179.9 **2b**, 140.8 **3b**) corresponding to the bridging phosphido groups^{16–25,29} and two upfield (δ 32.8 **2b**, 36.8 **3b**) to the terminal $PPhMe_2$ ligands.

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

Complex	$\nu(\text{CO})^a/\text{cm}^{-1}$	^1H NMR (δ) ^b	^{31}P NMR (δ) ^c
2a ^d	2000s, 1965s, 1948w, 1691m ^e	7.7–7.2 [m, 15H, Ph], 6.02 [ddd, $^3J(\text{PH})$ 16.2, $^3J(\text{P}'\text{H})$ 7.8, $^3J(\text{HH})$ 4.8, 1H, C(O)CHCH], 4.48 [dd, $^3J(\text{PH})$ 6.3, 1H, C(O)CHCH], 3.25 [d, $^3J(\text{PH})$ 11.0, 9H, P(OMe) ₃]	185.3 and 156.2 [s, br, $\mu\text{-PPh}_2$, P(OMe) ₃]
2b ^d	1998s, 1969s, 1947w, 1641m	7.8–6.8 [m, 20H, Ph], 6.00 [ddd, $^3J(\text{PH})$ 15.9, $^3J(\text{P}'\text{H})$ 7.6, $^3J(\text{HH})$ 4.5, 1H, C(O)CHCH], 4.46 [dd, $^3J(\text{PH})$ 6.1, 1H, C(O)CHCH], 1.32 [d, $^2J(\text{PH})$ 8.3, 3H, PPhMe], 1.26 [d, $^2J(\text{P}'\text{H})$ 8.1, 3H, PPhMe]	179.9 [s, br, $\mu\text{-PPh}_2$], 32.8 [s, br, PMe ₂ Ph]
3a ^d	As for 2a	7.7–7.2 [m, 15H, Ph], 5.76 [ddd, $^3J(\text{PH})$ 20.1, $^3J(\text{P}'\text{H})$ 17.7, $^3J(\text{HH})$ 4.8, 1H, C(O)CHCH], 4.38 [ddd, $^3J(\text{PH})$ 6.1, $^3J(\text{P}'\text{H})$ 2.5, 1H, C(O)CHCH], 3.54 [d, $^3J(\text{PH})$ 11.4, 9H, P(OMe) ₃]	154.1 and 147.1 [s, br, $\mu\text{-PPh}_2$, P(OMe) ₃]
3b ^d	As for 2b	7.8–6.8 [m, 20H, Ph], 5.78 [ddd, $^3J(\text{PH})$ 19.9, $^3J(\text{P}'\text{H})$ 17.9, $^3J(\text{HH})$ 4.5, 1H, C(O)CHCH], 4.19 [ddd, $^3J(\text{PH})$ 6.0, $^3J(\text{P}'\text{H})$ 3.0, 1H, C(O)CHCH], 1.48 [d, $^2J(\text{PH})$ 8.5, 3H, PPhMe], 1.41 [d, $^2J(\text{P}'\text{H})$ 8.3, PPhMe]	140.8 [s, br, $\mu\text{-PPh}_2$], 36.8 [s, br, PMe ₂ Ph]
4a ^d	2005m, 1990s, 1950s, 1683m	7.8–7.2 [m, 15H, Ph], 5.99 [dd, $^3J(\text{PH})$ 16.1, $^3J(\text{P}'\text{H})$ 8.0, 1H, C(O)CMeCH], 3.24 [d, $^3J(\text{PH})$ 11.0, 9H, P(OMe) ₃], 1.78 [d, $^4J(\text{PH})$ 4.0, 3H, C(O)CMeCH]	194.8 and 156.3 [s, br, $\mu\text{-PPh}_2$, P(OMe) ₃]
4b ^d	2004s, 1973s, 1946w, 1640m ^e	7.8–6.8 [m, 20H, Ph], 5.80 [dd, $^3J(\text{PH})$ 16.3, $^3J(\text{P}'\text{H})$ 4.0, 1H, C(O)CMeCH], 1.78 [d, $^4J(\text{PH})$ 2.7, 3H, C(O)CMeCH], 1.31 [d, $^2J(\text{PH})$ 8.3, 3H, PPhMe], 1.25 [d, $^2J(\text{P}'\text{H})$ 8.3, 3H, PPhMe]	180.2 [s, br, $\mu\text{-PPh}_2$], 11.9 [s, br, PMe ₂ Ph]
5a ^d	As for 4a	7.8–7.2 [m, 15H, Ph], 5.83 [dd, $^3J(\text{PH})$ 21.5, $^3J(\text{P}'\text{H})$ 17.9, 1H, C(O)CMeCH], 3.50 [d, $^3J(\text{PH})$ 11.2, 9H, P(OMe) ₃], 1.86 [d, $^4J(\text{PH})$ 4.0, 3H, C(O)CMeCH]	185.3 and 152.7 [s, br, $\mu\text{-PPh}_2$, P(OMe) ₃]
5b ^d	As for 4b	7.8–6.8 [m, 20H, Ph], 5.56 [dd, $^3J(\text{PH})$ 18.5, $^3J(\text{P}'\text{H})$ 15.2, 1H, C(O)CMeCH], 1.95 [d, $^4J(\text{PH})$ 2.7, 3H, C(O)CMeCH], 1.48 [d, $^2J(\text{PH})$ 8.5, 3H, PPhMe], 1.36 [d, $^2J(\text{P}'\text{H})$ 8.4, 3H, PPhMe]	137.8 [s, br, $\mu\text{-PPh}_2$], 31.8 [s, br, PMe ₂ Ph]
6a	2005m, 1990s, 1950s, 1683m	7.8–7.2 [m, 15H, Ph], 4.07 [dd, $^3J(\text{PH})$ 6.0, $^3J(\text{P}'\text{H})$ 4.0, 1H, C(O)CHCMe], 3.23 [d, $^3J(\text{PH})$ 9H, P(OMe) ₃], 1.95 [d, $^4J(\text{PH})$ 3.8, 3H, C(O)CHCMe]	176.3 [s, br, $\mu\text{-PPh}_2$], 138.8 [s, br, P(OMe) ₃]
6b	2004s, 1973s, 1946w, 1640m	Not recorded	183.1 [s, br, $\mu\text{-PPh}_2$], 15.4 [s, br, PMe ₂ Ph]
7a	2004s, 1956m, 1580w ^e	8.0–7.0 [m, 15H, Ph], 4.09 [ddd, $^3J(\text{PH})$ 37.4, $^3J(\text{P}'\text{H})$ 10.0, $^3J(\text{HH})$ 4.3, 1H, CHCHC(O)], 3.92 [ddd, $^3J(\text{PH})$ 4.3, $^3J(\text{P}'\text{H})$ 4.3, 1H, CHCHC(O)], 3.60 [d, $^3J(\text{PH})$ 11.4, 9H, P(OMe) ₃], 3.47 [d, $^3J(\text{PH})$ 10.9, 9H, P(OMe) ₃]	165.7 [s, P(OMe) ₃], 147.6 [s, P(OMe) ₃], 33.9 [s, PPh ₂ CHCHC(O)]
7b	2009s, 1960s, 1579m	Not recorded	35.9 [s, PPh ₂ CHCHC(O)], 18.2 [s, br, PMe ₂ Ph], 7.4 [s, br, PMe ₂ Ph]
8a	2015s, 1967s, 1588m	8.0–7.0 [m, 15H, Ph], 3.95 [dd, $^2J(\text{PH})$ 8.2, $^3J(\text{PH})$ 5.8, 1H, CHCMeC(O)], 3.63 [d, $^3J(\text{PH})$ 11.5, 9H, P(OMe) ₃], 3.51 [d, $^3J(\text{PH})$ 10.8, 9H, P(OMe) ₃], 1.41 [s, 3H, CHCMeC(O)]	168.1 [s, P(OMe) ₃], 147.2 [s, P(OMe) ₃], 30.8 [s, PPh ₂ CHCMeC(O)]
8b	2010s, 1960s, 1579m ^e	8.0–6.9 [m, 10H, Ph], 3.67 [dd, $^2J(\text{PH})$ 6.4, $^3J(\text{P}'\text{H})$ 6.3, 1H, CHCMeC(O)], 1.63 [d, $^3J(\text{PH})$ 7.9, 3H, PPhMe], 1.45 [d, $^3J(\text{PH})$ 8.3, 3H, PPhMe], 1.42 [d, 3H, $^4J(\text{PH})$ 1.7, CMeCHC(O)], 1.41 [d, $^3J(\text{PH})$ 8.0, 3H, PPhMe], 1.06 [d, $^3J(\text{P}'\text{H})$ 8.3, 3H, PPhMe]	37.2 [s, PPh ₂ CHCMeC(O)], 11.5 [s, br, PMe ₂ Ph], 3.3 [s, PMe ₂ Ph]
9a	2020s, 1971s, 1575m	8.0–7.0 [m, 15H, Ph], 4.16 [dd, $^3J(\text{PH})$ 37.2, $^3J(\text{P}'\text{H})$ 9.3, 1H, CMeCHC(O)], 3.52 [d, $^3J(\text{PH})$ 11.4, 9H, P(OMe) ₃], 3.36 [d, $^3J(\text{PH})$ 11.4, 9H, P(OMe) ₃], 1.41 [d, $^3J(\text{PH})$ 8.9, 3H, CMeCHC(O)]	167.0 [s, br, P(OMe) ₃], 143.2 [s, br, P(OMe) ₃], –29.6 [s, PPh ₂ CMeCHC(O)]
9b	2014s, 1970s, 1576m	7.8–6.9 [m, 25H, Ph], 3.97 [m, 1H, CMeCHC(O)], 1.42 [s, br, CMeCHC(O)], 1.33 [s, br, 12H, PPhMe]	38.3 [s, PPh ₂ CMeCHC(O)], 16.0 [s, br, PMe ₂ Ph], 0.8 [s, br, PMe ₂ Ph]
10	1995s, 1942s, 1580m	7.8–7.0 [m, 30H, Ph], 3.82 [ddd, $^3J(\text{PH})$ 37.4, $^3J(\text{PH})$ 8.8, $^3J(\text{HH})$ 4.0, 1H, CHCHC(O)], 3.65 [m, 1H, CHCHC(O)], 3.40 [d, $^3J(\text{PH})$ 11.2, 9H, P(OMe) ₃]	146.2 [s, br, P(OMe) ₃], 55.4 [s, br, PPh ₃], 35.6 [s, PPh ₂ CHCHC(O)]

^a Recorded in *n*-hexane solution. ^b ^1H chemical shifts (δ) in ppm relative to SiMe₄ (0.0 ppm), coupling constants in Hz in CDCl₃ at 293 K. ^c ^{31}P chemical shifts (δ) in ppm relative to external 85% H₃PO₄ (0.0 ppm), $\{^1\text{H}\}$ -gated decoupled, measured in CDCl₃ at 293 K. Deduct 140.2 from tabulated values in order to reference relative to external P(OMe)₃. ^d Complex pairs (**2a,3a**), (**2b,3b**), (**4a,5a**) and (**4b,5b**) are inseparable mixtures of mono-substituted species. ^e Recorded in CH₂Cl₂.

In the ^1H NMR spectrum of **2b/3b** two pairs of signals for the olefinic protons are observed; the more downfield signals (*ca.* δ 5.9) are assigned to the $\mu\text{-SPhC(O)CHCH}$ proton and the more upfield (*ca.* δ 4.4) to the $\mu\text{-SPhC(O)CHCH}$ proton.²⁷ For both the downfield resonances three-bond couplings to the other vinyl proton, the phosphido-phosphorus atom and the terminal phosphorus bound ligand lead to the resonances taking the form of doublets of doublets of doublets (ddd). In contrast, the more upfield resonances take the form of doublets of doublets (dd) (**2b**) and doublets of doublets of doublets (**3b**). The absence of a third coupling for **2b** suggests that the site of the terminal phosphine ligand is such that there are more than three bonds between it and the vinyl proton. On this basis **2b** is

assigned the molecular structure described above in which there are four bonds between the $\mu\text{-SPhC(O)CHCH}$ proton and the terminal phosphine ligand. The presence of a third coupling for **3b** for the corresponding proton, however, suggests the structure illustrated in Scheme 1 in which the phosphine is positioned on the cobalt atom in closer proximity to this proton (*i.e.* through three bonds). A similar location of a phosphine ligand to that in **3b** has been reported for the structurally related complex [Co₂($\mu\text{-PPh}_2$){ $\mu\text{-}\eta^1(\text{P})\text{:}\eta^1(\text{C})\text{:}\eta^2(\text{C})\text{-PPh}_2\text{C(O)CHCH}\}$ }(CO)₃(PPh₃)] and indeed a similar $^3J(\text{PH})$ coupling is observed for the corresponding proton.¹⁹

Microanalysis of the mixture of **2b** and **3b** is consistent with the two complexes having the same composition while the FAB

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

Co(1)–Co(2)	2.483(2)	Co(1)–S	2.266(4)
Co(1)–P(1)	2.234(4)	Co(1)–P(2)	2.182(4)
Co(1)–C(1)	1.97(1)	Co(2)–C(1)	1.98(1)
Co(2)–P(2)	2.135(4)	S–C(3)	1.92(1)
Co(2)–C(2)	2.12(1)	C(1)–C(2)	1.42(2)
C(2)–C(3)	1.41(2)	C(3)–O(3)	1.20(2)
C–O (carbonyl)	1.14(1)–1.16(2)	Co–C (carbonyl)	1.73(2)–1.76(2)
S–Co(1)–Co(2)	83.0(1)	P(1)–Co(1)–Co(2)	123.7(1)
P(1)–Co(1)–S	89.3(1)	P(2)–Co(1)–Co(2)	54.0(1)
P(2)–Co(1)–S	132.3(1)	P(2)–Co(1)–P(1)	97.8(1)
C(1)–Co(1)–Co(2)	51.1(4)	C(1)–Co(1)–S	86.8(4)
C(1)–Co(1)–P(1)	173.8(4)	C(1)–Co(1)–P(2)	81.4(4)
C(11)–Co(1)–Co(2)	140.6(5)	C(11)–Co(1)–S	114.7(5)
P(2)–Co(2)–Co(1)	55.8(1)	C(1)–Co(2)–P(2)	82.6(4)
C(1)–Co(2)–Co(1)	51.1(4)	C(2)–Co(2)–P(2)	122.8(4)
C(2)–Co(2)–Co(1)	78.4(3)	C(21)–Co(2)–Co(1)	144.9(5)
C(2)–Co(2)–C(1)	40.4(5)	C(12)–P(1)–Co(1)	115.5(5)
C(3)–S–Co(1)	99.1(5)	C(13)–P(1)–Co(1)	119.8(5)
Co(2)–P(2)–Co(1)	70.2(1)	Co(2)–C(1)–Co(1)	77.8(4)
C(2)–C(1)–Co(1)	117.7(9)	C(2)–C(1)–Co(2)	75.2(7)
C(1)–C(2)–Co(2)	64.4(7)	C(3)–C(2)–Co(2)	101.1(9)
C(3)–C(2)–C(1)	123(1)	C(2)–C(3)–S	110(1)

mass spectrum reveals a single molecular ion peak along with fragmentation peaks corresponding to the loss of up to three carbonyl ligands.

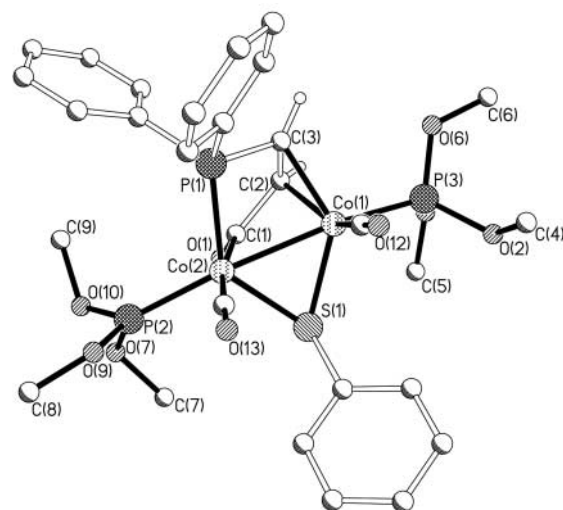
On the basis of the close similarity of the spectroscopic data, structures similar to **2b** are postulated for **2a**, **4a** and **4b** (with L bound to the metallacyclic Co) while complexes **3a**, **5a**, **5b**, **6a** and **6b** are ascribed structures similar to **3b** (with L bound to the Co atom not in the metallacycle). For **5** and **6**, which are structurally identical apart from the disposition of the inequivalent R' and R groups, the orientation of the vinyl group is assigned on the basis of a comparison of the ¹H NMR data with that for **3**. In a similar way, the disposition of the R groups in **4** is determined by comparison with the corresponding data for **2**. While complexes **4/5** are inseparable, complexes **6** can be isolated cleanly and do not isomerise to **4/5** even on prolonged standing (2–3 days) in solution.

A general feature of the inseparable complexes **2/3** and **4/5** is the presence of up to six resonances in the terminal carbonyl regions of their ¹³C–{¹H} NMR spectra at 293 K corresponding to three signals per isomer. This would suggest that at this temperature the carbonyl groups are inequivalent. Indeed, this is a feature that has also been observed in the ¹³C NMR spectra of the precursor complexes **1a** and **1b** in each of which four distinct resonances are displayed.²⁷ Due to the broadness of these signals for **2/3** and **4/5**, however, no coupling to geminal phosphorus centres could be detected.

2.2 Reaction of **2/3**, **4/5** or **6** with L at 383 K

The reactions of [Co₂(μ-PPh₂){μ-η¹(S):η¹(C):η²(C)-SPhC(O)-CR'CR'}(CO)₃(L)] [R' = R = H; L = P(OMe)₃, **2a/3a**, PPhMe₂ **2b/3b**], [R' = Me, R = H; L = P(OMe)₃, **4a/5a**, PPhMe₂ **4b/5b**] and [Co₂(μ-PPh₂){μ-η¹(S):η¹(C):η²(C)-SPhC(O)CR'CR'}(CO)₃(L)] [R' = Me, R = H; L = P(OMe)₃, **6a**, PPhMe₂ **6b**] with excess (up to 5 equivalents) L, at 383 K in toluene for 1 h gives the green complexes [Co₂(μ-SPh){μ-η¹(P):η¹(C):η²(C)-PPh₂-CR'CR'C(O)}(CO)₂(L)₂] [R' = R = H; L = P(OMe)₃, **7a**, PPhMe₂ **7b**], [R' = Me, R = H; L = P(OMe)₃, **8a**, PPhMe₂ **8b**] and [Co₂(μ-SPh){μ-η¹(P):η¹(C):η²(C)-PPh₂CR'CR'C(O)}(CO)₂(L)₂] [R' = Me, R = H; L = P(OMe)₃, **9a**, PPhMe₂ **9b**] in combined high yield (Scheme 1). Reaction of **2a/3a** with triphenylphosphine gives the mixed phosphine–phosphite species [Co₂(μ-SPh){μ-η¹(P):η¹(C):η²(C)-PPh₂CHCHC(O)}(CO)₂{P(OMe)₃}(PPh₃)] **10** in 78% yield.

All the complexes have been characterised by ¹H, ¹³C, ³¹P NMR and IR spectroscopy and by mass spectrometry and microanalysis (see Table 1 and Experimental section) and, in

**Fig. 3** Molecular structure of **7a** including the atom numbering scheme. Hydrogen atoms have been omitted for clarity.

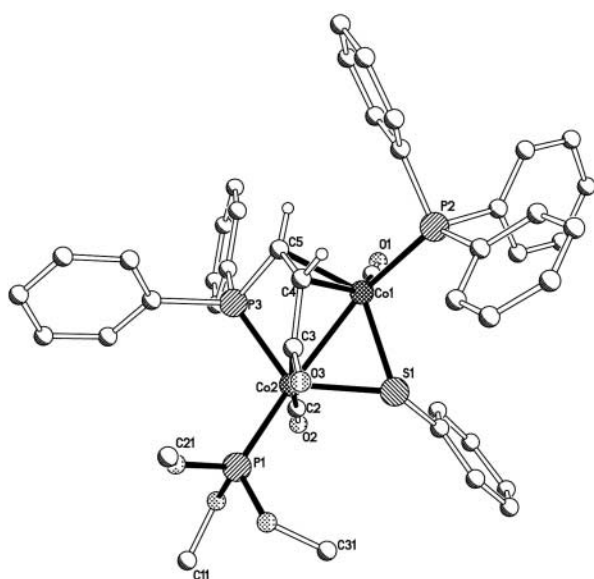
addition, complexes **7a** and **10** have been the subjects of single X-ray diffraction studies.

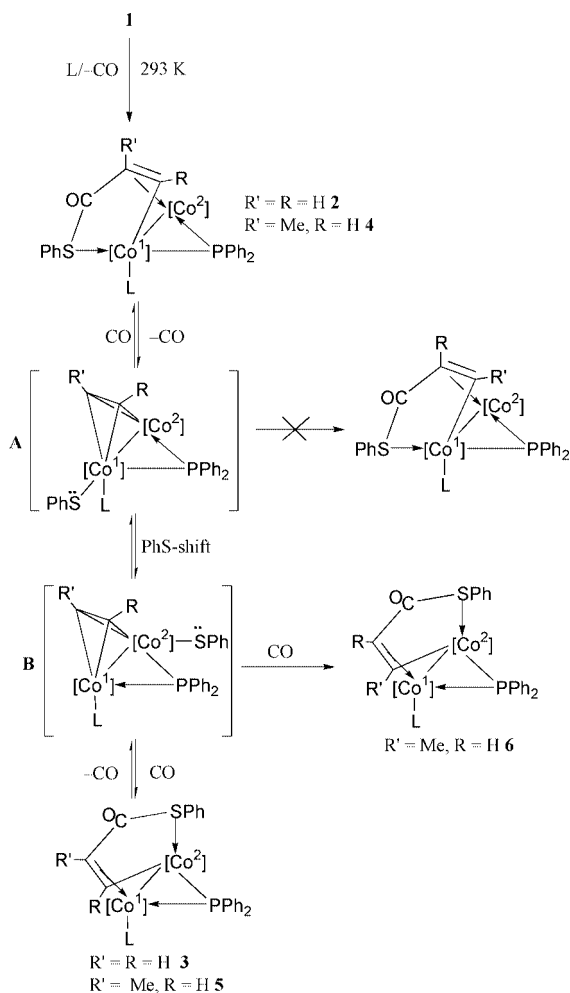
The molecular structure of complex **7a** is illustrated in Fig. 3; selected bond distances and angles for both are listed in Table 3. In complex **7a** the Co–Co single bond [2.466(2)] is bridged by SPh and PPh₂CHCHC(O) ligands such that one Co atom [Co(2)] is incorporated into a five-membered Co–P–C=C–C metallacycle whose unsaturated C–C bond is π-coordinated to the second Co atom [Co(1)]. The P–C=C–C system is folded so as to make the Co–Co and the C=C axes almost perpendicular. The thiolato group bridges the two metal centres symmetrically [Co(1)–S(1) 2.238(2) and Co(2)–S(1) 2.251(2)]. Both Co(1) and Co(2) atoms are bound by P(OMe)₃ ligands occupying sites *trans* to the metal–metal bond [P(2)–Co(2)–Co(1) 163.3(8), P(3)–Co(1)–Co(2) 162.4(1)°]. The relative configuration of the phosphorus donor ligands can be regarded as pseudo-*cis* with a torsion angle of 7°. A single carbonyl ligand completes the distorted octahedral coordination environment at each metal centre.

A partial determination of the molecular structure of complex **10** was made;³⁰ this is depicted in Fig. 4. The X-ray analysis is consistent with the proposed structure but the poor quality of the data precludes discussion of the structural details.

Table 3 Selected bond distances (Å) and angles (°) for **7a**

Co(1)–Co(2)	2.466(2)	Co(2)–S(1)	2.251(2)
Co(1)–S(1)	2.238(2)	C(1)–C(2)	1.47(1)
Co(2)–P(1)	2.194(2)	P(1)–C(3)	1.796(7)
Co(2)–C(1)	2.002(8)	C(1)–O(1)	1.231(7)
C(2)–C(3)	1.424(9)	Co(1)–C(2)	2.058(2)
Co(1)–C(3)	2.023(2)	Co(2)–P(2)	2.171(2)
Co(1)–P(3)	2.149(2)	Co(2)–C(2)	1.803(8)
Co–C(carbonyl)	1.768(8)–1.803(8)		
C(12)–Co(1)–P(3)	98.5(1)	P(1)–Co(2)–S(1)	130.5(1)
C(12)–Co(1)–S(1)	105.2(3)	C(13)–Co(2)–Co(1)	101.5(2)
P(3)–Co(1)–S(1)	110.2(1)	C(1)–Co(2)–Co(1)	68.7(2)
C(12)–Co(1)–Co(2)	96.8(2)	P(1)–Co(2)–Co(1)	74.5(8)
P(3)–Co(1)–Co(2)	162.4(1)	P(2)–Co(2)–Co(1)	163.3(8)
S(1)–Co(1)–Co(2)	57.0(1)	S(1)–Co(2)–Co(1)	56.4(1)
C(1)–Co(2)–P(2)	97.3(2)	C(3)–P(1)–Co(2)	94.9(3)
C(13)–Co(2)–P(1)	98.5(3)	Co(1)–S(1)–Co(2)	66.2(1)
C(1)–Co(2)–P(1)	80.6(3)	C(2)–C(1)–Co(2)	108.9(4)
P(2)–Co(2)–P(1)	113.3(1)	C(1)–C(2)–C(3)	116.9(7)
C(1)–Co(2)–S(1)	76.7(2)	C(2)–C(3)–P(1)	109.2(6)
P(2)–Co(2)–S(1)	112.8(1)		





Scheme 2 Proposed pathway for 'ring-flip' interconversion and formation of **2–6** from **1**. [Co] = Co(CO)₂ or Co(CO), L = P(OMe)₃ or PPhMe₂.

related mixed-metal systems²⁶ and then reform the metallacycle *via* SPh, CO and alkyne coupling. The formation of the isomers **5** and **6**, in which the disposition of the R substituents on the vinyl group is reversed, can be understood as resulting from insertion of the CO or SPh group (see Fig. 1) into one or other of the metal–carbon bonds between Co(2) and the alkyne-bridge in **B**. On the other hand, it is not clear why an isomer of **4** with the R substituents on the vinyl group reversed is not formed *via* the same process. It is noteworthy that a similar regioselectivity is observed in the formation of **1b** from the reaction of [Co₂(μ-MeCCH)(CO)₆] with PPh₂(SPh).²⁷

Although we were unable to detect by solution NMR spectroscopy any of the postulated intermediate species in the formation of **2–6**, related complexes containing the proposed or similar bridging ligands have been isolated and demonstrated to undergo related bond-forming and bond-breaking reactions. For example, reversible coupling of alkynes with CO on bimetallic centres has been well documented^{19,27–29,31–35} while recent reports have disclosed thiolate-alkyne coupling.^{25,26} In addition, the 'ring-flip' mechanism proposed here can be compared to the shift of a hydride and an oscillation of a η¹:η²-vinyl group between two metal centres detected by Deeming *et al.*³⁶

Scheme 3 illustrates a plausible pathway for the formation of **7–10**. Addition of L' to all mono-substituted structural types **2–6** is proposed to give a pair of common bis-substituted intermediates **C** and **D**. As in Scheme 2 these intermediates arise *via* fragmentation of the SPhC(O)CRCR ligand and contain transverse μ-η²:η²-alkyne and pendant thiolate groups. For **C**, however, exchange of a thiolate group with a bridging

phosphido group can then take place to give **E**, followed by coupling of the alkyne, CO and a phosphide groups to give **7–10**. Since the phosphide group may couple with the alkyne by insertion into either of two Co(1)–C bonds, two regiochemistries of the resulting vinyl group are possible and, indeed, observed in **8** and **9**. In Scheme 3 we propose initial phosphide rather than CO insertion, as we have previously isolated μ-PPh₂CRCR-bridged dicobalt complexes from alkyne-bridged precursor complexes and moreover, have observed the related carbonylation reaction of these complexes.¹⁹ The subsequent insertion of CO in Scheme 3 must be irreversible, as treatment of **7a** with ¹³CO at 383 K does not result in labelling of the ketonic carbonyl group. The reason for the absence of an isomer of **10** in which the phosphorus donor ligands have exchanged positions is unclear, but the reduced steric demands of a P(OMe)₃ group over a PPh₃ group at the crowded metallacyclic Co atom may be significant.

3 Conclusions

The reaction of phosphorus donor ligands (L) with the asymmetrically bridged **1** is much more complex than the simple substitution of carbonyl groups by the L ligands. Indeed, substitution of the carbonyl ligands does occur but with the effect of inducing two types of intramolecular rearrangement reaction. Firstly, the orientation of the R groups on the vinyl unit of the sulfur-containing Co–S–C–C=C metallacycle in **1b** can be reversed on mono-substitution at moderate temperatures (293 K). Secondly, the metallacycle, Co–S–C–C=C, in **1** can be converted to a phosphorus-containing Co–P–C–C=C metallacycle, in **7–10**, on bis-substitution at elevated temperatures (383 K).

4 Experimental

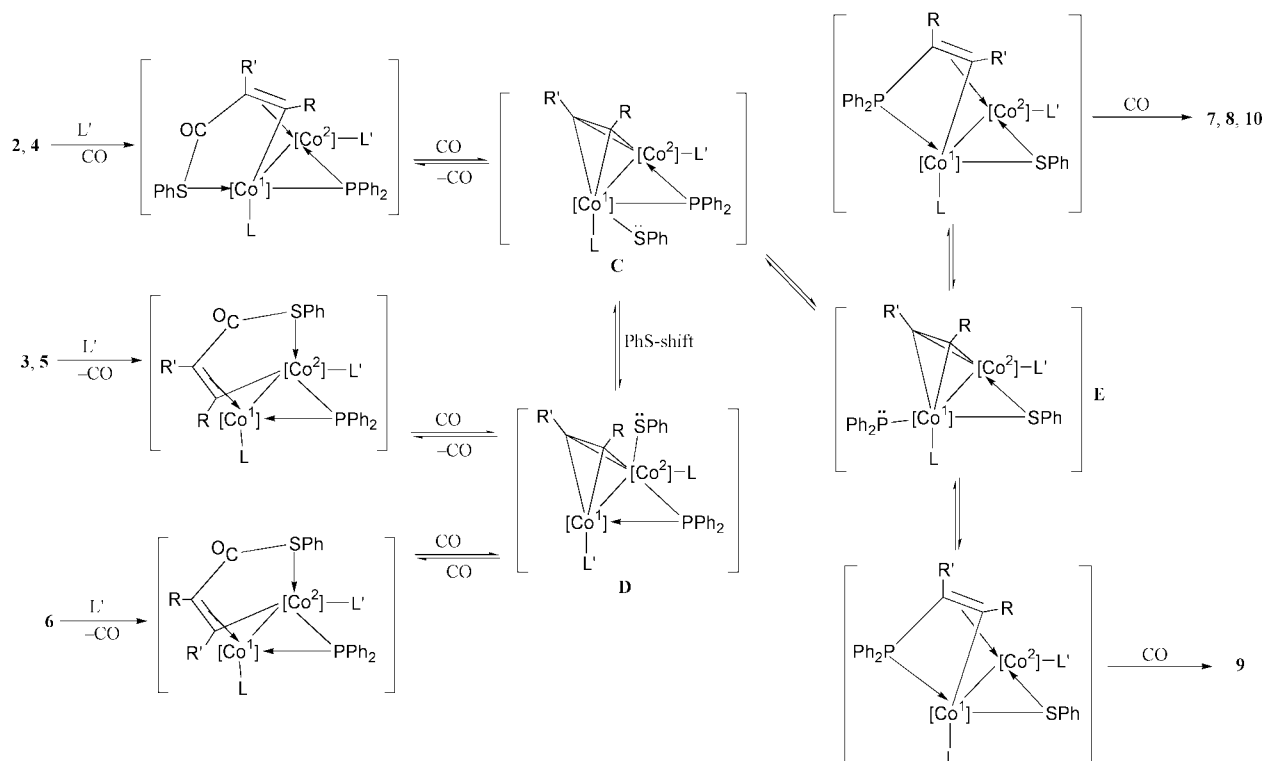
4.1 General techniques and reagents

All reactions were carried out under an atmosphere of dry, oxygen-free nitrogen, using standard Schlenk techniques. Solvents were distilled under nitrogen from appropriate drying agents and degassed prior to use.³⁷ Infrared spectra were recorded in dichloromethane solution in 0.5 mm NaCl cells, using a Perkin-Elmer 1710 Fourier-transform spectrometer. Fast atom bombardment (FAB) mass spectra were recorded on a Kratos MS 890 instrument using 3-nitrobenzyl alcohol as a matrix. ¹H, ¹³C and ³¹P spectra were recorded on either a Bruker WM 250 spectrometer or a Bruker AM 400 spectrometer. 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.

Unless otherwise stated all reagents were obtained from commercial suppliers and the compounds [Co₂(μ-PPh₂){μ-η¹(S):η¹(C):η²(C)-SPhC(O)C(R')C(R)(CO)₄}] (R' = R = H **1a**; R' = Me, R = H **1b**) were prepared by literature methods.²⁷

4.2 Room temperature reactions of **1a** with L

(i) **L = P(OMe)₃**. To a solution of [Co₂(μ-PPh₂){μ-η¹(S):η¹(C):η²(C)-SPhC(O)CHCH}(CO)₄] **1a** (0.300 g, 0.52 mmol) in toluene (50 cm³) was added P(OMe)₃ (0.20 cm³, 1.70 mmol) in toluene (50 cm³). The reaction mixture was stirred at 293 K for 4 h and after removal of the solvent under reduced pressure, purified by TLC using hexane–dichloromethane (2:1) as eluent. This gave in addition to a small amount of unreacted starting material, the inseparable isomeric purple crystalline complexes [Co₂(μ-PPh₂){μ-η¹(S):η¹(C):η²(C)-SPhC(O)CHCH}(CO)₃-{P(OMe)₃}] **2a/3a** (0.315 g, 90%). Compounds **2a/3a**: NMR (CDCl₃, 293 K): ¹³C{¹H composite pulse decoupled}, (**2a**)



Scheme 3 Proposed pathway to rearranged complex **10** from **2a/3a**. [Co] = Co(CO)₂ or Co(CO), L = P(OMe)₃, L' = PPh₃.

δ 208.6 [s, CoCO], 205.7 [s, CoCO], 203.7 [s, CoCO], 180.8 [d, $^3J(\text{PC})$ 22, SPhC(O)CHCH], 142–124 [m, Ph], 124.6 [dd, $^2J(\text{PC})$ 50, $^2J(\text{P}'\text{C})$ 35, SPhC(O)CHCH], 68.0 [s, SPhC(O)CHCH] and 52.3 [d, $^2J(\text{PC})$ 6 Hz, P(OMe)₃]. (**3a**) δ 207.9 [s, CoCO], 203.4 [s, CoCO], 202.5 [s, CoCO], 181.8 [d, $^3J(\text{PC})$ 22, SPhC(O)CHCH], 142–124 [m, Ph], 116.3 [dd, $^2J(\text{PC})$ 46, $^2J(\text{P}'\text{C})$ 31, SPhC(O)CHCH], 62.1 [s, SPhC(O)CHCH] and 51.8 [d, $^2J(\text{PC})$ 4 Hz, P(OMe)₃]. Fast atom bombardment (FAB) mass spectrum, m/z 674 (M^+) and ($\text{M}^+ - n\text{CO}$) ($n = 1-3$). Anal. Calc. for C₂₇H₂₆Co₂O₇P₂S: C, 48.1; H, 3.9. Found: C, 48.3; H, 4.0%.

(ii) **L = PPhMe₂**. As above in (i) using PPhMe₂ (0.20 cm³, 1.40 mmol). Eluted with hexane–dichloromethane (10:1) gave **2b/3b** (0.291 g, 83%). Compounds **2b/3b**: Anal. Calc. for C₃₂H₂₈Co₂O₄P₂S: C, 55.81; H, 4.07. Found: C, 55.63; H, 4.12%. FAB mass spectrum, m/z 688 (M^+) and ($\text{M}^+ - n\text{CO}$) ($n = 1-3$).

4.3 Room-temperature reactions of **1b** with **L**

(i) **L = P(OMe)₃**. To a solution of [Co₂(μ -PPh₂) $\{\mu$ - $\eta^1(\text{S})$: $\eta^1(\text{C})$: $\eta^2(\text{C})$ -SPhC(O)CMeCH $\}(\text{CO})_4$] **1b** (0.300 g, 0.51 mmol) in toluene (50 cm³) was added P(OMe)₃ (0.20 cm³, 1.70 mmol) in toluene (50 cm³). The reaction mixture was stirred at 293 K for 4 h and after removal of the solvent under reduced pressure, purified by TLC using hexane–dichloromethane (2:1) as eluent. This gave in addition to a small amount of unreacted starting material, the inseparable isomeric purple crystalline complexes [Co₂(μ -PPh₂) $\{\mu$ - $\eta^1(\text{S})$: $\eta^1(\text{C})$: $\eta^2(\text{C})$ -SPhC(O)CMeCH $\}(\text{CO})_3$ - $\{\text{P(OMe)}_3\}$] [**L = 4a/5a** (0.154 g, 44%)] and the red crystalline complex [Co₂(μ -PPh₂) $\{\mu$ - $\eta^1(\text{S})$: $\eta^1(\text{C})$: $\eta^2(\text{C})$ -SPhC(O)CHCH $\}(\text{CO})_3$ $\{\text{P(OMe)}_3\}$] **6a** (0.126 g, 36%). Compounds **4a/5a**: NMR (CDCl₃, 293 K): $^{13}\text{C}\{^1\text{H}$ composite pulse decoupled), (**4a**) δ 209.4 [s, CoCO], 203.9 [s, CoCO], 202.3 [s, CoCO], 177.3 [d, $^3J(\text{PC})$ 16, SPhC(O)CMeCH], 142–127 [m, Ph and SPhC(O)CMeCH], 68.1 [s, SPhC(O)CMeCH], 51.7 [d, $^2J(\text{PC})$ 4 Hz, P(OMe)₃] and 23.7 [s, SPhC(O)CMeCH]; (**5a**) δ 208.0 [s, CoCO], 204.6 [s, CoCO], 203.0 [s, CoCO], 181.5 [d, $^3J(\text{PC})$ 20, SPhC(O)CMeCH], 147.2 [dd, $^2J(\text{PC})$ 50, $^2J(\text{P}'\text{C})$ 34, SPhC(O)CMeCH], 142–127 [m, Ph], 66.6 [s, SPhC(O)CMeCH], 52.3 [d, $^2J(\text{PC})$ 6 Hz, P(OMe)₃] and 23.2 [s, SPhC(O)CMeCH]. Anal.

Calc. for C₂₈H₂₈Co₂O₇P₂S: C, 55.81; H, 4.07. Found: C, 55.63; H, 4.12%. FAB mass spectrum, m/z 688 (M^+) and ($\text{M}^+ - n\text{CO}$) ($n = 1-3$). Compound **6a**: FAB mass spectrum, m/z 688 (M^+) and ($\text{M}^+ - n\text{CO}$) ($n = 1-3$).

(ii) **L = PPhMe₂**. As above in (i) using PPhMe₂ (0.20 cm³, 1.40 mmol). Elution with hexane–dichloromethane (10:1) gave **4b/5b** (0.143 g, 40%) and **6b** (0.144 g, 40%). Compounds **4b/5b**: FAB mass spectrum, m/z 702 (M^+) and ($\text{M}^+ - n\text{CO}$) ($n = 1-3$). Compound **6b**: FAB mass spectrum, m/z 702 (M^+) and ($\text{M}^+ - n\text{CO}$) ($n = 1-3$).

4.4 Thermolytic reactions of **2/3** with **L**

(i) **2a/3a with P(OMe)₃ (L)**. To a solution of [Co₂(μ -PPh₂) $\{\mu$ - $\eta^1(\text{S})$: $\eta^1(\text{C})$: $\eta^2(\text{C})$ -SPhC(O)CHCH $\}(\text{CO})_3$ $\{\text{P(OMe)}_3\}$] **2a/3a** (0.200 g, 0.29 mmol) in toluene (50 cm³) was added a solution of P(OMe)₃ (0.20 cm³, 1.70 mmol) in toluene (50 cm³). The reaction mixture was stirred at 383 K for 1 h and after removal of the solvent under reduced pressure the mixtures were purified by TLC using hexane–ethyl acetate (10:1) as eluent. This gave in addition to a small amount of unreacted starting material, the green complex [Co₂(μ -SPh) $\{\mu$ - $\eta^1(\text{P})$: $\eta^1(\text{C})$: $\eta^2(\text{C})$ -PPh₂CHCHC(O) $\}(\text{CO})_2$ $\{\text{P(OMe)}_3\}_2$] **7a** (0.171 g, 75%). Compound **7a**: NMR (CDCl₃, 293 K): $^{13}\text{C}\{^1\text{H}$ composite pulse decoupled), δ 224.2 [s, PPh₂CHCHC(O)], 207.1 [s, CoCO], 203.1 [s, CoCO], 144–125 [m, Ph], 72.0 [s, br, PPh₂CHCHC(O)], 51.7 [m, br, P(OMe)₃] and 31.9 [m, br, PPh₂CHCHC(O)]. Anal. Calc. for C₂₉H₃₅Co₂O₉P₃S: C, 45.2; H, 4.6; P, 12.1. Found: C, 45.4; H, 4.5; P 12.0%. FAB mass spectrum, m/z 770 (M^+) and ($\text{M}^+ - n\text{CO}$) ($n = 1-3$).

(ii) **2b/3b with PPhMe₂ (L)**. As above in (ii) using **2a/3b** (0.200 g, 0.29 mmol) and PPhMe₂ (0.20 cm³, 1.40 mmol). Elution with hexane–dichloromethane (2:1) gave **7b** (0.181 g, 78%). Compound **7b**: NMR (CDCl₃, 293 K): $^{13}\text{C}\{^1\text{H}$ composite pulse decoupled), δ 226.8 [s, PPh₂CHCHC(O)], 208.8 [s, CoCO], 203.9 [s, CoCO], 144–125 [m, Ph], 72.0 [s, br, PPh₂CHCHC(O)], 32.3 [m, br, PPh₂CHCHC(O)] and 18.2 [d, $^2J(\text{PC})$ 18 Hz, PPhMe₂]. FAB mass spectrum, m/z 798 (M^+) and ($\text{M}^+ - n\text{CO}$) ($n = 1-3$).

Table 4 X-Ray crystallographic and data processing parameters for **2b** and **7a**^a

Complex	2b	7a
Formula	C ₃₂ H ₂₈ Co ₂ O ₄ P ₂ S	C ₂₉ H ₃₅ Co ₂ O ₉ P ₃ S
<i>M</i>	687.98	750.2
Crystal size/mm	0.38 × 0.32 × 0.23	1.0 × 1.0 × 1.0
Temperature/K	293(2)	295(2)
Crystal system	Monoclinic	Triclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 1̄ (no. 2)
<i>a</i> /Å	13.648(2)	9.360(4)
<i>b</i> /Å	16.213(3)	10.433(5)
<i>c</i> /Å	13.934(3)	19.106(8)
<i>a</i> /°	90	85.51(3)
<i>β</i> /°	100.46(2)	77.05(3)
<i>γ</i> /°	90	67.33(3)
<i>V</i> /Å ³	3032(1)	1678(1)
<i>Z</i>	4	2
<i>D</i> _c /g cm ^{−3}	1.508	1.485
<i>F</i> (000)	1408	752
<i>μ</i> (Mo-Kα)/cm ^{−1}	12.3	12.42
<i>θ</i> range/°	3.00–25.00	2.50–22.50
Limiting <i>hkl</i> indices	−15 to 15, 0–18, 0–16	−10 to 2, −11 to 10, −20 to 20
Reflections collected	5782	5023
Independent reflections	2402 [<i>I</i> > 3σ(<i>I</i>)]	4402 [<i>R</i> _{int} = 0.01]
Max. and min. transmission	1.000 and 0.658	1.000 and 0.916
Data/restraints/parameters	2402/0/352	5023/0/423
GOF ^b of fit on <i>F</i> ²	—	1.53
Final <i>R</i> indices ^c		
<i>I</i> > 2σ(<i>I</i>)	<i>R</i> = 0.0689, <i>R</i> ' = 0.0682 ^d	<i>R</i> ₁ = 0.0501, <i>R</i> _w = 0.0782
All data	—	<i>R</i> ₁ = 0.0625, <i>R</i> _w = 0.0853
Largest diff. peak and hole/e Å ^{−3}	0.743 and −0.852	1.13 and −1.01

^a Data common to all compounds: Mo-Kα (*λ* = 0.71073 Å). ^b GOF = [Σw(*F*_o² − *F*_c²)/(*n* − *p*)]^{1/2} where *n* = number of reflections and *p* = total number of parameters. ^c *R*₁ = Σ||*F*_o| − |*F*_c||/Σ|*F*_o|, w*R*₂ = [Σw(*F*_o² − *F*_c²)²/Σw(*F*_o²)²]^{1/2}, w^{−1} = [σ²(*F*_o)² + (*aP*)² + *bP*], *P* = [max(*F*_o², 0) + 2(*F*_c²)]/3; *R* = Σ(Δ*F*)/Σ(*F*_o); *R*' = [Σw(Δ*F*)²/Σw(*F*_o)²]^{1/2}; w^{−1} = σ²(*F*). ^d *I* > 3σ(*I*).

4.5 Thermolytic reactions of **4/5** with **L**

(i) **4a/5a** with **P(OMe)₃ (L)**. To a solution of [Co₂(μ-PPh₂)-{μ-η¹(S):η¹(C):η²(C)-SPhC(O)CMeCH}(CO)₃{P(OMe)₃}] **4a/5a**, (0.200 g, 0.29 mmol) in toluene (50 cm³) was added P(OMe)₃ (0.20 cm³, 1.70 mmol) in toluene (50 cm³). The solution was stirred at 383 K for 1 h and after removal of the solvent under reduced pressure the mixture was purified by TLC using hexane–ethyl acetate (10:1) as eluent. This gave in addition to a small amount of unreacted starting material, the green complexes [Co₂(μ-SPh){μ-η¹(P):η¹(C):η²(C)-PPh₂-CHCMeC(O)}(CO)₂{P(OMe)₃}₂] **8a** (0.136 g, 60%) and [Co₂(μ-SPh){μ-η¹(P):η¹(C):η²(C)-PPh₂CMeCHC(O)}(CO)₂-{P(OMe)₃}₂] **9a** (0.027 g, 12%). Compound **8a**: NMR (CDCl₃, 293 K): ¹³C{¹H composite pulse decoupled}, δ 224.3 [s, PPh₂-CHCMeC(O)], 206.5 [s, CoCO], 203.2 [s, CoCO], 144–124 [m, Ph], 72.1 [d, ²*J*(PC) 26.7, PPh₂CHCMeC(O)], 51.8 [m, br, P(OMe)₃], 31.6 [d, ¹*J*(PC) 41.2 Hz, PPh₂CHCMeC(O)] and 15.1 [s, PPh₂CHCMeC(O)]. Anal. Calc. for C₃₀H₃₇Co₂O₉P₃S: C, 45.9; H, 4.7. Found: C, 45.9; H, 4.7%. FAB mass spectrum, *m/z* 784 (*M*⁺) and (*M*⁺ − *n*CO) (*n* = 1–3). Compound **9a**: Anal. Calc. for C₄₀H₄₁Co₂O₃P₃S: C, 59.1; H, 5.1. Found: C, 59.0; H, 5.1%. FAB mass spectrum, *m/z* 812 (*M*⁺) and (*M*⁺ − *n*CO) (*n* = 1–3).

(ii) **4b/5b** with **PPhMe₂ (L)**. As above in (i) using **4b/5b** (0.200 g, 0.28 mmol) and PPhMe₂ (0.20 cm³, 1.40 mmol). Elution with hexane–dichloromethane (2:1) gave green **8b** (0.127 g, 56%) and **9b** (0.180 g, 8%). Compound **8b**: FAB mass spectrum, *m/z* 784 (*M*⁺) and (*M*⁺ − *n*CO) (*n* = 1–3). Compound **9b**: FAB mass spectrum, *m/z* 812 (*M*⁺) and (*M*⁺ − *n*CO) (*n* = 1–3).

4.6 Thermolytic reactions of **6** with **L**

(i) **6a** with **P(OMe)₃ (L)**. To a solution of [Co₂(μ-PPh₂)-{μ-η¹(S):η¹(C):η²(C)-SPhC(O)CHCMe}(CO)₃{P(OMe)₃}] **6a** (0.200 g, 0.29 mmol) in toluene (50 cm³) was added P(OMe)₃ (0.20 cm³, 1.70 mmol) in toluene (50 cm³). The solution was

stirred at 383 K for 1 h and after removal of the solvent under reduced pressure the mixture was purified by TLC using hexane–ethyl acetate (10:1) as eluent. This gave in addition to a small amount of unreacted starting material, the green complex [Co₂(μ-SPh){μ-η¹(P):η¹(C):η²(C)-PPh₂CHCMeC(O)}(CO)₂-{P(OMe)₃}₂] **8a** (0.136 g, 60%) and [Co₂(μ-SPh){μ-η¹(P):η¹(C):η²(C)-PPh₂CMeCHC(O)}(CO)₂{P(OMe)₃}₂] **9a** (0.027 g, 12%).

(ii) **6b** with **PPhMe₂**. As above in (i) using **6b** (0.200 g, 0.28 mmol) and PPhMe₂ (0.20 cm³, 1.40 mmol). Elution with hexane–dichloromethane (2:1) gave green **8b** (0.127 g, 56%) and **9b** (0.180 g, 8%).

4.7 Thermolytic reaction of **2a/3a** with **PPh₃**

Triphenylphosphine (0.050 g, 0.19 mmol) was added to [Co₂(μ-PPh₂){μ-η¹(S):η¹(C):η²(C)-SPhC(O)CHCH}(CO)₃-{P(OMe)₃}] **2a/3a** (0.100 g, 0.15 mmol) in toluene (50 cm³) and the reaction mixture stirred for 1 h at 383 K. The solvent was removed under reduced pressure and the mixture purified by preparative TLC using hexane–ethyl acetate (10:1) as eluent to yield the green complex [Co₂(μ-SPh){μ-η¹(P):η¹(C):η²(C)-PPh₂CHCMeC(O)}(CO)₂{P(OMe)₃}₂] **10** (0.105 g, 78%). Compound **10**: Anal. Calc. for C₄₄H₄₁Co₂O₆P₃S: C, 58.15; H, 4.51. Found: C, 58.08; H, 4.53%. FAB mass spectrum, *m/z* 908 (*M*⁺) and (*M*⁺ − *n*CO) (*n* = 1–3).

4.8 Crystal structure analysis of complexes **2b** and **7a**

Suitable single crystals were mounted on glass fibres with epoxy-resin, and transferred to an X-ray diffractometer. Details of the data-collection procedures, structure solution and refinements are presented in Table 4.

X-Ray intensity data for **2b** were collected on a Philips PW1100 four-circle diffractometer. Lorentz-polarisation and absorption corrections were applied to the data of all the compounds. The positions of the metal atoms in **2b** were

deduced from Patterson syntheses. The remaining non-hydrogen atoms and H(1) and H(2) were revealed from subsequent difference-Fourier syntheses. Refinement was based on F_o^2 . The phenyl rings were constrained to refine as rigid hexagons. The positions of the hydrogen atoms on C(1) and C(2) were obtained from a difference-Fourier map based on low angle data ($\theta < 20^\circ$), and were included without refinement. The remaining hydrogen atoms were placed in idealised positions; all hydrogen atoms were assigned displacement parameters of 0.1 \AA^2 . After initial refinement with isotropic displacement parameters empirical absorption corrections³⁹ were applied to the data. All non-hydrogen atoms were assigned anisotropic displacement parameters in the final cycles of full-matrix least-squares refinement.

X-Ray intensity data for **7a** were measured on a Siemens R3m/V diffractometer. The structure was solved by direct methods and refined by blocked full-matrix least-squares analysis;⁴⁰ phenyl hydrogens were placed in idealised positions and allowed to ride on the relevant carbon atoms. Positional disorder was detected for four oxygens of the trimethylphosphite groups with 43 and 57% of occupancy, respectively; only one of them was studied isotropically.

CCDC reference number 186/2284 for **2b** and code KumKei for **7a** (see ref. 28).

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