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Ring-Expansion Reactions of Ligand-Bridged Dinuclear Cobalt Complexes with Alkynes and with Allene: Crystal and Molecular Structures of $[Co_2\{\mu\text{-}PPh_2CHCHC(O)CHCHPPh_2\}(CO)_4]$ and $[Co_2\{\mu\text{-}PPh_2CHCHC(O)C(CH_2)_2\}(\mu\text{-}PPh_2)(CO)_3]$

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The bis(phosphido)-bridged complex $[Co_2(\mu\text{-}PPh_2)_2(CO)_6]$ (**1**) undergoes regiospecific insertion reactions with alkynes, $RC{\equiv}CR'$, to give, depending on the nature of R and R′, new ligand-bridged dinuclear complexes of the type $[Co_2(\mu\text{-}PPh_2CRCR')(\mu\text{-}PPh_2)(CO)_4]$ ($R = R' = CO_2Me$, **2**) or $[Co_2\{\mu\text{-}PPh_2CRCR'C(O)\}(\mu\text{-}PPh_2)(CO)_4]$ ($R' = R = H$, **3a**; $R' = Ph$, $R = H$, **3b**; $R' = SiMe_3$, $R = H$, **3c**; $R' = Me$, $R = H$, **3d**; $R' = CH_2OH$, $R = H$, **3e**; $R' = R = CO_2Me$, **3f**). Complexes **3a–f**, which contain the $\mu\text{-}PPh_2CRCR'C(O)$ ligand incorporated into a five-membered metallacyclic ring with one of the Co atoms, react regiospecifically with alkynes, $R''C{\equiv}CR'''$, to give $[Co_2\{\mu\text{-}PPh_2CRCR'C(O)CR''CR'''PPh_2\}(\mu\text{-}PPh_2)(CO)_4]$ ($R' = R = R'' = R''' = H$, **4a**; $R' = R = R'''$, $R'' = Me$, **4b**; $R' = R'' = Ph$, $R = R''' = H$, **4c**; $R' = Ph$, $R = R'' = R''' = H$, **4d**; $R' = Ph$, $R = R''' = H$, $R'' = Me$ **4e**; $R' = R = R'' = R''' = CO_2Me$, **4f**; $R' = SiMe_3$, $R = R''' = H$, $R'' = Me$, **4g**; $R' = SiMe_3$, $R = R''' = H$, $R'' = Ph$, **4h**), in which the new bridging ligand is part of a nine-membered dimetallacyclic ring. Complex **3a** ($R = R' = H$) also reacts with allene to give $[Co_2\{\mu\text{-}PPh_2CHCHC(O)CHCMePPh_2\}(\mu\text{-}PPh_2)(CO)_4]$ **4b′** (an isomer of **4b**) and $[Co_2\{\mu\text{-}PPh_2CHCHC(O)C(CH_2)_2\}(\mu\text{-}PPh_2)(CO)_3]$ **5**. The structures of **4a** and of the hexane solvate of **5** have been determined. Compound **4a** crystallizes in the monoclinic space group $P2_1/n$ with $a = 15.586(3)$ Å, $b = 18.882(6)$ Å, $c = 20.867(7)$ Å, $\beta = 95.80(3)°$, $V = 6109.6$ Å^3, and $Z = 8$, while $\mathbf{5}\cdot 1/2C_6H_{14}$ crystallizes in the monoclinic space group $P2_1/a$ with $a = 24.903(8)$ Å, $b = 14.674(5)$ Å, $c = 9.249(5)$ Å, $\beta = 96.17(2)°$, $V = 3360(2)$ Å^3, and $Z = 4$. Final R and R_w values were 0.032 and 0.036 (**4a**) and 0.036 and 0.044 (**5**) based on 4117 (**4a**) and 2469 (**5**) observations, respectively.

Introduction

Although bridging phosphido ligands are often used to stabilize dinuclear complexes with respect to fragmentation into mononuclear species, they can themselves participate in chemical reactions. In particular there are now several well-documented examples of the insertion of alkynes into phosphido-bridges in dinuclear complexes.[1-13] For the most part such reactions lead to the formation of new dinuclear complexes with bridging ligands derived from the phosphido group, one or more molecules of the alkyne, and also sometimes other ligands (e.g. CO or $C{\equiv}CR$) which were present in the original complex. Thus for example the complex $[(CO)_4Ru(\mu\text{-}PPh_2)Co(CO)_3]$ reacts regiospecifically with $RC{\equiv}CR'$ to give $[RuCo\{\mu\text{-}PPh_2C(O)CRCR'\}(\mu\text{-}CO)(CO)_5]$ ($R = H$, $R' = Ph$, Bu^t or H; $R = SiMe_3$, $R' = H$), in which the bridging ligand and the Ru atom form a five-membered $\overline{RuPPh_2C(O)CR{=}CR'}$ metallacyclic ring with the unsaturated C–C bond η^2-

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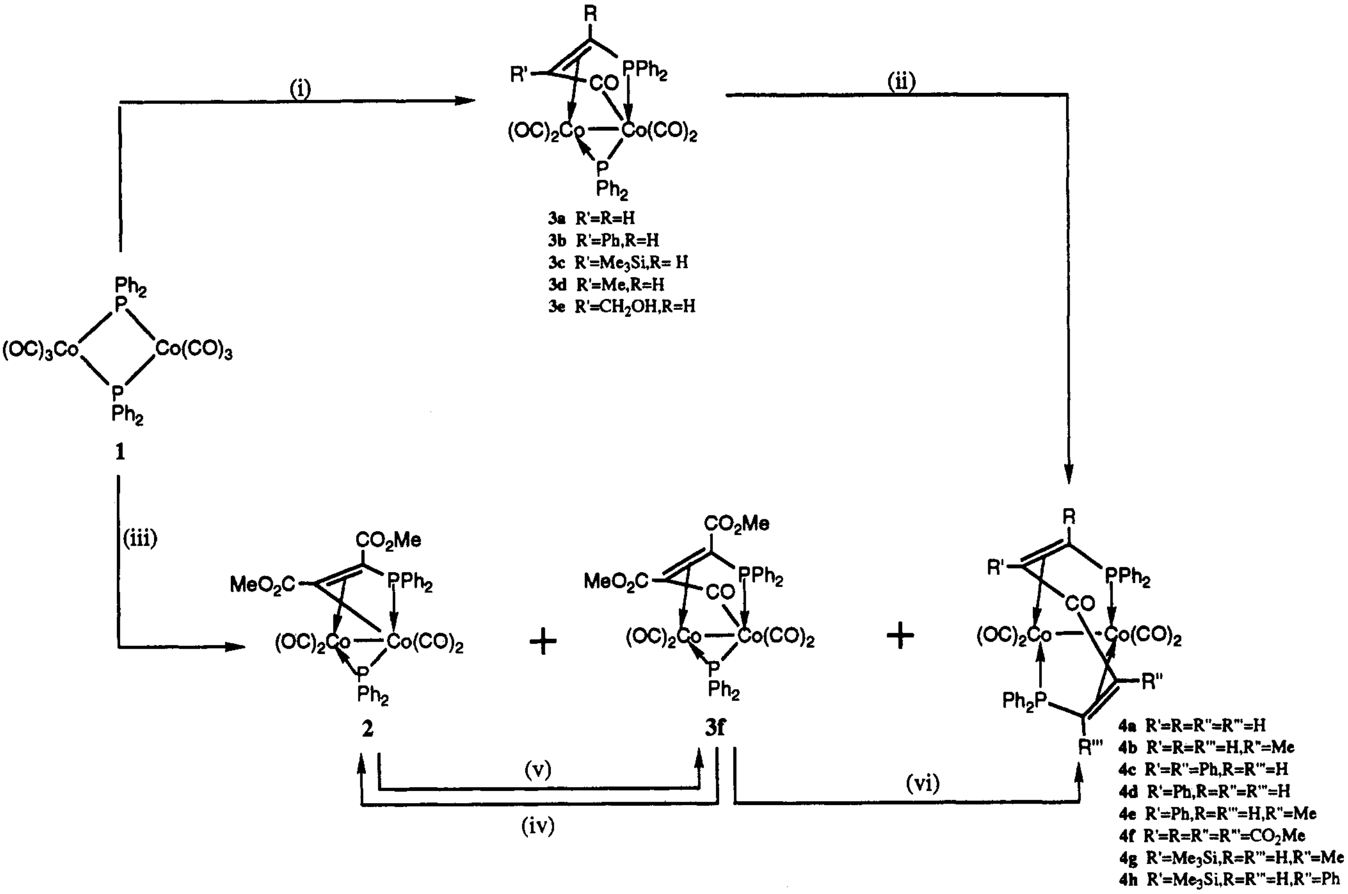

Figure 1. Reagents: (i) R′C≡CR/293 K, (ii) R″C≡CR‴/Δ (no reaction for R″ = R‴ = Ph), (iii) $C_2(CO_2Me)_2$/293 K, (iv) Δ,[14] (v) CO/Δ,[14] (vi) $C_2(CO_2Me)_2$/Δ/CO.

coordinated to the Co atom.[2] These complexes decarbonylate on thermolysis to give the four-membered ring-containing complexes [RuCo(μ-PPh_2CRCR′)(μ-CO)$(CO)_5$]. Although insertion reactions of this type most commonly lead to the formation of complexes with four-membered and five-membered metallacyclic rings, larger rings can also be formed. Thus the reaction of alkynes, RC≡CR′, with the di-iron acetylide complex [Fe_2(μ-C≡CBu^t)(μ-PPh_2)$(CO)_6$] gives [Fe_2{μ-PPh_2C(O)CBu^{t}CCRCR′}$(CO)_5$] in which the bridging ligand is part of an eight-membered dimetallacyclic ring.[8]

In previous work we have described the reactions of [Co_2(μ-alkyne)$(CO)_6$] with P_2Ph_4 which lead to new dinuclear cobalt complexes containing four-membered and five-membered metallacyclic rings derived from the coupling of the alkyne with a PPh_2 moiety and, for the complexes containing five-membered rings, with CO as well.[14] An alternative synthetic strategy for these compounds might be the reaction of [Co_2(μ-PPh_2)$_2$$(CO)_6$] (1), with alkynes, and in this paper we present a study of this reaction. The ready transformation of 1 to [Co_3(μ-PPh_2)$_3$$(CO)_6$][15] suggests that the bonds to the bridging phosphido groups are relatively easily broken, and indeed a variety of insertion products are obtained when 1 is reacted with alkynes. These contain new bridging ligands which form part of four-, five-, or nine-membered rings incorporating one or both of the metal centers. When unsymmetrical alkynes are employed, the reactions proceed regiospecifically and the origins of this regiospecificity are explored. The further reactions of one of the insertion products, [Co_2{μ-PPh_2CHCHC(O)}(μ-PPh_2)$(CO)_4$] **3a**, with alkynes and with allene have also been studied.

Results and Discussion

The reaction of a toluene solution of [Co_2(μ-PPh_2)$_2$$(CO)_6$] (1) with acetylene at room temperature gives the complex [Co_2{μ-PPh_2CHCHC(O)}(μ-PPh_2)$(CO)_4$] (**3a**) in near-quantitative yield. This reaction may be contrasted with the reaction of [Co_2(μ-HC≡CH)$(CO)_6$] with P_2Ph_4 which gives [Co_2{μ-PPh_2C(O)CHCH}(μ-PPh_2)$(CO)_4$] as the major product, although **3a** is also obtained in low yield.[14] The reactions of [Co_2(μ-PPh_2)$_2$$(CO)_6$] (1) with other alkynes, RC≡CR′, also in toluene at room temperature, give the complexes [Co_2{μ-PPh_2CRCR′C(O)}(μ-PPh_2)$(CO)_4$] (R = H, R′ = Ph, **3b**; R = H, R′ = $SiMe_3$, **3c**; R = H, R′ = Me, **3d**; R = H, R′ = CH_2OH, **3e**). Complex **3b** has previously been synthesized from the reaction of [Co_2(μ-HC≡CPh)$(CO)_6$] with P_2Ph_4 and its structure determined by an X-ray diffraction study.[14] The structures of the new complexes **3c–e** (Figure 1) are assigned on the basis of their spectroscopic properties which are closely similar to those of **3b**. The unsymmetrical alkynes which give complexes **3b–e** react regiospecifically and only the product isomers with the bulkier alkyne substituent attached to the carbon atom remote from the PPh_2 group are formed (Figure 1).

The room temperature reaction of [Co_2(μ-PPh_2)$_2$$(CO)_6$] (1) with dimethylacetylenedicarboxylate (dmad) gives, in addition to the five-membered metallacyclic ring-containing complex **3f**, the four-membered ring complex **2**

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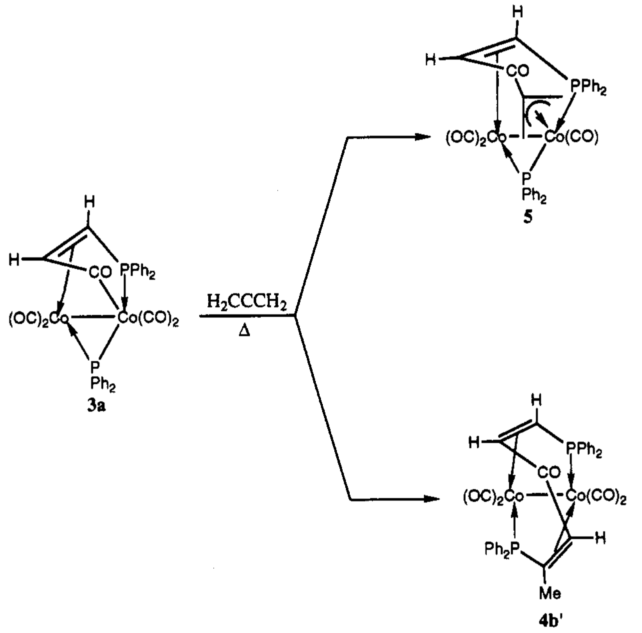

Figure 2. Products from the reaction of $[Co_2\{\mu\text{-}PPh_2CHCHC(O)\}(\mu\text{-}PPh_2)(CO)_4]$ (**3a**) with H_2CCCH_2.

and the nine-membered ring complex **4f**. We have previously reported the complexes **2** and **3f** as two of the products of the thermolysis at 363 K of $[Co_2\{\mu\text{-}C_2(CO_2Me)_2\}(\mu\text{-}P_2Ph_4)(CO)_4]$.[14] Complex **2** was postulated as an intermediate in the formation of complex **3f** and indeed complex **2** is partially converted to complex **3f** under CO when heated to 333 K. This conversion, however, does not take place at room temperature and the formation of complex **2**, from the reaction of **1** with dmad at room temperature, is thus more reasonably postulated as proceeding via the decarbonylation of complex **3f**.

The further reaction of the complexes **3** with the alkynes $R''C{\equiv}CR'''$ in toluene at 353 K gives rise to the complexes $[Co_2\{\mu\text{-}PPh_2CRCR'C(O)CR''CR'''PPh_2\}(CO)_4]$ (**4**), and the new complexes prepared by this route are shown in Figure 1. As mentioned above, complex **4f** is also obtained directly (with **3f** and **2**) in the room temperature reaction of **1** with $C_2(CO_2Me)_2$.

The structures of the complexes **4a–h** are assigned on the basis of spectroscopic data (see Table I and Experimental Section) and an X-ray diffraction study of **4a**. Crystals suitable for analysis were grown by slow evaporation of a dichloromethane/hexane solution of the complex. In the crystals two independent molecules (**A** and **B**) have been found. A view of the molecule **A** is shown in Figure 3 together with the atom numbering scheme; selected bond distances and angles are given in Table II and the atomic coordinates in Table IV. The two molecules differ only in the orientation of the phenyl rings and will therefore be described together. Average values of the corresponding structural parameters will be discussed.

Each independent molecule possesses an idealized C_2 symmetry, with the 2-fold noncrystallographic axis passing through the midpoint of the Co–Co bond and colinear with the carbonyl included in the bridging ligand. The molecule is chiral as is the precursor five-membered ring complex $[Co_2\{\mu\text{-}PPh_2CHCHC(O)\}(\mu\text{-}PPh_2)(CO)_4]$ (**3a**). As crystallization occurs in a centrosymmetric space group, a racemic mixture of both enantiomers of the molecules **A** and **B** are present in the crystals.

The $PPh_2CH{=}CHC(O)CH{=}CHPPh_2$ ligand bridges the two Co atoms through the P-termini, forming a nine-membered dimetallacyclic ring. The conjugated alkene system is $\eta^2{:}\eta^{2'}$-coordinated to the two metal centers. Each Co atom bears two carbonyl groups and formally receives four additional electrons, two from the Co–P σ-interaction and two from the π-interaction with the C=C system directly bound to the phosphorus linked to the other metal atom. The nine-membered ring is folded over so that the two C=C and the Co–Co axes are approximately perpendicular, as already seen in the five-membered metallacyclic ring in the complex $[Co_2\{\mu\text{-}PPh_2CHCPhC(O)\}(\mu\text{-}PPh_2)(CO)_4]$ (**3b**).[14] The bridging ligand is made up of a strictly planar moiety [C(6)C(7)O(7)C(8) in molecule **A** and C(39)C(40)O(40)C(41) in molecule **B**, respectively] and two PC=CC groups which are both nearly planar. The torsion angles within each of these two moieties range from 17.5 to 23°.

As in **3b**, there is an appreciable retention of double bond character in the conjugated olefin [1.431 Å, av], but in **4a** a certain degree of delocalization can be observed throughout the two PC=CC groups of the ring [=C–C(O) bond length 1.475 Å, av]. The P–C(alkene) distances are slightly shorter than the P–C(phenyl) distances, [1.784 vs 1.831 Å, av].

The Co–P bond distances, 2.191 Å, are comparable to those found in other dicobalt complexes containing inserted phosphido moieties.[3,4,11,13,14] An interesting feature of the structure of **4a** is the relatively short intramolecular distances between each cobalt atom and the remote phosphorus atom of the metallacyclic ring [Co(1)–P(2) and Co(2)–P(1) in molecule **A**, 2.872(2) and 2.841(2) Å; Co(3)–P(4) and Co(4)–P(3) in molecule **B**, 2.833(2) and 2.821(2) Å]. This feature can reasonably be ascribed to steric constraints imposed by the conformation adopted by the bridging ligand and has been previously observed also in complex **3b** [Co–P, 2.858(5) Å].

The Co–C(carbonyl) bond lengths do not show any appreciable variations in lengths depending on the cis or trans position with respect to the Co–Co bond. The value of the Co–Co distance, 2.655(1) Å, is much longer than that found in **3b**, 2.513(7) Å av, perhaps because this latter complex additionally possesses a bridging phosphido ligand.

Four terminal ν(CO) bands are visible in the IR spectrum of **4a**. In addition a lower frequency band is observed at 1636 cm^{-1}; this is assigned to the inserted carbonyl group. The ^1H NMR spectrum of **4a** shows a doublet at δ 4.29 with $^3J(HH)$ 8.2 Hz due to the two PPh_2CH protons [no geminal $^2J(PH)$ was observed]. A peak at δ 3.66 broadened by second-order effects takes the approximate form of a doublet of doublets with $^3J(PH)_{trans}$ 32.6 Hz. This signal is assigned to the $CHC(O)CH$ protons.

The structures of the complexes **4b–h** (Figure 1) are assigned on the basis of their spectroscopic properties (see Table I and Experimental Section) and a comparison of these properties with those of **4a**. These structures reveal that, in each case, the reaction of **3** with unsymmetrical alkynes is regiospecific and that the added alkyne is oriented within the nine-membered dimetallacyclic ring such that the more bulky substituent is furthest from the PPh_2 group to which the alkyne becomes attached. Thus, for example, the formation of **4e** can be achieved by the reaction of either **3d** with $PhC{\equiv}CH$ or **3b** with $MeC{\equiv}CH$. Interestingly, the reaction of complex **3b** with the sym-

Table I. Infrared and ^{1}H NMR Data for the New Complexes

compound	ν(CO),[a] cm^{-1}	^{1}H NMR[b] (δ)
3d, [Co$_2${μ-PPh$_2$CHC(SiMe$_3$)C(O)}(μ-PPh$_2$)(CO)$_4$]	2045 m, 2011 s, 2003 sh, 1969 m, 1638 w	8.2–7.2 (m, 20 H, Ph), 4.50 [dd, ^2J(PH) 6.1, ^3J(P′H) 1.9, 1 H, PPh$_2$C*H*], –0.3 (s, 9 H, SiMe$_3$)
3e, [Co$_2${μ-PPh$_2$CHCMeC(O)}(μ-PPh$_2$)(CO)$_4$]	2046 m, 2012 s, 2004 sh, 1969 m, 1618 w[c]	8.0–7.2 (m, 20 H, Ph), 4.57 [dd, ^2J(PH) 2.8, ^3J(P′H) 2.8, 1 H, PPh$_2$C*H*], 1.36 (s, 3 H, Me)
3f, [Co$_2${μ-PPh$_2$CHC(CH$_2$OH)C(O)}(μ-PPh$_2$)(CO)$_4$]	2049 m, 2017 s, 2008 sh, 1975 m, 1608[c]	8.2–7.2 (m, 20 H, Ph), 4.68 [dd, ^2J(PH) 2.8, ^3J(P′H) 2.8, 1 H, PPh$_2$C*H*], 3.61 [dd, J(H$_a$H$_b$) 12.3, J(H$_c$H$_b$) 6.5, 1 H, CH$_a$*H*$_b$OH$_c$], 3.56 [dd, J(H$_c$H$_a$) 6.5, 1 H, C*H*$_a$H$_b$OH$_c$], 2.18 (t, 1 H, CH$_a$H$_b$O*H*$_c$)
4a, [Co$_2${μ-PPh$_2$CHCHC(O)CHCHPPh$_2$}(CO)$_4$]	2034 m, 2015 s, 1990 m, 1972 w, 1636 w	8.0–7.3 (m, 20 H, Ph), 4.29 [d, ^3J(HH) 8.2, 2 H, PPh$_2$C*H*CH], 3.66 [dd, ^3J(PH) 32.6, 2 H, PPh$_2$CHC*H*][d]
4b, [Co$_2${μ-PPh$_2$CHCHC(O)CMeCHPPh$_2$}(CO)$_4$]	2032 m, 2012 s, 1988 m, 1968 w, 1627 w	8.0–7.2 (m, 20 H, Ph), 4.28 (s, 1 H, PPh$_2$C*H*CMe), 4.21 [dd, ^3J(HH) 7.8, ^2J(PH) 0.9, 1 H, PPh$_2$C*H*CH], 3.80 [ddd, ^3J(PH) 33.3, ^3J(PH) 1.1, 1 H, PPh$_2$CHC*H*], 1.26 (s, 3 H, Me)[d]
4b,′ [Co$_2${μ-PPh$_2$CHCHC(O)CHCMePPh$_2$}(CO)$_4$]	2029 m, 2011 s, 1985 m, 1964 w, 1636 w	8.1–7.3 (m, 20 H, Ph), 4.32 [dd, ^3J(HH) 8.4, ^2J(PH) 1.1, 1 H, PPh$_2$C*H*CH], 3.54 [dd, ^3J(PH) 30.2, ^3J(P′H) 1.5, 1 H, PPh$_2$CMeC*H*], 3.48 [ddd, ^3J(PH) 29.9, ^3J(P′H) 1.9, 1 H, PPh$_2$CHC*H*], 1.81 [dd, ^3J(PH) 9.3, ^4J(P′H) 6.5, 3 H, Me]
4c, [Co$_2${μ-PPh$_2$CHCPhC(O)CPhCHPPh$_2$}(CO)$_4$]	2033 m, 2016 s, 1989 m, 1971 w, 1609 w[c]	8.2–6.6 (m, 30 H, Ph), 5.29 [dd, ^2J(PH) 1.1, ^3J(P′H) 1.1, 2 H, PPh$_2$C*H*CPh]
4d, [Co$_2${μ-PPh$_2$CHCPhC(O)CHCHPPh$_2$}(CO)$_4$]	2033 m, 2014 s, 1988 m, 1969 w, 1606 w[c]	8.1–6.5 (m, 25 H, Ph), 5.10 (s, 1 H, PPh$_2$C*H*CPh), 4.43 [dd, ^3J(HH) 8.3, ^2J(PH) 1.1, 1 H, PPh$_2$C*H*CH], 3.99 [ddd, ^3J(PH) 33.2, ^3J(P′H) 1.1, 1 H, PPh$_2$CHC*H*]
4e, [Co$_2${μ-PPh$_2$CHCPhC(O)CMeCHPPh$_2$}(CO)$_4$]	2031 m, 2011 s, 1985 m, 1968 w, 1608 w[c]	8.2–6.6 (m, 25 H, Ph), 5.02 (s, br, 1 H, PPh$_2$C*H*CPh), 4.43 (s, br, 1 H, PPh$_2$C*H*CMe), 1.33 (s, 3 H, Me)[d]
4f, [Co$_2${μ-PPh$_2$C$_2$(CO$_2$Me)$_2$C(O)C$_2$(CO$_2$Me)$_2$PPh$_2$}(CO)$_4$]	2052 w, 2040 s, 2008 m, 1983 w, 1733 m, 1724 m, 1606 w[c]	8.1–7.3 (m, 20 H, Ph), 3.51 (s, 6 H, Me), 2.96 (s, 6 H, Me)
4g, [Co$_2${μ-PPh$_2$CHC(SiMe$_3$)C(O)CMeCHPPh$_2$}(CO)$_4$]	2027 m, 2005 s, 1978 m, 1961 w, 1592 w[c]	8.1–7.2 (m, 20 H, Ph), 4.31 [d, ^2J(PH) 2.1, 1 H, PPh$_2$C*H*CMe], 1.21 (s, 3 H, Me), 4.20 [s, 1 H, PPh$_2$C*H*C (SiMe$_3$)], –0.20 (s, 9 H, SiMe$_3$)
4h, [Co$_2${μ-PPh$_2$CHC(SiMe$_3$)C(O)CPhCHPPh$_2$}(CO)$_4$]	2029 m, 2008 s, 1982 m, 1964 w, 1583 w[c]	8.1–6.6 (m, 25 H, Ph), 4.99 (s, 1 H, PPh$_2$C*H*CPh), 4.60 [s, 1 H, PPh$_2$C*H*C(SiMe$_3$)], –0.16 (s, 9 H, SiMe$_3$)
5, [Co$_2${μ-PPh$_2$CHCHC(O)C(CH$_2$)$_2$}(μ-PPh$_2$)(CO)$_3$]	2025 m, 1971 s, 1630 w	7.6–6.8 (m, 20 H, Ph), 4.48 [ddd, ^3J(PH) 28.5, ^3J(HH) 8.1, ^3J(P′H) 2.1, 1 H, PPh$_2$CHC*H*], 3.67 [ddd, ^2J(PH) 1.8, ^3J(P′H) 1.8, 1 H, PPh$_2$C*H*CH], 2.83 [s, 1 H, C(C*H*$_2$)$_2$], 2.62 [d, J(PH) 12.9, 1 H, C(C*H*$_2$)$_2$], 2.04 [d, J(HH) 4.6, 1 H, C(C*H*$_2$)$_2$], 1.49 [m, 1 H, C(C*H*$_2$)$_2$]

[a] Infrared spectrum recorded in hexane solution unless otherwise indicated. [b] Chemical shifts (δ) in ppm, coupling constants in hertz, recorded in CD$_2$Cl$_2$ unless otherwise indicated. [c] Recorded in CH$_2$Cl$_2$ solution. [d] Recorded in CDCl$_3$ solution.

metrical alkyne PhC≡CPh gave only unreacted starting material and decomposition products. The formation in this particular reaction of a complex of type **4**, which would necessarily have a phenyl group on the carbon adjacent to the PPh$_2$ group, is presumably too sterically demanding.

Two possible pathways for the formation of the nine-membered dimetallacyclic ring-containing complexes **4** from the five-membered metallacyclic ring complexes **3** are shown in Scheme I. Path a and path b differ according to whether the alkyne inserts into the Co–C(O) bond or into a Co–P bond of the remaining phosphido group. Either would be compatible with the observed regiospecificity, although this is more obvious in path a in which the bulky phosphido group presumably prefers to become attached to the less sterically hindered end of the alkyne. The reaction of unsymmetrical alkynes, RC≡CR′, with C$_2$H$_4$ and CO in the presence of Co$_2$(CO)$_8$ to give CH$_2$CH$_2$CRCR′C(O) also proceeds, however, such that the more bulky R′ substituent is adjacent to the carbonyl group.[18] Carbon–carbon bond formation [path a] or carbon–phosphorus bond formation [path b] completes the formation of the nine-membered dimetallacyclic ring and is accompanied by coordination of the second C═C bond to give **4**.

To explore the scope of the reaction of complexes of type **3** with small unsaturated organic molecules, the reaction of **3a** with allene has also been studied (Figure 2).

A solution of [Co$_2${μ-PPh$_2$CHCHC(O)}(μ-PPh$_2$)(CO)$_4$] (**3a**) in toluene was heated to 338 K and allene was slowly bubbled through the solution for 45 min. After this time some polymerization of the allene was evident. Two products were isolated from the reaction, purple [Co$_2${μ-PPh$_2$CHCHC(O)CHCMePPh$_2$}(CO)$_4$] (**4b′**) (13%) and black [Co$_2${μ-PPh$_2$CHCHC(O)C(CH$_2$)$_2$}(μ-PPh$_2$)(CO)$_3$] (**5**) (35%). Both complexes have been characterized spectroscopically (see Table I and Experimental Section) and in addition complex **5** has been the subject of an X-ray determination (Figure 4).

Crystals of **5** suitable for an X-ray determination were obtained by slow evaporation of a dichloromethane/hexane solution of the complex. The crystals were found to contain hexane molecules of crystallization. The molecular structure of **5** is depicted in Figure 4 together with the atom numbering scheme; selected bond distances and angles are listed in Table III and atomic coordinates in Table V. The allene ligand has inserted in **3a** via its central carbon atom into the Co–C(O) bond of the PPh$_2$CH═CHC(O)Co

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(18) See, for example, Pályi, G.; Varadi, G.; Markó, L. In *Stereochemistry of Organometallic and Inorganic Compounds*; Bernal, I., Ed.; Elsevier: Amsterdam, 1986; Vol. 1, p 389, and refs therein.

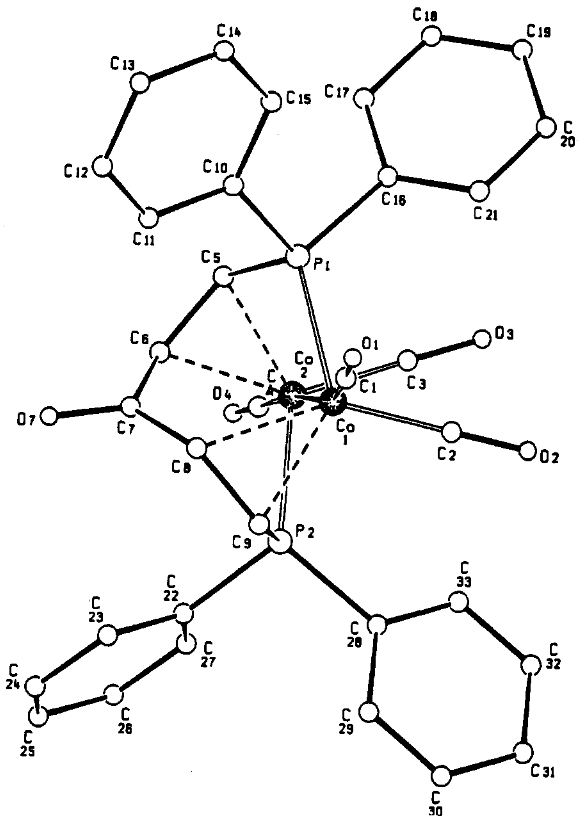


Figure 3. Molecular structure of one of the two independent molecules of complex [$Co_2\{\mu$-$PPh_2CHCHC(O)CHCHPPh_2\}(CO)_4$] (**4a**) including the atom numbering scheme.

Table II. Selected Bond Distances (Å) and Angles (deg) for 4a

molecule A		molecule B	
Co(1)–Co(2)	2.665(1)	Co(3)–Co(4)	2.665(1)
Co(1)–P(1)	2.182(2)	Co(3)–P(3)	2.194(2)
Co(2)–P(2)	2.195(2)	Co(4)–P(4)	2.180(2)
Co(1)–C(1)	1.795(6)	Co(3)–C(34)	1.785(6)
Co(1)–C(2)	1.782(6)	Co(3)–C(35)	1.782(7)
Co(1)–C(8)	2.060(5)	Co(3)–C(41)	2.071(6)
Co(1)–C(9)	2.036(5)	Co(3)–C(42)	2.056(5)
Co(2)–C(3)	1.776(6)	Co(4)–C(36)	1.782(6)
Co(2)–C(4)	1.776(7)	Co(4)–C(37)	1.780(7)
Co(2)–C(5)	2.047(5)	Co(4)–C(38)	2.037(5)
Co(2)–C(6)	2.069(6)	Co(4)–C(39)	2.053(5)
P(1)–C(5)	1.789(5)	P(3)–C(38)	1.778(5)
P(2)–C(9)	1.787(6)	P(4)–C(42)	1.781(6)
C(5)–C(6)	1.428(7)	C(38)–C(39)	1.440(8)
C(6)–C(7)	1.473(8)	C(39)–C(40)	1.481(8)
C(7)–O(7)	1.221(7)	C(40)–O(40)	1.224(7)
C(7)–C(8)	1.476(8)	C(40)–C(41)	1.471(8)
C(8)–C(9)	1.441(8)	C(41)–C(42)	1.426(8)
P–C(phenyl)	1.812(5)–1.852(5)		
Co(2)–Co(1)–P(1)	71.0(1)	Co(4)–Co(3)–P(3)	70.2(1)
Co(1)–Co(2)–P(2)	71.7(1)	Co(3)–Co(4)–P(4)	70.8(1)
Co(1)–P(1)–C(5)	100.7(2)	Co(3)–P(3)–C(38)	101.2(2)
P(1)–C(5)–C(6)	120.3(4)	P(3)–C(38)–C(39)	117.7(4)
C(5)–C(6)–C(7)	124.6(5)	C(38)–C(39)–C(40)	121.5(5)
C(6)–C(7)–O(7)	118.9(5)	C(39)–C(40)–O(40)	118.2(5)
O(7)–C(7)–C(8)	118.2(5)	O(40)–C(40)–C(41)	119.3(5)
C(6)–C(7)–C(8)	122.9(5)	C(39)–C(40)–C(41)	122.5(5)
C(7)–C(8)–C(9)	122.4(5)	C(40)–C(41)–C(42)	124.9(5)
C(8)–C(9)–P(2)	116.8(4)	C(41)–C(42)–P(4)	120.6(4)
Co(1)–C(1)–O(1)	175.5(6)	Co(3)–C(34)–O(34)	175.8(6)
Co(1)–C(2)–O(2)	176.4(6)	Co(3)–C(35)–O(35)	178.7(7)
Co(2)–C(3)–O(3)	176.9(5)	Co(4)–C(36)–O(36)	175.6(5)
Co(2)–C(4)–O(4)	179.6(5)	Co(4)–C(37)–O(37)	176.4(6)

Table III. Selected Bond Distances (Å) and Angles (deg) for 5

Co(1)–Co(2)	2.657(2)	P(1)–C(16)	1.819(8)
Co(1)–P(1)	2.174(2)	P(2)–C(4)	1.782(7)
Co(2)–P(1)	2.135(2)	P(2)–C(22)	1.808(7)
Co(2)–P(2)	2.173(2)	P(2)–C(28)	1.825(8)
Co(1)–C(1)	1.758(10)	C(1)–O(1)	1.134(12)
Co(1)–C(2)	1.792(9)	C(2)–O(2)	1.135(11)
Co(1)–C(4)	2.054(8)	C(3)–O(3)	1.130(10)
Co(1)–C(5)	2.046(8)	C(4)–C(5)	1.404(11)
Co(2)–C(3)	1.773(8)	C(5)–C(6)	1.453(12)
Co(2)–C(7)	1.999(8)	C(6)–O(4)	1.217(10)
Co(2)–C(8)	2.121(9)	C(6)–C(7)	1.507(12)
Co(2)–C(9)	2.066(9)	C(7)–C(8)	1.394(13)
P(1)–C(10)	1.833(8)	C(7)–C(9)	1.392(12)
Co(2)–Co(1)–P(1)	51.3(1)	C(5)–C(6)–C(7)	121.2(7)
Co(1)–Co(2)–P(1)	52.6(1)	C(7)–C(6)–O(4)	117.6(8)
Co(1)–Co(2)–P(2)	71.0(1)	C(6)–C(7)–C(8)	119.2(7)
Co(1)–P(1)–Co(2)	76.1(1)	C(6)–C(7)–C(9)	123.6(8)
Co(2)–P(2)–C(4)	97.6(3)	C(8)–C(7)–C(9)	116.5(8)
P(2)–C(4)–C(5)	127.0(6)	Co(1)–C(1)–O(1)	177.0(8)
C(4)–C(5)–C(6)	132.9(8)	Co(1)–C(2)–O(2)	176.8(8)
C(5)–C(6)–O(4)	121.0(8)	Co(2)–C(3)–O(3)	177.9(8)

metallacycle with concomitant elimination of a terminal carbonyl ligand. The new $PPh_2CH{=}CHC(O)C(CH_2)_2$ ligand is bound to the Co(2) atom through a σ-bond via the terminal P(2) atom, to the Co(1) atom via an η^2-interaction through the internal C(4)–C(5) double bond, and to the Co(2) atom via an η^3-interaction through the terminal allylic system. The phosphido ligand bridges almost symmetrically the two Co atoms. Co(1) and Co(2) are additionally bound by two and one terminal carbonyl groups, respectively. The Co–Co distance [2.657(2) Å] is closely comparable with that found in **4a** [2.665(1) Å] as is the Co(2)–P(2) distance of the inserted phosphido moiety, [2.173(2) Å].

In the $PPh_2CH{=}CHC(O)C(CH_2)_2$ ligand the C(5)C(6)C(7)O(4) moiety is strictly planar and P(2)C(4)C(5)C(6) is also almost planar [torsion angle 4.6°]; the two groups are practically coplanar being tilted by 7.0(3)°. The C(7)C(8)C(9) allylic group forms a dihedral angle of 67.4(5)° with the C(5)C(6)C(7)O(4) moiety.

As in **4a**, the olefinic C(4)–C(5) bond, 1.404(11) Å, preserves appreciable double bond character and a certain degree of delocalization can be observed throughout the PC=CC group as indicated by the values of the C(5)–C(6) and P(2)–C(4) distances, 1.453(12) and 1.782(7) Å, respectively, this latter distance being slightly shorter than the P–C(phenyl) distances [1.808(7) and 1.825(8) Å]. As in **4a** and in **3b** the intramolecular distance for Co(1)–P(2), 2.831(3) Å, is relatively short.

The structure of **4b′** (Figure 2) is assigned by comparison of its spectroscopic properties with those of the isomeric complex **4b** (see Table I and Experimental Section). The two complexes **4b** and **4b′** differ only in the position of the Me group in the nine-membered dimetallacycle. In **4b** the Me group is positioned on the olefinic carbon remote from the phosphido group and in **4b′** on the olefinic carbon adjacent to the phosphido group.

The IR spectrum of **4b′** in hexane solution is very similar to that recorded for **4b** (see Table I and Experimental Section). In addition to four terminal ν(CO) bands, a lower frequency band at 1636 cm^{-1} is assigned to the inserted carbonyl ligand. Figure 5 shows the ^1H NMR spectrum for complex **4b′** and, for comparative purposes, that for the isomeric complex **4b** in the regions ascribed to the olefinic protons of the relevant nine-membered metallacycles. In the spectrum of **4b′** two signals are observed corresponding to two inequivalent C*H*C(O) protons. A resonance centered at δ 3.54 with $^3J(PH)_{trans}$ 30.2 Hz and

Table IV. Fractional Atomic Coordinates for the Non-Hydrogen Atoms of the Complex 4a

atom	x	y	z	atom	x	y	z
Co(1)	–0.24468(5)	0.17583(4)	0.06274(3)	Co(3)	0.24956(5)	0.21655(4)	0.15366(3)
Co(2)	–0.37040(5)	0.27196(4)	0.04981(4)	Co(4)	0.12909(5)	0.11598(4)	0.14084(4)
P(1)	–0.28613(9)	0.19022(8)	–0.03945(7)	P(3)	0.17564(9)	0.22514(8)	0.05875(7)
P(2)	–0.30057(10)	0.28400(8)	0.14594(7)	P(4)	0.17387(10)	0.12876(8)	0.24255(7)
O(1)	–0.1054(3)	0.0782(2)	0.0395(2)	O(34)	0.3918(3)	0.1164(3)	0.1538(2)
O(2)	–0.3447(3)	0.0704(2)	0.1263(2)	O(35)	0.3633(4)	0.3388(3)	0.1490(2)
O(3)	–0.5020(3)	0.1615(3)	0.0433(2)	O(36)	0.2266(3)	0.0200(2)	0.0659(2)
O(4)	–0.4941(4)	0.3881(3)	0.0503(3)	O(37)	–0.0039(3)	0.0124(3)	0.1631(3)
O(7)	–0.1452(3)	0.3729(2)	0.0263(2)	O(40)	0.0224(3)	0.3101(2)	0.1819(2)
C(1)	–0.1586(4)	0.1155(3)	0.0511(3)	C(34)	0.3345(4)	0.1532(3)	0.1537(3)
C(2)	–0.3076(4)	0.1132(3)	0.1016(3)	C(35)	0.3183(4)	0.2917(4)	0.1510(3)
C(3)	–0.4487(4)	0.2034(3)	0.0458(3)	C(36)	0.1915(4)	0.0584(3)	0.0963(3)
C(4)	–0.4458(4)	0.3425(4)	0.0503(3)	C(37)	0.0474(4)	0.0528(3)	0.1523(3)
C(5)	–0.3270(3)	0.2788(3)	–0.0394(2)	C(38)	0.0758(3)	0.1866(3)	0.0746(2)
C(6)	–0.2849(3)	0.3311(3)	0.0021(3)	C(39)	0.0455(3)	0.2003(3)	0.1363(3)
C(7)	–0.1962(4)	0.3251(3)	0.0333(3)	C(40)	0.0747(4)	0.2630(3)	0.1751(3)
C(8)	–0.1655(3)	0.2633(3)	0.0725(3)	C(41)	0.1637(4)	0.2707(3)	0.2053(3)
C(9)	–0.1992(3)	0.2457(3)	0.1323(3)	C(42)	0.2094(3)	0.2184(3)	0.2445(2)
C(10)	–0.2027(3)	0.1840(2)	–0.0963(2)	C(43)	0.1567(2)	0.3140(2)	0.0257(2)
C(11)	–0.1317(3)	0.2292(2)	–0.0879(2)	C(44)	0.2261(2)	0.3515(2)	0.0053(2)
C(12)	–0.0668(3)	0.2246(2)	–0.1290(2)	C(45)	0.2139(2)	0.4200(2)	–0.0189(2)
C(13)	–0.0728(3)	0.1746(2)	–0.1786(2)	C(46)	0.1322(2)	0.4510(2)	–0.0228(2)
C(14)	–0.1438(3)	0.1294(2)	–0.1869(2)	C(47)	0.0628(2)	0.4134(2)	–0.0024(2)
C(15)	–0.2087(3)	0.1340(2)	–0.1458(2)	C(48)	0.0751(2)	0.3449(2)	0.0218(2)
C(16)	–0.3737(2)	0.1372(2)	–0.0792(2)	C(49)	0.2087(2)	0.1770(2)	–0.0103(2)
C(17)	–0.4192(2)	0.1613(2)	–0.1361(2)	C(50)	0.2969(2)	0.1695(2)	–0.0152(2)
C(18)	–0.4838(2)	0.1195(2)	–0.1679(2)	C(51)	0.3253(2)	0.1341(2)	–0.0678(2)
C(19)	–0.5030(2)	0.0535(2)	–0.1430(2)	C(52)	0.2656(2)	0.1061(2)	–0.1155(2)
C(20)	–0.4575(2)	0.0293(2)	–0.0861(2)	C(53)	0.1775(2)	0.1136(2)	–0.1105(2)
C(21)	–0.3929(2)	0.0712(2)	–0.0543(2)	C(54)	0.1490(2)	0.1491(2)	–0.0580(2)
C(22)	–0.2789(3)	0.3730(2)	0.1782(2)	C(55)	0.2647(3)	0.0791(2)	0.2804(2)
C(23)	–0.1966(3)	0.4027(2)	0.1813(2)	C(56)	0.3028(3)	0.1008(2)	0.3406(2)
C(24)	–0.1829(3)	0.4718(2)	0.2036(2)	C(57)	0.3715(3)	0.0623(2)	0.3714(2)
C(25)	–0.2515(3)	0.5113(2)	0.2229(2)	C(58)	0.4020(3)	0.0022(2)	0.3422(2)
C(26)	–0.3338(3)	0.4816(2)	0.2198(2)	C(59)	0.3638(3)	–0.0194(2)	0.2820(2)
C(27)	–0.3475(3)	0.4125(2)	0.1975(2)	C(60)	0.2952(3)	0.0190(2)	0.2511(2)
C(28)	–0.3339(2)	0.2381(2)	0.2164(2)	C(61)	0.0926(3)	0.1161(2)	0.3004(2)
C(29)	–0.2792(2)	0.2397(2)	0.2736(2)	C(62)	0.0248(3)	0.1643(2)	0.3009(2)
C(30)	–0.3024(2)	0.2046(2)	0.3280(2)	C(63)	–0.0376(3)	0.1551(2)	0.3436(2)
C(31)	–0.3804(2)	0.1680(2)	0.3253(2)	C(64)	–0.0323(3)	0.0976(2)	0.3858(2)
C(32)	–0.4351(2)	0.1663(2)	0.2682(2)	C(65)	0.0354(3)	0.0493(2)	0.3853(2)
C(33)	–0.4118(2)	0.2014(2)	0.2137(2)	C(66)	0.0978(3)	0.0586(2)	0.3426(2)

$^3J(P'H)$ 1.5 Hz is assigned to a $PPh_2CMeC\mathit{H}C(O)$ proton. A doublet of doublets of doublets at a similar chemical shift, δ 3.48, with $^3J(PH)_{trans}$ 29.9, $^3J(HH)$ 8.4, and $^3J(P'H)$ 1.9 Hz is assigned to a $PPh_2CHC\mathit{H}C(O)$ proton. The $PPh_2C\mathit{H}CHC(O)$ proton is observed as a doublet of doublets at δ 4.32 with $^2J(PH)$ 1.1 Hz.

In the $^{31}P\{^1H\}$ NMR spectrum of **4b′** two resonances corresponding to inserted phosphido groups are observed. One signal at δ −130.7, of almost identical shift to that observed in **3a** and of similar shift to those of the two phosphorus atoms in **4b**, is assigned to the $\mathit{P}Ph_2CH$ phosphorus. The other signal at δ −113.1 is assigned to the $\mathit{P}Ph_2CMe$ phosphorus atom.

The radically different nature of the products, **4b′** and **5**, suggests that the reaction mechanisms involved in the formation of each from **3a** are not the same. The formation of **5** can be viewed as an insertion of allene into the Co–C(O) bond of the five-membered metallacycle in **3a**. The formation of **4b′** is more difficult to rationalize but must involve an insertion of allene via its central carbon atom into the Co–P bond of the phosphido bridge, in order to account for the presence of the Me substituent on the carbon atom adjacent to the Ph_2P group. This insertion must be accompanied at some point by a 1,3 H-shift and one possible sequence is shown in Scheme II. The fact that **4b** and **4b′** are both accessible, albeit by different synthetic routes, suggests that the regiospecificity observed in the formation of each is kinetic in origin.

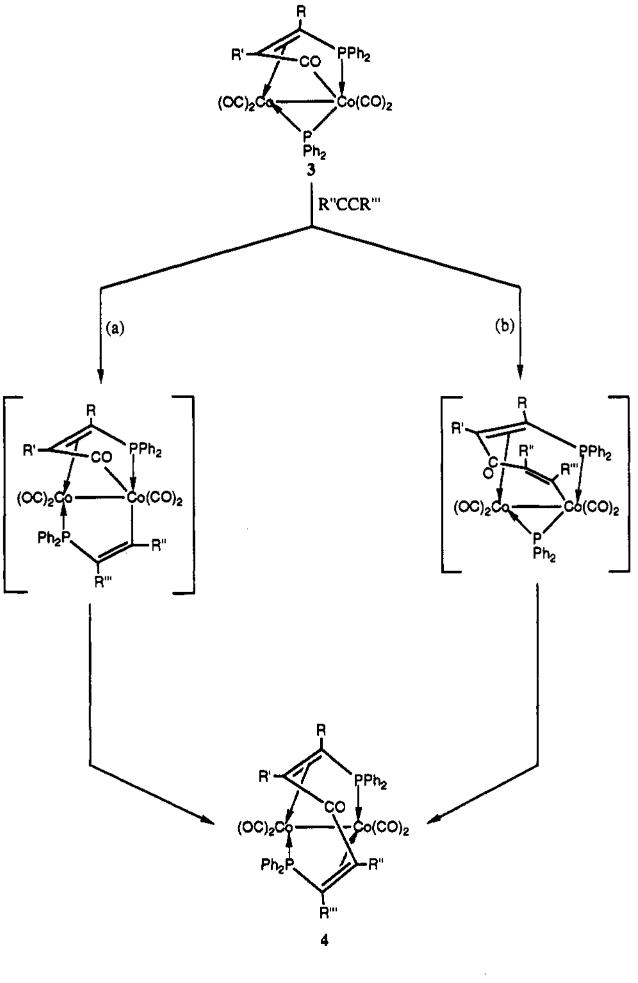
Summary

It has been shown that both of the phosphido bridges in $[Co_2(\mu\text{-}PPh_2)_2(CO)_6]$ (**1**) will readily undergo insertion reactions. In the first instance insertion of an alkyne and a carbonyl ligand into one phosphido bridge generates the five-membered metallacyclic ring-containing complexes **3**. These complexes can be induced to insert a second alkyne molecule to give the nine-membered dimetallacyclic ring-containing complexes **4**. Both of the above reactions were found to be regiospecific for all the examples studied. Allene also undergoes an insertion reaction with **3a** to give two products. One of these products contains a bridging ligand with a coordinated allyl group formed by insertion of allene into the Co–C(O) bond of the five-membered metallacycle in **3a**. The other product $[Co_2\{\mu\text{-}PPh_2CHCHC(O)CHCMePPh_2\}(CO)_4]$ (**4b′**) contains a nine-membered dimetallacyclic ring with a methyl substituent positioned differently from that in the isomeric complex **4b** obtained on reaction of $[Co_2\{\mu\text{-}PPh_2CHCHC(O)\}(\mu\text{-}PPh_2)(CO)_4]$ (**3a**) with MeC≡CH.

Experimental Section

Unless otherwise stated 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

Scheme I. Two Possible Mechanistic Pathways for the Formation of Complexes 4a–h Represented by a and b



coated with a 0.25-mm layer of silica or on 1-mm silica plates prepared at the University Chemical Laboratory, Cambridge; products are presented in order of decreasing R_f values.

The instrumentation used to obtain spectroscopic data has been described previously.[20] Phosphorus-31 NMR chemical shifts are given relative to $P(OMe)_3$ with upfield shifts negative. All coupling constants (*J*) are given in hertz. All NMR spectra were recorded at 293 K. Elemental analyses were performed at Cambridge.

(i) Preparation of $[Co_2(\mu\text{-}PPh_2)_2(CO)_6]$ (1). The complex $[Co_2(\mu\text{-}PPh_2)_2(CO)_6]$ (1) was generated in situ using a modification of Geoffroy's procedure.[15] A 100-mL Roth autoclave fitted with a glass liner was charged with toluene (50 mL) and $Co_2(CO)_8$ (0.80 g, 2.30 mmol). A 1-dram vial was taped to the inside of the liner, and PPh_2H (0.80 mL, 4.30 mmol) was then added to it. The autoclave was sealed, purged with CO, pressured to 80 atm, and heated to 383 K. On reaching this temperature the autoclave was carefully tipped upside down a few times and shaken. After 1 day at 383 K the autoclave was allowed to cool. When the sample was required, the CO pressure was released and the toluene solution of $[Co_2(\mu\text{-}PPh_2)_2(CO)_6]$ (1) decanted. This solution could generally be used for subsequent reactions without further workup. If necessary, however, any traces of oligomeric $[Co(PPh_2)(CO)_3]_x$ can be removed by chromatography on silica gel under red light using the procedure outlined by Geoffroy and co-workers.[15]

(ii) Reaction of $[Co_2(PPh_2)_2(CO)_6]$ (1) with RC≡CR' (R = H, R' = H, Ph, Me_3Si, Me, or CH_2OH and R = R' = CO_2Me). (a) A solution of the complex $[Co_2(\mu\text{-}PPh_2)_2(CO)_6]$ (1) (0.276 g, 0.346 mmol) in toluene (50 mL) was purged with acetylene for 5 h at 293 K. After removal of the solvent in vacuo, the residue was dissolved in the minimum quantity of CH_2Cl_2 and adsorbed onto silica. The silica was pumped dry and added to the top of a chromatography column [Kieselgel 60 (70–230 mesh)]. Elution with hexane/CH_2Cl_2 (1:1) gave red-brown $[Co_2\{\mu\text{-}PPh_2CHCHC(O)\}(\mu\text{-}PPh_2)(CO)_4]$ (**3a**) (0.186 g, 86%).

(b) A solution of the complex $[Co_2(\mu\text{-}PPh_2)_2(CO)_6]$ (1) (0.300 g, 0.457 mmol) in toluene (50 mL) was charged with a 5-fold excess of phenylacetylene and stirred at 293 K for 15 h. Purification was as in a. Elution with hexane/CH_2Cl_2 (1:1) gave red-brown $[Co_2\{\mu\text{-}PPh_2CHCPhC(O)\}(\mu\text{-}PPh_2)(CO)_4]$ (**3b**) (0.230 g, 69%).

(c) A solution of the complex $[Co_2(\mu\text{-}PPh_2)_2(CO)_6]$ (1) (0.340 g, 0.518 mmol) in toluene (50 mL) was charged with a 5-fold excess of (trimethylsilyl)acetylene and stirred for 15 h at 293 K. Purification was as in a. Elution with hexane/CH_2Cl_2 (1:1) gave red-brown $[Co_2\{\mu\text{-}PPh_2CHC(SiMe_3)C(O)\}(\mu\text{-}PPh_2)(CO)_4]$ (**3c**) (0.280 g, 74%). Anal. Calcd for $C_{34}H_{30}Co_2O_5P_2Si$ (**3c**): C, 56.2; H, 4.2; P, 8.5. Found: C, 56.4; H, 4.3; P, 8.2. Fast atom bombardment (FAB) mass spectrum, *m/z* 726 (M^+), $M^+ - n$CO (*n* = 0–5). NMR ($CDCl_3$): ^{13}C (^1H composite pulse decoupled) δ 219.1 [d, *J*(PC) 17, $PPh_2CHC(SiMe_3)$*C*(O)], 207.4 (s, 2 CO), 200.5 (s, 2 CO), 142–127 (m, Ph), 77.8 [d, *J*(PC) 27, $PPh_2CHC(SiMe_3)$], 46.5 [d, *J*(PC) 32, $PPh_2CHC(SiMe_3)$], −2.5 [s, $PPh_2CHC(Si\mathit{Me}_3)$]; ^{31}P (^1H-gated decoupled) δ 16.5 (s, μ-PPh_2), −86.3 [s, μ-$PPh_2CHC(SiMe_3)C(O)$].

(d) The complex $[Co_2(\mu\text{-}PPh_2)_2(CO)_6]$ (1) (0.200 g, 0.305 mmol) in toluene (50 mL) was purged slowly with methylacetylene for 45 min at 293 K and then left to stir in an atmosphere of the gas overnight. Purification was as in a. Elution with hexane/CH_2Cl_2 (1:1) gave unreacted $[Co_2(\mu\text{-}PPh_2)_2(CO)_6]$ (1) (0.058 g) and red-brown $[Co_2\{\mu\text{-}PPh_2CHCMeC(O)\}(\mu\text{-}PPh_2)(CO)_4]$ (**3d**) (0.063 g, 31%). Complex **3d**: FAB mass spectrum, *m/z* 668 (M^+), $M^+ - n$CO (*n* = 0–5). NMR ($CDCl_3$): ^{13}C (^1H composite pulse decoupled) δ 216.0 [s, $PPh_2CHCMeC(O)$], 207.1 (s, 2 CO), 203.0 (s, 2 CO), 143–128 (m, Ph), 83.5 [d, *J*(PC) 34, $PPh_2CHCMeC(O)$], 46.6 [d, *J*(PC) 40, $PPh_2CHCMeC(O)$], 19.1 [d, ^3J(PC) 9, $PPh_2CHC\mathit{Me}C(O)$]; ^{31}P (^1H-gated decoupled) δ 20.8 (s, μ-PPh_2), −95.7 [s, μ-$PPh_2CHCMeC(O)$].

(e) The complex $[Co_2(\mu\text{-}PPh_2)_2(CO)_6]$ (1) (0.200 g, 0.305 mmol) was dissolved in toluene (50 mL) and a 3-fold excess of propargyl alcohol added, and the solution was stirred at 293 K for 15 h. Purification was as in a. Elution with hexane/CH_2Cl_2 (1:1) gave red-brown $[Co_2\{\mu\text{-}PPh_2CHC(CH_2OH)C(O)\}(\mu\text{-}PPh_2)(CO)_4]$ (**3e**) (0.136 g, 65%). Complex **3e**: FAB mass spectrum, *m/z* 684 (M^+), $M^+ - n$(CO) (*n* = 0–5). NMR: ^{13}C (CD_2Cl_2, ^1H composite pulse decoupled) δ 219.0 [s, $PPh_2CHC(CH_2OH)$*C*(O)], 207.1 (s, 2 CO),

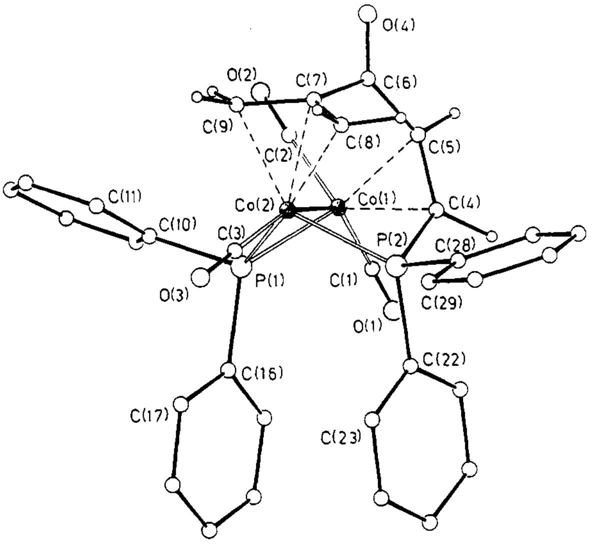


Figure 4. Molecular structure of the complex $[Co_2\{\mu\text{-}PPh_2CHCHC(O)C(CH_2)_2\}(\mu\text{-}PPh_2)(CO)_3]$ (**5**) including the atom numbering scheme.

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(19) Mays, M. J.; Solan, G. A., unpublished results.

(20) Caffyn, A. J. M.; Mays, M. J.; Raithby, P. R. *J. Chem. Soc., Dalton Trans.*, **1991**, 2349.

Table V. Fractional Atomic Coordinates ($\times 10^4$) with Esd's in Parentheses for the Non-Hydrogen Atoms of the Complex 5

	x/a	*y/b*	*z/c*
Co(1)	1898(1)	1063(1)	4646(1)
Co(2)	2295(1)	9(1)	2678(1)
P(1)	1466(1)	192(1)	3012(2)
P(2)	2464(1)	1425(1)	2212(2)
O(1)	1190(3)	2596(5)	4948(7)
O(2)	1708(3)	8(5)	7227(7)
O(3)	2195(3)	−1016(4)	−21(7)
O(4)	3068(3)	152(4)	6754(7)
C(1)	1471(4)	2004(6)	4795(9)
C(2)	1788(4)	396(6)	6210(10)
C(3)	2244(3)	−619(5)	1031(8)
C(4)	2525(3)	1833(5)	4037(8)
C(5)	2693(3)	1334(5)	5301(9)
C(6)	2893(4)	410(6)	5543(9)
C(7)	2854(3)	−280(5)	4331(9)
C(8)	3143(4)	−137(7)	3141(10)
C(9)	2484(4)	−995(6)	4215(11)
C(10)	1084(3)	−756(5)	3690(8)
C(11)	1198(4)	−1648(5)	3382(10)
C(12)	902(4)	−2351(7)	3908(11)
C(13)	499(4)	−2180(8)	4717(12)
C(14)	392(4)	−1292(8)	5087(12)
C(15)	676(4)	−584(7)	4551(10)
C(16)	985(3)	594(5)	1531(8)
C(17)	895(3)	100(7)	247(8)
C(18)	537(4)	400(7)	−893(10)
C(19)	263(4)	1196(8)	−767(11)
C(20)	339(4)	1690(7)	482(11)
C(21)	698(3)	1394(6)	1613(10)
C(22)	1993(3)	2181(5)	1184(8)
C(23)	1801(3)	1906(6)	−210(8)
C(24)	1456(4)	2456(7)	−1087(10)
C(25)	1298(4)	3279(7)	−594(11)
C(26)	1488(4)	3571(7)	781(11)
C(27)	1840(3)	3019(5)	1664(10)
C(28)	3075(3)	1703(5)	1376(8)
C(29)	3181(4)	1268(6)	122(9)
C(30)	3632(4)	1472(7)	−539(10)
C(31)	3978(4)	2119(7)	46(11)
C(32)	3887(4)	2562(7)	1290(11)
C(33)	3434(4)	2349(6)	1976(10)
C(34)	201(22)	4079(42)	2644(54)
C(35)	333(24)	4991(38)	2899(66)
C(36)	255(24)	4861(38)	4722(66)
C(37)	−255(10)	5139(20)	5278(34)
C(38)	233(24)	5122(37)	6597(61)
C(39)	44(25)	5096(39)	8109(67)

202.2 (s, 2 CO), 136–128 (m, Ph), 88.3 [d, *J*(PC) 28, $PPh_2CHC(CH_2OH)C(O)$], 63.4 [d, *J*(PC) 9, $PPh_2CHC(CH_2OH)C(O)$], 43.1 [d, *J*(PC) 33, $PPh_2CHC(CH_2OH)C(O)$]; ^{31}P ($CDCl_3$, ^1H-gated decoupled) δ 20.3 (s, μ-PPh_2), −96.3 [s, μ-$PPh_2CHC(CH_2OH)C(O)$].

(f) The complex $[Co_2(\mu\text{-}PPh_2)_2(CO)_6]$ (**1**) (0.140 g, 0.213 mmol) was dissolved in hexane (60 mL), a 5–10-fold excess of dmad added, and the solution stirred at 293 K for 15 h. After removal of the solvent in vacuo, the residue was redissolved in the minimum of CH_2Cl_2 and separated by preparative TLC. Elution with CH_2Cl_2 gave red $[Co_2\{\mu\text{-}PPh_2C(CO_2Me)C(CO_2Me)\}(\mu\text{-}PPh_2)(CO)_4]$ (**2**) (0.055 g, 35%), orange $[Co_2\{\mu\text{-}PPh_2C(CO_2Me)C(CO_2Me)C(O)\}(\mu\text{-}PPh_2)(CO)_4]$ (**3f**) (0.014 g, 9%), and purple-red crystalline $[Co_2\{\mu\text{-}PPh_2C_2(CO_2Me)_2C(O)C_2(CO_2Me)_2PPh_2\}(CO)_4]$ (**4f**) (0.032 g, 16%). Anal. Calcd for $C_{41}H_{32}Co_2O_{13}P_2$ (**4f**): C, 54.0; H, 3.5. Found: C, 54.5; H, 4.2. FAB mass spectrum: *m/z* 912 (M^+), $M^+ - n$CO (*n* = 0–4). NMR ($CDCl_3$): ^{31}P (^1H-gated decoupled) δ −121.8 [s, μ-$\{PPh_2C(CO_2Me)C(CO_2Me)\}_2C(O)$].

(iii) Reactions of $[Co_2\{\mu\text{-}PPh_2CRCR'C(O)\}(\mu\text{-}PPh_2)(CO)_4]$ with R″C≡CR‴ (R″ = H, R‴ = H, Me, or Ph and R″ = R‴ = CO_2Me). (a) The complex $[Co_2\{\mu\text{-}PPh_2CHCHC(O)\}(\mu\text{-}PPh_2)(CO)_4]$ (**3a**) (0.090 g, 0.144 mmol) was dissolved in toluene (40 mL) and the solution purged slowly with acetylene at 353 K for 2 h. After removal of the solvent in vacuo, the residue was separated by TLC. Elution with hexane/CH_2Cl_2 (2:3) gave purple crystalline $[Co_2\{\mu\text{-}PPh_2CHCHC(O)CHCHPPh_2\}(CO)_4]$ (**4a**) (0.045 g, 46%). Anal. Calcd for $C_{33}H_{24}Co_2O_5P_2$ (**4a**): C, 58.2; H, 3.5; P, 9.1. Found: C, 58.4; H, 3.5; P, 9.2. FAB mass spectrum; *m/z* 680 (M^+) and $M^+ - n$CO (*n* = 0–4). NMR ($CDCl_3$): ^{13}C (^1H composite pulse decoupled) δ 203.5 (s, 2 CO), 202.5 [d, ^2J(PC) 25, 2 CO], 199.6 [s, HCC(O)CH], 140–128 (m, Ph), 64.1 [s, $(PPh_2CHCH)_2C(O)$], 34.8 [d, ^1J(PC) 50, $(PPh_2CHCH)_2C(O)$]; ^{31}P (^1H-gated decoupled) δ −130.5 [s, μ-$(PPh_2CHCH)_2CO$].

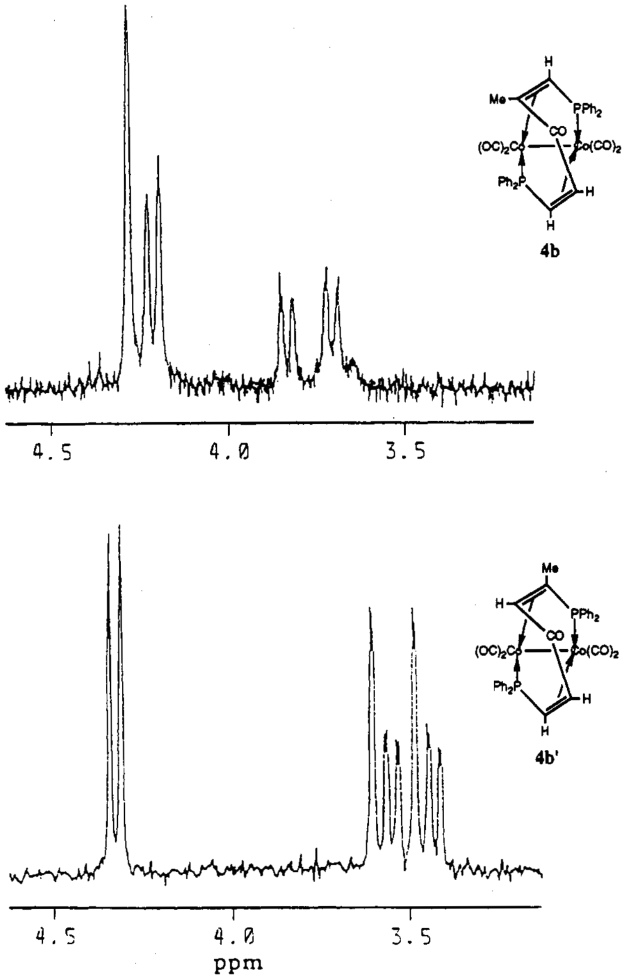
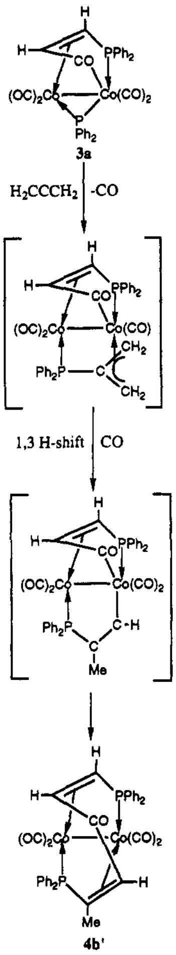


Figure 5. ^1H NMR spectra for the isomeric complexes **4b** and **4b′** in the olefinic proton region.

(b) The complex $[Co_2\{\mu\text{-}PPh_2CHCHC(O)\}(\mu\text{-}PPh_2)(CO)_4]$ (**3a**) (0.150 g, 0.229 mmol) was dissolved in toluene (50 mL) and the solution purged slowly with methylacetylene and 353 K for 1 h then stirred for one further hour. Purification as in a resulted in purple crystalline $[Co_2\{\mu\text{-}PPh_2CHCHC(O)CMeCHPPh_2\}(CO)_4]$ (**4b**) (0.065 g, 41%). Complex **4b**: FAB mass spectrum, *m/z* 694 (M^+), $M^+ - n$CO (*n* = 0–4). NMR ($CDCl_3$): ^{13}C (^1H composite pulse decoupled) δ 203.7 (s, 2CO), 203.4 [s, CHC(O)CMe], 200.1 (s, 2 CO), 136–128 (m, Ph), 76.0 [s, $PPh_2CHCMeC(O)$], 64.7 [s, $PPh_2CHCHC(O)$], 42.3 [dd, *J*(PC) 41, *J*(PC) 10, $PPh_2CHCMeC(O)$], 33.3 [dd, *J*(PC) 37, *J*(PC) 13, $PPh_2CHCHC(O)$], 24.7 [d, *J*(PC) 8, Me]; ^{31}P (^1H-gated decoupled) δ −129.5 [s, μ-$PPh_2CHCHC(O)CMeCHPPh_2$], −134.6 [s, μ-$PPh_2CHCHC(O)CMeCHPPh_2$].

(c) The complex $[Co_2\{\mu\text{-}PPh_2CHCPhC(O)\}(\mu\text{-}PPh_2)(CO)_4]$ (**3b**) (0.150 g, 0.205 mmol) was dissolved in toluene (50 mL), a 5–10-fold excess of phenylacetylene added, and the solution stirred at 353 K for 2 h. Purification was as in a. Elution with hexane/CH_2Cl_2 (1:1) gave purple $[Co_2\{\mu\text{-}PPh_2CHCPhC(O)CPhCHPPh_2\}(CO)_4]$ (**4c**) (0.077 g, 45%). Anal. Calcd for $C_{45}H_{32}Co_2O_5P_2$ (**4c**): C, 64.9; H, 3.9; P, 7.5. Found: C, 64.7; H, 4.1; P, 8.1. FAB mass spectrum: *m/z* 832 (M^+), $M^+ - n$(CO) (*n* = 0–4). NMR ($CDCl_3$): ^{13}C (^1H composite pulse decoupled) δ 203.3 (s, 2CO), 201.4 [s, $(PPh_2CHCPh)_2CO$], 198.3 (s, 2CO), 144–128 (m, Ph), 81.4 [s,

Scheme II. Possible Sequence for the Formation of 4b′ from the Reaction of [Co$_2${μ-PPh$_2$CHCHC(O)}(μ-PPh$_2$)(CO)$_4$] (3a) with Allene



(PPh$_2$CHCPh)$_2$CO], 35.5 [d, *J*(PC) 30, (PPh$_2$CHCPh)$_2$CO]; ^{31}P (^{1}H-gated decoupled) δ −139.1 [s, μ-(*P*Ph$_2$CHCPh)$_2$CO].

(d) A solution of the complex [Co$_2${μ-PPh$_2$CHCPhC(O)}(μ-PPh$_2$)(CO)$_4$] (**3b**) (0.150 g, 0.205 mmol) in toluene (50 mL) was purged with acetylene for 2 h at 353 K. Purification as in a gave purple [Co$_2${μ-PPh$_2$CHCPhC(O)CHCHPPh$_2$}(CO)$_4$] (**4d**) (0.071 g, 46%). Complex **4d**: FAB mass spectrum, *m*/*z* 756 (M$^+$), M$^+$ − *n*(CO) (*n* = 0–4). NMR (CDCl$_3$): ^{13}C (^{1}H composite pulse decoupled), δ 203.9 (s, 2CO), 202.4 [s, CPhC(O)CH], 199.2 (s, 1 CO), 198.6 (s, 1 CO), 143–126 (m, Ph), 79.8 [s, PPh$_2$CHCPhC(O)], 66.2 [s, PPh$_2$CHCHC(O)], 37.0 [d, *J*(PC) 37, PPh$_2$CHCPhC(O)], 33.1 [d, *J*(PC) 26, PPh$_2$CHCHC(O)]; ^{31}P (^{1}H-gated decoupled) δ −133.2 [s, μ-*P*Ph$_2$CHCPhC(O)], 136.2 [s, μ-*P*Ph$_2$CHCHC(O)].

(e) A solution of the complex [Co$_2${μ-PPh$_2$CHCPhC(O)}(μ-PPh$_2$)(CO)$_4$] (**3b**) (0.150 g, 0.205 mmol) in toluene (50 mL) was purged with methylacetylene for 1 h at 353 K and stirred for one further hour. Purification was as in a. Elution with hexane/CH$_2$Cl$_2$ (4:6) gave purple [Co$_2${μ-PPh$_2$CHCPhC(O)CMeCHPPh$_2$}(CO)$_4$] (**4e**) (0.066 g, 42%). Complex **4e**: FAB mass spectrum, *m*/*z* 770 (M$^+$), M$^+$ − *n*(CO) (*n* = 0–4). NMR: ^{13}C (CD$_2$Cl$_2$, ^{1}H composite pulse decoupled) δ 204.0 (s, 2 CO), 202.8 [s, CMeC(O)CPh], 200.3 (s, 1 CO), 199.6 (s, 1 CO), 145–126 (m, Ph), 80.0 [s, CMeC(O)CPh], 78.3 [s, CMeC(O)CPh], 40.6 [dd, *J*(PC) 39, *J*(P′C) 13, PPh$_2$CHCPhC(O)], 35.5 [dd, *J*(PC) 40, *J*(P′C) 13, PPh$_2$CHCMeC(O)], 26.6 [d, *J*(PC) 9, PPh$_2$CHC*Me*C(O)]; ^{31}P (CDCl$_3$, ^{1}H-gated decoupled) δ −135.3 [s, μ-PPh$_2$CHCMeC(O)CPhCH*P*Ph$_2$], −137.4 [s, μ-PPh$_2$CHCMeC(O)CPhCHPPh$_2$].

(f) The complex [Co$_2${μ-PPh$_2$CHCMeC(O)}(μ-PPh$_2$)(CO)$_4$] (**3d**) (0.080 g, 0.120 mmol) was dissolved in toluene (30 mL), a 5–10-fold excess of phenylacetylene added, and the solution stirred at 353 K for 2 h. Purification as in a. Elution with hexane/CH$_2$Cl$_2$ (4:6) gave [Co$_2${μ-PPh$_2$CHCMeC(O)CPhCHPPh$_2$}(CO)$_4$] (**4e**) (0.038 g, 41%).

(g) The complex [Co$_2${μ-PPh$_2$C(CO$_2$Me)C(CO$_2$Me)C(O)}(μ-PPh$_2$)(CO)$_4$] (**3f**) (0.070 g, 0.091 mmol) was dissolved in CO-purged toluene (30 mL) and a 5-fold excess of dmad added. The CO purge was continued as the solution was stirred at 343 K for 3 h. Purification was as in a. Elution with hexane/CH$_2$Cl$_2$ (1:1) gave red [Co$_2${μ-PPh$_2$C(CO$_2$Me)C(CO$_2$Me)}(μ-PPh$_2$)(CO)$_4$] (**2**) (0.013 g, 19%) and purple [Co$_2${μ-PPh$_2$C$_2$(CO$_2$Me)$_2$C(O)C$_2$(CO$_2$Me)$_2$PPh$_2$}(CO)$_4$] (**4f**) (0.019 g, 23%).

(h) The complex [Co$_2${μ-PPh$_2$CHC(SiMe$_3$)C(O)}(μ-PPh$_2$)(CO)$_4$] (**3c**) (0.150 g, 0.210 mmol) was dissolved in toluene (50 mL). The solution was purged slowly with methylacetylene for 1 h at 353 K and stirred for one further hour. Purification was as in a. Elution with hexane/CH$_2$Cl$_2$ (1:1) gave purple [Co$_2${μ-PPh$_2$CHC(SiMe$_3$)C(O)CMeCHPPh$_2$}(CO)$_4$] (**4g**) (0.070 g, 44%). Complex **4g**: FAB mass spectrum, *m*/*z* 766 (M$^+$), M$^+$ −*n*CO (*n* = 0–4). NMR: ^{13}C (CD$_2$Cl$_2$, ^{1}H composite decoupled) δ 204.5 (s, 2CO), 203.6 [s, CMe*C*(O)C(SiMe)$_3$], 202.7 (s, 1 CO), 200.4 (s, 1 CO), 141–128 (m, Ph), 77.3 [s, PPh$_2$CHCMeC(O)], 74.6 [s, PPh$_2$CH*C*(SiMe$_3$)C(O)], 40.5 [dd, *J*(PC) 31, *J*(P′C) 12, PPh$_2$CHCMeC(O)], 39.3 [dd, *J*(PC) 39, *J*(P′C) 12, PPh$_2$CHC(SiMe$_3$)C(O)], 26.2 [d, *J*(PC) 10, PPh$_2$CHC*Me*C(O)], −1.0 [s, PPh$_2$CHC(Si*Me*$_3$)C(O)]; ^{31}P (CDCl$_3$, ^{1}H-gated decoupled) δ −123.3 [s, μ-*P*Ph$_2$CHC(SiMe$_3$)C(O)CMeCHPPh$_2$], −136.5 [s, μ-PPh$_2$CHC(SiMe$_3$)C(O)CMeCH*P*Ph$_2$].

(i) The complex [Co$_2$(μ-PPh$_2$CHC(SiMe$_3$)C(O)}(μ-PPh$_2$)(CO)$_4$] (**3c**) (0.150 g, 0.210 mmol) was dissolved in toluene (50 mL), a 5-fold excess of phenylacetylene added, and the solution stirred at 353 K for 2 h. Purification was as in a. Elution with hexane/CH$_2$Cl$_2$ (1:1) gave purple [Co$_2${μ-PPh$_2$CHC(SiMe$_3$)C(O)CPhCHPPh$_2$}(CO)$_4$] (**4h**) (0.074 g, 43%). Complex **4h**: FAB mass spectrum, *m*/*z* 828 (M$^+$), M$^+$ − *n*CO (*n* = 0–4). NMR: ^{13}C (CD$_2$Cl$_2$, ^{1}H composite decoupled) δ 204.5 (s, 1 CO), 203.2 (s, 1 CO), 202.6 [s, C(SiMe$_3$)C(O)CPh], 201.6 (s, 1 CO), 199.2 (s, 1 CO), 145–126 (m, Ph), 79.3 [s, PPh$_2$CH*C*PhC(O)], 76.5 [s, PPh$_2$CH*C*(SiMe$_3$)C(O)], 39.8 [dd, *J*(PC) 30, *J*(P′C) 12, PPh$_2$CHCPhC(O)], 33.3 [dd, *J*(PC) 41, *J*(P′C) 13, PPh$_2$CHC(SiMe$_3$)C(O)], −0.9 [s, PPh$_2$CHC(Si*Me*$_3$)C(O)]; ^{31}P (CDCl$_3$, ^{1}H-gated decoupled) δ −129.6 [s, μ-*P*Ph$_2$CHCPhC(O)C(SiMe$_3$)CHPPh$_2$], −139.1 [s, μ-PPh$_2$CHCPhC(O)C(SiMe$_3$)CH*P*Ph$_2$].

(iv) Attempted Reaction of [Co$_2${μ-PPh$_2$CHCPhC(O)}(μ-PPh$_2$)(CO)$_4$] (3b) with PhC≡CPh. The complex [Co$_2${μ-PPh$_2$CHCPhC(O)}(μ-PPh$_2$)(CO)$_4$] (**3b**) (0.050 g, 0.068 mmol) was dissolved in toluene (25 mL) and diphenylacetylene introduced in a 5-fold excess. The solution was stirred at 353 K for 3 h. IR and spot TLC of the resulting reaction mixture indicated the presence of only starting material **3b** and unidentified decomposition products.

(v) Reaction of [Co$_2${μ-PPh$_2$CHCHC(O)}(μ-PPh$_2$)(CO)$_4$] (3a) with Allene. The complex [Co$_2${μ-PPh$_2$CHCHC(O)}(μ-PPh$_2$)(CO)$_4$] (**3a**) (0.137 g, 0.219 mmol) was dissolved in toluene (40 mL) and heated to 338 K. The solution was then purged with allene for 45 min. Some signs of polymerization of the allene were evident. After removal of the solvent in vacuo, the residue was repeatedly extracted with CH$_2$Cl$_2$. The extracts were combined, and solvent was removed in vacuo. The residue was redissolved in the minimum of CH$_2$Cl$_2$ and separated by preparative TLC. Elution with hexane/CH$_2$Cl$_2$ (1:1) gave purple crystalline [Co$_2${μ-PPh$_2$CHCHC(O)CHCMePPh$_2$}(CO)$_4$] (**4b′**) (0.020 g, 13%) and dark purple crystalline [Co$_2${μ-PPh$_2$CHCHC(O)C(CH$_2$)$_2$}(μ-PPh$_2$)(CO)$_3$] (**5**) (0.049 g, 35%). Anal. Calcd for C$_{24}$H$_{26}$Co$_2$O$_5$P$_2$ (**4b′**): C, 58.8; H, 3.8. Found: C, 58.8; H, 3.7. FAB mass spectrum: *m*/*z* 694 (M$^+$), M$^+$ − *n*(CO) (*n* = 0–4). NMR (CDCl$_3$): ^{31}P (^{1}H-gated decoupled) δ −113.1 [s, μ-*P*Ph$_2$CMeCHC(O)CHCHPPh$_2$], −130.7 [s, μ-PPh$_2$CMeCHC(O)CHCH*P*Ph$_2$]. Anal. Calcd for C$_{33}$H$_{26}$Co$_2$O$_4$P$_2$ (**5**): C, 59.5; H, 3.9; P, 9.3. Found: C, 59.1; H, 4.1; P, 9.1. FAB mass spectrum: *m*/*z* 666 (M$^+$), M$^+$ − *n*(CO) (*n* = 0–3). NMR (CDCl$_3$): ^{31}P (^{1}H-gated decoupled) δ 80.2 (s, μ-PPh$_2$), −141.3 [s, μ-PPh$_2$CHCHC(O)C(CH$_2$)$_2$].

Table VI. Summary of Crystallographic Data for Complexes 4a and 5

	4a	5
formula	$C_{33}H_{24}Co_2O_5P_2$	$C_{33}H_{26}Co_2O_4P_2 \cdot {}^1/_2C_6H_{14}$
fw	680.20	709.47
cryst syst	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/a$
a, Å	15.586(3)	24.903(8)
b, Å	18.882(6)	14.674(5)
c, Å	20.867(7)	9.249(5)
β, deg	95.80(3)	96.17(2)
V, Å^3	6109.6	3360(2)
Z	8	4
d_{calcd}, g cm^{-3}	1.48	1.40
cryst dimens, mm	0.25 × 0.35 × 0.40	0.17 × 0.20 × 0.25
temp, K	293	293
μ (Mo K*α*), cm^{-1}	11.60	11.15
F(000)	2767	1460
radiatn, Å	Mo K*α*, 0.710 73	Mo K*α*, 0.710 73
diffractometer	Enraf-Nonius CAD4	Siemens AED
range *θ* collcd, deg	2.5–25	3–25
no. of unique rflns	6263	6168
no. of obsd data $[I > 2\sigma(I)]$	4117	2469
R	0.032	0.036
R_w	0.036	0.044

(vi) Crystal Structure Determinations of the Complexes 4a and 5. The crystallographic data are summarized in Table VI. Data were collected at room temperature on an Enraf-Nonius CAD4 (**4a**) and on a Siemens AED (**5**) diffractometers using the graphite-monochromated (**4a**) and the niobium-filtered (**5**) Mo K_α radiation and the $\theta/2\theta$ (**4a**) and $\theta/2\theta$ (**5**) scan type. An empirical correction for absorption was applied only to **4a** (maximum and minimum values for the transmission factors were 1 and 0.79).[21] Only the observed reflections were used in the structure solution and refinement.

The structures were solved by direct and Fourier methods and refined by full-matrix least squares, first with isotropic and then with anisotropic thermal parameters in the last cycles for all the non-hydrogen atoms except those of the hexane molecule of solvation found in **5**. The hexane molecule, running on the inversion center, was found disordered and distributed in two positions of equal occupancy factor. Phenyl rings of **4a** were treated as rigid groups. All hydrogen atoms of **4a** were included in calculated positions and refined "riding" on the corresponding carbon atoms; four different thermal parameters were attributed to the alkyne and phenyl H-atoms of the two independent molecules, respectively, which converged to 0.09(1), 0.11(1) Å^2 for molecule **A** and 0.09(1), 0.13(1) Å^2 for molecule **B**. The hydrogen atoms of **5**, except those of the phenyl groups, were clearly localized in the final ΔF map and refined isotropically; those of the phenyl groups were placed at their geometrically calculated positions and refined "riding" on the corresponding carbon atoms; those of the solvent molecule were not taken into account. In the last cycles of refinement a weighting scheme $w = 1.2/\sigma^2(F_o)$ was applied to **4a** and $w = [\sigma^2(F_o) + gF_o^2]^{-1}$ to **5** with $g = 0.0031$ at convergence. Final R and R_w values were 0.032 and 0.036 (**4a**) and 0.036 and 0.044 (**5**), respectively. The SHELX-76 and SHELXS-86 systems of computer programs were used.[22,23] Atomic scattering factors, corrected for anomalous dispersion, were taken from ref. 24. Final atomic coordinates for the non-hydrogen atoms of **4a** and **5** are given in Tables IV and V, respectively.

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Supplementary Material Available: Tables of hydrogen atom coordinates (Table SI) and anisotropic thermal parameters for the non-hydrogen atoms (Table SII) for **4a** and tables of hydrogen atom coordinates (Table SIII) and anisotropic thermal parameters for the non-hydrogen atoms (Table SIV) for **5** (9 pages). Ordering information is given on any current masthead page.

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