# Reactions of the Heteronuclear Alkyne-bridged Cobalt–Molybdenum Complex $[(OC)_3Co\{\mu\text{-}C_2(CO_2Me)_2\}Mo(CO)_2(\eta^5\text{-}C_5H_5)]$ with $PPh_2H$, $P_2Ph_4$ and $PPh_2(SPh)$†

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The complex $[(OC)_3Co\{\mu\text{-}C_2(CO_2Me)_2\}Mo(CO)_2(\eta^5\text{-}C_5H_5)]$ **1** reacts preferentially at the Co atom with $PPh_2H$, $P_2Ph_4$ and $PPh_2(SPh)$ to give initially the mono-substituted products $[L(OC)_2Co\{\mu\text{-}C_2(CO_2Me)_2\}Mo(CO)_2(\eta^5\text{-}C_5H_5)]$ [L = $PPh_2H$ **2**, $P_2Ph_4$ **3** or $PPh_2(SPh)$ **4**]. In the case of $PPh_2H$ further reaction takes place at the Mo atom to give the bis-substituted product $[(HPh_2P)(OC)_2Co\{\mu\text{-}C_2(CO_2Me)_2\}Mo(CO)(\eta^5\text{-}C_5H_5)(PPh_2H)]$ **5**. Thermolysis of the substituted derivatives **2**–**5** results in either P–H, P–P or P–S bond cleavage. Thus for **2**, the isomeric species $[(\eta^5\text{-}C_5H_5)(OC)Mo\{\mu\text{-}C(CO_2Me){=}CH(CO_2Me)\}(\mu\text{-}PPh_2)Co(CO)_2]$ **6** and $[(OC)_2Co\{\mu\text{-}C(CO_2Me){=}CH(CO_2Me)\}(\mu\text{-}PPh_2)Mo(CO)(\eta^5\text{-}C_5H_5)]$ **7** are obtained, whereas **3** gives $[(OC)_2Co\{\mu\text{-}PPh_2C(CO_2Me){=}C(CO_2Me)\}(\mu\text{-}PPh_2)Mo(CO)(\eta^5\text{-}C_5H_5)]$ **8**, in which the Co atom is incorporated into a four-membered metallacycle. Thermolysis of **4** gives $[(\eta^5\text{-}C_5H_5)(OC)Mo\{\mu\text{-}PPh_2C(CO_2Me){=}C(CO_2Me)\}(\mu\text{-}SPh)Co(CO)_2]$ **9** (in which the Mo atom is incorporated into a four-membered metallacycle) and thermolysis of **5** gives $[(\eta^5\text{-}C_5H_5)(OC)Mo\{\mu\text{-}C(CO_2Me){=}CH(CO_2Me)\}(\mu\text{-}PPh_2)Co(CO)(PPh_2H)]$ **10**. Complex **6** can be converted to **10** by reaction with $PPh_2H$. The crystal structures of compounds **6** and **8** have been determined.

The reactions of transverse alkyne-bridged dicobalt and dimolybdenum complexes of general formula $[Co_2(\mu\text{-}RCCR')(CO)_6]$ and $[Mo_2(\mu\text{-}RCCR')(CO)_4(\eta^5\text{-}C_5H_5)_2]$ (R, R′ = alkyl, aryl or H) with $P_2Ph_4$ and with $PPh_2H$ have been previously studied and shown to lead to a variety of phosphido-bridged complexes *via* P–P or P–H cleavage.[1–4] The bridging alkyne ligand is often involved in these reactions in a manner which depends on the nature of R and R′. Thus, we recently reported that the reaction of the dicobalt system with $P_2Ph_4$ gives three main types of derivatives, $[Co_2(\mu\text{-}PPh_2CRCR')(\mu\text{-}PPh_2)(CO)_4]$, $[Co_2\{\mu\text{-}PPh_2CRCR'C(O)\}(\mu\text{-}PPh_2)(CO)_4]$ and $[Co_2\{\mu\text{-}PPh_2C(O)CRCR'\}(\mu\text{-}PPh_2)(CO)_4]$.[1] The choice of R and R′ governs which one or combination of these products results in any particular reaction. The reaction of the biphosphine $P_2Ph_4$ with the dimolybdenum complex also produces a wide variety of compounds depending on the nature of R and R′.[2]

Reactions of the alkyne-bridged cobalt and molybdenum species with secondary phosphines to give phosphido-bridged bimetallics requires the cleavage of a P–H bond. The site to which the cleaved hydrogen atom migrates can however vary. Thus, the reaction of $[Mo_2(\mu\text{-}HCCH)(CO)_4(\eta^5\text{-}C_5H_5)_2]$ with $PPh_2H$ yields the complex $[(\eta^5\text{-}C_5H_5)(OC)Mo(\mu\text{-}HCCHCHO)(\mu\text{-}PPh_2)Mo(CO)(\eta^5\text{-}C_5H_5)]$ *via* the migration of the hydrogen atom onto a carbonyl ligand to give a CHO group which then adds to the alkyne.[4] With the cobalt complex $[Co_2\{\mu\text{-}C_2(CO_2Me)_2\}(CO)_6]$, however, migration of the hydrogen atom to an alkyne carbon atom gives $[Co_2\{\mu\text{-}C(CO_2Me){=}CH(CO_2Me)\}(\mu\text{-}PPh_2)(CO)_4]$.[3]

The reaction of the ligand $PPh_2(SPh)$ with transverse alkyne-bridged complexes can also lead to phosphido-bridged complexes *via* P–S bond cleavage, and we recently reported the reaction of this ligand with $[Co_2(\mu\text{-}HCCH)(CO)_6]$ to yield $[Co_2\{\mu\text{-}SPhC(O)CHCH\}(\mu\text{-}PPh_2)(CO)_4]$.[5] In general, however, reactions of this ligand with organo-transition metal complexes have been little studied.

We have now studied the reactions of $PPh_2H$, $P_2Ph_4$ and $PPh_2(SPh)$ with the heteronuclear alkyne-bridged cobalt–molybdenum complex $[(OC)_3Co\{\mu\text{-}C_2(CO_2Me)_2\}Mo(CO)_2(\eta^5\text{-}C_5H_5)]$[6] in order to investigate the relative reactivities of the two different metal sites. In addition to carbonyl substitution, reactions involving P–H, P–P and P–S bond cleavage are observed (Scheme 1).

## Results and Discussion

(*a*) *Reaction of* $[(OC)_3Co\{\mu\text{-}C_2(CO_2Me)_2\}Mo(CO)_2(\eta^5\text{-}C_5H_5)]$ **1** *with* $PPh_2H$.—Reaction of $[(OC)_3Co\{\mu\text{-}C_2(CO_2Me)_2\}Mo(CO)_2(\eta^5\text{-}C_5H_5)]$ **1** with $PPh_2H$ at 313 K in toluene gives, in addition to unreacted starting material, $[(HPh_2P)(OC)_2Co\{\mu\text{-}C_2(CO_2Me)_2\}Mo(CO)_2(\eta^5\text{-}C_5H_5)]$ **2** and $[(HPh_2P)(OC)_2Co\{\mu\text{-}C_2(CO_2Me)_2\}Mo(CO)(\eta^5\text{-}C_5H_5)(PPh_2H)]$ **5** in 52 and 13% yields respectively. Complexes **2** and **5** have been characterised spectroscopically (see Table 1 and Experimental section).

The $^{31}P\text{-}\{^1H\}$ NMR spectrum of **2** displays a singlet which is assigned to a $PPh_2H$ bound to a cobalt atom, the shift being similar to that observed in the corresponding dicobalt complex.[3] The $^{13}C\text{-}\{^1H\}$ NMR spectrum of **2** at 293 K exhibits two terminal carbonyl resonances, one at a higher chemical shift (δ 224.2), typical of molybdenum-bound carbonyls, and the other at a lower chemical shift (δ 204.7) typical of cobalt-bound carbonyls. The cobalt-bound carbonyl resonance is also considerably broader, due to the quadrupolar nature of the $^{59}Co$ nucleus. The presence of only two signals suggests either that the cyclopentadienyl group on the Mo atom and the secondary phosphine group on the Co atom reside in pseudo-axial positions (Scheme 1) or that there is fluxionality at this temperature. This fluxionality could take the form of a localised site-exchange of the two carbonyl groups around the cobalt and molybdenum atoms or could represent a process involving a trigonal twist of the three terminal ligands on each metal atom.[1]

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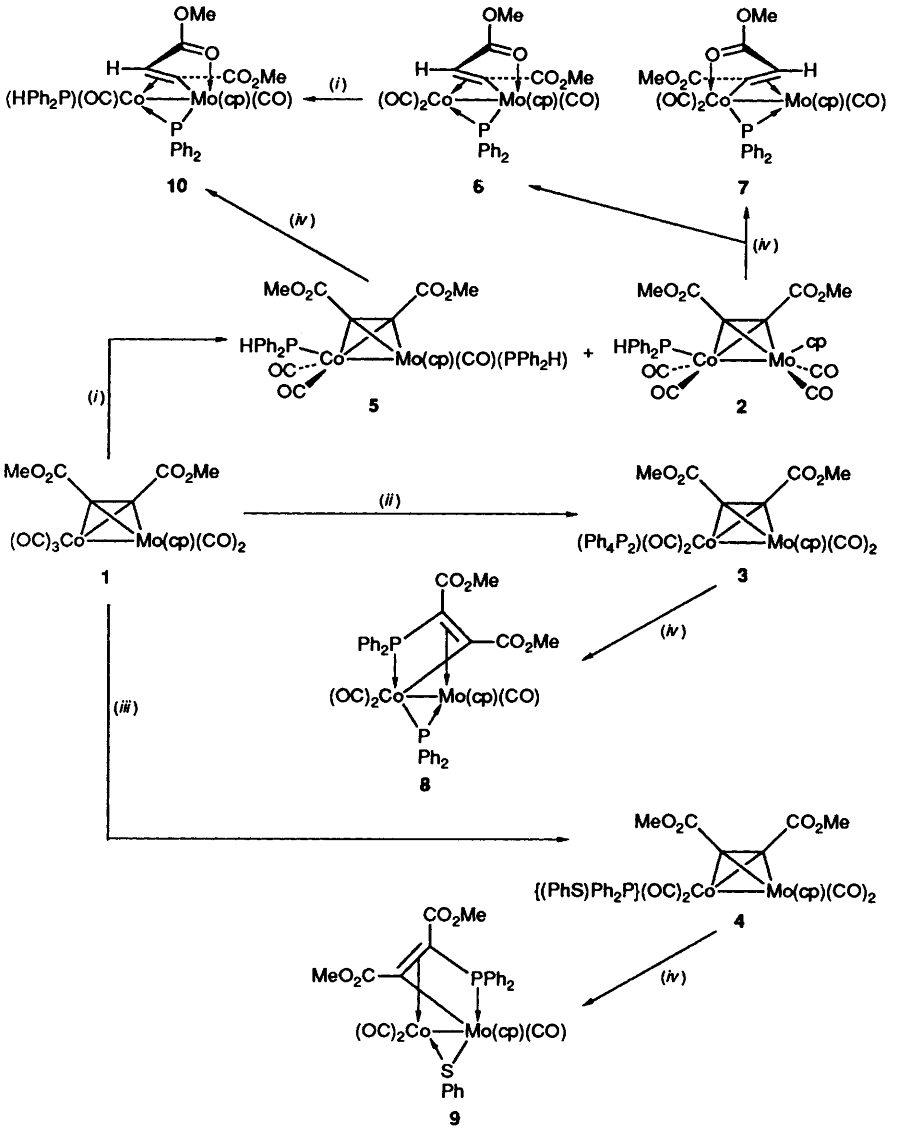
† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.



Scheme 1 Products from the reactions of $[(OC)_3Co\{\mu\text{-}C_2(CO_2Me)_2\}Mo(CO)_2(\eta^5\text{-}C_5H_5)]$ 1 with $PPh_2H$, $P_2Ph_4$ and $PPh_2(SPh)$; (*i*) $PPh_2H$, heat; (*ii*) $P_2Ph_4$, heat; (*iii*) $PPh_2(SPh)$, heat; (*iv*) heat. cp = Cyclopentadienyl

The $^{13}C\text{-}\{^1H\}$ NMR spectrum at 293 K of the related unsymmetrical trimethylsilylacetylene complex $[(HPh_2P)(OC)_2Co\{\mu\text{-}HCC(SiMe_3)\}Mo(CO)_2(\eta^5\text{-}C_5H_5)]$ [7] shows four CO signals, two in the Mo–CO region and two in the Co–CO region.* This implies that the CO groups on each metal atom are inequivalent and rules out a fluxional process involving localised site-exchange in this complex and presumably in 2. The result does not, however, distinguish between non-fluxionality and fluxionality *via* a trigonal twist process.

The $^{31}P\text{-}\{^1H\}$ NMR spectrum of 5 is consistent with two terminally bound $PPh_2H$ groups, the lower field resonance being assigned to a molybdenum-bound phosphorus atom. The $^{13}C\text{-}\{^1H\}$ NMR spectrum recorded at 293 K again shows two carbonyl resonances attributed to molybdenum- and cobalt-bound carbonyls. The low field molybdenum-bound carbonyl (δ 235.0) has been shifted 10.8 ppm downfield with respect to its position in 2 whereas the cobalt-bound carbonyl is only shifted by 0.7 ppm. In the IR spectrum of 5 three ν(CO) bands are observed in the region 2000–1800 $cm^{-1}$. The lowest energy band at 1825 $cm^{-1}$ is assigned to the lone carbonyl on molybdenum and the two higher energy bands (1984 and 1948 $cm^{-1}$) to the two terminal carbonyls on the cobalt atom.

(*b*) *Reaction of* $[(OC)_3Co\{\mu\text{-}C_2(CO_2Me)_2\}Mo(CO)_2(\eta^5\text{-}C_5H_5)]$ 1 *with* $Ph_2PL$ (L = $PPh_2$ or SPh).—Reaction of $[(OC)_3Co\{\mu\text{-}C_2(CO_2Me)_2\}Mo(CO)_2(\eta^5\text{-}C_5H_5)]$ 1 with $Ph_2PL$ (L = $PPh_2$ or SPh) at 313 K in toluene gives, in addition to unreacted starting material, the complexes $[(LPh_2P)(OC)_2Co\{\mu\text{-}C_2(CO_2Me)_2\}Mo(CO)_2(\eta^5\text{-}C_5H_5)]$ (L = $PPh_2$ 3 or SPh 4) respectively. Both complexes 3 and 4 have been characterised spectroscopically (see Table 1 and Experimental section).

The $^{31}P\text{-}\{^1H\}$ NMR spectrum of complex 3 is consistent with the presence of a terminal $P_2Ph_4$ ligand. Doublet resonances are observed for each phosphorus, with a large coupling constant [*J*(PP) *ca.* 313 Hz], implying a one-bond phosphorus–phosphorus coupling. The broadness of the lower-field resonance is due to the quadrupolar $^{59}Co$ and is indicative of a phosphorus atom directly bound to cobalt. The $^{31}P\text{-}\{^1H\}$ NMR spectrum of 4 displays a broad singlet resonance as expected if $PPh_2(SPh)$ is bound directly to the cobalt atom through phosphorus. The $^{13}C\text{-}\{^1H\}$ NMR spectra of 3 and 4 in the

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* $[(HPh_2P)(OC)_2Co\{\mu\text{-}HCC(SiMe_3)\}Mo(CO)_2(\eta^5\text{-}C_5H_5)]$: $^{13}C$ NMR ($CD_2Cl_2$, $^1H$ composite pulse decoupled), δ 230.8 (s, MoCO) 228.9 (s, MoCO), 2092 (s, CoCO) and 207.0 (s, CoCO).

**Table 1** Infrared, $^1$H and $^{31}$P NMR data for the complexes

| Compound | ν(CO)$^a$/cm$^{-1}$ | $^1$H NMR (δ)$^b$ | $^{31}$P NMR (δ)$^c$ |
|---|---|---|---|
| **2** | 2033m, 2000vs, 1974s 1960 (sh), 1704w$^d$ | 7.6–7.3 (m, 10 H, Ph), 6.24 [d, $^1J$(PH) 361, 1 H, Co–PPh$_2$*H*], 5.38 (s, 5 H, cp), 3.49 (s, 6 H, Me) | −113.6 (s, CoPPh$_2$H) |
| **3** | 2026m, 1993s, 1967s, 1950 (sh), 1693w | 7.5–7.0 (m, 20 H, Ph), 5.25 (s, cp), 3.19 (s, 6 H, Me) | −96.5 [d, $^1J$(PP) 313, Co*P*Ph$_2$PPh$_2$], −141.3 (d, CoPPh$_2$*P*Ph$_2$) |
| **4** | 2029m, 1997s, 1971s, 1953 (sh), 1695w | 7.6–6.6 (m, 15 H, Ph), 5.34 (s, cp), 3.27 (s, 6 H, Me) | −52.3 (CoPPh$_2$SPh) |
| **5** | 1984s, 1948m, 1825w, 1685w | 7.4–7.2 (m, 20 H, Ph), 5.82 [d, br, $^1J$(PH) ≈350, 2 H, Mo–PPh$_2$*H* and Co–PPh$_2$*H*], 4.88 (s, 5 H, cp) | −98.1 (s, MoPPh$_2$H), −107.3 (s, CoPPh$_2$H) |
| **6** | 2008s, 1967s, 1684w, 1668w, 1544w | 7.5–7.1 (m, 10 H, Ph), 5.40 (s, 5 H, cp), 4.04 [d, $^3J$(PC) 4.2, 1 H, C*H*CO$_2$Me], 3.55 (s, 3 H, Me), 3.22 (s, 3 H, Me) | 38.3 (s, μ-PPh$_2$) |
| **7** | 2003s, 1968s, 1950 (sh), 1682w, 1548w | 7.7–7.2 (m, 10 H, Ph), 5.50 (s, 5 H, cp), 4.61 (s, 1 H, C*H*CO$_2$Me), 3.75 (s, 3 H, Me), 2.91 (s, 3 H, Me) | 64.0 (s, μ-PPh$_2$) |
| **8** | 2022vs, 1978s, 1925s, 1682m | 8.1–6.9 (m, 20 H, Ph), 4.84 (s, 5 H, cp), 3.55 (s, 3 H, Me), 2.90 (s, 3 H, Me) | 19.1 [d, $^2J$(PP) 116, μ-PPh$_2$], −153.0 [d, μ-PPh$_2$C(CO$_2$Me)] |
| **9** | 2033s, 1987s, 1953w 1693m | 7.9–7.0 (m, 15 H, Ph), 4.97 [d, $^3J$(PH) 1.5, 5 H, cp], 3.83 (s, 3 H, Me), 3.61 (s, 3 H, Me) | −145.6 [s, PPh$_2$C(CO$_2$Me)] |
| **10** | 1956s, 1907w, 1674w, 1654w, 1542w | 7.7–6.9 (m, 20 H, Ph), 5.47 [dd, $^1J$(PH) 342, $^3J$(P′H) 3.7, 1 H, Co–PPh$_2$*H*], 5.46 (s, cp), 3.55 (s, 3 H, Me), 3.37 (s, 3 H, Me), 3.07 [dd, $^3J$(PH) 10.9, $^3J$(P′H) 4.1, 1 H, C*H*CO$_2$Me] | 1.8 (s, μ-PPh$_2$), −87.7 (s, CoPPh$_2$H) |

$^a$ Recorded in CH$_2$Cl$_2$ solution. $^b$ Proton chemical shifts (δ) relative to SiMe$_4$(δ = 0), coupling constants in Hz in CDCl$_3$ at 293 K. $^c$ Phosphorus-31 chemical shifts (δ) relative to external P(OMe)$_3$ (δ = 0.0) (upfield shifts negative), {$^1$H}-gated decoupled, measured in CDCl$_3$ at 293 K. $^d$ Recorded in *n*-hexane solution.

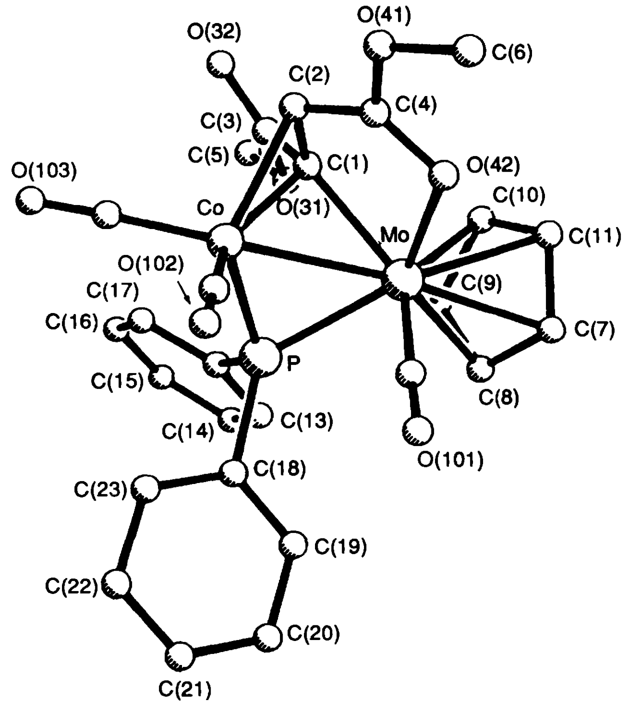


**Fig. 1** Molecular structure of [(η$^5$-C$_5$H$_5$)(OC)Mo{μ-C(CO$_2$Me)=CH(CO$_2$Me)}(μ-PPh$_2$)Co(CO)$_2$] **6** including the atom numbering scheme. Hydrogen atoms have been omitted for clarity

carbonyl region recorded at 293 K are similar to that of **2** showing two singlet resonances attributed to molybdenum- and cobalt-bound carbonyl groups.

Interestingly, no bis-substituted products analogous to **5** are observed in the reaction of **1** with P$_2$Ph$_4$ or PPh$_2$(SPh). The potentially unfavourable interaction of these more bulky ligands with the η$^5$-C$_5$H$_5$ group on Mo presumably inhibits substitution at this metal atom. A similar preference is observed for substitution at cobalt in the reaction of the related complex [(η$^5$-C$_5$H$_5$)(OC)$_2$Mo{μ-C$_2$(CF$_3$)$_2$}Co(CO)$_3$] with triphenylphosphine.[8] In contrast, the bis(alkyne) complex [(η$^5$-C$_5$H$_5$)(OC)Mo{μ-C$_2$(CF$_3$)$_2$}$_2$Co(CO)$_2$] was observed to react with PEt$_3$ to give only the molybdenum substituted derivative.[9]

(*c*) *Thermolysis of* [(HPh$_2$P)(OC)$_2$Co{μ-C$_2$(CO$_2$Me)$_2$}Mo(CO)$_2$(η$^5$-C$_5$H$_5$)] **2**.—The thermolysis of the secondary phosphine complex **2** at 338 K in toluene gives, in addition to unreacted starting material, the phosphido-, vinyl-bridged isomeric complexes [(η$^5$-C$_5$H$_5$)(OC)Mo{μ-C(CO$_2$Me)=CH(CO$_2$Me)}(μ-PPh$_2$)Co(CO)$_2$] **6** and [(OC)$_2$Co{μ-C(CO$_2$Me)=CH(CO$_2$Me)}(μ-PPh$_2$)Mo(CO)(η$^5$-C$_5$H$_5$)] **7** in 29 and 34% yields respectively. Both complexes **6** and **7** have been characterised spectroscopically (see Table 1 and Experimental section). Complex **6** has also been the subject of a single crystal X-ray structural analysis.

The molecular structure of **6** is shown in Fig. 1; selected bond distances and angles are given in Table 2 and atomic coordinates in Table 3. The molecule consists of (η$^5$-C$_5$H$_5$)Mo(CO) and Co(CO)$_2$ units linked by a Mo(1)–Co(1) bond, a phosphido bridge and virtually planar $\overline{\text{Mo–C=C–C=O}}$ five-membered molybdacylic ring π-co-ordinated through the carbon–carbon double bond to Co(1).

The vinyl group is σ-bonded to Mo(1) through C(1) [2.165(5) Å] and asymmetrically π-bonded to Co through C(1) [1.964(5) Å] and C(2) [2.080(5) Å]. The C(1)–C(2) bond distance [1.425(7) Å] is similar to that in related complexes.[3,10,11] A *trans* configuration is adopted by the methylcarboxylate groups, with O(42) co-ordinated to Mo [2.210(4) Å]. This type of bridging ligand is also observed in [(OC)$_3$Co{μ-C(CO$_2$Me)=CH(CO$_2$Me)}Fe(CO)$_3$][10] and [Co$_2${μ-C(CO$_2$Me)=CH(CO$_2$Me)}(μ-PPh$_2$)(CO)$_4$][3] in which oxygen co-ordination is to the Fe and Co respectively, whereas in complex **6** it is to Mo. As with the complex [Co$_2${μ-C(CO$_2$Me)=CH(CO$_2$Me)}(μ-PPh$_2$)(CO)$_4$] asymmetric bridging of the metal–metal bond by the phosphido ligand is observed. In the case of **6**, however, the asymmetry is more significant [Co–P 2.174(2), Mo–P 2.398(2) Å] with the P–Mo bond distance *ca.* 0.22 Å longer than the P–Co

**Table 2** Selected bond lengths (Å) and angles (°) for complex **6**

| | | | |
|---|---|---|---|
| Mo–Co | 2.684(1) | Co–C(2) | 2.080(5) |
| Mo–C(101) | 2.015(6) | Co–C(102) | 1.785(6) |
| Mo–O(42) | 2.210(4) | Co–C(1) | 1.964(5) |
| Mo–C(7) | 2.321(7) | P–C(18) | 1.833(5) |
| Mo–C(8) | 2.242(6) | P–C(12) | 1.822(5) |
| Mo–C(9) | 2.261(6) | C(1)–C(2) | 1.425(7) |
| Mo–C(10) | 2.324(6) | C(2)–C(4) | 1.428(7) |
| Mo–C(11) | 2.364(6) | C(1)–C(3) | 1.484(7) |
| Mo–P | 2.398(2) | C(4)–O(42) | 1.250(7) |
| Mo–C(1) | 2.165(5) | C(4)–O(41) | 1.328(7) |
| Co–P | 2.174(2) | O(31)–C(5) | 1.450(6) |
| Co–C(103) | 1.756(6) | O(41)–C(6) | 1.454(8) |
| C(102)–O(102) | 1.127(8) | C(101)–O(101) | 1.132(7) |
| C(103)–O(103) | 1.149(8) | | |
| Co–Mo–P | 50.3(1) | P–Co–C(2) | 127.8(1) |
| P–Mo–C(1) | 78.5(1) | C(1)–Co–C(2) | 41.2(2) |
| Co–Mo–C(1) | 46.3(1) | Mo–P–Co | 71.7(1) |
| Co–Mo–O(42) | 81.2(1) | Mo–C(1)–Co | 80.9(2) |
| C(101)–Mo–O(42) | 81.9(2) | Mo–C(1)–C(2) | 109.8(3) |
| C(1)–Mo–O(42) | 75.8(2) | Co–C(1)–C(2) | 73.8(3) |
| Mo–Co–P | 58.0(1) | Mo–C(1)–C(3) | 133.1(4) |
| Mo–Co–C(102) | 104.7(2) | Co–C(1)–C(3) | 117.5(3) |
| P–Co–C(102) | 105.8(2) | C(2)–C(1)–C(3) | 116.7(4) |
| Mo–Co–C(103) | 149.7(2) | Co–C(2)–C(1) | 65.0(3) |
| P–Co–C(103) | 103.9(2) | Co–C(2)–C(4) | 106.9(4) |
| Mo–Co–C(1) | 52.8(1) | C(1)–C(2)–C(4) | 113.9(4) |
| P–Co–C(1) | 88.6(1) | C(2)–C(4)–O(42) | 122.1(5) |
| C(102)–Co–C(1) | 141.2(2) | Mo–O(42)–C(4) | 111.8(3) |
| Mo–Co–C(2) | 75.9(1) | | |

distance. This is in accord with the smaller covalent radius of Co compared to Mo. The Co–Mo bond length [2.684(1) Å] is similar to that for the corresponding bond in the majority of other structurally characterised Co–Mo complexes containing bridging organic ligands.[6,8,12]

The IR spectrum of **6** displays three absorptions at 1684, 1668 and 1544 cm$^{-1}$ corresponding to ν(C=O) bands of the ester group. The absorption band at lowest wavenumber is due to the ester group co-ordinated to the molybdenum atom.[3,10,11] The two higher wavenumber bands are both consistent with unco-ordinated ester absorptions. In the $^{13}$C-{$^1$H} NMR spectrum the α carbon of the vinyl group appears as a doublet at δ 133.3 with $^2J$(PC) 24 Hz and the β carbon as a doublet at δ 47.2 with $^2J$(PC) 4 Hz. The $^{31}$P-{$^1$H} NMR spectrum displays a singlet at δ 38.3 consistent with the presence of a phosphido ligand bridging two metal–metal bonded centres.[13]

The proposed structure of complex **7** $[(OC)_2Co\{\mu\text{-}C(CO_2Me)\text{=}CH(CO_2Me)\}Mo(CO)(\eta^5\text{-}C_5H_5)]$ (Scheme 1) is based on spectroscopic evidence. It resembles that for complex **6** in that it contains a phosphido bridge and a five-membered π-co-ordinated metallacycle. It differs, however, in that co-ordination of the oxygen is to the Co instead of the Mo atom.

The IR spectrum of **7** shows two absorptions corresponding to ν(C=O) bands of the ester groups at 1682 and 1548 cm$^{-1}$, the latter indicating the oxygen co-ordination. The $^1$H NMR spectrum in $CDCl_3$ at 293 K shows, in addition to resonances for phenyl and cyclopentadienyl groups, a singlet at δ 4.61 corresponding to the proton on the vinyl group. A doublet rather than a singlet might have been expected due to the close proximity of the μ-$PPh_2$ group; however, in the complex $[(\eta^5\text{-}C_5H_5)_2Mo_2\{\mu\text{-}HCCHC(O)Ph\}(\mu\text{-}PPh_2)(CO)_2]$, where a similar proton environment exists, only a very small coupling of 1.5 Hz is reported.[4] Two separate $^1$H NMR singlets for the methyl groups in **7** are also observed. The $^{31}$P-{$^1$H} NMR spectrum displays a singlet at δ 64.0 consistent with a μ-$PPh_2$ bridge. In the $^{13}$C-{$^1$H} NMR spectrum at 293 K the three CO groups give rise to three separate resonances, the most downfield being a doublet with a coupling constant of 15 Hz, at a chemical shift characteristic of a molybdenum-bound carbonyl. The α- and the β-carbon of the vinyl group appear as singlets at δ 156.4 and 49.5 respectively.

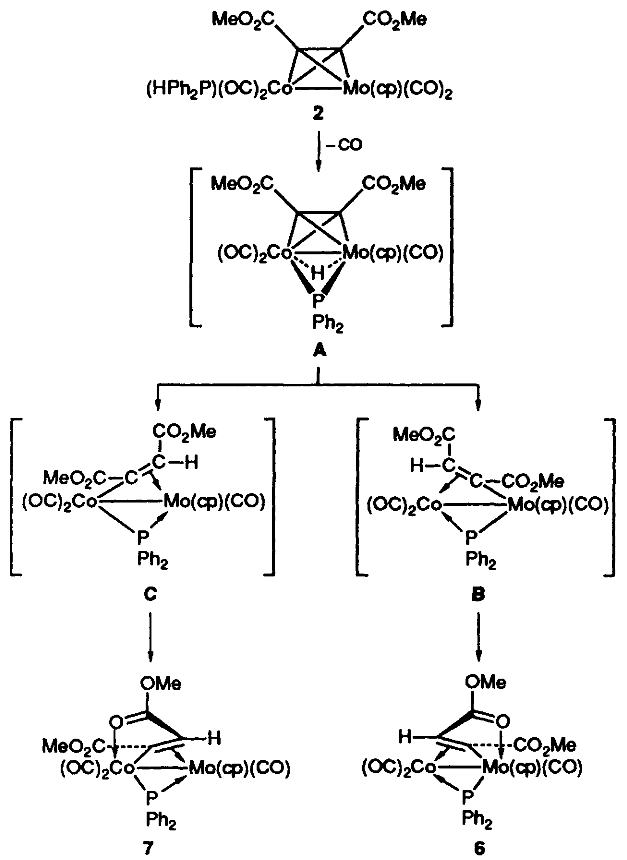
**Table 3** Fractional atomic coordinates ( × 10$^5$) for complex **6**

| Atom | *x* | *y* | *z* |
|---|---|---|---|
| Mo | 1 352(4) | 40 097(2) | 74 455(3) |
| Co | 20 546(7) | 51 817(4) | 74 658(4) |
| P | 27 518(13) | 39 797(7) | 74 997(7) |
| C(101) | 3 981(57) | 39 725(32) | 62 255(33) |
| O(101) | 5 120(50) | 39 330(29) | 55 377(25) |
| C(102) | 20 783(62) | 54 741(33) | 64 137(36) |
| O(102) | 21 437(57) | 56 551(32) | 57 511(28) |
| C(103) | 35 359(74) | 56 796(32) | 79 588(36) |
| O(103) | 45 296(59) | 59 974(28) | 82 653(31) |
| C(1) | 6 906(51) | 49 353(28) | 83 074(28) |
| C(2) | 2 235(56) | 56 574(29) | 79 580(31) |
| C(3) | 12 688(51) | 49 464(31) | 91 825(30) |
| C(4) | −9 519(57) | 55 933(33) | 73 392(32) |
| O(31) | 15 933(38) | 42 391(21) | 94 812(19) |
| O(32) | 14 108(40) | 55 265(23) | 95 966(21) |
| O(41) | −15 995(43) | 62 455(22) | 70 834(24) |
| O(42) | −13 839(36) | 49 538(21) | 70 586(21) |
| C(5) | 21 942(62) | 42 064(37) | 103 287(31) |
| C(6) | −27 531(72) | 61 924(38) | 64 274(41) |
| C(7) | −14 367(76) | 29 690(38) | 72 135(42) |
| C(8) | −487(70) | 27 203(32) | 74 425(43) |
| C(9) | 1 615(65) | 30 133(32) | 83 475(39) |
| C(10) | −10 752(58) | 34 464(32) | 85 033(36) |
| C(11) | −20 472(60) | 34 167(36) | 78 129(41) |
| C(12) | 38 787(48) | 35 697(28) | 83 574(27) |
| C(13) | 39 175(61) | 27 800(32) | 84 759(33) |
| C(14) | 47 422(66) | 24 459(35) | 91 153(36) |
| C(15) | 55 707(62) | 29 063(40) | 96 605(36) |
| C(16) | 55 820(60) | 36 838(37) | 95 596(33) |
| C(17) | 47 365(54) | 40 312(33) | 89 127(30) |
| C(18) | 37 786(52) | 36 310(30) | 66 455(28) |
| C(19) | 35 709(59) | 29 070(32) | 62 883(33) |
| C(20) | 44 097(69) | 26 625(38) | 56 597(36) |
| C(21) | 54 578(72) | 31 494(44) | 53 867(37) |
| C(22) | 56 896(74) | 38 538(44) | 57 251(41) |
| C(23) | 48 462(65) | 41 073(36) | 63 560(35) |

The proposed mechanism for the formation of complexes **6** and **7**, shown in Scheme 2, is similar to that postulated for the formation of $[Co_2\{\mu\text{-}C(CO_2Me)\text{=}CH(CO_2Me)\}(\mu\text{-}PPh_2)(CO)_4]$ *via* thermolysis of $[Co_2\{\mu\text{-}C_2(CO_2Me)_2\}(CO)_5(PPh_2H)]$.[3] Initial oxidative addition of the P–H bond of the cobalt-co-ordinated diphenylphosphine and loss of a molybdenum-bound carbonyl to give the phosphido-hydrido-bridged intermediate **A**, followed by migration of the hydride to one of the alkyne carbon atoms, would allow the formation of the co-ordinatively unsaturated μ-vinyl species **B** and **C**. Co-ordination of the carbonyl oxygens from the μ-vinyl groups of **B** and **C** then gives the eighteen-electron complexes **6** and **7** respectively.

(*d*) *Thermolysis of* $[(HPh_2P)(OC)_2Co\{\mu\text{-}C_2(CO_2Me)_2\}Mo(CO)(\eta^5\text{-}C_5H_5)(PPh_2H)]$ **5**.—The thermolysis of the bis-substituted secondary phosphine complex **5** at 338 K in toluene gives, in addition to unreacted starting material, the complex $[(\eta^5\text{-}C\,H_5)(OC)Mo\{\mu\text{-}C(CO_2Me)\text{=}CH(CO_2Me)\}(\mu\text{-}PPh_2)Co(CO)(PPh_2H)]$ **10** in 59% yield. Complex **10** has been characterised spectroscopically (see Table 1 and Experimental section).

In the IR spectrum of **10** a ν(CO) band at 1542 cm$^{-1}$ is ascribed to a co-ordinated methylcarboxylate group. As with complex **6**, there are two absorptions in the unco-ordinated methylcarboxylate region. The $^{31}$P-{$^1$H} NMR spectrum of **10** shows two resonances, the downfield signal (δ 1.8) being characteristic of a μ-$PPh_2$ bridge between two metal–metal bonded centres and the upfield signal (δ −87.7) being characteristic of a terminally bound secondary phosphine



**Scheme 2** Possible mechanism for the formation of complexes **6** and **7** on thermolysis of [(HPh$_2$P)(OC)$_2$Co{μ-C$_2$(CO$_2$Me)$_2$}Mo(CO)$_2$(η$^5$-C$_5$H$_5$)] **2**, cp = cyclopentadienyl

group, with the broadness of the latter signal being attributed to bonding to Co. In the $^1$H NMR spectrum, the vinyl proton appears as a doublet of doublets centred at δ 3.07. The smaller coupling of 4.1 Hz is attributed to a three-bond coupling to the bridging phosphido group, similar to that observed in complex **6**, and the larger [$^3J$(PH) 10.9 Hz] to coupling to a cobalt-bound diphenylphosphine ligand. On this basis **10** is assigned a structure analogous to that proposed for **6**, with a PPh$_2$H ligand replacing one of the carbonyl groups on cobalt. An alternative isomeric structure in which the bridging organic ligand adopts the configuration in **7** rather than that in **6** can be discounted, since the vinyl proton would then be separated from the PPh$_2$H ligand by four bonds rather than three. It is unlikely that a P–H coupling as large as 10.9 Hz would be observed in these circumstances. Presumably the presence of the cobalt-bound diphenylphosphine in some way inhibits the formation of a species isomeric with **10** in which oxygen-co-ordination is to the cobalt atom. The $^{13}$C-{$^1$H} NMR spectrum of **10** is in accord with the structure suggested, in that two terminal CO signals are observed, the doublet signal at lower field [$^2J$(PC) 13 Hz] being characteristic of a molybdenum-bound carbonyl and the unresolved broader signal at higher field being due to the cobalt-bound CO. The α carbon of the vinyl group appears as a doublet centred at δ 124.5 with $^2J$(PC) 25 Hz.

In an attempt to show that complex **10** is simply a diphenylphosphine-substituted derivative of complex **6**, a pure sample of **6** was treated with 1 equivalent of PPh$_2$H. After heating at 338 K in toluene for 20 h complex **10** was indeed formed in 50% yield along with unreacted starting material. No product was isolated in which the phosphine had displaced the co-ordinated carboxylate oxygen or substituted the molybdenum-bound carbonyl. This result is not unexpected since literature reports show a similar tendency for substitution in related dimetallic complexes to take place at the metal atom not co-ordinated by the carboxylate group.[3,10] However, a recent study of CO substitution by phosphines in [(OC)$_3$Fe{μ-C(CO$_2$Me)=CH(CO$_2$Me)}Co(CO)$_3$] shows that a carbonyl ligand on the metal co-ordinated by the carboxylate oxygen can be replaced when a relatively bulky phosphine (PPh$_3$) is used.[11]

(*e*) *Thermolysis of* [(LPh$_2$P)(OC)$_2$Co{μ-C$_2$(CO$_2$Me)$_2$}-Mo(CO)$_2$(η$^5$-C$_5$H$_5$)] (L = PPh$_2$ **3** *or* SPh **4**).—The thermolysis of the biphosphine complex **3** at 328 K in toluene gives, in addition to unreacted starting material, the phosphido-bridged complex [(OC)$_2$Co{μ-PPh$_2$C(CO$_2$Me)=C(CO$_2$Me)}(μ-PPh$_2$)-Mo(CO)(η$^5$-C$_5$H$_5$)] **8** in 45% yield. Thermolysis of complex **4** in refluxing toluene yielded the thiolato-bridged complex [(η$^5$-C$_5$H$_5$)(OC)Mo{μ-PPh$_2$C(CO$_2$Me)=C(CO$_2$Me)}(μ-SPh)-Co(CO)$_2$] **9** in 51% yield along with unreacted starting material.

Both complexes **8** snd **9** have been spectroscopically characterised (see Table 1 and Experimental section). Complex **8** has also been the subject of a single crystal X-ray structural analysis.

The molecular structure of **8** is shown in Fig. 2; Table 4 lists the bond lengths and angles and Table 5 the atomic coordinates. The Mo–Co single bond [2.735(2) Å] is bridged by a phosphido ligand and by a vinyl ligand which is σ-bonded to Co [Co–C(1) 2.042(8) Å] and asymmetrically π-bound to Mo [Mo–C(1) 2.085(11), Mo(1)–C(2) 2.271(9) Å]. The β-substituent of the vinyl group is a diphenylphosphido moiety which is itself co-ordinated to Co [Co–P(1) 2.219(2) Å] thus forming a $\overline{\text{Co–C=C–P}}$ four-membered metallacyclic ring. Similar ligands have previously been obtained by the insertion of alkynes into phosphido-bridged complexes.[14–18] The synthesis of complex **8** resembles that of [Mo$_2$(μ-Cl)(μ-PPh$_2$CHCH)(CO)$_2$-(η$^5$-C$_5$H$_5$)$_2$] and [Co$_2$(μ-PPh$_2$CRCR)(μ-PPh$_2$)(CO)$_4$] (R = CO$_2$Me or Ph) which both involve the insertion of a phosphido group into a metal–carbon bond of a μ-alkyne complex.[1,19] The smaller covalent radius of Co compared to Mo accounts, as in **6**, for the asymmetric bridging of the two metal centres in **8** by the PPh$_2$ ligand [Mo–P(2) 2.411(2) *vs.* Co–P(2) 2.210(3) Å].

The spectroscopic properties of **8** are in agreement with the solid-state structure being maintained in solution, with a medium intensity IR band at 1682 cm$^{-1}$ being assigned to ν(C=O) of the methylcarboxylate groups. In the $^{31}$P-{$^1$H} NMR spectrum two doublet resonances with $J$(PP) 116 Hz are observed with the downfield signal at δ 19.1 being consistent with a phosphido bridge and the upfield signal at δ −153.0 being typical of a μ-PPh$_2$ ligand which has become part of a four-membered metallacycle.[1,14–19] In the $^{13}$C-{$^1$H} NMR spectrum recorded at 293 K three resonances are observed in the CO region; the characteristically sharper lower-field signal is ascribed to a molybdenum-bound carbonyl and takes the form of a doublet with $^2J$(PC) 9 Hz. The cobalt-bound carbonyls give two distinct broader signals indicating a lack of fluxionality at the cobalt atom.

The proposed structure of [(η$^5$-C$_5$H$_5$)(OC)Mo{μ-PPh$_2$C-(CO$_2$Me)=C(CO$_2$Me)}(μ-SPh)Co(CO)$_2$] **9** (Scheme 1) is based on spectroscopic evidence. It resembles the structure for complex **8**, containing a four-membered metallacyclic ring, but differs in that in **9** the Mo atom rather than the Co atom as in **8** is incorporated into the metallacycle and a thiolato instead of a phosphido group bridges the two metal centres. Thus, the $^{31}$P-{$^1$H} NMR spectrum of the complex shows a singlet at δ −145.6 which is typical of a μ-phosphido group combined with an alkyne such that it is part of a four-membered $\overline{\text{P–C=C–M}}$ metallacyclic ring.[1,14–19] The $^{13}$C-{$^1$H} NMR spectrum of **9** confirms that the CO$_2$Me groups are inequivalent. The β carbon of the vinyl group gives a resonance centred at δ 38.5 with $^1J$(PC) 47 Hz. The α carbon of the vinyl group displays a doublet at δ 107.5 with $^2J$(PC) 11 Hz. As with complex **8** three signals are seen in the terminal carbonyl region, the lower field molybdenum-bound carbonyl (δ 235.4), however, takes the

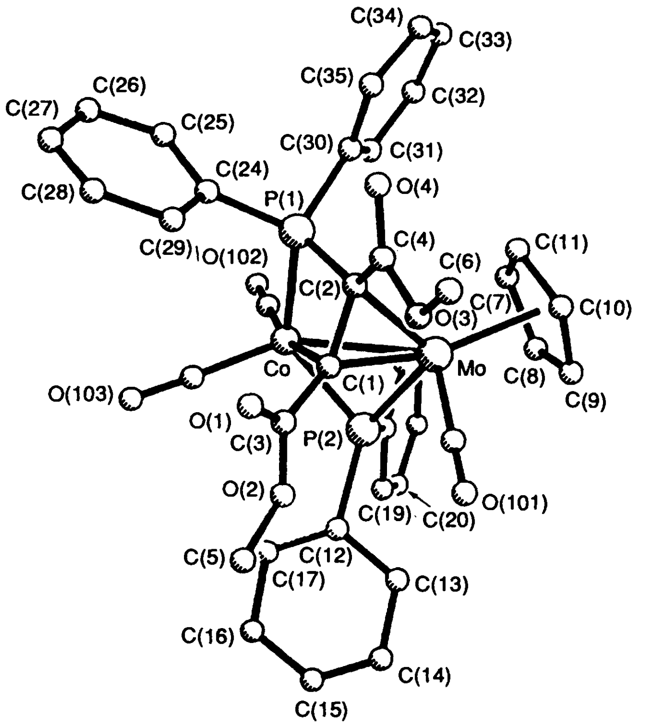


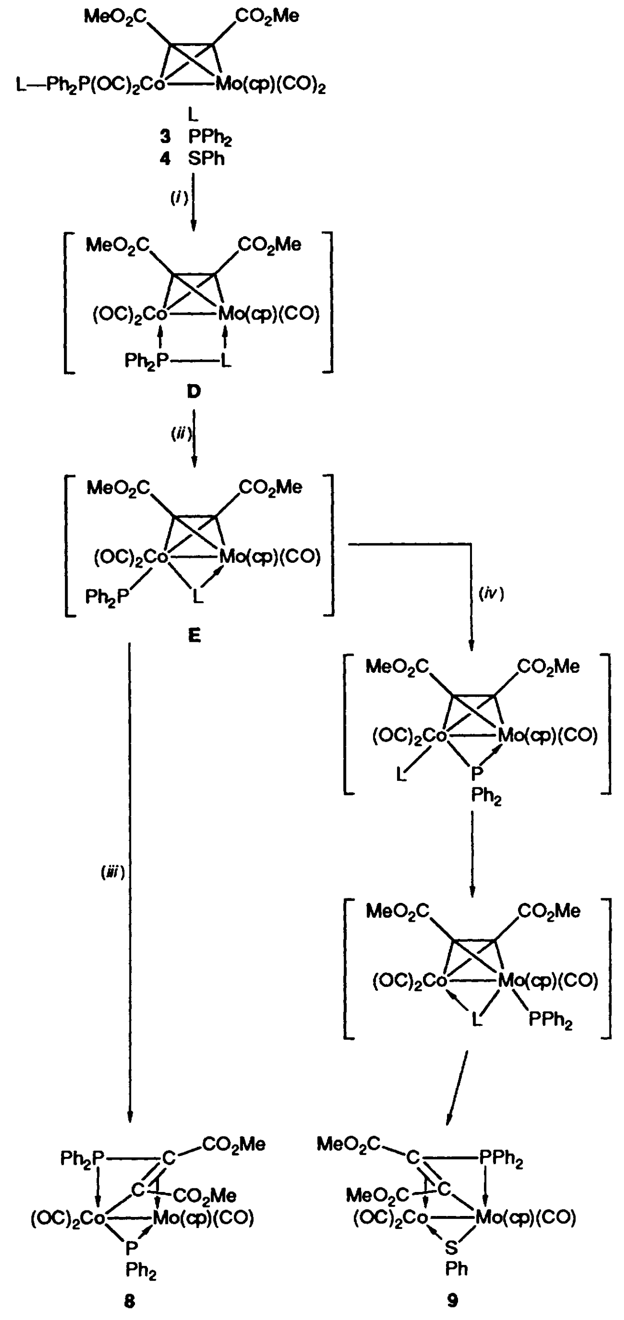
**Fig. 2** Molecular structure of $[(OC)_2Co\{\mu\text{-}PPh_2C(CO_2Me){=}C(CO_2Me)\}(\mu\text{-}PPh_2)Mo(CO)(\eta^5\text{-}C_5H_5)]$ **8** including the atom numbering scheme. Hydrogen atoms have been omitted for clarity

**Table 4** Selected bond distances (Å) and angles (°) for complex **8**

| | | | |
|---|---|---|---|
| Mo–Co | 2.735(2) | Co–C(103) | 1.772(14) |
| Mo–P(2) | 2.411(2) | Co–C(1) | 2.042(8) |
| Mo–C(101) | 1.962(8) | P(1)–C(2) | 1.770(9) |
| Mo–C(1) | 2.085(11) | P(1)–C(24) | 1.812(11) |
| Mo–C(2) | 2.271(9) | P(1)–C(30) | 1.828(9) |
| Co–P(1) | 2.219(2) | P(2)–C(12) | 1.817(8) |
| Co–P(2) | 2.210(3) | P(2)–C(18) | 1.851(9) |
| Co–C(102) | 1.753(8) | C(1)–C(2) | 1.474(11) |
| C(1)–C(3) | 1.463(12) | C(2)–C(4) | 1.483(12) |
| C(101)–O(101) | 1.132(10) | C(102)–O(102) | 1.157(10) |
| C(103)–O(103) | 1.145(19) | | |
| Co–Mo–P(2) | 50.4(1) | Mo–C(1)–Co | 83.0(3) |
| Co–Mo–C(101) | 114.0(4) | Mo–C(1)–C(2) | 77.2(6) |
| Co–Mo–C(1) | 47.8(2) | Co–C(1)–C(2) | 98.9(5) |
| Co–Mo–C(2) | 64.4(2) | Mo–C(1)–C(3) | 138.9(7) |
| P(2)–Mo–C(2) | 111.7(3) | Co–C(1)–C(3) | 121.8(7) |
| C(1)–Mo–C(2) | 39.3(3) | C(2)–C(1)–C(3) | 123.7(7) |
| Mo–Co–P(1) | 79.5(1) | Mo–C(2)–P(1) | 103.7(4) |
| Mo–Co–P(2) | 57.2(1) | Mo–C(2)–C(1) | 63.6(5) |
| P(1)–Co–P(2) | 135.8(1) | P(1)–C(2)–C(1) | 100.3(6) |
| Mo–Co–C(1) | 49.2(3) | Mo–C(2)–C(4) | 119.9(7) |
| P(1)–Co–C(1) | 71.7(2) | P(1)–C(2)–C(4) | 125.0(6) |
| P(2)–Co–C(1) | 84.8(3) | C(1)–C(2)–C(4) | 127.5(6) |
| Co–P(1)–C(2) | 84.3(2) | Mo–C(7)–C(8) | 71.9(6) |
| Mo–P(2)–Co | 72.4(1) | | |

form of a doublet with *J*(PC) 12 Hz, characteristic of a two-bond phosphorus–carbon coupling, and consistent with the phosphido fragment of the metallacycle being co-ordinated to the Mo atom. This is further supported by the $^1H$ NMR spectrum in which the signal assigned to the $\eta^5\text{-}C_5H_5$ group is split into a doublet with $^3J(PH)$ 1.5 Hz.

A plausible mechanism for the formation of **8** is outlined in Scheme 3. A similar mechanistic scheme was proposed for the formation of the dicobalt species $[Co_2(\mu\text{-}PPh_2CRCR)(\mu\text{-}PPh_2)(CO)_4]$ (R = $CO_2Me$ or Ph) but in this case the dicobalt analogue of intermediate **D** was isolated as a stable complex.[1] In step (*i*), adoption of a bridging mode by the $P_2Ph_4$ ligand and loss of a carbonyl group leads to the formation of intermediate **D**. The cleavage of a P–P bond in step (*ii*) permits phosphido-bridge formation along with a pendant phosphido group to give intermediate **E**. The attack of the pendant phosphido group at one end of the alkyne then gives the desired product **8** [step (*iii*)].



**Scheme 3** Possible mechanisms for the formation of complexes **8** and **9** on thermolysis of **3** and **4** respectively; (*i*) heat, –CO; (*iii*) L = $PPh_2$; (*iv*) L = SPh

The thermolysis of **4** to give **9** requires the transfer of the co-ordinated phosphorus from the cobalt to the molybdenum atom. It is possible that the mechanism for the formation of **9** is similar to that proposed for **8** up to the point of formation of intermediate **E**. One possible route from this point which accommodates the transfer of the phosphido group from one metal to the other is also shown in Scheme 3. A similar interchange of a SPh with a $PPh_2$ group in a dimetallic complex has been proposed previously.[5]

**Table 5** Fractional atomic coordinates ( × $10^5$) for complex **8**

| Atom | *x* | *y* | *z* |
|---|---|---|---|
| Mo | 24 619(8) | 21 135(6) | 18 717(5) |
| Co | 35 010(13) | 28 395(10) | 30 007(7) |
| P(1) | 17 824(25) | 45 012(19) | 26 891(15) |
| P(2) | 41 286(25) | 9 884(19) | 27 912(14) |
| C(101) | 39 514(117) | 15 686(75) | 6 969(63) |
| O(101) | 47 965(83) | 12 767(60) | 98(44) |
| C(102) | 27 485(105) | 27 534(84) | 41 968(58) |
| O(102) | 22 923(89) | 27 230(81) | 49 898(45) |
| C(103) | 50 971(127) | 31 396(88) | 29 338(64) |
| O(103) | 60 929(105) | 33 713(82) | 29 087(63) |
| C(1) | 38 589(95) | 30 463(75) | 16 097(53) |
| C(2) | 24 011(87) | 39 593(67) | 15 814(53) |
| C(3) | 52 999(98) | 30 394(76) | 9 840(55) |
| C(4) | 19 725(100) | 46 412(77) | 7 625(58) |
| O(1) | 55 010(79) | 38 369(59) | 4 992(54) |
| O(2) | 64 040(67) | 20 033(54) | 10 147(46) |
| O(3) | 27 685(77) | 40 770(57) | −191(41) |
| O(4) | 10 048(74) | 55 934(55) | 8 012(46) |
| C(5) | 78 531(107) | 18 559(99) | 4 149(79) |
| C(6) | 24 192(129) | 46 917(95) | −8 312(62) |
| C(7) | 1 042(107) | 20 353(84) | 27 698(69) |
| C(8) | 10 379(122) | 9 350(95) | 24 549(77) |
| C(9) | 14 168(127) | 10 007(95) | 14 707(88) |
| C(10) | 6 881(126) | 22 040(101) | 12 022(79) |
| C(11) | −1 101(110) | 28 077(94) | 20 498(75) |
| C(12) | 60 776(104) | 720(75) | 23 094(60) |
| C(13) | 64 404(125) | −7 290(92) | 16 735(61) |
| C(14) | 79 150(177) | −14 829(108) | 13 637(79) |
| C(15) | 90 161(146) | −14 916(116) | 16 781(106) |
| C(16) | 86 674(134) | −6 972(109) | 23 109(110) |
| C(17) | 72 080(120) | 671(87) | 26 303(86) |
| C(18) | 35 762(96) | 710(75) | 38 081(58) |
| C(19) | 45 608(113) | −10 137(82) | 40 059(63) |
| C(20) | 41 226(123) | −16 561(88) | 47 857(69) |
| C(21) | 27 161(123) | −12 687(92) | 53 621(72) |
| C(22) | 17 081(121) | 2 101(103) | 51 563(70) |
| C(23) | 21 277(111) | 4 814(91) | 44 081(62) |
| C(24) | 21 505(97) | 58 062(73) | 26 460(60) |
| C(25) | 15 336(130) | 64 919(92) | 33 840(71) |
| C(26) | 19 445(155) | 74 088(100) | 33 841(95) |
| C(27) | 29 910(147) | 76 699(97) | 26 448(104) |
| C(28) | 35 667(136) | 70 538(101) | 18 817(95) |
| C(29) | 31 722(122) | 61 005(88) | 18 655(73) |
| C(30) | −2 384(99) | 49 207(75) | 32 251(57) |
| C(31) | 8 246(110) | 43 512(93) | 40 079(68) |
| C(32) | −23 375(128) | 45 940(107) | 43 754(80) |
| C(33) | −32 963(126) | 54 837(104) | 39 328(82) |
| C(34) | −27 662(120) | 60 615(101) | 31 680(76) |
| C(35) | −12 406(112) | 58 136(87) | 28 058(67) |

In the only other reported case of the reaction of a μ-alkyne complex with $PPh_2(SPh)$ co-ordination and P–S bond cleavage is followed by the incorporation of the SPh group into a five-membered metallacycle and by phosphido-bridge formation to give the complex $[Co_2\{\mu\text{-}SPhC(O)CHCH\}(\mu\text{-}PPh_2)(CO)_4]$.[5] This result may be contrasted with the formation of complex **9** in which it is the $PPh_2$ fragment which is incorporated into the bridging metallacycle and the SPh fragment which bridges the two metal centres. This difference suggests that bimetallic complexes containing bridging four-membered metallathiacyclic rings may be less stable than complexes containing metallaphosphacyclic rings of the same size. Whereas there are several examples in the literature of bridging four-membered metallacyclic rings incorporating $PPh_2$ fragments, those incorporating SPh fragments are rare.[20]

## Experimental

All reactions were carried out under a nitrogen atmosphere using standard Schlenk techniques. Solvents were distilled under nitrogen from appropriate drying agents and degassed prior to use. Preparative thin-layer chromatography (TLC) was carried out on commercial Merck plates with a 0.25 mm layer of silica, or on 1 mm silica plates prepared at the University Chemical Laboratory, Cambridge. Column chromatography was performed on Kieselgel 60 (70–230 mesh) or (230–400 mesh). Products are given in order of decreasing $R_f$ values.

The instrumentation used to obtain spectroscopic data has been described previously.[21] Unless otherwise stated all reagents were obtained from commercial suppliers and used without further purification. The compounds $[(OC)_3Co\{\mu\text{-}C_2(CO_2Me)_2\}Mo(CO)_2(\eta^5\text{-}C_5H_5)]$ **1**,[6] $P_2Ph_4$,[22] and $PPh_2(SPh)$[23] were prepared by literature methods.

(*i*) *Reaction of* $[(OC)_3Co\{\mu\text{-}C_2(CO_2Me)_2\}Mo(CO)_2(\eta^5\text{-}C_5H_5)]$ **1** *with* $PPh_2H$.—The complex $[(OC)_3Co\{\mu\text{-}C_2(CO_2Me)_2\}Mo(CO)_2(\eta^5\text{-}C_5H_5)]$ **1** (0.80 g, 1.59 mmol) was dissolved in toluene (50 $cm^3$) and $PPh_2H$ (0.28 $cm^3$, 1.59 mmol) was added. The solution was heated at 313 K for 2 h. The solvent was removed on a rotary evaporator and 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. Elution with hexane–ethyl acetate (4:1) gave unreacted $[(OC)_3Co\{\mu\text{-}C_2(CO_2Me)_2\}Mo(CO)_2(\eta^5\text{-}C_5H_5)]$ **1** (0.11 g, 14%), followed by red crystalline $[(HPh_2P)(OC)_2Co\{\mu\text{-}C_2(CO_2Me)_2\}Mo(CO)_2(\eta^5\text{-}C_5H_5)]$ **2** (0.55 g, 52%). Further elution of the column with hexane–ethyl acetate (7:3) gave green crystalline $[(HPh_2P)(OC)_2Co\{\mu\text{-}C_2(CO_2Me)_2\}Mo(CO)(\eta^5\text{-}C_5H_5)(PPh_2H)]$ **5** (0.17 g, 13%). Complex **2** (Found: C, 48.9; H, 3.5. $C_{27}H_{22}CoMoO_8P$ requires C, 49.1; H, 3.4%); fast atom bombardment (FAB) mass spectrum, *m/z* 660 ($M^+$) and $M^+ - n$CO ($n$ = 0–4). NMR ($CDCl_3$): $^{13}C$ ($^1H$ composite pulse decoupled), δ 224.2 (s, 2MoCO), 204.7 (s, 2CoCO), 173.7 (s, $CO_2Me$), 133–128 (m, Ph), 90.6 (s, cp), 71.9 (s, $CCO_2Me$) and 52.0 (s, Me). Complex **5** (Found: C, 55.2; H, 4.1. $C_{38}H_{33}CoMoO_7P_2$ requires C, 55.7; H, 4.0%); FAB mass spectrum, *m/z* 818 ($M^+$) and $M^+ - n$CO ($n$ = 0–3). NMR ($CDCl_3$): $^{13}C$ ($^1H$ composite pulse decoupled), δ 235.0 (s, br, 1MoCO), 205.4 (s, 2CoCO), 176.0 (s, $CO_2Me$), 133–128 (m, Ph), 92.9 (s, cp), 70.0 (s, br, $CCO_2Me$) and 51.7 (s, Me).

(*ii*) *Reaction of* $[(OC)_3Co\{\mu\text{-}C_2(CO_2Me)_2\}Mo(CO)_2(\eta^5\text{-}C_5H_5)]$ **1** *with* $P_2Ph_4$.—The complex $[(OC)_3Co\{\mu\text{-}C_2(CO_2Me)_2\}Mo(CO)_2(\eta^5\text{-}C_5H_5)]$ **1** (0.80 g, 1.59 mmol) was added to a solution of $P_2Ph_4$ (0.59 g, 1.59 mmol) in toluene (60 $cm^3$). The solution was heated at 313 K for 4 h. After removal of the solvent on a rotary evaporator 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. Elution with hexane–ethyl acetate (4:1) gave unreacted $[(OC)_3Co\{\mu\text{-}C_2(CO_2Me)_2\}Mo(CO)_2(\eta^5\text{-}C_5H_5)]$ **1** 0.08 g, 10%) and orange crystalline $[(Ph_4P_2)(OC)_2Co\{\mu\text{-}C_2(CO_2Me)_2\}Mo(CO)_2(\eta^5\text{-}C_5H_5)]$ **3** (0.74 g, 54%) and several other compounds in very low yield. Complex **3**: mass spectrum, *m/z* 844 ($M^+$) and $M^+ - n$CO ($n$ = 0–4). NMR ($CDCl_3$): $^{13}C$ ($^1H$ composite pulse decoupled), δ 223.0 (s, 2MoCO), 205.7 (s, br, 2CoCO), 172.3 (s, $CO_2Me$), 135–127 (m, Ph), 90.3 (s, cp), 69.3 (s, $CCO_2Me$) and 51.5 (s, Me).

(*iii*) *Reaction of* $[(OC)_3Co\{\mu\text{-}C_2(CO_2Me)_2\}Mo(CO)_2(\eta^5\text{-}C_5H_5)]$ **1** *with* $PPh_2(SPh)$.—The complex $[(OC)_3Co\{\mu\text{-}C_2(CO_2Me)_2\}Mo(CO)_2(\eta^5\text{-}C_5H_5)]$ **1** (0.80 g, 1.59 mmol) was dissolved in toluene (50 $cm^3$) and $PPh_2(SPh)$ (0.47 g, 1.59

**Table 6** Crystallographic data and structure parameters for the complexes **6** and **8**

| | **6** | **8** |
|---|---|---|
| | C$_{26}$H$_{22}$CoMoO$_7$P | C$_{38}$H$_{31}$CoMoO$_7$P$_2$ |
| *M* | 632.3 | 816.4 |
| Crystal symmetry | Monoclinic | Triclinic |
| Space group | $P2_1/n$ (no. 14) | $P\bar{1}$ (no. 2) |
| $a$/Å | 9.181(2) | 10.135(2) |
| $b$/Å | 17.287(6) | 12.598(3) |
| $c$/Å | 16.257(6) | 15.402(3) |
| $\alpha$/° | | 80.07(3) |
| $\beta$/° | 93.92(3) | 71.06(3) |
| $\lambda$/° | | 66.39(3) |
| $U$/Å$^3$ | 2574(2) | 1702(1) |
| $Z$ | 4 | 2 |
| $D_c$/g cm$^{-3}$ | 1.631 | 1.593 |
| $F$(000) | 1272 | 828 |
| Crystal colour and habit | Dark green prism | Red prism |
| Crystal dimensions/mm | 0.38 × 0.25 × 0.31 | 0.38 × 0.21 × 0.19 |
| $\mu$(Mo-K$\alpha$)/mm$^{-1}$ | 1.237 | 1.000 |
| $2\theta$ scan range/° | 5.0–45.0 | 7.0–50.0 |
| Scan mode | $\omega$–$2\theta$ | $\omega$–$\theta$ |
| Total number of reflections | 3384 | 5341 |
| Number of unique data | 2633 [$F > 4\sigma(F)$] | 3984 [$F > 5\sigma(F)$] |
| Absorption correction | $\psi$ Scans | Face indexing |
| Maximum, minimum, transmission factors | 0.253, 0.273 | 0.808, 0.866 |
| Number of parameters refined | 325 | 442 |
| Largest and mean $\Delta/\sigma$ | 0.032, 0.006 | 0.004, 0.001 |
| $R$ | 0.034 | 0.082 |
| $R'$ | 0.038 | 0.108 |
| Goodness of fit | 1.14 | 1.76 |
| Weighting scheme | $w^{-1} = \sigma^2(F) + 0.0005F^2$ | $w^{-1} = \sigma^2(F) + 0.0030F^2$ |
| Largest difference peak/e Å$^{-3}$ | 0.35 | 1.95 |
| Largest difference hole/e Å$^{-3}$ | $-0.65$ | $-1.59$ |

mmol) added. The solution was heated to 313 K for 16 h. After removal of the solvent, column chromatographic separation eluting with hexane–ethyl acetate (4:1), gave red crystalline [{(PhS)Ph$_2$P}(OC)$_2$Co{μ-C$_2$(CO$_2$Me)$_2$}Mo(CO)$_2$(η$^5$-C$_5$H$_5$)] **4** (0.68 g, 56%) and a trace of starting material. Complex **4** (Found: C, 51.1; H, 3.5. C$_{33}$H$_{26}$CoMoO$_8$PS requires C, 51.6; H, 3.4%): mass spectrum, *m*/*z* 768 ($M^+$) and $M^+ - n$CO ($n$ = 0–4). NMR (CDCl$_3$): $^{13}$C ($^1$H composite pulse decoupled), δ 223.2 (s, 2MoCO), 205.0 (s, 2CoCO), 172.5 (s, *C*O$_2$Me), 136–127 (m, Ph), 90.4 (s, cp), 70.2 (s, *C*CO$_2$Me) and 51.7 (s, Me).

(*iv*) *Thermolysis of* [(HPh$_2$P)(OC)$_2$Co{μ-C$_2$(CO$_2$Me)$_2$}-Mo(CO)$_2$(η$^5$-C$_5$H$_5$)] **2**.—A solution of the complex [(HPh$_2$-P)(OC)$_2$Co{μ-C$_2$(CO$_2$Me)$_2$}Mo(CO)$_2$(η$^5$-C$_5$H$_5$)] **2** (0.40 g, 0.61 mmol) in toluene (40 cm$^3$) was heated at 338 K for 48 h. After removal of solvent on a rotary evaporator the residue was dissolved in the minimum quantity of CH$_2$Cl$_2$ and applied to the base of TLC plates. Elution with hexane–ethyl acetate (4:1) gave bright green crystalline [(η$^5$-C$_5$H$_5$)(OC)Mo{μ-C(CO$_2$-Me)=CH(CO$_2$Me)}(μ-PPh$_2$)Co(CO)$_2$] **6** (0.13 g, 34%) and brown crystalline [(OC)$_2$Co{μ-C(CO$_2$Me)=CH(CO$_2$Me)}-(μ-PPh$_2$)Mo(CO)(η$^5$-C$_5$H$_5$)] **7** (0.11 g, 29%) followed by unreacted [(HPh$_2$P)(OC)$_2$Co{μ-C$_2$(CO$_2$Me)$_2$}Mo(CO)$_2$(η$^5$-C$_5$H$_5$)] **2** (0.02 g, 5%). Complex **6**: mass spectrum, *m*/*z* 632 ($M^+$) and $M^+ - n$CO ($n$ = 0–3). NMR (CDCl$_3$): $^{13}$C ($^1$H composite pulse decoupled), δ 245.4 [d, *J*(PC) 13, MoCO], 209.3 (s, 1CoCO), 208.3 (s, 1CoCO), 189.1 (s, *C*O$_2$Me), 178.5 [d, *J*(PC) 5, *C*O$_2$Me], 145–127 (m, Ph), 133.3 [d, *J*(PC) 24, *C*(CO$_2$Me)=CH(CO$_2$Me)], 92.2 (s, cp), 54.0 (s, Me), 51.1 (s, Me) and 47.2 [d, *J*(PC) 4 Hz, *C*H(CO$_2$Me)]. Complex **7** (Found: C, 49.3; H, 4.0; P, 4.5. C$_{26}$H$_{22}$CoMoO$_7$P requires C, 49.4; H, 3.5; P, 4.9%); FAB mass spectrum, *m*/*z* 632 ($M^+$) and $M^+ - n$CO ($n$ = 0–3). NMR (CDCl$_3$): $^{13}$C ($^1$H composite pulse decoupled), δ 227.7 [d, *J*(PC) 15 Hz, MoCO], 217.6 (s, 1CoCO), 201.4 (s, 1CoCO), 180.7 (s, *C*O$_2$Me), 178.0 (s, *C*O$_2$Me), 156.4 [s, *C*(CO$_2$Me)CH(CO$_2$Me)], 143–127 (m, Ph), 92.2 (s, cp), 53.1 (s, Me), 51.9 (s, Me) and 49.5 [s, *C*H(CO$_2$Me)].

(*v*) *Thermolysis of* [(Ph$_4$P$_2$)(OC)$_2$Co{μ-C$_2$(CO$_2$Me)$_2$}Mo-(CO)$_2$(η$^5$-C$_5$H$_5$)] **3**.—Complex **3** (0.40 g, 0.47 mmol) was dissolved in toluene (40 cm$^3$). The solution was heated at 328 K for 22 h. After removal of the solvent on the rotary evaporator, TLC separation eluting with CH$_2$Cl$_2$, gave unreacted starting material [(Ph$_4$P$_2$)(OC)$_2$Co{μ-C$_2$(CO$_2$Me)$_2$}Mo(CO)$_2$(η$^5$-C$_5$H$_5$)] **3** (0.032 g) and green-brown crystalline [(OC)$_2$Co{μ-PPh$_2$C(CO$_2$Me)=C(CO$_2$Me)}(μ-PPh$_2$)Mo(CO)(η$^5$-C$_5$H$_5$)] **8** (0.17 g, 45%). Complex **8** (Found: C, 55.3; H, 3.9. C$_{38}$H$_{31}$CoMoO$_7$P$_2$ requires C, 55.9; H, 3.8%); mass spectrum, *m*/*z* 816 ($M^+$) and $M^+ - n$CO ($n$ = 0–3). NMR (CDCl$_3$): $^{13}$C ($^1$H composite pulse decoupled), δ 232.1 [d, *J*(PC) 9, MoCO], 210.1 (s, 1CoCO), 203.4 (s, 1CoCO), 175.4 (s, *C*O$_2$Me), 172.1 (s, *C*O$_2$Me), 146–127 (m, Ph), 98.2 [m, Ph$_2$PC(CO$_2$Me)-*C*(CO$_2$Me)], 91.6 (s, cp), 51.0 (s, Me), 50.7 (s, Me) and 36.9 [d, *J*(PC) 37 Hz, Ph$_2$P*C*(CO$_2$Me)C(CO$_2$Me)].

(*vi*) *Thermolysis of* [{(PhS)Ph$_2$P}(OC)$_2$Co{μ-C$_2$(CO$_2$Me)$_2$}-Mo(CO)$_2$(η$^5$-C$_5$H$_5$)] **4**.—Complex **4** (0.60 g, 0.78 mmol) was dissolved in toluene (50 cm$^3$). The solution was heated to reflux for 0.5 h. After removal of the solvent on a rotary evaporator, TLC separation eluting with hexane–ethyl acetate (4:1) gave green crystalline [(η$^5$-C$_5$H$_5$)(OC)Mo{μ-PPh$_2$C(CO$_2$Me)=C(CO$_2$Me)}(μ-SPh)Co(CO)$_2$] **9** (0.29 g, 51%) and unreacted [{(PhS)Ph$_2$P}(OC)$_2$Co{μ-C$_2$(CO$_2$Me)$_2$}Mo(CO)$_2$(η$^5$-C$_5$H$_5$)] **4** (0.042 g, 7%). Complex **9** (Found: C, 51.7; H, 3.6; P, 3.9. C$_{32}$H$_{26}$CoMoO$_7$PS requires C, 51.9; H, 3.5; P, 4.2%): mass spectrum, *m*/*z* 740 ($M^+$) and $M^+ - n$CO ($n$ = 0–3). NMR (CDCl$_3$): $^{13}$C ($^1$H composite pulse decoupled), δ 235.4 [d, *J*(PC) 12, MoCO], 206.6 (s, 1CoCO), 204.4 (s, 1CoCO), 179.5 [d, *J*(PC) 12, *C*O$_2$Me], 170.6 (s, *C*O$_2$Me), 145–125 (m, Ph), 107.5 [d, *J*(PC) 11, PPh$_2$C(CO$_2$Me)*C*(CO$_2$Me)], 91.4 (s, cp), 51.7 (s, Me), 51.5 (s, Me) and 38.5 [d, *J*(PC) 47 Hz, PPh$_2$*C*-(CO$_2$Me)C(CO$_2$Me)].

(*vii*) *Thermolysis of* [(HPh$_2$P)(OC)$_2$Co{μ-C$_2$(CO$_2$Me)$_2$}-Mo(CO)(η$^5$-C$_5$H$_5$)(PPh$_2$H)] **5**.—Complex **5** (0.200 g, 0.24

mmol) was dissolved in toluene (30 $cm^3$). The solution was heated to 338 K for 48 h. After removal of solvent on a rotary evaporator, TLC separation eluting with hexane–ethyl acetate (4:1), gave green-brown crystalline $[(\eta^5\text{-}C_5H_5)(OC)Mo\{\mu\text{-}C(CO_2Me)=CH(CO_2Me)\}(\mu\text{-}PPh_2)Co(CO)(PPh_2H)]$ **10** (0.11 g, 59%) and traces of unreacted $[(HPh_2P)(OC)_2Co\{\mu\text{-}C_2(CO_2Me)_2\}Mo(CO)(\eta^5\text{-}C_5H_5)(PPh_2H)]$ **5**. Complex **10**: mass spectrum, *m*/*z* 790 ($M^+$) and $M^+ - n$CO ($n$ = 0–2). NMR ($CDCl_3$): $^{13}C$ ($^1H$ composite pulse decoupled), δ 251.1 [d, *J*(PC) 13, MoCO], 214.2 (s, CoCO), 188.4 [d, *J*(PC) 7, $\mathit{C}O_2Me$], 180.6 (s, $\mathit{C}O_2Me$), 145–128 (m, Ph), 124.5 [d, *J*(PC) 25 Hz, $\mathit{C}(CO_2Me)=CH(CO_2Me)$], 91.8 (s, cp), 53.7 (s, Me), 50.7 (s, Me) and 47.0 (s, $\mathit{C}HCO_2Me$).

(*viii*) *Reaction of* $[(\eta^5\text{-}C_5H_5)(OC)Mo\{\mu\text{-}C(CO_2Me)=CH(CO_2Me)\}(\mu\text{-}PPh_2)Co(CO)_2]$ **6** *with* $PPh_2H$.—Complex **6** (0.077 g, 0.117 mmol) was dissolved in toluene (10 $cm^3$) and $PPh_2H$ (0.02 $cm^3$, 0.117 mmol) added. The solution was heated to 338 K for 20 h. After removal of the solvent on a rotary evaporator, TLC separation eluting with hexane–ethyl acetate (4:1), gave green-brown crystalline $[(\eta^5\text{-}C_5H_5)(OC)Mo\{\mu\text{-}C(CO_2Me)=CH(CO_2Me)\{(\mu\text{-}PPh_2)Co(CO)(PPh_2H)]$ **10** (0.048 g, 50%) and unreacted $[(\eta^5\text{-}C_5H_5)(OC)Mo\{\mu\text{-}C(CO_2Me)=CH(CO_2Me)\}(\mu\text{-}PPh_2)Co(CO)_2]$ **6** (0.005 g).

(*ix*) *Crystal Structure Analyses of Complexes* **6** *and* **8**.—Intensity data of compound **6** were collected on a Siemens R3m/V diffractometer and on a Stoe Stali four-circle diffractometer for compound **8**, with graphite-monochromated Mo-Kα radiation (λ = 0.710 73 Å). Three check reflections were monitored periodically throughout data collection and showed no significant variations. The two structures were solved by a combination of direct methods and Fourier difference techniques, and refined by full-matrix least-squares analysis. All the non-hydrogens atoms were assigned anisotropic thermal parameters. Phenyl and cyclopentadienyl H atoms were placed in idealised positions (C–H 0.96 Å) and allowed to ride on the relevant C atom. Weighting schemes were applied, and analysis of the variation of the sum of $w\Delta^2$ ($\Delta = F_o - F_c$) according to $F_o$ and sinθ indicated that they were appropriate in each case. The quality of data for **8** was poor due to repeated diffractometer malfunction during data collection. The highest residual peaks in the difference map lay close to metal atom positions, and could not be interpreted as being chemically sensible. Crystal data and structure parameters are given in Table 6. Calculations were carried out on a Micro-Vax II computer using the SHELXTL PLUS package.[24]

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

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