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Synthesis of three-membered metallaphosphaheterocycles and their ring opening with Ph_2PH on mixed-metal molybdenum–cobalt centres †

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Treatment of the alkyne-bridged molybdenum–cobalt complexes $[(\eta^5\text{-}C_5H_5)(OC)_2Mo(\mu\text{-}R^1CCR^2)Co(CO)_3]$ ($R^1 = R^2 = CO_2Me$ **1a**; $R^1 = H$, $R^2 = Bu^t$ **1b**) with the phosphinoalkyne $Ph_2PC{\equiv}CPh$ in refluxing toluene gave regiospecifically the phosphino-substituted butadiene-containing complexes $[(\eta^5\text{-}C_5H_5)(OC)Mo\{\mu\text{-}CR^2{=}CR^1CPh{=}C(PPh_2)\}Co(CO)_2]$ ($R^1 = R^2 = CO_2Me$ **2a**; $R^1 = H$, $R^2 = Bu^t$ **2b**) in moderate yield. Single crystal X-ray diffraction studies of **2a** and **2b** reveal the phosphorus and molybdenum centres to be constrained into three-membered metallaphosphaheterocycles. Reaction of **1a** with $Ph_2PC{\equiv}CBu^t$ has previously been shown to lead to P–C bond cleavage but, in contrast, reaction of **1b** with this phosphinoalkyne under the same conditions affords two products, $[(\eta^5\text{-}C_5H_5)(OC)Mo\{\mu\text{-}CBu^t{=}CHCBu^t{=}C(PPh_2)\}Co(CO)_2]$ **2c**, the analogue of **2a** and **2b** as the minor product, and $[(\eta^5\text{-}C_5H_5)(OC)Mo\{\mu\text{-}CBu^t{=}CHCBu^t{=}C(PPh_2O)\}Co(CO)_2]$ **3**, as the major product. This major product is derived from **2c** by oxidation of the phosphorus centre, with the P=O unit so formed then being incorporated into a four-membered Mo–O=P–C metallacycle. The reactivity of **2a** and **2b** towards diphenylphosphine has been examined and found to follow two different pathways. On reaction of **2a** with Ph_2PH in refluxing toluene the three-membered metallaphosphaheterocycle opens to give the vinyl-bridged complex $[(\eta^5\text{-}C_5H_5)(OC)Mo\{\mu\text{-}C(CO_2Me)C(CPh{=}CHPPh_2)C(OMe)O\}(\mu\text{-}PPh_2)Co(CO)]$ **4** while the vinylidene-bridged species $[(\eta^5\text{-}C_5H_5)(OC)Mo\{\mu\text{-}C{=}CPhCH(CH_2Bu^t)PPh_2\}(\mu\text{-}PPh_2)_2Co(CO)]$ **5** is isolated in the corresponding reaction of **2b**. In addition to **2a** and **2b**, single crystal X-ray diffraction studies have been performed on **3**, **4** and **5**. Possible reaction pathways for the formation of the new complexes are proposed and discussed.

1 Introduction

The reactivity of alkyne-bridged ditransition metal complexes towards alkynes has long been the focus for considerable research activity, due in part to the connection of such reactions to metal-mediated cyclooligomerisation processes.[1] In some cases organometallic products are isolated in which one, two or three molecules of the added alkyne have coupled with the bridging alkyne to form condensed ligands.[1–5] This occurs, for instance, in the reaction of the dimethyl acetylenedicarboxylate-bridged molybdenum–cobalt complex $[(\eta^5\text{-}C_5H_5)(OC)_2Mo\{\mu\text{-}C_2(CO_2Me)_2\}Co(CO)_3]$ **1a** with $HC{\equiv}C(CO_2Me)$ affording $[(\eta^5\text{-}C_5H_5)(OC)Mo\{\mu\text{-}C(CO_2Me){=}C(CO_2Me)C(CO_2Me){=}CH\}Co(CO)_2]$, in which one molecule of the free alkyne has effectively inserted selectively into a molybdenum–carbon(alkyne) bond in **1a** (Fig. 1).[5a]

Recently, we have investigated some reactions of complex **1a** with the phosphinoalkyne $Ph_2PC{\equiv}CBu^t$, and found that, instead of direct coupling with the bridging ligand, P–C(alkyne) bond cleavage occurs to give, after subsequent P–C and C–C bond forming steps, the complex $[(\eta^5\text{-}C_5H_5)(OC)_2Mo\{\mu\text{-}Bu^tCCC(CO_2Me){=}C(CO_2Me)PPh_2\}Co(CO)_2]$ (Fig. 1).[6] Indeed, phosphorus–carbon(alkyne) bond cleavage reactions are a feature of the reactivity of phosphinoalkynes towards transition metal carbonyl complexes, with the resulting PR_2 and $C{\equiv}CR$ fragments often participating in further coupling reactions.[7–9] However, insertion of an intact phosphinoalkyne into a metal–carbon bond of a bridging alkyne is, to the knowledge of the authors, unprecedented. Moreover, studies of the reaction chemistry of alkyne-bridged bimetallic complexes with phosphinoalkynes remain uncommon.[6,10,11]

By simple variation in the nature of the substituent R on the $Ph_2PC{\equiv}CR$ substrate, or the substituents R^1 and R^2 on the bridging alkyne in $[(\eta^5\text{-}C_5H_5)(OC)_2Mo(\mu\text{-}R^1CCR^2)Co(CO)_3]$ **1**, we have been able to effect insertion reactions to give novel butadiene-co-ordinated molybdenum–cobalt complexes containing strained three-membered metallaphosphaheterocycles, the reactivity of which has been probed with diphenylphosphine.

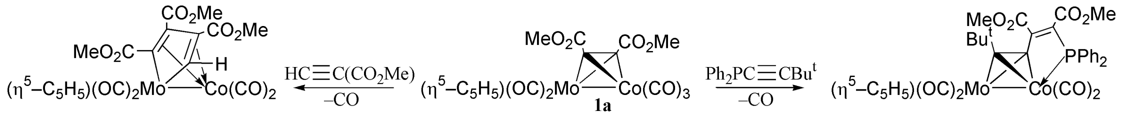

Fig. 1 Products from the reactions of complex **1a** with $HC{\equiv}C(CO_2Me)$ [ref. 5*a*] and $Ph_2PC{\equiv}CBu^t$ [ref. 6].

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† Dedicated to the memory of Dr Ron Snaith.

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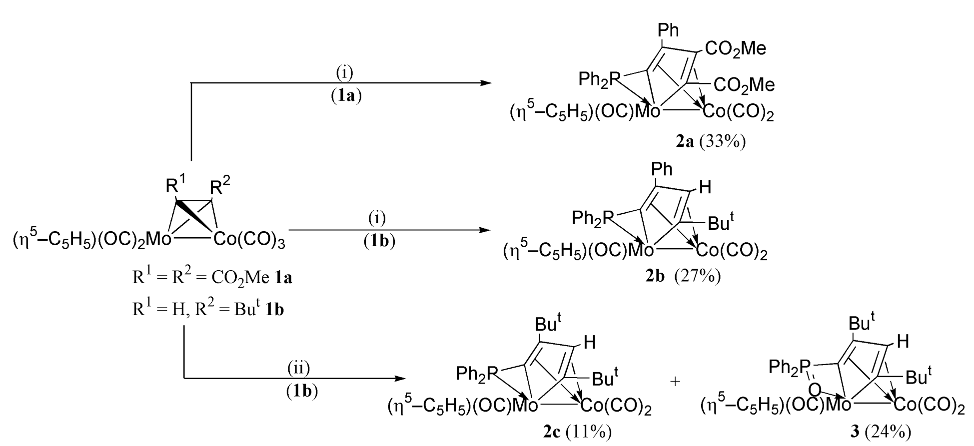
Table 1 Infrared, ^1H and ^{31}P NMR data for the new complexes **2**–**5**

Compound	$\nu(CO)^a/cm^{-1\,a}$	^1H NMR $(\delta)^b$	^{31}P NMR $(\delta)^c$
2a	2037vs, 1989s, 1841br	7.7–6.8 [m, 15H, Ph], 5.10 [d, ^3J(PH) 1.3, 5H, Cp], 3.76 [s, 3H, CO_2*Me*], 3.73 [s, 3H, CO_2*Me*]	−31.0 [s, μ-C(CO_2Me)=C(CO_2Me)CPh=C(PPh_2)]
2b	2000vs, 1956s, 1828br	7.7–7.2 [m, 15H, Ph], 7.03 [s, 1H, CH], 5.10 [s, 5H, Cp], 1.20 [s, 9H, Bu^t]	−27.8 [μ-CBu^t=CHCPh=C(PPh_2)]
2c	2004vs, 1950m, 1810br	7.9–7.2 [m, 10H, Ph], 6.40 [d, ^4J(PH) 4, 1H, CH], 5.00 [s, 5H, Cp], 1.31 [s, 9H, Bu^t], 1.20 [s, 9H, Bu^t]	−22.9 [μ-CBu^t=CHCBu^t=C(PPh_2)]
3	1986vs, 1938vs, 1115w (P–O)	7.8–7.4 [m, 10H, Ph], 6.10 [d, ^4J(PH) 6.5, 1H, CH], 4.80 [s, 5H, Cp], 1.30 [s, 9H, Bu^t], 1.01 [s, 9H, Bu^t]	63.5 [μ-CBu^t=CHCBu^t=C(PPh_2O)]
4	1964vs, 1916w, 1651w, 1581w	7.5–7.2 [m, 26H, Ph and μ-C(CO_2Me)C(CPh-C*H*PPh_2)C(OMe)O], 5.47 [d, ^3J(PH) 2.2, 5H, Cp], 3.67 [s, 3H, CO_2*Me*], 3.12 [s, 3H, CO_2*Me*]	136.4 [s, μ-PPh_2], 63.1 [s, μ-C(CO_2Me)C(CPh=CHPPh_2)C(OMe)O]
5	1958vs, 1924m	7.8–6.6 [m, 35H, Ph], 5.1 [s, 5H, Cp], 0.81 [m, 2H, μ-CCPhCH(C*H*$_2$$Bu^t$)$PPh_2$], 0.56 [dd, ^3J(HH) 17.0, ^2J(PH) 3.8, 1H, μ-CCPh-C*H*(CH_2Bu^t)PPh_2], −0.05 [s, 9H, Bu^t]	92.3 [d, ^2J(PP) 111, μ-PPh_2 *trans* to the ring], 89.6 [s, μ-PPh_2], 78.3 [d, μ-C=CPhCH(CH_2Bu^t)PPh_2]

[a] Recorded in *n*-hexane solution. [b] ^1H chemical shifts in ppm relative to $SiMe_4$ (0.0 ppm), coupling constants in Hz in $CDCl_3$ at 293 K. [c] ^{31}P chemical shifts in ppm relative to 85% external H_3PO_4 (0.0 ppm) (upfield shifts negative). Spectra were {^1H}-gated decoupled and measured in $CDCl_3$ at 293 K.



Scheme 1 *Reagents and conditions*: (i) $Ph_2PC{\equiv}CPh$, 383 K, C_6H_5Me; (ii) $Ph_2PC{\equiv}CBu^t$, 383 K, C_6H_5Me.

2 Results and discussion

(a) Reaction of [(η^5-C_5H_5)(OC)$_2$Mo(μ-R^1CCR^2)Co(CO)$_3$] with $Ph_2PC{\equiv}CR$

The reaction of [(η^5-C_5H_5)(OC)$_2$Mo(μ-R^1CCR^2)Co(CO)$_3$] (R^1 = R^2 = CO_2Me **1a**; R^1 = H, R^2 = Bu^t **1b**) with $Ph_2PC{\equiv}CPh$ in toluene at 383 K affords, respectively, in addition to unchanged starting material, the complexes [(η^5-C_5H_5)(OC)Mo{μ-CR^2=CR^1CPh=C(PPh_2)}Co(CO)$_2$] (R^1 = R^2 = CO_2Me **2a**; R^1 = H, R^2 = Bu^t **2b**) as the only products in 27–33% yield (Scheme 1). Complexes **2a** and **2b** have been characterised spectroscopically (see Table 1 and Experimental section) and, in addition, their molecular structures have been determined by single crystal X-ray diffraction. The structures are illustrated in Figs. 2 and 3 while Table 2 lists selected bond distances and angles.

Crystals of complexes **2a** and **2b** suitable for X-ray diffraction were obtained by slow evaporation of a CH_2Cl_2–hexane solution at 273 K. The structure of **2a** consists of two independent molecules (*A* and *B*) within the unit cell with the only appreciable difference between them being the orientation of the phenyl and CO_2Me groups. The bond parameters for *A* and *B* are essentially the same and only *A* will be discussed throughout the following; bond lengths and angles are listed in Table 2 separately for the two molecules *A* and *B*. Owing to the similarity of structures **2a** and **2b** they will be discussed together.

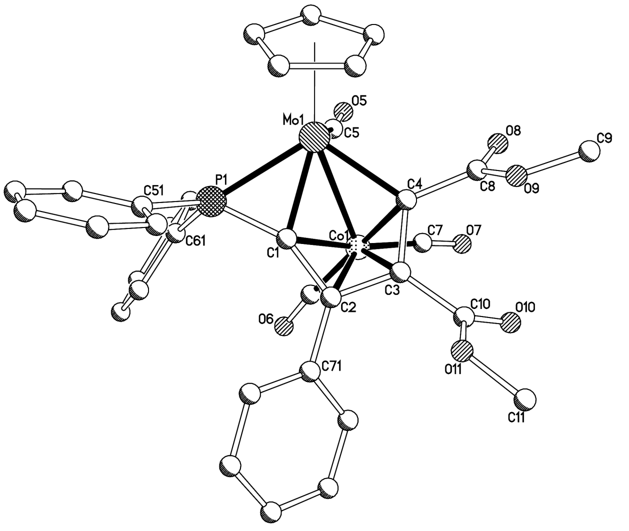


Fig. 2 Molecular structure of complex **2a** including the atom numbering scheme. Hydrogen atoms have been omitted for clarity.

The metal atoms are linked by a Mo–Co bond [Mo(1)–Co(1) 2.694(1) (**2a**), 2.724(2) (**2b**) Å][12] and are bridged by an unsaturated diphenylphosphino-substituted butadiene ligand [CR^2=CR^1CPh=C(PPh_2)] (R^1 = R^2 = CO_2Me **2a**; R^1 = H, R^2 = Bu^t **2b**). The cobalt atom is bound terminally by two carbonyl groups and the molybdenum by a carbonyl and a η^5-cyclopentadienyl ligand. The terminal carbon atoms (C_α) of the butadiene ligand [C(1) and C(4)] are σ-bonded to Mo to give a metallacyclopentadiene ring while co-ordination to the cobalt atom is

Table 2 Selected bond distances (Å) and angles (°) for [(η^5-C_5H_5)(OC)Mo{μ-CR^2=CR^1CPh=C(PPh_2)}Co$(CO)_2$] ($R^1 = R^2 = CO_2Me$ **2a**; R^1 = H, R^2 = Bu^t **2b**)

	2a		
	Molecule A	Molecule B	**2b**
Mo(1)–Co(1)	2.694(1)	2.710(1)	2.724(2)
Mo(1)–P(1)	2.403(2)	2.400(2)	2.416(4)
Mo(1)–C(1)	2.063(7)	2.067(7)	2.043(9)
Mo(1)–C(4)	2.175(7)	2.186(7)	2.250(8)
Mo(1)–C(5)	1.956(8)	1.966(8)	1.963(9)
Mo(1)–$(C_5H_5)_{centroid}$	2.007(7)	2.021(7)	2.010(5)
P(1)–C(1)	1.719(7)	1.716(8)	1.705(8)
C(1)–C(2)	1.444(10)	1.428(10)	1.446(10)
C(2)–C(3)	1.423(10)	1.432(10)	1.412(11)
C(3)–C(4)	1.443(10)	1.442(10)	1.413(11)
C(4)–$C(8)_{CO_2Me}$	1.495(10)	1.482(10)	—
C(4)–$C(8)_{Bu^t}$	—	—	1.550(12)
Co(1)–C(1)	2.082(7)	2.114(7)	2.032(8)
Co(1)–C(2)	2.092(7)	2.118(7)	2.109(8)
Co(1)–C(3)	2.071(7)	2.081(7)	2.106(9)
Co(1)–C(4)	2.011(7)	2.011(8)	2.076(9)
Co(1)–C(6)	1.774(9)	1.785(8)	1.753(9)
Co(1)–C(7)	1.776(8)	1.781(8)	1.739(10)
C–O (carbonyl)	1.137–1.176	1.127–1.161	1.137–1.169
Mo(1)–C(1)–P(1)	78.3(3)	78.1(3)	79.7(3)
P(1)–Mo(1)–C(1)	44.5(2)	44.4(2)	44.0(2)
Mo(1)–P(1)–C(1)	57.2(2)	57.5(2)	56.3(3)
Mo(1)–C(1)–C(2)	127.8(5)	128.3(5)	126.1(6)
Co(1)–Mo(1)–$(C_5H_5)_{centroid}$	160.8(6)	160.4(6)	165.1(6)
C(1)–C(2)–C(3)	107.4(6)	108.5(6)	108.1(7)
C(2)–C(3)–C(4)	113.9(6)	112.1(6)	117.3(7)
C(3)–C(4)–Mo(1)	119.5(5)	120.8(5)	114.6(6)
C(51)–P(1)–C(61)	106.0(3)	105.8(3)	104.9(4)
C(7)–Co(1)–C(6)	93.5(4)	91.4(4)	92.1(4)
C(71)–C(2)–C(1)	127.1(6)	120.9(6)	125.3(7)

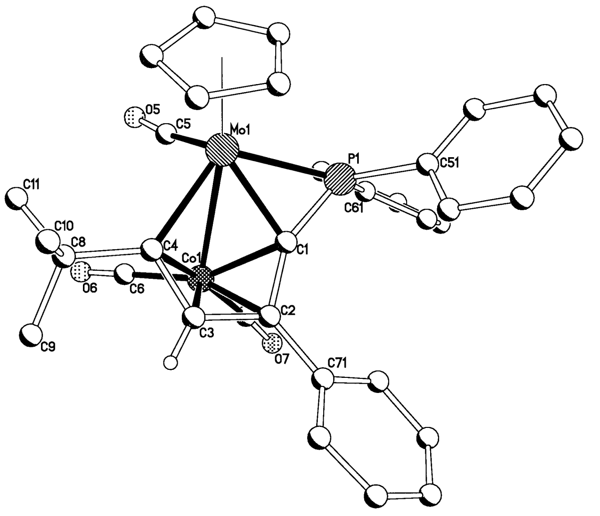
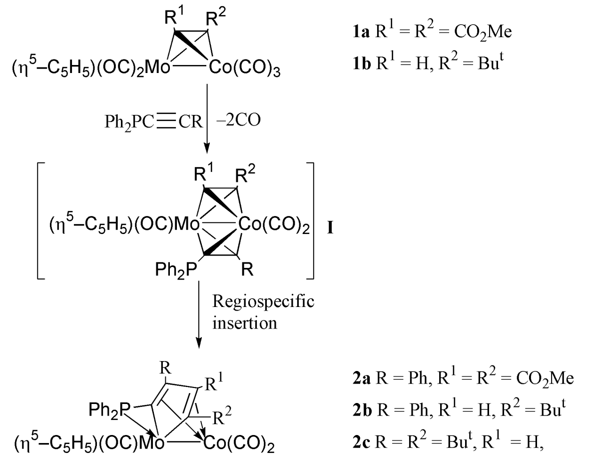


Fig. 3 Molecular structure of complex **2b** including the atom numbering scheme. All hydrogen atoms except for H3 have been omitted for clarity.

achieved through the butadiene π bonds. In addition, one C_α atom of the organic bridging ligand [C(1)] possesses a diphenylphosphino group which co-ordinates to the molybdenum atom to form a strained three-membered metallacycle [Mo(1)–P(1)–C(1) 57.2(2) **2a**, 56.3(3)° **2b**]. Owing to the phosphine co-ordination, the carbon atom C(1) is closer to molybdenum [Mo(1)–C(1) 2.063(7) **2a**, 2.043(9) Å **2b**] than the other σ-bonded carbon atom C(4) [Mo(1)–C(4) 2.175(7) **2a**, 2.250(8) Å **2b**]. The Ph_2PCCPhR [R = $C_2(CO_2Me)_2$ **2a**, CHCBu^t **2b**] moiety of the bridging ligand may also be viewed as a 'phospha-allene' co-ordinated through both P=C and C=C bonds, in that the P(1)–C(1) bond is short [1.719(7) **2a**, 1.705(8) Å **2b**] indicating a bond order greater than unity.[13] The C–C bond distances within the butadiene [C(1)–C(2) 1.444(10), C(2)–C(3) 1.423(10), C(3)–C(4) 1.443(10) **2a**; 1.446(10), 1.412(11), 1.413(11) Å **2b**] are similar indicating delocalisation over the system, as previously observed for related molybdenum–cobalt systems.[5] The co-ordination of a related diphenylphosphino-substituted butadiene ligand to a bimetallic backbone has been reported for [Mn_2(μ-PPh_2CHCHCHCH)(μ-PPh_2)$(CO)_5$]; in this case, however, the phosphine moiety is not constrained into a three-membered ring.[14] A number of examples of crystallographically characterised bimetallic complexes containing the diphenylphosphino fragment incorporated into a three-membered M–P–C ring have been reported. Notably, the M–P–C angles in **2a** and **2b** fall in the bottom of the range.[15]

The spectroscopic properties of complexes **2a** and **2b** are in accordance with the solid state properties being maintained in solution, with a single sharp upfield resonance [δ −31.0 (**2a**), −27.8 (**2b**)] in the ^{31}P-{^{1}H} NMR spectra being assigned to the phosphorus atom of the molybdenaphosphaheterocycle. In the ^{13}C-{^{1}H} spectrum four separate resonances are observed for the olefinic carbon atoms [δ 157.8, 151.1, 114.3, 114.1 (**2a**); 187.0, 152.6, 116.0, 112.3 (**2b**)] consistent with the unsymmetrical nature of the butadiene ligand. In the case of **2b** two terminal carbonyl resonances have been resolved at δ 240.0 and 202.0, the former chemical shift being typical of a molybdenum-bound carbonyl group and the latter a cobalt-bound carbonyl group.[5] In the ^{1}H NMR, in addition to signals for the cyclopentadienyl and phenyl groups, two separate resonances of equal integration are seen for the methyl carboxylate groups of the butadiene ligand for **2a** while for **2b** two resonances of relative integral 1 : 9 are seen for the CH and *tert*-butyl protons at δ 7.03 and 1.20 respectively.

The mechanism by which complexes **2a** and **2b** are formed from **1** is uncertain. However, the regiospecific insertion of the phosphinoalkyne into a molybdenum–carbon(alkyne) bond in a manner similar to that observed for the reactions of **1** with alkynes[5] would seem the most likely pathway. Scheme 2 shows a plausible proposal involving initial substitution of one carbonyl ligand on each of the molybdenum and cobalt atoms in **1** by a molecule of $Ph_2PC{\equiv}CR$ (intermediate **I**) which binds to both metal centres through the alkyne moiety in an $\eta^2:\eta^2$ fashion. Insertion of the alkyne functionality of the phosphinoalkyne into a Mo–C(alkyne) bond of **I** with concomitant co-ordination of the phosphino group to molybdenum affords **2**. It is noteworthy that Davidson has previously demonstrated a related conversion of a bis(alkyne)-bridged molybdenum–cobalt complex (*cf.* **I**) into a butadiene-bridged species.[16]



Scheme 2 A possible reaction pathway to account for the formation of complex **2** from **1**.

Table 3 Selected bond lengths (Å) and angles (°) for $[(\eta^5\text{-}C_5H_5)(OC)Mo\{\mu\text{-}CBu^t{=}CHCBu^t{=}C(PPh_2O)\}Co(CO)_2]$ **3**

Mo(1)–Co(1)	2.684(1)	C(3)–C(4)	1.405(4)
Mo(1)–C(4)	2.185(3)	C(4)–C(8)	1.560(4)
Mo(1)–C(5)	1.996(3)	Co(1)–C(1)	2.044(3)
Mo(1)–$(C_5H_5)_{centroid}$	1.996(3)	Co(1)–C(2)	2.104(3)
P(1)–C(1)	1.745(3)	Co(1)–C(3)	2.088(3)
C(1)–C(2)	1.401(4)	Co(1)–C(4)	2.086(3)
C(2)–C(3)	1.454(4)	Co(1)–C(6)	1.728(3)
Co(1)–C(7)	1.751(3)	P(1)–O(1)	1.535(2)
Mo(1)–O(1)	2.264(2)	Mo(1)–C(1)	2.155(3)
C–O (carbonyl)	1.147–1.152		
Mo(1)–C(1)–P(1)	93.7(1)	O(1)–P(1)–C(1)	98.9(1)
Co(1)–Mo(1)–$(C_5H_5)_{centroid}$	155.9(2)	C(1)–C(2)–C(3)	110.6(2)
		C(2)–C(3)–C(4)	119.8(3)
P(1)–Mo(1)–C(1)	37.5(2)	C(3)–C(4)–Mo(1)	112.4(2)
Mo(1)–P(1)–C(1)	48.8(1)	P(1)–C(1)–Co(1)	116.4(2)
Mo(1)–C(1)–C(2)	118.8(2)	C(7)–Co(1)–C(6)	91.0(2)
Mo(1)–O(1)–P(1)	95.7(1)	C(12)–C(2)–C(1)	129.0(2)

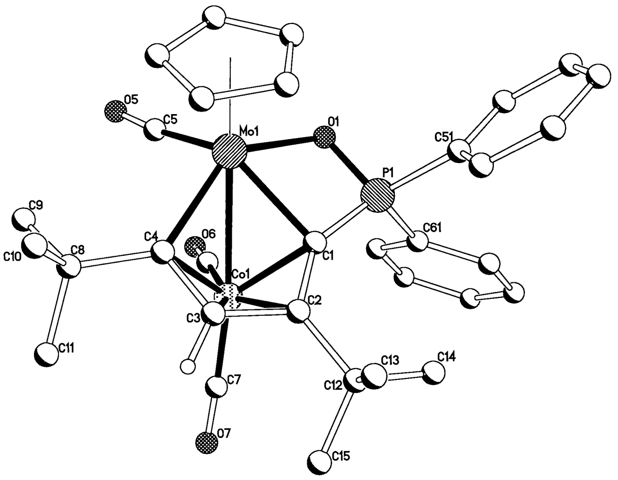


Fig. 4 Molecular structure of complex **3**. Details as in Fig. 3.

Clearly the nature of the substituent R on the substrate $Ph_2PC{\equiv}CR$ influences the type of reaction products isolated. This is most clearly shown by the contrasting reaction of complex **1a** with $Ph_2PC{\equiv}CPh$ as compared to $Ph_2PC{\equiv}CBu^t$. While coupling of the bridging alkyne with the β-carbon of the phosphinoalkyne occurs with $Ph_2PC{\equiv}CPh$ (Schemes 1 and 2), cleavage of the P–C(alkyne) bond occurs in the reaction with $Ph_2PC{\equiv}CBu^t$ (Fig. 1).[6] Based on these observations it might have been anticipated that the reaction of $[(\eta^5\text{-}C_5H_5)(OC)_2Mo(\mu\text{-}HCCBu^t)Co(CO)_3]$ **1b** with $Ph_2PC{\equiv}CBu^t$ would give a product analogous to that obtained in the reaction of **1a** with this phosphinoalkyne. However, the reaction in toluene at 383 K instead affords $[(\eta^5\text{-}C_5H_5)(OC)Mo\{\mu\text{-}CBu^t{=}CHCBu^t{=}C(PPh_2)\}Co(CO)_2]$ **2c**, the analogue of **2a** and **2b**, as the minor product (11%) and $[(\eta^5\text{-}C_5H_5)(OC)Mo\{\mu\text{-}CBu^t{=}CHCBu^t{=}C(PPh_2O)\}Co(CO)_2]$ **3** as the major product (24%) (Scheme 1). Complex **2c** has been characterised on the basis of the close similarity in its spectroscopic properties to those of **2a** and **2b** (see Table 1 and Experimental section) while **3** has been the subject of a single crystal X-ray diffraction study.

The molecular structure of complex **3** is depicted in Fig. 4; Table 3 lists selected bond distances and angles. The molecule comprises $(\eta^5\text{-}C_5H_5)(OC)Mo$ and $Co(CO)_2$ units linked by a Mo–Co bond [Mo(1)–Co(1) 2.684(1) Å][12] and bridged by a diphenylphosphine oxide-substituted butadiene ligand $[\mu\text{-}CBu^t{=}CHCBu^t{=}C(PPh_2O)]$. The butadiene σ-bonds to molybdenum *via* C(1) and C(4) and π-bonds to cobalt *via* the butadiene double bonds [C(1)=C(2) and C(3)=C(4)] in a fashion similar to that in **2a** and **2b** and elsewhere.[5] The substituent on C(1) is a phosphine oxide group which binds to molybdenum to form a four-membered metallacyclic ring Mo(1)–C(1)–P(1)=O(1). The phosphorus–oxygen bond [P(1)–O(1) 1.535(2) Å] of the ligand retains substantial multiple bond character. It is much shorter than expected for a P–O single bond [1.71 Å][17] and instead is in agreement with the average bond length of the P–O bond in phosphates at 1.54 Å.[18] The Mo(1)–O(1)–P(1) angle in **3** [95.7(1)°] is smaller than those found in crystallographically characterised molybdenum complexes containing monodentate (range: 142.0–171.9°)[19] and other chelating (range: 119.7–156.1°) phosphine oxide ligands,[20] but compares well with the Mn–O–P angle (92.7°) in the vinylphosphonato complex $[Mn\{(NC)_2C{=}CP(OPr^i)_2{=}O\}(dppe)(CO)_2]$.[21] The rather small angle in **3** is presumably a consequence of the requirements of the four-membered chelate ring. The small Mo(1)–O(1)–P(1) angle means that the phosphorus atom is held close to the molybdenum centre and allows some direct metal–phosphorus interaction [Mo(1)···P(1) 2.859(1) Å]. Burford *et al.* have discussed the relationship between bond distances and angles and the extent of pπ–dπ bonding and proposed that extensive Mo=O=P bonding occurs in compounds where the P–O–Mo linkage approaches linearity.[22] However, in **3** the chelate ring necessarily disrupts the π bonding to the metal and indeed the Mo(1)–O(1) distance [2.264(2) Å] falls at the top end of the range for other known Mo–O distances in phosphine oxide complexes (usually in the range: 2.09–2.24 Å).[19,20]

In the FAB mass spectrum of complex **3** a molecular ion peak is observed along with fragmentation peaks corresponding to the loss of up to three carbonyl groups. The IR spectrum in hexane shows, in addition to two terminal carbonyl bands, an intense band at 1115 cm^{-1}; a band at a very similar wavenumber has been assigned to the P–O stretch in a related complex.[23] The $^{31}P\text{-}\{^1H\}$ NMR spectrum displays a singlet at δ 63.5, shifted downfield by *ca.* 85 ppm when compared with that of **2c**. In the ^1H NMR spectrum the CH proton on the butadiene ligand is observed as a doublet at δ 6.10 with $^4J(PH)$ 6.5 Hz.

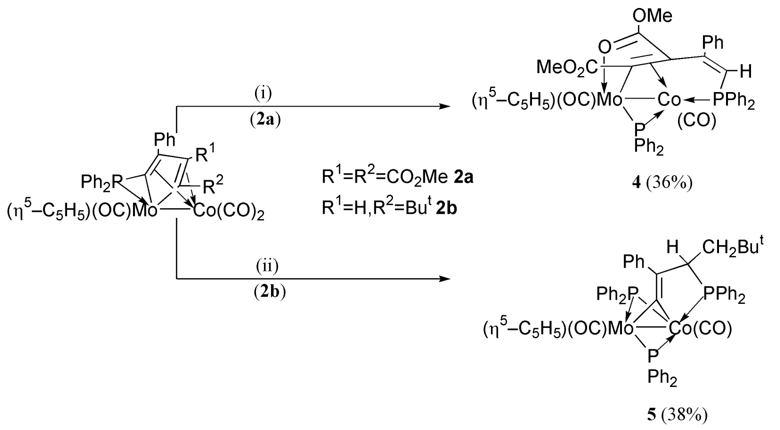
The origin of the oxygen atom in complex **3** is uncertain but is probably derived from adventitious oxygen in the reaction mixture or on work-up on silica TLC plates. It is a notable feature that only in the reaction of **1b** with *tert*-butyl substituted phosphinoalkyne the oxidation occurs. There is no evidence that a similar reaction occurs for **1a** or **1b** with $Ph_2PC{\equiv}CPh$.

(b) Reaction of $[(\eta^5\text{-}C_5H_5)(OC)Mo\{\mu\text{-}CR^2{=}CR^1CPh{=}C(PPh_2)\}Co(CO)_2]$ with Ph_2PH

The reactions of $[(\eta^5\text{-}C_5H_5)(OC)Mo\{\mu\text{-}CR^2{=}CR^1CPh{=}C(PPh_2)\}Co(CO)_2]$ ($R^1 = R^2 = CO_2Me$ **2a**; $R^1 = H$, $R^2 = Bu^t$ **2b**) with diphenylphosphine in refluxing toluene for 24 h gave $[(\eta^5\text{-}C_5H_5)(OC)Mo\{\mu\text{-}C(CO_2Me)C(CPh{=}CHPPh_2)C(OMe)O\}(\mu\text{-}PPh_2)Co(CO)]$ **4** and $[(\eta^5\text{-}C_5H_5)(OC)Mo\{\mu\text{-}C{=}CPhCH(CH_2Bu^t)PPh_2\}(\mu\text{-}PPh_2)_2Co(CO)]$ **5** respectively as the sole products in yields of between 36 and 38%. In the case of the reaction of **2b** the yield was maximised by employing two equivalents of Ph_2PH (Scheme 3). Both complexes have been characterised by ^1H, $^{31}P\text{-}\{^1H\}$, $^{13}C\text{-}\{^1H\}$ NMR, IR spectroscopy and by mass spectrometry and microanalysis (see Table 1 and Experimental section). In addition they have been the subject of single crystal X-ray diffraction studies.

The molecular structure of complex **4** is shown in Fig. 5, while selected bond distances and angles are listed in Table 4. The molecule consists of $(\eta^5\text{-}C_5H_5)(OC)Mo$ and Co(CO) units linked by a single Mo(1)–Co(1) bond [2.654(2) Å].[12] This bond is bridged asymmetrically by the phosphido group [Mo(1)–P(1) 2.433(2), Co(1)–P(1) 2.189(2) Å] and by a vinyl group in which the α-carbon is σ-bonded to molybdenum [Mo(1)–C(5) 2.181(6) Å] and the carbon–carbon double bond is π-bonded to cobalt [Co(1)–C(5) 1.927(6), Co(1)–C(6) 2.072(6) Å].

The β-carbon of the vinyl group has two substituents namely methyl carboxylate and vinylphosphine. The former



Scheme 3 *Reagents and conditions*: (i) Ph_2PH, 383 K, C_6H_5Me; (ii) $2Ph_2PH$, 383 K, C_6H_5Me.

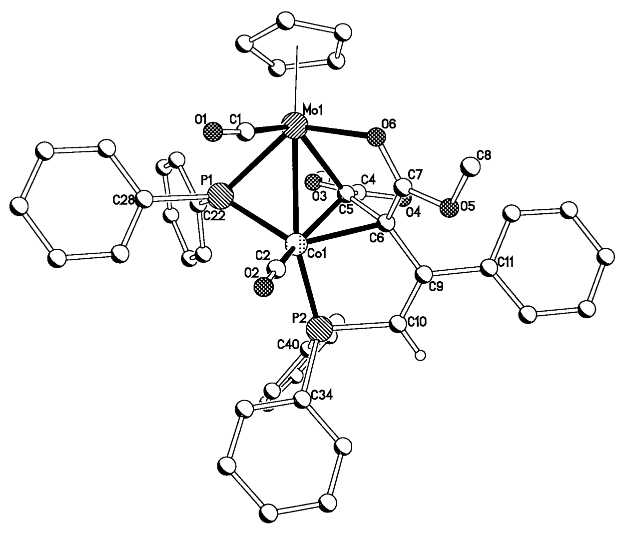


Fig. 5 Molecular structure of complex **4** including the atom numbering scheme. All hydrogen atoms except for H10 have been omitted for clarity.

co-ordinates to molybdenum *via* the oxygen atom [Mo(1)–O(6) 2.219(4) Å] to form a slightly puckered five-membered molybdenacyclic ring Mo–C=C–C=O [C(5) sitting 0.45 Å out of Mo(1)C(6)C(7)O(6) plane][24] while the latter co-ordinates to cobalt *via* the phosphorus atom to form a seven-membered dimetallacyclic Mo–C=C–C=C–P–Co ring. Unlike the unsaturated double bonds in complexes **2a** and **2b** the non-co-ordinated carbon–carbon double bond [C(9)–C(10)] in **4** maintains its double bond character [1.338(9) Å].

The spectroscopic properties of complex **4** are consistent with the solid-state properties being maintained in solution. The IR spectrum displays, in addition to terminal carbonyl bands, two absorptions at 1651 and 1581 cm^{-1} corresponding to carbonyl bands of the ester group. The band at lower wavenumber can be attributed to the ester group co-ordinated to the molybdenum atom.[12b] The FAB mass spectrum shows a molecular ion peak and sequential fragmentation peaks resulting from the loss of two carbonyl groups. The ^1H NMR spectrum shows multiplets in the region δ 7.5–7.2 attributable to the phenyl hydrogen atoms of the phosphido, phosphine and the olefinic hydrogen. The doublet at δ 5.47 with $^3J(PH)$ 2.2 Hz is assigned to the cyclopentadienyl ring on the molybdenum atom while the singlets at δ 3.67 and 3.12 are assigned respectively to the co-ordinated and unco-ordinated methyl carboxylate groups. Two signals are seen in the $^{31}P\text{-}\{^1H\}$ NMR spectrum at δ 63.1 and 136.4, the downfield signal being assigned to a bridging phosphido group and the upfield signal to the phosphorus atom incorporated into a metallacycle.[12b,c,h]

Table 4 Selected bond lengths (Å) and angles (°) for $[(\eta^5\text{-}C_5H_5)(OC)Mo\{\mu\text{-}C(CO_2Me)C(CPh{=}CHPPh_2)C(OMe)O\}(\mu\text{-}PPh_2)Co(CO)]$ **4**

Mo(1)–C(5)	2.181(6)	Mo(1)–O(6)	2.219(4)
Mo(1)–P(1)	2.433(2)	Mo(1)–Co(1)	2.654(2)
Co(1)–C(5)	1.927(6)	Co(1)–C(6)	2.072(6)
Co(1)–P(1)	2.189(2)	Co(1)–P(2)	2.205(2)
C(4)–O(4)	1.217(8)	C(4)–C(5)	1.467(8)
C(5)–C(6)	1.446(8)	O(5)–C(7)	1.320(7)
C(6)–C(7)	1.442(9)	C(6)–C(9)	1.512(8)
O(6)–C(7)	1.255(7)	C(9)–C(10)	1.338(9)
Mo(1)–$(C_5H_5)_{centroid}$	1.986(5)	Mo(1)–C(1)	1.998(8)
Co(1)–C(2)	1.762(8)		
C(5)–Mo(1)–O(6)	75.8(2)	C(7)–C(6)–C(9)	119.8(5)
O(6)–Mo(1)–P(1)	130.4(1)	P(1)–Co(1)–P(2)	119.7(1)
P(1)–Mo(1)–Co(1)	50.8(1)	P(2)–Co(1)–Mo(1)	153.3(1)
C(1)–Co(1)–P(1)	88.9(2)	C(9)–C(10)–P(2)	118.8(5)
P(1)–Co(1)–Mo(1)	54.1(2)	Co(1)–C(5)–Mo(1)	80.2(2)
Co(1)–Mo(1)–$(C_5H_5)_{centroid}$	159.7(3)	C(10)–P(2)–Co(1)	100.2(2)
		C(10)–C(9)–C(6)	119.2(6)
Co(1)–P(1)–Mo(1)	69.9(1)	C(7)–O(6)–Mo(1)	112.8(4)
C(6)–C(5)–C(4)	121.4(6)	C(6)–C(6)–C(9)	123.1(5)

Table 5 Selected bond lengths (Å) and angles (°) for species $[(\eta^5\text{-}C_5H_5)(OC)Mo\{\mu\text{-}C{=}CPhCH(CH_2Bu^t)PPh_2\}(\mu\text{-}PPh_2)_2Co(CO)]$ **5**

Mo(1)–Co(1)	2.600(2)	Mo(1)–C(51)	2.116(13)
Mo(1)–P(1)	2.439(3)	Mo(1)–P(2)	2.406(4)
Co(1)–C(51)	1.982(11)	Co(1)–P(3)	2.158(4)
Co(1)–P(1)	2.208(4)	Co(1)–P(2)	2.218(3)
P(3)–C(49)	1.869(11)	C(47)–C(48)	1.57(2)
C(48)–C(49)	1.56(2)	C(49)–C(50)	1.51(2)
C(50)–C(51)	1.35(2)	Mo(1)–$(C_5H_5)_{centroid}$	1.998(2)
Mo(1)–C(1)	2.010(13)	Co(1)–C(2)	1.754(13)
C(1)–Mo(1)–C(51)	127.8(5)	C(50)–C(51)–Mo(1)	155.7(9)
Co(51)–Mo(1)–P(1)	67.8(3)	C(51)–Mo(1)–P(2)	69.3(4)
P(1)–Mo(1)–Co(1)	51.9(1)	P(2)–Mo(1)–P(1)	103.9(1)
P(1)–Co(1)–P(2)	119.1(1)	P(2)–Mo(1)–Co(1)	52.4(1)
P(3)–Co(1)–Mo(1)	133.5(1)	P(3)–Co(1)–P(1)	117.8(1)
P(2)–Co(1)–Mo(1)	59.3(1)	P(3)–Co(1)–P(2)	108.3(1)
Co(1)–P(2)–Mo(1)	68.2(1)	P(1)–Co(1)–Mo(1)	60.3(1)
Co(1)–Mo(1)–$(C_5H_5)_{centroid}$	151.3(7)	Co(1)–P(1)–Mo(1)	67.8(1)
		C(50)–C(49)–P(3)	102.4(8)
C(51)–C(50)–C(52)	124.4(11)	C(51)–C(50)–C(49)	119.4(10)
C(52)–C(50)–C(49)	116.2(10)	C(50)–C(51)–Co(1)	125.6(9)

The molecular structure of complex **5** is depicted in Fig. 6, while selected bond distances and angles are listed in Table 5. The structure consists of a short molybdenum–cobalt bond [2.600(2) Å][12] linking the $(\eta^5\text{-}C_5H_5)(OC)Mo$ and Co(CO) units and bridged by two phosphido groups and by C(51) which forms part of a phosphine-substituted vinylidene ligand $[C{=}CPhCH(CH_2Bu^t)PPh_2]$. This vinylidene ligand wraps

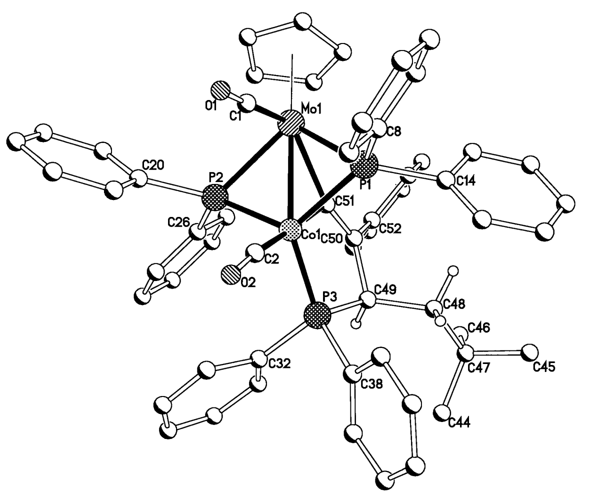


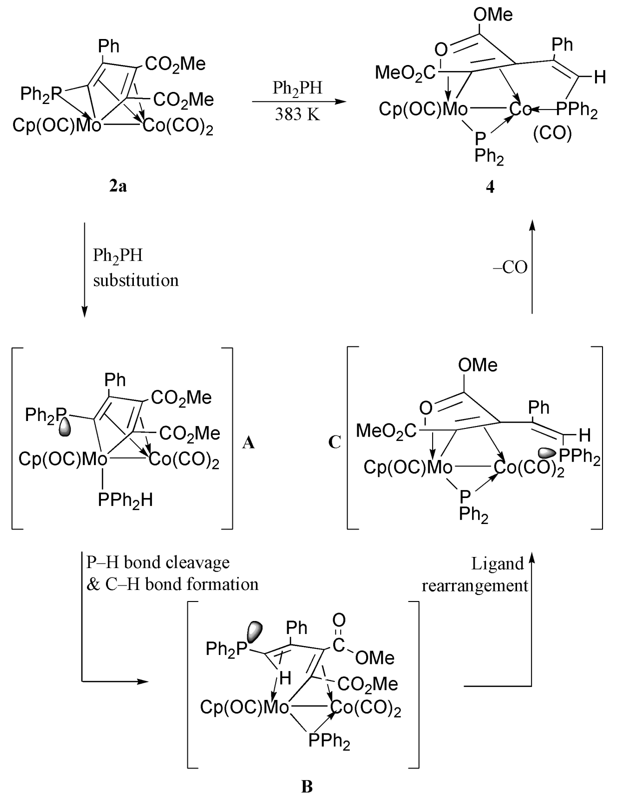
Fig. 6 Molecular structure of complex **5** including the atom numbering scheme. All hydrogen atoms except for H49, H48A and H48B have been omitted for clarity.

around to co-ordinate through the phosphorus centre to cobalt so as to form a five-membered [Co(1)–C(51)=C(50)–C(49)–P(3)] chelate ring. The C(51) atom is asymmetrically bound to the two metals, the Co(1)–C(51) bond distance being 1.982(11) Å as compared to the Mo(1)–C(51) distance of 2.116(13) Å. The C(51)–C(50) bond distance of 1.35(2) Å is typical of C=C bond distances in other μ-vinylidene ligands.[25] Further evidence of the sp^2 hybridised nature of the C(50) carbon atom comes from the angles around C(50). The C(49)–C(50)–C(51) angle is 119.4(10)°, C(49)–C(50)–C(52) is 116.2(10)° and C(52)–C(50)–C(51) is 124.4(11)°, close to those required for idealised sp^2 hybridisation. The Co(1)–C(51)=C(50)–C(49)–P(3) chelate ring is almost planar (maximum deviation from planarity, C(49) 0.147 Å) and the remaining bond distances within the ring are consistent with single bonds.

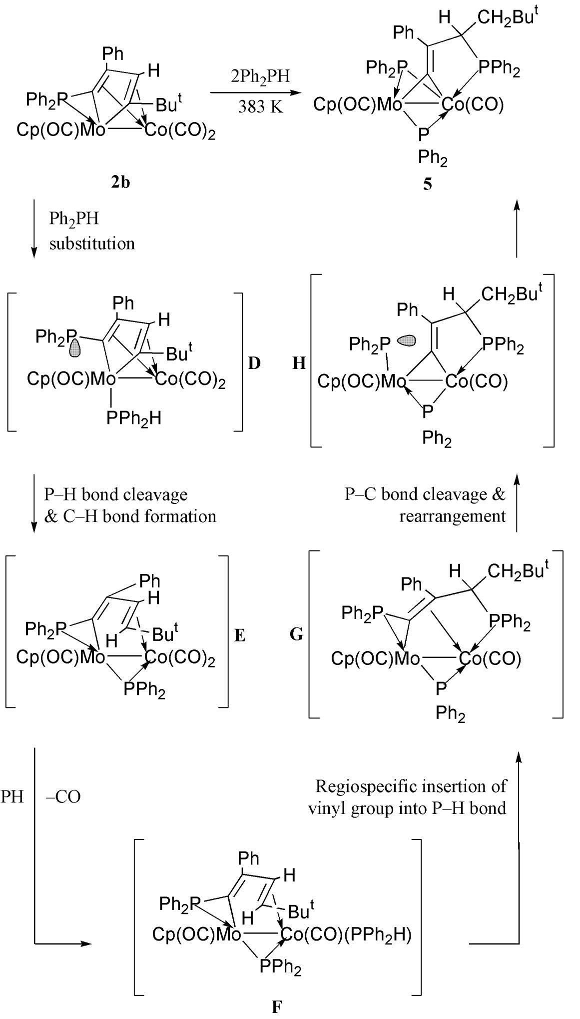
The solution state spectroscopic data for complex **5** are consistent with the solid-state structure being maintained in solution. Three phosphorus resonances are seen in the ^{31}P-{^{1}H} NMR spectrum, the more downfield signals at δ 92.3 and 89.6 being assigned to the phosphido groups, the former of which takes the form of a doublet [^2J(PP) 111 Hz] and has further been assigned to the phosphido group *trans* to the ring phosphorus. The more upfield doublet at δ 78.3 is assigned to the ring phosphorus atom. In the ^{1}H NMR spectrum, in addition to phenyl, cyclopentadienyl and *tert*-butyl resonances, a doublet of doublets at δ 0.56 with ^3J(HH) 17.0 and ^2J(PH) 3.8 Hz is assigned to the μ-C=CPhC*H*(CH$_2$Bu^t)PPh$_2$ proton. A multiplet at δ 0.81 is assigned to the methylene protons of the μ-C=CPhCH(C*H*$_2$Bu^t)PPh$_2$ ligand, the complexity of which results from the overlapping of signals due to inequivalent coupled C(H$_a$)(H$_b$) protons.

The explanation as to why the reactions of complexes **2a** and **2b** with diphenylphosphine do not follow the same course is uncertain. Possible reaction pathways for the formation of **4** and **5** are illustrated in Schemes 4 and 5 respectively. In Scheme 4 ring opening of the metallaphosphaheterocycle in **2a** occurs on co-ordination of a molecule of Ph$_2$PH to the molybdenum centre to give **A**. This is followed by oxidative addition of the P–H bond at the molybdenum to form PPh$_2$ and H ligands; reductive elimination and migration of the H atom to the phosphino-substituted terminal vinyl carbon atom of the butadiene ligand leads to **B**. A ligand rearrangement occurs with the ketonic oxygen atom of the CO$_2$Me substituent displacing the molybdenum-bound vinyl group to give **C**, this being followed by co-ordination of the pendant phosphino group to cobalt and concomitant CO loss to afford **4**.

In Scheme 5 complex **2b** undergoes similar initial Ph$_2$PH substitution (intermediate **D**) and oxidative addition steps. In



Scheme 4 A possible reaction pathway to account for the formation of complex **4** from **2a** (Cp = η^5-C$_5$H$_5$).



Scheme 5 A possible reaction pathway to account for the formation of complex **5** from **2b**.

contrast to that in Scheme 4, migration of the resultant H ligand occurs to the non-phosphino-substituted terminal vinyl carbon atom of the butadiene ligand to give **E**. Substitution of a terminal cobalt carbonyl group by a second molecule of Ph$_2$PH gives **F** which is then followed by regiospecific insertion of the π-bonded vinyl group into the P–H bond of the co-ordinated phosphine to give **G**. Ring opening of the metallaphosphaheterocycle in **G** by scission of the P–C bond and ligand rearrangement gives **H** which may be followed by co-ordination of the terminal phosphide in **H** to the cobalt to afford the co-ordinatively saturated species **5**.

It is noteworthy that we have recently reported the conversion of a bridging Ph$_2$PCR=CR group into a Ph$_2$PCR=CHR ligand by thermally induced P–H bond cleavage of a terminally bound diphenylphosphine ligand and migration of the resultant hydrogen atom to the α-carbon of the co-ordinated vinyl group, a step that relates to the conversion of **A**/**D** into **B**/**E** respectively.[26]

3 Conclusion

By variation of either the nature of the R substituent on the phosphinoalkyne Ph$_2$PC≡CR or of the substituents on the bridging alkyne ligand in complex **1**, the selective insertion of a molecule of Ph$_2$PC≡CR into a molybdenum–carbon(alkyne) bond can be achieved to give butadiene-co-ordinated complexes containing highly strained three-membered metallaphosphaheterocycles; the facility for ring opening has been probed with diphenylphosphine and found to follow two different reaction pathways.

4 Experimental

(a) General techniques

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.[27] Infrared spectra were recorded in hexane solution in 0.5 mm NaCl cells using a Perkin-Elmer 1710 Fourier-transform spectrometer, fast atom bombardment (FAB) mass spectra on a Kratos MS 890 instrument using 3-nitrobenzyl alcohol as a matrix and proton (reference to SiMe$_4$) and ^{31}P NMR spectra on either a Bruker WM250 or AM400 spectrometer, ^{31}P-NMR chemical shifts being referenced to 85% H$_3$PO$_4$. Preparative thin-layer chromatography (TLC) was carried out on commercial Merck plates with a 0.25 mm layer of silica, or on 1 mm silica plates prepared at the University Chemical Laboratory, Cambridge. Column chromatography was performed on Kieselgel 60 (70–230 or 230–400 mesh). Products are given in order of decreasing R_f values. Elemental analyses were performed at the University Chemical Laboratory, Cambridge.

Unless otherwise stated all reagents were obtained from commercial suppliers and used without further purification. The syntheses of [(η^5-C$_5$H$_5$)(OC)$_2$Mo(μ-R^{1}CCR^2)Co(CO)$_3$] (R^1 = R^2 = CO$_2$Me **1a**; R^1 = H, R^2 = Bu^t **1b**)[5a] and Ph$_2$PC≡CR (R = Bu^t or Ph)[28] have been reported previously.

(b) Reaction of [(η^5-C$_5$H$_5$)(OC)$_2$Mo{μ-C$_2$(CO$_2$Me)$_2$}Co(CO)$_3$] 1a with Ph$_2$PC≡CPh

To a solution of [(η^5-C$_5$H$_5$)(OC)$_2$Mo{μ-C$_2$(CO$_2$Me)$_2$}Co(CO)$_3$] **1a** (1.20 g, 2.4 mmol) in toluene (70 cm^3) was added Ph$_2$PC≡CPh (0.71 g, 2.5 mmol) and the resulting solution stirred at 383 K for 4 h. After removal of the volatiles under reduced pressure, the mixture was absorbed onto the minimum quantity of silica, added to the top of a chromatography column and purified with hexane–ethyl acetate (4 : 1) as eluent. This gave, in addition to a small amount of starting material, the brownish yellow crystalline complex [(η^5-C$_5$H$_5$)(OC)Mo{μ-C(CO$_2$Me)C(CO$_2$Me)CPhC(PPh$_2$)}Co(CO)$_2$] **2a** (0.58 g, 33%). FAB mass spectrum: *m*/*z* 732 (M^+) and $M^+ - n$CO (*n* = 1–3). NMR (CDCl$_3$): ^{13}C (^{1}H composite pulse decoupled), δ 177.1 [s, *C*O$_2$Me], 167.0 [d, ^3J(PC) 5, *C*O$_2$Me], 157.8 [d, ^2J(PC) 11, μ-*C*(CO$_2$Me)=C(CO$_2$Me)CPhC(PPh$_2$)], 151.1 [d, ^3J(PC) 4, μ-C(CO$_2$Me)=*C*(CO$_2$Me)CPhC(PPh$_2$)], 127–136 [m, Ph], 114.3 [d, ^2J(PC) 11, μ-C(CO$_2$Me)=C(CO$_2$Me)*C*PhC(PPh$_2$)], 114.1 [d, ^1J(PC) 18 Hz, μ-C(CO$_2$Me)=C(CO$_2$Me)CPh*C*(PPh$_2$)], 93.2 [s, C$_5$H$_5$], 52.5 [s, CO$_2$*Me*] and 51.5 [s, CO$_2$*Me*].

(c) Reaction of [(η^5-C$_5$H$_5$)(OC)$_2$Mo(μ-HCCBu^t)Co(CO)$_3$] 1b with Ph$_2$PC≡CPh

The complex [(η^5-C$_5$H$_5$)(OC)$_2$Mo(μ-HCCBu^t)Co(CO)$_3$] **1b** (0.70 g, 1.50 mmol) was dissolved in toluene (70 cm^3) and Ph$_2$PC≡CPh (0.44 g, 1.53 mmol) introduced. After stirring at 383 K for 2 h the volatiles were removed under reduced pressure. The resulting brown residue was absorbed onto the minimum amount of silica, added to the top of a chromatography column and purified with hexane–ethyl acetate (5 : 1) as eluent. This gave the brownish yellow crystalline complex [(η^5-C$_5$H$_5$)(OC)Mo{μ-CBu^{t}CHCPhC(PPh$_2$)}Co(CO)$_2$] **2b** (0.28 g, 27%) (Found: C, 59.9; H, 4.5. C$_{34}$H$_{30}$CoMoO$_3$P requires C, 60.7; H, 4.5%). FAB mass spectrum: *m*/*z* 672 (M^+) and $M^+ - n$CO (*n* = 1–3). NMR (CDCl$_3$): ^{13}C (^{1}H composite pulse decoupled), δ 240.0 [s, Mo–CO], 202.0 [s, Co–CO], 187.0 [s, μ-*C*Bu^t=CHCPh=C(PPh$_2$)], 152.6 [s, μ-CBu^t=*C*HCPh=C(PPh$_2$)], 137–127 [m, Ph], 116.0 [s, μ-CBu^t=CH*C*Ph=C(PPh$_2$)], 112.3 [d, ^3J(PC) 19, μ-CBu^t=CHCPh=*C*(PPh$_2$)], 91.6 [s, C$_5$H$_5$], 43.2 [s, *C*Me$_3$] and 33.5 [s, C*Me*$_3$].

(d) Reaction of [(η^5-C$_5$H$_5$)(OC)$_2$Mo(μ-HCCBu^t)Co(CO)$_3$] 1b with Ph$_2$PC≡CBu^t

To a solution of [(η^5-C$_5$H$_5$)(OC)$_2$Mo(μ-HCCBu^t)Co(CO)$_3$] **1b** (0.49 g, 1.10 mmol) in toluene (70 cm^3) was added Ph$_2$PC≡CBu^t (0.30 g, 1.12 mmol) and the resulting solution stirred at 383 K for 6 h. After removal of the volatiles under reduced pressure, the residue was purified by preparative TLC using hexane–ethyl acetate (5 : 1) as eluent. This gave orange complex [(η^5-C$_5$H$_5$)(OC)Mo{μ-CBu^{t}CHCBu^{t}C(PPh$_2$)}Co(CO)$_2$] **2c** (0.08 g, 11%) and brown complex [(η^5-C$_5$H$_5$)(OC)Mo{μ-CBu^{t}CHCBu^t-C(PPh$_2$O)}Co(CO)$_2$] **3** (0.16 g, 24%). Complex **2c** (Found: C, 58.1; H, 5.2. C$_{32}$H$_{34}$CoMoO$_3$P·CH$_2$Cl$_2$ requires C, 58.9; H, 5.3%): FAB mass spectrum *m*/*z* 654 (M^+) and $M^+ - n$CO (*n* = 1–3); NMR (CDCl$_3$) ^{13}C (^{1}H composite pulse decoupled), δ 240.4 [s, Mo–CO], 203.3 [s, Co–CO], 187.3 [s, μ-*C*Bu^t=CHCBu^t=C(PPh$_2$)], 167.7 [s, μ-CBu^t=CH*C*Bu^t=C(PPh$_2$)], 149.9 [s, μ-CBu^t=*C*HCBu^t=C(PPh$_2$)], 135–125 [m, Ph], 112.3 [d, ^3J(PC) 21 Hz, μ-CBu^t=CHCBu^t=*C*(PPh$_2$)], 91.5 [s, C$_5$H$_5$], 43.0 [s, *C*Me$_3$], 38.7 [s, *C*Me$_3$], 33.5 [s, C*Me*$_3$] and 32.4 [s, C*Me*$_3$]. Complex **3** (Found: C, 56.9; H, 5.38. C$_{32}$H$_{34}$CoMoO$_4$P requires C, 57.5; H, 5.13%): FAB mass spectrum *m*/*z* 668 (M^+) and $M^+ - n$CO (*n* = 1–3). NMR (CDCl$_3$) ^{13}C (^{1}H composite pulse decoupled), δ 205.0 [s, Co–CO], 191.5 [s, μ-*C*Bu^t=CHCBu^t=C(PPh$_2$O)], 133–127 [m, Ph], 109.1 [d, ^3J(PC) 10 Hz, μ-CBu^t=*C*HCBu^t=C(PPh$_2$O)], 92.0 [s, C$_5$H$_5$], 45.1 [s, *C*Me$_3$], 36.7 [s, *C*Me$_3$], 34.8 [s, C*Me*$_3$] and 32.1 [C*Me*$_3$].

(e) Reaction of [(η^5-C$_5$H$_5$)(OC)Mo{μ-C(CO$_2$Me)C(CO$_2$Me)-CPhC(PPh$_2$)}Co(CO)$_2$] 2a with Ph$_2$PH

To a solution of [(η^5-C$_5$H$_5$)(OC)Mo{μ-C(CO$_2$Me)C(CO$_2$Me)-CPhC(PPh$_2$)}Co(CO)$_2$] **2a** (0.33 g, 0.45 mmol) in toluene (50 cm^3) was added diphenylphosphine (0.10 cm^3, 0.57 mmol). After stirring at 383 K for 24 h, the volatiles were removed under reduced pressure and the residue purified by preparative TLC using hexane–ethyl acetate (3 : 1) as eluent. This gave, in addition to a small amount of unchanged starting material, the greenish crystalline complex [(η^5-C$_5$H$_5$)(OC)Mo{μ-C(CO$_2$Me)-C(CPhCHPPh$_2$)C(OMe)O}(μ-PPh$_2$)Co(CO)] **4** (0.14 g, 36%)

Table 6 Crystallographic and data processing parameters for complexes **2a**, **2b**, **3**, **4** and **5**

	2a	**2b**	**3**	**4**	**5**
Empirical formula	$C_{34}H_{26}CoMoO_7P$	$C_{34}H_{30}CoMoO_3P$	$C_{32}H_{34}CoMoO_4P$	$C_{45}H_{37}CoMoO_6P_2\cdot CH_2Cl_2\cdot CH_3OH$	$C_{57}H_{52}CoMoO_2P_3\cdot CH_2Cl_2\cdot 1.5C_6H_{14}$
Formula weight	732.39	672.42	668.43	1007.52	1230.95
Crystal system	Triclinic	Monoclinic	Monoclinic	Monoclinic	Triclinic
Space group	$P\bar{1}$	$P2_1/c$	$P2_1/n$	$P2_1/c$	$P\bar{1}$
a/Å	15.502(2)	10.771(19)	10.989(4)	20.676(7)	15.460(5)
b/Å	21.848(3)	28.163(12)	12.810(7)	18.323(4)	18.534(5)
c/Å	10.290(1)	11.014(12)	21.045(3)	12.021(6)	11.506(5)
α/°	91.85(1)				103.78(3)
β/°	108.33(1)	119.27(5)	102.80(2)	102.79(3)	91.12(3)
γ/°	71.29(1)				76.21(3)
U/Å^3	3124.3(7)	2914(6)	2888.9(12)	4441(3)	3107(2)
Z	4	4	4	4	2
μ(Mo-Kα)/mm^{-1}	1.031	1.088	1.099	0.899	0.674
Reflections collected	11453	7863	6969	10808	19369
Independent reflections	11008 ($R_{int} = 0.058$)	5102 ($R_{int} = 0.051$)	6629 ($R_{int} = 0.029$)	7844 ($R_{int} = 0.057$)	10516 ($R_{int} = 0.123$)
Final $R1$, wR_2 $I > 2\sigma(I)$	0.0531, 0.1095	0.0701, 0.1743	0.0387, 0.0932	0.0569, 0.1085	0.1044, 0.2871
all data	0.1353, 0.1596	0.1059, 0.2035	0.0543, 0.1019	0.1412, 0.1449	0.1962, 0.3402

Data in common: graphite-monochromated Mo-Kα radiation, $\lambda = 0.71073$ Å, 180(2) K, refinement based on F^2.

(Found: C, 57.8; H, 4.2. $C_{45}H_{37}CoMoO_6P_2\cdot CH_2Cl_2$ requires C, 60.2; H, 4.6%). FAB mass spectrum: m/z 890 (M^+) and $M^+ - n$CO ($n = 1$ or 2). NMR ($CDCl_3$): ^{13}C (^1H composite pulse decoupled), δ 209.7 [s, Mo–CO], 201.4 [s, Co–CO], 185.3 [s, *C*O$_2$Me], 182.5 [s, *C*O$_2$Me], 166.4 [d, ^2J(PC) 22, μ-C(CO$_2$-Me)=*C*(CPh=CHPPh$_2$)C(OMe)O], 139–126 [m, Ph and μ-C(CO$_2$Me)=*C*(CPh=*C*HPPh$_2$)C(OMe)O], 92.5 [s, C_5H_5], 53.6 [s, CO$_2$*Me*] and 49.6 [CO$_2$*Me*].

(f) Reaction of [(η^5-C$_5$H$_5$)(OC)Mo{μ-CBu^{t}CHCPhC(PPh$_2$)}-Co(CO)$_2$] 2b with Ph$_2$PH

To a solution of [(η^5-C$_5$H$_5$)(OC)Mo{μ-CBu^{t}CHCPhC(PPh$_2$)}-Co(CO)$_2$] **2b** (0.30 g, 0.44 mmol) in toluene (50 cm^3) was added diphenylphosphine (0.20 cm^3, 1.15 mmol). The solution was stirred at 383 K for 24 h. After removal of the volatiles under reduced pressure, the mixture was purified by preparative TLC using hexane–ethyl acetate (3 : 1) as eluent. This gave, in addition to a small amount of unchanged starting material, the reddish crystalline complex [(η^5-C$_5$H$_5$)(OC)Mo{μ-CCPhCH-(CH$_2$Bu^t)PPh$_2$}(μ-PPh$_2$)$_2$Co(CO)] **5** (0.18 g, 38%). FAB mass spectrum: m/z 1016 (M^+) and $M^+ - n$CO ($n = 1$ or 2). NMR ($CDCl_3$): ^{13}C (^1H composite pulse decoupled), δ 136–125 [m, Ph], 91.6 [s, μ-C=*C*PhCH(CH$_2$Bu^t)PPh$_2$], 88.2 [s, C_5H_5], 64.5 [s, μ-C=CPh*C*H(CH$_2$Bu^t)PPh$_2$], 42.7 [s, *C*Me$_3$], 30.0 [d, ^2J(PC) 28 Hz, μ-C=CPhCH(*C*H$_2$Bu^t)PPh$_2$] and 29.7 [s, C*Me*$_3$].

(g) Crystal structure determinations of complexes 2a, 2b, 3, 4 and 5

X-Ray intensity data were collected with Rigaku AFC5R (complexes **2a** and **4**) and AFC7R diffractometers (**2b** and **3**) and a Rigaku RAXIS-IIC image plate (**5**). Details of data collection, refinement and crystal data are listed in Table 6. All data were corrected for Lorentz-polarisation factors. Semi-empirical absorption corrections based on φ scans[29] were applied to the data for **2a**, **2b**, **3** and **4**; no absorption correction was applied to the data for **5**.

For all the complexes the positions of the metal atoms and most non-hydrogen atoms were located from direct methods, and the remaining non-hydrogen atoms revealed from subsequent Fourier difference syntheses. Refinement was based on F^2.[30] Hydrogen atoms were placed in idealised positions and refined using a riding model or as rigid methyl groups.

In complex **5** two molecules of poorly resolved hexane solvate were observed in the asymmetric unit and one was modelled as disordered over two sites; extensive common distance constraints had to be applied to both molecules during the refinement process in order to preserve sensible geometry.

CCDC reference number 186/2147.

See http://www.rsc.org/suppdata/dt/b0/b004594m/ for crystallographic files in .cif format.

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References

1 R. S. Dickson and P. J. Fraser, *Adv. Organomet. Chem.*, 1974, **12**, 323; R. S. Dickson and G. R. Tailby, *Aust. J. Chem.*, 1971, **23**, 229; U. Krüerke and W. Hübel, *Chem. Ber.*, 1961, **94**, 2829; E. M. Arnett, *J. Am. Chem. Soc.*, 1964, **86**, 4729.

2 S. Slater and E. L. Muetterties, *Inorg. Chem.*, 1980, **19**, 3337; S. A. R. Knox, R. F. D. Stansfield, F. G. A. Stone, M. J. Winter and P. Woodward, *J. Chem. Soc.*, *Dalton Trans.*, 1982, 173; A. M. Boileau, A. G. Orpen, R. F. D. Stansfield and P. Woodward, *J. Chem. Soc.*, *Dalton Trans.*, 1982, 187; R. J. Baxter, G. R. Knox, P. L. Pauson and M. D. Spicer, *Organometallics*, 1999, **18**, 197.

3 M. J. Winter, in *The Chemistry of the Metal–Carbon Bond*, eds. R. R. Hartley and S. Patai, John Wiley & Sons, Chichester, 1985, vol. 3, pp. 259–294; M. J. Winter, *Adv. Organomet. Chem.*, 1989, **29**, 101.

4 Q. Feng, M. L. H. Green and P. Mountford, *J. Chem. Soc.*, *Dalton Trans.*, 1992, 217.

5 (*a*) R. Yanez, N. Lugan and R. Mathieu, *Organometallics*, 1990, **9**, 2998; (*b*) F.-E. Hong, I.-R. Lue, S. C. Lo and C. C. Lin, *J. Organomet. Chem.*, 1995, **495**, 97; (*c*) W. Hirpo, M. D. Curtis and J. W. Kampf, *Organometallics*, 1994, **13**, 3360.

6 J. E. Davies, M. J. Mays, P. R. Raithby, K. Sarveswaran and G. P. Shields, *J. Organomet. Chem.*, 1999, **573**, 180.

7 A. J. Carty, *Pure Appl. Chem.*, 1982, **54**, 113; A. A. Cherkas, L. H. Randall, S. A. MacLaughlin, G. N. Mott, N. J. Taylor and A. J. Carty, *Organometallics*, 1988, **7**, 969; A. J. Carty, D. Nucciarone, S. A. MacLaughlin and N. J. Taylor, *Organometallics*, 1988, **7**, 106.

8 M. H. A. Benvenutti, M. D. Vargas, D. Braga, F. Grepioni, E. Parisini and B. E. Mann, *Organometallics*, 1993, **12**, 2955; M. H. A. Benvenutti, M. D. Vargas, D. Braga, F. Grepioni, B. E. Mann and S. Naylor, *Organometallics*, 1993, **12**, 2947; M. D. Vargas, R. M. S. Periera, D. Braga and F. Grepioni, *J. Chem. Soc.*, *Chem. Commun.*, 1993, 1008.

9 B. J. Bobbie, N. J. Taylor and A. J. Carty, *J. Chem. Soc.*, *Chem. Commun.*, 1991, 1511; E. Sappa, A. Pasquinelli, A. Tiripicchio and M. Tiripicchio Camellini, *J. Chem. Soc.*, *Dalton Trans.*, 1989, 601.

10 J. C. Jeffery, R. M. S. Pereira, M. D. Vargas and M. J. Went, *J. Chem. Soc.*, *Dalton Trans.*, 1995, 1805.

11 R. S. Dickson, T. de Simone, R. J. Parker and G. D. Fallon, *Organometallics*, 1997, **16**, 1531.

12 Single metal–metal bond distances for organo-bridged Co–Mo bimetallic complexes range from 2.68 to 2.90 Å. See refs. 5 and 6

and (*a*) G. Barrado, J. Li, D. Miguel, J. A. Perez-Martinez, V. Riera, C. Bois and Y. Jeannin, *Organometallics*, 1994, **13**, 2330; (*b*) A. Martin, M. J. Mays, P. R. Raithby and G. A. Solan, *J. Chem. Soc.*, *Dalton Trans.*, 1993, 1431; (*c*) S. L. Ingham, M. J. Mays, P. R. Raithby, G. A. Solan, B. V. Sundavadra, G. Conole and M. Kessler, *J. Chem. Soc.*, *Dalton Trans.*, 1994, 3607; (*d*) S. D. Jensen, B. H. Robinson and J. Simpson, *Organometallics*, 1986, **5**, 1690; (*e*) L. C. Song, J.-Y. Shen, Q.-M. Hu, B.-S. Han, R.-J. Wang and H.-G. Wang, *Inorg. Chim. Acta*, 1994, **219**, 93; (*f*) J.-C. Tsai, R. A. Wheeler, M. A. Khan and K. M. Nicholas, *Organometallics*, 1991, **10**, 1344; (*g*) M. Gruselle, H. El Hafa, M. Nikolski, G. Jaouen, J. Vaissermann, L.-J. Li and M. J. McGlinchey, *Organometallics*, 1993, **12**, 4917; (*h*) J. D. King, M. J. Mays, G. E. Pateman, P. R. Raithby, M. A. Rennie, G. A. Solan, N. Choi, G. Conole and M. McPartlin, *J. Chem. Soc.*, *Dalton Trans.*, 1999, 4447.

13 N. J. Grist, G. Hogarth, S. A. R. Knox, B. R. Lloyd, D. A. V. Morton and A. G. Orpen, *J. Chem. Soc.*, *Chem. Commun.*, 1988, 673.

14 L. Manojlovic-Muir, M. J. Mays, K. W. Muir and K. W. Woulfe, *J. Chem. Soc.*, *Dalton Trans.*, 1992, 1531; D. Braga, A. J. M. Caffyn, M. C. Jennings, M. J. Mays, L. Manojlovic-Muir, P. R. Raithby, P. Sabatino and K. W. Woulfe, *J. Chem. Soc.*, *Chem. Commun.*, 1989, 1401.

15 M–P–C angles range from 56.3 to 68.7°, see for example ref. 13 and G. M. Dawkins, M. Green, J. C. Jeffery and F. G. A. Stone, *J. Chem. Soc.*, *Chem. Commun.*, 1980, 1120; G. M. Dawkins, M. Green, J. C. Jeffery, C. Sambale and F. G. A. Stone, *J. Chem. Soc.*, *Dalton Trans.*, 1983, 499; J. A. Clucas, M. M. Harding, B. S. Nicholls and A. K. Smith, *J. Chem. Soc.*, *Dalton Trans.*, 1985, 1835; F. A. Cotton, J. A. M. Canick, R. L. Luck and K. Vidyasagar, *Organometallics*, 1991, **10**, 352; K.-B. Shiu, S.-W. Jean, H.-J. Wang, S.-L. Wang, F.-L. Liao, J.-C. Wang and L.-S. Liou, *Organometallics*, 1997, **16**, 114; A. D. Horton, M. J. Mays and P. R. Raithby, *J. Chem. Soc.*, *Chem. Commun.*, 1985, 247.

16 J. L. Davidson, *J. Chem. Soc.*, *Dalton Trans.*, 1983, 1667.

17 D. W. J. Cruickshank, *J. Chem. Soc.*, 1961, 5486.

18 D. E. C. Corbridge, *Phosphorus: An Outline of its Chemistry, Biochemistry, and Technology*, 3rd edn., Elsevier, Amsterdam, 1985, ch. 1.

19 R. J. Butcher, B. R. Penfold and E. Sinn, *J. Chem. Soc.*, *Dalton Trans.*, 1979, 668; D. M. Baird, P. E. Fanwick and T. Barwick, *Inorg. Chem.*, 1985, **24**, 3753; F. A. Cotton and R. Poli, *Inorg. Chem.*, 1986, **25**, 3624; F. A. Cotton, M. Kohli, R. L. Luck and J. V. Silverson, *Inorg. Chem.*, 1993, **32**, 1868; C. D. Garner, N. C. Howlader, F. E. Mabbs, A. T. McPhail and K. D. Onan, *J. Chem. Soc.*, *Dalton Trans.*, 1978, 1848; C. Limberg, M. Büchner, K. Heinz and O. Walter, *Inorg. Chem.*, 1997, **36**, 872; J. Chatt, R. Choukroun, J. Dilworth, J. Hyde, P. Vella and J. Zubieta, *Transition Met. Chem.*, 1979, **4**, 59.

20 T. Tanase, T. Igoshi and Y. Yamamoto, *Inorg. Chim. Acta*, 1997, **256**, 61; P. K. Baker, M. G. B. Drew and M. M. Meehan, *J. Chem. Soc.*, *Dalton Trans.*, 1999, 765; M. A. Bakar, A. Hill, D. L. Hughes and G. J. Leigh, *J. Chem. Soc.*, *Dalton Trans.*, 1989, 1417; P. M. Boorman, H. -B. Kraatz and M. Parvez, *Polyhedron*, 1993, **12**, 601; A. Herbowski, T. Lis and E. A. Deutsch, *J. Organomet. Chem.*, 1993, **460**, 25; P. Dahlke, J. C. Jeffery, M. D. Mortimer and F. G. A. Stone, *Polyhedron*, 1992, **11**, 1587.

21 M. G. Newton, N. S. Pantaleo, R. B. King and S. P. Diefenbach, *J. Chem. Soc.*, *Chem. Commun.*, 1979, 55.

22 N. Burford, B. W. Royan, R. E. V. H. Spence, T. S. Cameron, A. Linden and R. D. Rogers, *J. Chem. Soc.*, *Dalton Trans.*, 1990, 1521.

23 S. L. Brock and J. M. Mayer, *Inorg. Chem.*, 1991, **30**, 2138.

24 For related M–C=C–C=O rings see D. Mantlo, J. Suades, F. Dahan and R. Mathieu, *Organometallics*, 1990, **9**, 2933; G. R. Doel, N. D. Feasey, S. A. R. Knox, A. G. Orpen and J. Webster, *J. Chem. Soc.*, *Chem. Commun.*, 1986, 542; A. J. P. Domingos, B. F. G. Johnson, J. Lewis and G. M. Sheldrick, *J. Chem. Soc.*, *Chem. Commun.*, 1973, 912; F. J. Garcia Alonso, V. Riera, M. A. Ruiz, A. Tiripicchio and M. Tiripicchio Camellini, *Organometallics*, 1992, **11**, 370; A. J. M. Caffyn, M. J. Mays, G. Conole, M. McPartlin and H. R. Powell, *J. Organomet. Chem.*, 1992, **436**, 83; I. Moldes, J. Ros, R. Mathieu, X. Solans and M. Font-Bardia, *J. Organomet. Chem.*, 1992, **423**, 65.

25 M. I. Bruce, *Chem. Rev.*, 1991, **91**, 197.

26 J. D. King, M. J. Mays, C. -Y. Mo, P. R. Raithby, M. A. Rennie, G. A. Solan, T. Adatia and G. Conole, *J. Organomet. Chem.*, 2000, **601**, 271.

27 W. L. F. Armarego and D. D. Perrin, *Purification of Laboratory Chemicals*, Butterworth Heinemann, Oxford, 4th edn., 1996.

28 A. J. Carty, N. K. Hota, T. N. Ng, H. A. Patel and T. J. O'Connor, *Can. J. Chem.*, 1971, **49**, 2706.

29 A. C. T. North, D. C. Phillips and F. S. Matthews, *Acta Crystallogr.*, *Sect. A*, 1968, **24**, 351.

30 G. M. Sheldrick, SHELXL 93, University of Göttingen, 1993.