Phosphorus–Carbon Bond Formation in Dimolybdenum Alkyne Complexes induced by Oxidative Addition of Chlorodiphenylphosphine

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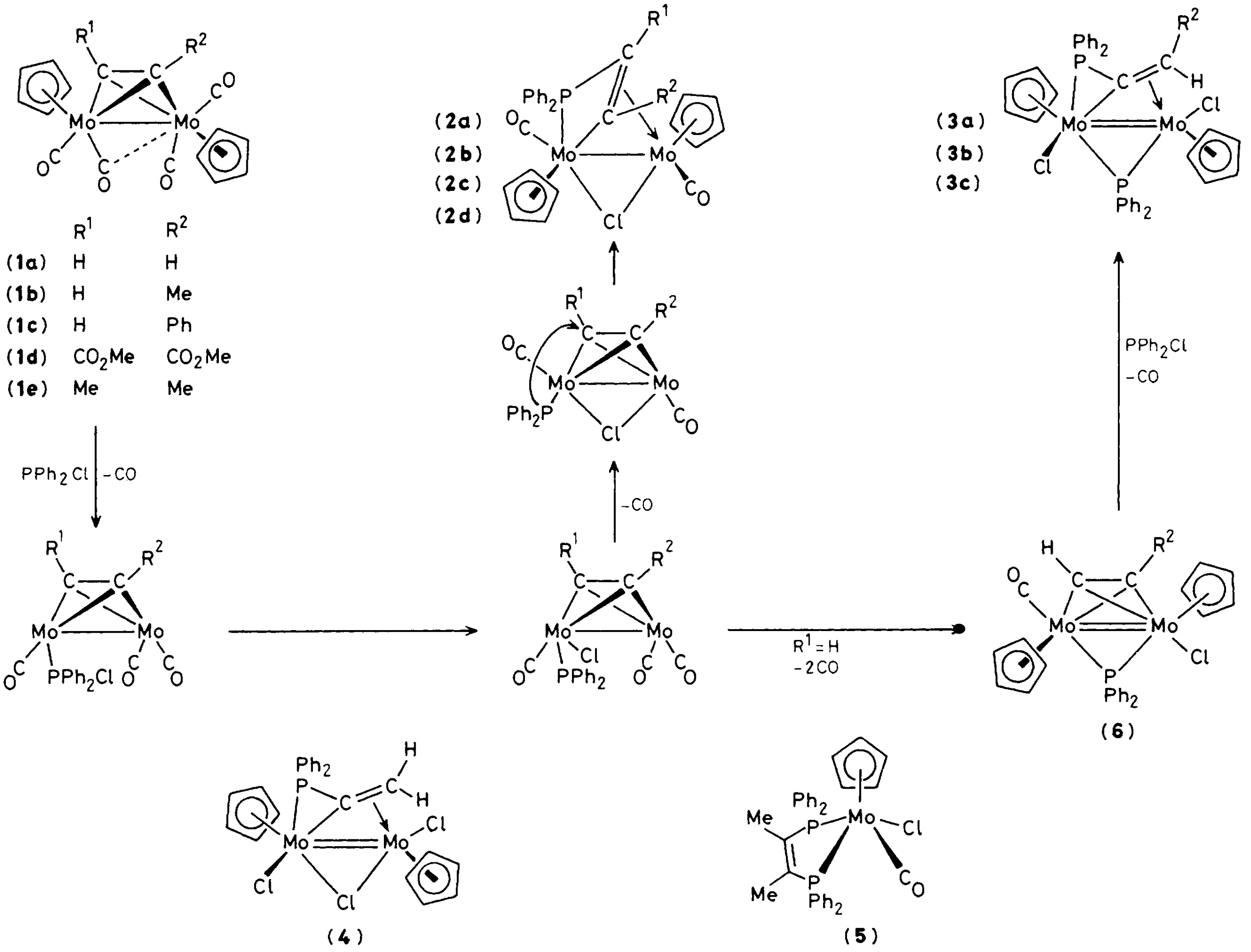
The reaction of $[Mo_2(CO)_4(\mu\text{-}R^1C_2R^2)(\eta\text{-}C_5H_5)_2]$ (R^1,R^2 = H, alkyl, or aryl) with PPh_2Cl proceeds *via* P–Cl bond cleavage and coupling of the diphenylphosphido group with the alkyne in one of three different ways depending on the nature of R^1 and R^2; two of the resulting complexes, $[Mo_2(\mu\text{-}Cl)\{\mu\text{-}Ph_2PC(H){=}CH\}(CO)_2(\eta\text{-}C_5H_5)_2]$ and $[Mo_2Cl_2(\mu\text{-}PPh_2)(\mu\text{-}Ph_2PC{=}CHMe)(\eta\text{-}C_5H_5)_2]$ have been characterised by *X*-ray analysis.

The cleavage of phosphorus–hydrogen, phosphorus–phosphorus, and phosphorus–carbon bonds at dimetallic centres are well known reactions which lead to a wide variety of dinuclear transition metal complexes.[1—3] In contrast, the cleavage of phosphorus–halogen bonds remains relatively unexplored[4] and has not been previously reported for dimetallic complexes containing bridging organic ligands. In this communication we report the reaction of chlorodiphenylphosphine with the dimolybdenum alkyne complexes $[Mo_2(CO)_4(\mu\text{-}R^1C_2R^2)(\eta\text{-}C_5H_5)_2]$ (**1a**—**e**). These reactions, which involve novel examples of phosphorus–carbon bond formation and unprecedented transformations of the alkyne ligands, suggest that a more general study of oxidative addition reactions of this type is warranted.

Treatment of $[Mo_2(CO)_4(\mu\text{-}R^1C_2R^2)(\eta\text{-}C_5H_5)_2]$ (R^1 = H, R^2 = H, Me, Ph) (**1a**—**c**)[5] with PPh_2Cl (1—2 equiv., refluxing toluene, 17 h) affords the chromatographically separable complexes $[Mo_2(\mu\text{-}Cl)(\mu\text{-}Ph_2PCR^1CR^2)(CO)_2(\eta\text{-}C_5H_5)_2]$ (**2a**—**c**) and $[Mo_2Cl_2(\mu\text{-}PPh_2)(\mu\text{-}Ph_2PC{=}CR^1R^2)(\eta\text{-}C_5H_5)_2]$ (**3a**—**c**) in low to moderate yields (see Scheme 1). In the reaction with (**1a**) a species related to (**3a**), $[Mo_2Cl_2(\mu\text{-}Cl)(\mu\text{-}Ph_2PC{=}CH_2)(\eta\text{-}C_5H_5)_2]$ (**4**), is also obtained and is the major product. Similar reactions of the disubstituted alkyne complexes (**1d**) ($R^1 = R^2 = CO_2Me$) and (**1e**) ($R^1 = R^2$ = Me) with



Scheme 1. Structural formulae for the new complexes with some possible reaction pathways. For (**6**), only (**6c**) was isolated.

PPh_2Cl lead to (**2d**) and (**5**) respectively as the only isolable compounds. All new complexes were characterised by analysis and standard spectroscopic methods.†

The occurrence of phosphido–alkyne coupling in orange, crystalline, slightly air-sensitive (**2a**) was clearly shown by its n.m.r. spectra, and subsequently confirmed by an *X*-ray diffraction study, the results of which are summarised in Figure 1 and its caption.‡ The Mo–Mo single bond [2.871(1) Å] is bridged by a chloride ligand and by a μ-vinyl ligand which is σ-bonded to Mo(1) [Mo(1)–C(2) 2.207(9) Å] and asymmetrically π-bound to Mo(2) [Mo(2)–C(1) 2.212(8), Mo(2)–C(2) 2.074(8) Å]. One of the β-substituents of this vinyl ligand is the diphenylphosphido group which is itself co-ordinated to Mo(1) [Mo(1)–P(1) 2.467(2) Å], thus forming a four-membered MoCCP ring. Similar ligands have previously been formed by the insertion of alkynes into phosphido-bridged complexes,[6] but this is the first example resulting from the insertion of a phosphido group into a μ-alkyne complex. The n.m.r. spectra of (**2b**) and (**2c**) reveal the presence of a single isomer of each, in which the phosphido group is joined to the CH terminus of the unsymmetrical alkyne, *i.e.* the coupling process is regiospecific.

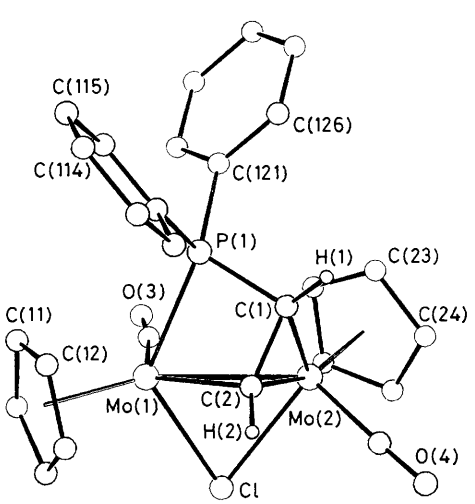


Figure 1. The structure of $[Mo_2(\mu\text{-}Cl)(\mu\text{-}Ph_2PC(H)C(H))(CO)_2(\eta^5\text{-}C_5H_5)_2]$ (**2a**). Principal bond lengths (Å) and angles (°) are: Mo(1)–Mo(2) 2.871(1), Mo(1)–P(1) 2.467(2), Mo(1)–Cl 2.496(2), Mo(1)–C(2) 2.207(9), Mo(1)–C(3) 1.919(10), Mo(2)–Cl 2.480(2), Mo(2)–C(1) 2.212(8), Mo(2)–C(2) 2.074(8), Mo(2)–C(4) 1.951(11), P(1)–C(1) 1.782(10), P(1)–C(111) 1.833(5), P(1)–C(121) 1.813(6), C(1)–C(2) 1.463(10), C(3)–O(3) 1.188(13), C(4)–O(4) 1.145(14); range Mo(1)–C(Cp) 2.303(21)—2.373(20), range Mo(2)–C(Cp) 2.273(10)–2.390(13). C(111)–P(1)–Mo(1) 118.1(2), C(111)–P(1)–C(1) 108.3(4), C(121)–P(1)–Mo(1) 127.9(2), C(121)–P(1)–C(1) 114.0(3), C(121)–P(1)–C(111) 100.4(3), P(1)–C(1)–Mo(2) 104.6(4), C(2)–C(1)–Mo(2) 65.0(4), C(2)–C(1)–P(1) 97.8(6), Mo(2)–C(2)–Mo(1) 84.2(3), C(1)–C(2)–Mo(1) 106.0(6), C(1)–C(2)–Mo(2) 75.2(5) (Cp = cyclopentadienyl).

The disubstituted alkyne complex (**1d**) similarly affords (**2d**), but in contrast the but-2-yne complex (**1e**) yields only traces of the analogous product (**2e**); instead the main product is the mononuclear complex $[MoCl(CO)\{cis\text{-}Ph_2PC(Me){=}C(Me)PPh_2\}(\eta\text{-}C_5H_5)]$ (**5**), in which incorporation of *two* phosphido groups[7] has occurred to give the chelating ligand *cis*-2,3-bis(diphenylphosphino)but-2-ene.[8] Although at present we have no direct evidence that (**5**) is formed *via* the species (**2e**), this seems plausible despite the fact that the complexes (**2a—d**) appear inert to further reaction with PPh_2Cl.

The ^1H and ^{13}C n.m.r. spectra of (**3a—c**), isolated as air-stable, purple, crystalline solids, likewise indicated phosphido–alkyne linkage and also that a 1,2-hydrogen shift had occurred on the alkyne, *e.g.* the observation of a doublet of quartets (1H) and a doublet (3H) for the CHMe group in (**3b**). Figure 2 depicts the structure of one of the two independent molecules in the unit cell of (**3b**)‡ as determined by *X*-ray diffraction. The two molybdenum atoms, now both formally Mo^{III}, are each ligated by a C_5H_5 ring and a terminal chloride, and are linked by a formal double bond [mean Mo(1)–Mo(2) 2.792(1) Å]. This bond is spanned by a diphenylphosphido bridge and an α-phosphino vinyl ligand which is a 5 electron donor. There has been a shift of the H-atom from C(1) to C(2), and C(1) is now bonded to a second PPh_2 group; this links to Mo(1) thus forming a three-membered MoCP ring. The rather short P(2)–C(1) bond length [1.724(12) Å] is consistent with an alternative view of this ligand as a phospha-allene.[9] This unusual co-ordination mode is reflected in the high-field ^{31}P n.m.r. shift of P(2) [a doublet at −243.3 p.p.m. relative to $P(OMe)_3$ = 0.0 p.p.m.]. A similar signal, a singlet, comprises the ^{31}P n.m.r. spectrum of (**4**), and elemental analysis indicates that this complex is directly

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† *Selected spectroscopic data* [i.r. in CH_2Cl_2, n.m.r. in $CDCl_3$ unless otherwise stated, coupling constants in Hz; ^{31}P n.m.r. shifts are relative to $P(OMe)_3$ = 0.0 p.p.m.]:

(**2a**) ν(CO) 1865 cm^{-1}; ^1H n.m.r. δ 6.47 (dd, J_{HH} 4.7, J_{HP} 10.1), 3.85 (dd, J_{HH} 4.7, J_{HP} 10.5); ^{13}C n.m.r. 110.7 (d, J_{CP} 28, μ-CH), 30.6 (d, J_{CP} 42, CH); ^{31}P n.m.r. −130.3 p.p.m.

(**2b**) ν(CO) 1864 cm^{-1}; ^1H n.m.r. δ 3.57 (d, J_{HP} 6.8, CH), 2.86 (d, J_{HP} 3.5, CMe); ^{31}P n.m.r. −132.7 p.p.m.

(**2c**) ν(CO) 1875 cm^{-1}; ^1H n.m.r. δ 4.16 (d, J_{HP} 6.8, CH); ^{13}C n.m.r. 122.8 (d, J_{CP} 20, CPh), 29.3 (d, J_{CP} 40, CH); ^{31}P n.m.r. −130.1 p.p.m.

(**3a**) ^1H n.m.r. δ 4.80 (td, $J_{H\mu\text{-}P}$ 0.9, $J_{HH} = J_{HP}$ = 3.8, 1H of CH_2), 2.27 (ddd, $J_{H\mu\text{-}P}$ 0.7, J_{HP} 8.5, J_{HH} 3.8, 1H of CH_2); ^{31}P n.m.r. 38.9 (d, J_{PP} 47, μ-P), −247.2 (d, J_{PP} 47) p.p.m.

(**3b**) ^1H n.m.r. δ 3.05 (dq, J_{HH} 6.4, J_{HP} 10.6, CH), 2.63 (d, J_{HH} 6.4, Me); ^{13}C n.m.r. 154.5 (d, J_{CP} 16, μ-C), 73.3 (d, J_{CP} 13, *C*HMe); ^{31}P n.m.r. 42.5 (d, J_{PP} 58, μ-P), −243.3 (d, J_{PP} 58) p.p.m.

(**3c**) ^1H n.m.r. δ 3.44 (d, J_{HP} 10.3, C*H*Ph); ^{13}C n.m.r. (CD_2Cl_2) 134.2 (d, J_{CP} 48, μ-C) 72.0 (d, J_{CP} 13, *C*HPh); ^{31}P n.m.r. 39.7 (d, J_{PP} 54, μ-P), −227.3 (d, J_{PP} 54) p.p.m.

(**4**) ^1H n.m.r. δ 3.60 (dd, J_{HP} 1.6, J_{HH} 5.0, 1H of CH_2), 2.21 (dd, J_{HH} 5.0, J_{HP} 6.8, 1H of CH_2); ^{13}C n.m.r. (CD_2Cl_2) 149.2 (s, μ-C), 40.4 (d, J_{CP} 12, CH_2); ^{31}P n.m.r. −249.1 p.p.m.

(**5**) ν(CO) 1866 cm^{-1}; ^1H n.m.r. δ 2.05 (dd, J_{HP} 5.9 and 1.1, Me), 1.79 (dd, J_{HP} 7.1 and 0.6, Me); ^{13}C n.m.r. 152.7 (t, J_{CP} 37, *C*Me), 152.5 (t, J_{CP} 40, *C*Me); ^{31}P n.m.r. −31.5 (d, J_{PP} 34), −44.9 (d, J_{PP} 34) p.p.m.

(**6c**) ν(CO) 1970 cm^{-1}; ^1H n.m.r. δ 9.13 (s, μ-CH); ^{13}C n.m.r. 121.5 (s, *C*Ph) 111.7 (s, μ-CH); ^{31}P n.m.r. 12.2 p.p.m.

Satisfactory elemental analyses were obtained for all new compounds, and in most cases molecular ions were observed in their fast-atom bombardment mass spectra.

‡ *Crystal data* for (**2a**): $C_{26}H_{22}ClMo_2O_2P$, *M* = 624.68, monoclinic, space group $P2_1/n$, *a* = 17.735(3), *b* = 10.023(2), *c* = 14.790(3) Å, β = 112.54(2)°, *U* = 2428.25 $Å^3$, *F*(000) = 1240, μ(Mo-K_α) = 11.08 cm^{-1}, *Z* = 4, D_c = 1.71 g cm^{-3}, *R* = 0.0424, for 2420 reflections with $I/\sigma(I) >$ 3.0.

Crystal data for (**3b**): $C_{37}H_{34}Cl_2Mo_2P_2$, *M* = 803.33, triclinic, space group $P\bar{1}$ (No. 2), *a* = 21.263(4),, *b* = 17.675(3), *c* = 9.970(2) Å, α = 81.02(2), β = 106.22(2), γ = 111.32(2)°, *U* = 3345.36 $Å^3$, *F*(000) = 1616, μ(Mo-K_α) = 9.28 cm^{-1}, *Z* = 4, D_c = 1.60 g cm^{-3}; *R* = 0.0578 for 6192 reflections with $I/\sigma(I) >$ 3.0.

Data were collected on a Philips PW1100 diffractometer in the θ range 3—25°. Lorentz-polarisation and absorption corrections were applied. One of the cyclopentadienyl ligands of (**2a**) is disordered, and this disorder was successfully modelled. Anisotropic thermal parameters were assigned to the non-hydrogen atoms of (**2a**), except for the carbon atoms of the phenyl rings, and to Mo, P, Cl, C(1), C(2), and C(02) of (**3b**). Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

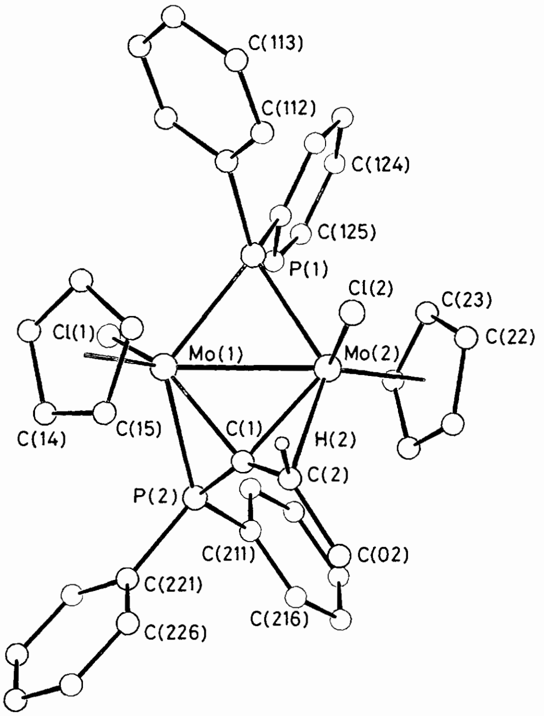

Figure 2. The structure of one of the two virtually identical independent molecules of $[Mo_2Cl_2(\mu\text{-}PPh_2)(\mu\text{-}Ph_2PC{=}CHMe)(\eta^5\text{-}C_5H_5)_2]$ (**3b**). Mean principal bond lengths (Å) and angles (°) are: Mo(1)–Mo(2) 2.792(1), Mo(1)–P(1) 2.428(3), Mo(1)–P(2) 2.441(3), Mo(1)–Cl(1) 2.450(5), Mo(1)–C(1) 2.140(10), Mo(2)–P(1) 2.385(3), Mo(2)–Cl(2) 2.472(4), Mo(2)–C(1) 2.124(9), Mo(2)–C(2) 2.304(10), P(1)–C(111) 1.836(7), P(1)–C(121) 1.853(9), P(2)–C(1) 1.724(12), P(2)–C(211) 1.814(10), P(2)–C(221) 1.816(6), C(1)–C(2) 1.409(18), C(2)–C(02) 1.502(15); range Mo(1)–C(Cp) 2.293(15)—2.410(14), range Mo(2)—C(Cp)$_2$ 281(14)—2.408(14). C(1)–P(2)–Mo(1) 58.8(3), C(211)–P(2)–Mo(1) 132.1(3), C(211)–P(2)–C(1) 120.0(5), C(221)–P(2)–Mo(1) 120.0(3), C(221)–P(2)–C(1) 113.1(5), C(221)–P[2)–C(211) 104.4(4), Mo(2)–C(1)–Mo(1) 81.8(3), P(2)–C(1)–Mo(1) 77.6(5), P(2)–C(1)–Mo(2) 125.0(6), C(2)–C(1)–Mo(1) 132.1(8), C(2)–C(1)–Mo(2) 78.6(6), C(2)–C(1)–P(2) 147.5(7), C(1)–C(2)–Mo(2) 64.6(5), C(02)–C(2)–Mo(2) 124.9(9), C(02)–C(2)–C(1) 121.9(9).

related to (**3a**) by the replacement of the μ-PPh$_2$ group by a third chloride ligand.

Some insight into the formation of (**3**) can be gained by treatment of (**1c**) with one equivalent of PPh$_2$Cl (refluxing toluene, 6 h, relatively dilute conditions) which allows the isolation of an intermediate complex (**6c**).† On heating with further PPh$_2$Cl, (**6c**) is rapidly converted into (**3c**). This process is evidently facile since only traces of an analogous complex can be isolated from (**1b**); even with one equivalent of PPh$_2$Cl, (**3b**) is the major product.

A plausible mechanism for the reaction is shown in Scheme 1. We propose that the key step is oxidative addition of PPh$_2$Cl followed by migration to a bridging position of *either* the chloride ligand [leading to (**2**)] *or* the phosphido group [leading to (**6**) and ultimately (**3**)].

No evidence for P–C bond formation was found in the reactions of (**1**) with PPh$_3$,[10] PPh$_2$H,[10] or P$_2$Ph$_4$.[11] Its occurrence in the products (**2**)—(**5**) attests to the markedly different reactivity obtained with PPh$_2$Cl.

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