Co-ordinated Phospholes from the coupling of Alkynes with Bridging Phosphido Ligands: the Crystal and Molecular Structures of $[Co_2\{\mu\text{-}\eta^2\text{:}\eta^{2'}\text{-}C_4(CO_2Me)_4PPh_2\}(\mu\text{-}PPh_2)(CO)_4]$, $[Mn_2(\eta^4\text{-}C_4H_4PPh_2)(\mu\text{-}PPh_2)(CO)_6]$, and $[Mn_2(\mu\text{-}\eta^5\text{-}C_4H_4PPh_2)(\mu\text{-}PPh_2)(CO)_5]$

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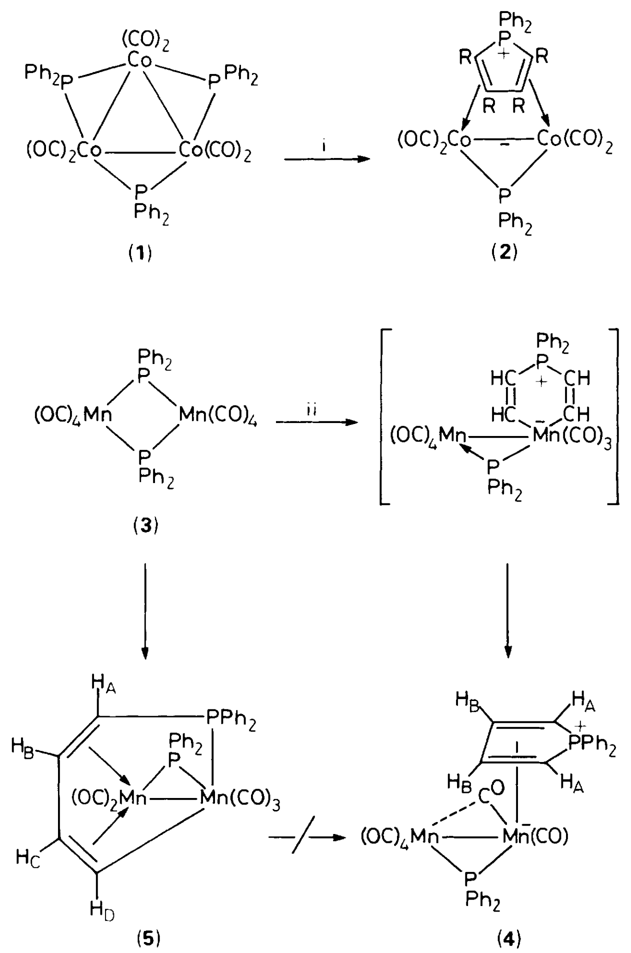
Reaction of μ-phosphido complexes with alkynes can lead to complexes with quaternised phosphole ligands; by this means a cobalt complex, $[Co_2\{\mu\text{-}\eta^2\text{:}\eta^{2'}\text{-}C_4(CO_2Me)_4PPh_2\}(\mu\text{-}PPh_2)(CO)_4]$, and a manganese complex, $[Mn_2(\eta^4\text{-}C_4H_4PPh_2)(\mu\text{-}PPh_2)(CO)_6]$, in which the phosphole adopts respectively a terminal and a bridging mode, have been prepared and characterised by *X*-ray analysis as has a related manganese complex, $[Mn_2(\mu\text{-}\eta^5\text{-}C_4H_4PPh_2)(\mu\text{-}PPh_2)(CO)_5]$.

Although bridging phosphido ligands can inhibit fragmentation in reactions of dinuclear and polynuclear metal complexes, they are by no means always inert.[1] Thus reaction of $\mu\text{-}PR_2$ complexes [R = alkyl or aryl] with alkynes can give rise to products containing new bridging ligands made up from the phosphido group, the alkyne and often CO as well if this is present in the original complex.[2—7] In all reported examples, however, only one of the metal–phosphorus bonds is cleaved and the new bridging ligand remains co-ordinated through phosphorus to one of the metal centres. We now show that reactions of this type can lead to cleavage of both metal–phosphorus bonds and to the formation of quaternised phosphole ligands which can be co-ordinated in either a terminal or a bridging mode.

Reaction of a toluene solution of $[Co_3(\mu\text{-}PPh_2)_3(CO)_6]$[8] (**1**) with an excess of dimethylacetylenedicarboxylate at 40 °C gave the red complex $[Co_2\{\mu\text{-}\eta^2\text{:}\eta^{2'}\text{-}C_4(CO_2Me)_4PPh_2\}(\mu\text{-}PPh_2)(CO)_4]$ (**2**)† (Scheme 1) in *ca.* 40% yield along with traces of an uncharacterised brown complex.



Scheme 1. *Reagents and conditions*: i, excess $C_2(CO_2Me)_2$ in toluene at 40 °C; ii, excess C_2H_2, $h\nu$ in CH_2Cl_2 at 18 °C.

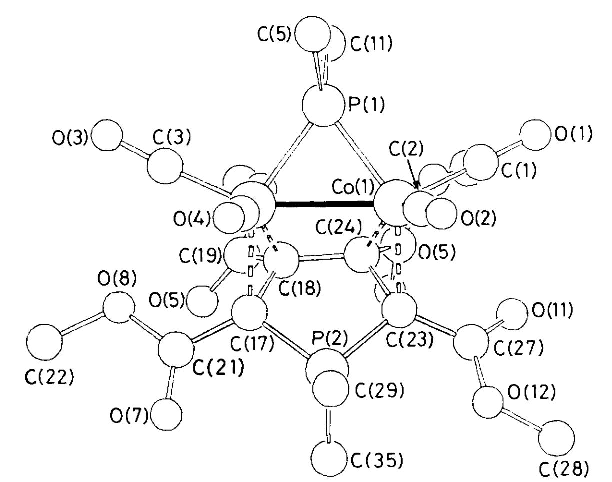


Figure 1. The molecular structure of $[Co_2\{\mu\text{-}\eta^2\text{:}\eta^{2'}\text{-}C_4(CO_2Me)_4PPh_2\}(\mu\text{-}PPh_2)(CO)_4]$ (**2**). Bond parameters: Co(1)–Co(2) 2.580(1), Co(1)–P(1) 2.178(2), Co(2)–P(1) 2.178(2), Co(2)–C(17) 2.03(1), Co(2)–C(18) 2.01(1), Co(1)–C(23) 2.03(1), Co(1)–C(24) 2.00(1), C(17)–C(18) 1.47(1), C(18)–C(24) 1.49(1), C(23)–C(24) 1.48(1), P(2)–C(17) 1.80(1), P(2)–C(23) 1.79(1) Å; C(17)–P(2)–C(23) 95.2(3), P(2)–C(23)–C(24) 108.0(4), C(23)–C(24)–C(18) 113.0(5), C(17)–C(18)–C(24) 113.2(5), P(2)–C(17)–C(18) 107.6(4)°.

† *Selected spectroscopic data*: [i.r. (ν_{CO} cm^{-1}) measured in CH_2Cl_2 solution; ^1H and ^{31}P n.m.r. in CD_2Cl_2 or $CDCl_3$ solution, ^{31}P shifts relative to $P(OMe)_3$ at 0 p.p.m. with upfield shifts negative; *J* in Hz]. (**2**), ν_{CO} 2038m, 2014s, 1991m, 1744m; ^1H n.m.r. δ 3.43 (s, 6H, CO_2Me), 3.37 (s, 6H, CO_2Me); ^{31}P n.m.r. δ 24.6 (br. s, $\mu\text{-}PPh_2$), −90.8 [s, $\mu\text{-}C_4(CO_2Me)_4PPh_2$]. (**4**), ν_{CO} 2047s, 1973sh, 1953br., 1933sh; ^1H n.m.r. δ 4.60 (dd, J_{PH} 18.6, 2.4, 2H, H_B), 2.00 (d, J_{PH} 19.1, 2H, H_A); ^{31}P n.m.r. δ 58.9 (s, $\mu\text{-}PPh_2$), −103.1 (s, $\eta^4\text{-}C_4PPh_2$). (**5**), ν_{CO} 2019m, 1956s, 1895m; ^1H n.m.r. δ 10.80 (dd, $^3J_{H_CH_D}$ 8.1, $^3J_{PH_D}$ 2.0, 1H, H_D), 8.02—6.76 (m, 22H, Ph, H_B, H_C), 3.07 (d, J_{PH} 9.2, 1H, H_A); ^{31}P n.m.r. δ 111.5 (s, $\mu\text{-}PPh_2$), −83.7 [s, $\mu\text{-}\eta^5\text{-}C_4H_4PPh_2$].

The *X*-ray structural determination of (**2**) (Figure 1)‡ shows that the two Co atoms are μ_2-η^2:$\eta^{2'}$-co-ordinated by a $C_4R_4PPh_2$ group (R = CO_2Me) in a similar manner to the *cis*-butadiene ligand in $[Cp_2Co_2(CO)(\mu$-η^2:$\eta^{2'}$-$C_4H_6)]$.[9] The C_4 unit in (**2**) adopts a planar configuration (max. C-atom deviation ± 0.03 Å) with the P atom 0.3 Å above the mean plane of the ring away from the metal atoms.

In a related experiment the photolytic reaction of $[Mn_2(\mu$-$PPh_2)_2(CO)_8]$[10] (**3**) with acetylene in CH_2Cl_2 solution gave $[Mn_2(\eta^4$-$C_4H_4PPh_2)(\mu$-$PPh_2)(CO)_6]$ (**4**)† (13%) and $[Mn_2(\mu$-η^5-$C_4H_4PPh_2)(\mu$-$PPh_2)(CO)_5]$ (**5**)† (2%) together with traces of several uncharacterised species. *X*-Ray structure analysis of (**4**) (Figure 2)‡ shows that the phosphole ligand is η^4-bonded to only one of the manganese atoms as in the mononuclear complex $[Mn\{\eta^4$-$C_4(CO_2Me)_4PMe_2\}$-$(CO)_3]$.[11] The phosphole C_4 unit is again planar (max. C-atom deviation ± 0.002 Å) with the P atom 0.066 Å above this plane, on the opposite side to the metal atoms.

X-Ray analysis of (**5**) (Figure 3)‡ shows that the two manganese atoms are bridged by a PPh_2 ligand and a $C_4H_4PPh_2$ ligand which is formally derived from a μ-PPh_2 group in (**3**) by a double insertion of acetylene into one of the metal phosphorus bonds.

Although ring closure in (**5**), involving carbon–phosphorus bond formation, could lead to (**4**) in the presence of CO we have been unable to effect this transformation either thermally or photolytically. Accordingly we suggest that a more likely route to (**4**) [and by analogy to (**2**)] is *via* insertion of one molecule of acetylene into each of the metal–phosphorus bonds of one of the μ-PPh_2 groups, with ring closure then resulting from carbon–carbon bond formation (Scheme 1). Similar processes are well established for μ-CO ligands[12,13] but have not been previously documented for μ-PR_2 ligands.

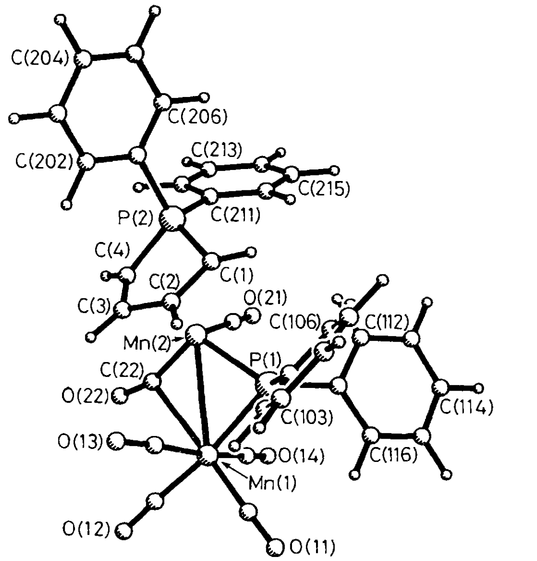


Figure 2. The molecular structure of $[Mn_2(\eta^4$-$C_4H_4PPh_2)(\mu$-$PPh_2)(CO)_5(\mu$-$CO)]$ (**4**). Bond parameters: Mn(1)–Mn(2) 2.839(1), Mn(1)–P(1) 2.270(1), Mn(2)–P(1) 2.247(1), Mn(2)–C(1) 2.165(4), Mn(2)–C(2) 2.085(4), Mn(2)–C(3) 2.078(5), Mn(2)–C(4) 2.160(5), C(1)–C(2) 1.435(7), C(1)–P(2) 1.750(5), C(2)–C(3) 1.408(7) C(3)–C(4) 1.436(7), C(4)–P(2) 1.747(5) Å; Mn(1)–P(1)–Mn(2) 77.9(1), Mn(1)–C(22)–Mn(2) 80.3(4), P(2)–C(1)–C(2) 107.6(3), C(3)–C(2)–C(1) 111.6(4), C(4)–C(3)–C(2) 111.3(4), P(2)–C(4)–C(3) 107.8(4), C(4)–P(2)–C(1) 89.3(2)°.

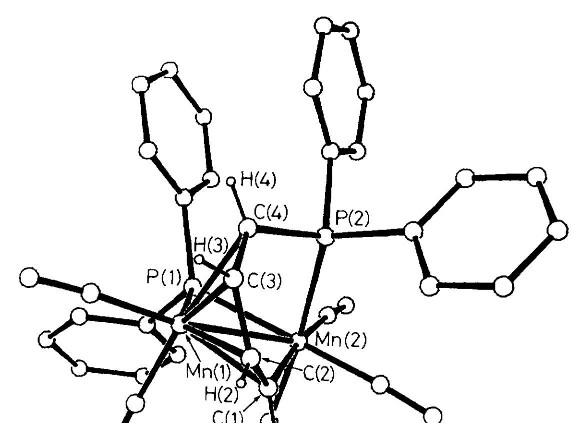


Figure 3. The molecular structure of $[Mn_2(\mu$-η^5-$C_4H_4PPh_2)(\mu$-$PPh_2)(CO)_5]$ (**5**). Bond parameters: Mn(1)–Mn(2) 2.706(2), Mn(1)–P(1) 2.175(3), Mn(2)–P(1) 2.379(3), Mn(1)–C(1) 1.992(8), Mn(1)–C(2) 2.116(10), Mn(1)–C(3) 2.140(8), Mn(1)–C(4) 2.237(8), Mn(2)–C(1) 2.107(8), C(1)–C(2) 1.380(13), C(2)–C(3) 1.398(13), C(3)–C(4) 1.401(11), C(4)–P(2) 1.795(8), P(2)–Mn(2) 2.304(2) Å; Mn(2)–Mn(1)–P(1) 57.1(1), Mn(1)–P(1)–Mn(2) 72.8(1), Mn(2)–Mn(1)–C(1) 50.6(3), Mn(1)–C(1)–Mn(2) 82.6(3), Mn(2)–C(1)–C(2) 134.4(7), Mn(1)–C(1)–C(2) 75.3(6), C(1)–C(2)–C(3) 122.2(9), C(2)–C(3)–C(4) 121.4(8), C(3)–C(4)–P(2) 122.7(6), C(4)–P(2)–Mn(2) 100.4(3)°.

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‡ *Crystal data*: (**2**) $C_{40}H_{32}Co_2O_{12}P_2$, M = 884.49, triclinic, space group $P\bar{1}$, a = 12.334(3), b = 14.879(8), c = 10.823(4) Å, α = 91.01(3), β = 93.68(4), γ = 100.30(2)°, U = 1949(3) Å^3, Z = 2, $F(000)$ = 904, $\mu(\text{Mo-}K_\alpha)$ = 9.30 cm^{-1}, θ-range 2.5—25°, 7233 reflections collected, final R value 0.051 (R_w = 0.053) for 3423 out of 5694 independent reflections $[I_0 > 2\sigma I_0]$ collected by the ω/2θ scan method. Absorption correction was applied by the Walker and Stuart method[15] (correction range 0.91—1.0). 50% positional disorder was detected for one of the methylcarboxylate groups. (**4**) $C_{34}H_{24}Mn_2O_6P_2$, M = 700.35, monoclinic, space group $C2/c$, a = 17.406(2), b = 15.744(1), c = 23.504(2) Å, β = 93.93(1)°, U = 6426(2) Å^3, Z = 8, $F(000)$ = 2736, D_c = 1.447 g cm^{-3}, $\mu(\text{Mo-}K_\alpha)$ = 8.58 cm^{-1}; R (R_w) = 0.041 (0.043) for 3070 unique absorption corrected reflections $[I > 2.5\sigma(I)]$ measured on a Stoe 4-circle diffractometer at 297 K (4576 measured reflections, $5 \leqslant 2\theta \leqslant 45°$, ω/θ scan mode, Mo-$K_\alpha$, λ = 0.71069 Å). The structure was solved by direct methods and refined by blocked full-matrix least-squares (phenyl rings treated as rigid groups with C–H = 1.08 Å), phosphole hydrogens directly located and refined with a common isotropic displacement parameter. (**5**) $C_{33}H_{24}Mn_2O_5P_2$, M = 672.4, monoclinic, space group $P2_1/c$, a = 10.560(1), b = 12.326(1), c = 23.026(3) Å, β = 97.91(1)°, U = 2968.5(6) Å^3, Z = 4, D_c = 1.504 g cm^{-3}, $F(000)$ = 1368, $\mu(\text{Mo-}K_\alpha)$ = 9.62 cm^{-1}, R (R_w) = 0.042 (0.048) for 2134 unique absorption-corrected intensities $[I \geqslant 3\sigma I]$ measured on a CAD4 diffractometer at 297 K (5882 measured reflections, $2 \leqslant \theta \leqslant 25°$, θ—2θ scan mode, Mo-$K_\alpha$, λ = 0.71069 Å). The structure was solved by heavy-atom method and refined by full-matrix least-squares (phenyl rings treated as rigid groups with C–C = 1.38 and C–H = 0.96 Å). The butadiene hydrogens were found in a difference map and their positional and isotropic thermal parameters were refined. 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.

Quaternised phospholes with two aryl substituents on phosphorus are not easy to synthesise by other routes,[11,14] and the synthetic utility of this reaction is under investigation.

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