Generation of a μ_3-Vinylidene Ligand *via* Step-wise Cleavage of 1,1-Bis(diphenylphosphino)ethylene at Di- and Tri-iron Centres

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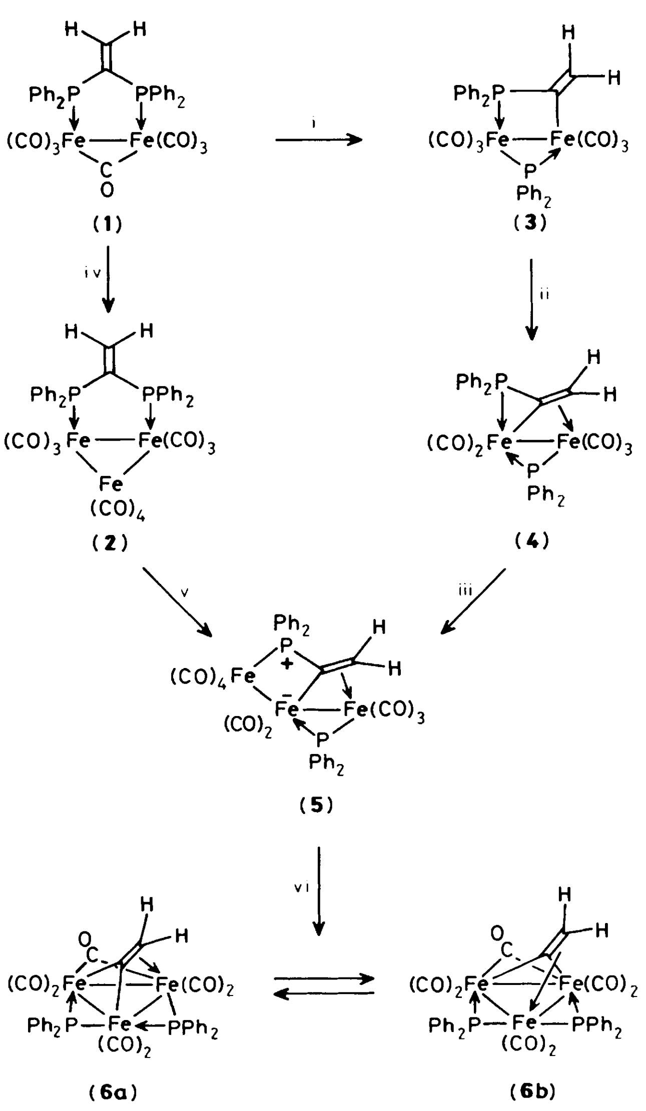
Through a sequence of thermally- and photochemically-induced steps the 1,1-bis(diphenylphosphino)ethylene ligand in $[Fe_2(CO)_7\{\mu\text{-}(Ph_2P)_2CCH_2\}]$ or $[Fe_3(CO)_{10}\{\mu\text{-}(Ph_2P)_2CCH_2\}]$ is fragmented to generate the μ_3-vinylidene complex $[Fe_3(CO)_6(\mu\text{-}CO)(\mu\text{-}PPh_2)_2(\mu_3\text{-}CCH_2)]$; the structures of the latter and of two 'phospha-allene' precursors $[Fe_2(CO)_5(\mu\text{-}PPh_2)(\mu\text{-}Ph_2PCCH_2)]$ and $[Fe_3(CO)_9(\mu\text{-}PPh_2)(\mu_3\text{-}Ph_2PCCH_2)]$ have been established by *X*-ray diffraction.

Recently we reported that bis(diphenylphosphino)methane undergoes cleavage of a single $P\text{–}CH_2$ bond when the complex $[Fe_2(CO)_7(\mu\text{-}Ph_2PCH_2PPh_2)]$ is heated, yielding $[Fe_2(CO)_6(\mu\text{-}PPh_2)(\mu\text{-}Ph_2PCH_2)]$.[1] Phosphorus–carbon ($sp^2$) bonds are generally more readily cleaved than $P\text{–}C(sp^3)$ bonds,[2] and we have therefore subsequently investigated the thermolysis of the new 1,1-bis(diphenylphosphino)ethylene (dppee) complexes $[Fe_2(CO)_7(\mu\text{-dppee})]$ (**1**) and $[Fe_3(CO)_{10}(\mu\text{-dppee})]$ (**2**). We report that fragmentation of $(Ph_2P)_2CCH_2$ is indeed more extensive; both $P\text{–}CCH_2$ bonds are cleaved in step-wise fashion to afford discrete phosphido and vinylidene ligands. The first cleavage may be accomplished at a di-iron centre, but the second requires three iron atoms and produces μ_3-vinylidene (see Scheme 1).

Complex (**1**)† is readily prepared (95%) by treating dppee with $[Fe_2(CO)_9]$ in tetrahydrofuran (thf) for 3 h, followed by the addition of $[Fe(CO)_5]$ and overnight photolysis. The η^1-dppee complex $[Fe(CO)_4(dppee)]$[3] is detected as an intermediate. Photolysis of (**1**) for 5 days in the presence of $[Fe(CO)_5]$ affords (**2**)† in 45% yield.

In boiling heptane complex (**1**) loses a CO ligand, inducing cleavage of a $P\text{–}CCH_2$ bond to enable the dinuclear metal centre to regain its full complement of 34 valence electrons. This generates the $\mu\text{-}\eta^2$-'phospha-allene' complex $[Fe_2(CO)_6(\mu\text{-}PPh_2)(\mu\text{-}Ph_2PCCH_2)]$ (**3**),† containing an unusual Fe_2PC four-membered ring with exocyclic double bond. The latter is brought into co-ordination *via* photochemically-induced loss of a second CO, yielding the α-phosphinovinyl complex $[Fe_2(CO)_5(\mu\text{-}PPh_2)(\mu\text{-}Ph_2PCCH_2)]$ (**4**),† the struc-



Scheme 1. *Reagents and conditions*: i, heptane reflux, 2 h, 45%; ii, u.v., toluene, 16 h, 90%; iii, $Fe(CO)_5$, u.v., toluene, 5 h, 80%; iv, $Fe(CO)_5$, u.v., toluene, 5 days, 45%; v, heptane reflux, 1 min, 50%; vi, heptane reflux, 1 h, 85%.

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† The new complexes were characterised by elemental analyses and mass, i.r. (CH_2Cl_2 solution), and n.m.r. (^1H, ^{13}C, and ^{31}P, coupling constants in Hz, $CDCl_3$ solution unless otherwise stated) spectra. *Selected data* for (**1**): red crystals, ν(CO) at 2044s, 1990s, 1979s, 1942m, 1923m, and 1759w cm^{-1}; ^1H n.m.r. (CD_2Cl_2) δ 6.14 [t, *J*(HP) 21, CH_2]; $^{13}C\{^1H\}$ n.m.r. (CD_2Cl_2) δ 136.1 (s, br, $C\mathit{C}H_2$) and 145.6 [t, *J*(CP) 21, $\mathit{C}CH_2$]; ^{31}P n.m.r. (CD_2Cl_2) δ 68.4s p.p.m.

(**2**): green crystals, ν(CO) at 2060s, 1995s, 1955m, and 1815w, br cm^{-1}; ^1H n.m.r. δ 5.80 [t, *J*(HP) 22, CH_2]; $^{13}C\{^1H\}$ n.m.r. (C_6D_6) δ 138.9 (s, br, $C\mathit{C}H_2$) and 153.4 [t, *J*(CP) 24, $\mathit{C}CH_2$; ^{31}P n.m.r. δ 60.7s p.p.m.

(**3**): yellow crystals, ν(CO) at 2054s, 2013s, 1990s, 1967m, and 1952m cm^{-1}; ^1H n.m.r. δ 6.27 [dd, *J*(HP) 6 and 26, 1H of CH_2] and 6.49 [dd, *J*(HP) 3 and 52, 1H of CH_2]; $^{13}C\{^1H\}$ n.m.r. (C_6D_6) δ 142.2 [t, *J*(CP) 8, $C\mathit{C}H_2$] and 146.0 [dd, *J*(CP) 14 and 28, $\mathit{C}CH_2$]; ^{31}P n.m.r. δ 24.1 [d, *J*(PP) 24, $PCCH_2$] and 177.5 p.p.m. [d, *J*(PP) 24, μ-P].

(**4**): orange crystals, ν(CO) at 2038s, 1988s, 1959m, and 1927m cm^{-1}; ^1H n.m.r. δ 2.94 [ddd, *J*(HH) 5, *J*(HP) 2 and 17, 1H of CH_2] and 3.74 [q, *J*(HH) = *J*(HP) 5, 1H of CH_2]; $^{13}C\{^1H\}$ n.m.r. (C_6D_6) δ 54.3 [dd, *J*(CP) 8 and 15, $C\mathit{C}H_2$] and 151.8 [dd, *J*(CP) 28 and 33, $\mathit{C}CH_2$]; ^{31}P n.m.r. δ −44.6 [d, *J*(PP) 44, $PCCH_2$] and 168.2 p.p.m. [d, *J*(PP) 44, μ-P].

(**5**): purple crystals, ν(CO) at 2069s, 2036s, 1994sh, 1984s, and 1919w cm^{-1}; ^1H n.m.r. δ 2.15 [ddd, *J*(HH) 4, *J*(HP) 4 and 29, 1H of CH_2] and 3.36 [ddd, *J*(HH) 4, *J*(HP) 8 and 21, 1H of CH_2]; $^{13}C\{^1H\}$ n.m.r. (C_6D_6) δ 56.7 [t, *J*(CP) 8, $C\mathit{C}H_2$] and 150.3 [t, *J*(CP) 30, $\mathit{C}CH_2$]; ^{31}P n.m.r. δ 9.6 [d, *J*(PP) 10, $PCCH_2$] and 179.7 p.p.m. [d, *J*(PP) 10, μ-P].

(**6**): dark green crystals, ν(CO) at 2038s, 2005sh, 1995s, 1975s, 1957sh, and 1880w, br cm^{-1}; ^1H n.m.r. (in $[^2H_8]$ toluene at 80 °C) δ 3.83 [t, *J*(HP) 2, CH_2]; $^{13}C\{^1H\}$ n.m.r. (in $[^2H_8]$ toluene at 80 °C) δ 95.6 [t, *J*(CP) 5, $C\mathit{C}H_2$] and 141.3 [dd, *J*(CP) 29 and 46, $\mathit{C}CH_2$]; ^{31}P n.m.r. (in $[^2H_8]$ toluene at 100 °C) δ 279.1s, (in $[^2H_8]$ toluene at −40 °C) δ 267.5 [d, *J*(PP) 64], 274.7s, and 305.7 [d, *J*(PP) 64].

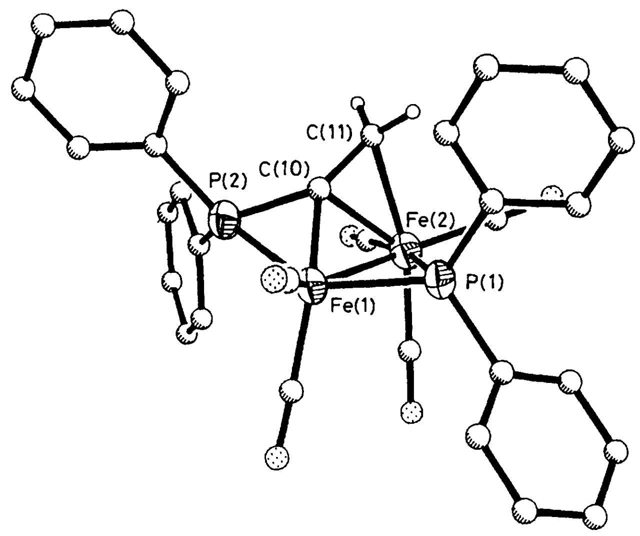

Figure 1. Molecular structure of (**4**). Phenyl group hydrogens are omitted for clarity. Important dimensions include: bond lengths (Å) Fe(1)–Fe(2) 2.658(1), Fe(1)–P(1) 2.166(1), Fe(2)–P(1) 2.268(1), Fe(1)–P(2) 2.205(1), Fe(1)–C(10) 1.908(4), Fe(2)–C(10) 2.108(4), Fe(2)–C(11) 2.161(4), P(2)–C(10) 1.746(4), C(10)–C(11) 1.392(5); bond angles (°) Fe(1)–P(2)–C(10) 56.3(1), Fe(1)–C(10)–P(2) 74.1(1), Fe(1)–P(1)–Fe(2) 73.6(1).

ture of which was determined by an *X*-ray diffraction study.[‡] The results are summarised in Figure 1 and in its caption.

The di-iron centre of (**4**) is bridged by diphenylphosphido and μ-$\eta^2,\eta^{2'}$-Ph_2PCCH_2 ligands. The latter may also be viewed as a 'phospha-allene,' co-ordinated through both P=C and C=C bonds, in that the P(2)–C(10) bond is short [1.746(4) Å], indicating a P–C bond order greater than unity, and the P–C–C backbone is bent [P(2)–C(10)–C(11) 144.2°]; *cf.* similar distortion in μ-$\eta^2,\eta^{2'}$-allene complexes.[4] A striking feature of (**4**) is the presence of a three-membered FePC ring which is apparently under strain [*e.g.* Fe(1)–P(2)–C(10) angle is only 56.3(1)°] and is consequently readily opened. Thus, treatment of (**4**) with [$Fe(CO)_5$] under u.v. irradiation results in the smooth insertion of an $Fe(CO)_4$ fragment into the Fe(1)–P(2) bond to afford [$Fe_3(CO)_9(\mu$-$PPh_2)(\mu_3$-$Ph_2PCCH_2)$] (**5**)[†] in high yield. The structure of (**5**) was established by *X*-ray diffraction, as shown in Figure 2.[‡]

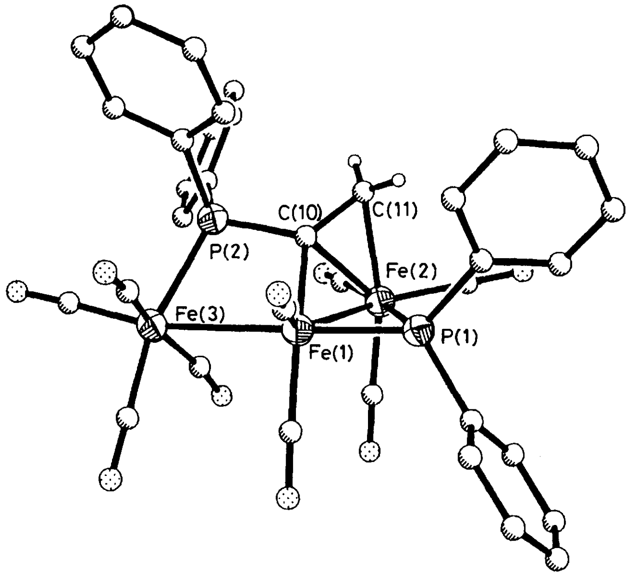

Figure 2. Molecular structure of (**5**). Phenyl group hydrogens are omitted for clarity. Important dimensions include: bond lengths (Å) Fe(1)–Fe(2) 2.655(1), Fe(1)–Fe(3) 2.828(1), Fe(1)–P(1) 2.143(1), Fe(2)–P(1) 2.246(1), Fe(3)–P(2) 2.254(1), Fe(1)–C(10) 1.926(4), Fe(2)–C(10) 2.116(4), Fe(2)–C(11) 2.129(4), P(2)–C(10) 1.783(5), C(10)–C(11) 1.400(6); bond angles (°) Fe(3)–P(2)–C(10) 106.0(1), Fe(1)–C(10)–P(2) 100.8(2), Fe(1)–P(1)–Fe(2) 74.4(1).

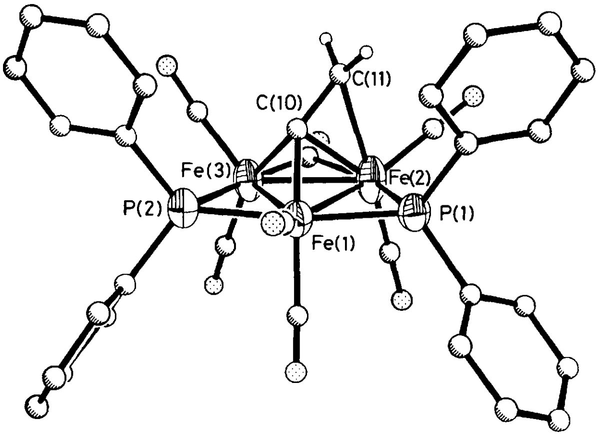

Figure 3. Molecular structure of (**6a**). Phenyl group hydrogens are omitted for clarity. Important dimensions include: bond lengths (Å) Fe(1)–Fe(2) 2.551(1), Fe(1)–Fe(3) 2.557(1), Fe(2)–Fe(3) 2.490(2), Fe(1)–P(1) 2.205(2), Fe(2)–P(1) 2.188(2), Fe(1)–P(2) 2.206(2), Fe(3)–P(2) 2.210(2), Fe(1)–C(10) 1.881(7), Fe(2)–C(10) 2.063(7), Fe(3)–C(10) 1.984(8), Fe(2)–C(11) 2.302(8), C(10)–C(11) 1.352(12); bond angles (°) Fe(1)–P(1)–Fe(2) 71.0(1), Fe(1)–P(2)–Fe(3) 70.8(1).

The ligand conformations and gross molecular geometry of (**5**) show surprisingly little change from those in (**4**). The principal effect of the $Fe(CO)_4$ insertion into the Fe(1)–P(2) bond is to allow relaxation of the Fe(1)–C(10)–P(2) bond angle from 74.1(1)° in (**4**) to 100.8(2)° in (**5**). In addition, the geometry at P(2) is less strained [*e.g.* Fe(3)–P(2)–C(10) is now 106.0(1)°] and the P(2)–C(10) bond is lengthened [to 1.783(5) Å].

The shortness of the P(2) · · · Fe(1) trans-annular distance [2.859(2) Å] in (**5**) suggested that upon heating (to drive off CO) a second P–CCH_2 bond might be cleaved [*i.e.*

[‡] *Crystal data* for (**4**): $C_{31}H_{22}Fe_2O_5P_2$, $M = 648.15$, monoclinic, space group $P2_1/n$ (No. 14), $a = 12.500(7)$, $b = 15.869(3)$, $c = 15.001(5)$ Å, $\beta = 100.98(4)°$, $U = 2921(2)$ Å^3, $T = 294$ K, $Z = 4$, $D_c = 1.474$ g cm^{-3}, $F(000) = 1320$, μ(Mo-K_α) = 11.37 cm^{-1}. Final $R = 0.041$ for 3412 unique, observed [$I > 1.5\sigma(I)$], absorption-corrected intensities with $3 < 2\theta < 50°$.

Crystal data for (**5**): $C_{35}H_{22}Fe_3O_9P_2$, $M = 816.02$, monoclinic, space group $P2_1/n$ (No. 14), $a = 11.145(4)$, $b = 16.745(5)$, $c = 18.577(6)$ Å, $\beta = 93.37(2)°$, $U = 3461(2)$ Å^3, $T = 294$ K, $Z = 4$, $D_c = 1.566$ g cm^{-3}, $F(000) = 1648$, μ(Mo-K_α) = 13.84 cm^{-1}. Final $R = 0.043$ for 3658 unique, observed [$I > 1.5\sigma(I)$], absorption-corrected intensities with $4 < 2\theta < 50°$.

Crystal data for (**6a**): $C_{33}H_{22}Fe_3O_7P_2$, $M = 759.99$, monoclinic, space group $P2_1/n$ (No. 14), $a = 13.378(3)$, $b = 14.813(4)$, $c = 16.686(4)$ Å, $\beta = 103.85(2)°$, $U = 3211(2)$ Å^3, $T = 294$ K, $Z = 4$, $D_c = 1.572$ g cm^{-3}, $F(000) = 1536$, μ(Mo-K_α) = 14.81 cm^{-1}. Final $R = 0.069$ for 4287 unique, observed [$I > 1.5\sigma(I)$], absorption-corrected intensities with $4 < 2\theta < 50°$. Intensity data were collected for unique portions of reciprocal space using Mo-K_α *X*-radiation ($\lambda = 0.71069$ Å) on Nicolet R3m diffractometers.

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.

P(2)–C(10)] and the P(2)–Fe(1) bond re-created. This proved to be the case. In refluxing heptane two molecules of CO are lost from (**5**), requiring P–CCH_2 cleavage and iron–iron bond formation in order that the valence electron count is maintained, resulting in the formation of the μ_3-vinylidene species [$Fe_3(CO)_6(\mu$-$CO)(\mu$-$PPh_2)_2(\mu_3$-$CCH_2)$] (**6**).† N.m.r. spectra reveal that complex (**6**) exists in solution as two isomers, (**6a**) and (**6b**), differing only in which of the two types of iron atom is η^2-co-ordinated by the vinylidene group, and also that these interconvert rapidly on the n.m.r. time scale above room temperature, *i.e.* there is fluxional rotation of the vinylidene about the iron triangle. An *X*-ray diffraction study established that the favoured solid state structure is (**6a**) (see Figure 3 and caption).‡

In (**6a**), the asymmetric isomer, the Fe_3 triangle is edge-bridged by two PPh_2 groups and one CO, and asymmetrically capped by a μ_3-vinylidene moiety fully separated from phosphorus [P(2) · · · C(10) 2.671 Å]. The vinylidene is essentially σ-bonded to Fe(1) and Fe(3) and co-ordinated *via* an asymmetric η^2 interaction to Fe(2), such that its C–C axis makes an angle of 38.6° with the normal to the Fe_3 plane.

The sequence (**1**) → (**3**) → (**4**) → (**5**) → (**6**) comprises the step-wise fragmentation of 1,1-bis(diphenylphosphino)ethylene at a di-iron centre, for the first P–CCH_2 bond cleavage, and at a tri-iron centre, for the second. However, the same end can be achieved entirely, and easily, at a tri-iron centre. In boiling heptane [$Fe_3(CO)_{10}(\mu$-dppee)] (**2**) is converted within one minute into complex (**5**), the precursor of (**6**), which is the sole product of another hour of heating. It is noteworthy that in the transformation (**2**) → (**5**) → (**6**) the P–C cleavages are accompanied by the opening and closing of the Fe_3 triangle.

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References

1 N. M. Doherty, G. Hogarth, S. A. R. Knox, K. A. Macpherson, F. Melchior, and A. G. Orpen, *J. Chem. Soc., Chem. Commun.*, 1986, 540.

2 P. E. Garrou, *Chem. Rev.*, 1985, **85**, 171.

3 J. A. Clucas, R. H. Dawson, P. A. Dolby, M. M. Harding, K. Pearson, and A. K. Smith, *J. Organomet. Chem.*, 1986, **311**, 153.

4 C. G. Kreiter, M. Leyendecker, and W. S. Sheldrick, *J. Organomet. Chem.*, 1986, **302**, 35, and references therein.