

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

Nigel J. Grist, Graeme Hogarth, Selby A. R. Knox, Brian R. Lloyd, David A. V. Morton, and A. Guy Orpen

Department of Inorganic Chemistry, The University, Bristol BS8 1TS, U.K.

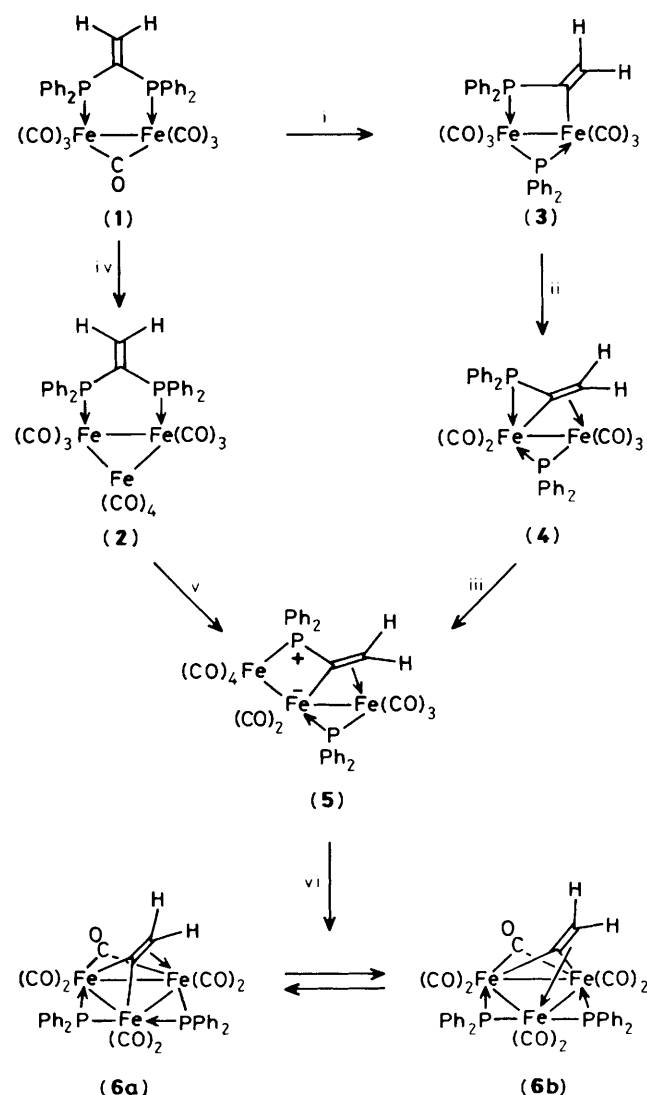
Through a sequence of thermally- and photochemically-induced steps the 1,1-bis(diphenylphosphino)ethylene ligand in $[\text{Fe}_2(\text{CO})_7(\mu\text{-(Ph}_2\text{P)}_2\text{CCH}_2)]$ or $[\text{Fe}_3(\text{CO})_{10}(\mu\text{-(Ph}_2\text{P)}_2\text{CCH}_2)]$ is fragmented to generate the μ_3 -vinylidene complex $[\text{Fe}_3(\text{CO})_6(\mu\text{-CO})(\mu\text{-PPh}_2)_2(\mu_3\text{-CCH}_2)]$; the structures of the latter and of two 'phospha-allene' precursors $[\text{Fe}_2(\text{CO})_5(\mu\text{-PPh}_2)(\mu\text{-Ph}_2\text{PCCH}_2)]$ and $[\text{Fe}_3(\text{CO})_9(\mu\text{-PPh}_2)(\mu_3\text{-Ph}_2\text{PCCH}_2)]$ have been established by X-ray diffraction.

Recently we reported that bis(diphenylphosphino)methane undergoes cleavage of a single P-CH₂ bond when the complex $[\text{Fe}_2(\text{CO})_7(\mu\text{-Ph}_2\text{PCH}_2\text{PPh}_2)]$ is heated, yielding $[\text{Fe}_2(\text{CO})_6(\mu\text{-PPh}_2)(\mu\text{-Ph}_2\text{PCH}_2)]$.¹ Phosphorus-carbon (sp²) bonds are generally more readily cleaved than P-C(sp³) bonds,² and we have therefore subsequently investigated the thermolysis of the new 1,1-bis(diphenylphosphino)ethylene (dppee) complexes $[\text{Fe}_2(\text{CO})_7(\mu\text{-dppee})]$ (1) and $[\text{Fe}_3(\text{CO})_{10}(\mu\text{-dppee})]$ (2). We report that fragmentation of $(\text{Ph}_2\text{P})_2\text{CCH}_2$ is indeed more extensive; both P-CCH₂ 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 $[\text{Fe}_2(\text{CO})_9]$ in tetrahydrofuran (thf) for 3 h, followed by the addition of $[\text{Fe}(\text{CO})_5]$ and overnight photolysis. The η^1 -dppee complex $[\text{Fe}(\text{CO})_4(\text{dppee})]$ ³ is detected as an intermediate. Photolysis of (1) for 5 days in the presence of $[\text{Fe}(\text{CO})_5]$ affords (2)[†] in 45% yield.

In boiling heptane complex (1) loses a CO ligand, inducing cleavage of a P-CCH₂ 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 $[\text{Fe}_2(\text{CO})_6(\mu\text{-PPh}_2)(\mu\text{-Ph}_2\text{PCCH}_2)]$ (3),[†] containing an unusual Fe₂PC 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 -phosphinovinylic complex $[\text{Fe}_2(\text{CO})_5(\mu\text{-PPh}_2)(\mu\text{-Ph}_2\text{PCCH}_2)]$ (4),[†] the struc-



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

[†] 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, $\nu(\text{CO})$ at 2044s, 1990s, 1979s, 1942m, 1923m, and 1759w cm^{-1} ; ^1H n.m.r. (CD_2Cl_2) δ 6.14 [t, $J(\text{HP})$ 21, CH_2]; $^{13}\text{C}\{^1\text{H}\}$ n.m.r. (CD_2Cl_2) δ 136.1 (s, br, CCH_2) and 145.6 [t, $J(\text{CP})$ 21, CCH_2]; ^{31}P n.m.r. (CD_2Cl_2) δ 68.4s p.p.m.

(2): green crystals, $\nu(\text{CO})$ at 2060s, 1995s, 1955m, and 1815w, br cm^{-1} ; ^1H n.m.r. δ 5.80 [t, $J(\text{HP})$ 22, CH_2]; $^{13}\text{C}\{^1\text{H}\}$ n.m.r. (C_6D_6) δ 138.9 (s, br, CCH_2) and 153.4 [t, $J(\text{CP})$ 24, CCH_2]; ^{31}P n.m.r. δ 60.7s p.p.m.

(3): yellow crystals, $\nu(\text{CO})$ at 2054s, 2013s, 1990s, 1967m, and 1952m cm^{-1} ; ^1H n.m.r. δ 6.27 [dd, $J(\text{HP})$ 6 and 26, 1H of CH_2] and 6.49 [dd, $J(\text{HP})$ 3 and 52, 1H of CH_2]; $^{13}\text{C}\{^1\text{H}\}$ n.m.r. (C_6D_6) δ 142.2 [t, $J(\text{CP})$ 8, CCH_2] and 146.0 [dd, $J(\text{CP})$ 14 and 28, CCH_2]; ^{31}P n.m.r. δ 24.1 [d, $J(\text{PP})$ 24, PCCH_2] and 177.5 p.p.m. [d, $J(\text{PP})$ 24, $\mu\text{-P}$].

(4): orange crystals, $\nu(\text{CO})$ at 2038s, 1988s, 1959m, and 1927m cm^{-1} ; ^1H n.m.r. δ 2.94 [ddd, $J(\text{HH})$ 5, $J(\text{HP})$ 2 and 17, 1H of CH_2] and 3.74 [q, $J(\text{HH}) = J(\text{HP})$ 5, 1H of CH_2]; $^{13}\text{C}\{^1\text{H}\}$ n.m.r. (C_6D_6) δ 54.3 [dd, $J(\text{CP})$ 8 and 15, CCH_2] and 151.8 [dd, $J(\text{CP})$ 28 and 33, CCH_2]; ^{31}P n.m.r. δ -44.6 [d, $J(\text{PP})$ 44, PCCH_2] and 168.2 p.p.m. [d, $J(\text{PP})$ 44, $\mu\text{-P}$].

(5): purple crystals, $\nu(\text{CO})$ at 2069s, 2036s, 1994sh, 1984s, and 1919w cm^{-1} ; ^1H n.m.r. δ 2.15 [ddd, $J(\text{HH})$ 4, $J(\text{HP})$ 4 and 29, 1H of CH_2] and 3.36 [ddd, $J(\text{HH})$ 4, $J(\text{HP})$ 8 and 21, 1H of CH_2]; $^{13}\text{C}\{^1\text{H}\}$ n.m.r. (C_6D_6) δ 56.7 [t, $J(\text{CP})$ 8, CCH_2] and 150.3 [t, $J(\text{CP})$ 30, CCH_2]; ^{31}P n.m.r. δ 9.6 [d, $J(\text{PP})$ 10, PCCH_2] and 179.7 p.p.m. [d, $J(\text{PP})$ 10, $\mu\text{-P}$].

(6): dark green crystals, $\nu(\text{CO})$ at 2038s, 2005sh, 1995s, 1975s, 1957sh, and 1880w, br cm^{-1} ; ^1H n.m.r. (in $^2\text{H}_8$ toluene at 80°C) δ 3.83 [t, $J(\text{HP})$ 2, CH_2]; $^{13}\text{C}\{^1\text{H}\}$ n.m.r. (in $^2\text{H}_8$ toluene at 80°C) δ 95.6 [t, $J(\text{CP})$ 5, CCH_2] and 141.3 [dd, $J(\text{CP})$ 29 and 46, CCH_2]; ^{31}P n.m.r. (in $^2\text{H}_8$ toluene at 100°C) δ 279.1s, (in $^2\text{H}_8$ toluene at -40°C) δ 267.5 [d, $J(\text{PP})$ 64], 274.7s, and 305.7 [d, $J(\text{PP})$ 64].

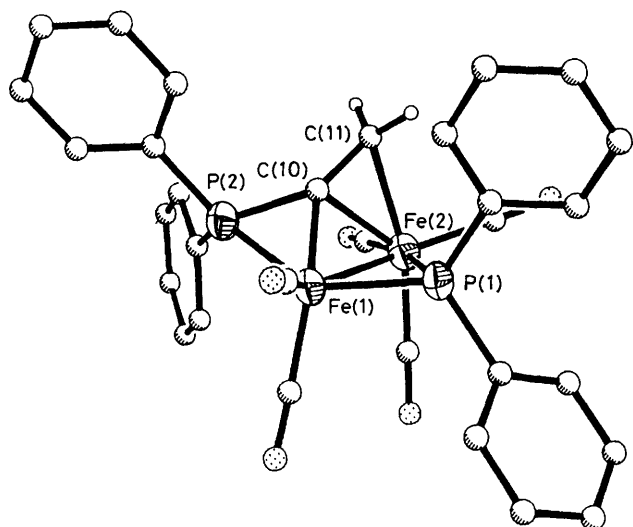


Figure 1. Molecular structure of (4). Phenyl group hydrogens are omitted for clarity. Important dimensions include: bond lengths (Å) Fe(1)–Fe(2) 2.658(1), Fe(1)–P(1) 2.166(1), Fe(2)–P(1) 2.268(1), Fe(1)–P(2) 2.205(1), Fe(1)–C(10) 1.908(4), Fe(2)–C(10) 2.108(4), Fe(2)–C(11) 2.161(4), P(2)–C(10) 1.746(4), 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 $\mu\text{-}\eta^2,\eta^{2'}\text{-Ph}_2\text{PCCH}_2$ 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 $\mu\text{-}\eta^2,\eta^{2'}\text{-allene}$ 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 [Fe₃(CO)₉($\mu\text{-PPh}_2$)($\mu_3\text{-Ph}_2\text{PCCH}_2$)] (5)[†] in high yield. The structure of (5) was established by *X*-ray diffraction, as shown in Figure 2.‡

‡ *Crystal data for (4):* C₃₁H₂₂Fe₂O₅P₂, *M* = 648.15, monoclinic, space group P2₁/n (No. 14), *a* = 12.500(7), *b* = 15.869(3), *c* = 15.001(5) Å, β = 100.98(4)°, *U* = 2921(2) Å³, *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* > 1.5σ(*I*)], absorption-corrected intensities with 3 < 2θ < 50°.

Crystal data for (5): C₃₅H₂₂Fe₃O₉P₂, *M* = 816.02, monoclinic, space group P2₁/n (No. 14), *a* = 11.145(4), *b* = 16.745(5), *c* = 18.577(6) Å, β = 93.37(2)°, *U* = 3461(2) Å³, *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* > 1.5σ(*I*)], absorption-corrected intensities with 4 < 2θ < 50°.

Crystal data for (6a): C₃₃H₂₂Fe₃O₇P₂, *M* = 759.99, monoclinic, space group P2₁/n (No. 14), *a* = 13.378(3), *b* = 14.813(4), *c* = 16.686(4) Å, β = 103.85(2)°, *U* = 3211(2) Å³, *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* > 1.5σ(*I*)], absorption-corrected intensities with 4 < 2θ < 50°. Intensity data were collected for unique portions of reciprocal space using Mo-*K*_α *X*-radiation (λ = 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.

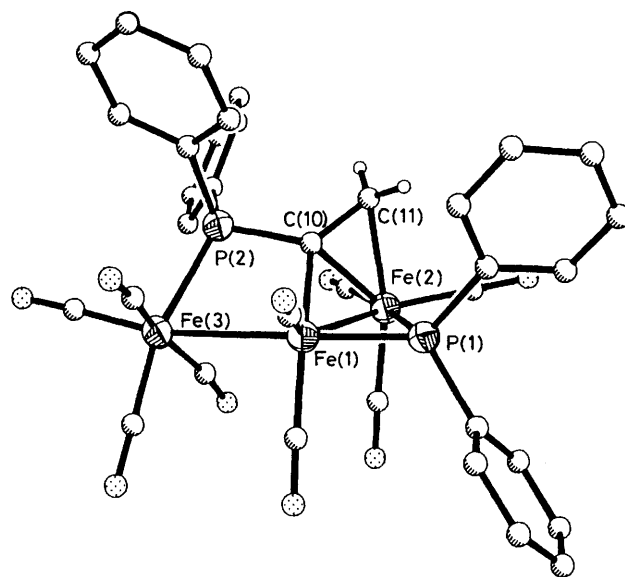


Figure 2. Molecular structure of (5). Phenyl group hydrogens are omitted for clarity. Important dimensions include: bond lengths (Å) Fe(1)–Fe(2) 2.655(1), Fe(1)–Fe(3) 2.828(1), Fe(1)–P(1) 2.143(1), Fe(2)–P(1) 2.246(1), Fe(3)–P(2) 2.254(1), Fe(1)–C(10) 1.926(4), Fe(2)–C(10) 2.116(4), Fe(2)–C(11) 2.129(4),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

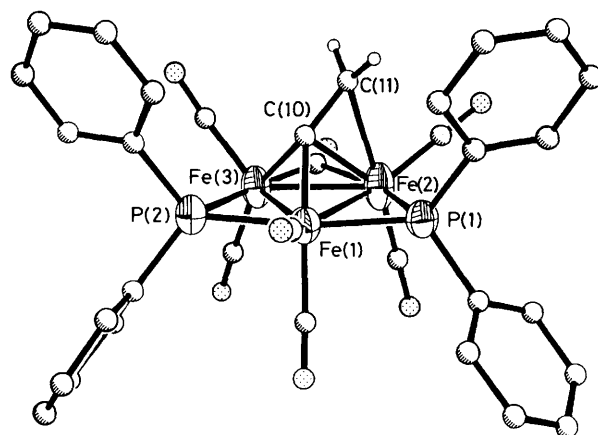


Figure 3. Molecular structure of (6a). Phenyl group hydrogens are omitted for clarity. Important dimensions include: bond lengths (Å) Fe(1)–Fe(2) 2.551(1), Fe(1)–Fe(3) 2.557(1), Fe(2)–Fe(3) 2.490(2), Fe(1)–P(1) 2.205(2), Fe(2)–P(1) 2.188(2), Fe(1)–P(2) 2.206(2), Fe(3)–P(2) 2.210(2), Fe(1)–C(10) 1.881(7), 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–CCH₂ bond might be cleaved [*i.e.*

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–CCH₂ 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 [Fe₃(CO)₆(μ -CO)(μ -PPh₂)₂(μ_3 -CCH₂)] (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 Fe₃ triangle is edge-bridged by two PPh₂ 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 Fe₃ plane.

The sequence (1) → (3) → (4) → (5) → (6) comprises the step-wise fragmentation of 1,1-bis(diphenylphosphino)ethyl-

ene at a di-iron centre, for the first P–CCH₂ 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 [Fe₃(CO)₁₀(μ -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 Fe₃ triangle.

We are grateful to the S.E.R.C. for the award of Research Studentships (to N. J. G., G. H., and D. A. V. M.) and for support, and N.A.T.O. for a travel grant.

Received, 23rd December 1987; Com. 1842

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.