

Transformations of alkynyl ligands at iron centres: alkenyl formation *via* addition of PPh₃ and enyne generation *via* head-to-head coupling and addition of benzene

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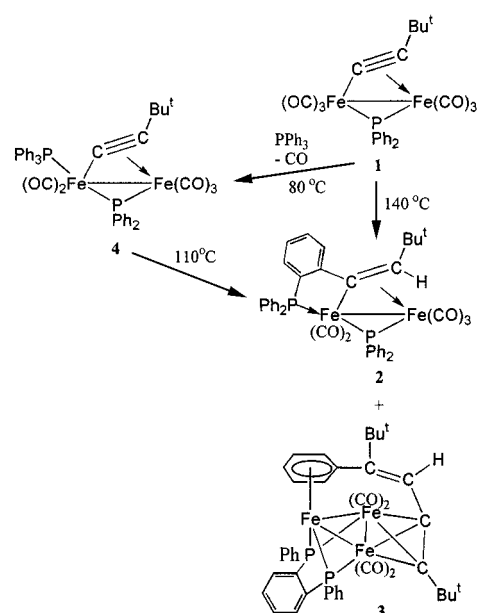
Thermolysis of Fe₂(CO)₆(μ-PPh₂)(μ-C₂Bu^t) affords the binuclear alkenyl complex Fe₂(CO)₅(μ-PPh₂)(μ-*o*-Ph₂PC₆H₄C=CHBu^t) and the trinuclear arene complex Fe₃(CO)₄(μ₃-*o*-PhPC₆H₄PPh){μ₃-C(Bu^t)CCH=CBu^t-η⁶-C₆H_{5}}} both resulting from a number of novel transformations including C–C bond formation and C–H and C–P bond cleavage and reformation.

Binuclear iron triad acetylide complexes such as M₂(CO)₆(μ-PPh₂)(μ-C≡CR) have recently been exploited as novel precursors for the synthesis of multimetallic polycarbon materials *via* intermolecular coupling of alkynyl ligands.^{1–4} For example, thermolysis of Ru₂(CO)₆(μ-PPh₂)(μ-C≡CR) (R = Ph, Bu^t) affords several tetra ruthenium clusters with C₄ chains formed by head-to-head or head-to-tail ynyl coupling, the nature of which depends on the acetylide substituent.^{1,2} Similarly, in a remarkably specific, high yield reaction, the diiron complex Fe₂(CO)₆(μ-PPh₂)(μ-C≡CPh) has been shown independently by ourselves³ and Mays and coworkers⁴ to undergo head-to-head carbon–carbon coupling generating the unusual tetrairon cluster Fe₄(CO)₈(μ-PPh₂)₂(μ₄-C≡CPh)₂ in which the face capping acetylides are linked through the tetrairon core by a short [1.596(4) Å] carbon–carbon contact. In an effort to extend this chemistry to other polycarbon systems we have studied the analogous thermolysis of Fe₂(CO)₆(μ-PPh₂)(μ-C≡CBu^t) **1**. To our surprise, we have discovered that this leads to two new complexes formed *via* unprecedented transformations including carbon–carbon bond formation, and carbon–hydrogen and carbon–phosphorus bond cleavage and reformation. We describe herein the characterisation of these novel compounds Fe₂(CO)₅(μ-PPh₂)(μ-*o*-Ph₂PC₆H₄C=CHBu^t) **2** and Fe₃(CO)₄(μ₃-*o*-PhPC₆H₄PPh){μ₃-C(Bu^t)CCH=CBu^t-η⁶-C₆H_{5}}} **3**.

Heating a toluene solution of **1** at 140 °C for 30 h resulted in a gradual darkening of the solution and disappearance of **1** as shown by IR spectroscopy, and led after chromatography to the isolation of orange Fe₂(CO)₅(μ-PPh₂)(μ-*o*-Ph₂PC₆H₄C=CHBu^t) **2** (35%) and green Fe₃(CO)₄(μ₃-*o*-PhPC₆H₄PPh){μ₃-C(Bu^t)CCH=CBu^t-η⁶-C₆H_{5}}} **3** (10%) (Scheme 1). Spectroscopic data[†] and X-ray crystallography[‡] established full details of the molecular structures and the nature of the coupled organic fragments.

Complex **2** (Fig. 1) is binuclear, the diiron centre being bridged by phosphido and alkenyl ligands. The latter carries the *tert*-butyl substituent at the β-carbon as expected, while the α-carbon is attached to the *ortho*-position of a 2-diphenylphosphino-C₆H₄ group and is *cis* to the Bu^t substituent. The diphenylphosphido functionality is coordinated to Fe(1) as a two-electron ligand. The two phosphorus ligands subtend an angle of 159.39(4)° at Fe(1) accounting for the relatively large phosphorus–phosphorus coupling constant of 75 Hz and the unique alkenyl proton lies *endo* to the phosphido bridge. While the structural features of the alkenyl group are similar to those

of related diiron μ-alkenyl complexes the formation of a 2-diphenylphosphino-C₆H₄ substituent at C_α is quite unex-



Scheme 1

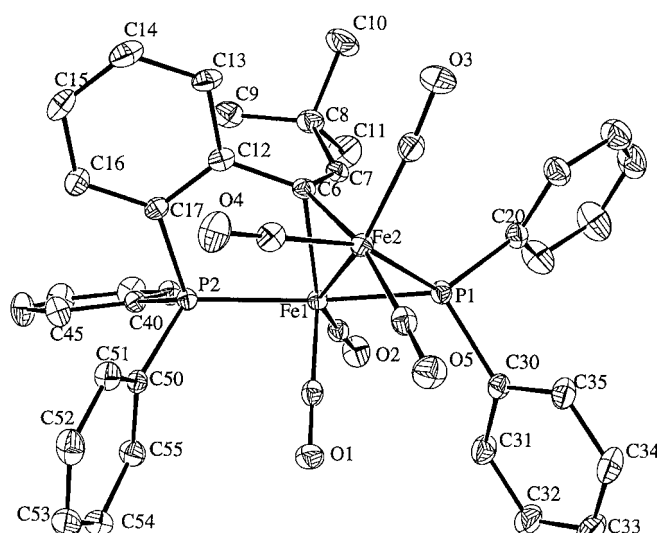


Fig. 1 Molecular structure of **2** with selected bond lengths (Å): Fe(1)–Fe(2) 2.5877(6), Fe(1)–P(1) 2.2220(10), Fe(1)–P(2) 2.2588(10), Fe(2)–P(1) 2.2269(10), Fe(1)–C(6) 2.080(3), Fe(1)–C(7) 2.307(3), Fe(2)–C(6) 2.020(3), C(6)–C(7) 1.383(5).

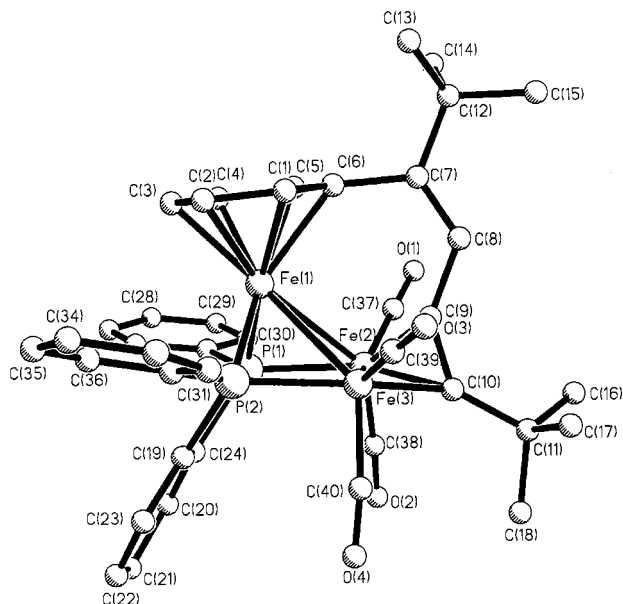


Fig. 2 Molecular structure of **3** with selected bond lengths (Å): Fe(1)–Fe(2) 2.696(2), Fe(1)–Fe(3) 2.689(3), Fe(2)–Fe(3) 2.438(2), Fe(1)–P(1) 2.184(4), Fe(1)–P(2) 2.191(4), Fe(2)–P(1) 2.165(4), Fe(3)–P(2) 2.155(4), Fe(1)–C(1) 2.119(14), Fe(1)–C(2) 2.097(13), Fe(1)–C(3) 2.104(12), Fe(1)–C(4) 2.089(11), Fe(1)–C(5) 2.142(12), Fe(1)–C(6) 2.156(12), Fe(2)–C(9) 2.020(11), Fe(3)–C(9) 1.982(12), Fe(2)–C(10) 2.041(11), Fe(3)–C(10) 2.034(11), C(1)–C(2) 1.412(18), C(2)–C(3) 1.374(18), C(3)–C(4) 1.411(18), C(4)–C(5) 1.398(17), C(5)–C(6) 1.461(17), C(1)–C(6) 1.433(17), C(6)–C(7) 1.490(17), C(7)–C(8) 1.294(16), C(8)–C(9) 1.469(16), C(9)–C(10) 1.335(16).

pected. Formally the new hydrocarbyl ligand can be derived from **1** by loss of CO and addition of PPh₃ across the alkynyl ligand. Indeed **2** is an isomer of Fe₂(CO)₅(PPh₃)(μ-PPh₂)(μ-C≡CBu^t) **4**.⁵ The latter is formed upon addition of PPh₃ to **1** under benzene reflux and we have now shown in a separate experiment that **4** cleanly converts to **2** in refluxing toluene. This may imply that upon thermolysis of **1**, PPh₃ is released which subsequently reacts with **1** to afford **2**.

The structure of trinuclear **3** (Fig. 2) is quite unprecedented and highly unusual for an Fe₃ cluster. It consists of a triiron core, one edge of which [Fe(2)–Fe(3) 2.438(2) Å] is significantly shorter than the other two [Fe(1)–Fe(2) 2.696(2), Fe(1)–Fe(3) 2.689(3) Å]. One face of the cluster is capped by an *ortho*-phenylenebis(phenylphosphido) bridge,⁶ while the second is spanned by a new enyne ligand namely 2,2,7,7-tetramethyl-3-phenylocta-3-en-5-yne. The acetylinic triple bond acts as a four-electron donor, binding in perpendicular fashion to the short iron–iron vector, while the phenyl ring is coordinated as an η⁶-ligand to Fe(1). The average iron–carbon (2.118 Å) and carbon–carbon (1.415 Å) bond lengths for the η⁶-ligand fall within the ranges associated with mononuclear iron–arene complexes.⁷ All bonds to the substituted aryl carbon C(6) are elongated with respect to the other carbons in the ring, an effect probably due to the strain imposed on the hydrocarbyl ligand to maximise metal–alkyne bonding. Two iron centres also bear two carbonyls giving the cluster the expected 48-electron count. Although there is no crystallographic plane of symmetry, the molecule has an approximate plane containing Fe(1)C(3)C(6)C(7)C(8)C(9)C(10) and bisecting Fe(2)–Fe(3) and P(1)–P(2) hence accounting for the relatively simple NMR data.

While the precise mechanism of formation of **2** and **3** from **1** is unknown, the nature of the new ligands and the nuclearity of

3 imply key bond breaking and bond making processes: (i) P–C(Ph) cleavage of a μ-PPh₂ bridge and scavenging of released phenyl groups by phosphido and hydrocarbyl ligands; (ii) addition of a C–H bond of a phenylphosphine across a coordinated triple bond—we believe that this observation is unprecedented; (iii) head-to-head coupling of acetylide ligands and intermolecular condensation at binuclear metal centres; (iv) coupling of PPh₂ and PPh fragments *via* orthophosphination of a phenyl ring to afford a six-electron donor PhPC₆H₄PPh ligand in **3**; (v) loss of carbonyl groups and η⁶-coordination of an aryl substituent to afford a carbonyl free iron atom. Again, we are unaware of any comparable reacton.

We are currently examining the thermal and photochemical transformations of other binuclear phosphido bridged acetylides to gain further insights into the factors governing these novel processes.

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Notes and references

† *Spectroscopic data*: for **2**: IR (C₆H₁₄) ν(CO) 2030s, 1977vs, 1967m, 1954s, 1932m cm⁻¹; ¹H NMR (CDCl₃): δ 8.0–7.1 (m, Ph, 24H), 3.36 (dd, *J* 9.1, 2.5, 1H, H_β), 0.29 (s, 9H, Bu^t); ³¹P NMR (CDCl₃): δ 179.8 (d, *J* 75, μ-PPh₂), 73.4 (d, *J* 75, PPh₂) (85% H₃PO₄); MS(FAB+) *m/z* 781 (M + 1); Anal. Calc. for Fe₂C₄₁H₃₄O₅P₂·0.25CH₂Cl₂: C, 61.78, H, 4.31. Found: C, 62.21, H 4.24%. For **3**: IR (C₆H₁₄) ν(CO) 1981s, 1954s, 1915s, 1909m cm⁻¹; ¹H NMR (CDCl₃): δ 8.01 (s, 4H, Ph), 7.97 (s, 1H, C=CH), 7.53 (s, 6H, Ph), 6.87 (s, 4H, Ph), 6.30 (t, *J* 6.2, 1H, Ar), 4.43 (m, 2H, Ar), 4.30 (d, *J* 5.0, 2H, Ar), 1.89 (s, 9H, Bu^t), 1.04 (s, 9H, Bu^t); ³¹P NMR (CDCl₃): δ 225.0 (s) (85% H₃PO₄); MS(FAB+) *m/z* 813 (M + 1); Anal. Calc. for Fe₃C₄₀H₃₈O₄P₂: C, 59.11; H, 4.68. Found: C, 59.48; H, 4.53%.

‡ *Crystal data*: for **2**: X-ray intensity data were collected on a Siemens CCD diffractometer using Mo-Kα radiation and the ω-scan mode; *T* = 173 K, Fe₂C₄₁H₃₄O₅P₂, *M_r* = 780.35, monoclinic, space group *P*2₁/*n*, *a* = 11.8359(10), *b* = 17.5456(11), *c* = 17.3929(11) Å, β = 92.545(5)°, *F*(000) = 1612, *D_c* = 1.436 g cm⁻³, *Z* = 4, μ = 0.93 mm⁻¹, 2θ(max) = 57.5°, *R*(*R_w*) = 0.0480 (0.0470) for 5812 reflections [*I* > 2.5σ(*I*)] and 587 parameters.

For **3**: X-ray intensity data were collected on a Nonius KappaCCD diffractometer using Mo-Kα radiation and the φ scan mode; *T* = 100 K, Fe₃C₄₀H₃₈O₄P₂, *M_r* = 812.19, monoclinic, space group *I*a, *a* = 13.6479(14), *b* = 35.838(3), *c* = 15.1837(18) Å, β = 90.55(5)°, *F*(000) = 3344, *D_c* = 1.453 g cm⁻³, *Z* = 8, μ = 1.28 mm⁻¹, 2θ(max) = 50°, *R*(*R_w*) = 0.1089 (0.1737) for 11982 reflections [*I* > 2σ(*I*)] and 884 parameters. There are two independent molecules in the asymmetric unit but they do not differ significantly. CCDC 182/1294.

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