Synthesis of $Fe_4(CO)_8(\mu\text{-}PPh_2)_2(\mu_4\text{-}\eta^1,\eta^1,\eta^2,\eta^2\text{-}C_2Ph)_2$ *via* coupling of acetylides at a binuclear centre: a molecule with through-the-cluster carbon–carbon bonding?

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Thermolysis of $Fe_2(CO)_6(\mu\text{-}PPh_2)(\mu\text{-}\eta^1,\eta^2\text{-}C_2Ph)$ affords the rectangular cluster $Fe_4(CO)_8(\mu\text{-}PPh_2)_2(\mu_4\text{-}\eta^1,\eta^1,\eta^2,\eta^2\text{-}C_2Ph)_2$ with two face-capping acetylides linked through the Fe_4 face by a short carbon–carbon contact: reaction with CO leads to $Fe_3(CO)_8\{\mu\text{-}Ph_2PC(CPh){=}C(CPh)PPh_2\}$ as a result of C–C and C–P bond-forming processes.

The acetylide group (–C≡CR) is an extremely versatile ligand capable of binding to one or more metal centres in a variety of coordination modes, donating up to 5 electrons to a cluster centre.[1] In fact, metal acetylides and polyacetylides have recently emerged as promising molecules and precursors for advanced materials and there is now intense interest in both carbon-rich polyacetylide complexes and multimetallic systems where the π-electrons of the polyunsaturated fragment are used for additional coordination. One strategy for the synthesis of polymetallic arrays is to effect the coupling of multi-site bound acetylides and we have recently described the generation of a series of new tetraruthenium clusters from bimetallic precursors.[2] Herein we describe the high yield synthesis of the symmetrical rectangular tetrairon cluster $Fe_4(CO)_8(\mu\text{-}PPh_2)_2(\mu_4\text{-}\eta^1,\eta^1,\eta^2,\eta^2\text{-}C_2Ph)_2$ **2** *via* dimerisation and CO loss on thermolysis of $Fe_2(CO)_6(\mu\text{-}PPh_2)(\mu\text{-}\eta^1,\eta^2\text{-}C_2Ph)$ **1**. The molecule **2** has two face-capping acetylides with a short 'through-the-cluster' C_α–C_α distance such that the two acetylides resemble a PhC_4Ph diyne. Complex **2** undergoes a further facile conversion to $Fe_3(CO)_8\{\mu\text{-}\eta^2,\eta^4,\eta^2\text{-}Ph_2PC(CPh)C(CPh)PPh_2\}$ *via* acetylide–phosphido coupling.

Heating a toluene solution of $Fe_2(CO)_6(\mu\text{-}PPh_2)(\mu\text{-}\eta^1,\eta^2\text{-}C_2Ph)$[3] **1** at 140 °C for 2 h results in a darkening of the solution and the appearance of new ν(CO) bands at 2004 and 1976 cm^{-1} in the IR spectrum. After removal of solvent and washing with hexane, $Fe_4(CO)_8(\mu\text{-}PPh_2)_2(\mu_4\text{-}\eta^1,\eta^1,\eta^2,\eta^2\text{-}C_2Ph)_2$ **2** was isolated as a dark red solid in 90% yield.† The simplicity of the IR spectrum and the presence of a single resonance in the $^{31}P\{^1H\}$ NMR spectrum at δ 252.2 were suggestive of high symmetry. The precise nature of **2** was established by a crystallographic study (Fig. 1).‡

The molecule is centrosymmetric and consists of a rectangle of iron atoms characterised by Fe–Fe distances of 2.5282(4) [Fe(1)–Fe(2)] and 2.8652(5) Å [Fe(1a)–Fe(2)], short edges being bridged symmetrically by phosphido ligands [Fe(1)–P(1) 2.1996(7); Fe(2)–P(1) 2.2010(7) Å]. Each face of the rectangle is capped by an acetylide ligand which is σ-bonded to two metal atoms [Fe(1)–C(5a) 1.992(2); Fe(2)–C(5a) 2.002(2) Å] and π-bonded to the other two [Fe(1)–C(5) 2.143(2); Fe(2)–C(5) 2.141(2); Fe(1)–C(6) 2.030(2); Fe(2)–C(6) 2.001(2) Å]. Although several clusters with μ_4-acetylides on M_4 faces are known,[4] we are unaware of any examples where two such moieties are bound on opposite faces of an M_4 rectangle. Within each acetylide ligand the C_α–C_β distance [C(5)–C(6) 1.383(3) Å] is similar to that found in $Ru_5(CO)_{13}(\mu\text{-}PPh_2)(\mu_4\text{-}\eta^1,\eta^1,\eta^2,\eta^2\text{-}C_2Ph)$ [1.342(11) Å] where the acetylide is also coordinated on an M_4 face.[5] The most noteworthy feature of **2** is the C(5)–C(5a) distance of 1.596(4) Å, indicative of a direct through-space interaction between the two C_α carbon atoms. Indeed this distance could be interpreted as indicative of a C–C single bond elongated somewhat *via* interactions of C(5) and C(5a) with the iron atoms. The metallic valence electron count (MVEC) of **2** is 62 or 64 electrons depending on whether the hydrocarbyl ligands $(C_2Ph)_2$ are acting as one 8-electron donor diyne or as two 5-electron donor acetylides. Extended Hückel computations show that the LUMO for **2** lies 1.99 eV above the HOMO, ensuring the stability of **2** for an MVEC of 64 electrons. This model for the electronic structure of **2**, with the acetylides contributing 10 electrons to the MVEC, does not require any through-space C···C bonding. Nevertheless, a strongly positive C_α-C_α overlap population (+0.66) is computed, reflecting a significant attractive interaction between the C_α atoms capping the metallic core. Both size and electronic factors contribute to the short C···C contact in**2**. A smaller P···P overlap population of 0.226, indicative of a P···P interaction across the cluster face in $Fe_4(CO)_{12}(\mu_4\text{-}PH)_2$ has been calculated by Halet and coworkers.[6] The EHMO calculations on **2** also revealed that the negative charge on C_β was significantly higher than that on C_α (−0.21 *vs.* + 0.20). Consistent with this, in the $^{13}C\{^1H\}$ NMR spectrum of **2**, C_α [δ 143.23(d); J_{P-C} 23.0 Hz] is much more deshielded than C_β [δ 95.21(s)].

In light of the interaction between C_α atoms in **2** we investigated whether formal coupling of the two acetylides to a diyne could be induced. While **2** is stable to prolonged reflux at 160 °C, bubbling CO through a toluene solution at 100 °C leads

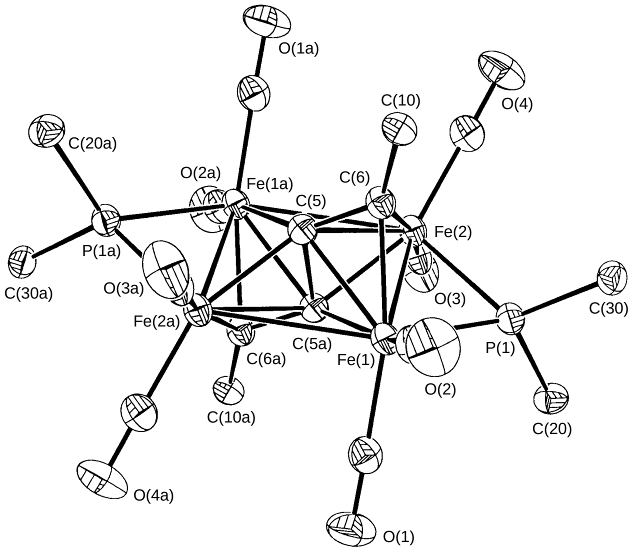


Fig. 1 Molecular structure of **2** with selected bond lengths (Å) and angles (°): Fe(1)–Fe(2) 2.5282(4), Fe(1)–Fe(2a) 2.8652(5), Fe(1)–P(1) 2.1996(7), Fe(2)–P(1) 2.2010(7), Fe(1)–C(5a) 1.9916(22), Fe(2)–C(5a) 2.0018(23), Fe(1)–C(5) 2.1429(22), Fe(2)–C(5) 2.1407(22), Fe(1)–C(6) 2.0296(22), Fe(2)–C(6) 2.0008(23), C(5)–C(6) 1.383(3), C(5)–C(5a) 1.596(4); Fe(1)–P(1)–Fe(2) 70.130(22), C(5)–C(6)–C(10) 130.77(21)

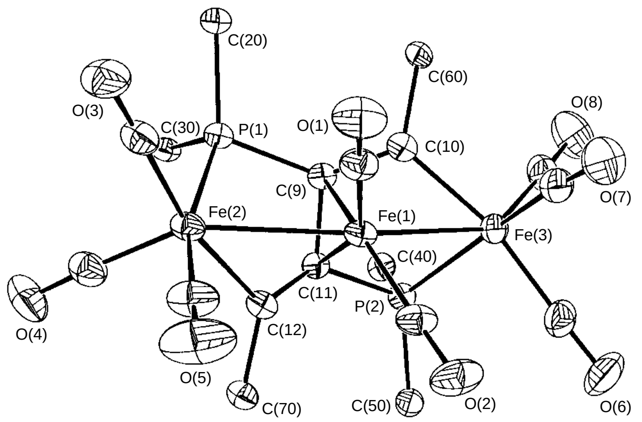
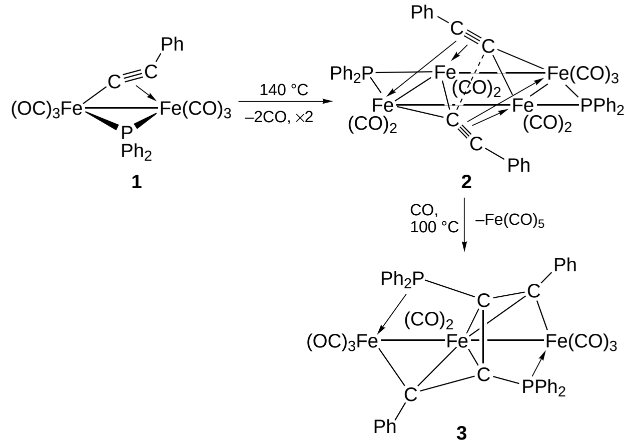


Fig. 2 Molecular structure of **3** with selected bond lengths (Å) and angles (°): Fe(1)–Fe(2) 2.6327(15), Fe(1)–Fe(3) 2.6506(15), Fe(2)–P(1) 2.247(2), Fe(3)–P(2) 2.258(2), Fe(1)–C(9) 2.037(6), Fe(1)–C(10) 2.104(7), Fe(1)–C(11) 2.038(6), Fe(3)–C(10) 2.004(7), Fe(1)–C(12) 2.108(6), Fe(2)–C(12) 2.029(6), C(9)–C(10) 1.422(9), C(11)–C(12) 1.418(9), C(9)–C(11) 1.485(9), P(1)–C(9) 1.821(6), P(2)– C(11) 1.821(6); Fe(2)–Fe(1)–Fe(3) 153.37(5)

to the rapid appearance of new IR bands and the isolation after workup of $Fe_3(CO)_8\{\mu\text{-}Ph_2PC(CPh){=}C(CPh)PPh_2\}$ **3** in 65% yield as a cherry-red solid.§ The ^{31}P NMR spectrum showed only a single resonance (δ 67.1) well upfield of **2**, suggesting that P–C coupling had occurred. An X-ray analysis revealed the molecular structure shown in Fig. 2.‡

The molecule consists of a near linear triiron backbone [Fe(2)–Fe(1)–Fe(3), 153.37(5)°] with the two outer atoms carrying three carbonyls and the central iron atom carrying two. This metal core [Fe(1)–Fe(2) 2.6327(15), Fe(1)–Fe(3) 2.6506(15) Å] is spanned by an unusual bis-2,3-diphenylphosphinodiyne which has resulted from the coupling of both of the phosphido bridges and the two acetylide ligands. To our knowledge, this diphosphine has not previously been synthesised. The coupling of the acetylides is through the two α-carbon atoms as might be expected from their close proximity in **2**. The phosphido groups also couple to the α-carbons and each is coordinated to a single outer iron centre. This new bridging ligand acts as 10-electron donor to the cluster, which then has the expected 50-electron count for a linear trimetallic complex. A closer look at the bond lengths within the diphosphine ligand reveals that the C(9)–C(11) distance of 1.485(9) Å is only 0.11 Å shorter than the corresponding C_α-C_α distance found in **2**, while the C(9)–C(10) and C(11)–C(12) lengths of 1.422(9) and 1.418(9) Å are somewhat longer than those in the precursor. It is interesting to note that binuclear **1**[3] results from the reaction of $Fe_3(CO)_{12}$ with the phosphinoalkyne, Ph_2PC_2Ph, and thus the overall transformation of this ligand *via* **1** and **2** to give **3** (Scheme 1) represents the metal-mediated C_α–C_α coupling of two phosphinoalkynes.



Scheme 1

We are currently exploring both the mechanism of formation of **2** and the broader implication of acetylide coupling at polynuclear centres for the synthesis of new polyyne clusters.

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Footnotes and References

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† Spectroscopic data for **2**: IR (CH_2Cl_2) ν(CO) 2004s, 1976m cm^{-1}; ^1H NMR ($CDCl_3$): δ 8.4–6.5 (m, Ph); ^{31}P NMR ($CDCl_3$): δ 252.2 (s) (85% H_3PO_4); ^{13}C NMR ($CDCl_3$): δ 213.36 (d, *J* 4.7, CO), 211.05 (d, *J* 10.7, CO), 143.23 (d, *J* 23.0, C_α), 136–125 (m, Ph), 95.21 (s, C_β): MS(FAB+) *m/z* 1020; Anal. Calc. for $Fe_4C_{48}H_{30}P_2O_8$. C, 56.47, H, 2.94. Found: C, 55.43, H, 2.76%.

‡ *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 = 293 K $Fe_4C_{48}H_{30}P_2O_8$, M_r = 1020.09, triclinic, space group $P\bar{1}$, a = 9.3789(10), b = 11.2897(10), c = 12.1423(10) Å, α = 104.14(1), β = 101.70(1), γ = 114.35(1)°, D_c = 1.588 g cm^{-3}, $F(000)$ = 517, Z = 1, μ = 1.46 mm^{-1}, 2θ(max) = 48°, R (R_w) = 2.8% (4.0%) for 2930 reflections [$I > 2.5\sigma(I)$] and 323 parameters. For **3**: intensity data: Siemens CCD diffractometer using Mo-Ka radiation and ω-scan mode; T = 293 K $Fe_3C_{48}H_{32}P_2O_8$, M_r = 982.23, triclinic, space group $P\bar{1}$, a = 11.1911(10), b = 11.6675(15), c = 16.9642(12) Å, α = 97.960(10), β = 93.137(10), γ = 94.407(10)°, $F(000)$ = 1003, D_c = 1.495 g cm^{-3}, Z = 2, μ = 1.11 mm^{-1}, 2θ(max) = 49°, R (R_w) = 5.59% (6.70%) for 6857 reflections [$I > 2\sigma(I)$] and 567 parameters. CCDC 182/567.

§ Spectroscopic data for **3**; IR(CH_2Cl_2) ν(CO) 2049m, 2025s, 1979m, 1968m(sh), 1911w cm^{-1}; ^1H NMR ($CDCl_3$): δ 7.8–6.5 (m, Ph); ^{31}P NMR ($CDCl_3$): 67.08 (s) ppm (85% H_3PO_4): MS(FAB+) m/z 964; Anal.Calcd. for $Fe_3C_{48}H_{30}P_2O_8.H_2O$, C, 58.66, H, 3.05; Found, C, 58.20, H, 3.13 %.

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