Single and Double Carbon–Carbon Bond Formation in an Ethenylidene Bridged Di-iron Complex. *X*-Ray Crystal Structure of a 3,3-Dicyanoallenylidene Bridged Di-iron Complex

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Tetracyanoethylene reacts with $[Cp_2Fe_2(\mu\text{-}CO)(\mu\text{-}P\text{–}P)(\mu\text{-}C{=}CH_2)]$ ($Cp{=}\eta^5\text{-}C_5H_5$) [P–P = 1,2-bis(diphenylphosphino)ethane = dppe, or P–P = bis(diphenylphosphino)methane = dppm] to give the μ-3,4,4-tricyanobuta-1,3-dienylidene complexes $[Cp_2Fe_2\ (\mu\text{-}CO)(\mu\text{-}P\text{–}P)\ \{\mu\text{-}C{=}CH\text{–}C(CN){=}C(CN)_2\}]$ exhibiting strong absorption in their visible spectra, and the μ-dicyanoallenylidene complex $[Cp_2Fe_2(\mu\text{-}CO)(\mu\text{-}P\text{–}P)\{\mu\text{-}C{=}C{=}C(CN)_2\}]$ whose structure has been determined by *X*-ray diffraction (P–P = dppe).

Pursuing our studies of the reactions of unsaturated cyanocarbons with alkenylidene bridged di-iron complexes,[1] we wish to report herein a further example of a buta-1,3-dienylidene bridged complex, with promising optical properties, as well as the first example of a di-iron complex containing a bridging allenylidene ligand.

The new† green complex $[Cp_2Fe_2(\mu\text{-}CO)(\mu\text{-}dppe)(\mu\text{-}C{=}CH_2)]$ (**2**) ($Cp = \eta^5\text{-}C_5H_5$, dppe = $Ph_2P\text{–}CH_2\text{–}CH_2\text{–}PPh_2$), prepared in 80% yield by refluxing the ethenylidene complex[2] $[Cp_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}C{=}CH_2)]$ (**1**) and dppe in toluene (see Scheme 1), reacts instantaneously with a stoicheiometric amount of tetracyanoethylene (tcne) (dichloromethane, room temperature, dinitrogen atmosphere) to give an intense violet solution. Column chromatography of the reaction mixture gives first a green band, then a violet one. The latter is shown to contain, by comparison with the previously[1b] *X*-ray characterised $[Cp_2Fe_2(CO)_2(\mu\text{-}CO)\{\mu\text{-}C{=}CH\text{–}C(CN){=}C(CN)_2\}]$, the 3,4,4-tricyanobuta-1,3-dienylidene bridged di-iron complex† $[Cp_2Fe_2(\mu\text{-}CO)(\mu\text{-}dppe)\{\mu\text{-}C{=}CH\text{–}C(CN){=}C(CN)_2\}]$ (**3**) (yield 60%). Whereas all the other diphosphine bridged di-iron complexes described herein are green to green–brown, (**3**) exhibits an intense violet colour. A strong band is observed in its visible absorption spectrum (λ_{max} = 539 nm, ε = 25 700 l mol^{-1} cm^{-1}), and this is in connection with the use of the electron withdrawing tricyanobutadienyl unit in the design of organic dyes:[3] here, its association with the strongly electron donating $Cp_2Fe_2(\mu\text{-}CO)(\mu\text{-}dppe)$ moiety leads to a new class of organometallic dyeing materials.

The green crystalline complex (**4**), isolated from the first band (yield 17%) exhibited analytical and spectroscopic features that did not unambiguously define its nature† (i.r. band at 1837 cm^{-1} that could not be assigned to any carbonyl absorption; ^{13}C n.m.r. triplet due to coupling to ^{31}P at δ 173, and singlets at δ 201 and 39). The structure of (**4**) was determined by an *X*-ray diffraction analysis‡ (see Figure 1). Compound (**4**) is the rare 3,3-dicyanoallenylidene bridged di-iron complex $[Cp_2Fe_2(\mu\text{-}CO)(\mu\text{-}dppe)\{\mu\text{-}C{=}C{=}C(CN)_2\}]$. The dicyanoallenylidene ligand bridges symmetrically the two iron atoms (at a single bond distance) in the μ-σ,σ (2e) mode as observed in the case of dimanganese,[4a] ditungsten,[4c] and mixed manganese–iron[4b] complexes. This differs from the dimolybdenum complex[4d] $[Cp_2Mo_2(CO)_4\{\mu\text{-}C{=}C{=}C(CH_3)_2\}]$ where the μ-σ,η^2 (4e) mode is adopted.

Striking features in the structure of (**4**) are (i), the almost equal bonding parameters of the CO and $C{=}C{=}C(CN)_2$ bridging ligands with respect to the di-iron core; (ii), a

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† The new complexes gave satisfactory elemental analyses and/or spectroscopic data in accord with their proposed structure.

Selected spectroscopic data (i.r. and vis. in CH_2Cl_2, n.m.r. in $CDCl_3$ unless stated otherwise, coupling constants in Hz): $[Cp_2Fe_2(\mu\text{-}CO)(\mu\text{-}dppe)(\mu\text{-}C{=}CH_2)]$ (**2**): green–brown crystals, i.r. $\nu_{(CO)}$ 1705 (br) cm^{-1}; ^{1}H n.m.r. δ 6.81 (br-t, $^4J_{PH}$ 3, 2H, $\mu\text{-}C{=}CH_2$), 4.16 (10H, C_5H_5); $^{31}P\{^1H\}$ n.m.r. δ 69.1 (s); ^{13}C n.m.r. δ 297.1 (t, $^2J_{PC}$ 15, $\mu\text{-}C{=}CH_2$), 288.6 (t, $^2J_{PC} \approx 30$, μ-CO), 123.6 (t, $^1J_{CH}$ 155, $\mu\text{-}C{=}CH_2$), 86.3 (d, $^1J_{CH}$ 176, C_5H_5), 20.8 (dt, $^1J_{PC}$ 26, $^1J_{CH}$ 132, $\text{–}CH_2\text{–}P{<}$).

$[Cp_2Fe_2(\mu\text{-}CO)(\mu\text{-}dppe)\{\mu\text{-}C{=}CH\text{–}C(CN){=}C(CN)_2\}]$ (**3**): violet crystals, i.r. $\nu_{(CN)}$ 2195 (m), $\nu_{(CO)}$ 1740 (m-br), $\nu_{(C{=}C)}$ 1445 (s-br) cm^{-1}; ^{1}H n.m.r. δ 9.39 (t, $^4J_{PH}$ 1.9, 1H, $\mu\text{-}C{=}CH\text{–}$), 4.61 (s, 10H, C_5H_5); $^{31}P\{^1H\}$ n.m.r. δ 61.8 (s); ^{13}C n.m.r. [0.075 M $Cr(acac)_3$] δ 378.5 (t, $^2J_{PC}$ 16, $\mu\text{-}C{=}$), 283.8 (t, $^2J_{PC}$ 29, μ-CO), 141.0 (d, $^1J_{CH}$ 154, $\mu\text{-}C{=}CH\text{–}$), 121.7 [s, $\mu\text{-}C{=}CH\text{–}C(CN){=}C(CN)_2$], 117.6, 116.9, 116.2 (s, CN), 89.2 (d, $^1J_{CH}$ 178, C_5H_5) 58.3 [s, $\mu\text{-}C{=}CH\text{–}C(CN){=}C(CN)_2$], 20.8 (dt, $^1J_{PC}$ 30, $^2J_{PH}$ 145, $\text{–}CH_2\text{–}P{<}$); vis. λ_{max} 539 nm (ε 25 700 l mol^{-1} cm^{-1}).

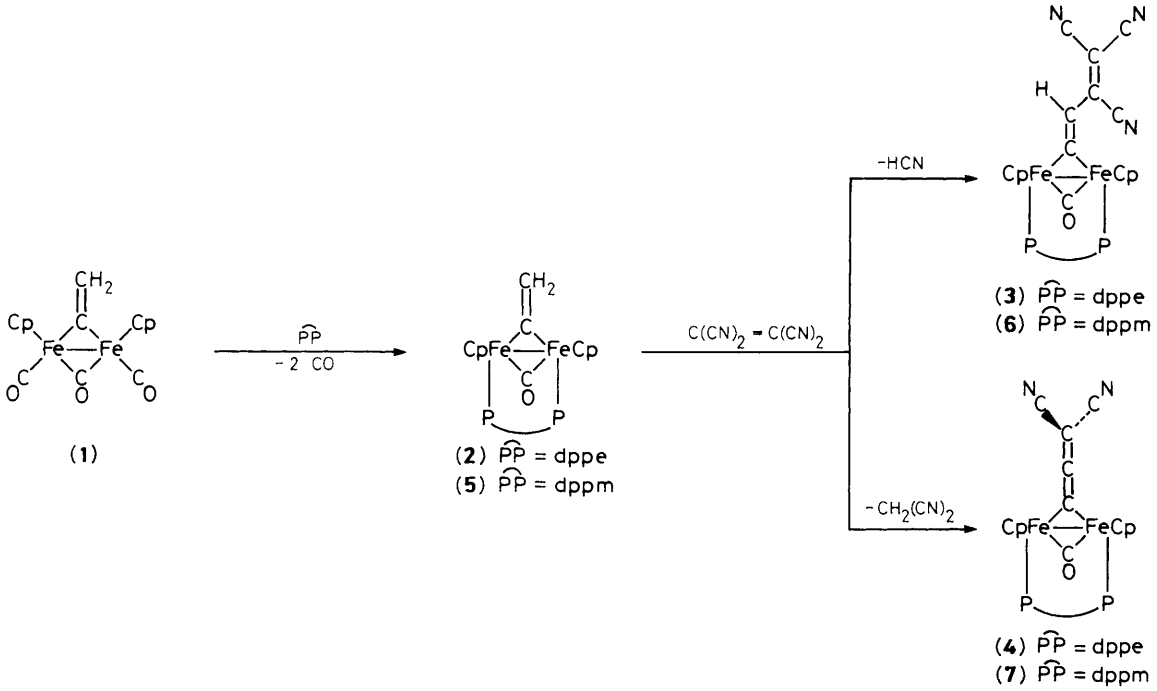
$[Cp_2Fe_2\ (\mu\text{-}CO)(\mu\text{-}dppe)\{\mu\text{-}C{=}C{=}C(CN)_2\}]$ (**4**): green crystals, i.r. $\nu_{(CN)}$ 2200, 2190 (m), $\nu_{(\mu\text{-}C{=}C{=}C{<})}$ 1837 (m), $\nu_{(CO)}$ 1737 (m-br cm^{-1}); ^{1}H n.m.r. δ 4.39 (C_5H_5); $^{31}P\{^1H\}$ n.m.r. δ 63.6 (s); $^{13}C\{^1H\}$ n.m.r. [0.075 M $Cr(acac)_3$] δ 280.2 (t, $^2J_{PC}$ 15, μ-CO), 201.2 [s, $\mu\text{-}C{=}C{=}C(CN)_2$], 173.1 [t, $^2J_{PC}$ 17, $\mu\text{-}C{=}C{=}C(CN)_2$], 119.3, 117.4 (s, CN), 86.1 (s, C_5H_5), 39.5 [s, $\mu\text{-}C{=}C{=}C(CN)_2$], 20.9 (d, $^1J_{PC}$ 27, $\text{-}CH_2\text{–}P{<}$).

$[Cp_2Fe_2(\mu\text{-}CO)(\mu\text{-}dppm)(\mu\text{-}C{=}CH_2)]$ (**5**): green crystals, i.r. $\nu_{(CO)}$ 1705 (br) cm^{-1}; ^{1}H n.m.r. δ 6.58 (t, $^4J_{PH}$ 3.2, 2H, $\mu\text{-}C{=}CH_2$), 4.31 (s, 10H, C_5H_5); $^{31}P\{^1H\}$ n.m.r. δ 87.9 (s).

$[Cp_2Fe_2(\mu\text{-}CO)(\mu\text{-}dppm)\{\mu\text{-}C{=}CH\text{–}C(CN){=}C(CN)_2\}]$ (**6**): violet crystals, i.r. $\nu_{(CN)}$ 2195 (s), $\nu_{(CO)}$ 1755 (m-br), $\nu_{(C{=}C)}$ 1445 (s-br) cm^{-1}; ^{1}H n.m.r. δ 9.32 (t, $^4J_{PH}$ 2.2, 1H, $\mu\text{-}C{=}CH\text{–}$), 4.68 (s, 10H, C_5H_5); $^{31}P\{^1H\}$ n.m.r. δ 79.6 (s); $^{13}C\{^1H\}$n.m.r. [0.075 M $Cr(acac)_3$] δ 379.0 (t, $^2J_{PC}$ 17, μ-C), 280.5 (t, $^2J_{PC}$ 14, μ-CO), 140.1 (s, $\mu\text{-}C{=}CH\text{–}$), 120.8 [s, $\mu\text{-}C{=}CH\text{–}C(CN){=}C(CN)_2$], 117.5, 116.6, 115.8 (s,CN), 88.8 (s, C_5H_5), 57.7 [s, $\mu\text{-}C{=}CH\text{–}C(CN){=}C(CN)_2$], 25.2 (t, $^1J_{PC}$ 26, ${>}P\text{–}CH_2\text{–}P{<}$).

$[Cp_2Fe_2(\mu\text{-}CO)(\mu\text{-}dppm)\{\mu\text{-}C{=}C{=}C(CN)_2\}]$ (**7**): green crystals, i.r. $\nu_{(CN)}$ 2200, 2190 (m), $\nu_{(\mu\text{-}C{=}C{=}C)}$ 1835 (m), $\nu_{(CO)}$ 1740 (m-br)cm^{-1}; ^{1}H n.m.r. δ 4.53 (s, 10H, C_5H_5); $^{31}P\{^1H\}$ n.m.r. δ 82.4 (s); $^{13}C\{^1H\}$n.m.r. δ 282.9 (t, $^2J_{PC}$ 15, μ-CO), 199.3 [s, $\mu\text{-}C{=}C{=}C(CN)_2$], 176.0 [t, $^2J_{PC}$ 19, $\mu\text{-}C{=}C{=}C(CN)_2$], 119.4, 117.2 (s, CN), 86.3 (s, C_5H_5), 40.4 [s, $\mu\text{-}C{=}C{=}C(CN)_2$], 26.1 (t, $^1J_{PC}$ 23, ${>}P\text{–}CH_2\text{–}P{<}$).

‡ *Crystal data* for $Fe_2P_2C_{42}H_{34}ON_2$, CH_2Cl_2 (**4**): M = 840.3, monoclinic; space group *C*2/c, a = 22.222(8), b = 13.677(5), c = 25.746(9)Å, β = 103.44(3)°, U = 7610.4(8)Å^3, Z = 8, D_x = 1.467 Mg m^{-3}, $\lambda(\text{Mo-}K_\alpha)$ = 0.71069Å, μ = 10.2 cm^{-1}, $F(000)$ = 3456, T = 296 K; R = 0.048, R_w = 0.045 for 3550 independent [$I > 2\sigma(I)$] diffractometer (Enraf-Nonius CAD4) reflections out of 6786 measured (h 0—26, k 0—16, l −30—30, $2\theta \leq 50°$, $\omega/2\theta$ = 1 scan). The structure was solved by direct methods; all non-hydrogen atoms and a CH_2Cl_2 molecule were located after a difference Fourier map. All atoms were refined isotropically (R = 0.08) then anisotropically (R = 0.060). At this stage, the majority of hydrogen atoms were defined from a difference Fourier map (0.43—0.12 eÅ^{-3}), the others being defined from calculation. The best full matrix refinement (x,y,z, βij, non-hydrogen atoms and x,y,z hydrogen atoms) gave R = 0.048, R_w = 0.045. 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.



Scheme 1

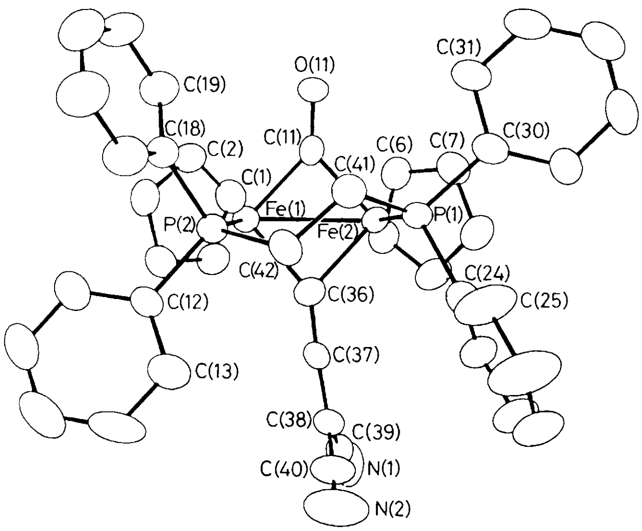


Figure 1. ORTEP drawing of [$Cp_2Fe_2(\mu\text{-}CO)(\mu\text{-}dppe)\{\mu\text{-}C{=}C{=}C(CN)_2\}$] (**4**). Relevant bond distances (Å) and angles (°): Fe(1)–Fe(2) 2.515(1), Fe(1)–C(11) 1.913(6), Fe(2)–C(11) 1.922(6), Fe(1)–C(36) 1.916(6), Fe(2)–C(36) 1.937(6), C(11)–O(11) 1.186(4), C(36)–C(37) 1.258(5), C(37)–C(38) 1.345(6); Fe(1)–C(11)–Fe(2) 81.9(2), Fe(1)–C(36)–Fe(2) 81.5(2), C(36)–C(37)–C(38) 173.8(5).

somewhat short C(36)–C(37) bond [1.258(5) Å] indicating a bond order between two and three, whereas the C(37)–C(38) bond [1.345(6) Å] remains a normal double carbon–carbon bond.[4c] These observations may explain some relevant ^{13}C n.m.r. spectroscopic data such as (i), the comparable magnitude of the phosphorus to carbon ($^2J_{PC}$) coupling constants between dppe and the bridgehead carbons of CO($^2J_{PC}$ 15 Hz) and $C{=}C{=}C(CN)_2$ ($^2J_{PC}$ 17 Hz); (ii), the 'surprising low field' resonance (δ 173) of the bridgehead carbon of the dicyanoallenylidene ligand, comparable to that of a bridging alkylidene carbon.[5]

To our knowledge, this is the first time that the conversion of an ethenylidene (C_2 fragment) bridged complex into an allenylidene (C_3 fragment) has been observed, with a double carbon–carbon bond being formed. This is completely new compared with previously known syntheses.[4] A close observation of the ^1H n.m.r. spectrum of the reaction mixture shows malononitrile (δ 3.6) to be the other product of this reaction. The radical anion tcne$^{-\bullet}$ has been identified by its characteristic e.s.r. spectrum as the sole radical species, and examination of the redox properties [cyclic voltammetry (c.v.), dichloromethane, Bu_4NPF_6 as supporting electrolyte, glassy carbon electrode, scan rate 0.2 V s^{-1}, and $Fc^{+\bullet}/Fc$ as reference potentials] of tcne ($E_{1/2}$ [tcne/tcne$^{-\bullet}$] = −0.17 V) and complex (**2**) ($E_{1/2}$[(**2**)/(**2**)$^{+\bullet}$] = −0.40 V) support a single electron transfer as the first step of these reactions.

The bis(diphenylphosphino)methane (dppm) analogues of (**2**), (**3**), and (**4**), respectively (**5**), (**6**), and (**7**), have also been prepared,† albeit in lower yield for (**6**) (see Scheme 1).

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