

Stepwise Synthesis of Tropone from Ethyne and Carbon Monoxide at a Di-iron Centre: Crystal Structure of $[\text{Fe}_2(\text{CO})_4(\mu\text{-C}_6\text{H}_6\text{CO})(\mu\text{-Ph}_2\text{PCH}_2\text{PPh}_2)]$

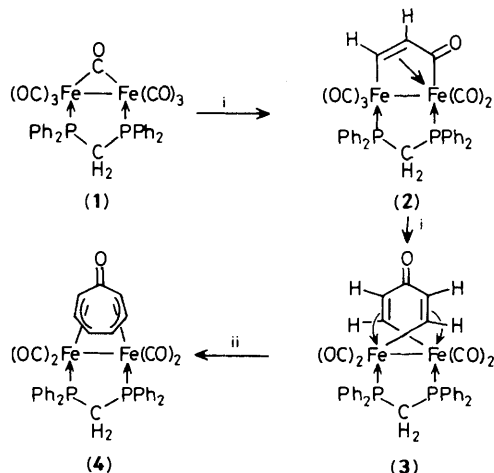
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Treatment of $[\text{Fe}_2(\text{CO})_7(\mu\text{-dppm})]$ (dppm = $\text{Ph}_2\text{PCH}_2\text{PPh}_2$) with ethyne under u.v. irradiation results in the stepwise linking of one, two, and three molecules of ethyne with carbon monoxide, yielding $[\text{Fe}_2(\text{CO})_5(\mu\text{-C}_2\text{H}_2\text{CO})(\mu\text{-dppm})]$, $[\text{Fe}_2(\text{CO})_4(\mu\text{-C}_4\text{H}_4\text{CO})(\mu\text{-dppm})]$, and the tropone complex $[\text{Fe}_2(\text{CO})_4(\mu\text{-C}_6\text{H}_6\text{CO})(\mu\text{-dppm})]$; the structure of the latter has been established by X-ray diffraction.

The reactions of alkynes with metal carbonyls have proved a valuable source of cyclic carbonyl-containing organic compounds, such as cyclopentadienones, quinones, lactones, and cycloheptatrienone (tropone).¹ For example, it has been known for over 25 years that treatment of $[\text{Fe}_2(\text{CO})_9]$ or $[\text{Fe}_3(\text{CO})_{12}]$ with ethyne yields (tropone)tricarbonyliron, from which the hydrocarbon is readily displaced.² However,

no other species were detected in these reactions and the manner of the tropone ring formation has remained obscure. We now report that substitution of bis(diphenylphosphino)methane (dppm) into $[\text{Fe}_2(\text{CO})_9]$ results in the stabilisation of the di-iron centre, permitting the isolation of a di-iron tropone complex and the intermediates in its construction.

U.v. irradiation (500 W mercury vapour lamp, silica vessel) of a toluene solution of $[\text{Fe}_2(\text{CO})_7(\mu\text{-dppm})]$ (1)³ while purging with ethyne gives the complexes $[\text{Fe}_2(\text{CO})_5(\mu\text{-C}_2\text{H}_2\text{CO})(\mu\text{-dppm})]$ (2),[†] $[\text{Fe}_2(\text{CO})_4(\mu\text{-C}_4\text{H}_4\text{CO})(\mu\text{-dppm})]$



Scheme 1. Reagents: i, u.v., $-\text{CO}$, $+\text{HC}_2\text{H}$; ii, u.v., $+\text{HC}_2\text{H}$.

[†] The new complexes were characterised by elemental analyses and 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: (2), red crystals, $\nu(\text{CO})$ at 2043m, 1975s, 1960sh, 1923w, 1747w, and 1725w cm^{-1} ; ^1H n.m.r. δ 3.63 [dd, $J(\text{HH})$ 7, $J(\text{HP})$ 2, CHCHCO] and 8.63 [ddd, $J(\text{HH})$ 7, $J(\text{HP})$ 4 and 19, CHCHCO]; $^{13}\text{C}\{^1\text{H}\}$ n.m.r. δ 44.8 [d, $J(\text{CP})$ 11, CHCHCO], 168.4 [d, $J(\text{CP})$ 22, CHCHCO], and 210.6 (s, CHCHCO); $^{31}\text{P}\{^1\text{H}\}$ n.m.r. ($[\text{C}_6\text{H}_6]$ toluene) δ 52.03 and 67.92 [AB q, $J(\text{PP})$ ca. 117]. (3), orange crystals, $\nu(\text{CO})$ at 2010m, 1985s, 1950s, and 1657m cm^{-1} ; ^1H n.m.r. δ 3.86 [d, $J(\text{HH})$ 7, 2H, CHCHCO] and 8.17 [q, $J(\text{HH}) = J(\text{HP}) = 7$, 2H, CHCHCO]; $^{13}\text{C}\{^1\text{H}\}$ n.m.r. δ 80.0 [t, $J(\text{CP})$ 3, CHCHCO], 177.8 [t, $J(\text{CP})$ 7, CHCHCO], and 204.4 (s, CHCHCO); ^{31}P n.m.r. δ 50.85 (s). (4), brown crystals, $\nu(\text{CO})$ at 1994m, 1962s, 1935w, 1907sh, and 1551w cm^{-1} ; ^1H n.m.r. δ 3.09 [d, $J(\text{HH})$ 7, 2H], 3.93 (s, br, 2H), and 4.36 (s, br, 2H) ($\text{C}_6\text{H}_6\text{CO}$); $^{13}\text{C}\{^1\text{H}\}$ n.m.r. δ 61.2, 66.3, 71.7 (singlets, $\text{C}_6\text{H}_6\text{CO}$), and 191.3 (s, $\text{C}_6\text{H}_6\text{CO}$); $^{31}\text{P}\{^1\text{H}\}$ n.m.r. δ 59.06 (s).

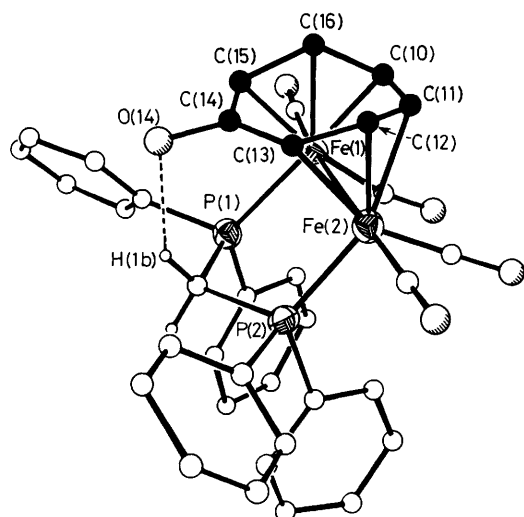


Figure 1. Molecular structure of (4), with tropone and phenyl group hydrogens omitted for clarity. Important bond lengths (Å) include: Fe(1)–Fe(2) 2.950(1), Fe(1)–P(1) 2.242(1), Fe(2)–P(2) 2.235(1), Fe(1)–C(15) 2.134(6), Fe(1)–C(16) 2.034(5), Fe(1)–C(10) 2.173(5), Fe(2)–C(11) 2.177(6), Fe(2)–C(12) 2.025(5), Fe(2)–C(13) 2.133(6), C(14)–O(14) 1.261(7), C(14)–C(15) 1.471(8), C(15)–C(16) 1.420(8), C(16)–C(10) 1.385(8), C(10)–C(11) 1.453(8), C(11)–C(12) 1.395(8), C(12)–C(13) 1.420(8), C(13)–C(14) 1.436(8).

(3),[†] and $[\text{Fe}_2(\text{CO})_4(\mu\text{-C}_6\text{H}_6\text{CO})(\mu\text{-dppm})]$ (4)[†] as air-stable crystalline products. Complex (2) was obtained in optimum yield (63%) after about 1 h, complex (3) (28%) after 2 h, and complex (4) (25%) after 4 h. This indication of a (1) → (2) → (3) → (4) sequence of formation (see Scheme 1) was confirmed by the reaction of (2) and (3) separately with ethyne, when (3) and (4) were produced respectively. Reaction of (1) with tropone under u.v. irradiation does not afford (4) directly.

The molecular structures of (2) and (4) (as its 1,2-dichloroethane solvate) were determined by X-ray diffraction. That of (2) is described in the accompanying communication,⁴ which outlines the thermally-induced isomerisation of the complex; the results for (4) are shown in Figure 1 and in its caption.[‡]

The di-iron unit of (4), which features an unusually long Fe–Fe bond [2.950(1) Å], is symmetrically bridged by dppm

and tropone ligands, with each iron atom carrying two terminal CO ligands. The tropone interacts with each iron in an η^3 manner as a di- η -allyl ligand. As a consequence the tropone ring is considerably distorted from planarity. The large Fe–Fe distance may in part be due to the demands of the tropone in this η^3, η^3 binding mode. The μ -dppm ligand adopts an unusual geometry, with the $\text{Fe}_2\text{P}_2\text{CH}_2$ ring folded in an envelope conformation which allows close approach of the methylene hydrogen H(1b) to the tropone oxygen [H(1b)···O(14) 2.32 Å] in a weak C–H···O interaction.

Complexes $[\text{Fe}_2(\text{CO})_6(\mu\text{-C}_4\text{R}_4\text{CO})]$, analogous to (3), are obtained from iron carbonyls and substituted alkynes,⁵ but they do not react further to yield tropone complexes and no precursor of type (2) has been characterised. On the other hand, while type (2) metallacycles have been obtained by the linking of ethyne with CO at another di-iron centre⁶ (and also Ru_2 ,⁶ FeRu ,⁷ and FePt ⁸ centres), these systems do not link a second ethyne to generate a species like (3). Only in the sequence (1) → (2) → (3) → (4) of Scheme 1 is the nature of the step-wise build-up of tropone clearly revealed, and seen to occur at a dinuclear metal centre. Presumably, the reaction of an unsubstituted iron carbonyl with ethyne follows a similar sequence to give an analogue of (4), $[\text{Fe}_2(\text{CO})_6(\mu\text{-C}_6\text{H}_6\text{CO})]$, which disintegrates under the reaction conditions to afford the observed product (tropone)tricarbonyliron.² In contrast, the tropone ligand appears firmly bound in (4); treatment of the complex with CO or Me_3NO does not effect its release.

We suggest that the tropone in (4) is created by successive co-ordination of ethyne to vacant sites on iron, made available by photochemically-induced release of CO [from (1) and (2)] or an olefinic double bond [from (3)], followed by rapid carbon–carbon bond formation. Preliminary study of reactions of (1), (2), and (3) with unsymmetrically substituted alkynes indicates that derivatives of (2), (3), and (4) are produced, the nature of which promises to shed light on the factors controlling the carbon–carbon bond-formation processes.

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[‡] Crystal data for (4) (1,2-dichloroethane solvate): $\text{C}_{36}\text{H}_{28}\text{Fe}_2\text{O}_5\text{P}_2\cdot\text{C}_2\text{H}_4\text{Cl}_2$, $M = 813.2$, orthorhombic, space group $P2_12_12_1$ (No. 19), $a = 11.589(3)$, $b = 15.822(4)$, $c = 19.428(7)$ Å, $U = 3562(2)$ Å³, $T = 294$ K, $Z = 4$, $D_c = 1.51$ g cm⁻³, $F(000) = 1664$, graphite-monochromated Mo- K_α X-radiation, $\lambda = 0.71069$ Å, $\mu(\text{Mo-}K_\alpha) = 10.9$ cm⁻¹. The structure was solved by heavy atom methods and refined by least squares to $R 0.040$ for 2972 unique, observed, profile-fitted, absorption-corrected data measured in one octant of reciprocal space for $3 < 2\theta < 50^\circ$. The handedness of the crystal studied was confirmed by refinement [$\eta = 1.2(5)$]. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.