Synthesis and Crystal Structure of An Unusual Trinuclear Ferracyclobutene Complex, $Fe_3(CO)_8[Ph_2PC_4(CF_3)_2](PPh_2)$

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Summary The molecular structure of a ferracyclobutene complex $Fe_3(CO)_8(Ph_2PC_4(CF_3)_2)(PPh_2)$, obtained from the room-temperature reaction of $Fe_3(CO)_{12}$ with $Ph_2PC{\equiv}CCF_3$, has been determined by X-ray crystallographic techniques.

A FASCINATING and recurring feature of the reactions of alkynes with metal carbonyls is the formation of organometallic ring systems *via* oligomerization of the acetylene. Thus 1,1,1-tricarbonylferracyclopentadiene-π-tricarbonyliron complexes are major components in the mixture of products obtained from the reaction of $Fe_3(CO)_{12}$ with alkynes.[1] Metallocyclopentadienes have also been characterized for rhodium,[2] iridium,[3] and palladium.[4] A few six-membered metallocyclic rings are known and, recently, a seven-membered nickelacycloheptatriene complex $Ni[C_6(CF_3)_6][AsPhMe_2]_2$ has been described.[5]

We have characterized the first example of a ferracyclobutene complex, $Fe_3(CO)_8[Ph_2PC_4(CF_3)_2](PPh_2)$ (I) as one of several products from the reaction of $Fe_3(CO)_{12}$ with

$Ph_2PC{\equiv}CCF_3$. Compound (I) is a rare example of a complex containing an acyclic dimerized acetylene.

Careful chromatography of the mixture obtained from the reaction of $Fe_3(CO)_{12}$ with $Ph_2PC{\equiv}CCF_3$ (L), in benzene at room temperature affords small amounts of (I) as well as the following products: $Fe_3(CO)_{11}L$, $Fe_3(CO)_{10}L_2$, $Fe(CO)_3L_2$, $Fe_3(CO)_8(Ph_2P)[Ph_2PC_4(CF_3)_2]$[6] (II) and two, as yet, uncharacterized trinuclear complexes. The complexes (I) and (II) can also be obtained by warming $Fe_3(CO)_{10}L_2$ in benzene. Physical measurements (i.r., n.m.r., mass spectra and Mössbauer spectra) on (I) and (II) suggest a marked similarity in the structures of the two complexes. An X-ray structure determination was undertaken and has revealed the isomeric nature of the two compounds.

Crystal data: $Fe_3(CO)_8[Ph_2PC_4(CF_3)_2](PPh_2),C_6H_6$, $M = 1026{\cdot}2$. Red triclinic crystals, space group $P\bar{1}$, $a = 11{\cdot}738(6)$, $b = 14{\cdot}110(6)$, $c = 14{\cdot}753(4)$ Å, $\alpha = 97{\cdot}26(3)$, $\beta = 92{\cdot}35(4)$, $\gamma = 112{\cdot}31(4)^\circ$, $U = 2231{\cdot}9(1{\cdot}6)$ Å^3, $D_m = 1{\cdot}5$ g cm^{-3}, $Z = 2$, $D_c = 1{\cdot}527$. The structure has been refined to $R = 0{\cdot}079$ for the 4059 observed reflections measured with a computer-controlled diffractometer, using graphite-monochromatized Mo-K_α-radiation.

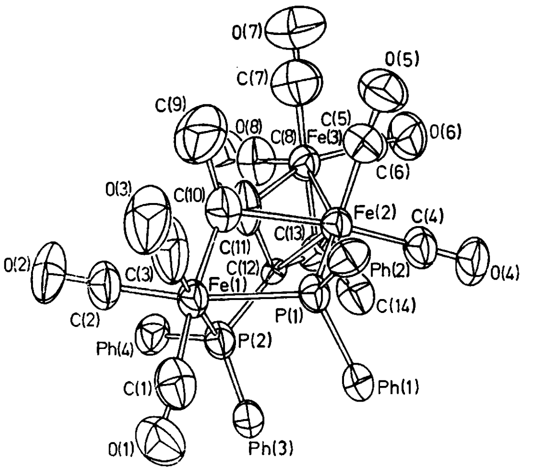
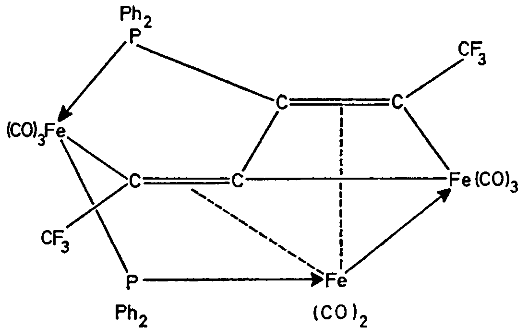


FIGURE. A view of the $Fe_3(CO)_8[Ph_2PC_4(CF_3)_2](Ph_2P)$ molecule showing the molecular shape, atomic numbering, and the thermal ellipsoids.

The structure and atomic numbering are illustrated in the Figure. The dimerization of two phosphino-acetylene molecules has produced a *trans*-butadiene unit. The carbon atoms C(11) and C(13) of the butadiene unit are co-ordinated to Fe(3) forming a nearly planar ferracyclobutene ring. The Fe–C distances [Fe(3)–C(11) of 2·021(13) and Fe(3)–C(13) of 1·959(12) Å] are comparable to the Fe–C distances in (II) (av. 1·964 Å) and other ferracyclopentadiene complexes.[7] However, the Fe(3)–C(11)–C(12)–C(13) ring is quite unsymmetrical [C(11)–C(12) is 1·535(16) Å and C(12)–C(13) is 1·240(14) Å] because of the multiple character of the C(12)–C(13) bond. Fe(3) is also linked to Fe(2) *via* a metal–metal bond of 2·514(3) Å which is similar to the Fe(2)–Fe(3) distance of 2·554(2) Å in (II), and the distances of 2·531(2) and 2·534(2) Å reported for *cis*- and *trans*-$(\pi\text{-}C_5H_5)_2Fe_2(CO)_4$, respectively.[8] The Fe(2) atom is also bonded in π-fashion to the *trans*- C(10)–C(11) and C(12)–C(13) multiple bonds. The Fe(1)–Fe(2) and Fe(1)–Fe(3) distances are both greater than 3·45 Å which precludes any metal–metal bonding between these atoms.



The presence of a bridging phosphido group between Fe(1) and Fe(2) implies a cleavage of the P–C(*sp*) bond of the parent phosphino-acetylene, which is somewhat surprising considering the mild reaction conditions. However, accumulating evidence[6,9] suggests that P–C bond rupture is a common feature of reactions between phosphino-acetylenes and iron carbonyls. Presumably, the strain induced by attempting to co-ordinate both the phosphorus atom and the alkyne unit simultaneously leads to P–C bond cleavage.

A consideration of the molecular structure leads to a valence-bond representation (A) for (I) which is very similar to that proposed for (II).[6] The similarities of the chemical bonding in (I) and (II) raise the question of whether the isomers might be interconvertible under appropriate experimental conditions. Finally, it is noteworthy that while (I) and (II) are both formed in the reaction of $Fe_3(CO)_{12}$ with $Ph_2PC{\equiv}CCF_3$, ferracyclobutene complexes analogous to (I) have not yet been isolated from the reaction of $Fe_3(CO)_{12}$ with other acetylenes.

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