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Preliminary communication

SYNTHESIS AND X-RAY STRUCTURE OF $Fe_2(CO)_6[P(C_6F_5)_2]$-$[(C_6F_5)_2PC_4(C_6H_5)_2]$: A NEW TYPE OF ORGANOIRON COMPLEX CONTAINING A 3-ELECTRON DONOR PHOSPHORUS HETEROCYCLE

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Summary

A new five-membered phosphorus heterocycle coordinated to two iron atoms in the binuclear complex $Fe_2(CO)_6[(C_6F_5)_2PC_4(Ph)_2]P(C_6F_5)_2$ is formed in the reaction of $Fe_2(CO)_9$ with $(C_6F_5)_2PC{\equiv}CPh$. An X-ray structural study revealed that the heterocycle, a derivative of 1-bis(pentafluorophenyl)-phosphonia-2,5-diphenyl-2,4-cyclopentadiene functions as a symmetrical *dihapto*, bridging 3*e* ligand in I.

The coupling of acetylenes promoted by transition metal carbonyls has led to the characterisation of several unusual, cyclic hydrocarbon ligands often stabilised by coordination to a metal*. The possible use of heteroatom-substituted acetylenes in the analogous synthesis of new heterocyclic ligands has, by comparison, received little attention**. We describe herein the structure of a binuclear complex $Fe_2(CO)_6[(C_6F_5)_2P][(C_6F_5)_2PC_4(Ph)_2]$ (I) in which a heterocyclic 3,4-*dihapto*-1-phosphoniacyclopentadiene ligand formed in the reaction of the phosphinoacetylene $(C_6F_5)_2PC{\equiv}CPh$ with $Fe_2(CO)_9$ is coordinated as a 3-electron donor to a diiron hexacarbonyl moiety. Although a number of examples are known where a two carbon fragment can be formally considered as an unsymmetrical 3-electron donor [3], the symmetrical h^2 bonding in I appears unprecedented.

The sealed tube reaction of $(C_6F_5)_2PC{\equiv}CPh$ with $Fe_2(CO)_9$ at 75° in benzene gave, after chromatography on alumina, a red diamagnetic compound analyzing as I together with smaller quantities of a yellow complex of unknown structure. The infrared spectrum of I (CCl_4; 2063vs 2034vs, 2002s 1996s 1981w cm^{-1}) indicated a symmetrical binuclear structure in agreement with the

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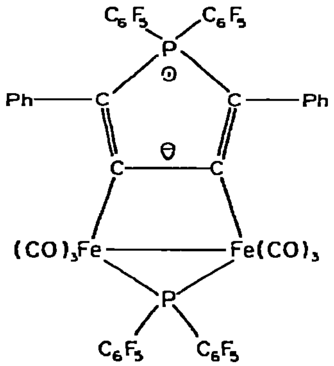
[*] For recent reviews see ref. 1.

[**] A number of metallocycles and linear dimers with phosphorus substituents have been synthesized in this way. See for example ref. 2.



(I)

appearance of only one pair of Mössbauer lines (δ 0.28; Δ 0.28 mm s^{-1}) typical of iron atoms in equivalent, near octahedral environments. Since the IR spectrum did not correspond with the spectra of other binuclear phosphinoacetylene complexes, an X-ray study of I was undertaken. Crystals of I (from CH_2Cl_2/benzene) are monoclinic, space group $P2_1/c$, a = 16.183(11), b = 11.524(18), c = 24.546(25) Å, β = 98.76(14)°; Z = 4; ρc = 1.779, ρm = 1.80 g cm^{-3}. The structure was solved by a combination of Patterson and Fourier techniques using the intensities of 4296 ($I \geqslant 3\sigma(I)$) observed reflections measured via the stationary crystal-stationary counter method out to $2\theta \leqslant 45°$ on a GEXRD6 automatic diffractometer with Mo-K_α radiation. Refinement by full matrix least squares techniques with anisotropic thermal parameters for all non-hydrogen atoms has reduced R, the usual residual, to 0.087.

An ORTEP plot of the molecular structure is shown in Fig. 1. Each iron atom in the binuclear complex is coordinated in pseudooctahedral fashion to 3 carbonyl groups, a bridging bis(pentafluorophenyl)phosphide, one carbon atom of a symmetrical 1-bis(pentafluorophenyl)phosphonia-2,5-diphenyl-2,4-cyclopentadiene and a second iron atom via a metal—metal bond of length 2.697 (2) Å. The principal structural feature is the planar, five-membered phosphorus heterocycle*. The C(7)—C(8) (1.38(2) Å) and C(9)—C(10) (1.37(2) Å) distances are significantly shorter (3σ) than the C(8)—C(9) bond length (1.44(2) Å) while the P(2)—C(7) (1.79(1) Å) and P(2)—C(10) (1.82(1) Å) distances are comparable to P—C(sp^2) single bond lengths in the $MePh_3P^+$ cation [4] and related phosphonium salts [5]. Thus the ring system can be envisaged as a phosphoniadiene rather than an ylide. The bonding of the heterocycle to the iron atoms is of interest since an electron count indicates that if the bridging phosphide utilizes its 3-electron donor capacity the organic ligand must behave as a 3-electron donor for both iron atoms to obey the 18e rule. The iron carbon distances (Fe(1)—C(8) of 1.99(1) Å and Fe(2)—C(9) of 1.97(1) Å) are 0.1 Å shorter than the predicted Fe—C(sp^2) single bond length [6] but rather similar to Fe—C distances in ferracyclopentadiene rings [7] where some degree of multiple bonding may be present. In view of the geometrical features of the phosphoniadiene and the near planarity of the Fe(1)—Fe(2)—C(9)—C(8) ring**and the heterocycle, the metal—

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*Atomic displacements from a least squares plane through the heterocycle are as follows: P(2) (0.010 Å); C(7) (0.013 Å); C(8) (—0.039 Å); C(9) (0.049 Å); C(10) (—0.034 Å).

**Maximum displacements from a least squares plane are Fe(1) (—0.056 Å); Fe(2) (0.057 Å); C(8) (—0.108 Å); C(9) (—0.107 Å).

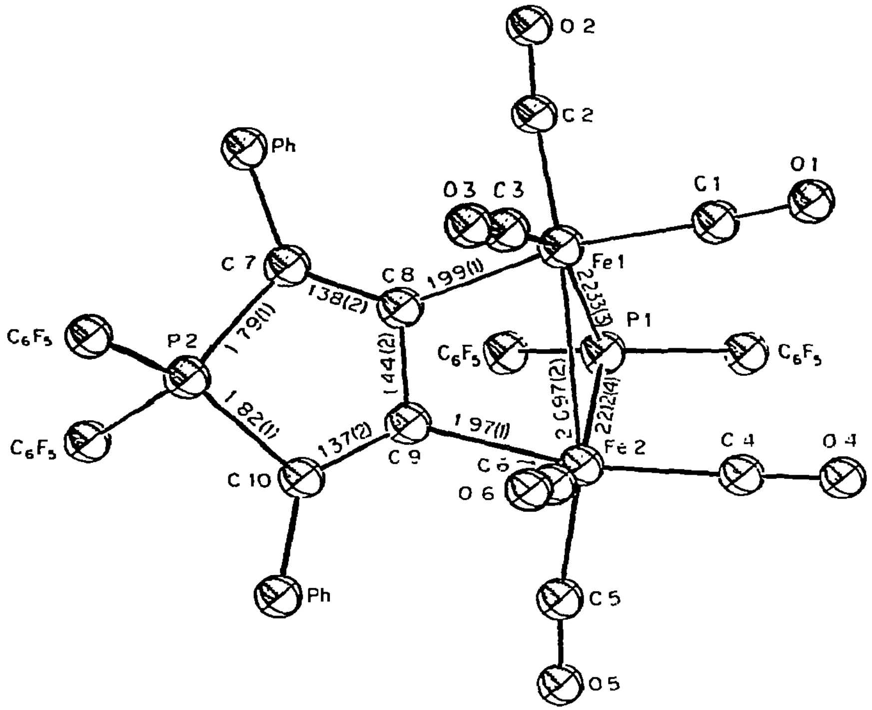

Fig. 1. A view of the molecular structure of $Fe_2(CO)_6[P(C_6F_5)_2][(C_6F_5)_2PC_4(C_6H_5)_2]$ drawn by the programme ORTEP. For the sake of clarity only one carbon atom of each C_6F_5 or C_6H_5 ring is shown.

ring bonding could with some justification be described in terms of the structure I. In this context, the formulation of I as a phosphonium salt complex bears a formal resemblance to the stabilized alkyls prepared by Schmidbauer and coworkers from methylenetrimethyl phosphorane [8].

The synthesis of a phosphacycle from two molecules of $(C_6F_5)_2PC{\equiv}CPh$ implies the cleavage of two P—C(*sp*) bonds and the coupling of two PhC≡C-moieties. We believe that the formation of I may proceed via cycloaddition of a phosphinoacetylene to a σ—π-acetylide complex analogous to $Fe_2(CO)_6(C{\equiv}CPh)$-PPh_2 [3b], followed by a rearrangement. Experiments designed to test this hypothesis and the synthesis of other phosphacycles via metal carbonyl reactions are in progress.

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