Structural Characterisation of an Acetylenic Diphosphine Derivative of π-Cyclopentadienyliron Dicarbonyl Dimer: an Unusual Mössbauer Effect

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Summary Mössbauer spectroscopy has failed to detect the nonequivalent iron atoms in the novel compound $[(\pi\text{-}C_5H_5)_2Fe_2(CO)_3]_2\cdot Ph_2PCCPPh_2$ which has been characterised by i.r., n.m.r., and X-ray studies.

RECENT interest in ditertiary phosphine derivatives of cyclopentadienyl metal carbonyls[1] and in the use of Mössbauer spectroscopy for the structural characterisation of organometallic molecules[2] prompts us to report our spectral and X-ray diffraction results for a product of the reaction of bis(diphenylphosphino)acetylene (DPPA) with $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2$.

The u.v. irradiation of a benzene or acetone solution of $[\pi\text{-}C_5H_5Fe(CO)_2]_2$ and DPPA yields green crystals of a compound analysing as $[(\pi\text{-}C_5H_5)_2Fe_2(CO)_3]_2$DPPA (I). The i.r. spectrum of (I) suggests the presence of both terminal and bridging carbonyl groups (mull: 1953s, 1910w, 1765w, 1724s; benzene solution: 1960m,br, 1780m, 1732vs; *cf.* $(\pi\text{-}C_5H_5)_2Fe_2(CO)_4$[3] mull: 2000sh,w, 1965s, 1950s, 1782s, 1770s; benzene solution: 1998m, 1953m, 1803sh, 1783s). The absence of any absorption at 2100 cm.$^{-1}$ argues against a monodentate diphosphine.[4] In the n.m.r. spectrum of a benzene solution, two cyclopentadienyl resonances occur as a singlet (τ 5·78) and a doublet (τ 5·61, $^3J_{PH}$ 1·8 Hz.). The above data and the ligand geometry[4] suggest the structure shown in the Figure.

The Mössbauer spectra at 295 and 77° K showed quadrupole splittings of 1·95 and 1·94 mm./sec. with isomer shifts (compared with sodium nitroprusside) of 0·45 and 0·53 mm./sec. Line widths for the two quadrupole split lines were 0·24 mm./sec. and 0·26 mm./sec. at 295° K and 0·28 mm./sec. and 0·31 mm./sec at 75° K compared with 0·26 mm./sec. for sodium nitroprusside at room temperature. These values are similar to the related parameters in other iron carbonyl complexes[2] (although the larger quadrupole splittings suggest a more asymmetric iron atom) but are unexpected for a structure with two nonequivalent iron atoms. An X-ray crystal structure study of (I) was undertaken to resolve the conflict in the n.m.r., i.r. and Mössbauer studies.

Crystal data: $Fe_4(CO)_6(C_5H_5)_4Ph_2PCCPPh_2$, monoclinic, a = 10·135(5), b = 23·293(13), c = 9·794(4) Å, β = 107·99 (4)°, D_m = 1·54 g./cm.^{3}, D_c = 1·58 g./cm.^{3}. Z = 2; space group $P2_1/c$ (No. 14).

The intensities of 1392 non-zero independent reflections were measured using Cu-K_α radiation. The structure was solved by the heavy-atom method and refined by least-squares methods (iron and phosphorus atoms with anisotropic thermal parameters) to an R of 11·5%.

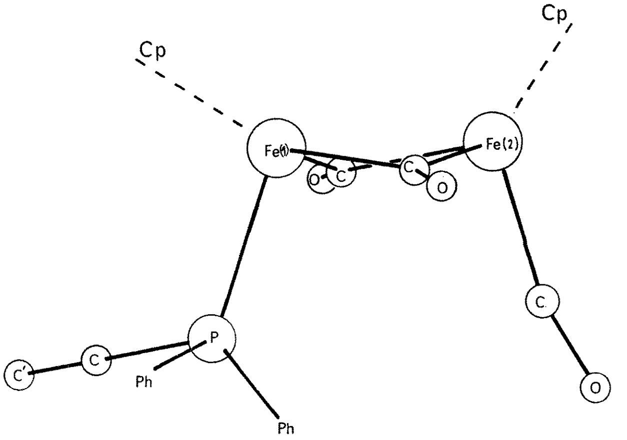

FIGURE. *Idealized view of half of the* $[(\pi\text{-}C_5H_5)_2Fe_2(CO)_3]_2\cdot Ph_2PCCPPh_2$ *molecule. A centre of symmetry exists between* C *and* C′. *The* $\pi\text{-}C_5H_5$ *groups are represented by* Cp.

The molecule consists of two $Fe_2(CO)_3(\pi\text{-}C_5H_5)_2$ units linked by a DPPA molecule situated on a centre of symmetry; see Figure. The $Fe_2(CO)_2$ ring is nonplanar with a dihedral angle of 20°. The two $\pi\text{-}C_5H_5$ rings are *cis* relative to the Fe–Fe bond. The Fe–Fe distance of 2·54 Å compares favourably with the distance found in other molecules.[5a] The average Fe–C ($\pi\text{-}C_5H_5$ ring) distance of 2·15 Å, which is longer than in other $\pi\text{-}C_5H_5$–Fe compounds,[5b] may be rationalized in terms of steric repulsion between the $\pi\text{-}C_5H_5$ rings and the phenyl groups of the DPPA.

In an attempt to explain the Mössbauer data, isomer shifts for the nonequivalent iron atoms were calculated.[2b] Requisite partial shifts were taken from the literature and a value for DPPA (δ = 0·055 mm./sec.) was evaluated from data on related DPPA complexes.[6] Calculated isomer shifts are [Fe(1) = 0·539; Fe(2) = 0·556]. Although this difference is extremely small and beyond resolution, two resonances would still be observable if there were different electric field gradients at the two sites. Since this is not the case, we conclude that DPPA has much the same effect on the electronic environment of the metal as a terminal CO group. These data clearly illustrate the dangers which can arise from the inference of structure based solely on Mössbauer data, particularly when large organic groups such as π-C_5H_5 are present.

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[1] R. J. Haines, A. L. DuPreez, and G. T. W. Wittmann, *Chem. Comm.*, 1968, 611.

[2] (a) W. R. Cullen, D. A. Harbourne, B. V. Liengne, and J. R. Sams, *Inorg. Chem.*, 1969, **8**, 95; (b) R. H. Herber, *Prog. Inorg. Chem.*, 1967, **8**, 1.

[3] A. R. Manning, *J. Chem. Soc.* (*A*), 1968, 1319.

[4] A. J. Carty and A. Efraty, *Inorg. Chem.*, 1969, **8**, 543.

[5] (a) M. R. Churchill, *Inorg. Chem.*, 1967, **6**, 191; (b) M. R. Churchill and J. Wormald, *Inorg. Chem.*, 1969, **8**, 716.

[6] T. Birchall, A. J. Carty, and T. W. Ng, to be published.