The *cis*-Isomer of Bis-(π-cyclopentadienyldicarbonyliron)

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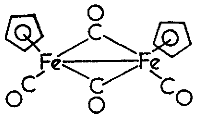
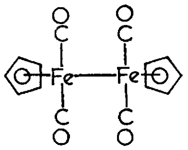
Summary The existence of the *cis*-isomer of [π-$C_5H_5Fe(CO)_2]_2$ in the solid state has been established by i.r. and *X*-ray methods.

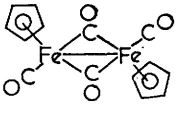
THE i.r. spectrum of bis-(π-cyclopentadienyldicarbonyliron) has been interpreted[1] as indicating the presence, in solution, of the *cis*-isomer (I), the non-bridged isomer (II), and the *trans*-isomer (III). Until now† only the *trans*-isomer (III) has been known in the solid state.[2]



(I)



(II)



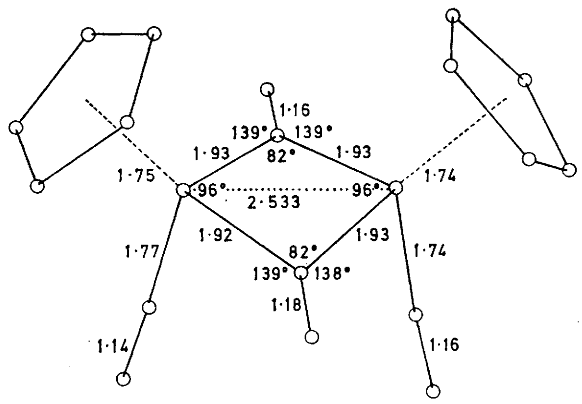
(III)

We have found that recrystallisation of the commercially available dimer from either methylene chloride or ethyl acetate at −78° gives crystals of the *cis*-isomer (I). These crystals have the same colour, general appearance, and decomposition point as those of (III), and the solution i.r. and mass spectra of both crystalline forms are very similar. However, the i.r. spectra taken in KBr discs show major differences in the ν_{CO} region [(I): 1971vs, 1930vs, 1797sh, 1765vs; (III): 1950vs, 1931vs, 1930sh, 1765vs, 1752vs, 1726sh], the probable δ_{CH} region [(I): 853, 844, 832, 828; (III): 839, 827], and the probable $\delta_{MCO}/\nu_{MC(1)}$ region [(I): 611, 594, 561, 540, 520; (III): 589, 561, 539 cm^{-1}].

The results of a single-crystal *X*-ray diffraction study have confirmed that the crystals isolated at low temperature are indeed of the *cis*-isomer.

Crystal data: $[C_5H_5Fe(CO)_2]_2$, monoclinic, $a = 8{\cdot}880(2)$, $b = 12{\cdot}301(3)$, $c = 13{\cdot}140(3)$ Å, $\beta = 108{\cdot}64(1)°$, $D_m = 1{\cdot}73$, $D_c = 1{\cdot}73$ g./cm^3, $Z = 4$. Space group $P2_1/c$. 1549 independent intensities, Mo-K_α radiation, scintillation counting by diffractometry. Structure solved by heavy-atom method, refined by block-diagonal least-squares techniques with anisotropic thermal parameters to $R = 0{\cdot}058$.

The molecular structure is shown in the Figure.



FIGURE

The molecule has an almost totally eclipsed configuration and the basic structure is very similar to that reported[4] for the isoelectronic anion $[B_9C_2H_{11}Fe(CO)_2]_2^{2-}$ except that the Fe–Fe separation is shorter and the carbonyl bridge symmetrical. The mean Fe–C distance to the rings is 2·12 Å comparable to the 2·13 Å observed in the anion, and as in that complex the angles Fe–Fe–Cp (135°) are considerably larger than the values observed in single-ring complexes.[5] This is caused by repulsions between the hydrogen atoms of the two cyclopentadienyl rings. The bridging $Fe_2(CO)_4$ group is non-planar, the dihedral angle about the Fe–Fe axis being 16°.

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† Very recently[3] the structure of an acetylenic diphosphine derivative of the dimer has been reported where the cyclopentadienyliron dicarbonyl moieties are in the *cis*-conformation.

[1] A. R. Manning, *J. Chem. Soc.* (*A*), 1968, 1319; R. D. Fischer, A. Vogler, and K. Noack, *J. Organometallic Chem.*, 1967, **7**, 135; K. Noack, *ibid.*, p. 150; F. A. Cotton and G.Yagupsky, *Inorg. Chem.*, 1967, **6**, 15; K. Noack, *J. Inorg. Nuclear Chem.*, 1963, **25**, 1383; F. A. Cotton, H. Stammreich, and G. Wilkinson, *ibid.*, 1959, **9**, 3.

[2] O. S. Mills, *Acta Cryst.*, 1958, **11**, 620.

[3] A. J. Carty, T. W. Ng, W. Carter, G. Palenik, and T. Birchall, *Chem. Comm.*, 1969, 1101.

[4] P. T. Greene and R. F. Bryan, *Acta Cryst.*, 1969, *A* **25**, S170.

[5] R. F. Bryan, *J. Chem. Soc.* (*A*), 1967, 192.