The Preparation and Crystallographic Characterization of *trans*-1,4-Bis(dicarbonyl-π-cyclopentadienyliron)buta-1,3-diene: a Complex with an Anomalous Proton Magnetic Resonance Spectrum†

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THE mildly exothermic reaction of π-$C_5H_5Fe(CO)_2Na$ with *cis*-3,4-dichlorocyclobutene[1] in tetrahydrofuran produces (in 60—70% yield) the orange crystalline complex $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2C_4H_4$ confirmed by analysis. The room temperature ^1H n.m.r. spectrum (in tetrahydrofuran) shows two sharp singlets at τ 3·76 and 5·05 (relative intensity 2 : 5). This preliminary information led us to believe that the material was some unusual type of cyclobutadiene complex, and prompted an *X*-ray crystallographic investigation of the material.

Crystal data: $C_{18}H_{14}Fe_2O_4$, $M = 405\cdot70$, monoclinic, $a = 6\cdot794(5)$, $b = 11\cdot471(10)$, $c = 11\cdot787(7)$ Å, $\beta = 113\cdot14(2)$, $U = 844\cdot7$ Å^3, $D_m = 1\cdot60(1)$, $Z = 2$, $D_c = 1\cdot596$; space group $P2_1/c$ (No. 14), requiring the molecule to be centrosymmetric. Complete three-dimensional diffraction data to $\sin\theta = 0\cdot38$ [Mo-K_α radiation; $\lambda = 0\cdot7107$ Å] were collected with a 0·01°-incrementing Buerger automated diffractometer, and the structure was solved by means of conventional Patterson, Fourier, and least-squares refinement procedures. All atoms (including hydrogen) have been located, the final *R* being 5·48% for 989 independent non-zero reflections.

The complex is *trans*-1,4-bis(dicarbonyl-π-cyclopentadienyliron)buta-1,3-diene (Figure 1). The molecule has exact C_i symmetry and the Fe–C(1)–C(2)–C(2′)–C(1′)–Fe′ system is closely planar, as are the π-cyclopentadienyl rings. The Fe–C(1) bond length (1·987 ± 0·005 Å) is 0·12 Å shorter than the Fe–C single bond in $(\pi\text{-}C_5H_5)Fe(CO)_2$-$(\sigma\text{-}C_5H_5)$,[2] thus indicating partial double-bond character in this Fe–C linkage. (This is in keeping with previous studies which have shown metal–carbon bond contraction in perfluoroalkyls,[3] acyls,[4] and aryls.[5]) Carbon–carbon bond lengths

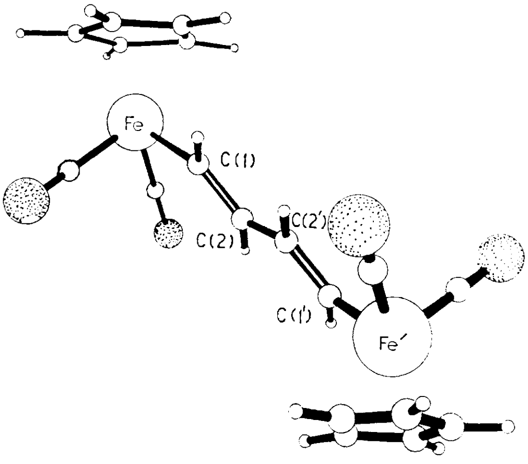

FIGURE 1

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† An independent crystallographic study of this molecule has also been made by Professor R. E. Davis (following Communication).

within the butadiene fragment are: C(1)–C(2) = C(1′)–C(2′) = 1·340 ± 0·007 and C(2)–C(2′) 1·450 ± 0·011 Å. All other dimensions are in the usual ranges.

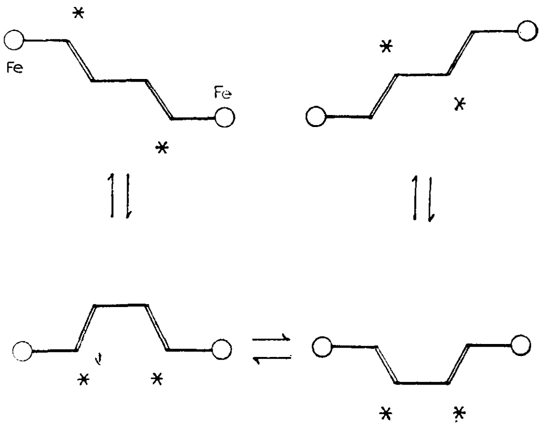

FIGURE 2

The i.r. spectrum in the solid (KBr pellet) and in solution (tetrahydrofuran or *sym*-$C_2H_2Cl_4$) are essentially identical, special features being two carbonyl stretches (~2000 and ~1950 cm.$^{-1}$) and a band at ~1515 cm.$^{-1}$, possibly due to a carbon–carbon double bond. [A similar absorption is observed for $(\pi\text{-}C_5H_5)Fe(CO)_2(\sigma\text{-}C_2H_3)$.[6]]

The remaining problem with the compound is to understand its ^1H n.m.r. spectrum. The peak at τ 5·05 is evidently due to the protons of the π-cyclopentadienyl system, so that the sharp singlet at τ 3·76 must include all four protons of the 1,4-disubstituted butadiene system.

Two explanations would appear possible:

(i) the protons on C(1) and C(2) are accidentally equivalent. This seems unlikely due both to their difference in chemical environment, and to a comparison with $(\pi\text{-}C_5H_5)Fe(CO)_2(\sigma\text{-}C_2H_3)$ where the analogous proton resonances are at τ 3·07 and 4·68; (ii) the molecule is stereochemically non-rigid and some process allows the interconversion of C(1) and C(1′) with C(2) and C(2′). This seems rather more likely, especially since the τ 3·76 resonance is found to be broadened at −65° in tetrahydrofuran. Lack of solubility in appropriate solvents has so far precluded our obtaining a limiting spectrum, but Figure 2 shows a possible mechanism for interconversion of the C(1) and C(2) protons.

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