X-Ray Structure of the Non-classically Bonded Carbonium Ion $[\{(\eta^5\text{-}C_5H_5)Fe(CO)_2\}_2(C_3H_5)]^+$

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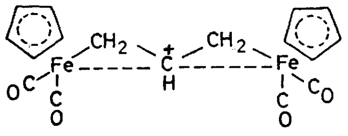
Summary In the cation $[\{(\eta^5\text{-}C_5H_5)Fe(CO)_2\}_2(C_3H_5)]^+$, each Fe atom is joined by a strong σ-bond to a CH_2 group and by a weak link to the β-CH group of the allylic system.

King and Bisnette[1] showed that a hydride ion could be removed from the β-CH_2 group of $[\{(\eta^5\text{-}C_5H_5)Fe(CO)_2\}_2(CH_2)_3]$ (I) to yield a stable cation (II). Subsequent studies on (II)[2] and related compounds[3] have led to the suggestion that the cation is 'fluxional' rather than in 'dynamic equilibrium' between extreme σ- and π-bonded forms.[1,2]

Crystals of the PF_6^- salt of (II) were prepared by crystallization from acetone. They are monoclinic, space group $P2_1/n$, $a = 16\cdot52(1)$, $b = 9\cdot96(1)$, $c = 12\cdot65(1)$ Å, $\beta = 108\cdot6(1)°$, $U = 1972\cdot5$ Å^3, $D_m = 1\cdot80(2)$ g cm^{-3}, $Z = 4$, $M = 540$. Data were measured on a Philips four-circle diffractometer with graphite-monochromated Mo-K_α radiation ($\lambda = 0\cdot7107$ Å) for θ between 3 and 25°. The structure was solved from the three-dimensional Patterson map and refined by block-diagonal least-squares to $R = 0\cdot073$ for 2548 observed data (Fe atoms, PF_6, and CO groups anisotropic, all H atoms included).†



(II)

The Figure shows the structure of the cation and gives important bond lengths and angles; (II) is best represented as having the positive charge isolated on the β-carbon atom, *i.e.* similar to compound (IIIB) of ref. 1 and (IB) of ref. 2 but with additional weak Fe ··· CH bonds. The Fe-CH_2 lengths exceed 2·08 Å, the value observed in (I).[4] However, the Fe ··· CH separations of 2·59 and 2·72 Å are considerably shorter than the analogous non-bonded Fe ··· CH_2 separation of 3·07 Å found in (I). The Fe ··· CH attractions cause both the reduction of the Fe–CH_2–C angle from 115 in (I) to 98 and 91° and an increase in the OC–Fe–CH_2 angle from 87 in (I) to 96 and 99° for the CO group *cis* to the β-CH group. The difference between the

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† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

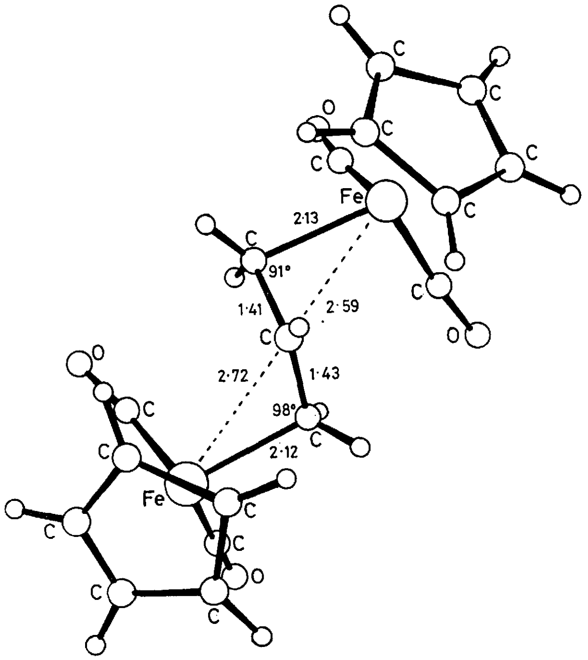

FIGURE. A projection of the cation (II) along the *y* axis. The cation closely approximates symmetry 2. Other angles of interest are: Fe $\cdots$ CH $\cdots$ Fe, 162 and CH_2–CH–CH_2, 126°. The C–C lengths in the cyclopentadienyl rings range between 1·36 and 1·43 Å while the Fe–C(cp) distances are between 2·08 and 2·12 Å. For the CO groups the ranges are: Fe–C, 1·77—1·78 and C–O, 1·13—1·15 Å.

two Fe $\cdots$ CH distances is probably caused by packing effects[5] because the lattice energy is of the same order of magnitude as the energy barrier to rotation about the CH_2–CH bond (14·6 kcal mol^{-1} in acetone) and the energy required to distort the structure to give unequal Fe $\cdots$ CH distances would not exceed *ca.* 1 kcal mol^{-1}. Weak Fe $\cdots$ CH interactions of this type have been postulated previously to explain various chemical reactions.[6]

This cation, which has been isolated in the crystal, is non-classically bonded with a rigid FeC_3Fe framework; thus the allylic hydrogens form an A_2B_2X system. One can conclude that this is the entity whose n.m.r. spectrum, measured at low temperatures [$(CD_3)_2CO$, −20 °C], shows the pattern of doublet of doublets at δ 2·25 (J_{AX} 14·0 and J_{AB} 2·8 Hz), doublet of doublets at δ 2·92 (J_{BX} 6·0 and J_{AB} 2·8 Hz), and triplet of triplets at δ 6·80 (J_{AX} 14·0 and J_{BX} 6·0 Hz) found for the PF_6^- salt of (II), which is typical of a rigid π-allylic A_2B_2X system.[7]

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