Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne
Printed in The Netherlands

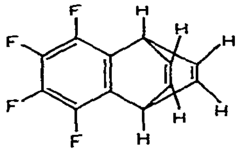
Preliminary communication

The structure of tetrafluorobenzobicyclo[2.2.2]octatrieneiron tricarbonyl, $C_{12}F_4H_6Fe(CO)_3$

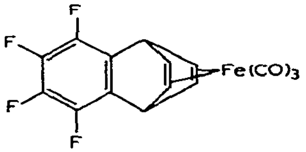
M.B. HURSTHOUSE, A.G. MASSEY, A.J. TOMLINSON* and D.S. URCH
Department of Chemistry, Queen Mary College, Mile End Road, London E.1. (Great Britain)

(Received December 6th, 1969)

Tetrafluorobenzobicyclo[2.2.2]octatriene (I) is formed by thermal decomposition of pentafluorophenyllithium or pentafluorophenylmagnesium bromide in benzene[1]. When refluxed with triiron dodecacarbonyl in petroleum ether, it forms a complex [$LFe(CO)_3$], which was assigned the structure (II) on the basis of spectroscopic studies. This has now been confirmed by a single crystal X-ray study, the preliminary results of which we now report.



(I)



(II)

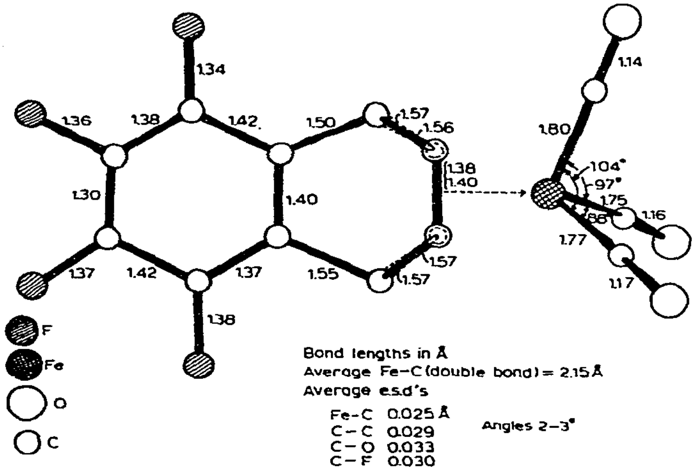
Well formed, orange-yellow crystals, obtained from 40/60 petroleum ether, belong to space group $P1$ with $a = 8.03(2)$, $b = 11.57(3)$, $c = 14.82(3)$Å, $\alpha = 90.0(3)$, $\beta = 103.0(3)$, $\gamma = 94.9(3)^\circ$. $D_m = 1.80$, $Z = 4$, $D_c = 1.77$ g·ml^{-1}. 1937 independent observed reflections were recorded by visual estimation from Weissenberg and precession photographs taken with MoK_α radiation. The structure was solved by standard heavy atom procedures and refined with isotropic temperature factors to a present R-factor of 0.13.

The geometries of the two molecules in the asymmetric unit are equivalent to within the limits of experimental error. Figure 1 shows a molecule viewed in the direction perpendicular to the mean plane of the tetrafluorobenzene part of the ligand. Some relevant bond parameters are included.

The coordination at the iron atom may be best described, at least geometrically, as square pyramidal with C_{14}, C_{15}, C_1 and C_4 forming the square base. If the mid points of the ethylene double bonds are chosen instead of C_1 and C_4, the Fe atom lies about 0.5Å above the mean basal plane. That no simple bonding scheme may be used is seen in

---

*Present address: University of Western Ontario, London, Ontario (Canada)



the spread of carbonyl–Fe–carbonyl angles and in the fact that an NMR study of this complex shows all four ethylenic protons to be equivalent.

However, we feel that the most convenient approach to a discussion of the bonding is to assume, in the first instance, that the atom adopts tetrahedral hybridisation of the 4*s* and 4*p* orbitals. Three hybrids are then used for bonding to the carbonyls and the fourth interacts with the diethylenic π-system.

The local symmetry of the two ethylenic bonds is C_{2v} and if the x axis is defined parallel to these, with the z axis pointing towards the Fe atom, then the bonding π orbitals on the double bonds belong to the irreducible representations a_1 and b_2, and the antibonding orbitals to a_2 and b_1. Considering now the local "T_d" symmetry about the Fe atom (*i.e.* assuming the diene system to be equivalent to a carbonyl group) the three carbonyl orbitals directed towards the Fe atom and the diethylenic a_1 orbital will belong to representations a_1 and t_2, and will form σ-bonds to the iron. π-Bonds will result from the six antibonding carbonyl orbitals and the b_1 and b_2 orbitals from the diethylenic group (e, t_1, t_2) interacting with the d orbitals on the iron (e and t_2). The neutral iron atom may be regarded as d^8, but the b_1 orbital is full so that the "inert gas rule" is in fact obeyed.

This simple picture will be somewhat perturbed by the large energy difference between the b_1 and b_2 orbitals and by the presence in the olefinic ligand of a fourth a_2 orbital which will interact with the $3d_{x^2-y^2}$ orbital on the iron. Even so, it would appear that the idea of tetrahedral hybridisation can be used as the basis for a simple description of the bonding in this molecule. The back donation through the π-bonds to the antibonding ethylenic orbitals accounts for the increase in length of the C=C bonds. Also it may be that the delocalisation of charge from the ethylenic bonds to the Fe atom causes the two olefinic groups to move closer together than they would be in the free ligand. We hope to investigate this possibility.

REFERENCES

1 S.C. Cohen, M.L.N. Reddy, D.M. Roe, A.J. Tomlinson and A.G. Massey, *J. Organometal. Chem.*, 14 (1968) 241.