The Electronic Structure of Trismethylenemethane Iron Tricarbonyl: Umbrella or Parachute?

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The synthesis of the trismethylenemethane iron tricarbonyl complex was reported by Emerson *et al.* in 1966.[1] The geometry of this compound in the gas phase was investigated in 1969 by Almenningen *et al.*,[2] using electron diffraction methods, and these authors pointed out some structural peculiarities which were not amenable to a simple explanation: in particular, it was questioned how the hypothetical planar $(CH_2)_3C$ radical could be distorted when bound to the $Fe(CO)_3$ fragment in such a way that the CH_2 carbons were displaced towards, and not away from, the iron atom (Fig. 1).

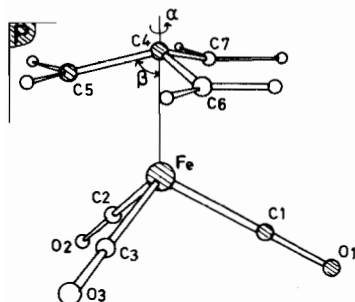Fig. 1. Geometry and numbering of the atoms.

The "attractive and repulsive regions of the bond energy *versus* (Fe···C) distance curve" were invoked[2] in order to explain this observation but it was surprising to find a stronger (Fe–C) bonding interaction for quite a long (2.123 Å) distance than for the shorter (1.938 Å) one. In other words, the question arose as to whether the real electronic structure of the complex was a so-called "umbrella" one (in which a fourth Fe–C strong bond existed along the iron–central carbon direction, this structure being supported by the "classical" relationship between interatomic distance and bond strength) or a "parachute" one (in which the Fe(0) atom would be at least hexacoordinated, that is, linked preferentially to the carbon atoms of the three CH_2 groups).

It is noteworthy that the latter structure (which is not in accord with the normal distance/bond strength relationship) was supported by a recent work of Finseth, Sourisseau and Miller[3] concerning the vibrational spectra and force field of the complex in question.

Thus the electronic structure of the trismethylenemethane iron tricarbonyl was investigated on the IBM 370/168 CNRS computer (CIRCE, Orsay–France) within the framework of the recently proposed extended CNDO/2 formalism.[4-7] The geometry which we used was that given by Almenningen[2] which is very similar to that of (CHC_6H_5)-$(CH_2)_2CFe(CO)_3$.[8]

Starting with an assumed planarity for the $(CH_2)_3C$ group, we first studied the variation of the total energy, E_{tot}, as a function of the angle of rotation, α (see Fig. 1) around the iron–central carbon direction: the staggered conformation was found to be more stable by 0.696 kJ mol^{-1} than the eclipsed one, in agreement with the experiment.[2]

Then, taking this staggered "planar" conformation as a standard, we studied the variation of E_{tot} as a function of the angle β (Fe–C$_4$–C$_5$) (equal to 90° for the reference). The minimum of the potential well was found at $\beta = 83°$, a value fairly close to the experimental one (76.4°).[2] In other words, theory provided naturally for a distorsion of the ligand atoms *towards* the iron atom. This being so, the electronic structure of the experimentally (staggered, 76.4°) observed conformation was computed: the net atomic charges Q_A, the Wiberg indices W_{AB}[9] and the bicentric components E_{AB} of the total energy (using Pople's partitioning[10]) are collected in Table I together with the corresponding Fe···C distances.

TABLE I. Net Atomic Charges, Wiberg Indices and Bicentric Components.

	Interatomic Distance (Å)	E_{AB} (u.a.)	W_{AB}
FeC$_1$	1.810	−0.31	0.60
FeC$_4$	1.938	−0.06	0.21
FeC$_5$	2.123	−0.30	0.46

Net Atomic Charges Q_A
Fe: 0.67; C$_1$: 0.09; C$_4$: 0.17; C$_5$: −0.30; O$_1$: −0.05; H: −0.01

The main result from these values is that there does not exist the expected simple, linear relation between bond strength – as measured by the E_{AB} – and interatomic distance. The E_{Fe-C_5} type terms are large, of the same order of magnitude as the E_{Fe-C_1} ones, despite the fact that the two corresponding Fe–C distances are extremely different (2.123 *versus* 1.810 Å). On the contrary, the intermediate Fe···C$_4$ distance corresponds surprisingly to an extremely weak bonding energy.

The reasons seem clear: the net atomic charges on Fe and C_4 are positive and there is a strong electrostatic repulsion (as supposed by Almenningen *et al.*) along the iron–central carbon line while, with respect to the negative net charge on the C_5-type atoms, a strong attractive component enhances the total E_{Fe-C_5} energy and consequently allows chemical bonds between Fe and the three C_5-type atoms to be set up.

The W_{Fe-C} Wiberg indices are small, as expected,[5] *i.e.* lower than unity. The same situation is observed for metal–carbon and metal–phosphorus bonds in metal carbonyls[5] and their phosphine derivatives[6,7] – in agreement with the correspondingly weak bond overlap populations obtained by *ab initio* calculations[11] and with the low force constants deduced from IR measurements.[12]

The total and differential isoenergy curve maps are shown in Figures 2 and 3, figure 3 emphasizing the general conclusions we have drawn above: taking as a reference the differential isoenergy curves along the Fe–C(0) bond, it is clear that the same situation occurs along the Fe–C_5 directions and not at all along the Fe–C_4 one, thus supporting the existence of a quasioctahedral coordination of the iron atom.
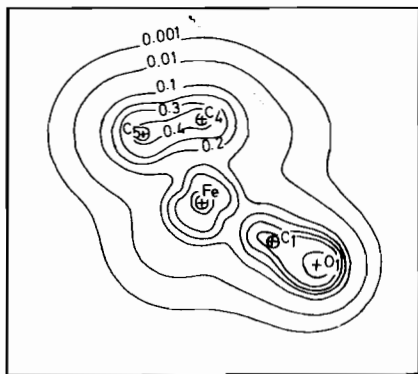

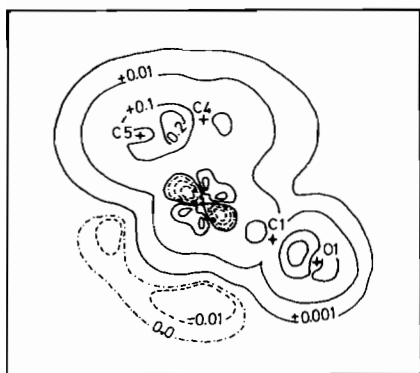Fig. 2. Total isoenergy curves map (within the P plane from figure 1).

Fig. 3. Differential isoenergy curves map (within the P plane from figure 1).

It may be noted that it would have been quite impossible to reach this conclusion from the total energy map, figure 2.

Our main conclusion is that one has to be extremely cautious to draw too much upon a relation between interatomic distance and bond strength in metal π-complexes with delocalised bonds. Indeed, in the case of the trismethylenemethane iron tricarbonyl complex, chemical bonds as generally defined exist for Fe–C distances equal to 2.123 Å while no bonding is found for the distance of 1.938 Å.*

Acknowledgments

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Note added in proof (July 7, 1976)

Examination of the $Fe(CO)_3$ and $(CH_2)_3C$ fragments molecular orbitals and of their relative energies (using Extended Hückel R. Hoffmann's work: *Inorg. Chem.*, 15, 1149 (1976)) indicates that one would expect stronger bonding of Fe to the outer three C atoms than to the central one; this is in complete agreement with our results and supports too the "parachute" electronic structure of $[(CH_2)_3C] Fe(CO)_3$. We thank Prof. R. G. Pearson for pointing this out to us.

*The above conclusion is supported by a study of the isoelectronic series from ethenylNi(CO)$_3$ to phenylCr(CO)$_3$[13] made by Dr. N. Fitzpatrick (University College, Dublin) during a recent visit to our Laboratory.