olysis,[1] oxidation to alcohols,[1] oxidation to ketones,[9c] amination,[9d] metalation,[9e] coupling with alkaline silver nitrate,[1] homologation,[9f] carbonylation[9g] to tertiary alcohols,[9h] ketones,[9i] aldehydes,[9j,k] methylol derivatives,[9l] acids,[9m] ring ketones,[9n] and polycyclics,[9o] propanalation,[9p-s] alkylation of α-halo-substituted esters[9t-v] and ketones,[9w-y] and the cyclopropane synthesis.[9z]

With the exception of the coupling reaction and the catalyzed propanalation reactions here described, these reactions appear to involve largely ionic or molecular pathways. The discovery that organoboranes can be made to participate in such clean free-radical addition processes opens up a major new area for exploration. Such a study is in progress.

(j) H. C. Brown, R. A. Coleman, and M. W. Rathke, *J. Amer. Chem. Soc.*, **90**, 499 (1968); (k) H. C. Brown, E. F. Knights, and R. A. Coleman, *ibid.*, **91**, 2144 (1969); (l) M. W. Rathke and H. C. Brown, *ibid.*, **89**, 2740 (1967); (m) H. C. Brown, G. W. Kabalka, and M. W. Rathke, *ibid.*, **89**, 4530 (1967); (n) H. C. Brown and E. Negishi, *ibid.*, **89**, 5477 (1967); (o) H. C. Brown and E. Negishi, *ibid.*, **89**, 5478 (1967); (p) A. Suzuki, A. Arase, H. Matsumoto, M. Itoh, H. C. Brown, M. M. Rogić, and M. W. Rathke, *ibid.*, **89**, 5708 (1967); (q) H. C. Brown, M. M. Rogić, M. W. Rathke, and G. W. Kabalka, *ibid.*, **89**, 5709 (1967); (r) H. C. Brown, M. M. Rogić, M. W. Rathke, and G. W. Kabalka, *ibid.*, **90**, 4165 (1968); (s) H. C. Brown, M. M. Rogić, M. W. Rathke, and G. W. Kabalka, *ibid.*, **90**, 4166 (1968); (t) H. C. Brown, M. M. Rogić, M. W. Rathke, and G. W. Kabalka, *ibid.*, **90**, 818 (1968); (u) H. C. Brown, M. M. Rogić, M. W. Rathke, and G. W. Kabalka, *ibid.*, **90**, 1911 (1968); (v) H. C. Brown and M. M. Rogić, *ibid.*, **91**, 2146 (1968); (w) H. C. Brown, M. M. Rogić, and M. W. Rathke, *ibid.*, **90**, 6218 (1968); (x) H. C. Brown, M. M. Rogić, H. Nambu, and M. W. Rathke, *ibid.*, **91**, 2147 (1969); (y) H. C. Brown and M. M. Rogić, *ibid.*, **91**, 4304 (1969); (z) H. C. Brown and S. Rhodes, *ibid.*, **91**, 2149 (1969).

(10) Graduate research assistant on Grant GM 10937 from the National Institutes of Health.

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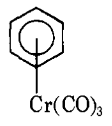
Bond Localization in Aromatic–Iron Carbonyl Complexes

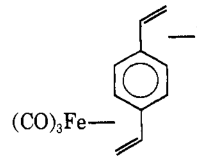
Sir:

The X-ray structural analysis of benzene–chromium tricarbonyl reveals that within experimental error the C–C bond distances of the benzene ring are equal[1,2] (1.40 Å). This molecule is then satisfactorily represented as in structure I, in which, by the standard convention, the circle implies uniform electron delocalization in the ring. We wish to report that in certain aromatic complexes containing the iron tricarbonyl moiety there is, in contrast to the above, a large degree of bond fixation in the ligand. This implies significant loss of π-electron delocalization, and the ligands are then better regarded as derivatives of 1,3,5-cyclohexatriene rather than of benzene.

Our interest in the present work stemmed from attempts to assign a suitable structural formula to *p*-divinylbenzene–diiron hexacarbonyl. This compound was first described by Stone and coworkers,[3] but, at the time it was reported, insufficient data were available to allow a detailed formulation. Using the effective atomic number rule as a guideline, several structures could be contemplated for this system. With an "aromatic" formulation analogous to I there is structure II or III; on the other hand, if classical structures were to be used then only formula IV is possible and a disposition of atoms similar to those in II is not feasible. In each case the two iron atoms could be *cis* or *trans* with respect to the ring. Initial nmr studies clearly indicated that the atoms are not disposed as in II, but the data were consistent with either formulation III or IV; this raised the question of possible bond fixation in the system. The implications of several X-ray studies of several iron tricarbonyl complexes containing aromatic ligands are now given.[4]



I



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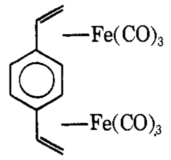

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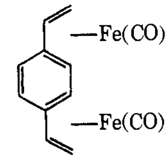
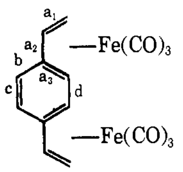
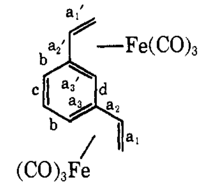


IV

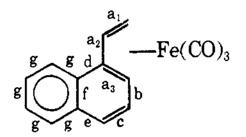
X-Ray analysis reveals the disposition of atoms in *p*-divinylbenzene–diiron hexacarbonyl,[3] *m*-divinylbenzene–diiron hexacarbonyl,[3] 1-vinylnaphthalene–iron tricarbonyl,[8] and 2-vinylnaphthalene–iron tricarbonyl[9] to be as indicated in formulas V–VIII, respectively. In the two diiron complexes the iron atoms are situated *trans* with respect to the ring. Bond distance data for these are summarized in Table I.



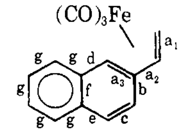
V



VI



VII



VIII

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(1) M. F. Bailey and L. F. Dahl, *Inorg. Chem.*, **4**, 1314 (1965).

(2) M. F. Bailey and L. F. Dahl, *ibid.*, **4**, 1298 (1965).

(3) T. A. Manuel, S. L. Stafford, and F. G. A. Stone, *J. Amer. Chem. Soc.*, **83**, 3597 (1961).

(4) Structure refinements are complete for *p*-divinylbenzene–diiron hexacarbonyl (V), *m*-divinylbenzene–diiron hexacarbonyl (VI), 1-vinylnaphthalene–iron tricarbonyl (VII), 2-vinylnaphthalene–iron tricarbonyl (VIII), and carbomethoxybenzocyclobutadiene–iron tricarbonyl (X) (R = COO CH_3), with final *R* values of 0.052, 0.043, 0.044, 0.052, and 0.093, respectively. Estimated standard deviations for these bonds are in the range 0.01–0.02 Å. Manuscripts reporting details of the structure determinations, final atomic parameters, and molecular geometry are in preparation.[5-7] The degree of reliability of the bond distances in Table I may also be seen from the reproducibility of the 18 Fe—C and the 18 C═O values. For all structures, single crystal intensity data were collected by the stationary crystal–stationary counter method on a General Electric XRD-5 diffractometer, using balanced filter pairs. All structures were solved by the heavy atom method and refined by block diagonal least-squares calculations.

(5) R. E. Davis, in preparation.

(6) M. Jenks and R. E. Davis, in preparation.

(7) J. D. Oliver and R. E. Davis, in preparation.

(8) T. A. Manuel, *Inorg. Chem.*, **3**, 1794 (1964).

(9) Prepared from 2-vinylnaphthalene and iron carbonyl.

Table I. Bond Distances (Å) of Iron Tricarbonyl Complexes

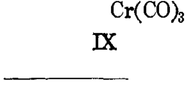
Bonds	V[a]	VI	VII	VIII[b] Molecule A	VIII[b] Molecule B
a_1, a_2, a_3	1.38, 1.42, 1.43	1.39, 1.41, 1.43	1.43, 1.43, 1.43	1.40, 1.41, 1.42	1.41, 1.41, 1.42
(a_1', a_2', a_3')		1.41, 1.42, 1.44			
b, b′	1.43	1.44, 1.44	1.45	1.44	1.46
c	1.31	1.33	1.33	1.33	1.31
d	1.45	1.47	1.46	1.45	1.45
e			1.43	1.46	1.46
f			1.44	1.41	1.43
g (av)			1.38 ± 0.03	1.39 ± 0.01	1.38 ± 0.01
Fe—C	1.78, 1.78, 1.80	1.79, 1.77, 1.80 1.77, 1.78, 1.79	1.77, 1.79, 1.81	1.79, 1.78, 1.80	1.80, 1.78, 1.79
C═O	1.14, 1.14, 1.14	1.14, 1.13, 1.13 1.15, 1.14, 1.13	1.14, 1.16, 1.12	1.13, 1.13, 1.13	1.13, 1.13, 1.13

[a] Crystals of the *p*-divinylbenzene complex have space group symmetry C2/c with $z = 4$, implying one-half molecule per asymmetric unit. A crystallographic twofold rotation axis passes through the midpoints of bonds c and d. [b] The space group symmetry of 2-vinylnaphthalene–iron tricarbonyl is $P2_1/c$ with $z = 8$. This corresponds to two independent molecules per asymmetric unit. These are referred to in Table I as "Molecule A" and "Molecule B."

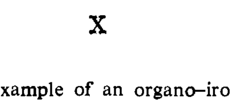
The most significant point which emerges from these data is that each ring attached to Fe contains one bond, not coordinated to iron, which has a length typical of that of an ethylenic bond (bond c); furthermore this particular bond is flanked by two significantly longer bonds. The data suggest that the aromaticity of the ring is largely destroyed through involvement of some of the "aromatic sextet" of electrons (formally four in the case of complexes V and VI) in coordination to the iron atom. It is of interest to note that in the naphthalene derivative the ring which is not involved in direct coordination retains its aromaticity.[10] It is also significant that the bond lengths of the two double bonds of the diene system coordinated to iron are similar to those in butadiene–iron tricarbonyl,[13] again suggesting no extensive delocalization of these with the other double bonds of the ring.

These findings are in accord with the rough qualitative observations concerning the stability of aromatic–iron tricarbonyl complexes. Thus styrene–iron carbonyl appears to be unstable. It has not yet been isolated and at least cannot be prepared under conditions which yield the divinylbenzene complexes. Apparently the concerted action of two iron tricarbonyl groups is required to overcome the benzene resonance energy. The destruction of the π-electron delocalization energy of one ring of naphthalene is energetically more favorable than for benzene, and in this case the monoiron complexes are stable.

The apparent effectiveness of an iron tricarbonyl group in localizing bonds in a hitherto aromatic ring is also seen in a comparison of the bond lengths in naphthalene–chromium tricarbonyl (IX) and the benzocyclobutadiene–iron tricarbonyl derivative X (R = COOCH$_3$).



IX



X

XI

In the naphthalene complex the lengths of the bonds in the ring not coordinated to the metal remain aromatic in character (Table II). However the corresponding bonds (c_1, d, c_2) in the iron complex display distinct alternation and have lengths typical of carbon sp^2–sp^2 double bonds and carbon sp^2–sp^2 single bonds.[14] This again suggests a major reduction in the π-electron delocalization as is implied in the formulation X. The alternation in the bond length in this complex is not merely a consequence of ring strain associated with fusion of the benzene ring to the four membered ring. The corresponding bond lengths for biphenylene (XI) (see ref *b* of Table II) suggest that this factor alone would produce, if anything, a slight alternation in the opposite manner to that observed in complex XI.

Table II. Bond Distances (Å) of IX, X, and XI

Bond	IX[a]	X	XI[b]
a_1, a_2	1.44, 1.40	1.47, 1.45	1.43
a_3, a_4	1.42, 1.40	1.49, 1.46	
a_5, a_6	1.44, 1.44		
b_1, b_2	1.45, 1.43	1.40, 1.41	1.37
c_1, c_2	1.39, 1.39	1.36, 1.33	1.42
d	1.41	1.48	1.38

[a] The crystal structure of the orthorhombic modification of naphthalene–chromium tricarbonyl has been reported by Kunz and Nowacki (V. Kunz and W. Nowacki, *Helv. Chim. Acta*, **50**, 1052 (1967)). This structure was also determined and has been further refined in this laboratory ($R = 0.062$, 1120 observed reflections, hydrogen atoms found but not included in calculations). The bond distance values cited are those derived in this laboratory, and have estimated standard deviations in the range 0.01–0.02 Å. [b] J. K. Fawcett and J. Trotter, *Acta Crystallogr.*, **20**, 87 (1966). Average values for each bond type are cited.

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(10) Another possible example of an organo–iron complex, whose bond length deviations from normal benzene values could be considered indicative of bond fixation, is the phenyl benzoferrole–iron tricarbonyl complex.[11] A related phenomenon is also seen in a *p*-methylbenzyl–cyclopentadienylmolybdenum dicarbonyl complex.[12]

(11) Y. Degre've, J. Meunier-Piret, M. Van Meerssche, and P. Piret, *Acta Crystallogr.*, 23, 119 (1967).

(12) F. A. Cotton and M. D. LaPrade, *J. Amer. Chem. Soc.*, **90**, 5418 (1968).

(13) O. S. Mills and G. Robinson, *Acta Crystallogr.*, **16**, 758 (1963).

(14) L. E. Sutton, Ed., "Tables of Interatomic Distances and Configurations in Molecules and Ions," Supplement, The Chemical Society, London, 1965, pp S 14s–15s.

(15) The authors thank the Robert A. Welch Foundation, the Petroleum Research Fund, the National Science Foundation, and the U. S. Army Research Office (Durham) for financial support.

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