

factors contrives to make the homotropylum structure substantially more stable than the cyclooctatrienyl one.

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The Molecular Structure of Bicyclo[3.2.1]octadienyliron Tricarbonyl Tetrafluoroborate¹

Sir:

The structure of the bicyclo[3.2.1]octadienyl cation (1) is of some theoretical interest since extensive charge delocalization is in principle available through nonclassical resonance forms symbolized by the aggregate structure (2). At present, the evidence for nonclassical carbonium ions rests principally,² and not without some dissent,³ on the rates and stereospecificities of solvolysis reactions believed to involve these intermediates.

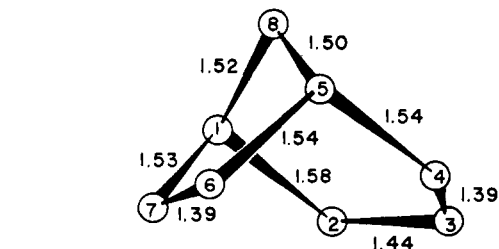
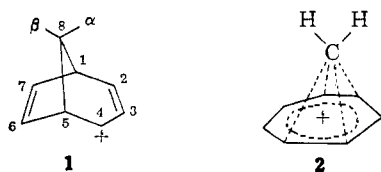


Figure 1. The complex cation projected on (010). Numbered atoms are carbon. Iron-carbon distances are 2.24, 2.26, 2.21, 2.17, and 2.09 Å. to C-6, C-7, C-2, C-4, and C-3, respectively. Iron-carbonyl distances average 1.76 Å.; C=O distances average 1.14 Å. All distances ± 0.03 Å. Average bond angles are: C-2,C-1,C-7, 102°; C-2,C-1,C-8, 108°; C-7,C-1,C-8, 100°; C-1, C-2,C-3, 118°; C-5,C-6,C-7, 109°; C-2,C-3,C-4, 119°; C-1,C-8, C-5, 105°; all $\pm 4^\circ$.

While stabilization of π -allyl and π -pentadienyl cationic systems by complexation with transition metals is a well-established phenomenon,⁴ its possible extension to include those charge-delocalized structures associated with nonclassical ions has not been examined. The cation 1 appeared particularly well suited to this purpose.

We wish to report the preparation of bicyclo[3.2.1]octadienyliron tricarbonyl tetrafluoroborate and a determination of its molecular structure in solution and in the crystalline state.

Bicyclo[3.2.1]octadiene (3) was prepared from norbornadiene by a synthetic route similar to that recently reported by Moore, Moser, and La Prade.⁵ Norbornadiene was converted in 38% yield to *exo*-3,4-dichlorobicyclo[3.2.1]octa-2,6-diene⁶ by treatment with ethyl trichloroacetate and sodium methoxide, and thence to 3, in 60% yield, by reduction with lithium in *t*-butyl alcohol.⁷ The infrared and n.m.r. spectra of the diene were in accord with published data,⁵ and hydrogenation gave bicyclo[3.2.1]octane, identical with an authentic sample of this substance.⁸

When the diene 3 was heated in methylcyclohexane solution in the presence of iron pentacarbonyl, bicyclo-

[3.2.1]octadieneiron tricarbonyl (4) was formed. This substance crystallized from methanol solution as pale yellow plates, m.p. 30–31°; infrared 4.92 and 5.11 μ (C≡O); ultraviolet $\lambda_{\text{max}}^{\text{EtOH}}$ 215 m μ (ϵ 22,400). *Anal.* Calcd. for C₁₁H₁₀O₃Fe: C, 53.71; H, 4.07. Found: C, 54.25; H, 4.30; mol. wt., 246 (mass spectroscopy).

Treatment of 4 with trityl fluoroborate in methylene chloride solution gave bicyclo[3.2.1]octadienyliron tricarbonyl tetrafluoroborate (5) as fine yellow needles which decompose above 175°; infrared 4.80, 4.93, and 4.97 μ (C≡O); ultraviolet $\lambda_{\text{max}}^{\text{EtOH}}$ 218 and 250 m μ (ϵ 13,500 and 7250). *Anal.* Calcd. for C₁₁H₉O₃FeBF₄: C, 39.82; H, 2.73. Found: C, 39.38; H, 2.85.

Crystals of the complex salt are monoclinic, space group P2₁/a, with four formula weights/cell. The cell dimensions are $a = 7.85 \pm 0.02$ Å., $b = 12.54 \pm 0.04$ Å., $c = 13.17 \pm 0.04$ Å., $\beta = 99.6 \pm 0.5^\circ$. X-Ray intensities were estimated visually from equi-inclination Weissenberg photographs for layers 0kl-7kl. Patterson, electron density, and difference maps were employed in the structure determination. Refinement of the structure was accomplished by full-matrix least-squares calculations. The present value of $R = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}$ is 0.12 for 886 nonzero reflections.

The crystal structure of the salt consists of discrete complex cations and somewhat disordered tetrafluoroborate anions. The molecular geometry of the complex cation is depicted in Figure 1, as viewed along the b axis. These data rule out the nonclassical structure 2 for the hydrocarbon portion of the cation.

Several other structural features of the complex deserve comment. The cation has approximate C_s symmetry across the plane containing C-3, C-8, Fe, C-11-O, and the midpoint of the C-6-C-7 double bond. The coordination about the metal atom is very nearly octahedral if the three-carbon bridge is taken as providing two coordination sites, the remaining apical positions being occupied by the isolated double bond and the three carbonyl groups.

(1) This research was supported by National Institutes of Health Grant No. G-5978, National Science Foundation Grant No. GP-1078, and in part by American Cancer Society Grant No. IN-29.

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(7) P. Bruck, D. Thompson, and S. Winstein, *Chem. Ind. (London)*, 405 (1960).

(8) We are indebted to Professor H. M. Walborsky for providing us with a sample of this compound.

Although a number of cyclic and acyclic π -pentadienyliron tricarbonyl salts are known,⁴ the present structure is unique in that the five-carbon unit comprising the cationic skeleton is not contained within a continuous carbon chain.⁹ As would be required for a symmetrically bound allyl group, the C-2-C-3 and C-3-C-4 bond lengths are equal within the present level of accuracy. These, with the C-6-C-7 bond, are as expected inter mediate between a single and a double bond. While the angles defined by C-1,C-2,C-3, C-2,C-3,C-4, and C-3,C-4,C-5 are close to the values expected for trigonally hybridized carbon atoms, it is significant that carbon atoms C-1 and C-5 are not coplanar with the allyl group but lie instead 0.52 Å. above the plane defined by C-2, C-3, and C-4.¹⁰ The displacement of bonds to the termini of the allyl group from trigonal toward tetrahedral geometry is comparable with, although smaller in degree than, the analogous distortions observed in several cyclic dieneiron tricarbonyl complexes.¹¹ It has been suggested^{11d} that these distortions are to be accounted for in terms of σ -bonding of the terminal carbon atoms of the butadiene group to the metal atom, but it is clear that such a description is less satisfactory in the present context, unless three-point attachment of the allyl group to a seven-coordinated metal atom be considered.^{11a} In any event, distortions in the σ -framework of the ligands which result in increased overlap of metal and carbon 2p-orbitals, as well as those imposed by the geometry of the ligand and induced by back bonding from the metal atom to antibonding levels in the ligand, cannot be neglected.

The structure of the complex cation does not appear to be significantly different in solution. Its n.m.r. spectrum displays signals at τ 5.05 (triplet, $J = 6$ c.p.s.), 5.32 (triplet, $J = 6$ c.p.s.), 5.76 (pair doublets, $J \approx J' = 2$ c.p.s.), and 6.62 (multiplet), assignable to H_3 , $H_{2,4}$, $H_{6,7}$, and $H_{1,5}$, respectively, and consistent with a structure for the cation essentially identical with that found in the crystalline state. Moreover, the couplings of $H_{8\alpha}$ (τ 8.86) and $H_{8\beta}$ (τ 8.30) (1) with the bridgehead protons ($H_{1,5}$) are unequal ($J_{\alpha,1} = 1$ c.p.s., $J_{\beta,1} = 4$ c.p.s., $J_{\alpha,\beta} = 12$ c.p.s.), in accord with the molecular geometry defined in Figure 1.¹²

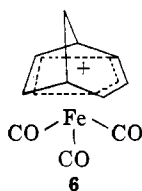
Acknowledgment. We thank the Computation Center

(9) Several π -allyliron tricarbonyl salts have recently been described by G. F. Emerson and R. Pettit, *J. Am. Chem. Soc.*, **84**, 4591 (1962), and G. F. Emerson, J. E. Mahler, and R. Pettit, *Chem. Ind. (London)*, 836 (1964).

(10) The dihedral angle between the least-squares plane fitted to C-1, C-2, C-4, and C-5 and the plane defined by C-2, C-3, and C-4 is 161°.

(11) (a) B. Dickens and W. N. Lipscomb, *J. Chem. Phys.*, **37**, 2084 (1962); (b) M. R. Churchill and R. Mason, *Proc. Chem. Soc.*, 226 (1964), (c) R. P. Dodge, *J. Am. Chem. Soc.*, **86**, 5429 (1964); (d) D. L. Smith and L. F. Dahl, *ibid.*, **84**, 1743 (1962).

(12) The pronounced deshielding of $H_{6,7}$ protons in the cation, as is evident from a comparison of the chemical shift of these protons with those in the neutral complex (τ ca. 6.7), suggests that contributions from more highly delocalized charged forms such as 6 may be important, although transmission of electronic effects through the ligand-metal orbitals cannot be discounted.



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Selective Catalysis of the Copolymer of 4(5)-Vinylimidazole and Acrylic Acid

Sir:

The efficiency of multicenter enzymatic catalysis is sometimes partially due to the electrostatic attraction that one of these functions exerts on a charged substrate. This could be the case with ribonuclease¹ and acetylcholinesterase.² For acetylcholinesterase a negatively charged site A besides a catalytic function B was recognized in the active site. The role of A was considered to be electrostatic attraction of the positively charged substrate, acetylcholine, which improved the catalytic action of group B from a "neighboring group position." While group A could be the carboxylate anion, group B (or part of it) was identified as imidazole.³

As a macromolecular model for acetylcholinesterase the copolymer of 4(5)-vinylimidazole and acrylic acid has been prepared. Partially protonated homopolymers of 4-vinylpyridine,^{4,5} 4(5)-vinylimidazole,⁶ and N-vinylimidazole⁷ were found effective with negatively charged substrates. Bell-shaped pH-rate profiles were realized⁵⁻⁷ since partial ionization optimized the cooperative effect of polymer charge and nucleophile concentration. Separation of the roles of electrostatic attraction and catalytic action between two different functional groups A and B in a copolymer makes it possible to vary independently the charge of the polymer and the concentration of catalytically active groups. The assistance of the charged groups to the catalytic functions must be through coiling of the polymer chain.⁸ A proper concentration of charged groups in the copolymer may produce optimal results.⁹ So far, the possibility to improve the catalytic action of a group B by its random copolymerization with a noncatalytic charged group A has not been validated. We wish to report the first example of a synthetic copolymer with a marked selective catalysis.

In benzene solution 0.0056 mole of 4(5)-vinylimidazole and 0.0053 mole of acrylic acid were polymerized at 70° for 12 hr. with azobisisobutyronitrile as an initiator. The copolymer was obtained in 55% con-

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(8) Cf. P. J. Flory, "Principles of Polymer Chemistry," Cornell University Press, New York, N. Y., 1953, p. 95.

(9) The effect of copolymer composition on catalytic action is now being investigated.