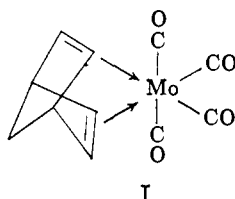


Resonances of carbonyl carbons have been more difficult to find. Some of our data are given in Table II. Conspicuously absent from the list of carbonyl resonances are those of manganese and cobalt compounds. These resonances must be split and broadened by spin-spin coupling with high-spin metal nuclei undergoing moderately rapid quadrupole-induced relaxation. In the spectrum of cyclopentadienylmanganese tricarbonyl, it has indeed been possible to observe a broad (about 170 c.p.s.), weak carbonyl resonance at about -28 p.p.m. from CS_2 . That the carbon-metal couplings in such compounds can be large is shown by the observation of a 116-c.p.s. splitting of the C^{13} satellites in the V^{51} resonance of the symmetrical $\text{V}(\text{CO})_6^-$ anion in a tetrahydrofuran solution of $[\text{Na}(\text{diglyme})_2][\text{V}(\text{CO})_6]$.

The C^{13} n.m.r. spectrum of bicyclo[2.2.1]heptadienemolybdenum tetracarbonyl (I) was found to have two resonances of approximately equal intensities in the carbonyl region. The carbon shieldings in the two types of carbonyl groups shown below must therefore



be different, but there is no way at present to associate a resonance with a particular pair of carbonyl groups.

The limited data available do not seem to provide firm grounds for any useful generalizations. A rough correlation between estimated metal-carbon bond orders and carbonyl carbon shieldings is suggested by these results, but more experimental studies are obviously required.

the ring E_1 bonding orbitals and metal hybrid orbitals. Back bonding between ring E_2 antibonding orbitals and filled metal d-orbitals is probably less important in these complexes.

P. C. Lauterbur
State University of New York
Stony Brook, Long Island, New York

R. B. King
Mellon Institute
Pittsburgh, Pennsylvania 15213
Received April 28, 1965

Homotropylium Ion and Its Molybdenum Tricarbonyl Complex¹

Sir:

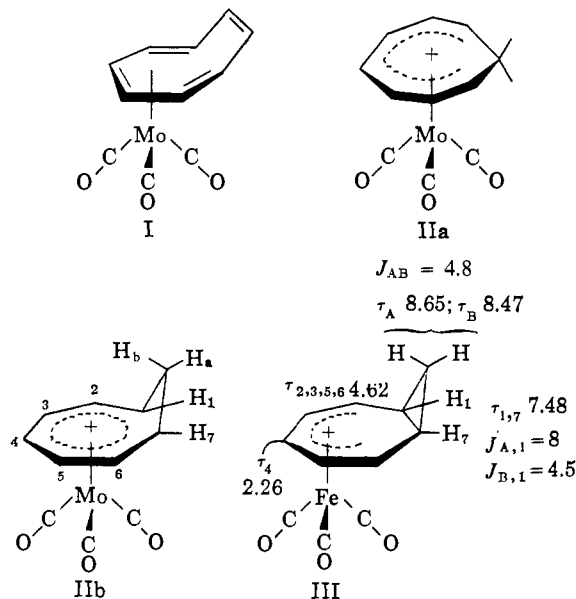
The different electronic requirements of transition metal atoms in their complexes exert a corresponding control on the resulting structure and thus constitute a powerful tool in the study of various aspects of homoconjugation, homoaromaticity, and nonclassical structures.²

We have now prepared for the first time the cyclooctatetraene complex $\text{C}_8\text{H}_8\text{Mo}(\text{CO})_3$ (I), in which this olefin is bound to a metal by six π -electrons on six carbon atoms ($6\pi-6\text{C}$). This complex can be protonated to examine the predicted $6\pi-7\text{C}$ electronic system in cation II. Especially interesting is the question whether II

(1) Research sponsored by U. S. Army Research Office (Durham) and the National Science Foundation G.P. 4175.

(2) S. Winstein, *et al.*, *J. Am. Chem. Soc.*, **81**, 6523 (1959); **83**, 3244 (1961); *Tetrahedron Suppl.*, **2**, 423 (1963).

is cyclooctatrienyl (IIa) or monohomotropylium (IIb) in character. It is of obvious importance to compare cation II with the related $\text{C}_8\text{H}_9^+\text{Fe}(\text{CO})_3$ cation (III) studied previously by Schrauzer³ and Wilkinson,⁴



and also the free C_8H_9^+ ion mentioned earlier by Pettit.⁵

Compound I is obtained as red crystals in 60–70% yield by stirring cyclooctatetraene with pale yellow diglyme-molybdenum tricarbonyl⁶ in hexane at 50° .

Anal. Calcd. for $\text{C}_{11}\text{H}_8\text{MoO}_3$: C, 46.50; H, 2.84; Mo, 33.77. Found: C, 46.74; H, 2.90; Mo, 33.36.

Nuclear magnetic resonance of I in toluene solution at 30° showed a broad band (half-width 25 c.p.s.) at $\tau 6.05$ (which became a sharp singlet at 80°).⁷ In concentrated H_2SO_4 I gives an n.m.r. spectrum summarized in Figure 1. This displays a 5:2:1:1 proton pattern with assignments as shown. Especially striking is the large chemical shift between "inside" and "outside" H_b and H_a methylene protons. From the spectrum of I in D_2SO_4 (Figure 1) it is evident that protonation is stereospecific, the proton added to the complex I becoming the "outside" proton H_a . This n.m.r. spectrum of $\text{C}_8\text{H}_9^+\text{Mo}(\text{CO})_3$ bears a striking resemblance to that of the parent cation from protonation of cyclooctatetraene in H_2SO_4 . As is clear from Figure 1 the spectrum of C_8H_9^+ in H_2SO_4 (also observed by Pettit⁵ for C_8H_9^+ in H_2SO_4 and $\text{C}_8\text{H}_9^+\text{SbCl}_6^-$ in MeNO_2) has the 5:2:1:1 pattern which in our hands was sufficiently well resolved to determine H_1-H_b , H_1-H_a , and H_a-H_b coupling constants. The chemical shift between H_b and H_a is even larger in the free ion (5.8 p.p.m.) than in the $\text{Mo}(\text{CO})_3$ complex (3.5 p.p.m.). In contrast, the n.m.r. spectrum of $\text{C}_8\text{H}_9^+\text{Fe}(\text{CO})_3$ in H_2SO_4 reported by Schrauzer³ and Wilkinson⁴ displays a 1:4:2:2 proton pattern with assignments as shown in III. In this complex, the

(3) G. N. Schrauzer, *J. Am. Chem. Soc.*, **83**, 2966 (1961).

(4) A. Davison, W. McFarlane, L. Pratt, and G. Wilkinson, *J. Chem. Soc.*, 4821 (1962).

(5) J. L. Rosenberg, J. E. Mahler, and R. Pettit, *J. Am. Chem. Soc.*, **84**, 2842 (1962).

(6) R. P. M. Werner and T. H. Coffield, *Chem. Ind. (London)*, 936 (1960).

(7) At lower temperature (-30°) the spectrum freezes to a complex pattern. This is therefore the first known complex of cyclooctatetraene whose proton magnetic resonance shows observable change from rapid to arrested valency tautomerism. We shall discuss more fully elsewhere the further study of this phenomenon and the structure of I.

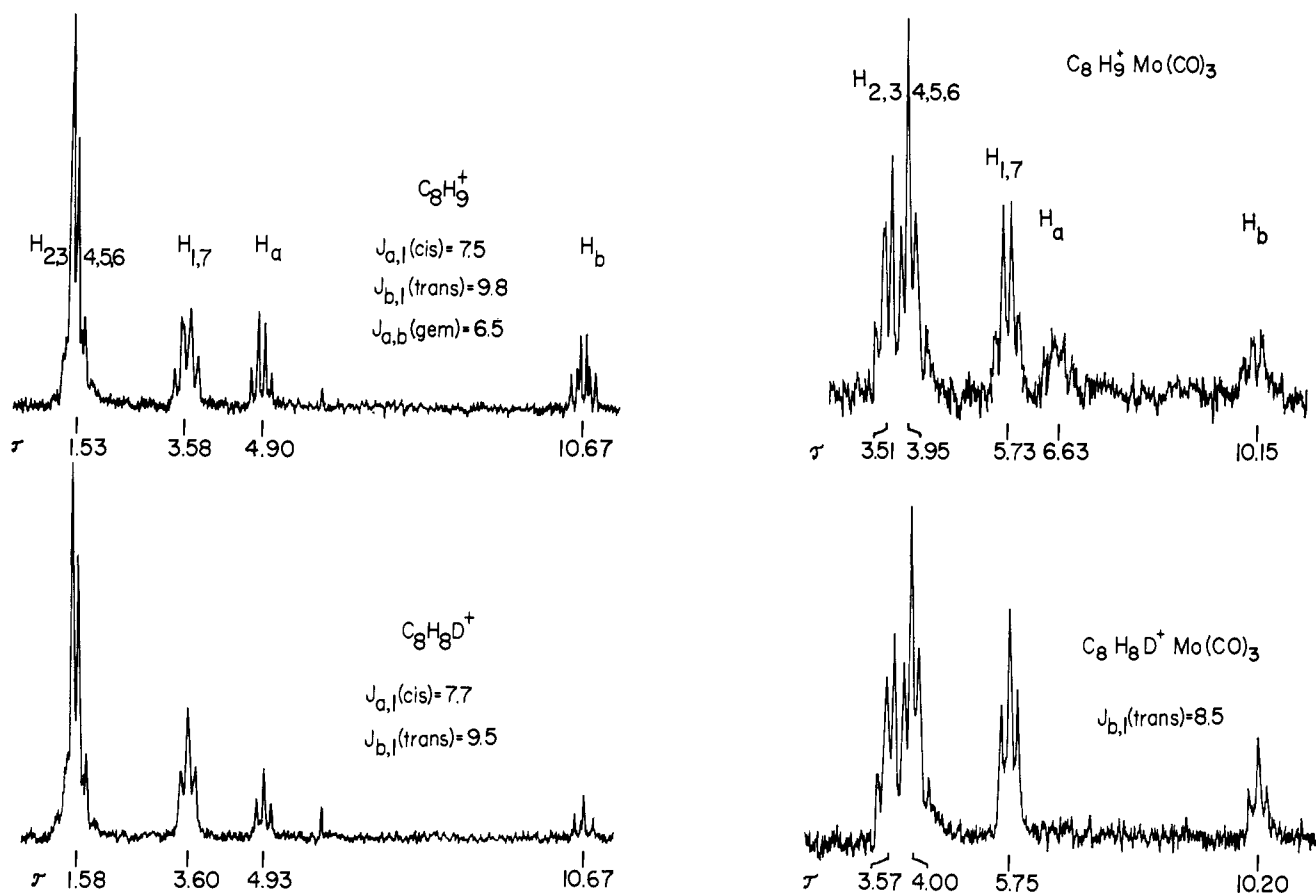


Figure 1. Proton n.m.r. spectra in concentrated H_2SO_4 ; Me_4Si external reference; Varian A-60.

methylene protons display nearly the same chemical shift.

The striking similarity between the n.m.r. spectra of the free ion and its $Mo(CO)_3$ complex and the contrast with that of the $Fe(CO)_3$ complex give one considerable insight into the electronic structure of each of the species. It seems evident that the $Fe(CO)_3$ complex may be represented to a fair approximation by the classical structure III, which was preferred by Wilkinson⁴ and which is in accord with the $4\pi-5C$ preference of the Fe atom. For the $Mo(CO)_3$ complex, the 6π -electronic preference of Mo limits the choice of structure to cyclooctatrienyl (IIa) or homotropylium (IIb). Only the latter seems able to account for the large observed chemical shift between the "inside" and "outside" H_b and H_a protons. This assignment is strengthened by analogy between the $Mo(CO)_3$ complex and the free ion. As regards the free $C_8H_9^+$ ion, the planar cyclooctatrienyl structure (type IIa) may be excluded because this would have magnetically equivalent H_a and H_b methylene protons. For a structure akin to III with a relatively fully formed cyclopropane ring we would expect the n.m.r. signal for $H_{1,7}$ to be at $\tau \sim 7$ or above, a *gem* $J_{a,b}$ of 4.5–5 c.p.s., and a *cis* $J_{a,1}$ (~ 8 c.p.s.) larger than the *trans* $J_{b,1}$ (~ 4.5 c.p.s.), by analogy with known cyclopropyl-substituted carbonium ions and other cyclopropane derivatives.⁸ Such a structure is excluded by the extensive deshielding of the $H_{1,7}$ protons (τ 3.6) and the pattern of the available coupling constants, *trans*

(8) N. C. Deno, *Progr. Phys. Org. Chem.*, **2**, 148 (1964); (b) E. Friedrich, unpublished work; (c) L. Ebersson and S. Winstein, *J. Am. Chem. Soc.*, in press; (d) J. D. Graham and M. T. Rogers, *ibid.*, **84**, 2249 (1962).

($J_{b,1} = 10$ c.p.s.) being larger than *cis* ($J_{a,1} = 7.5$ c.p.s.). On the other hand, we should note that the n.m.r. spectrum of the $Fe(CO)_3$ complex is just what would be expected for a structure of type III.

The available data strongly support nonclassical homotropylium structures for the free $C_8H_9^+$ ion and its $Mo(CO)_3$ complex IIb. These involve 1,7-orbital overlap of a type intermediate between σ and π , and the species may be called homoaromatic.² Ring currents associated with these structures presumably contribute to the large chemical shift between the "inside" and "outside" methylene protons.⁹

From the failure to observe a measurable rate of exchange of magnetic environments between the H_a and H_b methylene protons in the free cation, one can derive a minimum figure for the free energy difference between the nonclassical homotropylium ion (type IIb) and the classical planar cyclooctatrienyl cation (type IIa). From the line width of the H_a and H_b signals, it is clear that the rate constant for ring inversion must be well below 5 sec.^{-1} at room temperature.¹⁰ This corresponds to a ΔF^* greater than 16 kcal./mole. Thus, the blend of strain and delocalization energy¹¹

(9) Pettit⁵ recognized the indications of extensive involvement of the potential cyclopropane ring in the sense of the type IIb structure. On the other hand, in his recent review Deno^{8a} has employed the type III representation for $C_8H_9^+$. However, as we have already pointed out elsewhere,^{8c} he uniformly omits from his representations of cyclopropyl substituted carbonium ions any explicit indication of the extensive electron delocalization from the cyclopropyl group.

(10) This is substantially slower than the rate of ring inversion in a substituted cyclooctatetraene observed by F. A. L. Anet, A. J. R. Bourn, and Y. S. Lin, *J. Am. Chem. Soc.*, **86**, 3576 (1964).

(11) Simple HMO calculations for the IIa type structure (without a 1,7-interaction) give a π -electron energy ($E - 6\alpha$) of 8.055 β . Inclusion of a $\beta_{1,7}$ increases this figure; e.g., $\beta_{1,7} = 0.5\beta$ leads to a figure of 8.423 β for the energy.

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

Acknowledgment. We are grateful to Professor F. A. L. Anet for valuable suggestions and advice.

S. Winstein, H. D. Kaesz
C. G. Kreiter, Edwin C. Friedrich

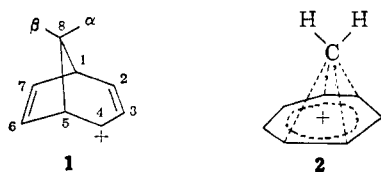
Contribution No. 1829 from the Department of Chemistry
University of California, Los Angeles, California 90024

Received June 1, 1965

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.



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-

(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.

(2) S. Winstein, *J. Am. Chem. Soc.*, **87**, 381 (1965), and preceding references, P. von R. Schleyer, *ibid.*, **86**, 1956 (1964).

(3) H. C. Brown and M. H. Rei, *ibid.*, **86**, 5008 (1964), and preceding references.

(4) J. E. Mahler and R. Pettit, *ibid.*, **85**, 3955 (1963), and references cited therein.

(5) W. R. Moore, W. R. Moser, and J. E. La Prade, *J. Org. Chem.*, **28**, 2200 (1963).

(6) R. C. DeSelms and C. M. Combs, *ibid.*, **28**, 2206 (1963).

(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.

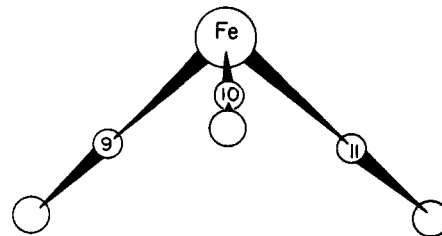
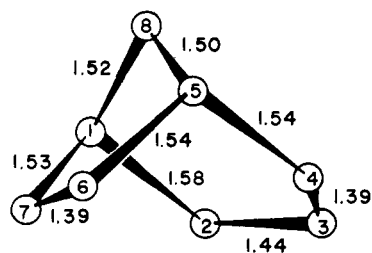


Figure 1. The complex cation projected on (010). Numbered atoms are carbon. Iron-carbon distances are 2.24, 2.26, 2.21, 2.17, and 2.09 Å, to C-6, C-7, C-2, C-4, and C-3, respectively. Iron-carbonyl distances average 1.76 Å.; C=O distances average 1.14 Å. All distances ± 0.03 Å. Average bond angles are: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

[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 \equiv 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 \equiv 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.