solved by conventional Patterson and Fourier techniques. At the present stage of isotropic full-matrix least-squares refinement $R = 0.094$ using 1482 reflections for which $I \geq 4\sigma(I)$. The anomalous dispersion of the chromium atom has been included.

The results show, by internal comparison with the known absolute configuration of the camphor moiety,[3] that sample B of Cr(+atc)$_3$ is the Λ-trans isomer, in agreement with previous assignments based on spectroscopic[4,5,10] and steric[4] arguments. This result is confirmed by a Bijvoet analysis of several Friedel pairs employing the anomalous dispersion of the chromium atom. Furthermore, employing the correlations of King and Everett,[5b] the correspondence of diastereoisomers of both Cr(+atc)$_3$ and Co(+atc)$_3$ is definitely established as follows: A, Δ-trans; B, Λ-trans; C, Λ-cis, D, Δ-cis. The Λ configuration and trans geometry of isomer B are clearly evident in the stereoview provided by Figure 1.

The Cr–O distances are all identical to within experimental error and average 1.97 (1) Å. The O–Cr–O angles within the individual chelate rings average 91.9 (1)°. The three carbon and two oxygen atoms defining each chelate ring are quite accurately coplanar with no atom deviating more than 0.04 Å from the least-squares plane in any instance. These chelate-ring planes are inclined to the planes defined by the chromium and two oxygen atoms by angles of 17.6, 16.3, and 15.5° for each of the three bidentate ligands. Dihedral coordination of this type by β-diketonate ligands has been noted before.[11]

Single-crystal electronic spectroscopy has shown that for the lowest energy ligand-field transition in Cr(acac)$_3$,[12] $^4A_2 \rightarrow (^4E_a + {}^4A_2)$, and Co(acac)$_3$,[13] $^1A_1 \rightarrow (^1E_a + {}^1A_2)$, the E_a component lies at higher energy in each case. This result, coupled with the CD data[5b] for the present tris-atc complexes, demonstrates that a positive CD band for the E_a component is diagnostic of the Λ absolute configuration in tris-β-diketonate complexes of chromium and cobalt. The assignment[14] of absolute configuration of diastereoisomers of the tris-β-diketonate complexes of cobalt(III) derived from the chiral natural products carvone and pulegone recently made on this basis is thus supported.

A complete description of this structure and an analysis of the factors governing stereoselectivity in this class of complex will be presented in a subsequent publication.

Acknowledgments. We thank Professor G. W. Everett, Jr., of the University of Kansas for supplying us with separated diastereoisomers, and the College of Science, The Pennsylvania State University, for an allocation of funds for computer time.

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(15) Petroleum Research Fund Predoctoral Fellow, 1969–1970.

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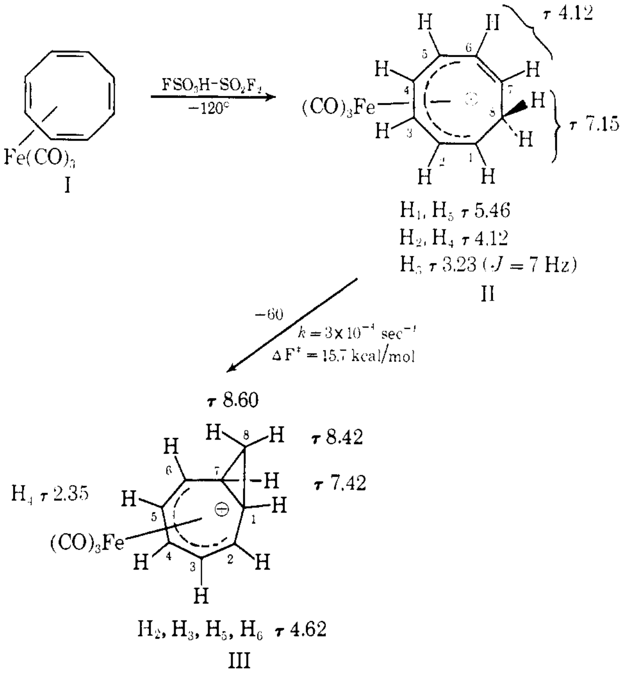
Direct Observation of the Cyclooctatrienyliron Tricarbonyl Cation and Its Electrocyclic Ring Closure to the Bicyclo[5.1.0]octadienyliron Tricarbonyl Cation

Sir:

There has been much recent interest in metal carbonyl complexes of carbonium ions.[1] Metal carbonyl complexes of the $C_8H_9^+$ cation generated from protonation of the corresponding cyclooctatetraene complexes have been especially interesting in that the electronic requirements of the metal dictate the structure of the cationic ligand.[2,3] For example, protonation of cyclooctatetraenemolybdenum tricarbonyl yields the homotropylium complex in which all six π electrons of the homotropylium ion are used in bonding to molybdenum. In contrast, protonation of cyclooctatetraeneiron tricarbonyl[2] I in sulfuric acid at 0° yields the ring-closed bicyclo[5.1.0]octadienyliron tricarbonyl complex III, in which the cyclopropane ring remains closed[4] and only the four π electrons of the pentadienyl system are needed for bonding to iron.

In this communication we report the preparation of a new $C_8H_9^+$ iron tricarbonyl complex, the cyclooctatrienyliron tricarbonyl complex[4] II, and a study of its electrocyclic ring closure to the bicyclic complex III.



Preparation of complex II is accomplished by low-temperature protonation of I. When I is dissolved in $FSO_3H–SO_2F_2$ (1:3, v:v) at −120° ion II is formed cleanly. The nmr spectrum[5] of this ion recorded at

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(1) For a review, see E. W. Abel and S. Tyfield, *Advan. Organometal. Chem.*, 8, 117 (1970).

(2) (a) A. Davison, W. McFarlane, L. Pratt, and G. Wilkinson, *Chem. Ind. (London)*, 553 (1961); (b) *J. Chem. Soc.*, 4821 (1962).

(3) (a) S. Winstein, H. D. Kaesz, C. G. Kreiter, and E. C. Friedrich, *J. Amer. Chem. Soc.*, 87, 3267 (1965); (b) R. Aumann and S. Winstein, *Tetrahedron Lett.*, 903 (1970); (c) for a review, see S. Winstein, *Quart. Rev., Chem. Soc.*, 23, 141 (1969).

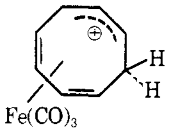
(4) Protonation of I was reported to give the cyclooctatrienyliron tricarbonyl complex: G. N. Schrauzer, *J. Amer. Chem. Soc.*, 83, 2966 (1961). However, work by Davison, *et al.*,[2] showed the structure to be the bicyclo[5.1.0]octadienyliron tricarbonyl complex, III.

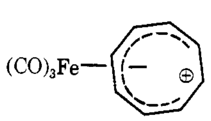
(5) All chemical shifts are in τ relative to internal CH_2Cl_2 taken as τ 4.70.

$-80°$ shows a one-proton triplet ($J = 7$ Hz) at τ 3.23 assigned to H_3, a four-proton multiplet at τ 4.12 assigned to H_2, H_4, H_6, and H_7, a two-proton multiplet at τ 5.46 for H_1 and H_5, and a two-proton multiplet at τ 7.15 assigned to the methylene protons at C_8. If the protonation is carried out in $FSO_3D-SO_2F_2$, the band at τ 7.15 is reduced to a relative intensity corresponding to one proton, confirming the assignment of this band to the methylene protons.

When the temperature of the $FSO_3H-SO_2F_2$ solution is raised, ion II undergoes a clean first-order ring closure to the previously reported[2] bicyclo[5.1.0]octadienyliron complex III. The first-order rate constant for appearance of III at $-60°$ is 3×10^{-4} sec^{-1}, corresponding to $\Delta F^{\ddagger} = 15.7$ kcal/mol.

The nmr spectrum of the intermediate complex clearly indicates that its structure is best described as II, in which the ligand contains a "free" double bond and a five-carbon pentadienyl system complexed to iron,[6] and not alternative structures such as IV, in which the ligand contains a free allylic cation and a diene moiety complexed to iron, or V, in which the iron is symmetrically disposed with respect to the ligand. The position and difference in chemical shifts of H_1, H_5 and H_2, H_4 are in accord with other cyclic pentadienyliron tricarbonyl complexes,[8–10] while the chemical shift of H_3 (τ 3.23) and the H_3–H_2 and H_3–H_4 coupling constants (7 Hz) are quite characteristic of the central proton in cationic pentadienyliron tricarbonyl complexes.[8,9,11] The chemical shift of protons H_6 and H_7 (*ca.* τ 4.12) is also appropriate for the protons on the unbound vinyl group, considering the chemical shift (*ca.* τ 4.5) of the protons of the free vinyl group in cyclooctatrieneiron tricarbonyl.[9,12]


IV


V

There has been much current interest and speculation about the effects which transition metals may have upon symmetry-controlled transformations of organic systems.[14] The present observation appears to be the first unambiguous case of an electrocyclic ring closure of an organic ligand bound to a transition metal.[15] The closure involves a six-π-electron system, and, therefore, the disrotatory mode of closure is symmetry allowed in the free ligand and is the mode observed[17] in the complex II. It is difficult to assess the exact effect of the metal on the activation energy for ring closure in this case since the analogous transformation of the unbound ligand has not been observed. (The free ligand is the nonclassical monohomotropylium ion.) Several disrotatory ring closures have been reported for cyclic trienes;[18] while the free energies of activation are generally higher (*ca.* 25 kcal/mol) than that observed for II, these neutral trienes serve as poor reference compounds.

Studies are currently in progress on the low-temperature protonations of derivatives of I, and the thermal isomerization of III at higher temperatures, as well as other symmetry-controlled isomerizations of organic molecules bound to transition metals.

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(6) Since signals for II are sharp at -40, no rapid 1,3 oscillations of iron are occurring with $\Delta F^{\ddagger} < ca.$ 11 kcal/mol to average H_1 with H_7, H_2 with H_6, and H_3 with H_5. The bonding in tropyliumiron tricarbonyl is postulated[7] to be similar to that in II (iron bound to a pentadienyl unit with a free double bond); however, the nmr of this complex shows all proton signals averaged to a singlet. This averaging probably occurs by 1,2 iron shifts rather than shifts of other orders (*e.g.*, 1,3).

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(10) The assignment of H_1, H_5 to the signal at τ 5.46 is further strengthened by the fact that H_3 appears as a clean triplet. In III, in which H_2, H_6 and H_3, H_5 have the same chemical shifts, H_4 appears as a quintet. This quintet, although originally interpreted[2] as equal coupling of H_4 to H_2, H_3, H_5, and H_6 is best explained by "virtual coupling" between H_4 and H_2, H_6 in the AA'BB'X system. If H_1, H_5 had the same chemical shift as H_2, H_4 in II, virtual coupling would again be expected to alter the triplet structure of H_3. We thank Dr. D. L. Harris for calling this to our attention.

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(12) A referee has suggested that structure IV remains a possibility for the low-temperature intermediate if the τ-3.23 resonance is assigned to the central proton of the free allylic cation, the τ-5.46 band to the terminal allylic protons, and the τ-4.12 band to the bound diene protons. Such an assignment can be ruled out by comparison of the assignments of the allylic protons to shifts of protons bound to other cyclic allylic cations. Typically, terminal allylic protons are at *ca.* τ 0 and to *low fields* of the central proton at *ca.* τ 2.[13]

(13) (a) A. F. Diaz, D. L. Harris, M. Sakai, and S. Winstein, *Tetrahedron Lett.*, in press; (b) P. M. Warner, Ph.D. Thesis, UCLA, 1970.

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(15) The present results and the limited data available[16] suggest that bicyclo[4.2.0]octadieneiron tricarbonyl may be formed by electrocyclic ring closure of cyclooctatrieneiron tricarbonyl.

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(17) The disrotatory closure of II may proceed in either of two ways to yield the cyclopropane ring cis or trans to the $Fe(CO)_3$. As in previous papers, the complex III is written with a *trans*-cyclopropane, but this stereochemistry has not been proved.

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Photoracemization of Optically Active Derivatives of [2.2]Paracyclophane[1]

Sir:

Earlier work[2] demonstrated that [2.2]paracyclophane underwent photolytic ring opening to give open-chain

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(1) The authors thank the National Science Foundation for a grant used in support of this research. M. H. Delton thanks the Regents of the University of California for a First Year Fellowship.

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