Low-Temperature Protonation of Cyclooctatetraeneiron Tricarbonyl and Methylcyclooctatetraeneiron Tricarbonyl. Generation and Observation of Cyclooctatrienyliron Tricarbonyl Cations

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Abstract: The low-temperature protonation (−120°) of cyclooctatetraeneiron tricarbonyl in FSO_3H-SO_2ClF is reported to yield initially the monocyclic cyclooctatrienyliron tricarbonyl cation which is observed by proton nmr at low temperatures. From an analysis of the nmr spectrum the structure of the monocyclic ion is shown to be II; other possible structures IV and V were conclusively eliminated. At −60° the monocyclic ion undergoes clean first-order electrocyclic ring closure ($k = 3 \times 10^{-4}$ sec^{-1}, $\Delta F^{\ddagger} = 15.7$ kcal/mol) to the previously observed bicyclo[5.1.0]octadienyliron tricarbonyl cation III. The low-temperature protonation of methylcyclooctatetraeneiron tricarbonyl, which exists predominantly as isomer VIII, is shown to yield two monocyclic complexes. From an analysis of the proton nmr spectra these are shown to be IXa (66%) and IXb (33%). At −62° IXa undergoes electrocyclic ring closure ($k = 3.5 \times 10^{-4}$ sec^{-1}, $\Delta F^{\ddagger} = 15.6$ kcal/mol) to bicyclic ion Xa, while IXb at −62° isomerizes to Xb ($k = 7 \times 10^{-4}$ sec^{-1}, $\Delta F^{\ddagger} = 15.3$ kcal/mol). From the fact that isomers IXa and IXb are formed from protonation of VIII it can be inferred that the C_6 and C_7 positions were the sites of initial protonation of VIII and, by analogy, must be the site of protonation of I. These data indicate that II is the initial product of protonation and rule out the possibility of initial formation of either IV or V followed by rapid rearrangement to III.

There has been much current interest and speculation, both theoretical and experimental, concerning the influence of transition metals upon the thermal isomerization of organic molecules.[1-4] This interest has concentrated particularly on those organic transformations which, in the absence of the metal, are formally orbital symmetry-forbidden reactions. From a theoretical point of view both Mango and coworkers[1] and Pettit and coworkers[2] have examined the question of whether orbital interactions between an organic molecule and a transition metal may remove symmetry restrictions such that normally symmetry-forbidden reactions become symmetry allowed. Each cites possible experimental examples and each concludes that under appropriate conditions such a "symmetry catalysis" by a transition metal of a concerted ligand transformation is a clear possibility. These theoretical aspects have been reviewed in detail.[1d-f, 2b]

From an experimental point of view many organic systems in the presence of a transition metal ion or complex have been reported to undergo transformations which correspond formally to symmetry-forbidden reactions and are synthetically useful in that regard.[2,3] However, in the majority of these cases the exact mechanism is unknown. Since the metal serves a catalytic role, and, in general, no intermediates are isolated in the reaction, it is difficult to draw conclusions concerning the intimate details of the mechanism. Although some reactions may ultimately prove to be true examples of concerted "symmetry catalyzed" reactions, recent work has indicated that some of these transformations probably proceed stepwise through discrete intermediates.[4]

In our studies in this field we have been focusing on the thermal chemistry of systems in which the rearranging ligand is initially bound to the metal and remains bound during the course of the isomerization. By restricting ourselves to such systems we at least remove several uncertainties concerning the course of the reaction and are possibly better able to judge whether or not a concerted mechanism is involved. In addition, these studies are directed at the general influence of the metal on the patterns of and barriers to thermal isomerization of organic systems regardless of whether such reactions represent a formally forbidden or allowed transformation.

The initial system we chose for study and wish to report on here is the formation of bicyclo[5.1.0]octadienyliron tricarbonyl from protonation of cyclooctatetraeneiron tricarbonyl (I), first reported by Davison, McFarlane, Pratt, and Wilkinson.[5] In the light of recently developed orbital symmetry concepts, it

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[1] (a) F. D. Mango and J. H. Schachtschneider, *J. Amer. Chem. Soc.*, **89**, 2484 (1967); (b) *ibid.*, **91**, 1030 (1969); (c) *ibid.*, **93**, 1123 (1971); (d) F. D. Mango, *Advan. Catal.*, 20, 291 (1969); (e) *Chem. Technol.*, **1**, 758 (1971); (f) "Transition Metals in Homogeneous Catalysis," G. N. Schrauzer, Ed., Marcel Dekker, New York, N. Y., 1971, Chapter 6.

[2] (a) W. Merk and R. Pettit, *J. Amer. Chem. Soc.*, **89**, 4787, 4788 (1967); (b) R. Pettit, H. Sugahara, J. Wristers, and W. Merk, *Discuss. Faraday Soc.*, **47**, 71 (1969); (c) G. S. Lewandos and R. Pettit, *Tetrahedron Lett.*, 789 (1971).

[3] (a) C. W. Bird, R. C. Cookson, and J. Hudec, *Chem. Ind. (London)*, 20 (1960); (b) C. W. Bird, D. L. Colinese, R. C. Cookson, J. Hudec, and R. O. Williams, *Tetrahedron Lett.*, 373 (1961); (c) G. N. Schrauzer, *Advan. Catal.*, **18**, 373 (1968), and references cited therein; (d) H. Hogeveen and H. C. Volger, *J. Amer. Chem. Soc.*, **89**, 2486 (1967); (e) H. Hogeveen and H. C. Volger, *Chem. Commun.*, 1133 (1967); (f) H. C. Volger and H. Hogeveen, *J. Amer. Chem. Soc.*, **91**, 218 (1969); (g) R. L. Banks and G. C. Bailey, *Ind. Eng. Chem., Prod. Res. Develop.*, **3**, 170 (1964); (h) N. Calderon, E. A. Ofstead, J. P. Ward, W. A. Judy, and K. W. Scott, *J. Amer. Chem. Soc.*, **90**, 4133 (1968); (i) W. B. Hughes, *ibid.*, **92**, 532 (1970); (j) J. C. Mol, F. R. Visser, and C. Boelhouwer, *J. Catal.*, **17**, 114 (1970); (k) J. Wristers, L. Brener, and R. Pettit, *J. Amer. Chem. Soc.*, **92**, 7499 (1970).

[4] (a) T. J. Katz and S. A. Cerefice, *ibid.*, **91**, 2405 (1969); (b) *ibid.*, **91**, 6519 (1969); (c) L. Cassar, P. E. Eaton, and J. Halpern, *ibid.*, **92**, 3515 (1970); (d) K. L. Kaiser, R. F. Childs, and P. M. Maitlis, *ibid.*, **93**, 1270 (1971); (e) L. A. Paquette, *Accounts Chem. Res.*, **4**, 280 (1971).

[5] (a) A. Davison, W. McFarlane, L. Pratt, and G. Wilkinson, *Chem. Ind. (London)*, 553 (1961); (b) *J. Chem. Soc.*, 4821 (1962); (c) G. N. Schrauzer, *J. Amer. Chem. Soc.*, **83**, 2966 (1961), also reported protonation of I but incorrectly assigned a monocyclic structure to the observed ion III.

Table I. Proton Chemical Shifts and Coupling Constants for Ions II, III, IXa, IXb, Xa, and Xb[a]

Ion	Chemical shifts[b]									Coupling constants[c]
Monocyclic ions[d]	H_1,H_5		H_4,H_2,H_6,H_7		H_3	$H_{8(exo, endo)}$		$-CH_3$		
II	5.42		4.05		3.10 (t)	7.13				$J_{3,2} = J_{3,4} = 7$, $J_{1,2} = 10$
IXa	5.48		4.07			7.05		7.28 (s)		
IXb	5.48		4.07		3.18 (d)	7.05		7.35 (s)		$J_{2,3} = 7$
Bicyclic ions[e]	H_2	H_3	H_5	H_6	H_4	H_1,H_7	$H_{8(exo)}$	$H_{8(endo)}$	CH_3	
III	4.52				2.18	7.36	8.50	8.32		$J_{8(exo)-8(endo)} = 4.8$[f] $J_{8(exo),1} = J_{8(exo),7} = 8$[f] $J_{8(endo),1} = J_{8(endo),7} = 4.5$[f]
Xa	4.95 (d)		4.58	4.32 (dd)	2.37 (d)	7.35	8.47		7.60	$J_{4,5} = 6$, $J_{1,2} = 7$, $J_{6,7} = 7$, $J_{5,6} = 10$
Xb	4.58					7.35	8.47		6.90	

[a] Spectra recorded on a Varian HA-100 MHz spectrometer. [b] Chemical shifts reported relative to internal CH_2Cl_2 taken as τ 4.70. s = singlet, d = doublet, t = triplet, dd = doublet of doublets. [c] Coupling constants in hertz. All coupling constants verified by double resonance techniques. [d] Spectra for monocyclic ions recorded at −80°. [e] Spectra for bicyclic ions recorded at −50°. [f] Values taken from ref 5b.

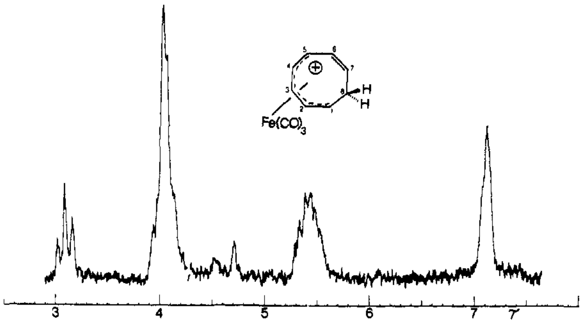

Figure 1. The 100-MHz proton nmr spectrum of cyclooctatrienyliron tricarbonyl (II) at −80° in FSO_3H-SO_2ClF. The internal standard $CHDCl_2$ appears at τ 4.70 while a trace of ion III is evident at τ 4.52.

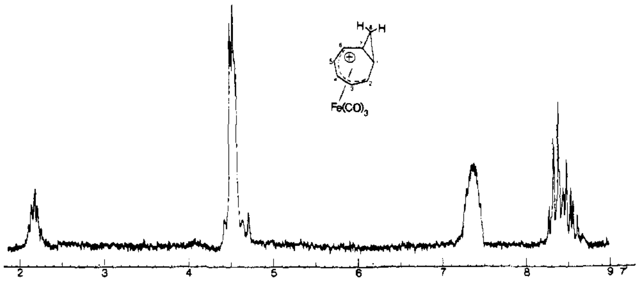

Figure 2. The 100-MHz proton nmr spectrum of bicyclo[5.1.0]-octadienyliron tricarbonyl (III) at −50° in FSO_3-SO_2ClF. The internal standard $CHDCl_2$ is evident at τ 4.70 while a trace of ion II remains as evidenced by the τ 4.05 signal.

seemed likely that formation of the bicyclic ion occurred *via* concerted electrocyclic ring closure of a monocyclic intermediate. Since techniques were available for protonation and observation of ionic species in strong acids at temperatures below −120°, it appeared feasible to possibly observe and study the monocyclic intermediate. In this paper we report the observation of such monocyclic intermediates from low-temperature protonation of I and methylcyclooctatetraeneiron tricarbonyl, the structure of these intermediates, and the observation of their electrocyclic ring closures to the bicyclic ions.[6] These studies also yield data on the energetics of the electrocyclic ring closure as well as insight into the detailed mechanism of protonation of the cyclooctatetraene complexes.

Results

Protonation of Cyclooctatetraeneiron Tricarbonyl (I). Protonation of I was accomplished either by dissolving the complex in FSO_3H-SO_2F_2 (1:3 v/v) under nitrogen at −120° or by adding a methylene-d_2 chloride solution of I (filtered and degassed) to a degassed FSO_3H-SO_2ClF solution at −125° followed by sealing under high vacuum (see Experimental Section). The latter technique was superior in producing solutions which gave sharp proton nmr signals with no observable line broadening due to paramagnetic impurities.

Using these techniques for protonation of I, a monocyclic intermediate assigned structure II (see below) could indeed be generated and observed at low temperatures by nmr. Solutions of II generated at −125° exhibited similar nmr spectra in the range of −120 to −80°; however, at −80° resolution was considerably better due to decreased solution viscosity. A typical spectrum is illustrated in Figure 1 and chemical shifts and coupling constants for II are summarized in Table I. When the temperature of the solution of II is raised, the ion undergoes a clean first-order ring closure to the previously reported[5] bicyclo[5.1.0]-octadienyliron tricarbonyl complex III. The first-order rate 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 III is shown in Figure 2 while nmr data for the ion are summarized in Table I.

Initially, three possible structures were considered for the observed low-temperature intermediate. These species were (a) ion II in which the ligand contains a five-carbon pentadienyl cation bound to iron and a "free" or unbound double bond, (b) ion IV which contains a free allylic cation and iron bound to a diene unit, and (c) ion V in which iron is bound to an allylic cation leaving an unbound diene moiety. These possibilities were considered for the reason that each had, to an extent, a literature analogy and each could arise from protonation of I at a rational position (see below). From analysis of the nmr data as detailed below structure II was the clear choice for the intermediate.

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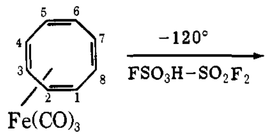
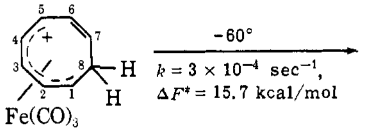
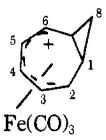
[6] Preliminary results of parts of this work have been reported: (a) M. Brookhart and E. R. Davis, *J. Amer. Chem. Soc.*, **92**, 7622 (1970); (b) *Tetrahedron Lett.*, 4349 (1971). (c) After our first communication concerning this work we learned that ion II had also been observed by D. A. T. Young, Ph.D. Thesis, UCLA, 1969. We thank Dr. Young for communicating his results to us.



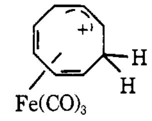
I



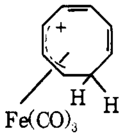
II



III

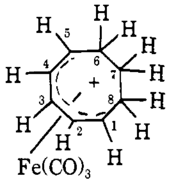


IV



V

The agreement of the nmr parameters as assigned in Table I with those expected for structure II is excellent. The chemical shift positions and differences of the H_1,$H_5(\alpha)$,H_2,$H_4(\beta)$, and the $H_3(\gamma)$ protons are in accord with other α, β, and γ protons of cyclic pentadienyliron tricarbonyl complexes.[5b,7-9] Perhaps the best model for II is the cyclooctadienyliron tricarbonyl complex VI reported by Wilkinson[8] for which the nmr data are summarized. The close correlation of these shifts with those of II is evident. The assignment of structure II is also strengthened on the basis of coupling constant analogies to pentadienyliron systems. The $J_{2,3}$ and $J_{3,4}$ of 7 Hz is that expected for a β,γ coupling, while the $J_{1,2}$ of 10 Hz is typical of the α,β cis coupling.[5b,10]



τ 7.5–8.5 (5 H)
τ 9.54 (1 H, quartet)

H_1,H_5, τ 5.53
H_2,H_4, τ 4.27
H_3, τ 2.73 (triplet)

VI

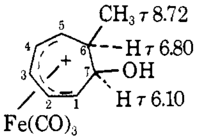
Although no direct analogies exist for the chemical shifts of the H_6 and H_7 of the unbound double bond, their position is approximately that expected based on the chemical shift (*ca.* τ 4.5) of the protons of the uncomplexed double bond in cyclooctatrieneiron tricarbonyl.[8] The methylene resonance (τ 7.13) is in accord with the expected value based on models such as VI. The assignment of this signal is further confirmed by protonation in DSO_3F-SO_2ClF which reduces the relative intensity of this band to one proton.[11]

Structure IV can be eliminated as a possibility by examining model cyclic allylic cations.[12] Based on these models, signals for H_5 and H_7 of the allylic system should appear in the *ca.* τ 0 region whereas the resonance for the central proton, H_6, would be expected in the τ 2 region. In addition, the H_1 chemical shift should be *ca.* τ 6.5 based on model cyclic diene complexes.[8] These shifts are clearly not in accord with those observed for the intermediate.

If structure V is assigned to the intermediate, then the τ 4.12 band must be assigned to the H_4–H_7 protons of the free diene, the τ 5.46 signal to H_1 and H_3, and the τ 3.23 triplet to H_2. From the data available on π-allyliron cations,[13] the difference in the H_1,H_3 and the H_2 shifts is too great and the H_2 resonance is at much lower fields than expected. Serious objections must also be raised against V on the basis of bonding considerations. As written, iron is two electrons short of the rare gas configuration even though these electrons are readily available for coordination from the cyclooctatrienyl ligand, a situation which apparently has no precedent.

Warming of ion III in FSO_3H-SO_2ClF solution to room temperature results ultimately in general decomposition of the sample. However, preparation of ion III in a degassed solution of 93% H_2SO_4 followed by warming to 35° for *ca.* 24 hr results in a new species being formed. This new species exhibits nmr signals at τ 3.08 (triplet), 4.18, 5.70, 6.10, 6.80, and 8.72 (doublet, $J = 6$ Hz) with relative integrated intensities of 1:2:2:1:1:3, respectively. All signals were somewhat broadened probably due to formation of paramagnetic impurities. The shift and pattern of the 3.08, 4.18, and 5.70 bands suggested that a pentadienyliron complex was retained while the three proton doublet at τ 8.72 seemed to indicate the formation of a methyl group. The new species is tentatively assigned structure VII which results from addition of water to the cyclopropane ring in III.[14]

H_1,H_5, τ 5.70
H_2,H_4, τ 4.18
H_3, τ 3.08



VII

A problem which we sought to solve was the *initial position* of protonation of I. Work by Davison[5b] in D_2SO_4 had shown that proton attack occurs trans to the metal with the entering proton (deuteron) finally occupying the "inside" or endo methylene position. This is in contrast to the exo stereospecificity observed for protonation of cyclooctatetraenemolybdenum tri-

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(7) H. J. Dauben, Jr., and D. J. Bertelli, *J. Amer. Chem. Soc.*, **83**, 497 (1961).

(8) W. McFarlane, L. Pratt, and G. Wilkinson, *J. Chem. Soc.*, 2162 (1963).

(9) The nmr data for III serve as a poor model for II. In III the H_2, H_3, H_5, and H_6 protons occur at nearly identical chemical shifts, a highly unusual feature for α and β protons in pentadienyliron complexes and one perhaps due to the cyclopropyl ring anisotropy. In addition, the γ proton, H_4, appears as a quintet. This quintet, although originally interpreted[5b] as equal coupling of H_4 to H_2, H_3, H_5, and H_6, is best explained as "virtual coupling" between H_4 and H_2,H_6 in the AA'BB'X system.

(10) (a) J. E. Mahler and R. Pettit, *J. Amer. Chem. Soc.*, **85**, 3955 (1963); (b) J. E. Mahler, D. H. Gibson, and R. Pettit, *ibid.*, **85**, 3959 (1963).

(11) As additional facts supporting resonance assignments in II we note that the γ hydrogen, H_4, appears as a clean triplet (no virtual coupling), indicating H_2,H_4 and H_1,H_5 must have different chemical shifts (see footnote 9) and that double resonance experiments show that the methylene protons (τ 7.13) are coupled to the H_1 proton (τ 5.42). Irradiation of the τ 7.13 signal reduces the τ 5.42 signal to a doublet of 10 Hz ($J_{1,2}$) superimposed on a multiplet.

(12) A. F. Diaz, D. L. Harris, M. Sakai, and S. Winstein, *Tetrahedron Lett.*, 303 (1971).

(13) G. F. Emerson and R. Pettit, *J. Amer. Chem. Soc.*, **84**, 451 (1962).

(14) The reaction of III at room temperature is in contrast to those of the ruthenium and osmium analogs of III reported by M. Cooke, P. T. Draggett, M. Green, B. F. G. Johnson, J. Lewis, and D. J. Yarrow, *Chem. Commun.*, 621 (1971).

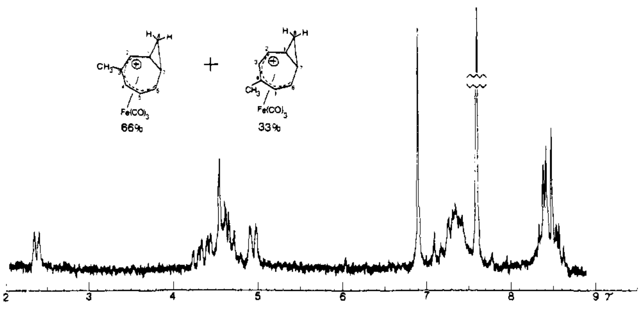


Figure 3. The 100-MHz proton nmr spectrum at −50° in FSO_3H–SO_2ClF of the mixture of ions Xa and Xb generated from rearrangement of IXa and IXb.

carbonyl[15] but similar to the protonation of cyclooctatetraene which is predominantly endo.[16] The observation of trans protonation of I clearly rules out a mechanism in which iron is initially protonated followed by proton migration to the ligand.

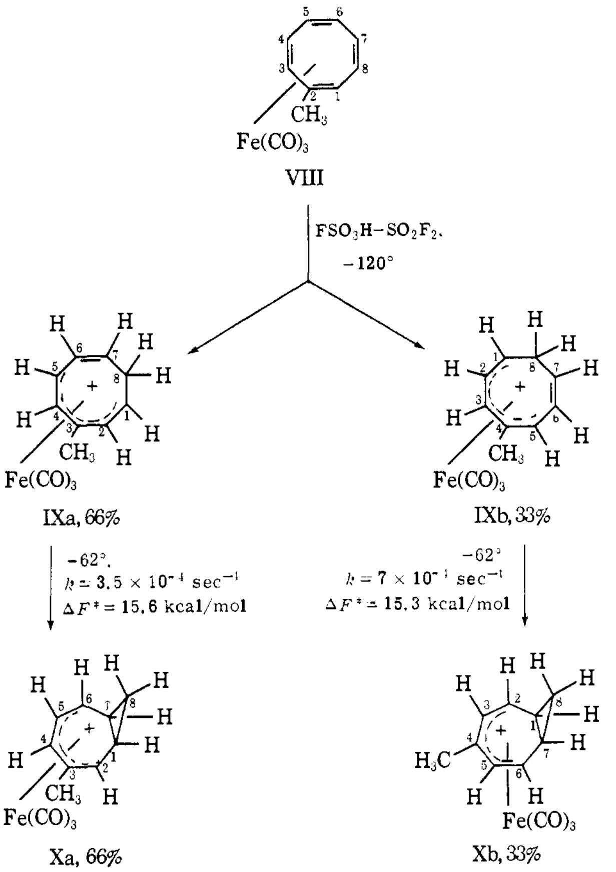
Even though it is clear that II is the first observed intermediate, IV or V could be precursors of II. For example, protonation at either equivalent "terminal" position of the unbound diene (C_5 or C_8) is reasonable and would yield ion IV which could rapidly isomerize to II. Similarly, in analogy with simple dieneiron tricarbonyl complexes, protonation may occur at C_1 or C_4 to yield initially ion V which could rapidly collapse to II.[17] Of course, if ion II is the first formed ion the protonation must occur initially at C_6 or C_7.

In order to determine the position of protonation, a ring label is needed. A deuterium label, even if it could be introduced into a specific position, is unsatisfactory since rapid iron migration about the ring would equilibrate the deuterium to all positions.[18,19] An ideal label proved to be the methyl substituent as described below.

Protonation of Methylcyclooctatetraeneiron Tricarbonyl (VIII). Anet[19] has demonstrated with an elegant deuterium-labeling experiment that VIII exists at −145° almost exclusively (≥90%) as the isomer shown with the methyl group bound to one of the internal carbons of the bound diene unit. In that the introduction of a methyl group creates a preponderance of one isomer, it becomes an ideal label for determining the initial position of protonation.

Protonation of VIII at −120° by either technique described above yields a clear yellow solution containing a mixture of monocyclic isomers. The nmr of this solution at −80° exhibits a τ 3.18 doublet (J = 7 Hz) and multiplets at τ 4.07, 5.48, and 7.05. The respective integrated intensities of these bands are 0.33, 3.7, 2.0, and 2.0. In addition, two methyl singlets appear at τ 7.28 and 7.35 in the ratio of 2:1 with a total integrated intensity of 3.0.

This system is best interpreted as a 2:1 mixture of complexes IXa and IXb. The appearance of two methyl singlets indicates the formation of two isomeric complexes in a *ca.* 2:1 ratio. Only a *single* band of relative intensity 0.33 appears in the region where the central proton, H_3, of the pentadienyl system of the monocyclic complexes should appear (*ca.* τ 3.1 in analogy with II). This clearly indicates that the major isomer (66%) must be IXa with a methyl substituent at C_3. The fact that the H_3 signal observed at τ 3.18 for the minor (33%) isomer is a doublet indicates that the methyl group in this isomer must be bound to a carbon adjacent to C_3. If this were not the case H_3 would appear as a triplet analogous to the H_3 signal for II. This minor isomer is assigned structure IXb. The data presented thus far would not rule out the isomer containing the methyl substituent at C_2, however; this structure is highly doubtful since the ring-closed product of the minor isomer corresponds to the assigned structure IXb and not to the isomer bearing the methyl substituent at C_2 (see below). The positions and integrated intensities of the remaining signals are in accord with these isomer assignments; the methylene (τ 7.05) and the H_1,H_5 (τ 5.48) resonances integrate as expected for two protons each while the τ 4.07 band assigned to H_2, H_4, H_6, and H_7 of both isomers integrates as predicted for *ca.* 3.7 protons. The nmr data for each isomer are summarized in Table I.



When the acid solution is warmed to −60° both monocyclic complexes IXa and IXb undergo ring closures to bicyclic complexes Xa (66%) and Xb (33%), respectively. The spectrum of this mixture is shown in Figure 3 and the nmr data for each ion are summarized in Table I. The excellent agreement of these data

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[15] S. Winstein, H. D. Kaesz, C. G. Kreiter, and E. C. Friedrich, *J. Amer. Chem. Soc.*, **87**, 3267 (1965).

[16] S. Winstein, C. G. Kreiter, and J. I. Brauman, *ibid.*, **88**, 2047 (1966).

[17] If protonation and iron migration were synchronous, neither ion IV nor V need be postulated as discrete intermediates to envision initial protonation at C_5,C_8 or C_1,C_4.

[18] (a) C. G. Kreiter, A. Maasbol, F. A. L. Anet, H. D. Kaesz, and S. Winstein, *J. Amer. Chem. Soc.*, **88**, 3444 (1966); (b) F. A. Cotton, A. Davison, and J. W. Faller, *ibid.*, **88**, 4507 (1966); (c) C. E. Keller, B. A. Shoulders, and R. Pettit, *ibid.*, **88**, 4760 (1966); (d) F. A. L. Anet, H. D. Kaesz, A. Maasbol, and S. Winstein, *ibid.*, **89**, 2489 (1967).

[19] F. A. L. Anet, *ibid.*, **89**, 2491 (1967).

with structures Xa and Xb substantiates the structural assignments of IXa and IXb. Two methyl singlets appear at τ 7.60 and 6.90 in a 2:1 ratio for the major IXa and minor IXb complexes. In the low-field region of the spectrum where H_4 resonances should appear, only a *single* band is observed, a doublet ($J_{4,5}$ = 6 Hz) at τ 2.37 now with relative intensity of 0.63 as expected for Xa. Since Xb contains a methyl substituent at C_4 no other H_4 resonance is observed. Due to perturbation of the methyl group, considerable spread in the H_2, H_3, H_5, and H_6 chemical shifts was observed for Xa which provides more detailed assignments and coupling constant data than in II. The H_2 signal of Xa appears as a doublet ($J_{1,2}$ = 7 Hz) at τ 4.95 (relative intensity 0.64) while H_6 of Xa appears at τ 4.32 (relative intensity 0.63) as a skewed quartet ($J_{6,7}$ = 7, $J_{6,5}$ = 10 Hz). (Coupling constant assignments were confirmed by double resonance experiments.) The H_2, H_3, H_5, and H_6 signals of Xb and the H_5 signal of IXa appear as a broad multiplet at *ca.* τ 4.58 with an integrated intensity of 2.0 (see Figure 3). The methylene resonance and the bridgehead resonances (H_1,H_7) appear at τ 8.47 and 7.35, respectively, each exhibiting integrated intensities of 2.0 as expected.

By carefully integrating the four methyl resonances and the τ 3.16 and 2.37 signals during the course of the rearrangement, the rate of ring closure for each individual isomer could be determined. At $-62°$ the first-order rate constant for closure of IXa to Xa is 3.5×10^{-4} sec^{-1} corresponding to $\Delta F^{\ddagger} = 15.7$ kcal/mol while the rate constant for ring closure of IXb to Xb is 7.0×10^{-4} sec^{-1}, $\Delta F^{\ddagger} = 15.3$ kcal/mol.

The formation of complexes IXa and IXb is consistent only with protonation of VIII at C_6 (33%) and C_7 (66%), the internal positions of the free diene moiety[20] (see Discussion). Regarding the methyl group as only a minor perturbation, the protonation of I must also occur at C_6 and C_7 which in I are equivalent.

Discussion

The ring closure of II to III appears to represent the first reported case of the observation of an electrocyclic ring closure of an organic ligand bound to a transition metal. The present case does not represent a normally symmetry-forbidden isomerization. The closure involves a six π-electron system, and therefore the disrotatory mode of closure is symmetry allowed for the free ligand and is the mode observed in the complex II. In this particular case it is difficult to assess the exact effect of the metal on the activation energy for ring closure since the analogous transformation in the free ligand has not been observed. The free ligand is of course the nonclassical homotropylium ion[21] in which the C_1–C_7 bond is neither a classical σ bond nor completely open, but a bond with both σ and π character. Although several disrotatory ring closures have been reported for cyclic trienes[22] and the activation energies are generally higher (*ca.* 25 kcal/mol), these closures serve as poor models for the cationic II to III closure.

Considering the unusual stability of pentadienyliron cations as compared to allylic cations, it is not surprising that II represents the structure of the monocyclic complex in which the iron is bound to a pentadienyl cation. The bonding in the tropyliumiron tricarbonyl cation is thought to be similar with the ligand best described as containing a free double bond and a pentadienyl cation bound to iron.[23]

Since signals for II are sharp at $-40°$, no rapid 1,3 oscillations of iron are occurring with activation energies less than *ca.* 11 kcal/mol. Such oscillations would average H_1 with H_7, H_2 with H_6, and H_3 with H_5. The 1,3-iron shift appears to be a process with a considerably higher activation energy than a 1,2 shift.[24] Cycloheptatrieneiron tricarbonyl exhibits no nmr line broadening due to 1,3 shifts at temperatures up to 100° ($\Delta F^{\ddagger} >$ *ca.* 20 kcal/mol, $-120°$)[25] while I is fluxional by virtue of 1,2-iron shifts simultaneous with bond shift ($\Delta F^{\ddagger} = 7.2$ kcal/mol).[18,19] The tropyliumiron tricarbonyl cation is fluxional[23] with iron migration no doubt occurring *via* 1,2 shifts. It is interesting to note that in the present case a 1,2 iron shift in II in fact corresponds to ring closure and formation of III.

The exact position of protonation of I is a question of considerable interest. Three of the four different possible positions appear to be plausible ones. If the complexed diene and the free diene are acting as independent functional groups, then one might expect the position of protonation to correspond to that observed for either a simple conjugated diene or a simple dieneiron tricarbonyl complex. A simple diene would of course protonate at the external carbons (C_5,C_8 in I) while a dieneiron tricarbonyl complex would also be expected to protonate at external positions (C_1,C_4 in I) based on literature analogies.[13,26] These positions of protonation correspond to initial formation of IV and V, respectively, either of which could rapidly rearrange to II. If there is substantial "coupling" of the two diene units, then protonation might be expected to occur at the internal carbons of the free diene (C_6,C_7 in I) to yield the first observed complex, II, initially. The experimental results indicate that this latter case applies and that protonation occurs at C_6 and C_7 in VIII. The argument for these positions of protonation is as follows. Formation of IXb can arise only from protonation at C_6 while isomer IXa can arise from protonation at either C_5 or C_7. Since positions C_6 and C_7 are equivalent in I (internal carbons of the unbound diene) it seems most reasonable that isomer IXa must arise from protonation of VIII at C_7 rather

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[20] The possibility that IXa and IXb arise from protonation of a minor isomer in equilibrium with VIII is remote. For the case of either the 1- or 5-methyl isomer of VIII, protonation would have to occur at two positions which are *nonequivalent* in I, while for the 6-methyl isomer protonation would have to occur at the unlikely 2 and 3 positions. In addition, protonation of VIII would probably be more rapid than the rate of conversion of VIII to a minor isomer.[19]

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than C_5. A second argument for protonation at C_7 and against protonation at C_5 is the absence of the 2-methyl isomer which would arise from protonation at C_8, a position essentially equivalent to C_5 (external carbons of the unbound diene). By analogy, I also protonates at C_6 and C_7 thus indicating that I, as regards attack by the proton, behaves neither as a free diene nor as an iron bound diene. These results suggest that for the electrophilic substitutions of I reported by Lewis,[27] attack of the electrophile probably also occurs at C_6 and C_7, a fact which may eventually prove valuable in predicting the products of electrophilic substitutions of substituted derivatives of I.

The fact that IXa is formed as the major isomer but yet undergoes ring closure at a slower rate than the minor isomer IXb suggests that IXa is more stable than IXb. Such a difference in stability would seem to imply that the positive charge at the central (γ) carbon in a cationic pentadienyliron complex may be somewhat greater than at the β carbon, but other factors may also be important in determining the difference in stability between IXa and IXb.[28]

Experimental Section

General. Low-temperature, high-resolution proton nmr spectra were recorded either on a Jeolco C-60HL spectrometer (60 MHz) or on a Varian HA-100 spectrometer (100 MHz). All spectra below −100° were recorded on the Jeolco instrument. Spin decoupling experiments were performed on the Varian instrument. For best resolution it was necessary to tune the spectrometers at low temperatures after thorough thermal equilibration with a sealed, degassed sample of $FSO_3H-SO_2ClF-CH_2Cl_2$. Infrared spectra were recorded in CS_2 solution on a Perkin-Elmer 421 spectrometer. Melting points are uncorrected and were obtained using a Buchi melting point apparatus.

Fluorosulfonic acid (Allied Chemical Co.) was twice distilled, divided into 0.5-ml portions and sealed in ampoules under nitrogen. A fresh ampoule was used for each ion preparation. Sulfuryl chloride fluoride (Allied Chemical) and sulfuryl fluoride (Matheson) were used as received.

Preparation of Ions. Method A.[29] Using this technique samples were prepared at low temperatures directly in nmr tubes and sealed under high vacuum. The basic apparatus used consisted of an nmr tube sealed to a 24/40 standard taper male joint thus allowing vacuum line operations. Between the joint and the nmr tube was a high vacuum stopcock which allowed the tube to be blanketed with nitrogen when not connected to the vacuum line. Initially the apparatus was flushed with purified nitrogen passed through the high vacuum stopcock and the nmr tube was then cooled to −78°. Distilled FSO_3H (0.15 ml) and SO_2ClF (0.30 ml) were condensed in the tube and mixed with a long glass rod. This solution was degassed on a vacuum line and removed under nitrogen to a low-temperature bath. A CD_2Cl_2 solution of the iron complex was then prepared by degassing 0.20 ml of CD_2Cl_2 and bulb to bulb distilling onto the iron complex (*ca.* 35 mg) which had been placed on a medium porosity glass frit. The CD_2Cl_2 solution of the complex was then sucked through the frit into a small Schlenk tube and stored under nitrogen until needed (see below). At this point a "buffer" layer of SO_2ClF (0.15 ml) was carefully condensed onto the top of the degassed FSO_3H-SO_2ClF solution which had cooled to −125°. The CD_2Cl_2 solution of the complex was then carefully added under nitrogen *via* a capillary dropper to the top of the SO_2ClF buffer layer. After the CD_2Cl_2 had completely cooled (*ca.* 15 sec), the layers were mixed rapidly with the glass stirring rod (which had remained in the nmr tube) until a homogeneous solution was obtained. The apparatus was then transferred to a vacuum line and the tube was sealed off at liquid nitrogen temperatures under high vacuum. The sealed tube was stored in liquid nitrogen until nmr spectra were recorded.

Method B. As above, ion samples were prepared directly in nmr tubes. Initially, the nmr tube was flushed for several minutes with purified nitrogen through a thinly drawn capillary tube inserted 7 cm into the nmr tube. The tube was continually flushed throughout the preparation of the ion. To this tube a finely ground solid sample of the iron complex (*ca.* 35 mg) was added. The tube was cooled to −120° and SO_2F_2 (0.5 ml) was condensed onto the complex. Distilled FSO_3H (0.2 ml) was added slowly with a capillary dropper. The acid was allowed to run slowly down the side of the cold tube so that it had cooled by the time it reached the SO_2F_2 solution. The mixture was stirred vigorously for *ca.* 15–20 min until all the solid complex had dissolved. The nitrogen capillary was quickly removed and the tube was immediately sealed with a pressure cap and further with parafilm. Spectra were recorded as quickly as possible; samples were stored for only a short time at −120°.

Methylcyclooctatetraene. Methylcyclooctatetraene was prepared from bromocyclooctatetraene[30] employing the lithium dimethylcopper reagent described by Corey.[31] To generate the lithium dimethylcopper, 52 ml of a 2.11 *M* solution of methyllithium in ether was added dropwise under nitrogen over 10 min to a rapidly stirring suspension of 10.37 g (0.0545 mol) of CuI in 50 ml of anhydrous ether cooled to 0°. After addition, the reaction was stirred 15 min at 0°. To this solution was added dropwise over 10 min 2.03 g (0.011 mol) of bromocyclooctatetraene in 15 ml of ether. After stirring at 0° for 3.0 hr, the solution was quenched by addition of 50 ml of saturated ammonium chloride solution. The resulting solution was filtered; the filtrate was extracted with ether. The ether extracts were washed with water and a saturated NaCl solution and were then dried over anhydrous K_2CO_3. Filtration and evaporation of the ether fraction yielded 1.05 g (0.009 mol) of methylcyclooctatetraene as a yellow oil (82% yield). The nmr (CS_2) of this material exhibited a 3-proton methyl singlet at τ 7.75 and a 7-proton band at τ 3.85 for the ring protons. The nmr spectrum indicated the compound was 95% pure and this sample was used without further purification for preparation of the iron complex.

Cyclooctatetraeneiron Tricarbonyl (I). I was prepared as previously described by Manuel and Stone.[32] The complex was sublimed twice [75° (0.1 mm)] before use.

Methylcyclooctatetraeneiron Tricarbonyl (VIII). A similar procedure to that employed by Anet[19] was used in the preparation of VIII.

To 25 ml of *n*-hexane was added 0.50 g (0.042 mol) of methylcyclooctatetraene and 1.54 g (0.041 mol) of diiron nonacarbonyl. This mixture was refluxed under nitrogen for 30 min and cooled to room temperature and the *n*-hexane was removed under vacuum to leave a red residue. The residue was chromatographed on a silica gel column with hexane to yield 0.605 g of deep red complex which was further purified by sublimation [85° (0.05 mm)] to yield 0.52 g (49%) of red crystals: mp 40°; ν_{CO} (CS_2) 2048, 1985, and 1967 cm^{-1}. The nmr spectrum (CS_2, internal TMS) is essentially identical with that reported[18c] showing a complex multiplet (6 H) at τ 4.2–5.3, a doublet (1 H, J = 10 Hz) at τ 5.67, and a methyl singlet (3 H) at τ 8.16.

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[28] As pointed out by a referee there are no data that indicate that the charge distribution in an iron-complexed pentadienyl ion is similar to the distribution in the uncomplexed ion.

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