15), 203 (13), 202 (100), 201 (15), 155 (16), 125 (12), 91 (77), 78 (20), 47 (14).

With Phenyllithium in 70:30 Benzene–Ether. 46. The reaction described above was conducted with 1.0 mmol of **33** and 1.03 mmol of commercial phenyllithium. The nmr spectrum of the crude reaction product obtained in 66% yield showed besides a singlet at τ 2.80 attributable to **47** only resonances due to **46** and hydrocarbon impurity from the commercial phenyllithium. This mixture was not further characterized.

Phenylphosphahomocuneane Oxide (33) with Methyllithium. 48. A 50-ml, three-necked, round-bottomed flask equipped with a nitrogen inlet, serum cap, stopper, and magnetic stirrer was flamed while purging with nitrogen. Phenylphosphahomocuneane oxide (**33**) (114 mg, 0.50 mmol) and 5 ml of anhydrous ether were added. While stirring the suspension rapidly, 0.5 ml (1.1 mmol) of methyllithium[73] in ether was added through the serum cap. The solid gave way to a yellow solution within 5 min. After 4 hr the reaction was quenched with 5 ml of H_2O, whereupon the yellow color discharged and gas evolved. The aqueous layer was extracted (3 × 10 ml) with chloroform and the combined organic layers were dried ($MgSO_4$) and stripped, leaving 140 mg of off-white crystalline material. Recrystallization from hexane and sublimation at 95° (0.05 mm) gave 80 mg (66%) of white crystals: mp 108–110°; mass spectrum (peaks $\geq 10\%$ intensity) m/e (rel intensity) 244 (M^+, 17), 243 (25), 166 (47), 165 (60), 141 (10), 140 (100), 139 (20), 125 (53), 105 (10), 104 (12), 103 (11), 91 (10), 79 (10), 78 (19), 77 (36), 51 (13), 47 (20).

Acknowledgments. We are grateful to the National Institutes of Health for support under Grants No. MH08912 and No. GM19173, to Badische Anilin und Sodafabrik, A.G., for gifts of cyclooctatetraene, to James C. Carnahan, Jr., for initially developing the improved syntheses shown in Scheme III, and to Jerome Groopman and Jeffrey Johnson for assisting in the syntheses.

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[73] This methyllithium was in ether solution and contained LiBr. It was obtained from Alfa Inorganics, Beverly, Mass.

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cis^4-Cyclononatetraeneiron Tricarbonyl. Its Synthesis, Thermal Rearrangement, and Low-Temperature Protonation[1]

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Received September 22, 1972

Abstract: The preparation and characterization of *cis*^{4}-cyclononatetraeneiron tricarbonyl (III) are reported. This complex is prepared from the reaction of *cis*-bicyclo[6.1.0]nonatriene either photochemically with iron pentacarbonyl or thermally with diiron nonacarbonyl. Additional complexes isolated and characterized from these reactions include *cis*-8,9-dihydroindeneiron tricarbonyl (IV), bicyclo[6.1.0]nonatrieneiron tricarbonyl (V), and the binuclear complex bicyclo[6.1.0]nonatrienediiron hexacarbonyl (VI). The *cis*^{4}-cyclononatetraeneiron tricarbonyl complex is stable for days at room temperature but at 101° undergoes electrocyclic ring closure to *cis*-dihydroindeneiron tricarbonyl (IV). The first-order rate constant for this process at 101° is 2.4×10^{-4} sec^{-1} corresponding to $\Delta F^{\ddagger} = 28.4$ kcal/mol. This is contrasted to the ring closure of *cis*^{4}-cyclononatetraene which occurs at 23° with a half-life of *ca.* 50 min ($\Delta F^{\ddagger}$ *ca.* 23 kcal/mol). Low-temperature protonation of cyclononatetraene complex III in FSO_3H–SO_2ClF is observed to occur at C_6 to yield the monocyclic cation X.

Over the past several years the chemistry of diene iron tricarbonyl complexes has received considerable attention and has proved to be interesting and varied. For the organic chemist, one valuable function of the iron tricarbonyl group has been to allow isolation of reactive polyolefins which are not normally stable at room temperature as their metal complexes. Among prominent examples of this phenomenon are cyclobutadieneiron tricarbonyl,[2] cyclopentadienoneiron tricarbonyl,[3] and norbornadien-7-oneiron tricarbonyl.[4]

A second aspect of the chemistry of iron diene complexes in which we have recently been interested is the thermal rearrangements of the bound organic ligands and the comparison of their thermal chemistry with the thermal chemistry of the uncomplexed organic systems. In this regard, we have recently reported the electrocyclic ring closure of 1,3,5-cyclooctatrieneiron tricarbonyl to bicyclo[4.2.0]octadieneiron tricarbonyl,[5] the ring closure of the cyclooctatrienyliron tricarbonyl cation to the bicyclo[5.1.0]octadienyliron tricarbonyl cation,[6] and the thermal conversion of bicyclo[5.1.0]octadieneiron tricarbonyl to bicyclo[4.2.0]octadieneiron tricarbonyl.[5a]

Interesting from both perspectives is the iron tricarbonyl complex of *cis*^{4}-cyclononatetraene (I). Although this tetraene has been prepared at low temperatures by several groups,[7–10] it is unstable relative to its

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[1] Research supported by the National Science Foundation (Grant GP-29580) and the North Carolina Board of Science and Technology.

[2] G. F. Emerson, L. Watts, and R. Pettit, *J. Amer. Chem. Soc.*, 87, 131 (1965).

[3] (a) M. L. H. Green, L. Pratt, and G. Wilkinson, *J. Chem. Soc.*, 989 (1960); (b) E. Weiss, W. Hübel, and R. Merenyi, *Chem. Ind. (London)*, 407 (1960).

[4] J. M. Landesberg and J. Sieczkowski, *J. Amer. Chem. Soc.*, **90**, 1655 (1968).

[5] (a) M. Brookhart, N. M. Lippman, and B. F. Lewis, Abstracts, 163rd National Meeting of the American Chemical Society, Boston, Mass., 1972, No. ORGN-16; (b) M. Brookhart, N. M. Lippman, and E. J. Reardon, Jr., *J. Organometal. Chem.*, in press.

[6] (a) M. Brookhart and E. R. Davis, *J. Amer. Chem. Soc.*, **92**, 7622 (1970); (b) D. A. T. Young, Ph.D. Thesis, UCLA, 1969; (c) M. Brookhart and E. R. Davis, *Tetrahedron Lett.*, 4349 (1971); (d) M. Brookhart, E. R. Davis, and D. L. Harris, *J. Amer. Chem. Soc.*, **94**, 7853 (1972).

[7] G. Boche, H. Boehme, and D. Martens, *Angew. Chem., Int. Ed. Engl.*, **8**, 594 (1969).

[8] P. Radlick and G. Alford, *J. Amer. Chem. Soc.*, **91**, 6529 (1969).

[9] A. G. Anastassiou, V. Orfanos, and J. H. Gebrian, *Tetrahedron Lett.*, 4491 (1969).

[10] S. Masamune, P. M. Baker, and K. Hojo, *Chem. Commun.*, 1203 (1969).

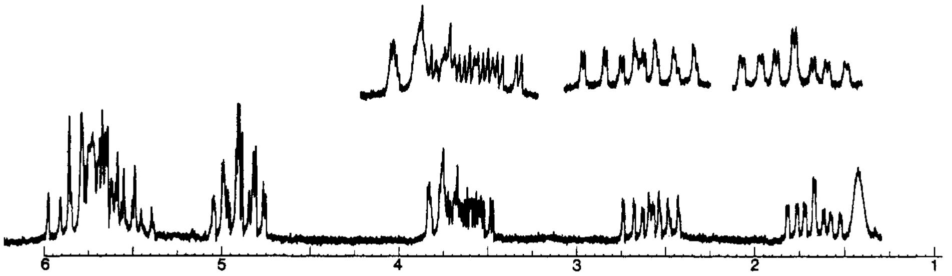
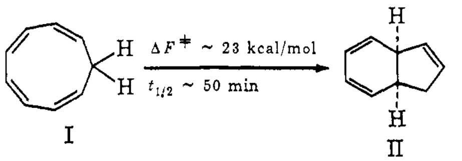


Figure 1. The 100-MHz pmr spectrum of cyclononatetraeneiron tricarbonyl in cyclohexane-d_{12}. The broad band at δ 1.43 is residual undeuterated solvent $C_6D_{11}H$.

ring-closed isomer, *cis*-8,9-dihydroindene (II), and



I

II

undergoes rapid electrocyclic ring closure to II at 23° ($t_{1/2} \sim 50$ min, $\Delta F^{\ddagger} \sim 23$ kcal/mol).[7,8,10]

In this paper we wish to report the isolation of *cis*^{4}-cyclononatetraeneiron tricarbonyl (III) and a study of its thermal rearrangement as well as the structure of the cation obtained from low-temperature protonation of III.

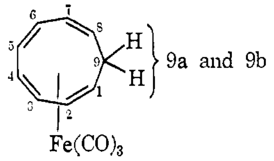
Results and Discussion

Preparation and Characterization of Complexes. Reaction of *cis*-bicyclo[6.1.0]honatriene either photochemically with iron pentacarbonyl or thermally with diiron nonacarbonyl yields a dark red mixture of comlexes from which *cis*^{4}-cyclononatetraeneiron tricarbonyl (III) can be isolated along with *cis*-8,9-dihydroindene-iron tricarbonyl (IV), bicyclo[6.1.0]nonatrieneiron tricarbonyl (V), and the binuclear complex bicyclo[6.1.0]-nonatrienediiron hexacarbonyl (VI).[11] Table I summarizes the relative yields for each procedure.

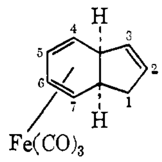
Table I

Method	Complex (% yields)			
	III	IV	V	VI
A,[d] thermal	12[a]	46[a]	15[a,b]	14[c]
B,[e] photochemical	35[c]	6[c]	15[c]	1[c]

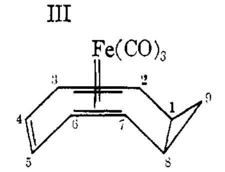
[a] Analyzed by glcp (6 ft × 0.25 in. 3% UCW-98 on 60–80 Chromosorb W) *vs.* internal standard; no significant rearrangement of III to IV occurred during analysis. [b] V decomposes in injection port and elutes as free ligand. [c] Isolated yield. [d] Method A: excess $Fe_2(CO)_9$, ether, 40 hr, 25°. [e] Method B: excess $Fe(CO)_5$, benzene, 4 hr, 40°, Hanovia 450-W lamp, Pyrex.



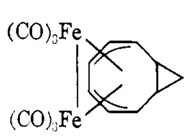
III



IV

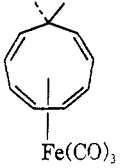


V



VI

The cyclononatetraeneiron tricarbonyl complex (III) was isolated as a crystalline yellow solid, mp 36–37°, showing strong infrared carbonyl absorptions at 2045 and 1975 (br) cm^{-1}, typical of iron tricarbonyl complexes. The 100-MHz pmr spectrum (C_6D_{12}) of III is illustrated in Figure 1 and shows signals at δ 1.68 (1 H), 2.60 (1 H), 3.61, 3.77 (overlapping, total 2 H), 4.79–5.07 (2 H), and 5.41–6.00 (4 H). The two nonequivalent methylene protons are assigned to the bands at δ 1.68 (H_{9a}) and 2.60 (H_{9b}). The triplet showing additional fine structure at δ 3.77 is assigned to H_4 and the highly coupled band centered at 3.61 (overlapping the 3.77 band) is assigned to H_1. These chemical shifts are typical of those of external protons of iron-complexed cyclic diene units[12] and assignments are further supported by decoupling experiments (see below). By analogy with other cyclic diene complexes,[12] the δ 4.79–5.07 resonance is assigned to the internal protons H_2 and H_3 of the bound diene, while the four free olefinic protons are assigned to the complex band at δ 5.41–6.00. Spin decoupling experiments further confirm these assignments and indicate $J_{9a,9b} = 14.5$, $J_{9a,1} = 5.2$, $J_{9b,1} = 11.0$, $J_{9a,8} = 9.5$, and $J_{9b,8} = 6.2$ Hz. The H_{9a} and H_{9b} protons also show additional long-range couplings of *ca.* 1.0 and 0.8 Hz, respectively. The fact that the external hydrogens of the bound diene (H_1 and H_4) are nonequivalent and that H_1 is strongly coupled to H_{9a} and H_{9b} clearly indicates the complex is the unsymmetrical species III in which the iron is bound to the 1,2 and 3,4 double bonds and not the symmetrical complex VII in which iron is bound to the 3,4 and 5,6 double bonds. Aside from nmr data, further proof that the ligand is *cis*^{4}-cyclononatetraene comes from cerium(IV) degradation of III. Reaction of III with ceric ammonium nitrate in acetone and work-up at −10° yield



VII

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(11) Using the nomenclature of F. A. Cotton [*J. Amer. Chem. Soc.*, **90**, 5412 (1968)], complex III is (1,2,3,4-*tetrahapto-cis*^{4}-cyclononatetraene)tricarbonyliron, IV is (2,3,4,5-*tetrahapto-cis*-bicyclo[4.3.0]nona-2,4,7-triene)tricarbonyliron, V is (2,3,6,7-*tetrahapto-cis*-bicyclo[6.1.0]-nonatriene)tricarbonyliron, and VI is (*hexahapto-cis*-bicyclo[6.1.0]-nontriene)hexacarbonyldiiron(*Fe–Fe*).

(12) M. L. Maddox, S. L. Stafford, and H. D. Kaesz, *Advan. Organometal. Chem.*, 3, 1 (1965).

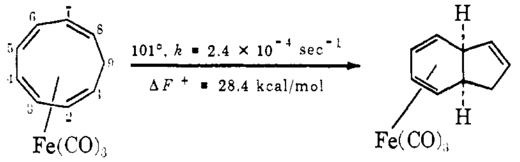
an oil whose pmr spectrum is consistent in detail with that reported for *cis*^{4}-cyclononatetraene.[8] Work-up at room temperature produces *cis*-8,9-dihydroindene (II) in 83% yield with no trace of the trans isomer (glpc). Since *trans,cis*^{3}- and *cis*^{4}-cyclononatetraenes electrocyclize respectively to the *trans*- and *cis*-8,9-dihydroindenes,[7–10] this result is also indicative of the *all-cis* assignment for the ligand in complex III.

The dihydroindene complex (IV) was isolated as a yellow oil exhibiting carbonyl bands in the infrared (CS_2) at 2045 and 1970 (br) cm^{-1} and complex pmr signals (CS_2, benzene internal standard δ 7.27) at δ 1.6–3.0 (4 H), 3.0–3.3 (2 H), and 5.1–5.5 (4 H). The δ 1.6–3.0 can clearly be assigned to H_{1a}, H_{1b}, H_8, and H_9 while the 3.0–3.3 signal is assigned to H_4 and H_7, the external protons of the bound diene, and the 5.1–5.5 signal to the internal protons H_5, H_6 and the free olefinic protons H_2, H_3. Further structural proof is derived from the observation that the identical complex is produced from the reaction of *cis*-dihydroindene in ether with $Fe_2(CO)_9$ and that *cis*-8,9-dihydroindene is produced in 70% yield when IV is degraded with ceric ammonium nitrate in ethanol at 0°.

The bicyclo[6.1.0]nonatriene complex V[13] was isolated as a yellow oil whose pmr spectrum (CS_2, benzene internal standard) exhibited a four proton multiplet at δ 0.95–1.80, a two proton doublet at 3.57 (J = 9.0 Hz), a two proton doublet at 4.08 (J = 9.0 Hz), and a two proton singlet at 5.48. The high field band (0.95–1.80) is assigned to the cyclopropane protons H_1, H_8, H_{9a}, and H_{9b}, while the low-field singlet (5.48) can be assigned to the equivalent free olefinic protons H_4 and H_5. The two doublets at δ 3.57 and 4.08 are due to the two sets of protons H_2, H_7 and H_3, H_6 on the bound vinyl groups ($J_{2,3} = J_{6,7} = 9.0$ Hz); however, the exact pairings are not clear. It might be anticipated that the H_3, H_6 set adjacent to the vinyl group would appear at lowest field and on that basis the δ 4.08 doublet is tentatively assigned to H_3, H_6 and the 3.57 doublet to H_2, H_7.[14] Since both doublets exhibit no additional observable coupling it can be inferred that $J_{3,4} = J_{5,6} \sim 0$ and $J_{1,2} = J_{7,8} \sim 0$. The observation that $J_{1,2} = J_{7,8} \sim 0$ indicates that the H_1, H_2 dihedral angle is *ca.* 90° and is evidence that the stereochemistry of the cyclopropane ring is cis to the iron tricarbonyl group as shown. Were the ring trans to the iron tricarbonyl group an observable H_1, H_2 coupling would be expected. It is of interest to note that in V iron is bound to the two terminal double bonds (2,3 and 6,7), whereas in all other cyclic conjugated triene and tetraene complexes (*e.g.*, 1,3,5-cyclooctatrieneiron tricarbonyl[15] and cyclooctatetraeneiron tricarbonyl[16]) iron prefers bonding to a 1,3 conjugated diene. This unusual bonding in V appears to be due to the steric incompatibility of the cis cyclopropane ring with an iron tricarbonyl group bound to the 1,3 diene unit.

The red-orange crystalline binuclear complex VI[17,19] exhibits pmr signals (CS_2, benzene standard) at δ 0.3–1.4 (H_{9a}, H_{9b}, H_1, H_8), 2.55 (H_2, H_7, doublet, $J_{2,3} = J_{6,7} = 8.2$ Hz), 3.8–4.25 (H_3, H_6), and 4.25–4.50 (H_4, H_5) and carbonyl stretching frequencies (CS_2) at 2060, 2049, 2037, 2015, 1990, 1975, and 1960 cm^{-1}. Further structural proof comes from mass spectral data (see Experimental Section).

Thermal Rearrangement of III. The relative thermal stabilities of complex III and *cis*^{4}-cyclononatetraene are of considerable interest. While cyclononatetraene undergoes rapid electrocyclic ring closure to dihydroindene at 23° ($t_{1/2} \sim 50$ min, $\Delta F^{\ddagger} = 23$ kcal/mol), complex III is stable for many days at room temperature. However, upon heating III at 101° in octane, isomerization to the *cis*-dihydroindene complex IV does occur. The rate of rearrangement could be conveniently studied by monitoring the relative amounts of III and IV by gas chromatography. At 101 ± 1° in rigorously degassed octane solution the isomerization obeys first-order kinetics and standard kinetic analysis yields a first-order rate constant $k = 2.4 \pm 0.2 \times 10^{-4}$ sec^{-1} corresponding to $\Delta F^{\ddagger} = 28.4 \pm 0.1$ kcal/mol. During the isomerization no free ligand could be detected and the yield of IV was essentially quantitative.



III

IV

The mechanism for the conversion of III to IV seems best interpreted as a unimolecular electrocyclic ring closure of the bound cyclononatetraene ligand.[21] The relative importance of all possible factors which might increase the activation energy for the ring closure of the bound ligand in III *vs.* the free tetraene are not clear. However, it should be noted that in closure of IV the iron, which is bound to the C_1–C_2–C_3–C_4 diene

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(13) (a) A rhodium complex of similar structure has been isolated: R. Grigg, R. Hayes, and A. Sweeney, *Chem. Commun.*, 1248 (1971). (b) Due to its thermal instability and chromatographic behavior, complex V has not yet been obtained sufficiently pure for characterization by means other than pmr and, hence, the structural assignment must be regarded as tentative.

(14) Consistent with this assignment is the fact that the vinyl protons in 1,5 cyclooctadieneiron tricarbonyl appear at δ 3.4; E. Koerner von Gustorf and J. C. Hagen, *Tetrahedron Lett.*, 3191 (1968).

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

(16) (a) F. A. L. Anet, H. D. Kaesz, A. Maasbol, and S. Winstein, *J. Amer. Chem. Soc.*, **89**, 2489 (1967); (b) F. A. L. Anet, *ibid.*, **89**, 2491 (1967).

(17) (a) The complex may not exhibit equivalent bonding to each iron as drawn but may be similar to the unsymmetrical binuclear complex of cyclooctatriene: F. A. Cotton and W. T. Edwards, *J. Amer. Chem. Soc.*, **91**, 843 (1969); (b) G. Deganello, H. Maltz, and J. Kozarich apparently have also synthesized this complex (unpublished results cited in ref 18a).[17c]

(17c) NOTE ADDED IN PROOF. Deganello, *et al.*, have also prepared complex III: G. Deganello, H. Maltz, and J. Kozarich, *J. Organometal. Chem.*, in press.

(18) (a) F. A. Cotton and G. Deganello, *J. Organometal. Chem.*, **38**, 147 (1972); (b) *J. Amer. Chem. Soc.*, **94**, 2142 (1972).

(19) The analogous complexes of cyclooctatetraene epoxide[20] and bicyclo[6.2.0]deca-2,4,6-triene[18] have been reported.

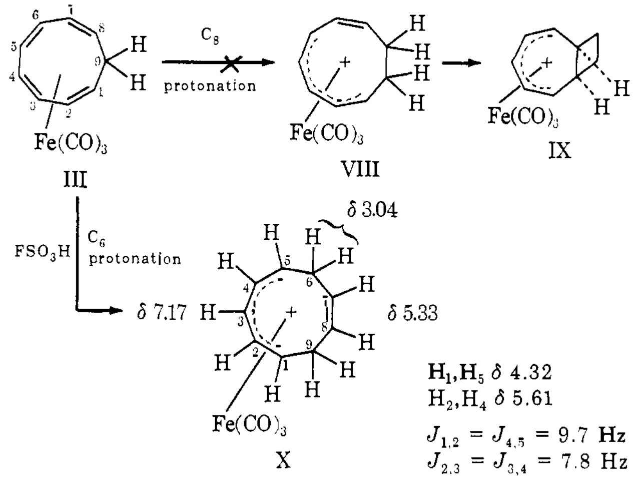
(20) H. Maltz and G. Deganello, *J. Organometal. Chem.*, **27**, 383 (1971).

(21) An alternate mechanism which results in the observed first-order kinetics would be one in which III undergoes reversible dissociation into I and $Fe(CO)_3$, free I undergoes ring closure to II followed by recombination of II with $Fe(CO)_3$ to yield IV. In addition to the fact that the $Fe(CO)_3$ species is an unattractive intermediate, this mechanism can be ruled out on energetic grounds. If it applied, the measured free energy of activation (28.4 kcal/mol) would represent the sum of the ΔF for the dissociation equilibrium III $\rightleftharpoons$ I + $Fe(CO)_3$ and the $\Delta F^{\ddagger}$ for ring closure of I. Since this latter value is *ca.* 23 kcal/mol, the ΔF for the dissociative equilibrium would be required to be *ca.* 5.4 kcal/mol. This value is obviously too low and not consistent with many aspects of the chemistry of diene iron tricarbonyl complexes (*e.g.*, the fact that the nmr of III itself indicates a "frozen" and not a "fluxional" structure in which iron migrates between the two diene units in III).

unit, must undergo essentially a 1,2 shift and in the product IV ends up bound to carbons which in III were numbered C_2–C_3–C_4–C_5. An example of a 1,2 shift of iron with simultaneous double bond migration is known and has been demonstrated to be a relatively facile process in that it is the mechanism for the rapid fluxional migration of iron in cyclooctatetraeneiron tricarbonyl complexes.[16] Such a requirement for 1,2 iron shift might be at least in part responsible for the increased free energy of activation of 5.4 kcal/mol for ring closure of III *vs.* I. A similar increase in the free energy of activation for the electrocyclic ring closure of 1,3,5-cyclooctatrieneiron tricarbonyl relative to 1,3,5-cyclooctatriene has been observed.[5]

Low-Temperature Protonation. The protonation of cyclononatetraene complex III is of considerable interest in light of much recent work on the protonation and electrophilic substitution of cyclic triene and cyclic tetraeneiron tricarbonyl complexes.[6,22] Several possibilities for the structure of the protonated species can be envisioned. For example, if proton addition occurs at C_8, ion VIII would be formed. This ion might then undergo ring closure to ion IX analogous to the ring closure of the cyclooctatrienyliron tricarbonyl cation.[6] However, if protonation occurs at C_6, ion X is formed (Scheme I).

Scheme I



Protonation of III at −120° in FSO_3H-SO_2ClF yields a clear yellow solution whose pmr spectrum at −67° exhibits signals (CH_2Cl_2 internal standard, δ 5.30) at δ 7.17 (1 H, triplet, J = 7.8 Hz), 5.61 (2 H, quartet, J = 7.8, 9.7 Hz), 5.33 (2 H, broad singlet), 4.32 (2 H, multiplet), and 3.04 (4 H, broad, unresolved band). The two-proton bands 5.61, 5.33 and 4.32 are symmetrical and each is clearly due to two *equivalent* protons. This fact rules out ion VIII in which each proton is in a different magnetic environment. The resonance positions and observed coupling constants are all consistent with that expected for X and assignments are illustrated above. The protons at δ 5.61 are coupled to the proton at δ 7.17 by 7.8 Hz and the protons at δ 4.32 by 9.7 Hz. Based on the coupling constants and chemical shifts in analogous pentadienyliron species,[6,22] the δ 4.32 signal must be assigned to the external (α) protons of the bound pentadienyl unit and the δ 5.61 band to the β protons. For ion X the signal at δ 5.33 must be assigned to the two equivalent free vinyl protons at C_7 and C_8, and this chemical shift is consistent with that expected for such protons.[6,22c] If ion IX were the observed species, then the δ 4.32 signal would have to be assigned to the bridgehead hydrogens and this signal is at a field value too low to be compatible with this assignment.[6,22a]

The observation of protonation at C_6, the β position of the double bond adjacent to the bound diene, is analogous to the position of protonation observed for other cyclic triene and tetraene complexes[6,22] (*e.g.*, cyclooctatetraeneiron tricarbonyl[6c,d] and cyclooctatrieneiron tricarbonyl[22c]), with the exception of troponeiron tricarbonyl which has been shown by Hunt to protonate at the external carbon of the bound diene unit.[22e]

Mechanisms of Formation of Complexes. Very little can yet be said about the detailed mechanisms of formation of III–VI. Although III rearranges to IV the rate is sufficiently slow so as to preclude this route for generation of IV under either set of reaction conditions. In the photolysis reaction, the small amount of IV might possibly arise from *cis*-dihydroindene present initially as a slight impurity and formed in additional amounts from the thermal rearrangement of the bicyclo[6.1.0]nonatriene. The binuclear complex VI does yield IV upon heating (toluene, 120°, 22 hr, 60%); however, its rate of thermal rearrangement is also sufficiently slow to preclude it as a precursor to IV in either the thermal or photochemical route.

The ring opening of vinylcyclopropanes with iron pentacarbonyl at 140° to yield diene complexes has been previously reported.[23] In these reactions a hydrogen migration in addition to ring opening is required to yield the observed complexes, in contrast to the present case where only ring opening is required.

One possibility suggested by the isolation of V is that the products may be controlled to some extent by the stereochemistry of attack of the reactive iron carbonyl species on the bicyclo[6.1.0]nonatriene system. For example, in the photolysis reaction where $Fe(CO)_4$ is probably the reactive species,[24] attack of $Fe(CO)_4$ cis to the cyclopropane may lead to V, while attack trans may lead to cyclopropane ring opening and eventually to III.

Experimental Section

General. Spectra were recorded using CS_2 solutions of the complexes unless otherwise noted. Infrared spectra were recorded on a Perkin-Elmer 421 spectrometer. Pmr spectra were taken routinely on a Jeolco C-60HL spectrometer (60 MHz) or, where noted, on a Varian HA-100 spectrometer. Decoupling experiments were performed on the HA-100 spectrometer. Chemical shifts are in δ relative to internal TMS taken as δ 0. High resolution mass

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spectra were obtained at the temperature and voltage indicated on a computer-interfaced A.E.I., Ltd., MS 902 mass spectrometer.[25] Melting points are uncorrected and were taken on a Büchi melting point apparatus. Preparative and analytical glpc were performed on a Hewlett-Packard 5750 research chromatograph using a thermal conductivity detector and helium as the carrier gas. Columns were aluminum packed with a 3% loading of either Carbowax 20M (6 ft × 1/8 in.) or silicone gum rubber UC-W98 (6 ft × 0.25 in.) on Chromosorb W (60–80 mesh). Nitrogen gas was purified by passing successively through concentrated sulfuric acid, potassium hydroxide pellets, and a heated column of BASF catalyst R3-11.

***cis*-Bicyclo[6.1.0]nona-2,4,6-triene.** This triene was prepared in 47% yield by the method of Katz and Garratt[26] or in 58% yield by the method of Staley and Henry[27] after a spinning-band distillation (bp 50–58° (7 Torr), lit.[2] bp 51° 7 Torr)). The product typically contained (glpc, CW 20M, 65°) 2–4% *cis*-8,9-dihydroindene as an impurity generated during distillation.

***cis*-8,9-Dihydroindene.** A neat sample of *cis*-bicyclo[6.1.0]-nonatriene (5.0 g) was heated under nitrogen for 3 hr at 100°. Analysis by glpc (CW 20 M, 65°) indicated 5% reactant, 81% *cis*-dihydroindene, and 14% *trans*-dihydroindene.[26,28] Distillation by spinning band gave pure (glpc, >99%) samples of the trans isomer (fraction I, 0.45 g, bp 39–41° (12 Torr), lit.[29] bp 54° (28 Torr)) and the cis isomer (fraction III, 3.75 g, bp 47° (13.5 Torr), lit.[26,30] bp 46° (11 Torr)).

Reaction of *cis*-Bicyclo[6.1.0]nona-2,4,6-triene and Diiron Nonacarbonyl. The iron carbonyl (16.9 g, 46.5 mmol), the triene (2.36 g, 20 mmol), tetradecane (internal standard 0.5 g), and 125 ml of ether were stirred under nitrogen for 40 hr at 25°. Analysis by glpc indicated the presence of 15% unreacted triene (CW 20M, 80°), 46% complex IV, and 12% complex III (UCW 98–110°). The mixture was filtered, washed well with hexane, and then concentrated under reduced pressure. The remainder of the volatiles were removed under high vacuum. Storage of the residual dark viscous oil at 0° for several days produced a crystalline mass which was separated and recrystallized from hexane to give 0.68 g of binuclear complex VI as orange crystals, mp 105° dec. Complex VI was identified as *cis*-bicyclo[6.1.0]nonatrienediiron hexacarbonyl: ir 2060, 2049, 2037, 2015, 1990, 1975, 1960 cm^{-1} ($\nu_{C\equiv O}$); pmr δ 0.3–0.8 (H_{9a}), 0.8–1.4 (H_1, H_8, H_{9b}), 2.55 (d, $J_{2,3}$ = 8.2 Hz, $H_{2,7}$)), 3.8–4.25 ($H_{3,6}$), 4.25–4.50 ($H_{4,5}$); *m/e* (100°, 70 eV) 370 (55), 342 (43), 314 (14), 286 (37), 258 (64), 230 (100), 204 (14), 202 (12), 174 (11), 134 (18), 117 (18);[31] exact mass spectrum, 397.9183 (calcd for $C_{15}H_{10}Fe_2O_6$, 397.9175).

The remaining oil was chromatographed on 80 g of activity I, neutral alumina to give 2.33 g of a mixture of complexes III and IV (hexane eluent) as a yellow oil and 0.42 g (20% benzene eluent) of complex VI. The mixture of III and IV was chromatographed on 200 g of activity II, basic alumina. Elution with hexane gave IV, a yellow oil identified as *cis*-8,9-dihydroindeneiron tricarbonyl:[33] ir 2045, 1970 (br) cm^{-1} ($\nu_{C\equiv O}$); pmr δ 1.6–3.0 (H_{1a}, H_{1b}, H_8, H_9), 3.0–3.3 (H_4, H_7), 5.1–5.5 (H_2, H_3, H_5, H_6); *m/e* (50°, 70 eV) 230 (12), 202 (9), 174 (6), 172 (50), 134 (5), 118 (6), 117 (10), 116 (10), 115 (14), 69 (100);[31] exact mass spectrum 257.9984 (calcd for $C_{12}H_{10}FeO_3$, 257.9979).

Later fractions were enriched in the minor component III, which by further fractional chromatography, was obtained in good purity as a yellow solid, mp 36–37°, and identified as *cis*^{4}-cyclononatetraeneiron tricarbonyl; ir 2045, 1975 (br) cm^{-1} ($\nu_{C\equiv O}$); pmr (C_6D_{12}, 100 MHz) δ 1.68 (H_{9a}), 2.60 (H_{9b}), 3.61 (H_1), 3.77 (H_4), 4.79–5.07 (H_2, H_3), 5.41–6.00 (H_5, H_6, H_7, H_8, $J_{9a,9b}$ = 14.5, $J_{9a,1}$ = 5.2, $J_{9b,1}$ = 11.0, $J_{9a,8}$ = 9.5, $J_{9b,8}$ = 6.2 Hz); *m/e* (50°, 70 eV) 258 (2), 230 (32), 202 (34), 174 (59), 172 (48), 148 (31), 146 (10), 134 (36), 130 (7), 122 (14), 121 (7), 118 (55), 117 (100), 116 (53), 115 (76), 108 (8), 103 (8), 91 (36), 89 (11), 78 (9);[31] exact mass spectrum 257.9985 (calcd for $C_{12}H_{10}FeO_3$, 257.9979).

Anal. Calcd: C, 55.85; H, 3.91; Fe, 21.64. Found: C, 55.77; H, 4.00; Fe, 21.61.

Complexes III and IV could also be collected *via* preparative glpc (UC-W98, 110°). While IV had eluted intact (pmr), III had partially rearranged to IV (*vide infra*) on the column as shown by pmr and reinjection.

Photolysis of *cis*-Bicyclo[6.1.0]nona-2,4,6-triene and Iron Pentacarbonyl. Iron pentacarbonyl (5.1 ml, 37 mmol), the triene (2.50 g, 22 mmol), and 150 ml of benzene were irradiated through Pyrex at 40° for 4 hr under nitrogen using a 450-W Hanovia lamp. The solvent was then removed under vacuum and the residue chromatographed on 250 g of activity II, basic alumina. The first fraction (hexane eluent) contained 1.20 g of yellow oil which contained minor amounts of III and IV but chiefly a new complex (V), *cis*-bicyclo[6.1.0]nona-2,4,6-trieneiron tricarbonyl identified by its pmr spectrum: δ 0.95–1.80 (m, H_1, H_8, H_{9a}, H_{9b}), 3.57 (d, $J_{2,3}$ = 9.0 Hz, H_2, H_7), 4.08 (d, $J_{2,3}$ = 9.0, H_3, H_6), 5.48 (bs, H_4, H_5). A second fraction (1.60 g) eluted with hexane was predominantly the cyclononatetraene complex III (pmr and glpc) but also contained complex IV. Elution with 3% benzene in hexane gave as the third fraction 0.05 g of crude binuclear complex VI. Further purification was accomplished by repeated fractional chromatography.

Reaction of *cis*-8,9-Dihydroindene and Diiron Nonacarbonyl. The iron carbonyl (2.54 g, 7.0 mmol) and the triene (0.80 g, 6.8 mmol) in 20 ml of ether were heated at reflux under nitrogen. After 1.5 hr nearly all the iron carbonyl had reacted and analysis by glpc showed <5% of triene remaining and the presence of a peak corresponding to complex IV. The mixture was chromatographed on 100 g of activity I, neutral alumina to give 0.49 g (28%) of a yellow oil spectrally identical with complex IV. No significant amount of any other complex was detected.

Ceric Ammonium Nitrate Oxidation of Complexes.[34] **A. Complex IV.** The complex (300 mg) in 20 ml of degassed absolute ethanol was cooled to 0°. Solid ceric ammonium nitrate was added in portions with shaking until evolution of gas ceased. The solution was diluted with 30 ml of cold hexane and quickly washed with brine solution. The colorless organic solution was dried over magnesium sulfate. After filtration the solvent was removed under vacuum to give 0.10 g of an oily residue which was identified by its pmr spectrum and glpc analysis as *cis*-8,9-dihydroindene.

B. The Tetraene Complex III. The complex (380 mg) was dissolved in 10 ml of degassed acetone and cooled to 0°. Solid ceric ammonium nitrate (1.7 g) was added in portions over a 20-min period until evolution of gas ceased. Hexane (60 ml) was then added, the mixture was shaken, and the layers were separated. The hexane layer was washed with brine, dried, and filtered. Removal of solvent under vacuum gave a greenish-yellow oil (145 mg, 83%). Analysis (pmr and glpc) confirmed the oil to be *cis*-8,9-dihydroindene contaminated with small amounts of higher molecular weight products but no trace of the trans isomer (glpc) or other C_9 isomers.

When the oxidation and work-up were performed at −10°, the oil exhibited two absorptions in its pmr spectrum (room temperature), a multiplet at δ 5.67 and a triplet at 3.01, J = 5.3 Hz. This spectrum was identical with the published spectrum of *cis*^{4}-cyclononatetraene.[8]

Thermal Rearrangement of Binuclear Complex VI. A solution of complex VI (333 mg) in 20 ml of toluene was flushed with nitrogen. After the solution was heated at 120° for 22 hr, the solvent was removed under vacuum and the residue chromatographed on 50 g of activity II, basic alumina. Elution with hexane produced 130 mg (60%) of complex IV.

Thermal Rearrangement of Complex III. The tetraene complex (227 mg) was dissolved in thoroughly degassed octane (1 ml), and the solution was placed in a small Schlenk tube. The solution was further degassed on a high vacuum line using three freeze–pump–thaw cycles and then heated at 101 ± 1° under a positive pressure of nitrogen. Aliquots were withdrawn by syringe at 10-min intervals and analyzed by glpc. Nearly base-line separation of the two complexes, III and IV, was achieved at 100° on the UC-W98 column. Retention times were 8 min for complex IV and 13 min for the

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(25) Mass spectra were obtained using the facilities of the Research Triangle Center for Mass Spectrometry, Research Triangle Park, N. C., supported by the Biotechnology Research Branch of the Division of Research Resources of NIH under Grant No. RR-330.

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tetraene complex III. Rearrangement of the tetraene complex during analysis at 100° broadened the tetraene peak, but did not contribute significantly to the area of the peak for the dihydroindene complex IV. No free ligand was detected by glpc during the course of the reaction. By standard analysis, the first-order rate constant was found to be $2.4 \pm 0.2 \times 10^{-4}$ sec^{-1} at 101°.

Low-Temperature Protonation of Complex III. The tetraene complex III (82 mg) in 0.2 ml of CD_2Cl_2 was protonated at $-120°$ using a degassed solution of FSO_3H and SO_2ClF (1:2, v/v). The details of this protonation technique have been described previously.[6d] The pmr spectrum of the ion observed at $-67°$ exhibits bands at δ 3.04 (4 H, broad singlet), 4.32 (2 H, mult.), 5.33 (2 H, broad singlet), 5.61 (2 H, quartet, J = 7.8, 9.8 Hz), and 7.17 (1 H, triplet, J = 7.8 Hz) and is assigned structure X.

Thermal Decomposition of 2-Chlorocyclobutanone[1]

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Abstract: The thermal decomposition of 2-chlorocyclobutanone has been studied at four different temperatures, and its rate of decomposition was found to be ~2.3 times as fast as that of cyclobutanone. The decomposition yields (1) ~94% of products from the ring fission modes, the ratio of C_2H_4 (plus chloroketene *via* mode a) to C_2H_3Cl (plus ketene *via* mode b) being ~6.5:1 with a slight temperature dependence; (2) ~3% of products from the decarbonylation process giving the C_3H_5Cl isomers and CO; (3) ~2% of products from the HCl elimination process, followed by fission or decarbonylation, giving acetylene, methylacetylene, and allene; and (4) ~1% of products which were not identified in gas chromatographic analysis. *Approximate* Arrhenius parameters are calculated for the ring fission, decarbonylation, and HCl elimination pathways.

The thermal decomposition of cyclobutanone (CB) has been shown to yield ethylene and ketene (>99%) and cyclopropane and CO (<1%).[2-4] The products arise from two consecutive, homogeneous thermal reactions which are first order above ~10 Torr pressure.[3,4] McGee and Schleifer inferred that both of the competing processes occur by "concerted" mechanisms on the basis of the energetics of decomposition reactions,[4] whereas Blades postulated biradical mechanisms.[3] The thermal decomposition of 2-*n*-propylcyclobutanone[5] and four of the six possible isomeric dimethylcyclobutanones (DMCB),[6] excluding optical isomers, also suggests that the decomposition processes are "concerted."

The present study was undertaken in order to observe any changes in the mechanism and rates of thermal decomposition of cyclobutanone caused by a chlorine atom substitution at the α position of cyclobutanone. This study is only a preliminary and limited step toward the complete study of the excited state chemistry of 2-chlorocyclobutanone (chloro-CB), and hence no attempt was made to obtain an *accurate* thermal rate of decomposition. The thermal decomposition of chloro-CB was found to differ from that of CB not only for the fission modes available (see Scheme I) but also for a new pathway available for HCl elimination.[7] This contrasts with the thermal decomposition of chlorocyclobutane which proceeds in a manner very similar to that of cyclobutene.[8]

Scheme I

Experimental Section

Preparation of 2-Chlorocyclobutanone. Chloro-CB was prepared by the method of Durig and Green.[9] Sulfuryl chloride (Eastman) (5.7 ml) in 20 ml of CCl_4 was slowly added to a stirred mixture of CB (5 g, Aldrich) and CCl_4 (35 ml) at 0°. The mixture was allowed to warm to room temperature and react for 30 hr. After removal of most of the volatile components by vacuum distillation at room temperature, chloro-CB was purified by preparative vpc on a Carbowax column (10 ft × 0.25 in.) at 90° and dried over 5A Linde molecular sieve. The ir spectrum was identical with the published spectrum.[9]

Chemicals. CB (Aldrich Chemical Co.) was used without further purification, as its impurities were found by vpc to be less than 0.005%. The following authentic chemical compounds were used for product identification by checking vpc retention times: C_2H_2, C_2H_4, cyclopropane, allene, methylacetylene, 1,3-butadiene, and C_2H_3Cl (all Matheson CP grade) *cis*- and *trans*-1-chloropropene (Chemical Samples and Columbia Organic Chemical Co.), 2-chloropropene (Chemical Procurement Lab., Inc.), and 3-chloropropene (Matheson Coleman and Bell). The trans isomer was the major component in the *cis*/*trans*-1-chloropropene mixture when the ir and nmr spectra were compared with the published spectra.[10,11] Chlorocyclopropane was made by the method of Dedio, *et al.*,[12] by the photochemical addition of chlorine gas to cyclopropane (both Matheson CP grade).

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