Diprotonation and Tautomerism in Olefin–Iron Carbonyl Complexes[1]

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Abstract: At low temperatures (*ca.* −78°) solutions of the iron tricarbonyl complexes of butadiene, 1-methylbutadiene, and 1,4-dimethylbutadiene in strong acid display a high-field signal in the ^{1}H nmr indicating the presence of hydrogen on the metal. The metal-bonded proton is in rapid exchange with a selected number of olefin protons. Evidence indicates that a second labile proton must also be associated with the complex and is responsible for the shift of first proton from olefin to metal. Through the metal complexes it is possible specifically to deuterate certain olefins. For the iron tricarbonyl complexes of cyclohexadiene and cycloheptadiene, diprotonation (at the metal and at the olefin) is observed under the same conditions. The metal–hydrogen signal in these complexes is also observed to average with certain olefin protons at slightly higher temperatures, owing to rapid exchange between mono- and diprotonated species.

A number of olefin–metal complexes are known to react with proton acids, in which reactions entering hydrogen becomes attached to the hydrocarbon group. For the complexes $C_7H_8Fe(CO)_3$,[2] $C_8H_8Fe(CO)_3$,[2] or $C_8H_8Mo(CO)_3$,[3] in which the olefin contains one or more double bonds not coordinated to the metal, evidence available thus far indicates that, in the methylene group which is formed on protonation, entering hydrogen is on the side of the metal (*endo*). Other complexes such as butadieneiron tricarbonyl, undergo protonation[4] in which one carbon atom is displaced from bonding to the metal in the formation of a π-methallyl group. We were prompted to follow the reaction of these complexes with acid at low temperatures to determine whether metal protonation such as has been demonstrated for a number of other olefin complexes[5] participated in these electrophilic substitutions.

Experimental Section

All manipulations were carried out under an inert atmosphere.

Materials. 1,3-Butadieneiron tricarbonyl and 1,3-pentadienyliron tricarbonyl were purchased from Alfa Inorganics, Inc., Beverly, Mass. To obtain optimum nmr resolution both for neat samples of the compounds and for further treatment with strong acid, it was necessary to chromatograph the commercial products in dry, oxygen-free *n*-hexane over dry, oxygen-free silica gel.

The following olefin complexes were prepared[6] by refluxing the diene ligand (purchased from Aldrich Chemical Co., Milwaukee, Wis.) with a one-third molar equivalent of triiron dodecacarbonyl (Alfa Inorganics) in *n*-heptane: *trans,trans*-1,4-dimethyl-1,3-butadieneiron tricarbonyl, 2,3-dimethyl-1,3-butadieneiron tricarbonyl, and 2-methyl-*trans*-4-isopropyl-1,3-butadieneiron tricarbonyl. The latter is obtained from 2,5-dimethyl-2,4-hexadiene.[6]

The initial mixture was refluxed for 2–4 hr until the green-black color of $Fe_3(CO)_{12}$ disappeared. The resulting amber-colored solutions were cooled and filtered and the solvent, residual diene, and $Fe(CO)_5$ removed at 1 Torr. The resulting oils were then chromatographed with *n*-hexane over silica gel. The structures were confirmed by comparison of their nmr and carbonyl infrared absorptions with the published values.[6]

Low-Temperature Protonation. Fluorosulfonic acid was distilled in an all-glass apparatus and sealed in ampoules under argon atmosphere. About 0.60–0.90 mmol of complex was placed in a nmr tube (5-mm diameter). The tube was then cooled to −80° and about 0.5 ml of dry SO_2 condensed in from a gas stream (all under a stream of argon). The diene complex was dissolved into the SO_2 by mixing with a glass rod and slight warming. Cold HSO_3F (about 1.5 mmol) was next added at −80° and the final solution obtained on further mixing. Deuteration studies were also carried out using DSO_3F (*ca.* 98% D) obtained from Diaprep Inc., Atlanta, Ga. 30301.

Instrumental. Nmr spectra were obtained with a Varian Associates A-60 or HA100 instruments as needed. Resonance positions are given in ppm relative to internal tetramethylsilane (TMS) at τ 10. The chemical shift values are considered to be accurate to ±0.05-ppm unit and the coupling constants to ±0.2 Hz. The temperatures at which nmr spectra were observed were determined by the relative shift of the two methanol resonances and are considered accurate to ±1°.

Infrared spectra in the metal–carbonyl stretching region were obtained with a Beckman IR-4 using LiF optics and solution cells fitted with CaF_2 windows. The absorption maxima are considered accurate to ±1 cm^{-1}. Calibration was obtained from the 1988.5-cm^{-1} line of water vapor in air.[7]

Mass spectra were obtained on an Associated Electrical Industries MS-9 spectrometer. For analysis of the deuterium content of 1,3-butadieneiron tricarbonyl, the instrument was operated at the lowest ionizing potential which would give a reasonably intense pattern for the parent ion (about 8 eV) in order to preclude hydrogen loss during the ionization process.[8] The spectrum was recorded under slow scan conditions.

Analysis of Mass Spectra. The analyses of the mass spectra were carried out for the parent multiplet and that of the fragments arising from loss of CO (diene·$Fe(CO)_n^+$, n = 3, 2, 1, and 0). The most intense peak in the parent multiplet for the undeuterated complex was at *m/e* 194 (as expected, see Table I). The other peaks appeared at the predicted relative intensities (within ±10%). In addition to errors arising from the measurement of the height of the smaller peaks, the presence of $Fe(CO)_5$ would make some contribution to the *m/e* 196 and other peaks.

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[1] This work was supported by U. S. Public Health Service Grant GM 14336.

[2] (a) A. Davison, W. McFarlane, L. Pratt, and G. Wilkinson, *J. Chem. Soc.*, 4821 (1962); (b) G. N. Schrauzer, *J. Amer. Chem. Soc.*, **83**, 2966 (1961).

[3] S. Winstein, H. D. Kaesz, C. G. Kreiter, and E. C. Friedrich, *ibid.*, 87, 3267 (1965).

[4] (a) F. J. Impastato and K. G. Ihrman, *ibid.*, **83**, 3726 (1961); (b) G. F. Emerson and R. Pettit, *ibid.*, **84**, 451 (1962). The former is a report on what has later been shown (see ref 6, below) to be *syn*-methallyl-(chloro)iron tricarbonyl in which the carbon skeleton of the olefin is related to *trans*-butadiene, while the latter is a report of the *anti*-methallyl(tricarbonyl)iron tetrafluoroborate, in which the carbon skeleton of the olefin is related to *cis*-butadiene (see Figure 1).

[5] (a) A. Davison, W. McFarlane, L. Pratt, and G. Wilkinson, *J. Chem. Soc.*, 3653 (1962); (b) most recently D. R. Falkowski, D. F. Hunt, C. P. Lillya, and M. R. Rausch, *J. Amer. Chem. Soc.*, **89**, 6387 (1967).

[6] (a) G. F. Emerson, J. E. Mahler, and R. Pettit, *Chem. Ind.* (London), 836 (1964); (b) G. F. Emerson, J. E. Mahler, R. Kochhar, and R. Pettit, *J. Org. Chem.*, **29**, 3620 (1964).

[7] *Cf.* band no. 50, Table 5: E. K. Plyler, A. Danti, L. R. Blaine, and E. D. Tidewell, *J. Res. Nat. Bur. Stand.*, *A*, **64**, 1 (1960).

[8] K. Biemann, "Mass Spectrometry: Organic Chemical Applications," McGraw-Hill Book Co., Inc., New York, N. Y., 1962.

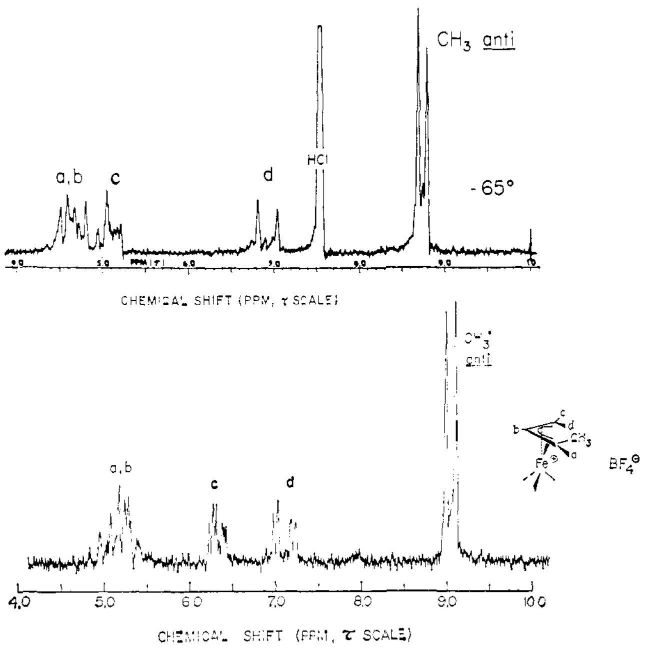


Figure 1. Proton nmr spectra, 60 Mc: upper spectrum, methallyl iron complex formed from butadieneiron tricarbonyl and HCl in SO_2 at $-65°$ (see text); lower spectrum, π-*anti*-methallyl(tricarbonyl)iron tetrafluoroborate, see ref 4b.

In the deuterated mixture, the peak of highest intensity was at *m/e* 195. The ratio of mono-D to all-proton derivative was calculated by solving two simultaneous equations for the intensities under the *m/e* 194 and 195 peaks, assuming they contained contributions only from these two species. From these, the intensities of the higher mass peaks were derived and the remaining observed intensity attributed to higher deuterated species. If these are significant, the calculation can be repeated with all components and the fit of calculated to observed intensities thus improved. For the present mixtures, the second calculation came well within experimental error of the first, and further iterations were not needed. Because of the possible presence of $Fe(CO)_5$, the assignment of dideuterated and higher species must be considered as an upper limit.

Table I. Distribution of Principal Isotopic Species in the Parent Peak Multiplet for Butadieneiron Tricarbonyl and Partially Deuterated Derivatives

Isotope combinations of Fe and C[a]	Rel abundance	H or D content			
		H_6	DH_5	D_2H_4	D_3H_3
$^{54}Fe^{12}C_7{}^{18}O_3$	0.054	192	193	194	195
$^{54}Fe^{13}C^{12}C_6{}^{18}O_3$	0.004	193	194	195	196
$^{56}Fe^{12}C_7{}^{18}O_3$	0.846	194	195	196	197
$^{56}Fe^{13}C^{12}C_6{}^{18}O_3$	0.071	195	196	197	198
$^{57}Fe^{12}C_7{}^{18}O_3$	0.020				
$^{57}Fe^{13}C^{12}C_6{}^{18}O_3$	0.002	196	197	198	199
Total	0.997				

[a] Only mono-^{13}C considered for this isotopic species.

The average of the intensities of the parent multiplet from several spectra of a deuterated sample (see discussion below) was as follows (*m/e* followed by observed intensity in arbitrary units): 192, 0.10; 193, 0.22; 194, 1.27; 195, 3.08; 196, 0.39; 197, 0.05; 198, <0.005. The composition of this sample was calculated to be: all proton, 28%; mono-D, 70%; di-D, 1.6% (upper limit); tri-D, 0.9% (upper limit). These results were confirmed within ±3% in the analysis of the multiplets arising from fragments due to loss of CO (in which the relative abundance of the components due to iron and carbon isotopes is slightly different than shown in the second column of Table I owing to the smaller carbon content).

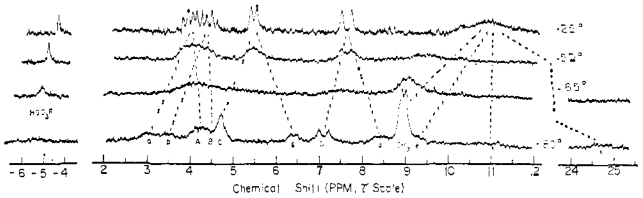


Figure 2. Proton nmr spectra, 60 Mc, for the protonation mixture containing HSO_3F and butadieneiron tricarbonyl in the ratio of 1.4:1.0; temperature varied as indicated.

Results and Discussion

The Reaction of Butadieneiron Tricarbonyl with Acids at Low Temperature. When we added any of a number of different acids in equimolar amount or less to a solution of butadieneiron tricarbonyl in SO_2 at low temperature (*ca.* $-60°$), nmr revealed a pattern typical of a methallyl complex. The spectrum obtained in the low-temperature protonation using HCl is shown on the upper trace of Figure 1, which is nearly identical with that obtained using a number of different acids, including H_2SO_4, HSO_3F, and CF_3COOH. If the diene is present in excess, nmr shows the presence of the methallyl and unreacted diene complexes. For comparison, the spectrum of *anti*-methallyl(tricarbonyl)iron tetrafluoroborate[4b] is shown as the lower trace on Figure 1. The two spectra are similar but not identical and the precise reasons for these differences are presently under study. It has been established, however, that in both cases *anti*-methallyl groups have been formed.

If, at low temperature, additional quantities of a strong acid such as HSO_3F or H_2SO_4 are added, the nmr spectrum is observed to change. A new set of peaks make their appearance which broaden and merge with resonances of the methallyl complex as the temperature is raised. For the mixture containing HSO_3F and complex in the ratio 1.4:1.0, the spectra at varying temperatures are shown in Figure 2. The peaks of the original methallyl complex (in the spectrum at lowest temperature) are labeled with capital letters corresponding to the assignment shown in Figure 1. The peaks of the new species are labeled with lower case letters, to correspond to assignments discussed below. Equilibrium is established between the methallyl complex and the new species. The two are rapidly interconverted at higher temperature as shown by the averaging of the two sets of signals. Because the concentration of the new species is proportional to excess acid, we assume it is diprotonated; however, the second proton must be in rapid equilibrium with those of excess acid, and the temperature dependence of the resonance at lowest field (τ *ca.* -5) supports this. At higher concentration of acid the resonances of the methallyl complex are no longer observed and a better defined spectrum of the new species is obtained; see Figure 3. Seven distinct resonances in addition to a peak for the excess acid are observed at $-86°$. The chemical shifts are as follows (τ values): H_a, 3.05; H_b, 3.56; H_c, 6.37; H_d, 8.33; H_e, 9.00; H_f, 10.86; H_h, 24.59. These correspond to one proton each. The peak for excess acid (τ *ca.* -5) is not shown in this figure. As the temperature is raised, bands e, f, and h are observed to broaden and then to coalesce into band g which appears at an averaged chemical shift position, τ 14.7.

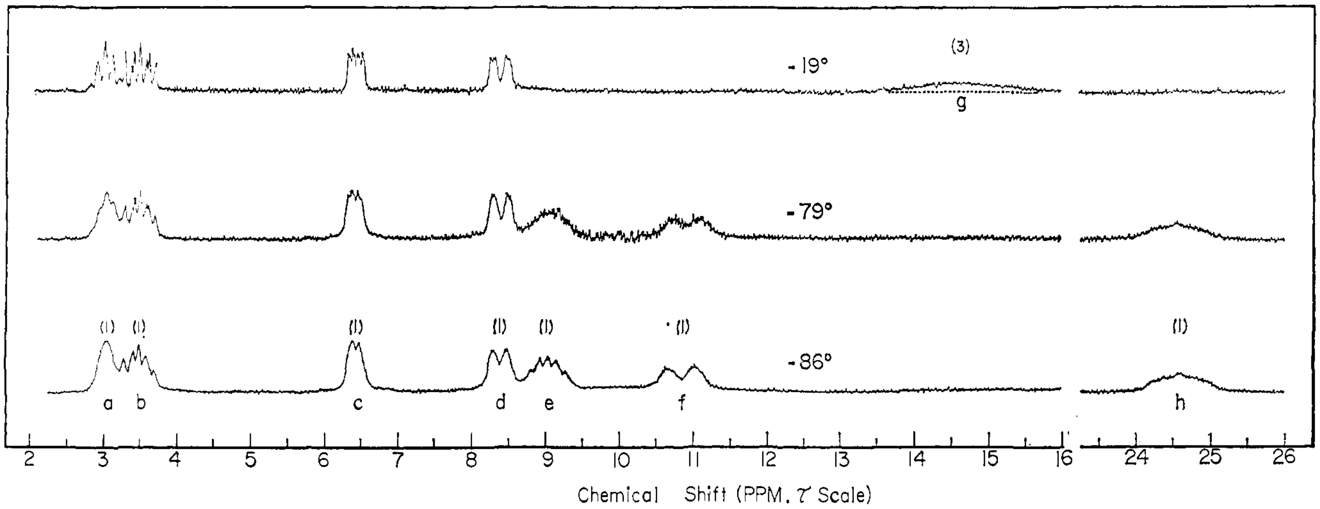
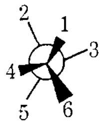
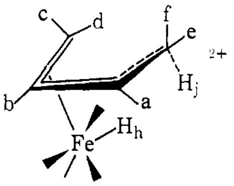


Figure 3. Proton nmr spectra, 60 Mc, for the protonation mixture containing butadieneiron tricarbonyl with a large excess of HSO_3F; temperature varied as indicated.

With excess strong acid, the equilibrium is shifted far to the side of the new species and the only remaining evidence of rapid interconversion between monoprotonated complex and the new species is the exchange of metal–proton with two protons on the ligand. As will be shown in the evidence cited below, the proton now observed on iron (H_h, τ 24.59) must be the one which was first attached to the methyl group in the monoprotonated (methallyl) complex.

For purposes of discussion it is necessary at this point to have reference to a structure for the new species, and we propose the formulation I based on the information discussed below. We assume approximately octahedral coordination around the iron, illustrated by the planar projection diagram to the left of structure I. The olefin (either as butadiene or a substituted allyl group) will occupy two positions, those numbered 1 and 2. Because of the observed exchange of the iron proton with two protons on the hydrocarbon group, we are prompted to choose a position for Fe–H closest to the olefin, namely position 3. However, for the diprotonated complexes of cyclic dienes (see below) a plane of symmetry would exist for such an isomer and the data require different placement of Fe–H (on positions 5 or 6). An equally acceptable fit of the observed spectra in the present case can be obtained with H_h at any of these three positions; however, the results of deuteration and some of the observations for the spectra of hexadiene complexes (discussed below) are best accommodated by the structure in which proton h is in position 3, as shown. The three carbonyl groups would occupy the remaining coordination positions.





I

The bands e and f must correspond to the terminal protons of the hydrocarbon group which participate in exchange with Fe–H. By analogy to resonances in other olefin complexes[9,10] we assign the band at higher field, f, to the inside proton and band e to the outside proton. Resonances c and d most logically become those of the other terminal CH_2 group as labeled in structure I. A rather large chemical shift difference is observed between the two inside protons d and f (2.53 ppm) and between the two outside protons c and e (2.63 ppm). We are led to conclude that there is some activity occurring around the terminal carbon atom carrying H_e and H_f which must account for this difference and which must also explain the exchange of these protons with Fe–H. The second proton, H_j, must attack the monoprotonated (methallyl) complex at saturated carbon. This causes a methyl proton to shift to iron (H_h). The second proton is in rapid exchange with excess acid and does not become equilibrated with protons (e and f) of the terminal carbon. To accommodate these data we write a weaker bond from the carbon to H_j; the electron pair represented by the dotted line may be in partial conjugation with the unsaturated group adjacent, and this could give intermediate hybridization for the terminal carbon atom between sp^3 and sp^2. The infrared spectra of this mixture at low temperature show two principal absorptions in the carbonyl region, a sharp band at 2132 cm^{-1} and a broad band which can be resolved into two shallow maxima at 2086 and 2075 cm^{-1}. These are shifted to higher energy from the bands in butadieneiron tricarbonyl (2050, 1978 cm^{-1}) as expected for a cationic species. An analogous high-energy pattern, 2126 (sharp) and 2076 (broad) cm^{-1}, is observed for cyclohexadieneiron tricarbonyl in strong acid medium. Since diprotonation is confirmed by nmr for this species (see below), the proposed structure for the butadiene complex receives further support.

H_h is equilibrated with H_e and H_f through the small amount of monoprotonated (methallyl) complex which is in rapid equilibrium with the diprotonated species. The sequence of attack of first and second protons receives further clarification in the study of cyclic diene complexes discussed below.

The remaining peaks, a and b, are assigned to the central protons of the olefin. Of these we would ex-

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(9) M. H. L. Green and P. L. I. Nagy, *J. Chem. Soc.*, 189 (1963).

(10) K. Vrieze, C. Maclean, P. Cossee, and C. W. Hilbers, *Rec. Trav. Chim. Pays-Bas*, **85**, 1077 (1966).

pect the one most strongly spin coupled to the exchanging protons e and f to show some broadening; thus, we assign the broadened band a to the proton adjacent to the exchanging methylene group. The other band shows slightly better resolution of spin–spin coupling peaks and is assigned to proton b, the one less strongly coupled to the exchanging protons.

At $-20°$, due to rapid exchange, protons e, f, and h become effectively spin decoupled from the other four, a, b, c, and d. The residual splittings of these four protons are well resolved and they may be analyzed separately as an ABMX system. The magnitudes of the coupling derived from an approximate analysis are given as follows. Band d is expected to show a large separation due to *trans* coupling of proton d with proton b, J_{bd} = 11.7 Hz. In addition we see a small splitting, due to the *gem* coupling, J_{cd} = 3.7 Hz. Band c will contain the *gem* coupling as well as the *cis* coupling, J_{bc} = 7.8 Hz. In addition the band shows further splitting due to $J_{ac} \sim 1.5$ Hz. Band b is approximately an octet due to coupling J_{db} from *trans* proton and to two *cis* couplings which are not equal but are close in value, J_{bc} (see above) and J_{ab} = 6.5 Hz. These coupling constants, obtained from the spectrum at $-30°$, are closer to the values of analogous coupling constants in allyl complexes,[11] $J_{gem} < 1$ Hz, $J_{cis} \approx 6.5$ Hz, and $J_{trans} \approx 12$ Hz, than they are for the analogous couplings in diene complexes,[12] $J_{gem} \approx 2.5$, $J_{cis} \approx 4.0$, and $J_{trans} \approx 8.5$ Hz.

At the lowest temperatures attainable in our medium the exchange of protons e, f, and h is slowed sufficiently that splitting of their resonances is observed though not completely resolved. The largest splitting, observed in both f and h, is $J_{fh} \simeq 22$ Hz. The additional splitting in the iron–hydrogen resonance corresponds to its interaction with the other terminal proton of the diene, $|J_{eh}| \simeq 14$ Hz.

Protons e and f show a splitting which can only be interpreted as the geminal coupling constant $J_{ef} \simeq 7$ Hz, indicating significant departure from sp^2 to sp^3 hybridization of the carbon on which they reside. Other splittings due to longer range interactions of protons e, f, and h with others in the molecule appear to be present but were not resolvable under the conditions of our experiments. In particular, the splitting J_{af} would have added valuable information about the conformation of protons on the terminal carbon.

Computer calculations of theoretical line shapes under exchange conditions were carried out for the protonated butadieneiron tricarbonyl using a program originally written by Saunders.[13] The three exchanging protons e, f, and h (see Figure 3) were first treated as a three-site system. Then each site was split up into "subsites" corresponding to the resolvable members of the spin multiplet of each of the three resonances. This resulted in an expansion of the problem to 13 sites, five for proton e and four each for protons f and h. Neglecting the additional (unresolvable) coupling is expected[14] to have little effect on the calculated line shapes at all but the slowest exchange rates, since the coupling constants are small compared to the chemical shifts between the various sites.

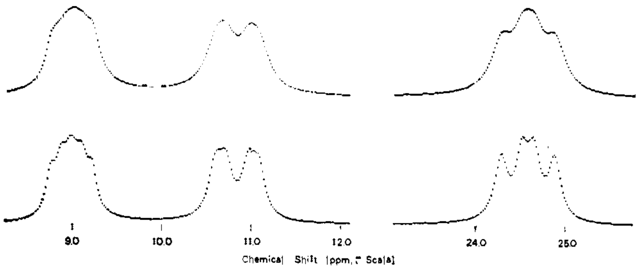

Figure 4. Calculated spectra for resonances e, f, and h of the spectrum shown in Figure 3 (see text); lower trace, $-86°$; upper trace, $-70°$.

In setting up the transition-probability matrix[15] it was further assumed that all of the coupling constants producing the observed fine structure in protons e, f, and h were of the same algebraic sign. Viscosity effects of natural line widths were included in the calculations by estimating the width of (nonexchanging) protons a and b.

The calculated spectra resulting from this analysis are shown in Figure 4. We considered these to have satisfactorily reproduced the features of the corresponding observed resonances (Figure 3). From these calculations we obtain rate constants for the intramolecular exchange of proton: 15 sec^{-1}, $-86°$; 30 sec^{-1}, $-79°$. A spectrum was also calculated for the merged resonance, g, at $-19°$ ($k = 1.4 \times 10^4$ sec^{-1}) with an equally acceptable fit of half-band width. These first-order rate constants give $\Delta F^{\ddagger}$ = 9.3 kcal/mol and $A = 1.5 \times 10^{12}$ sec^{-1}.

1,3-Butadieneiron Tricarbonyl in Strong Deuterio Acid Medium. In order further to elucidate the nature of the processes occurring in the protonated complex, 1,3-butadieneiron tricarbonyl in SO_2 solution was treated with fluorosulfonic acid-d_1 (98 atom % deuterium) and proton nmr spectra of the solutions were observed. The relative integrated intensities of the bands of the complex in the deuterio acid medium at various temperatures are shown in Table II. Because of the differences in the line widths of the various resonances, particularly at the lower temperatures, there is some uncertainty inherent in these measurements. In order to determine the approximate magnitude of this uncertainty, identical solutions were prepared using HSO_3F and the corresponding integrals recorded under identical instrumental conditions. These results are included in Table II for comparison. On the basis of proton nmr and mass spectral analyses of the neutral diene complex recovered after extensive deuteration (see below), the integrated intensities of protons a and b were assumed to remain constant to well within experimental error and the sum of their integrals was taken to represent *two* protons.

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[11] See Table XIII in the review article by M. L. Maddox, S. L. Stafford, and H. D. Kaesz, *Advan. Organometal. Chem.*, 3, 1 (1965); similar results are observed in a recent study of allyl complexes; see ref 10.

[12] Although the nmr spectra of many diene complexes have been reported (see ref 6 and 11), little coupling-constant data are available. We have compiled the coupling constants in the diene complexes which we studied here, which values are similar to those reported by R. Burton, L. Pratt, and G. Wilkinson, *J. Chem. Soc.*, 594 (1961), or in the iron complex obtained from methyl linoleate; see H. S. Gutowsky and J. Jonas, *Inorg. Chem.*, 4, 430 (1965).

[13] M. Saunders, *Tetrahedron Lett.*, 1699 (1963). The program is based on a model for exchange originally proposed by P. W. Anderson, *J. Phys. Soc. Jap.*, 9, 16 (1954), using the matrix representation of R. A. Sack, *Mol. Phys.*, 1, 163 (1958). The program was modified for use on the IBM 360 by Mr. Mark Henrichs of this department.

[14] S. Alexander, *J. Chem. Phys.*, 37, 967 (1962).

[15] M. Saunders in "Magnetic Resonance in Biological Systems," A. Ehrenberg, Ed., Pergamon Press, Ltd., Oxford, 1967, p 85.

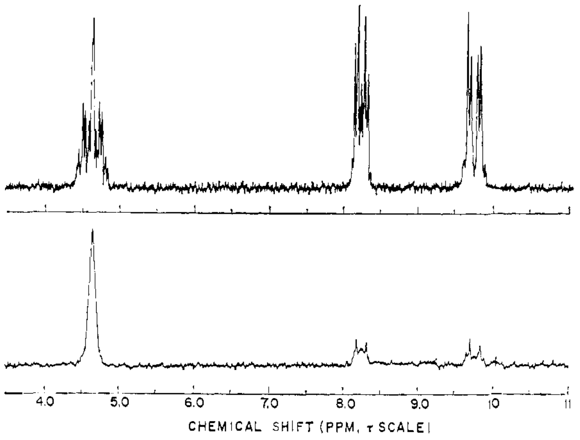

Figure 5. Proton nmr spectra, 60 Mc, $CDCl_3$ solution: upper trace, butadieneiron tricarbonyl, starting material; lower trace, material recovered from deuterio acid mixture, see text.

When the deuterated sample is prepared at −70 to −80° and maintained at these low temperatures, one observes that the *total* integrated intensity of the five bands c through h (*cf.* Figure 3 for identification) corresponds to 4.0 protons (within 10%, see Table II).

Table II. Relative Intensities. Proton Nmr of $C_4H_6Fe(CO)_3$ in DSO_3F–SO_2 and HSO_3F–SO_2

Time,[a] min	Temp, °C	Relative areas[b] c	d	e	f	h	Total
			DSO_3F–SO_2				
20	−80	0.96	0.92	0.63	0.70	0.68	3.89
115	−80	1.01	0.97	0.60	0.62	0.64	3.84
12	−40	0.85	0.83	0.71	0.61	0.69	3.69
85	−40	0.75	0.81	0.77	0.73	0.79	3.85
180	−40	0.75	0.79	0.77	0.77	0.92	4.00
			HSO_3F–SO_2				
20	−80	0.94	1.00	0.98	0.95	0.95	4.83
110	−40	0.94	0.98	1.00	0.91	0.98	4.82

[a] Cumulative time the solution was held at the stated temperature after addition of acid. [b] Based on the assumption that the integrated intensity of bands a and b corresponds to 2.0 protons (see text).

Only three resonances, e, f, and h, show any significant reduction in intensity and each of these is reduced to about $^2/_3$ the intensity observed for the corresponding peak in proton acid. This result indicates that there is rapid equilibration of entering deuterium over the three sites whose resonances are observed to broaden and eventually to merge at higher temperatures, as discussed above.

Another sample, similarly prepared, was allowed to warm to −40° and held at that temperature for various periods of time. The sample was cooled to −80° at intervals and its proton nmr spectrum observed. On the same basis as before, the total integrated intensity of the five bands c through h (*cf.* Figure 3), shown in Table II, is found to correspond to 4.0 protons, within our limits of experimental precision. However, in this case the intensities of resonances c and d show a significant decrease while those of e, f, and h show a trend in the opposite direction. After several hours at −40° all five bands seem to approach a uniform value of approximately 0.8 proton each. Thus, while a signal averaging shows rapid equilibration over three sites, the deuteration results show that on a longer time scale, entering hydrogen is equilibrated over *five* sites, *without* exchange of metal hydrogen with reservoir acid (the total integrated intensity of the resonances c through h remains constant at a value of approximately four). An explanation of this is given below in the discussion of a related process observed in the protonation of *trans*-2-*trans*-4-hexadieneiron tricarbonyl.

The neutral butadiene complex can be recovered from the strong acid medium by quenching the SO_2 solution in cold (0°) water and extracting the complex from the aqueous medium with a suitable organic solvent, *e.g.*, chloroform.[16] The deuterium content of the samples recovered from DSO_3F (through D_2O quench and $CDCl_3$ extraction) was also monitored using both mass spectrometry and proton nmr. Our analysis of the intensity pattern of the parent ion in the mass spectrum, obtained at low ionizing voltage (see Experimental Section), indicates that the recovered butadiene complex consists principally of $C_4H_6Fe(CO)_3$ (29 ± 2%) and $C_4H_5DFe(CO)_3$ (69 ± 2%), along with a small amount (at most, 1.5%) of $C_4H_4D_2Fe(CO)_3$. This result, moreover, is in excellent agreement with the integrated intensities of the proton nmr spectrum of the recovered butadiene complex; the total corresponds to approximately 5.3 protons, or 70% monodeuterium substituted.

Other samples exposed to deuterio acid for longer periods of time at −40° and similarly analyzed confirmed that incorporation of deuterium beyond the initial value is slow at this temperature. Samples held at −20°, however, do show additional deuterium uptake. (Above −20° decomposition of the sample becomes appreciable.) Again using the integrated intensities of the proton nmr spectrum of the quenched and recovered butadiene complex, it was found that after 5 days at −20° the total proton count in the terminal $=CH_2$ groups had fallen to 2.7. This corresponds to about 1.3 deuterium atoms per molecule and is to be compared with values of 0.7–0.8 deuterium incorporated at lower temperatures (see Table II).

One can more quickly increase deuterium content by subjecting the complex to several deuteration–quench cycles. The proton nmr spectrum of a sample which had undergone three such cycles is shown in Figure 5. The total integrated intensity of the terminal hydrogens corresponds to 0.9 proton relative to the value of 2.0 assumed for the inner hydrogens. Note that the resonances of the remaining protons on the terminal carbons are essentially doublets, indicating that the central carbon atoms are not significantly deuterated. This result provides further justification for our earlier assumption that the integrals of the inner protons taken as 2.0 can be used as a basis for evaluating the extent of deuteration at other positions.

Protonation and Deuteration of *trans*-Piperyleneiron Tricarbonyl. The spectrum of *trans*-piperyleneiron tricarbonyl in excess strong acid at low temperature is shown in Figure 6. The assignments are identified in

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(16) No significant proton exchange occurs during quenching of the strong acid mixtures with cooling. Use of D_2O on the proton–acid mixture did not produce any deuterated material. This is in complete agreement with the observations of Davison, McFarlane, Pratt, and Wilkinson[2a] who found that $C_7H_8D^+Fe(CO)_3$ does not exchange with excess proton acid as far as could be told after several hours in solution.

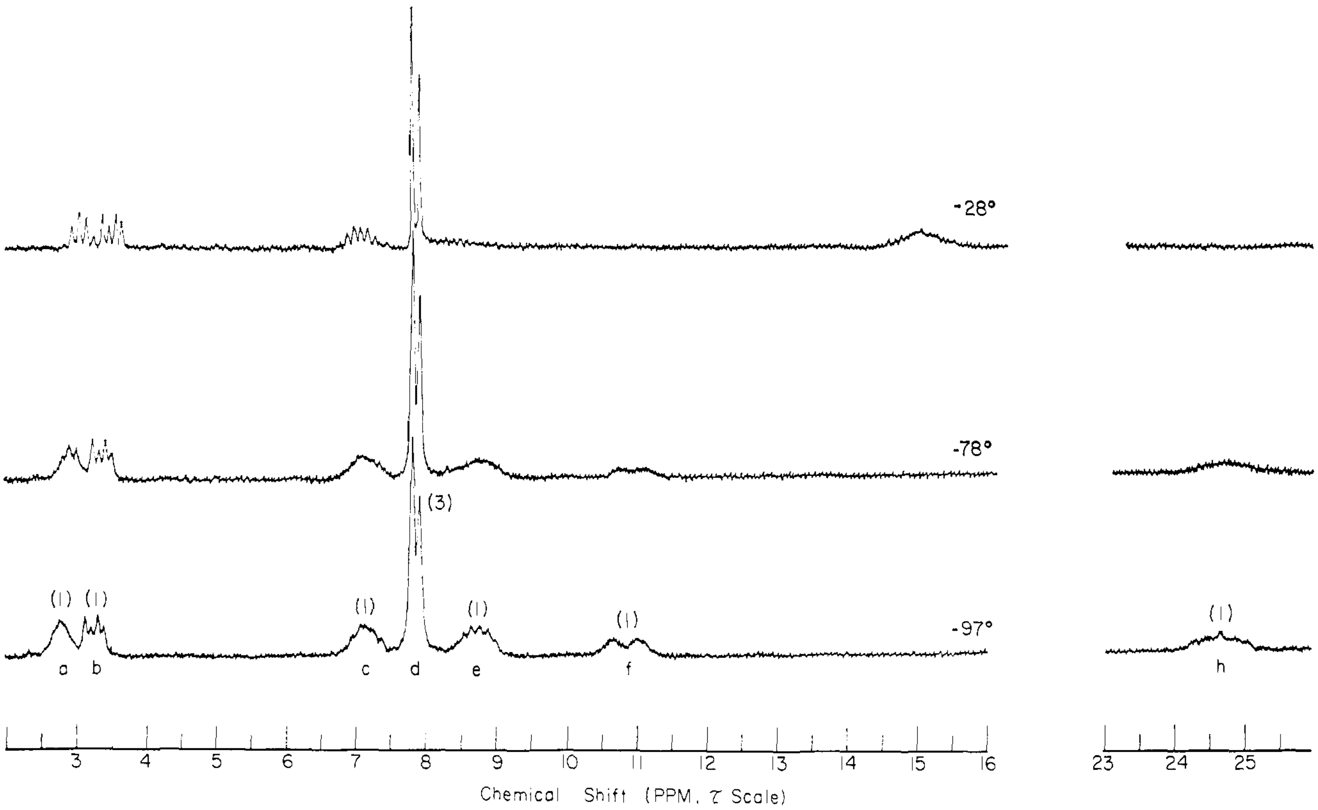
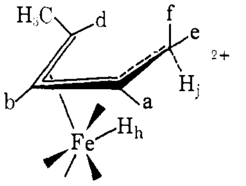


Figure 6. Proton nmr spectra, 60 Mc, for the protonation mixture containing *trans*-piperyleneiron tricarbonyl with a large excess of HSO_3F; temperature varied, as indicated.

structure II and the chemical shift values are as follows (τ values): H_a, 3.04; H_b, 3.50; CH_3, 8.20; H_d, 7.50; H_e, 8.95; H_f, 10.85; and H_h, 24.67. The coupling constants derived from first-order analysis are as follows (Hz): J_{ab} = 6.5; J_{bd} = 11.4; $J_{d\text{-}CH_3}$ = 6.2; J_{ef} $\approx$ 6; J_{eh} $\approx$ 11; J_{fh} $\approx$ 22.5.



II

The resonances for protons a, b, e, f, and h are very similar in their appearance to the analogous ones in the spectrum of protonated butadieneiron tricarbonyl, Figure 3. Proton resonances e, f, and h also broaden with increasing temperature and merge at −28° to a broad single resonance centered at τ 14.23 (relative area, 3). In place of the resonance for the *syn* proton, c, we observe a doublet centered on τ 8.20 (relative area 3) which represents the methyl group. The resonance of *anti*-proton d in the $=CH(CH_3)$ group is 1.2 ppm lower than the *anti* proton in the $=CH_2$ group, typical of the effect of *gem*-methyl groups in these complexes. Because of the similarity to the spectrum of the protonated butadiene complex, specifically in the signals a, b, f, and h discussed above, we felt confident that the isomer designated as structure II, rather than one in which H_j is associated with the $-CH(CH_3)$ group, is the principal species in solution.

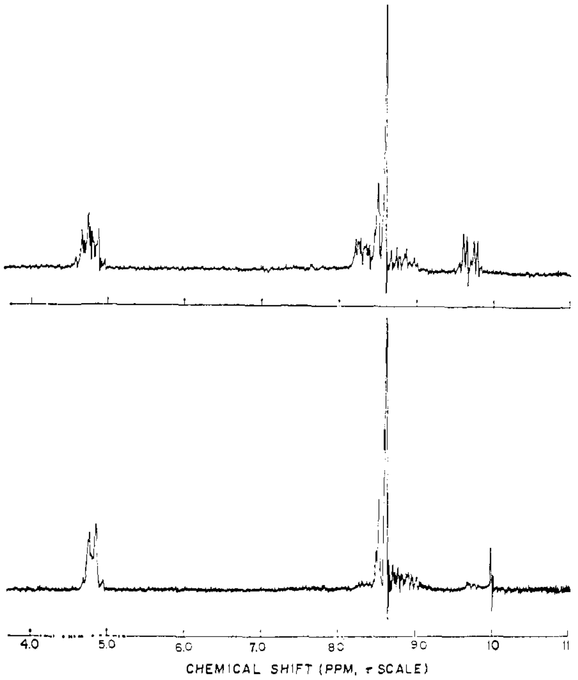


Figure 7. Proton nmr spectra, 60 Mc, $CHCl_3$ solution: upper trace, piperyleneiron tricarbonyl, starting material; lower trace, material recovered from deuterio acid mixture.

The spectra of the neutral *trans*-piperyleneiron tricarbonyl is shown in Figure 7, along with that of complex recovered after three cycles of deuteration at −20° and subsequent quenching (totaling to a period of 5 days exposure in deuterio acid). The assignments[17] for the

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(17) It is worth noting that the chemical shift of the *anti* proton of the $=CH(CH_3)$ group is about 0.9 ppm lower than the *anti* proton in the $=CH_2$ group.

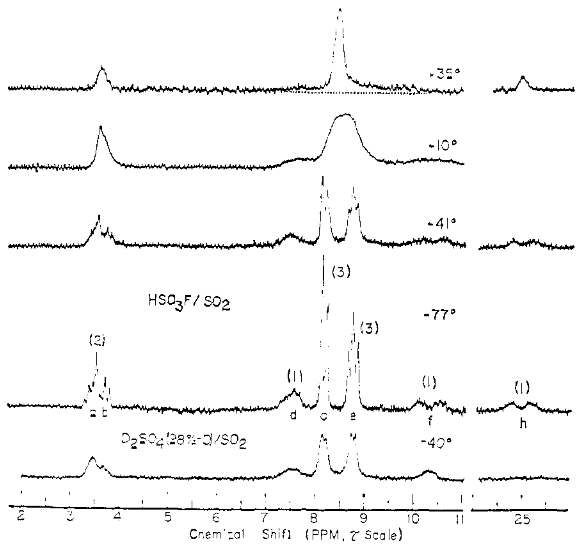
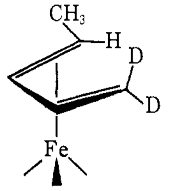


Figure 8. Proton nmr spectra, 60 Mc, for the protonation mixture containing *trans*-2-*trans*-4-hexadieneiron tricarbonyl; lowest trace, deuterio acid medium; upper traces, proton acid medium. Temperature varied, as indicated.

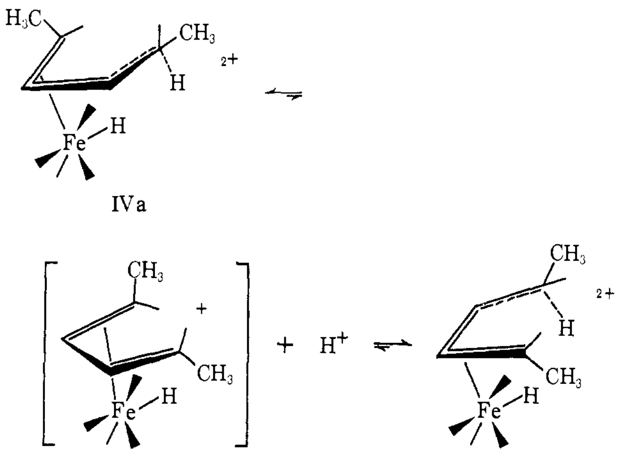
neutral complex are in agreement with what has been reported before.[6] Significant decrease in relative intensity in the lower spectrum is observed only for the protons of the $=CH_2$ group. Thus the specifically labeled complex III is the principal product of this reaction.



III

This was to be expected. Even if a $-CHD(CH_3)$ group were to be formed during tautomerization of the isomer in which the second D^+ was associated with the $-CH(CH_3)$ group (which in any case must be present only in very small equilibrium concentration), the first D^+ does not lose its chemical identity in the deuterioethyl group of the ethallyl complex.

Protonation and Deuteration of *trans*-2-*trans*-4-Hexadieneiron Tricarbonyl. The spectrum of *trans*-2-*trans*-4-hexadieneiron tricarbonyl in excess strong acid at low temperature is shown in Figure 8. The pertinent data are as follows. Chemical shifts (τ values, ppm): H_a, 3.41; H_b, 3.63; CH_3(c), 8.16; H_d, 7.50; CH_3(e), 8.74; H_f, 10.30; H_h, 24.64. Coupling constants (Hz): $J_{ab} \approx 5.5$; $J_{bd} = 10.5$; $J_{CH_3(c)-H_d} = J_{CH_3(e)-H_f} = 6.2$; $J_{CH_3(e)-H_h} = 5.5$; $J_{fh} = 22$. The most prominent feature in these spectra is the persistence of the Fe–H signal. This is a broad doublet centered around τ 24.64 at $-77°$ and becomes a broad singlet at $+35°$ without observable change in chemical shift. Furthermore, the resonance of H_a is not broadened at low temperature as it was in the spectra shown in Figures 3 and 5. As the solution is warmed the resonances of protons a and b, d and f, and those of the two CH_3 groups (c and e), are observed to broaden and merge. The Fe–H signal does not average with olefin protons because, even if tautomerism to terminal carbon were occurring, the identity of each proton is preserved. The observed averaging of the two terminal portions of the olefin was not sufficiently rapid to produce signal averaging in the complexes discussed above although such a mechanism was deduced through the deuteration experiments. The two terminal carbon atoms of the hydrocarbon can be equilibrated through a structure such as IVi, which would be either the transition state or an unstable intermediate between the monoprotonated and diprotonated species. As written, it is an isomer of the monoprotonated species which can collapse to give the ethallyl group at either end, or with shift of acid, can give the diprotonated species at either end. An analogous transition state or intermediate would be responsible for the observed (slow) exchange of deuterium over *five* sites in the deuterated butadiene complexes, discussed above.



IVa

IVi

IVb

The relatively constant position of the Fe–H resonance indicates that if Fe–H is tautomerizing on to the olefin, the fraction of the time spent at that site is very small, *ca.* 10^{-4}. A significant amount of time spent on the olefin should lower the resonance position of the proton by a measurable amount away from the typical Fe–H value and closer to the typical C–H value. The same consideration holds for the butadiene complex; the fact that the position of the merged peak (g) is at the average position calculated from the original Fe–H resonance and those of H_e and H_f tells us that there is very little change in the equilibrium concentration of metal-protonated complex in the mixture as the temperature is raised.

Cyclic Diene Complexes in Strong Acid Medium. The spectrum obtained when cyclohexadieneiron tricarbonyl (V) is placed in strong acid is shown in Figure 9. A pattern indicative of a cyclohexenyl group (see structure VIIa or b, below) as well as a metal–hydrogen is observed. The integrals total to ten hydrogens, in agreement with formulation of diprotonated complex, $[C_6H_9Fe(CO)_3 \cdot H]^{2+}$. Similar features are observed for cycloheptadieneiron tricarbonyl under the same conditions (except that the CH_2 region integrates to eight rather than six protons). The resonances a and c (τ 3.08 and 4.79, respectively) are due to the terminal protons, and b (τ 3.64) is that of the central proton, of the allyl moiety of the π-cyclohexenyl ring. The asymmetry in chemical shifts requires placement of iron–hydrogen in a position different from that proposed for the diprotonated complexes of acyclic dienes. Due to the slightly different behavior observed in these two

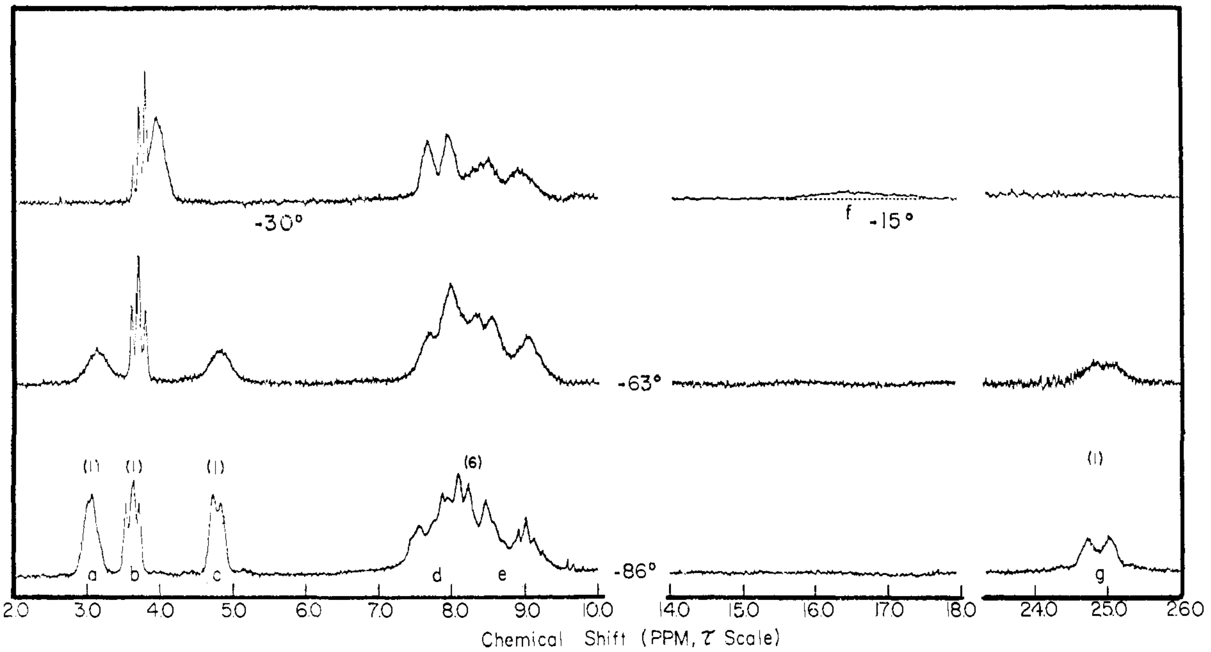
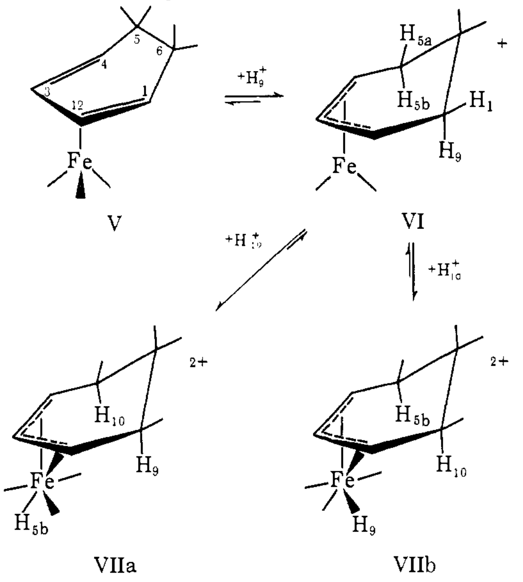


Figure 9. Proton nmr spectra, 60 Mc, for the protonation mixture containing 1,3-cyclohexadieneiron tricarbonyl with excess HSO_3F; temperature varied, as indicated.

sets of complexes, perhaps this difference can be accepted. The integrated intensities are indicated by the numbers in parentheses above several of the resonances in Figure 9; these are measured to a precision of ±5%.

On warming, most of the resonances broaden. At the highest temperature shown, signals for a and c have merged; together with the triplet, b, these still integrate to three protons. The methylene region (d and e) now represents five protons. Peak g has merged with the equivalent signal of one proton from the methylene region to produce a broad absorption labeled f, centered around τ 16.5; this integrates approximately to 1.6. In deuterio acid, resonances a, b, and c appear unchanged and, counting the total integral under these as 3.0, we obtain 4.7 for the integral under the methylene resonances, and 0.6 for resonance g. These observations may be accounted for by scheme illustrated in structures V through VII.



As in the case of the acyclic complexes, the first acid proton (labeled H_9^+, structure VI) must attack at a terminal carbon atom of the diene system (positions 1 or 4) of the neutral complex, V. Since the two positions are related by symmetry, it is necessary to follow the sequence of attack at only one of these, position 1. For reasons enumerated below and from data on the stereochemistry of known protonations,[3,4] we expect that the first proton must become the methylene hydrogen on the side of the metal (*endo*). Attack of the second proton (H_{10}^+) must occur at this saturated center (1) or its symmetry related equivalent (5). The *endo* hydrogen of the methylene adjacent to the allyl moiety is displaced onto the metal by entering proton, which takes its place on the hydrocarbon. In deuterio acid there is one chance in two that the hydrogen on the metal will be deuterium, in agreement with the integral for metal-H obtained in this medium. Attack of second proton is arbitrarily depicted as *endo*. However, until we are able to resolve the signals for *exo*- and *endo*-methylene protons, this point must remain uncertain. The permutation of hydrogen atoms in the various positions brought about by this mechanism is summarized in Table III.

Table III. Permutation of Hydrogen Atoms in Diprotonated Isomers of Cyclohexadieneiron Tricarbonyl

H[a]	Position in isomer VIIa	Position in isomer VIIb
H_1	*exo*-Outer methylene	*exo*-Outer methylene
H_2	Outer allyl *trans* to FeH	Outer allyl *cis* to FeH
H_3	Central allyl	Central allyl
H_4	Outer allyl *cis* to FeH	Outer allyl *trans* to FeH
H_{5a}	*exo*-Outer methylene	*exo*-Outer methylene
H_{5b}	FeH	*endo*-Outer methylene
H_{6a}	*exo*-Central methylene	*exo*-Central methylene
H_{6b}	*endo*-Central methylene	*endo*-Central methylene
H_9	*endo*-Outer methylene	FeH
H_{10}	*endo*-Outer methylene	*endo*-Outer methylene

[a] Hydrogen atoms are labeled according to their location on the neutral complex, structure V.

The signals observed at low temperatures are those of structures VIIa and VIIb. These are equivalent in the all-proton system. In deuterio acid, H_9^+ and H_{10}^+ are replaced by deuterium and the spectrum represents an equimolar mixture of D_2-VIIa and D_2-VIIb, in agreement with the integrals obtained.

Rapid deprotonation and return would equilibrate structures VIIa and VIIb and account for all the features observed in the spectra at higher temperatures. The outer allyl protons *cis* and *trans* to Fe–H would undergo exchange, as shown in Table III. The iron–hydrogen would exchange with only one methylene proton, in agreement with the integral of signal f (1.6) and its chemical shift which is half-way between the CH_2 and Fe–H regions. The integral does not quite come up to a value of two protons because of the broadness of the line. Due to decomposition of the sample, it was not possible to sharpen this resonance by increasing the temperature.

The central allyl proton, H_3, remains a sharp signal (triplet) coupled to the outer allyl protons. The intensity of this signal is skewed toward the average signal for the outer allyl protons at higher temperature due to a second-order effect. The signal for the methylene region is separated into two groups of resonances corresponding to central (2) and outer (3) protons. The two sharper signals at lower field must be associated with the central methylene protons since these are subject to less environmental change in the exchange.

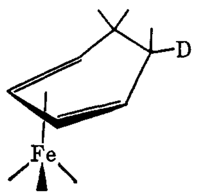
Deuteration also provides evidence for processes too slow to produce signal averaging in the nmr. The integrals in deuterio acid show little change up to 0° for several hours. Over longer periods at 0° small amounts of decomposition begin to broaden the peaks considerably. The progress of deuteration was therefore monitored in the neutral complexes recovered by quenching the mixtures; it has already been shown that exchange of ligand protons with H_2O or D_2O during quenching is negligible.[16] The undeuterated neutral complex shows three signals in the nmr,[12] τ 4.77 for the two inner diene protons, τ 6.86 for the two outer diene protons, and τ 8.37 for the four methylene protons. The integrals in the complex recovered from deuterio acid after several different periods of exposure are shown in Table IV.

Table IV. Proton Nmr Integrals for Cyclohexadieneiron Tricarbonyl Recovered from D_2SO_4–SO_2 Mixture

Time elapsed,[a] hr	Relative Integrals[b] Inner diene	Outer diene	Methylene
92	2.0	2.0	3.6
140	2.0	2.0	2.8
164	2.0	2.0	2.7

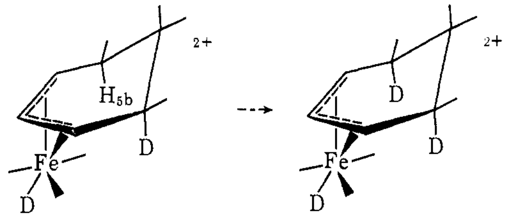
[a] Exposure to deuterio acid at 0°. [b] Proton signals in neutral complex, see text; precision is ±0.1.

An equilibrated mixture of dideuterated isomers D_2-VIIa and D_2-VIIb (structures VIIa and VIIb above with deuterium for H_9^+ and H_{10}^+) would give, on quenching, 50 mol % of a monodeuterated complex, D_1-V (arising from D_2-VIIa), and 50 mol % of the all-proton complex, V (arising from D_2-VIIb). This mixture would give integrals for the recovered complex in the ratios of 2.0:2.0:3.5, as observed in the product recovered after 92 hr in deuterio acid solution.



D_1-V

A greater amount of deuterium becomes incorporated over longer periods of time. At least one additional deuterium can be incorporated into the diprotonated complex by adding to the above mechanism a slow rotation of the cyclohexenyl group with respect to the other ligands. In D_2-VIIa this would not influence product, but in D_2-VIIb this would give rise to a new isomer, D_2-VIIc. As proton 5b eventually exchanges with reservoir acid in this isomer, the trideuterated D_3-VIIc is produced. Both D_3-VIIc and D_2-VIIa give rise to a monodeuterated cyclohexadiene complex on quenching. The ratios of the integrals in the product would thus be 2.0:2.0:3.0. Deuteration apparently proceeds beyond this point, but the condition of the sample begins to be a serious problem, and it is not possible to draw any further conclusions at this time.



D_2-VIIc D_3-VIIc

Summary and Conclusion

The evidence presented here indicates that cyclic diene complexes of iron tricarbonyl are diprotonated in strong acid. By inference, the same is strongly suggested for the acyclic diene complexes in the same medium. The averaging processes observed in these systems require that attack of *both* first and second proton occur on the hydrocarbon. During attack of second proton, the first proton or its symmetry-related equivalent (if one exists in the monoprotonated complex) is displaced from the hydrocarbon and is observed on the metal in the diprotonated species. In the complexes of the acyclic dienes, a separate signal has not been observed for the second proton; it is believed to be rapidly exchanging with the protons of excess acid. We have observed spectra at temperatures as low as −120° in SO_2ClF–HSO_3F; under these conditions all signals become broadened, but the resonance of acid proton is very much more so. Apparently, still lower temperatures will be required to resolve the signal, if any, of the proposed second proton. It may eventually be possible to settle this point if the appropriate medium can be found.

The second proton proposed in the protonated acyclic diene complexes is thus only weakly held to the terminal carbon of the organic group. One possible reason for this may reside in the stereochemistry around the iron atom. Structures have recently been reported for some π-allyl (σ-halo) iron tricarbonyl complexes.[18] No π-

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[18] A. N. Nesmeyanov, Yu. A. Ustynyuk, I. I. Kritskaya, and G. A. Shchembelow, *J. Organometal. Chem.*, **14**, 395 (1968), and references cited therein.

allyl derivative is known in which a substituent is present in the *anti* position of the terminal carbon while the metal also is bonded to *four* other ligands. It is apparent from the reported structural work[18] that a fully formed methyl group in the *anti* position on the π-allyl group would seriously interfere with the "axial" ligand (see position 3 in structure I, above). A minor structural adjustment in the cyclohexenyl complexes could be responsible for the difference. In these protonated derivatives, the second proton becomes sufficiently tightly bound to the carbon adjacent to the allyl moiety to give rise to a resonance typical of a methylene proton of the cyclohexyl ring, as observed. The solvent (SO_2) might also play a role in these systems. Studies on this and related systems are in progress to provide further elucidation of these phenomena.

Acknowledgment. We are indebted to Professors F. A. L. Anet and S. Winstein of this department for stimulating discussions, and to the following sources for support of departmental instruments used in this work: NSF GP-8223 (Varian HA-100 nmr spectrometer); Du Pont donation and NSF G-20207 (Varian A-60 nmr spectrometer); and NSF GP-3672 (AEI-MS9 mass spectrometer).

Chemistry of Macrocyclic Complexes of Cobalt(III). Acid Hydrolysis of Bidentate Carbonate and *cis–trans* Isomerization of Macrocyclic Complexes[1a,b]

John A. Kernohan and John F. Endicott[1c]

Contribution from the Department of Chemistry, Boston University,
Boston, Massachusetts 02215. *Received May 9, 1969*

Abstract: Rates have been determined for the relatively slow acid hydrolyses of $CoLCO_3^+$ complexes containing a macrocyclic tetracoordinate ligand L and bidentate carbonate. In the case that L is a cyclic tetramine (hexamethylcyclam = Curtis' tet*b*), the hydrolysis rate is slower by a factor of about 10^5 than the hydrolysis rate of the analogous $Co(en)_2CO_3^+$. This great disparity in rates most likely has its source in steric crowding of the fifth and sixth coordination positions by methyl groups of the ligand L. The immediate product of hydrolysis of Co(tet*b*)CO_3^+ appears to be *cis*-Co(tet*b*)$(OH_2)_2^{3+}$, but the kinetics are complicated by a chloride-catalyzed *cis* → *trans* isomerization reaction. The acid hydrolysis of Co(*trans*[14]diene)CO_3 (where *trans*[14]diene is Curtis' Schiff base amine) is intermediate in rate and gives *trans*-Co(*trans*[14]diene)$(OH_2)_2^{3+}$ as the first isolable product. It appears that the *cis* → *trans* isomerization for the latter complex is unusually fast. It is suggested that the presence of Co(III)–N(imine) groups in the macrocyclic ligand may stabilize the five-coordinated intermediate in the isomerization reaction.

Bidentate carbonate complexes have been reported recently for cobalt(III) complexes containing the tetradentate macrocyclic ligands 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane[2,3] and 5,7,7,12,14,14-hexamethyl-1,4,8,11-azacyclotetradeca-4,11-diene[5,6] (see Figure 1). The Co(*trans*[14]diene)CO_3^+ complex is one of the very few known complexes containing the *trans*[14]diene ligand in a folded (or *cis*) configuration; it is the only such cobalt(III) complex yet reported. In fact all reported complexes of Co^{III}(*trans*-[14]diene)X_2 and Co^{III}(tet*b*)X_2 for monodentate ligands X have a *trans* geometry despite the fact that many of these complexes have been prepared from Co(*trans*[14]diene)CO_3^+ and Co(tet*b*)CO_3^+, respectively. Since *cis*-Co^{III}(cyclam)X_2 complexes seem to be easily prepared and isomerize only slowly,[7,8] the relative difficulty in preparing *cis*-Co^{III}(*trans*[14]diene)X_2 and *cis*-Co^{III}(tet*b*)X_2 complexes might well be attributed to rather great steric strains (possibly between some of the six methyl groups and the fifth and sixth coordination positions) which result when the *trans*[14]diene and tet*b* ligands are folded.

We have found Co(*trans*[14]diene)CO_3^+ and Co(tet*b*)CO_3^+ to be very rugged complexes in aqueous solution. Their general inertness is particularly surprising when it is realized that the *trans*-Co^{III}(tet*b*)X_2 complexes are generally quite labile with respect to aquation of the ligand X.[9] In fact, Co(tet*b*)CO_3^+ is a most remarkable substance for its stability for hours in dilute acid solutions at room temperature and for its ready formation from *trans*-Co(tet*b*)$(OH_2)OH^{2+}$ in neutral solution.

In this paper we report our studies of the acid hydrolysis of Co(*trans*[14]diene)CO_3^+ and Co(tet*b*)CO_3^+. Several features of these macrocyclic ligand systems permit the examination of simple chemical reactions from an unusual point of view. The significance of steric interactions has been alluded to above and the manifestations of steric interactions are an important part of the

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(1) (a) Taken in part from the dissertation submitted by J. A. Kernohan to Boston University in partial fulfillment of the requirements of the Ph.D. (b) Supported in part by the Public Health Service (Grant AM 08737) and in part by a grant in aid from Boston University. (c) Correspondence may be addressed to J. F. E., Department of Chemistry, Wayne State University, Detroit, Mich. 48202.

(2) P. W. Whimp and N. F. Curtis, *J. Chem. Soc., A*, 1827 (1966).

(3) For the C-*dl* isomer of the ligand which Curtis[4] designates tet*b*.

(4) N. F. Curtis, *Coord. Chem. Rev.*, 3, 3 (1968).

(5) N. Sadasivan, J. A. Kernohan, and J. F. Endicott, *Inorg. Chem.*, 6, 770 (1967).

(6) Following Curtis' suggestion[4] this ligand will hereafter be referred to as *trans*[14]diene.

(7) C. K. Poon and M. L. Tobe, *J. Chem. Soc., A*, 1549 (1968).

(8) C. K. Poon and M. L. Tobe, *Inorg. Chem.*, 7, 2398 (1968).

(9) J. A. Kernohan, Ph.D. Dissertation, Boston University, 1969.