References and Notes

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Fluxional Behavior and Substituent Site Preferences in Cationic Monosubstituted Tropyliumiron Tricarbonyl Complexes

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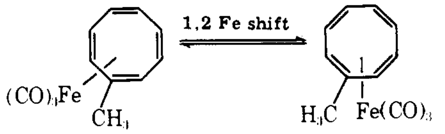
Abstract: The fluxional monosubstituted tropyliumiron tricarbonyl complexes, $RC_7H_6Fe(CO)_3^+$ (R = methyl, isopropyl, cyclopropyl, and phenyl), have been studied by variable temperature ^1H and ^{13}C NMR. Static systems can be observed at low temperatures (ca. −100 °C) and reveal the isomer distributions in the various ions studied and thus the substituent site preferences. For R = methyl, the 2-methyl, 3-methyl, and 6-methyl (vinyl substituted) ions can be observed in a ratio of ca. 43:7:50 at −100 °C. For R = isopropyl, no 3 isomer is observed and the 2-isopropyl:6-isopropyl ratio is ca. 15:85. When R = phenyl, the vinyl-substituted 6 isomer is the only species observed, while in contrast for R = cyclopropyl the 2 isomer predominates (80%) with the 6-cyclopropyl isomer as the minor component (20%). The substituent site preferences indicate that there is relatively little charge on the carbons of the metal-complexed pentadienyl ring, but among the three different sites, most positive charge resides at C_2, C_4. A fine balance of electronic vs. steric factors control the C_2:C_6 isomer ratio. The dynamic behavior of the complexes was studied at higher temperatures and, in general, three dynamic processes all occurring via 1,2 iron shifts could be observed. In order of increasing activation energies, these processes were (1) degenerate isomerization of the 2 isomer with its enantiomer via the symmetrical 3 isomer, (2) degenerate interconversion of the 6 isomer with its enantiomer, and (3) the interconversion of the equilibrating 2 and 3 isomers with the 6 isomer via the unobserved 1 isomer. Detailed rates and free energies of activation for these processes are given.

Introduction

Stereochemical nonrigidity is frequently encountered in transition metal π complexes in which the metal is bonded to a fragment of a completely conjugated cyclic polyolefin.[2] For such mononuclear complexes, the fluxionality is associated with a rapid metal migration around the ring, resulting in a number of thermally accessible degenerate configurations. This results in the "averaging" of all ring carbon and attached proton sites in the system, if migration is sufficiently rapid on the NMR time scale. Such metal migration is overwhelmingly of the 1,2 type, with concomitant π-bond reorganization.[2,3] When the polyene is substituted, structures generated by metal shifts are no longer degenerate, and are likely to differ in stability and hence be present in unequal amounts. Apparently only one thorough study of such a system has been conducted, that being the examination of monosubstituted cyclooctatetraene-$Fe(CO)_3$ (COT-$Fe(CO)_3$) complexes.[4] Anet demonstrated that methyl-COT-$Fe(CO)_3$ exists very largely (>90%) with the methyl group occupying the inside site of the bound diene unit as shown below.[4a,c] Other monosubstituted COT-$Fe(CO)_3$ complexes were examined and different substituents were found to prefer different sites.[4c] These results for an uncharged system suggested that the determination of site preferences in other systems could be quite illuminating with respect to the electronic properties of the bound unsaturated moiety.



Pentadienyl-$Fe(CO)_3$ cations are remarkably stable and have been subjected to extensive experimental[5,6] and theo-

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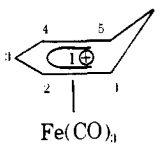
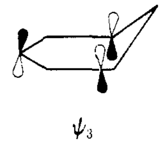
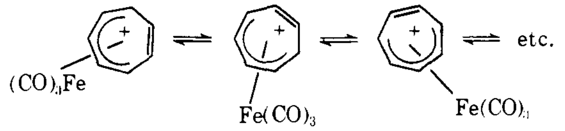
retical[7-9] scrutiny. In the latter connection, comparisons of (positive) charge densities in the complexed and uncomplexed pentadienyl fragment have been of primary interest.[7-9] For example, while molecular orbital results for uncomplexed cyclohexadienyl (benzenium) cations[7] place nearly equal charges at C_1, C_3, and C_5 with little at C_2 and C_4 (consistent with $C_6H_7^+$ ^{13}C NMR shifts),[10] the calculations for cyclohexadienyl-$Fe(CO)_3^+$ are consistent in the ordering of the charge pattern, viz., $C_{2,4} > C_3 > C_{1,5}$. This remarkable reversal in charge distribution can, in qualitative terms, be attributed to interaction of an occupied orbital on iron with the LUMO (ψ_3) of a dienyl cation. This interaction would supply electron density to $C_{1,5}$ and C_3 leaving $C_{2,4}$ relatively more positive.[8]

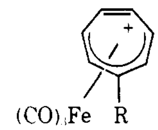




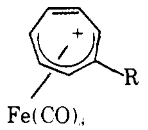
These calculations are supported by the ^{13}C chemical shifts for a range of pentadienyl-$Fe(CO)_3^+$ systems, and in particular for cyclohexadienyl-$Fe(CO)_3^+$ shown above: $C_{1,5}$ at 63 ppm, C_3 at 88 ppm, and $C_{2,4}$ at 101 ppm.[8,11] These results, implying appreciable charge disparity in the pentadienyl network, made examination of a fluxional system incorporating a pentadienyl-$Fe(CO)_3$ fragment a worthwhile goal, in anticipation that cation-stabilizing substituents in particular would exhibit definite site preferences. Monosubstituted tropylium-$Fe(CO)_3^+$ species would seem to be well credentialled in this regard, as the instantaneous structure of $C_7H_7Fe(CO)_3^+$ is known to be an iron-bound pentadienyl unit and a free double bond.[12,13] The system is fluxional and line-shape analyses are consistent with 1,2 iron shifts.



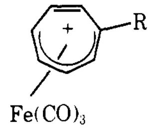
On substitution of R for H in $C_7H_7Fe(CO)_3^+$ four distinct isomers are possible as shown below. The relative stabilities of A-D, as judged by relative populations at an appropriate temperature, and the energetics of the interconversion should provide useful insights into the charge patterns and general structures of the ions. To relate our results to theoretical treatments of acyclic pentadienyl- and cyclohexadienyl-$Fe(CO)_3$ cations, it is necessary to demonstrate experimentally a close similarity between such ions and a pentadienyl-$Fe(CO)_3$ cation system incorporated in a seven-membered ring and formally conjugated with the uncomplexed double bond. The ^{13}C and ^1H chemical shifts, as well as the $^1J_{^{13}C-^1H}$ values (which are frequently regarded as indicative of carbon hybridization), show close agreement (vide infra) and we feel that application of the theoretical results to our systems is acceptable, though clearly not absolutely rigorous.



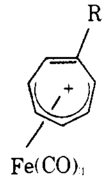
A



B



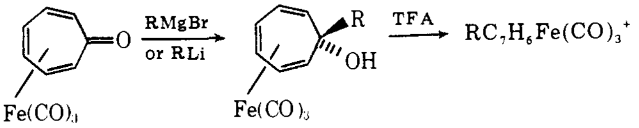
C



D

Results and Discussion

Synthesis of Ions. The precursors to the ions $RC_7H_6Fe(CO)_3^+$ were the alcohols which were obtained by alkylating troponeiron tricarbonyl with the appropriate Grignard or lithium reagent. The alcohols cleanly ionize in a trifluoroacetic acid containing medium to provide solutions of the ions.



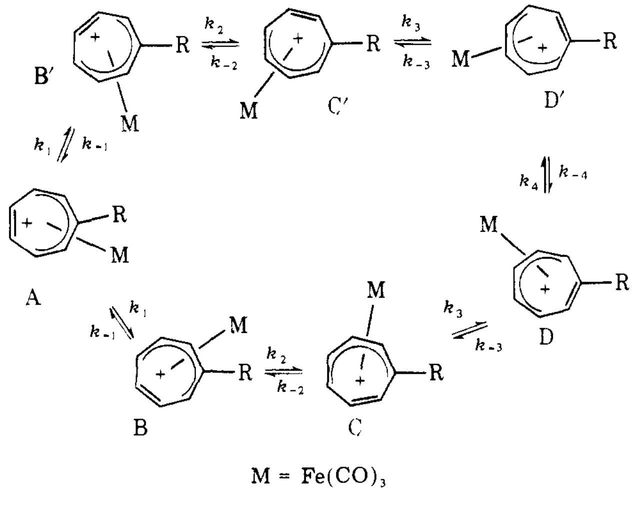
The alcohols were characterized by their ^1H and ^{13}C NMR spectra and the IR spectra in the carbonyl region were appropriate for $Fe(CO)_3$ systems. In the alkylation reactions only one alcohol isomer was formed and was assumed to be that resulting from exo attack by the reagent. This structural detail is of course lost on ionization. Conjugate addition to troponeiron tricarbonyl was not observed.

Methyltropylium-$Fe(CO)_3^+$. The methyltropyliumiron tricarbonyl cation was examined first and analysis of its behavior allows ready understanding of the phenyl, cyclopropyl, and isopropyl cases. Scheme I illustrates the four possible isomers of this cation, together with their possible modes of interconversion via consecutive 1,2-iron shifts. (B and B′ are enantiomers as well as C, C′ and D, D′.)

Before a detailed analysis of the rather complex temperature-dependent spectra is given, it will be useful to outline in general terms the proposed interpretations. At temperatures below ca. − 90 °C, three of the four possible isomers are detectable in the ^1H NMR spectrum, the symmetrical 3-methyl ion A, the 2-methyl ion B, and the 6-methyl ion D, in the approximate ratio of 7:43:50, respectively. As the temperature is raised, ions A, B, and B′ exhibit line broadening and eventually merge. A second averaging process, which is apparent at higher temperatures, corresponds to the degenerate process involving the 6-methyl ions, $D \rightleftharpoons D'$ via 1,2 iron shifts. At still higher temperatures, a third averaging process is observed, in which the equilibrating $B \rightleftharpoons A \rightleftharpoons B'$ ions begin to average with the $D \rightleftharpoons D'$ system. Let us examine these processes in detail.

Low-Temperature Limiting Spectrum. The presence of three of the four possible isomers at −102 °C is clearly indicated by the observation (see Figure 1) of separate methyl resonances at δ 1.51, 2.41, and 3.05 in the relative ratios of 50:43:7. Below −102 °C, the CH_3 signal of the minor isomer sharpens ($W_{1/2}$ $\sim$ 5 Hz at −124 °C) whereas other resonances are less resolved due to increased solution viscosity. The remaining ring signals fall into three distinct areas—those in the δ 4.3-5.5 range due to protons 1, 5, 6, 7; δ 5.8-6.5 for protons in the 2, 4 positions; δ 7.89-7.95 for protons at the 3 position. The numbering scheme is shown below. These "regional" assignments are consistent with data on many other cyclic pentadienyliron tricarbonyl ions, including those for tropyliumiron tricarbonyl

Scheme I



M = Fe(CO)3

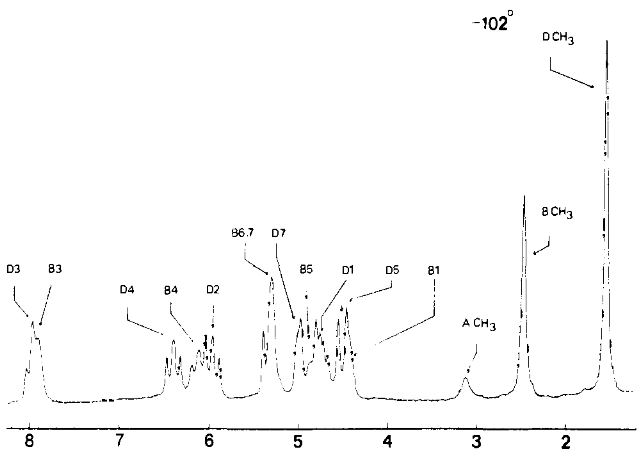
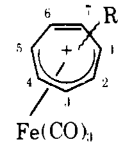
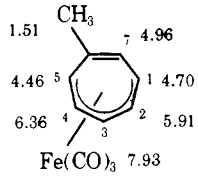


Figure 1. ¹H NMR of methyltropyliumiron tricarbonyl cation at −102 °C in TFA/SO_2/SO_2F_2. Resonance assignments are indicated.



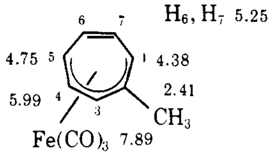
cation.[5,13] The major isomer with a methyl resonance at δ 1.51 is the vinylmethyl isomer D. Additional ¹H assignments are



D

δ 7.93 (H_3, t) (but overlapping another band, see below), 6.36 (H_4, t), 5.19 (H_2, t), 4.96 (H_7, narrow d), 4.70 (H_1, d of d) (skewed from overlap with another band), and 4.46 (H_5, d). All assignments were confirmed by decoupling experiments.[14]

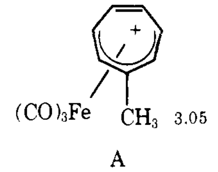
The next most abundant species (~43% at −102 °C with δ CH_3 at 2.41; see Figure 1) is isomer B, a conclusion based



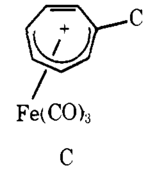
B

initially on the following: (a) The downfield resonances (~7.93) together integrate for one proton relative to the area sum of the two most intense CH_3 signals. This indicates that B has a proton at position 3 of the pentadienyl system, hence eliminating the 3-CH_3 isomer A. (b) Only *one* other signal, a triplet at δ 5.99 (overlapping the δ 5.91 band of D), appears in the δ 5.8–6.5 region in addition to the two (δ 5.91 and 6.31) already assigned to isomer D. This is consistent with a 2-CH_3 isomer. Decoupling experiments on B established the following: δ 7.89 (H_3, d), 5.99 (H_4, t, overlapping the δ 5.91 band of D), 5.25 (H_6, H_7, br, s), 4.75 (H_5, lies under δ 4.70 d of d of D), and 4.38 (H_1, narrow band overlapping upfield side of δ 4.46 doublet of D). An important observation was that irradiation at either δ 7.89 or δ 4.75 collapses H_4 (at δ 5.99) to a doublet. The assignment of the two-proton band at δ 5.25 to $H_{6,7}$ and the narrow one-proton band (δ 4.38) to H_1 is in accord with the expected lower field resonance of vinyl protons relative to H_1. In addition, the (free) vinyl protons in the parent C_7H_7-$Fe(CO)_3^+$ (acetone, −80 °C) resonate at δ 5.48.[13] The narrowness of the H_1 signal is expected, as the H_1-H_7 coupling is small and a vicinal proton (at position 2) is absent.

The minor isomer (~7% at −102 °C) with δ CH_3 at 3.05 is assigned to the symmetrical 3-methyl ion A rather than the remaining alternative 1-methyl ion C. The population of this ion is sufficiently low that no ring proton resonances can be observed. The distinction between A and C is made on the basis



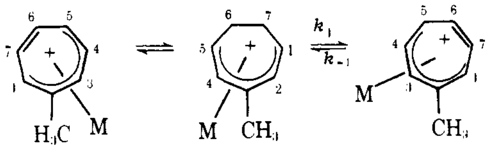
A



C

of a strong chemical shift analogy with other methyl-substituted pentadienyliron tricarbonyl cations. In particular, Birch[15] has reported a series of methyl-substituted cyclohexadienyliron tricarbonyl cations, and finds $\delta_{1\text{-}CH_3}$ at 1.90–1.96, $\delta_{2\text{-}CH_3}$ at 2.26–2.29, and $\delta_{3\text{-}CH_3}$ at 2.86–2.88. In the bicyclo[5.1.0]octadienyl-$Fe(CO)_3$ cations (in which the pentadienyl system is in a seven-membered ring) $\delta_{2\text{-}CH_3}$ is 2.40 while $\delta_{3\text{-}CH_3}$ is 3.10.[16] These comparisons direct the choice of A for the minor isomer, and this is in line with the ¹³C shift of the CH_3 group (vide infra) as well as higher temperature spectra.

Higher Temperature Spectra. The First Averaging Process. As the temperature is raised above −102 °C, the CH_3 signals at δ 2.41 and 3.05 each broaden and eventually merge (see −76 and −89 °C spectra, Figure 2) while the δ 1.51 CH_3 signal remains sharp. In the downfield region of the spectra, considerable changes also occur. Substantial broadening of the δ 5.99, 5.25, and 4.38 bands of B can be observed in the −89 and −76 °C spectra. The downfield resonance at δ 7.9 changes from a highly skewed triplet (from overlap of H_3, t in D and H_3, d, in B) to a more symmetrical triplet (H_3 in D), as H_3 of B has broadened almost into the base line (see −76 °C spectrum). Spectra in the −70 to 80 °C range provide confirmation of the structure and shift assignment of isomer D, as its resonances remain sharp at δ 7.93, 6.36, 5.91, 4.70, 4.96, and 4.46 while other ring proton resonances have broadened. This first process is postulated to involve rapid interconversion of B and minor isomer A and thus (since A is symmetric) degenerate averaging with enantiomer B′ as shown below, M = $Fe(CO)_3$. Such a process would average H_1 and H_3 of B with each other, and



B A B′

with H_2, H_4 of A. Analogously, H_4, H_7 of B will average with each other and with H_1, H_5 of A. Similar considerations apply to H_5, H_6 of B and H_6, H_7 of A. It is clear from coalescence of the methyl resonances that B is averaging with the minor isomer. If A is correctly assigned, the degenerate B ⇌ B′ averaging must also occur; however, if the minor isomer were in fact C then the B ⇌ B′ process would not occur together with the B ⇌ C process. Hence it is important to demonstrate that the B ⇌ B′ process occurs together with the process which averages B and the minor isomer, assigned structure A. Two approaches were used to demonstrate the B ⇌ B′ averaging process, the first being based on spin saturation transfer. At −89 °C where the lifetime of B would be relatively short (ca. 0.1 s) the δ 7.89 resonance (H_3) was irradiated. This resulted in saturation and disappearance of the δ 4.38 band assigned to H_1. This confirmed the H_1 ⇌ H_3 interconversion and thus the degenerate B ⇌ B′ interconversion. The second approach was to calculate where the averaged resonances should appear assuming a B

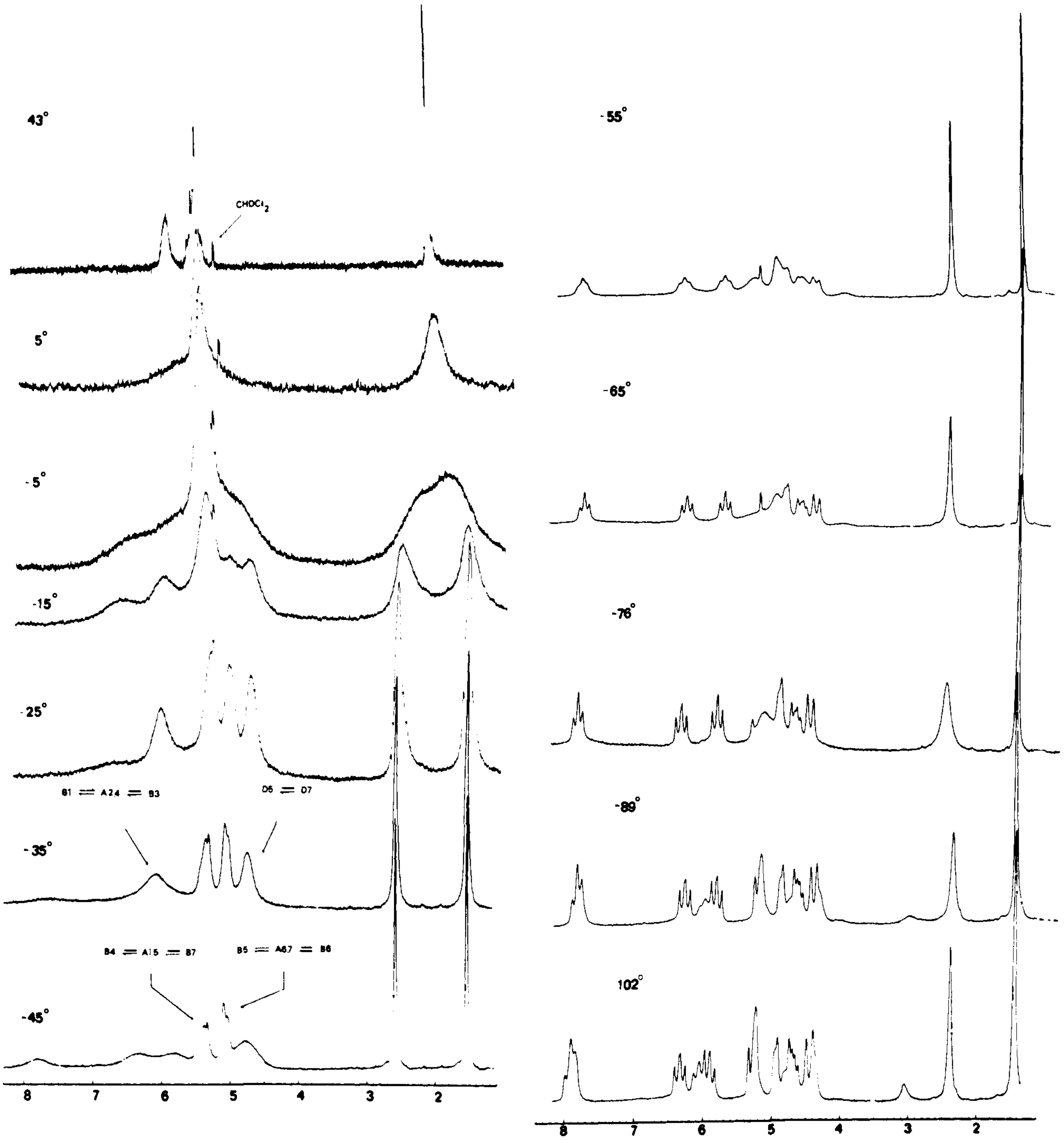


Figure 2. Variable-temperature ^1H NMR spectrum of methyltropyliumiron tricarbonyl from −102 to 43 °C. Solvent changes were necessary to span this temperature range and are indicated in the Experimental Section.

$\rightleftharpoons$ A $\rightleftharpoons$ B′ process. No signals for ring protons in A are observed, but good estimates can be made. Any error will not be crucial, as the abundance of A is known to be small. Hence estimating the shifts of A as H_2, H_4 ca. δ 5.9 H_1, H_5 ca. δ 4.6, and $H_{6,7}$ ca. δ 5.2, the weighted average bands which will appear at higher temperature can be calculated as δ 6.1 (for H_1, H_3 (B) + H_2, H_6 (A) + H_3, H_1 (B′)), ca. δ 5.5 (for H_4, H_7 (B) + H_1, H_5 (A) + H_7, H_4 (B′)), and ca. δ 5.0 (for H_5, H_6 (B) + H_6, H_7 (A) + H_6, H_5 (B′)). As the temperature is raised, the δ 5.5 and 5.0 bands should emerge and sharpen faster than the δ 6.1 band, as these arise from averaging of shifts less than 1 ppm apart (ca. 0.7 and 0.5 ppm, respectively) whereas the δ 6.1 band is primarily an average of H_1 and H_3 which are 3.5 ppm apart. Although a second averaging process (see below) is beginning to broaden the signals of isomer D, at −55 °C the δ 5.5 and 5.1 resonances can be seen emerging and at −45 °C the bands are clearly evident. In the −35 and −25 °C spectra, the δ 6.1 band has now emerged as expected and the δ 5.5 and 5.1 bands are considerably sharper. These observations are completely consistent with the B $\rightleftharpoons$ A $\rightleftharpoons$ B′ process.

The other alternative, a B $\rightleftharpoons$ C averaging process, would not result in averaging to three ring signals (since no symmetrical intermediate is involved), but would retain *six* unique ring protons. Since the minor isomer (C) would contribute little to the weighted average, the six coalesced ring signals would appear very close to those of static ion B. This prediction is clearly not observed.

Line-width measurements of the two methyl signals at various temperatures, and application of the slow exchange approximation ($k = \pi\Delta\nu$), provided rate constants k_1 and k_{-1}

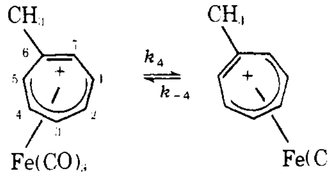
Table I. Summary of Rate Constants and Free Energies of Activation for Interconversions of Isomers of Methyltropyliumiron Tricarbonyl

process	k, s^{-1}	t, °C	$\Delta G^{\ddagger}$, kcal/mol	method of calculation
A → B (or B′)	4.7	−105	9.1	^{1}H, approx. slow exchange
(k_1)	11.0	−100	9.1	^{1}H, approx. slow exchange
	15.7	−95	9.2	^{1}H, approx. slow exchange
B (or B′) → A	4.7	−95	9.7	^{1}H, approx. slow exchange
(k_{-1})	12.6	−89	9.7	^{1}H, approx. slow exchange
	25	−80	9.8	^{13}C, approx. slow exchange
D ⇌ D′	3.1	−75	11.5	^{1}H, approx. slow exchange
($k_4 = k_{-4}$)	11.5	−65	11.5	^{1}H, approx. slow exchange
B, A, B′ $\underset{k_{-5}}{\overset{k_5}{\rightleftharpoons}}$ D, D′	6.3	−35	12.7	^{1}H, approx. slow exchange
	25	−25	12.7	^{1}H, approx. slow exchange
$k_5 = k_{-5}$	30	−27	12.7	^{13}C, approx. slow exchange
	90	−15	12.7	^{1}H, approx. slow exchange
	231	−5	12.7	^{1}H, coalescence
	314	0	12.8	^{13}C, coalescence
	541	5	12.7	^{1}H, fast exchange
	2074	20	12.7	^{1}H, fast exchange
	2950	28	12.8	^{13}C, fast exchange

(see Table I). Values determined for k_1 are 4.7 (−105 °C), 11 (−100 °C), and 15.7 s^{-1} (−95 °C) all corresponding to $\Delta G^{\ddagger} = 9.1$ kcal/mol. Values for k_{-1} were 4.7 (−95 °C) and 12.6 s^{-1} at −89 °C, yielding $\Delta G^{\ddagger} = 9.7$ kcal/mol. The ratio of A/(B + B′) is given by $k_1/2k_{-1} = 6.7$ (−95 °C), which agrees well with the ratio of areas of the methyl signals of 6.1/1.

The Second Averaging Process. Raising of the temperature above −65 °C reveals a second process manifested by the broadening of the ring proton signals of D (see, for example, −45 °C spectrum). Note that the CH_3 signal of D (δ 1.51) remains sharp up to −35 °C. The only plausible explanation of these observations is degenerate 1,2 iron shift which interconverts D with D′ and averages $H_5 \rightleftharpoons H_7$, $H_1 \rightleftharpoons H_4$, and $H_2 \rightleftharpoons H_3$ but does *not* affect the methyl signal, equivalent in D and D′.

The D ⇌ D′ averaging could be confirmed by spin saturation transfer experiments conducted at −55 °C where lines were beginning to broaden but all were clearly identifiable. Irradiation at δ 7.93 (H_3) results in saturation and disappearance of the δ 5.91 signal (H_2) while irradiation at δ 6.36 (H_4) results in disappearance of the δ 4.70 (H_1) band. A rate constant for D ⇌ D′ (k_4) can be estimated as 12 s^{-1} at −65 °C (providing $\Delta G^{\ddagger} = 11.5$ kcal/mol) by applying the slow exchange approximation to broadening of the δ 4.46 (H_5) doublet (see Table I).



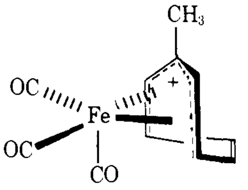
D D′

The Third Averaging Process. Before the D ⇌ D′ averaging process is complete, a third averaging process sets in and is evidenced by the broadening (−25, −15 °C spectra) and coalescence (ca. −5 °C) of the two methyl resonances. The high-temperature limiting spectrum is reached above 40 °C where the merged methyl resonances now appear as a sharp singlet at δ 2.2.

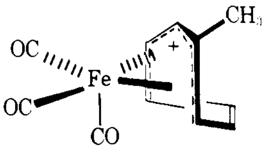
The behavior of the ring proton resonances above −25 °C is quite complex. In the −25 °C spectrum the resonances at δ 6.1, 5.5, and 5.0 are visible (due to the B ⇌ A ⇌ B′ process as noted earlier) while the band at δ 4.7 is associated with the averaging of H_5 (δ 4.46) with H_7 (δ 4.96) in the D ⇌ D′ process. Before a sufficiently high temperature is attained for the (H_1, H_4) and (H_2, H_3) averaged bands from the D ⇌ D′ process to emerge, the third averaging process has set in so that all bands begin to broaden again (see −15 and −5 °C spectra). The consequence of the rapid interconversion of all ions is that the two protons α to the methyl group in all ions become equivalent (H_2, H_4, of A, H_1, H_3 of B, and H_5, H_7 of D), as do the two β protons and the two γ protons. Calculating the weighted averages of the bands indicates that the α protons should ultimately appear at δ 5.8, H_β at δ 5.9, and H_γ at δ 6.3. These shifts are in approximate agreement with the observed high-temperature spectrum showing a four-proton resonance at δ 5.65 (H_α, H_β) and a two-proton band at δ 6.05 (H_γ). The deviation of observed from calculated values is not unexpected considering the likely change in the equilibrium distribution of the three ions in going from −100 to 43 °C and the solvent dependence of the chemical shifts. (Solvent changes are necessary to span these temperature ranges; see Experimental Section.)

Again, rate constants for the interconversion of the B ⇌ A ⇌ B′ set with the D ⇌ D′ set can be estimated at several temperatures. Since the ratio of the coalescing CH_3 groups is ca. 1:1 the forward and reverse rate constants are equal and at coalescence (ca. −5 °C) can be estimated to be 230 s^{-1} using $k_c = \pi(\nu 1 - \nu 2)/\sqrt{2}$. Employing the slow exchange approximation k can be estimated at 6.3 s^{-1} at −35 °C, 25 s^{-1} at −25 °C, and 90 s^{-1} at −15 °C. Using the fast exchange approximation, $k = \pi(\nu 1 - \nu 2)^2/2\delta\nu$, k was calculated to be 541 s^{-1} at 5 °C, 2074 s^{-1} at 20 °C and 3110 s^{-1} at 28 °C. These values provided $\Delta G^{\ddagger} = 12.7$ kcal/mol for the interconversion of the B ⇌ A ⇌ B′ system with the D ⇌ D′ set. The data are summarized in Table I. The 1-methyl ion C was not observed, but, as indicated in the general scheme, is logically implicated as the means of communication of the B ⇌ A ⇌ B′ and D ⇌ D′ systems, on the basis of 1,2 iron shifts.

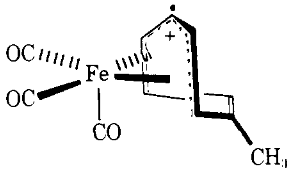
^{13}C Examination of Methyltropylium-Fe(CO)$_3^+$. The foregoing analysis based on ^{1}H NMR observations is completely supported and augmented by a tandem ^{13}C study. In the temperature range −95 to −105 °C (viscosity broadening of some peaks occurred at the lower temperature) spectra of SO_2F_2-TFA-CD_2Cl_2 solutions exhibited three CH_3 signals at 19.5, 23.0, and 26.2 ppm (based on CD_2Cl_2 at 53.6 ppm, external Me_4Si) with the former signal constituting ca. 50% of the total CH_3 intensity. The 23.0-ppm signal was quite minor (10%) and broader than the other two, and must be the methyl signal of minor isomer A. On intensity and chemical shift grounds,[17] the 19.5-ppm signal is associated with D, leaving the 26.2-ppm signal for isomer B. The other relatively simple zone of the spectrum is the carbonyl region. At −100 to −105 °C six resolved CO signals are observed and can be grouped into two sets of three on intensity grounds: 195.8, 196.1, and 210.1 (D) and 195.0, 197.6, and 210.0 ppm (B). This pattern is anticipated on the basis of the structures below for A, B, and D considered to be reasonable representations of these ions on the basis of known structural data.[18] For isomer D the higher field duo at 195.8 and 196.1 ppm is associated with the basal carbonyl groups, while the 195.0- and 197.6-ppm signals are associated with the basal carbonyls in B. Isomer A with a plane of symmetry should exhibit two carbonyl signals (ratio 2:1) but at the lowest practical temperature (−105 °C) these signals were not observed. In view of their low intensity and possible coincidence with the major signals, this is not surprising. The (internal) separation of the basal carbonyl signals in isomers D ($\Delta\delta$ = 0.24 ppm) and B ($\Delta\delta$ = 2.58 ppm) is interesting and consistent with a greater perturbation by a 2-CH$_3$ than a vinyl CH$_3$ (as in D) not involved in the pentadienyl Fe(CO)$_3^+$ fragment.



A



B



C

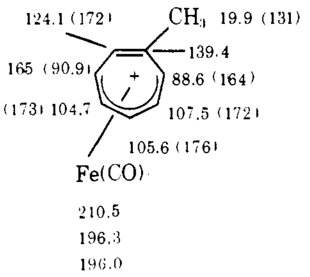
Assignment of the ring carbon resonances in the major isomers D and B is best considered in conjunction with the effects of increasing temperature on the spectral behavior. As the temperature is raised from ca. −100 °C to −70 °C significant changes occur in several regions of the spectrum. The CH$_3$ signals at 26.2 and 23.0 ppm exhibit initial broadening and at ca. −90 °C the minor 23.0-ppm signal has broadened into the base line. With increasing temperature the emerging averaged signal sharpens and at −53 to −60 °C is quite sharp (25.9 ppm). This observation of CH$_3$ signal averaging is mandatory for the B $\rightleftharpoons$ A $\rightleftharpoons$ B′ process discussed in detail previously, and confirms the assignments of the CH$_3$ signals to B and A. Over the range −105 to ∼−65°C the high-field CH$_3$ signal at 19.50 ppm remains sharp. Operation of the B $\rightleftharpoons$ A $\rightleftharpoons$ B′ process demands that changes occur in the CO part of the spectrum. The signals at 195.0 and 197.6 ppm assigned to the basal set in B exhibit substantial broadening at ca. −80 °C, while the signal at 210.0 ppm (apical CO in B) remains sharp and apparently unaltered. This behavior is consistent again with the B $\rightleftharpoons$ A $\rightleftharpoons$ B′ process, which would result in exchange of basal CO environments in B and B′, but would not affect the apical CO environment. (In principle the apical CO for B must average with the undetected apical CO resonance of A but changes in the resonance shape would be minimal considering the low abundance of A (<10%) and the likely near coincidence of these apical CO resonances.) From initial line broadening of the basal CO resonances in B (at ca. −80 °C) a rough rate constant for the B → A change (k_{-1}) is calculated to be ca. 25 s^{-1} at −80 °C ($\Delta G^{\ddagger} \simeq$ 9.9 kcal/mol) by using the slow exchange approximation ($k = \pi\Delta\nu$). This value is in sufficiently good agreement with k_{-1} = 12.6 s^{-1} (−89 °C, $\Delta G^{\ddagger} \simeq$ 9.7 kcal/mol) based on initial broadening of the CH$_3$(B) ^{1}H resonance to conclude that CO averaging and CH$_3$ averaging are both the result of the same process, viz., the 1,2 iron shift in the B $\rightleftharpoons$ A $\rightleftharpoons$ B′ process. CO scrambling in pentadienyl-Fe(CO)$_3^+$ systems, in which fluxionality in the organic moiety is impossible, is a relatively high-energy process, and frequently three sharp CO signals are observed as high as −50 °C for such unsymmetrical systems.[8,11] The facility of the specific CO interchange in the present system is at variance with this general observation and the averaging process is clearly associated with metal migration about the ring (vide infra).

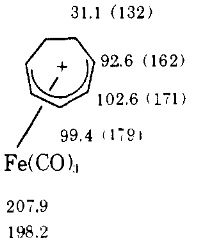
A low-intensity signal at 83.6 ppm is apparent in spectra at −95 to −100 °C and exhibits temperature dependence appropriate for minor isomer A. This signal is assigned to the equivalent 1,5 carbons of A, and the reasonableness of this assignment on chemical shift grounds will be apparent from subsequent discussion. Signals for C$_{2,4}$, C$_3$ (quaternary), and C$_{6,7}$ in A are not observed at −100 °C, but again would be expected to occur in regions dominated by the resonances of B and D (vide infra).

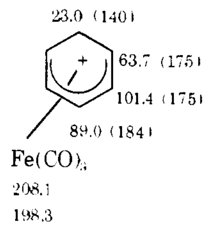
At −65 °C, the B $\rightleftharpoons$ A $\rightleftharpoons$ B′ process is well advanced and ring tertiary carbon resonances for B are now broad and not identifiable. However, as described above, signals for rapidly averaged CH$_3$ and the apical CO in the B $\rightleftharpoons$ A $\rightleftharpoons$ B′ system are observable. A signal at 126.5 ppm (−95 °C) undergoes broadening (−80 °C) and at −65 °C is relatively sharp again. This signal is assigned to the quaternary C$_2$ of B and its intermediate broadening is due to averaging with C$_3$ of A in the B $\rightleftharpoons$ A $\rightleftharpoons$ B′ system. Its unspectacular temperature dependence is due not only to averaging with C$_3$ in the least abundant A, but also because C$_3$ of A is predicted to have a very similar chemical shift (125–127 ppm) on the basis of known α effects of CH$_3$ in pentadienyl-Fe(CO)$_3^+$ systems.[19] However, spectra of the system at −76 to −65 °C are dominated by other resonances excluding those just discussed and associated with the B $\rightleftharpoons$ A $\rightleftharpoons$ B′ system. Prominent sharp resonances at 19.9, 88.6, 90.9, 104.7, 105.6, 107.5, 124.2, and 139.4 ppm are associated with CH$_3$ and ring carbons, and carbonyl resonances were observed at 196.0, 196.3, and 210.5 ppm (note the slightly different δ values at this temperature). These resonances are those of isomer D which on an NMR time scale is just beginning its degenerate interconversion with D′. This behavior leaves the CH$_3$ and quaternary (C$_6$) carbons in unchanged environments, and on warming from ca. −70 to −55 °C the signals at 19.9 and 139.4 ppm remain very sharp. Hence the 139.4-ppm signal is assigned to C$_6$ in D. Of the remaining signals, 124.2 ppm is appropriate for the vinyl carbon (C$_7$) while the groupings (88.6, 90.9) and (104.7, 105.6, and 107.5) are associated with C$_{1,5}$ and C$_{2,3,4}$, respectively, on the basis of data for several pentadienyl-Fe(CO)$_3^+$ ions[8,11,17,19] (see below for specific assignments).

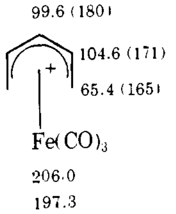
The relatively sharp nature of the signals at −65 °C of D permitted the acquisition of a proton-coupled spectrum (SO$_2$-TFA-CD$_2$Cl$_2$) which provides useful comparisons with other pentadienyl-Fe(CO)$_3^+$ ions. This spectrum confirmed the assignment of C$_6$ (139.4 ppm) in D, as this signal lacks a one-bond proton coupling, but does appear as a doublet ($J \sim$ 8 Hz) due to vicinal coupling to H$_1$. (Coupling to H$_4$ is clearly smaller as expected.) The remaining assigned signals[20a] and their one-bond couplings are shown below and compared with literature data on related ions ($^1J_{\text{C-H}}$ in parentheses).[8,11]

Comparison of these data with those presented for the other systems shows a regular trend in $^1J_{\text{C-H}}$ values for the pentadienyl carbons, in that the central carbon (C$_3$) has the largest value.[8,11] This adds confidence to the chemical shift assignments. It is also apparent there is a close similarity in the NMR data (shifts and J values) for the pentadienyl fragment of D and C$_7$H$_9$Fe(CO)$_3^+$ (lacking the double bond) as well as with the cyclic C$_6$H$_7$Fe(CO)$_3^+$ and the acyclic C$_5$H$_7$Fe-



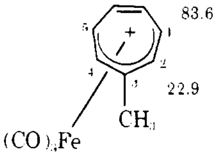




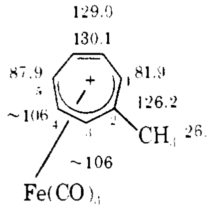


(CO)$_3^+$.[8,11,17] These data allow the conclusion that the pentadienyl-Fe(CO)$_3^+$ systems in these various ions have similar electronic structures, and in D the double bond is not strongly involved. This is consistent with the evidence already presented from ^{1}H coupling that the double bond fragment is tilted significantly from planarity.

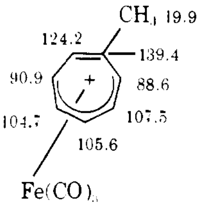
We can now return to the location and assignment of resonances for ion B in the low-temperature spectrum, having "isolated" the resonances for the major ion D. Shifts are shown below for A, B, and D. Distinction between the resonances at 81.9 and 87.9 ppm in B is suggested on the basis that a 2-CH$_3$ group in ions like B can exert a negative β effect.[19] The C$_3$ and C$_4$ resonances for B (given above as ~106 ppm) are largely obscured by the C$_{2,3,4}$ resonances of D and only an approximate value can be cited. For A, positive identification of only the CH$_3$ signal and C$_{1,5}$ (83.6 ppm) is possible.



A



B



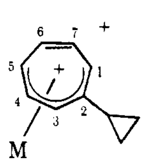
D

Analysis of the higher temperature processes is now given. As pointed out earlier, before either of the B ⇌ A ⇌ B′ or D ⇌ D′ processes is complete, another process sets in. This is evidenced by a broadening above −55 °C of both the CH$_3$ signals (of ca. equal intensity) associated with the above two processes, and coalescence at ca. −5 to 0 °C. The ring carbon resonances are broad and unresolved over this range. Applying the slow exchange approximation and the coalescence formula for broadening of the CH$_3$ signals, rate constants of 30 s^{-1} at −27 °C and 314 s^{-1} at 0 °C (coalescence) can be calculated. These may be compared with 6.3 (−35 °C), 25 (−25 °C), and 231 s^{-1} (−5 °C) calculated from the ^{1}H spectra (see Table I). As the temperature is further raised the averaging signals begin to sharpen (28 °C, k = 2950 s^{-1} using fast exchange formula) and at 45 °C the finally "averaged" spectrum is attained, exhibiting resonances at 23.5, 104.7, 106.8, 109.9, 133.5, and ca. 201 ppm. These changes herald the well-advanced third "averaging" process. These chemical shifts may be compared with the calculated "average" values based on ion populations of D (50%), B (40%), and A (10%). The agreement is satisfactory considering that temperature effects on ion equilibria and solvent effects on shifts have been ignored.

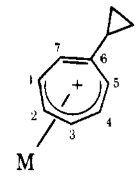
Chart I

cyclopropyltropylium-Fe(CO)$_3^+$

observed ions:



B$_\Delta$ (80%)



D$_\Delta$ (20%)

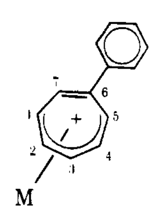
rates and free energies of activation:

$$B_\Delta \underset{k_1}{\overset{k_1}{\rightleftharpoons}} A_\Delta \underset{k_1}{\rightleftharpoons} B'_\Delta$$

k_1 = 12 s^{-1}, −80 °C $\Delta G^{\neq}$ = 10.2 kcal/mol

phenyltropylium-Fe(CO)$_3^+$

observed ion:



D$_\phi$ (>90%, −90 °C)

rates and free energies of activation:

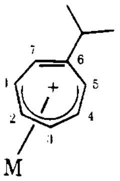
$$D_\phi \overset{k_4}{\rightleftharpoons} D'_\phi$$

$k_4 \simeq$ 10 s^{-1} (−50 °C), $\Delta G^{\neq}$ = 11.8 kcal/mol (from ^{1}H data)

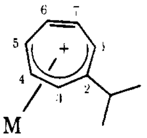
$k_4 \simeq$ 10 s^{-1} (−55 °C), $\Delta G^{\neq}$ = 11.6 kcal/mol (from ^{13}C data)

isopropyltropylium-Fe(CO)$_3^+$

observed ions:



D$_{i\text{-Pr}}$ (85%)



B$_{i\text{-Pr}}$ (15%)

rates and free energies of activation:

$B \underset{k_1}{\overset{k_1}{\rightleftharpoons}} A \rightleftharpoons B'$ k_1 = 14 s^{-1} (−80 °C), $\Delta G^{\neq} \simeq$ 10 kcal/mol

$D \overset{k_4}{\rightleftharpoons} D'$ k_4 = 11 s^{-1} (−60 °C) $\Delta G^{\neq}$ = 11.4 kcal/mol

$$[B, A, B'] \underset{k_{-5}}{\overset{k_5}{\rightleftharpoons}} [D, D']$$

k_5 = 80 s^{-1} (−15 °C), $\Delta G^{\neq}$ = 12.8 kcal/mol

k_{-5} = 20 s^{-1} (−15 °C), $\Delta G^{\neq}$ = 13.5 kcal/mol

Table II. ^1H and ^{13}C NMR Data for Monosubstituted Tropyliumiron Tricarbonyl Cations, $RC_7H_6Fe(CO)_3^+$

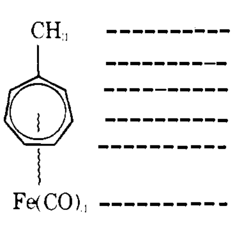
R	isomer	$^1H/^{13}C$ (°C)	positions, shifts[a] 1	5	2	4	3	6	7	other resonances
C_6H_5	D	^1H (−80)	4.98 (br d, 8)	4.98 (br d, 8)	6.23 (t, 7.5)	6.60 (t, 7.5)	8.26 (t, 7)		5.62 (d, 4)	C_6H_5 7.43 (br)
	D	^{13}C (−70)	82.3	84.8	104.7	105.6	107.5	134.7 or 140.7	123.7	C_6H_5 C_{para} 129.2 C_{ortho} 125.7, C_{meta} 129.4, C_{ipso} 134.7 or 140.7 CO's 195.0, 194.6, 208
c-C_3H_5	B	^1H (−75)	4.09 (br, s)	4.74 (br d, 6)		6.00 (t, 6)	7.79 (d, 6)	5.27	5.16	c-C_3H_5 α-H 2.11 β-H's 1.20
		^{13}C (−90)	73.2 (163)	88.0 (164)	135.8	103.9 (171)	101.8 (168)	130.1 (171)		c-C_3H_5 α-C 20.2 (168) β-C's 9.5 (165) 16.9 (165) CO's 195.5, 197.4, 210.4
	D[c]	^1H (−75)	4.70	4.90	6.70 (t, 7)	5.80 (t, 7)	7.51 (t, 6)		*b*	c-C_3H_5[b]
		^{13}C (−90)	*b*	96.4	105.7	102.1	105.8	121.7	*b*	c-C_3H_5 α-C 16.9 β-C's 6.5, 7.9 CO's 196.4, 196.7, 210.6
$CH(CH_3)_2$	D	^1H (−80)	4.70	4.39	5.98	6.23	7.99		4.88	-CH 2.06 CH_3's 0.87, 0.82 (d's, 7)
		^{13}C (−90)	84.1	86.6	106.9	104.1	105.5	150.3	119.8	-CH 31.8 CH_3's 19.1, 19.4 CO's 195.5, 195.2, 209.5
	B	^1H (−80)	*b*	*b*	*b*	*b*	*b*	*b*	*b*	-CH 2.93 -CH_3's 1.53 (d,d −90 °C, coalesces to d −60 °C)
		^{13}C (−80)	*b*	*b*	133.5	*b*	*b*	128.7		-CH 36.4 -CH_3's 22.3

[a] ^1H shifts are in parts per million downfield from Me_4Si relative to internal $CHDCl_2$ taken as δ 5.35. Multiplicities and coupling constants in hertz are shown in parentheses. ^{13}C shifts are in parts per million downfield from Me_4Si relative to internal CD_2Cl_2 taken as 53.6 ppm. Directly bonded ^{13}C–H coupling constants (Hz) are shown in parentheses where observed. [b] Resonances obscured by those of the major isomer. [c] Several ^1H and ^{13}C resonances located by observing spectra at higher temperatures where signals for isomer B are broad due to B ⇌ B′ averaging.

Table III. Isomer Distributions in $RC_7H_6Fe(CO)_3^+$

R[a]	% A	% B	% C	% D
CH_3	~7	~43	n.o.	50
C_6H_5	n.o.	n.o.[b]	n.o.	>95
c-C_3H_5	n.o.	~80	n.o.	~20
$(CH_3)_2CH$	n.o.	~15	n.o.	~85

[a] At −90 to −102 °C. n.o. = not observed. [b] At 40 °C chemical shift averages strongly suggest the presence of small amounts of B.



calcd av	obsd av
22.7	23.5
132.9	133.5
101.4	104.7
105.2	106.8
108.9	109.9
~200	~201

Phenyl-, Cyclopropyl-, and Isopropyltropylium-$Fe(CO)_3^+$ Systems. A similarly detailed ^1H and ^{13}C analysis of the phenyl, cyclopropyl, and isopropyl substituted systems has been carried out. The detailed arguments for isomer and chemical shift assignments, and rate analyses as well as selected spectra (^{13}C (−70 °C) and variable-temperature ^1H (−70 to 45 °C) spectra of phenyltropylium-$Fe(CO)_3^+$ and ^{13}C (−90 °C) spectra of the cyclopropyl and isopropyl substituted ions) are available as supplementary material. A summary of the resultant data is presented in Chart I and Table II.

Summary

The substituent site preferences in $RC_7H_6Fe(CO)_3^+$ for various R groups among the ions A–D are summarized in Table III.

Table IV. Free Energies of Activation[a] for Isomer Interconversion of Substituted Tropyliumiron Tricarbonyl Complexes, $RC_7H_6Fe(CO)_3^+$

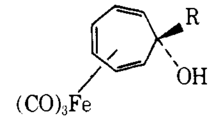
process	substituent CH_3	C_6H_5	-C_3H_5	*i*-C_3H_7
A → B (or B′)	9.1			
B (or B′) → A	9.7		10.2	9.7
D ⇌ D′	11.5	11.8		11.4
[D,D′] → [B,A,B′]	12.7			13.5
[B,A,B′] → [D,D′]	12.7			12.8

[a] All values in kcal/mol.

The clear trends that emerge are (1) for the four cases investigated ions B and D together constitute >90% of the isomer population for each R group; (2) ion A was observed only in the CH_3 case and then in low relative abundance; (3) ion C was not observed in any case.

In the CH_3 case it is remarkable that the energy differences between the ions are such that observation of three of the four ions is possible. The free-energy difference between A and B (−102 °C) is only ca. 0.23 kcal/mol while between A and D it is 0.26 kcal/mol, after correction for the statistical factor. The features responsible for such small energy differences must be discussed with caution, but focusing on the ions in which the pentadienyl unit is substituted, there is a definite preference for B followed by A, in line with the charge densities calculated for pentadienyl-$Fe(CO)_3^+$ outlined in the introduction. If methyl site preferences are determined in large part by charge densities, it appears that charge disparity between sites 2 and 3 is not large. This again is consistent with calculations by

Table V. Spectroscopic Data for $RC_7H_6OH\text{-}Fe(CO)_3$ Complexes[a]



R =	position 1	2	3	4	5	6	7	other
CH_3 (^1H)	3.46 (d)	5.48 (m)		3.07 (t)	5.85 (dd)	5.20 (dd)		1.42 (CH_3) 1.85 (OH)
(^{13}C)	72.6	83.7	94.9	54.1	127.5,	132.3	68.6	32.4 (CH_3), 210.4 (CO's)
C_6H_5 (^1H)	3.44 (d)	5.23, (m)	5.59 (m)	3.12 (br, t)	6.05 (dd)	5.23 (dd)		7.31 (Ar) 2.13 (OH)
(^{13}C)	73.2	83.7,	94.6	54.0	128.9,	131.3	73.1	124.8 (O) 128.4 (m) 127.1 (p) 147.2 (ipso) 210.2 (CO's)
c-C_3H_5 (^1H)	3.43 (dt)	5.47 (m)		3.00 (t)	5.88 (dd)	4.97 (dd)		0.38 (m) (β-H) 0.88 (m) (α-H) 1.57 (OH)
(^{13}C)	71.6	83.8,	94.4	54.0	129.30,	129.38	70.1	24.2 (α-C) 1.5, 1.7 (β-C) 210.5 (CO's)
i-C_3H_7 (^1H)	3.16 (dd)	5.50 (m)		2.93 (t)	5.90 (dd)	5.04 (dd)		0.96 (d, 7 5 Hz, CH_3) 0.83 (d, 7.5 Hz, CH_3) 1.80 (m, CH) 1.73 (OH)
(^{13}C)	67.8	85.1,	93.4	54.3	129.6,	130.7	74.2	17.0, 18.0 (CH_3's) 39.1 (CH) 210.6 (CO's)

[a] ^1H and ^{13}C spectra at 100 and 25.2 MHz, respectively, for $CDCl_3$ solutions referenced to Me_4Si or $CHCl_3$ (7.27). Signal patterns and coupling constants for ring protons were very similar for all alcohols. Careful determination for the methyl system yielded $J_{1,6} = 1.1$, $J_{5,6} = 10.5$, $J_{3,4} = 8.5$, $J_{4,5} = 8.5$, and $J_{1,2} = 8.2$Hz. The infrared spectra of all alcohols were quite similar and showed two strong CO bands at 1986 ± 3 (br) and 2048 ± 4 cm^{-1} (sharp).

Hoffmann[7] and Lillya[8] which indicate that charge density on the iron tricarbonyl moiety may be substantial.

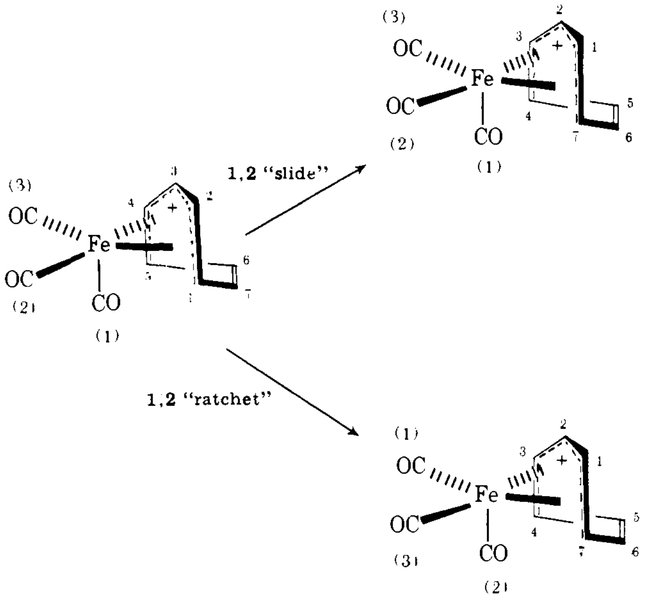
The phenyl and cyclopropyl cases represent an interesting contrast. Provided that the proper geometry can be attained, both substituents are very efficient at stabilizing positive charge, yet for the phenyl case ion D is highly favored while for cyclopropyl ion B is preferred (Table III). This again is consistent with weak positive character at C_2 and suggests that steric factors can markedly affect the B/D equilibrium ratio. However, it should be noted that chemical-shift comparisons for the B and D cyclopropyl ions show greater downfield shifts of the cyclopropyl resonances in B_Δ relatively to D_Δ. In the isopropyl system the equilibrium shifts to more strongly favor ion D relative to the methyl system. The larger steric requirement of isopropyl relative to methyl is presumably the important factor.

The above results suggest relatively little charge on the ring carbons and a fine balance of the electronic and steric factors of the substituents in determining the B:D ion distribution. The nonobservance of ion C would seem to be largely determined by electronic effects. More detailed discussion should await calculations on $C_7H_7Fe(CO)_3^+$ itself, and the availability of data for smaller but better cation-stabilizing substituents such as halogens or methoxy. Such data is being obtained. It would be equally useful to know substituent site preferences in the isoelectronic (neutral) $RC_7H_6Mn(CO)_3$ system, and work in this direction is beginning.

Although the fluxional behavior of many π-bound MC_nH_n systems has been examined and 1,2 shifts have been established,[1] there are several interesting aspects in this work. These concern the relative energetics of the $B \rightleftharpoons A \rightleftharpoons B'$, $D \rightleftharpoons D'$, and $[B, A, B'] \rightleftharpoons [D, D']$ interconversions summarized in Table IV. The free energy of activation for these processes must be associated with the necessary flattening of the ring for π-bound relocation as well as the 1,2 iron shift. The generally more facile $B \rightleftharpoons A \rightleftharpoons B'$ processes compared to $D \rightleftharpoons D'$ seems best explained by examining the ring-flattening component. For the D, D′ ions, flattening involves increased eclipsing R,H_5 interactions, whereas for the B, A, B′ ions the analogous interactions are vinylic H, H_1, which would be less severe. For the highest energy interconversion, $[D \rightleftharpoons D'] \rightleftharpoons [B \rightleftharpoons A \rightleftharpoons B']$, ion C is a necessary intermediate on the basis of 1,2 iron shifts. Since ion C is never observed and is therefore the highest energy isomer, this accounts for the greater activation energy for this process.

Energy comparisons for rearrangement in $C_7H_7Fe(CO)_3^+$ and $C_7H_7Mn(CO)_3$ are available, being $\Delta G^{\ddagger} \sim 11$ and 15 kcal/mol, respectively.[13] Whitesides and Budwick have associated this difference with the degree of back-bonding in the two cases, and a possible result was that the C_7 ring was more like a tropylium ion in the Fe case, but more like a cycloheptatrienyl anion in the Mn case.[13] Conclusions of this type would seem to have significant implications for relative substituent site preferences in the two systems, and are currently being explored.

A further interesting point concerning the fluxional behavior of the $RC_7H_6Fe(CO)_3^+$ systems is that, from analysis of the temperature dependence of the CO resonances, a detailed picture of the motion of the $Fe(CO)_3$ fragment around the C_7 ring is obtained. In the $B_R \rightleftharpoons A_R \rightleftharpoons B'_R$ process for R = CH_3 and c-C_3H_5 and in the $D_R \rightleftharpoons D'_R$ process for R = CH_3, Ph, and *i*-Pr the two nonequivalent basal CO signals average at the appropriate rates with each other but *not* with the apical CO signal, which remains sharp. These observations require that the $Fe(CO)_3^+$ fragment move around the C_7 ring with a "sliding" motion which maintains the identity of the apical



CO's and not with a rotating or "ratchet-type" motion which moves an apical CO to a basal position. Although all CO signals eventually average at higher temperatures,[8] this scrambling process is clearly not coupled with metal migration around the ring.

Experimental Section

Compounds. The alcohol precursors of the ions were synthesized by treating troponeiron tricarbonyl with an excess of the alkylating reagent at low temperature (−79 → −40 °C) followed by aqueous quenching and ether extraction. Generally the crude alcohol was chromatographed directly on basic alumina (activity III) eluting with pentane, or crystallized from pentane. The following procedure is illustrative.

7-Methyl-7-hydroxycycloheptatrieneiron Tricarbonyl. To a flame-dried three-necked 200-mL flask equipped with a N_2 inlet tube, magnetic stirring bar, and septum were added 100 mL of anhydrous degassed diethyl ether and 250 mg (1 mmol) of troponeiron tricarbonyl. The flask was cooled (−78 °C) and 2.5 mL of methyllithium (0.8 mol) was added slowly via syringe. The reaction mixture was stirred at −78 °C for 45 min and then quenched with an H_2O/ether/THF mixture. The reaction mixture was diluted with hexane and water, and the organic layer was separated, dried with Na_2SO_4, and concentrated (reduced pressure). The oily residue was diluted (degassed hexane) and filtered through glass wool. Cooling the hexane solution (0 °C) provided 210 mg of pale-yellow crystals of the title compound.

The alcohols were characterized by their 100-MHz ^1H, proton-decoupled ^{13}C, and IR spectra in the carbonyl region. These data are assembled in Table V.

The phenyl derivative, $C_{16}H_{12}O_4Fe$, was obtained as a solid and C, H analysis conducted. Anal. Calcd for $C_{16}H_{12}O_4Fe$: C, 59.25; H, 3.70. Found: C, 59.12; H, 3.93.

Preparation of Ions. The general procedure used was addition of a degassed CD_2Cl_2 solution of the alcohol to a degassed trifluoroacetic acid-solvent solution at −78 or 0 °C in a 5- or 10-mm NMR tube adapted for attachment to a vacuum line and/or manipulation under a N_2 atmosphere. The solutions were mixed (under N_2) with a long glass rod, and rose on burgundy solutions of the ions resulted. The tubes were then frozen, evacuated, and sealed at liquid N_2 temperatures. The solutions of ions generally exhibited good stability when kept for prolonged periods at −78 °C. Ions could also be formed with FSO_3H, but the samples were less stable, particularly at higher temperatures.

The particular solvents used and the respective temperature ranges of observation follow: TFA/SO_2F_2 (1:10, v:v), −135 to −105 °C; TFA/SO_2/SO_2F_2 (1:3:4, v:v) −105 to −75 °C; TFA/SO_2 (1:4, v:v) −65° to −5 °C; neat TFA, 0 to 50 °C.

All solutions were handled under a dry N_2 atmosphere.

All ^1H and ^{13}C spectra were recorded on a Varian XL-100 NMR spectrometer. CD_2Cl_2 provided the ^2H lock and served as secondary reference (53.6 and 5.35 ppm for ^{13}C and ^1H, respectively).

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Supplementary Material Available: A detailed analysis of the ^1H and ^{13}C NMR spectra of the phenyl-, isopropyl-, and cyclopropyltropylium-Fe$(CO)_3^+$ systems (including figures of spectra) (17 pages). Ordering information is given on any current masthead page.

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(14) Irradiation at δ 7.93 reduces the δ 6.36 and 5.91 signals to doublets; irradiation of δ 6.36 reduces δ 7.95 to a doublet and δ 4.46 to a singlet while irradiation at δ 5.91 reduces the signals at δ 7.93 and 4.70 to doublets. Irradiation at δ 4.70 collapses the signal at δ 5.91 to a doublet. Coupling constants determined from these double resonance experiments are summarized in the table and are consistent with previous data. An interesting result is the small value $^3J_{H_1-H_7}$ (4.2 Hz) for the vicinal coupling, and this is indicative of an increased H_1–H_7 dihedral angle, as required by a displacement of the ene fragment from the pentadienyl plane.
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(18) See ref 7 for a summary of structural information. In particular see P. M. Harrison, Ph.D. Thesis, University of Sheffield, 1968, as cited by R. Mason in XXIIIrd International Congress of Pure and Applied Chemistry, Boston, Mass., 1971, Special Lectures, Vol. 6, 1971, p 31. As regards structures A, B, and D notice that a 180° rotation of the basic C_7H_7 fragment with respect to the Fe$(CO)_3$ system does not alter any of the conclusions that follow.
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(20) (a) Some explanation of the specific assignments given for the pentadienyl (teritary) carbon resonances is required. Distinction between the 88.6- and 90.9-ppm resonances is based on considerations of long-range (vicinal) proton couplings and the anticipated effect on the major "doublet" appearance. Clearly C_5 is expected to experience vicinal couplings to H_7 and H_3 of substantial magnitude (both in planar fragments) as well as coupling to the methyl protons. On the other hand, C_1 would couple only with H_3, and hence the doublet pattern should be sharper. On this basis, the 88.6-ppm signal is assigned to C_5. (Recent careful studies[2D] on planar conjugated systems have provided the following J_{C-H} values: C_6H_6, $^1J = 158.7$, $^2J = 1.11$, $^3J = 7.58$; $C_7H_7^+$, $^1J = 166.79$; $^2J = 0$, $^3J = 9.99$ Hz.) Both show geminal (i.e., $^2J_{C-H}$) coupling to be much smaller than vicinal coupling ($^3J_{C-H}$). The signals clustered at 104.7, 105.6, and 107.5 ppm associated with $C_{2,3,4}$ were assigned as follows. Each component of the doublet at 105.6 ppm with separation 176 Hz ($^1J_{C-H}$) appeared as a reasonably well-resolved triplet ($J \sim 8$ Hz) appropriate for C_3, which would experience vicinal coupling to $H_{1,5}$. The doublet patterns for C_2 and C_4, each of which would experience only one strong vicinal coupling, should

be narrower and this is observed. (C_2 could experience coupling to H_7, but, in view of the bending away of the uncomplexed double bond, the coupling is expected to be reduced in comparison with coupling in a planar fragment). Distinction between C_2 and C_4 was made on the basis of higher temperature spectra. The $D \rightleftharpoons D'$ (degenerate) process exchanges C_3 with C_2 and spectra at −50 and −35 °C show that the 105.6-ppm signal (C_3) averages with the 104.7-ppm signal and not the remaining 107.5-ppm signal. Hence C_2 is at 104.7 ppm. (The averaged signal emerges quite quickly as the chemical shift separation is only ~1 ppm.) (b) H. Gunther, H. Seel, and M. E. Gunther, *Org. Magn. Reson.*, 11, 97 (1978).

Hexakis(pyridine)ruthenium(II) Tetrafluoroborate. Molecular Structure and Spectroscopic Properties

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Abstract: Hexakis(pyridine)ruthenium(II) tetrafluoroborate has been prepared by extended reflux of a methanol solution of $[RuHS_3(PPh_3)_2][BF_4]$ (S = CH_3OH or H_2O) and pyridine. Spectroscopic and electrochemical characterizations of this complex are reported. The observed ^1H and ^{13}C chemical shift values are discussed in terms of previous reports concerning NMR properties of complexed pyridine. A comparison of ruthenium-nitrogen force constants for pyridine and ammine ligands is based upon far-infrared vibrational data. Rationalization of the larger force constant evident in the case of pyridine is presented in terms of both σ and π interactions in the case of this unsaturated heterocyclic ligand. Assignment of a metal-to-ligand charge transfer band at 341 nm, in conjunction with electrochemical reduction potentials, provides data for a general qualitative molecular orbital scheme for a series of $[Ru(py)_n(NH_3)_{6-n}]^{2+}$ complexes (n = 6, 2, 1, 0). The electrochemistry of $[Ru(py)_6]^{2+}$ is virtually indistinguishable from that of the $[Ru(bpy)_3]^{2+}$ ion. Crystals of $[Ru(py)_6][BF_4]_2$ were found to be orthorhombic, space group $Pna2_1$, with a unit cell of dimensions a = 16.933 (27), b = 10.431 (7), and c = 18.197 (14) Å. The observed density is 1.54(2) g cm^{-3} while a density of 1.536 g cm^{-3} is calculated for $Z = 4$. The structure was refined to $R = 0.063$ and $R_w = 0.075$ using 2142 reflections with $I \geq 3\sigma(I)$. The $Ru(py)_6^{2+}$ cation exhibits Ru–N bond lengths in the range from 2.10 (1) to 2.14 (1) Å with an average length of 2.12 Å for the six metal-ligand bonds. The rotational orientation of the six planar ligands is such that the isolated cation belongs to the C_1 point group, i.e., there is clearly no symmetry operation present other than the identity itself.

Introduction

An extensive chemistry of ruthenium(II) complexes containing nitrogen donor ligands has been realized during the past decade.[1] The range of chemical properties accessible to such complexes is evident in the diverse properties of the two cationic derivatives $Ru(NH_3)_6^{2+}$ and $Ru(bpy)_3^{2+}$.

Hexaammineruthenium(II) is a classical octahedral coordination complex[2] containing six σ-only ammine ligands. One exceptional feature of this unit is the variety of reactions which form $Ru(NH_3)_5L^{2+}$ complexes[3] (where L is a π-acceptor ligand such as N_2, CO, RCN, etc.). This reactivity pattern implicates the $Ru(NH_3)_5^{2+}$ $(d\pi)^6$ fragment as a unit capable of extensive π donation to acceptor ligands. Such a conclusion is consistent with expectations for a low-spin d^6 system which has the optimal number of d electrons for bonding interactions with empty ligand π orbitals. Furthermore, the $Ru(NH_3)_5^{2+}$ moiety has no pathway available for the transfer of electron density from the metal to the five ammine ligands which are devoid of empty π-type orbitals, leaving only L as a $d\pi$ electron sink. Since effective electronegativity increases with an increase in oxidation state of the metal, the relatively low 2+ oxidation state of ruthenium (as compared to other common d^6 ions such as Co^{3+} and Rh^{3+}) enhances covalent π interactions with appropriate ligand orbitals where the metal furnishes the electron density. Thus the isolation of such noteworthy species as $Ru(NH_3)_5(N_2)^{2+}$ [4] can be rationalized in retrospect.

The tris(bipyridyl)ruthenium(II,III) couple is another octahedral ruthenium system which has attracted widespread attention owing to the unique redox and photochemical properties it displays.[5] The photoredox chemistry of this complex has been the subject of extensive research efforts directed toward the conversion of light into chemical and electrical energy.[6] The lifetime of the photochemical excited state is adequate to allow bimolecular electron transfer processes to occur which utilize the high-energy transient species as a reactant.[7]

Although reports of $M(py)_6^{n+}$ cations abound in the literature,[8] in only a few cases have crystalline solids been structurally characterized in which six pyridines remain bound to one metal ion. One study which confirmed the existence of $M(py)_6^{n+}$ in the solid state was reported for the Fe(II) cation.[9] The high-spin d^6 iron dication in the $[Fe(py)_6][Fe_4(CO)_{13}]$ structure conforms to T_h molecular symmetry as appropriate to minimize steric repulsions among the six ligands. Doedens and Dahl concluded that in the absence of distortional forces (such as hydrogen bonding or Jahn–Teller degeneracies) a transition metal bound to six identical C_{2v} ligands would presumably exist in the T_h molecular form.

In view of the current interest in the chemistry of octahedral ruthenium(II,III) complexes with nitrogen donor ligands we have synthesized $[Ru(py)_6][BF_4]_2$ and now report the molecular structure as determined by X-ray crystallographic techniques as well as other relevant spectroscopic data.

Although similar values of $10Dq$ characterize py and NH_3 as evidenced by their approximate equivalence in the spectrochemical series,[10] the metal–ligand interactions which produce these roughly equivalent d-orbital splittings are quite different for the two nitrogenous nucleophiles. The presence of vacant pyridine π^* molecular orbitals provides a potential pathway for π back-bonding from ruthenium(II) to the ligands in the hexakis(pyridine)ruthenium(II) complex. Thus, in spite of the similar distribution of six monodentate nitrogen donor

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