new signal appeared, which consisted of seven equally spaced lines with binomial intensities. The splitting is evidently due to fluorine hyperfine interaction in the ferrihexafluoride ion $(FeF_6)^{3-}$. Evidence for this complex in aqueous solutions was previously obtained from solvent extraction[5] data. Our esr results substantiate this evidence and provide a more direct means for a quantitative study of its properties.

Typical spectra, recorded at room temperature, corresponding to solutions containing 0.04 M $Fe(ClO_4)_3$ and varying amounts of NH_4F are shown in Figure 1. By comparison with simulated spectra the fluorine hyperfine splitting was found to be 23.0 G. This is very close to the fluorine isotropic hyperfine interaction in $(FeF_6)^{3-}$ observed[6] in the solids $KMgF_3$ (25.7 G) and $KCdF_3$ (24.3 G). No satellites due to ^{57}Fe were observed. The line width (peak-to-peak separation of the derivative curve) of a single hyperfine component was about 11 G and the g value was 2.0036. The esr spectra of $(FeF_6)^{3-}$ were sensitive to pH: at high NH_4F concentration (pH 8–9), well-resolved lines were observed, but when the pH was less than 5 the $(FeF_6)^{3-}$ resonance disappeared.

The spin Hamiltonian for the Fe^{3+} sextet in a nearly octathedral field is[7] (assuming only a small tetragonal distortion)

$$\mathcal{H} = g\beta HS + D\left(S_z^2 - \frac{35}{12}\right) + \frac{1}{6}a\left(S_x^4 + S_y^4 + S_z^4 - \frac{707}{16}\right)$$

In solutions the first term gives the position of the esr line which is normally close to that of the free electron, while the last two terms determine the line width. McGarvey[1] has shown that for Fe^{3+} the quartic term, a, contributes very little to the electronic relaxation, and the main effect on the line width arises from the modulation of the zero-field splitting parameter D. The relatively small line width observed in $(FeF_6)^{3-}$ is of the same order as that often found in Mn^{2+} complexes.[4,8,9] For the latter case it was proposed[10] that the electronic relaxation occurs by distortion of the symmetric structure of the complex *via* collisions with other molecules. If the same mechanism is also dominant in $(FeF_6)^{3-}$, an upper limit for the root-mean-square fluctuation of the zero-field parameter, D, may be calculated from the equation[4]

$$1/T_2 = 6.4D^2\tau$$

where T_2 is the transverse electronic relaxation time and τ is the mean lifetime between collisions ($\sim 2 \times 10^{-12}$ sec).[10] Substituting the experimental value for $1/T_2$ gives $\sqrt{\overline{D^2}} = 0.02\ \text{cm}^{-1}$.

The large width of the esr resonance of Fe^{3+} hydrate is partly due to dimerization[11] but may also be caused by large deviations from cubic symmetry of the monomeric species. This will result in a significant static zero-field splitting interaction which provides an effective relaxation mechanism.[1] This deformation can be caused by the formation of both inner- and outer-sphere ion-pair complexes or by the acid dissociation of the hydrate, thus forming species of the type $[Fe(OH)(H_2O)_5]^{2+}$. All three possibilities are quite likely for the Fe^{3+} hydrate. The situation with $(FeF_6)^{3-}$ is, however, quite different; here there is no strong tendency to complex with other ions, and the geometry of the complex is more symmetric and can better resist deformation by collisions with neighboring molecules. It is quite likely that other Fe^{3+} complexes having high symmetry and tightly bound ligands will also exhibit narrow esr lines in solutions.

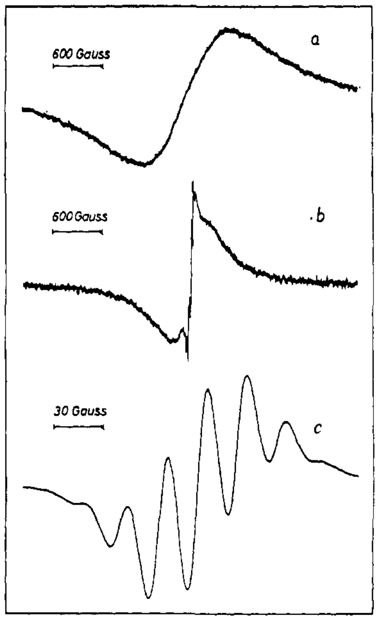

Figure 1. Fe^{3+} esr spectra in aqueous solutions. Spectrum a is for a 0.04 M $Fe(ClO_4)_3$ solution. Spectra b and c are for solutions containing the same amounts of $Fe(ClO_4)_3$ as in solution a and 0.36 and 2.0 M NH_4F, respectively. Note the different sweep width of spectrum c; at a greater sweep width of this spectrum no broad line signal was observed.

H. Levanon, G. Stein
Physical Chemistry Department, The Hebrew University
Jerusalem, Israel

Z. Luz
The Weizmann Institute of Science
Rehovot, Israel

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Mechanism of the Intramolecular Reorientation Process in σ-Cyclopentadienylmetal Complexes

Sir:

The facile rearrangement of metal–carbon bonds in σ-cyclopentadienylmetal complexes, which manifests intself in the nmr equivalence of cyclopentadienyl protons in these substances, has heretofore been regarded as proceeding through either a dipolar metal–

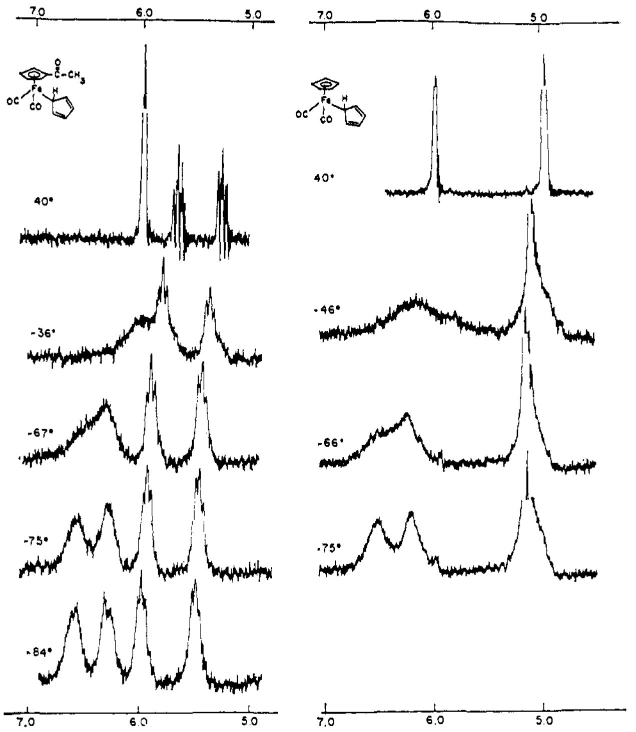
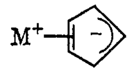


Figure 1. Nmr spectra of $(\pi\text{-}CH_3COC_5H_4)Fe(CO)_2(\sigma\text{-}C_5H_5)$ and $(\pi\text{-}C_5H_5)Fe(CO)_2(\sigma\text{-}C_5H_5)$ taken in CD_3COCD_3 solution at 60 Mc (scale in τ).

olefin complex transition state or intermediate (**1**)[1,2] or a partially dissociated polar state (**2**).[3]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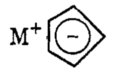
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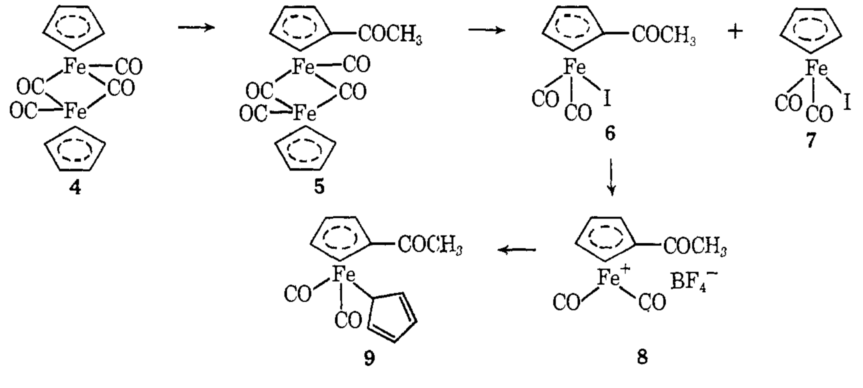
The process of proton averaging in $(\pi\text{-}C_5H_5)Fe(CO)_2(\sigma\text{-}C_5H_5)$ and in $(\pi\text{-}C_5H_5)Cr(NO)_2(\sigma\text{-}C_5H_5)$ has recently been shown to involve a series of rapid 1,2 shifts of the metal–carbon bond,[1,2] but a 1,3-shift mechanism has tentatively been advanced to account for the time-average equivalence of cyclopentadienyl protons in $(\sigma\text{-}C_5H_5)CuP(C_2H_5)_3$.[3] We now show that the transition state for the rearrangement of $(\pi\text{-}C_5H_5)Fe(CO_2)_2(\sigma\text{-}C_5H_5)$ (**3**) is essentially nonpolar and suggest that the rapid migration of metal–carbon bonds in σ-cyclopentadienylmetal complexes must in general take place by a series of 1,2 shifts which are more properly regarded as degenerate [1.5] sigmatropic rearrangements.[4]

It is well established that the oxidation potential associated with reversible electron transfer from the metal atom in ferrocenes is strongly dependent on the nature and number of ring substituents.[5] For example, the oxidation potential of acetylferrocene lies 0.25 V above that of the parent compound,[6] corresponding to an increase in the free-energy change for electron removal of almost 6 kcal/mol. These observations prompted us to examine the effect of acyl substitution of the π-cyclopentadienyl ring on the rearrangement of the σ-cyclopentadienyl ring since such substitution would be expected to render a dipolar transition state such as **1** or **2** less accessible, and hence retard the rearrangement of the σ-cyclopentadienyl ring.[7]

Acylation of $[\pi\text{-}C_5H_5Fe(CO)_2]_2$ (**4**) with boron trifluoride and acetic anhydride yielded the monoacyl derivative **5**, as purple crystals, mp 150° dec; ir (KBr) 2000, 1950, 1700, and 1680 cm^{-1}; nmr ($CDCl_3$) τ 7.47 (S, 3), 5.15 (S + t, 7), 4.81 (t, 2, J = 2 Hz). *Anal.* Calcd for $C_{16}H_{12}Fe_2O_5$: C, 48.48; H, 3.03. Found: C, 48.14; H, 3.11. Brief treatment of this substance with iodine in chloroform solution at 25° gave a mixture of the iodo compounds **6** and **7**, which were separated on alumina. Unlike **7**, which is converted to the σ-cyclopentadienyl derivative on treatment with sodium cyclopentadienide, similar treatment of **6** failed to produce any well-defined product. When, however, the iodo compound **6** was converted to the cation **8** by treatment with 1 equiv of silver trifluoroacetate, and this was immediately quenched with cyclopentadienide, the desired σ-cyclopentadienyl derivative **9** was obtained as yellow crystals: mp 110°; ir (KBr) 2020, 1955, 1920, 1665 cm^{-1}; nmr ($CDCl_3$, 30°) τ 7.65 (s, 3), 5.24 (t, 2, J = 2 Hz), 4.83 (t, 2, J = 2 Hz), 4.08 (s, 5). *Anal.* Calcd for $C_{14}H_{12}FeO_3$: C, 59.15; H, 4.22. Found: C, 59.18; H, 4.41.



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The nmr spectra of **3** and its acetyl derivative **9**, taken at several temperatures, are shown in Figure 1. A comparison of the spectra fails to reveal any marked difference in the temperature dependence of proton averaging for the three magnetically nonequivalent protons whose chemical shift differences are virtually identical for the two compounds. These results are clearly not in accord with a transition state for bond migration of the form **1** or **2** in which appreciable positive charge is developed on the metal atom. They are, however, consonant with the view that reaction occurs by way of an essentially nonpolar transition state, as has been depicted for sigmatropic rearrangements.[9]

The great facility with which these rearrangements occur, contrasted with the very much higher activation energies associated with [1.5] sigmatropic shifts of C–H bonds in substituted cyclopentadienes,[10] is most reasonably attributed to the relatively low bond energy of the Fe–C bond[11] and possibly as well to the more diffuse character of the metal orbital constituting the metal–carbon bond which would be expected to facilitate its continuous overlap with the cyclopentadienyl π orbitals in the course of the rearrangement.[12,13]

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Benzion Fuchs, Muhammad Ishaq, Myron Rosenblum
Department of Chemistry, Brandeis University
Waltham, Massachusetts 02154

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Formation of an Unstable Dinitrogen Complex of Ruthenium(II)

Sir:

Recently a dinitrogen complex of osmium(II), *cis*-$[Os(NH_3)_4(N_2)_2]Cl_2$, was reported, as was the failure to make an analogous complex of ruthenium(II).[1] We wish to report the formation of unstable $[Ru(en)_2(N_2)_2]^{2+}$ by means of reaction 1. Previous attempts to prepare metal–nitrogen complexes by the reaction of metal–azido compounds with nitrous acid were not successful.[2,3]

$$cis\text{-}[Ru(en)_2N_3N_2]^+ + HNO_2 \xrightarrow[\text{cold}]{} cis\text{-}[Ru(en)_2(N_2)_2]^{2+} + N_2O \quad (1)$$

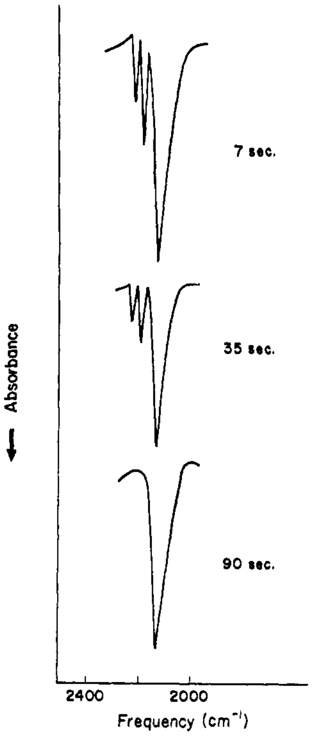

Figure 1. The infrared spectra of samples isolated after various periods from the reaction of nitrous acid on *cis*-$[Ru(N_3)(N_2)en_2]^+$.

Reaction 1 is extremely rapid even at 0°. The immediate (~7 sec) addition of a cold solution of $NaB(C_6H_5)_4$ to the reaction mixture results in the coprecipitation of the salts *cis*-$[Ru(en)_2(N_2)_2][B(C_6H_5)_4]_2$ and *cis*-$[Ru(en)_2H_2O(N_2)][B(C_6H_5)_4]_2$. Figure 1 shows the N–N stretching region of the ir spectra for such mixtures collected at various times. The bands at 2220 and 2190 cm^{-1} are assigned to the *cis*-dinitrogen complex, in accord with the two bands reported[1] for *cis*-$[Os(NH_3)_4(N_2)_2]Cl_2$. Also in agreement with this assignment is the observation that these bands decrease in intensity with increasing isolation time. Furthermore, in the solid state at room temperature the bands gradually disappear in about 30 min. These results show that a metal–nitrogen compound is formed by the reaction of a metal–azido complex with nitrous acid and that the dinitrogen complex *cis*-$[Ru(en)_2(N_2)_2]^{2+}$ is not very stable. If π bonding of the type $Ru \rightleftarrows N{=}\ddot{N}:$ is important in these systems, then it is reasonable that two nitrogens would have to share in such bonding and be held less firmly than in a corresponding system containing only one nitrogen. In agreement with this is the observation that the N–N stretching frequencies are higher for the dinitrogen complex *cis*-$[Ru(en)_2(N_2)_2]^{2+}$ (2220 and 2190 cm^{-1}) than for the mononitrogen cation *cis*-$[Ru(en)_2H_2ON_2]^{2+}$ (2130 cm^{-1}). Likewise the latter

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