The calculated k values should be meaningful when compared with each other, even if they are not meaningful in the absolute sense. From the calculated values for k, the rate of electron hopping between ferrocenyl and ferricenium groups is slower in Fc^+-Fc-Fc^+ than in Fc^+-Fc mainly because of the energetically different chemical sites in Fc^+-Fc-Fc^+. The rate differences involved are small, but worth noting, since they indicate that in ligand-bridged complexes where there are weak metal–metal interactions, rates of intramolecular electron transfer can be varied systematically by changing the chemical environments of the constituent ions.

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Registry No. Fc, 102-54-5; Fc-Fc, 1287-38-3; Fc-Fc-Fc, 1273-59-2; Fc-Fc-Fc-Fc, 1299-15-6; $(Fc)^+$, 12125-80-3; $(Fc\text{-}Fc)^+$, 51263-10-6; $(Fc\text{-}Fc\text{-}Fc)^+$, 53730-59-9; $(Fc\text{-}Fc\text{-}Fc)^{2+}$, 53730-60-2; $(Fc\text{-}Fc\text{-}Fc\text{-}Fc)^{2+}$, 53730-61-3.

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(30) In the calculations the sites of oxidation in the 1,1'-polyferrocene ions are specified since for the mixed-valence 1,1'-polyferrocene ions, more than one isomer can exist. The isomers differ with regard to the site(s) of oxidation, *e.g.*, Fc^+-Fc-Fc and Fc-Fc^+-Fc, and therefore may differ in free energy. If there are two isomers and they differ in free energy by 1 kcal or more, the experimental $E_{1/2}$ value measures essentially the half-cell potential for the reaction involving the isomer of lower free energy content. As a consequence, calculations such as those shown in Scheme I are expected to agree with $E_{1/2}$ only if (1) the isomers used are of lowest free energy or (2) the isomers used are one of a series of isomers differing only slightly in free energy content.
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Localized Scrambling of Carbonyl Ligands in Compounds with Metal-to-Metal Bonds

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We report the results of ^{13}C nmr investigations of (acenaphthylene)$Fe_2(CO)_5$ (**1**) and (cycloheptatriene)$Fe_2(CO)_6$ (**2**). In **1**, which has $Fe(CO)_2$ and $Fe(CO)_3$ groups connected by an Fe–Fe bond, the CO groups of $Fe(CO)_3$ scramble among themselves but do not exchange with those on the $Fe(CO)_2$ group, thus proving that the localized process is important in compounds with $Fe(CO)_3$–Fe type groups. In **2** scrambling also occurs, and, because of the very long Fe–Fe distance (2.87 Å), which would destabilize a bridged intermediate, it is believed that this system provides another example of localized scrambling within an (allyl)$Fe(CO)_3$–Fe type unit.

Introduction

It is now well established that in many binuclear,[1–9] trinuclear,[2,10] and tetranuclear[11–13] metal carbonyl compounds, carbonyl groups are scrambled by processes which involve their passage from one metal atom to another. In these processes they pass from bridging to terminal positions, and *vice versa*. It has also been shown that in some mononuclear organocarbonyl species which have nonequivalent CO groups within $M(CO)_3$ sets, rapid site exchange occurs by some process which is indistinguishable from and may well be the same in actuality

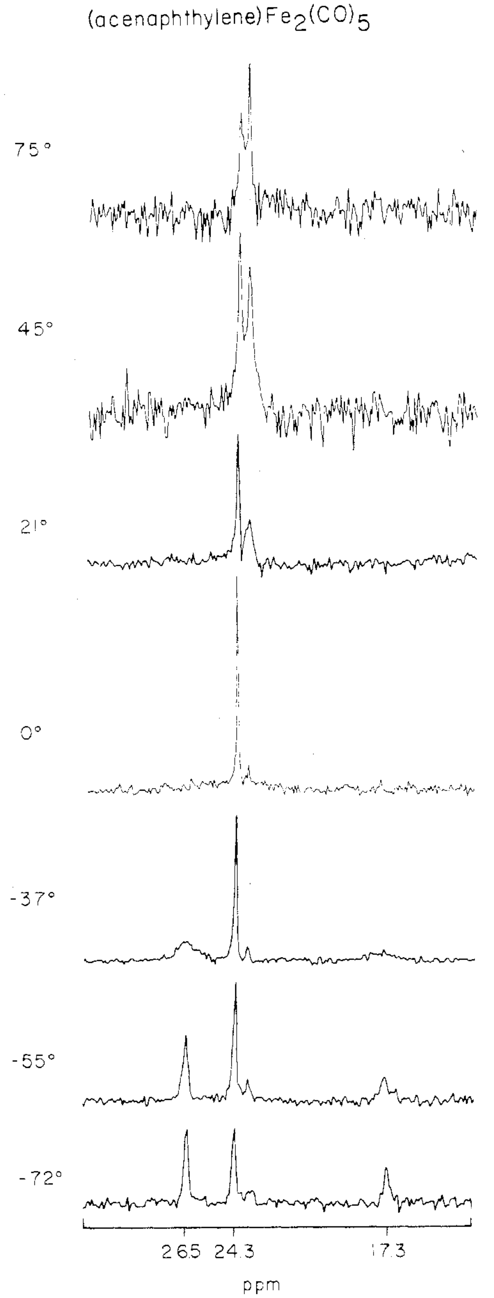


Figure 1. The ^{13}C nmr spectra of (acenaphthylene)$Fe_2(CO)_5$ in the CO region, at various temperatures. Those at 21° and below were recorded in Et_2O-CD_2Cl_2 (deuterium lock) and those above 21° in 2-methyltetrahydrofuran using an external lock. CS_2 was added as a chemical shift reference in each case.

as rotation of the set of CO groups about a quasi-threefold axis.[14-19]

We now wish to report some observations on two molecules which contain $(OC)_2Fe$–$Fe(CO)_3$ and $(OC)_3Fe$–$Fe(CO)_3$ groups bound to cyclic polyolefins. In these, namely, (acenaphthylene)$Fe_2(CO)_5$, **1**, and $(C_7H_8)Fe_2(CO)_6$, **2**, carbonyl scrambling occurs, even though there is no other fluxional process (*e.g.*, "ring whizzing") observed at any temperature. In **1** it is certain that only localized exchange in the $Fe(CO)_3$ set, equivalent to internal rotation of the $Fe(CO)_3$ set, takes place. In **2**, this is considered probable but has not yet been proved, since the form of labeling required to do so has not yet been accomplished.

Experimental Section

The compounds were prepared by methods described previously.[20,21]

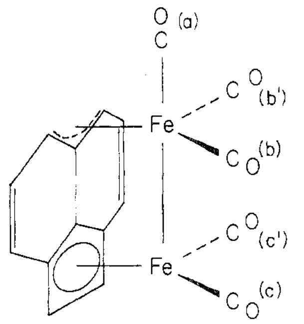
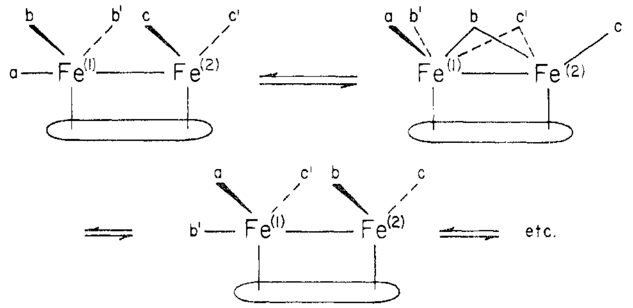


Figure 2. A diagrammatic, perspective view of the structure of (acenaphthylene)$Fe_2(CO)_5$, as reported by Churchill and Wormald.[22]

Scheme I



Molecule **1** was enriched to 10% by starting with enriched $Fe_3(CO)_{12}$ which was prepared by stirring $Fe_3(CO)_{12}$ in benzene under a ^{13}CO atmosphere for 24 hr. Solvents were dried over Na-K benzophenone and distilled just prior to use. Samples were always maintained in a nitrogen atmosphere.

Instrumental Measurements. The carbon-13 variable-temperature nmr spectra were recorded on a Jeol PFT-100/Nicolet 1080 Fourier transform spectrometer at 25.037 MHz. The solvents were freeze–thaw degassed and transferred to 10-mm diameter serum stoppered nmr tubes with a syringe. The temperature was set using a thermocouple placed inside an nmr tube in the probe and read on a Leeds and Northup Model 913 digital thermometer. The temperature was constant to ±2°. To accelerate longitudinal relaxation of the carbonyls,[2] 35 mg of $Cr(acac)_3$ was added to each tube. Solubility limited the sample concentrations to about 0.1 *M*.

Results and Discussion

Compound 1. The spectra obtained at various temperatures for the acenaphthylene complex, **1**, are shown in Figure 1. The structure of this compound has been shown to be that indicated in Figure 2 by X-ray crystallography,[22] with an unusually long Fe–Fe bond, 2.77 Å. For this structure, there are three nonequivalent types of CO groups, as indicated in Figure 2, in 1:2:2 ratio. The ^{13}C nmr spectrum below −60° is clearly in accord with this structure. As the temperature is raised, one of the signals remains unchanged, but the others, including the one of relative intensity 1, broaden and eventually coalesce into one signal of relative intensity 3 which then becomes sharp as the temperature is further raised.

There would appear to be only one acceptable explanation for these observations. The three CO groups, CO(a), CO(b), and CO(b'), on iron atom 1 are scrambling among themselves, while those on iron atom 2 remain there.

The possibility that all five CO groups might have engaged in mutual exchange *via* a doubly bridged intermediate, as indicated in Scheme I, is thus ruled out. While there may be other factors which prevent this from occurring, one factor which alone may be sufficient is the great length of the Fe–Fe bond and the probability that the bonding of each iron atom to its portion of the acenaphthylene ring system will make it very difficult for this bond to shorten. Because of this, the bridged intermediates in the processes represented in Scheme I would be disfavored.

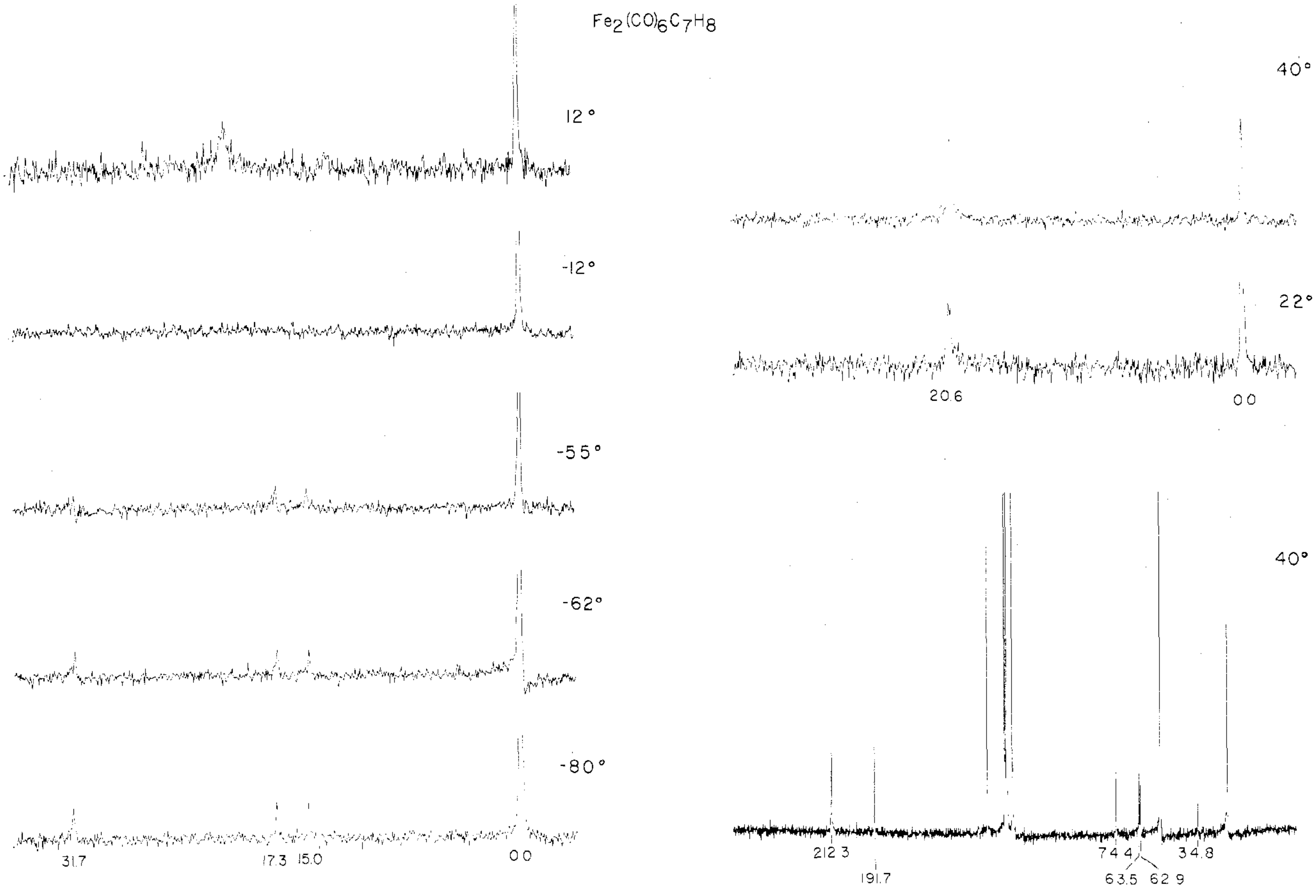


Figure 3. The spectra of $(C_7H_8)Fe_3(CO)_6$ at various temperatures. The spectra above room temperature were recorded in CH_2Cl_2–toluene whereas CH_2Cl_2 was used for the low-temperature spectra. An external deuterium lock was used in each case. The spectrum showing both the carbonyl and ring portions of the molecule was referenced to the downfield toluene peak and adjusted to a TMS scale by $\delta_{TMS} = 137.4 + \delta$. The spectra in the carbonyl region were referenced to CS_2.

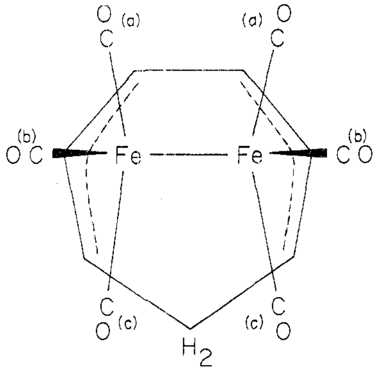


Figure 4. The molecular structure of $(C_7H_8)Fe_2(CO)_6$, as reported by Cotton, DeBoer, and Marks.[20]

It is not possible to determine from available data the intimate mechanism by which permutation of the a and b type CO groups on Fe(1) actually occurs. One possibility is a cyclic permutation due to a physical process of internal rotation of the three CO groups relative to the rest of the molecule. The only other pathway that seems at all plausible would be a succession of pairwise permutations of the types (abb') ⇄ (bab') and (abb') ⇄ (b'ba). It is our opinion that the rotatory process is the more likely, but it must be conceded that there is no proof of this.

Compound 2. The variable-temperature spectra for the cycloheptatriene molecule, **2**, are shown in Figure 3. The ^{13}C spectra at −60° are in complete agreement with the X-ray crystal structure[20] which is represented schematically in Figure 4. The mirror symmetry that is seen in the structure, with three different types of carbonyl groups, is manifested in the limiting spectrum which has three peaks of equal intensity. As the temperature is raised, the lines broaden *uniformly* and coalesce to a singlet at +40°. There are four kinds of carbon atoms in the ring, and their resonances are invariant with temperature, as were the ring proton resonances.[20]

Because of the equivalence of the two $Fe(CO)_3$ moieties in this compound, we cannot rule out, on the experimental evidence directly, the possibility that carbonyl scrambling might occur by a process comparable to that shown in Scheme I. However, in view of the result for compound **1** and the observation made in other cases[14–19] that organometal tricarbonyl groups undergo scrambling by a process localized within an individual $M(CO)_3$ group, such a localized process must be considered here also. Since the Fe–Fe distance here, 2.87 Å, is even longer than that in **1** and, again, the rigidity of the organic moiety would afford considerable resistance to the shortening presumably necessary to the attainment of a transitional structure having bridges, localized scrambling is the probable mechanism here. A further indication that localized scrambling is the more likely alternative is provided by our study[23] of $C_8H_{10}Fe_2(CO)_6$ in which local scrambling in each of the *non*equivalent $Fe(CO)_3$ groups is observed unambiguously, even though the Fe–Fe distance is much shorter,[24] *viz.*, 2.76 Å.

It is not possible to specify any of the finer details of the process. Thus, we cannot tell whether rearrangements on the two ends of the $Fe_2(CO)_6$ are correlated, or anticorrelated, or whether each end behaves independently of the other. As before, there is also the question of the type of permutation, *i.e.*, (abc) ⇄ (bca) ⇄ (cab) ⇄ (abc) or (abc) ⇄ (bac) ⇄ (bca) ⇄ (cba), etc.

Probably the simplest way to determine with certainty that delocalized scrambling (*i.e.*, passage of CO groups from one metal atom to the other *via* bridged intermediates) does not occur would be to prepare a molecule with nuclear spin labeling of the iron atoms. The practicality of this is now under study.

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Registry No. **1**, 53495-33-3; **2**, 51403-97-5.

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Charge-Transfer Spectra and Stability Constants of Ion Pairs of Hexaammineruthenium(III) and Halide Ions

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Stability constants and extinction coefficients for ion pairs between ruthenium(III) hexaammine and chloride, bromide and iodide ions were measured spectrophotometrically. The absorption spectra of the ruthenium(III) hexaammine halide ion pairs were measured in solutions of varying sodium halide concentration. The stability constants at zero ionic strength K^0_{IP} and the molar extinction coefficients $\Delta\epsilon$ at the maxima of the absorption peaks were evaluated as follows: $K^0_{IP} = 16 \pm 1\ M^{-1}$, $\Delta\epsilon$ 255 M^{-1} cm^{-1} for Cl$^-$; $K^0_{IP} = 11 \pm 1\ M^{-1}$, $\Delta\epsilon = 300\ M^{-1}$ cm^{-1} for Br$^-$; $K^0_{IP} = 10 \pm 1\ M^{-1}$, $\Delta\epsilon$ 251 and 252 M^{-1} cm^{-1} for I$^-$. $\Delta H°$ and $\Delta S°$ were also measured for the formation of the ion pair with the chloride ion. The spectra were interpreted as charge-transfer transitions from the halide ions to the ruthenium ion. The spectrum of the iodide ion pair consisting of two maxima was described as a superposition of two gaussians and a slightly blue-shifted $Ru(NH_3)_6^{3+}$ spectrum. The difference between the two maxima, 6590 cm^{-1}, was interpreted as the $^2P_{3/2}$–$^2P_{1/2}$ doublet splitting of the iodide ion. For the bromide ion, a similar procedure gave a doublet splitting of 2250 cm^{-1}. The transition energies of the $Ru(NH_3)_6^{3+},X^-$ ion pairs are compared to those of the analogous cobalt(III) complexes.

Introduction

Spectrophotometric investigations of ion pairs are possible in systems where a significant change in the absorption spectrum takes place upon the formation of the ion pair. Such a situation is likely to be obtained when a charge-transfer optical transition from the anion to the associated cation is possible.[1-3]

In our study of the base-catalyzed proton-exchange reactions of $Ru(NH_3)_6^{3+}$, its ion pair with hydroxide ion as well as the deprotonated species $Ru(NH_3)_5NH_2^{2+}$ was implicated in the exchange mechanism.[4] The formation of the latter species was indicated by the appearance of an additional absorption peak at 402 nm in basic solutions.[5] The problem of distinguishing between the absorption due to the ion pair and that due to the deprotonated species stimulated our interest in the spectra and stability of the ion pairs formed by $Ru(NH_3)_6^{3+}$. The results of a study of the ion pairs formed between $Ru(NH_3)_6^{3+}$ and halide ions are presented here.

Experimental Section

Materials. $Ru(NH_3)_6Cl_3$ (supplied by Johnson Matthey Chemicals) was either used without purification (batch no. 7) or recrystallized from 1 *N* HCl[6] (other batches). Identical results were obtained in either case. The other materials were of AR grade and were used without further purification.

Methods. $Ru(NH_3)_6Cl_3$ and NaI solutions were freshly prepared prior to each set of experiments. The pH of the iodide solutions was adjusted to 8 in order to reduce autoxidation of the iodide ion. The solutions were tested for traces of I_3^- ion by recording their absorbance near the absorption maxima of the triiodide ion at 226 and 352 nm.

Spectra of the $Ru(NH_3)_6Cl_3$–sodium halide mixtures were recorded as difference spectra with $Ru(NH_3)_6Cl_3$ solutions of identical concentration in the reference compartment. For the measurements of the entire absorption curves, including the short-wavelength region