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(63) The $Ni^{III} \rightarrow Ni^{II}$ redox couples can be made to appear reversible with cyclic voltammetry by incorporating slow potential-scan rates with an excess of $X^-$ ion present. The measured potentials probably correspond to the $[NiX_2L_2]^+ \rightleftarrows [NiX_2L_2]$ conversion involving formally six-coordinate nickel(II).
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(65) The isotropic hyperfine splittings $A_{iso}^{Cl}$ and $A_{iso}^{As}$ found for $[NiCl_2(diars)_2]^+$ in ref 10, taken with the atomic data given in Tables A3.1 and A3.2 by P. B. Ayscough, "Electron Spin Resonance in Chemistry", Methuen, London, 1967, show that only about 1.4–2% of the total unpaired electron density resides on the four As atoms taken together and about 2–4.6% on the two Cl atoms.
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# Intramolecular Rearrangement in ($\eta$-Diene)tricarbonyliron and -ruthenium Compounds. A Carbon-13 Nuclear Magnetic Resonance Study

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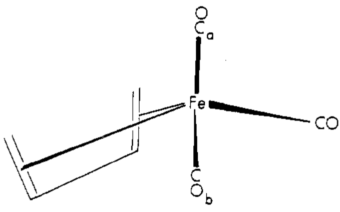
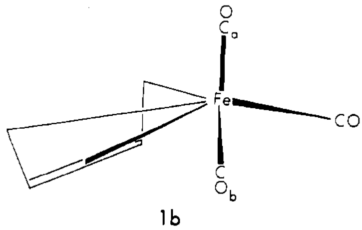
The fluxional behavior of a series of ($\eta$-diene)tricarbonyliron and ($\eta$-diene)tricarbonylruthenium complexes studied by variable-temperature $^{13}C$ NMR spectroscopy is reported. The difference in the rates of rearrangement between conjugated and nonconjugated dienes is noted. The increased activation barrier for carbonyl scrambling in ($\eta$-1,3-diene)tricarbonyliron complexes is attributed to the mixing in of "six-coordinate character" into these formally five-coordinate molecules. The dependence of the rearrangement energetics on the electronic structure of the conjugated diene is fully consistent with the above postulate. Possible mechanisms which are consistent with the permutational nature of the exchange are detailed and the apparent differences between conjugated and nonconjugated dienes are discussed. The variations in the averaged $^{13}C$ chemical shifts of the carbonyl groups can be satisfactorily accounted for by a metal→carbonyl $\pi$-back-bonding model. However, the individual carbonyl resonances observed in the low-temperature spectra are at odds with force constant calculations. This apparent discrepency is commented upon.

## Introduction

The study of intramolecular rearrangement in five-coordinate $d^8$ transition metal complexes has attracted a great deal of attention since the first unambiguous demonstration of the phenomenon in $(CF_3)Co(CO)_3PF_3$ by Udovich and Clark.[1] The studies, besides establishing the generality of the phenomenon,[2,3] have also provided important mechanistic insights into the nature of the dynamic process.[4,5] It is then interesting to observe that $Fe(CO)_5$[5a] and some of its derivatives ($\eta$-norbornadiene)tricarbonyliron,[6a] [bis(dimethylphosphino)ethane]tricarbonyliron,[6b] [bis(diphenylphosphino)methane]tricarbonyliron,[6c] $(R_3P)Fe(CO)_4$,[6a,d,e] $(py)Fe(CO)_4$,[6f] and $(CHO)Fe(CO)_4^-$ [6g] are conspicuous because of their low activation barriers for rearrangement and the consequent observation of time-averaged spectra even at the lowest accessible temperatures. Indeed, until recently, only in (1–4-$\eta$-cyclooctatetraene)tricarbonyliron,[7] ($\eta$-butadiene)$Fe(CO)_{3-x}(PF_3)_x$,[8] and ($\eta$-1,3-cyclohexadiene)$Fe(CO)_{3-x}(PF_3)_x$[9] has intramolecular rearrangement in an iron-containing five-coordinate molecule been demonstrated. Although the above complexes all contained a conjugated diene ligand, the importance of this structural unit on the activation barrier for rearrangement seemed to have been overlooked. Indeed, two previous reports[10] on the $^{13}C$ NMR of ($\eta$-butadiene)tricarbonyliron were concerned only with the question of whether **1a** or **1b** was a better representation of the bonding for the molecule in solution. No attempt was made to rationalize the observation of a single sharp resonance for the three carbonyl groups, which is clearly inconsistent with either **1a** or **1b** and the known tetragonal-pyramidal geometry of the complex[11] in the solid state. Nor was there a variable-temperature study initiated to verify whether the single line was due to accidental coincidence or nonrigid behavior.



1a



1b

We[12] and others[13] have recently reported a variable-temperature $^{13}C$ NMR study of **1** showing that in fact intramolecular rearrangement was responsible for the single $^{13}CO$ line observed at room temperature. In an attempt to understand the nature of the rearrangement process and the factors which determine the size of the barrier for rearrangement, we have extended our study to other ($\eta$-diene)-$M(CO)_3$ (M = Fe, Ru) complexes. Here we wish to describe the results of such an investigation. Recently, related work has also been reported by Clark et al.,[14] Whitesides et al.,[15] and Laszlo et al.[16]

## Experimental Section

($\eta$-Butadiene)tricarbonyliron was obtained from Alfa Inorganics. The following compounds were prepared and purified according to published procedures: ($\eta$-diene)$Fe(CO)_3$ [where diene = tetrakis(trifluoromethyl)cyclopentadienone,[17b] bicyclo[4.2.0]octa-2,4-diene,[17c] cycloheptadienone,[17d] tropone,[17d] cycloocta-1,3-diene,[17e] cycloocta-1,3,5-triene,[17c] norbornadiene,[17f] cycloocta-1,5-diene (1,5-COD),[17b] and tetrafluorobenzobicyclo[2.2.2.]octatriene[17g]] and ($\eta$-tetraphenylcyclopentadienone)tricarbonylruthenium.[17a]

The yield of [$\eta$-tetrakis(trifluoromethyl)cyclopentadienone]tricarbonylruthenium was improved from 10%[17a] to ca. 80% by reacting a 20-fold molar excess of hexafluoro-2-butyne with $Ru_3(CO)_{12}$ at 120 °C for 30 h in a stainless steel cylinder. ($\eta$-Tetraphenylcyclopentadienone)tricarbonyliron has been made[18] by refluxing tetraphenylcyclopentadienone with iron pentacarbonyl. It can also conveniently be prepared, in good yield, by stirring tetraphenylcyclopentadienone with the stoichiometric amount of $Fe_2(CO)_9$ in pentane for 12 h at room temperature. (1–4-$\eta$-Cycloheptatriene)tricarbonyliron[19] was conveniently made in greater than 80% yield without any need for further purification by refluxing stoichiometric amounts of cycloheptatriene and $Fe(CO)_5$ in an equal volume of methylcyclohexane for 3 days with efficient stirring. ($\eta$-1,3-Cyclohexadiene)tricarbonylruthenium was made by heating (1,5-COD)$Ru(CO)_3$[20] with an excess of cyclohexa-1,3-diene in benzene. The physical propeprties of the product were identical with those reported by Cowles et al.[21]

Carbon-13 NMR samples were prepared by dissolving 0.3–0.5 g of the compound (depending on solubility at low temperature) in 2 ml of an appropriate solvent (see Table I) in a serum stoppered 10-mm NMR tube. Carbon-13 NMR spectra were recorded on a deuterium-lock Bruker HFX-90/Nicolet 1085 FT spectrometer operating at 22.628 MHz. Solvent resonances were occasionally used as secondary standards and converted to TMS scale with the relations $\delta_{TMS} = \delta_{CS_2} + 192.75$, $\delta_{TMS} = \delta_{CD_3{}^{13}C(C_5D_5)} + 137.51$, $\delta_{TMS} = \delta_{CD_2Cl_2} + 55.27 - 0.0055T$ ($T$ in K), and $\delta_{TMS} = \delta_{(CD_3)^{13}CO} + 210.22 - 0.01452T$ ($T$ in K). The $^{57}Fe$–$^{13}C$ coupling constant was measured with a deuterium-lock Varian HA-100-15 interfaced with a Digilab FTS/NMR-3 data system using a 12-mm sample tube. Five hundred to one thousand pulses at tilt angles of 35° and 0.8-s repetition rates were collected. $Cr(acac)_3$ was occasionally added[6a] to reduce $T_1$'s until resonances with short $T_1$'s (i.e., $^{13}C$–H) just began to broaden.

Between five and ten spectra at 3–5 °C intervals were obtained in the exchange region. Temperature measurements were made with a Bruker temperature control unit, Model B-ST 100/700, and are expected to be constant to ±1 °C. Exchange rates were determined by visual comparison of experimental and computer-simulated[22] spectra. The nonexchanging $^{13}CO$ line width was used to estimate $T_2$*. The $^{13}CS_2$ line width was generally available as a $T_2$* check in the exchange region. Rate constants with an estimated 10% error and temperatures (±1 °C) could be correlated at a confidence level greater than 99% using the Eyring and Arrhenius expressions.

## Results

Figure 1 illustrates the NMR line broadening behavior observed in the carbonyl region for (1–4-$\eta$-cycloheptatriene)tricarbonyliron. Computer-generated spectra with exchange rates chosen to give the best visual fit to the observed spectra are also shown in the figure. As expected from an asymmetric diene, the low-temperature limiting spectrum shows three carbonyl resonances. By comparing this spectrum to those of (symmetric diene)$Fe(CO)_3$ complexes, the two closely spaced high-field lines are assigned to the basal and the low-field resonance to the apical carbonyl groups, respectively. It is clear that as the temperature is raised the resonances collapse in a symmetrical fashion and result in a high-temperature singlet whose resonance position is very close to the averaged value of the low-temperature resonances. Fluxional behavior is indicated.

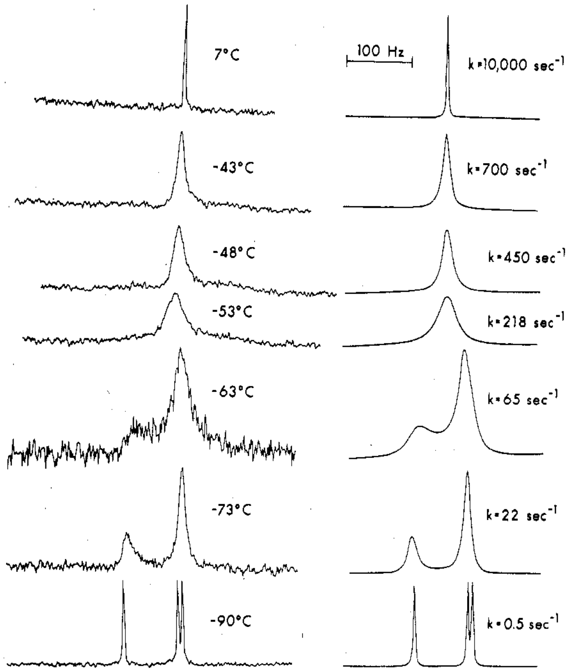


**Figure 1.** Variable-temperature $^{13}C$ NMR spectra of (1-4-$\eta$-cycloheptatriene)tricarbonyliron in the carbonyl region. Temperatures (°C) are shown on the observed spectra (left) and rate constants label the calculated spectra.

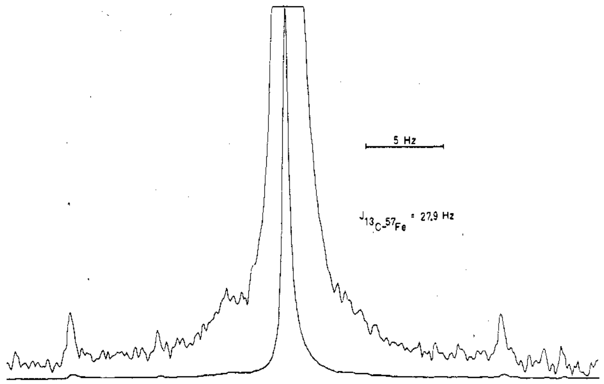


**Figure 2.** High-temperature averaged $^{13}CO$ line in ($\eta$-butadiene)tricarbonyliron shown at normal and with superimposed ordinate expansion. The two satellites flanking the main peak are due to $J_{^{57}Fe-^{13}C}$.

The high-temperature averaged $^{13}CO$ line in ($\eta$-butadiene)tricarbonyliron is shown at normal and with superimposed ordinate expansion in Figure 2. Iron-57 (2.2%, $I = {}^1/_2$) gives rise to clearly resolved $^{57}Fe$–$^{13}CO$ satellites. The observed $J_{^{57}Fe-^{13}C}$ of 27.9 Hz is similar to other $J_{^{57}Fe-^{13}CO}$ values measured: 23.4 Hz in $Fe(CO)_5$,[6e] 25.1 Hz in $(Me_3Si)_2Fe(CO)_4$.[23] The coupling between the iron and the carbonyl groups at the fast-exchange limit, together with the observed independence of the temperature-dependent spectral changes toward added free diene, is an indication of the intramolecularity of the rearrangement.

Chemical shift data in the carbonyl region for the conjugated dienes studied in this work are listed in Table I. All compounds except **2** and **3** show line broadening in the CO region typical of nonrigid molecules. The single resonance observed for compounds **2** and **3** remained sharp down to 183 and 206 K, respectively, indicating rapid fluxionality even at these temperatures or accidental degeneracy of the apical and basal carbonyl groups. The last possibility cannot be over-

Table I. $^{13}C$ Chemical Shifts for the Carbonyl Resonances and Associated Activation Parameters in (1–4-$\eta$-diene)$M(CO)_3$ Complexes (M = Fe, Ru)[a]

| | | | Limiting spectrum | | | | | Activation data[b] | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| No. | Diene | Solvent | Apical CO | Basal CO | $T$, K | Av spectrum | $T$, K | $\Delta H^{\ddagger}$ | $\Delta S^{\ddagger}$ | $\Delta G^{\ddagger}_{298}$ | $\Delta G^{\ddagger}_{298}$[e] |
| 1 | Butadiene | $CD_3COCD_3/CS_2$ | 217.4 | 211.3 | 193 | 213.2 | 273 | 9.1 | −4.6 | 10.5 | 10.0 |
| 2 | Tetraphenylcyclopentadienone[c] | $CD_2Cl_2$ | | | | 208.7 | 183 | | | | |
| 3 | Tetraphenylcyclopentadienone[c,d] | $CD_2Cl_2$ | | | | 194.1 | 206 | | | | |
| 4 | Tetrakis(trifluoromethyl)-cyclopentadienone | $CD_3COCD_3$ | 203.8 | 201.0 | 203 | 201.4 | 238 | 9.7 | −4.8 | 11.1 | 10.6 |
| 5 | Tetrakis(trifluoromethyl)-cyclopentadienone[d] | $CD_3COCD_3$ | 189.6 | 188.0 | 213 | 188.4 | 256 | 11.8 | −1.3 | 12.2 | 12.0 |
| 6 | Cyclohexa-1,3-diene | $CD_3COCD_3/CS_2$ | 216.7 | 211.9 | 172 | 213.7 | 223 | 10.1 | 4.3 | 8.8 | 9.2 |
| 7 | Cyclohexa-1,3-diene[d] | $C_6D_5CD_3$ | 202.8 | 197.9 | 203 | 199.1 | 303 | 10.9 | −5.6 | 12.5 | 11.9 |
| 8 | Bicycloclo[4.2.0]octadiene | $CD_3COCD_3/CS_2$ | 216.9 | 212.0 | 175 | 213.7 | 233 | 9.1 | −0.2 | 9.2 | 9.2 |
| 9 | Cycloheptatriene | $C_6D_5CD_3$ | 214.6 | $\begin{Bmatrix}210.9\\210.6\end{Bmatrix}$ | 183 | 211.9 | 280 | 10.8 | −0.1 | 10.4 | 10.4 |
| 10 | Cyclohepta-1,3-dienone | $CD_3COCD_3/CS_2$ | 215.4 | $\begin{Bmatrix}209.3\\207.5\end{Bmatrix}$ | 208 | 210.5 | 280 | 10.4 | −3.0 | 11.3 | 11.0 |
| 11 | Tropone | $CDCl_3$ | 216.0 | $\begin{Bmatrix}206.5\\205.4\end{Bmatrix}$ | 223 | 209.0 | 315 | 11.6 | −3.3 | 12.7 | 12.5 |
| 12 | Cycloocta-1,3-diene | $C_6D_5CD_3$ | 216.9 | 210.6 | 195 | 212.4 | 243 | 10.2 | −0.7 | 10.4 | 10.3 |
| 13 | Cyclooctatriene | $CD_2Cl_2$ | 215.3 | $\begin{Bmatrix}210.8\\209.5\end{Bmatrix}$ | 203 | 212.2 | 270 | 11.3 | 0.3 | 11.2 | 11.2 |

[a] Chemical shifts in ppm relative to TMS. [b] $\Delta H^{\ddagger}$ and $\Delta G^{\ddagger}_{298}$ in kcal/mol with associated error of $\pm 0.5$ kcal $mol^{-1}$; $\Delta S^{\ddagger}$ in eu with an error of ca. ±2 eu. [c] Single sharp line to the lowest accessible temperature. [d] For these three cases M = Ru; for all others M = Fe. [e] Calculated assuming $\log A = 13.2$.

looked especially in view of the fact that the chemical shift difference between apical and basal carbonyl groups in the tetrakis(trifluoromethyl)cyclopentadienone derivatives is substantially smaller than in the other ($\eta$-diene)$M(CO)_3$ complexes. Eyring activation parameters are also listed in Table I. Activation entropies are small and average to −2 eu for the 11 compounds studied. They are consistent with the observed intramolecularity of the rearrangement process. Large $\Delta S^{\ddagger}$ values were often associated with experimental problems such as poor signal to noise ratios, small chemical shift separations which result in a short exchange region, and poor resolution. For this reason we have also calculated and listed in Table I free energies of activation assuming $\Delta S^{\ddagger} = 0$ ($\log A = 13.2$) and are inclined to think that $\Delta G^{\ddagger}$ and not $\Delta H^{\ddagger}$ (or $E_a$) should be consulted and compared when trends in fluxionality for these compounds are to be discussed. Of course similar conclusions regarding the advantages of dealing with $\Delta G^{\ddagger}$ rather than $E_a$ have been reached by others.[24,25]

Free and complexed diene chemical shifts are listed in Table II. Upfield shifts of ca. 40 ppm for inner and ca. 65 ppm for outer diene carbons are found on coordination.[26] Other carbons in the diene ligand invariably shift upfield 5–10 ppm on coordination. This behavior is typical and has been noted in a number of organometallic systems, for instance, ($\eta$-arene)$Cr(CO)_3$[28] and *cis*-$(CH_3)_2Pt$($\eta$-diene).[29] Chemical shift data for some (nonconjugated diene)$Fe(CO)_3$ complexes are listed in Table III. No evidence for line broadening was observed for these complexes, even at the lowest accessible temperatures. Upfield coordination shifts of the olefinic carbons in these complexes vary from 45 ppm in (1,5-COD)$Fe(CO)_3$ to 107 ppm in ($\eta$-norbornadiene)$Fe(CO)_3$. It is interesting to note that the small coordination shift in (1,5-COD)$Fe(CO)_3$ is reflected in the somewhat thermal and oxidative instability of this compound. Upfield shifts of other carbons associated with the diene are also observed except for (1,5-COD)$Fe(CO)_3$ where the methylene carbons experience a downfield coordination shift. This has been noted previously for *cis*-$(CH_3)_2Pt$(1,5-COD).[29]

## Discussion

**Fluxional Behavior.** The identification of fluxional behavior in the reported complexes, together with the variable nature of the rearrangement barrier, brings to mind the following questions. First, what makes the activation barrier in complexes with conjugated dienes sufficiently large to be observable and what are the factors responsible for its increase on going from cyclohexa-1,3-diene to tropone? Second, what is the cause of the dramatic increase in fluxionality when a conjugated 1,3-diene is replaced by nonconjugated 1,4- and 1,5-dienes? We believe that the answers to both of these questions can be arrived at from a consideration of the bonding between the $Fe(CO)_3$ group and the respective diene moiety.

The bonding between a diene and a metal carbonyl fragment has been discussed by several workers[30] and is assumed to consist of two interdependent components. There is electron donation from the highest occupied MO of the ligand (HOMO) into empty metal d orbitals, which is complemented by back-donation of electron density from filled metal d orbitals into the lowest unoccupied orbital (LUMO) of the diene moiety. The relative importance of these two interactions will, of course, be determined by the energy separation between metal d orbitals and the HOMO and LUMO of the ligands, respectively.

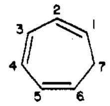
Armed with this information, let us first consider the case of conjugated 1,3-dienes. In Figure 3 we illustrate the energy of the HOMO and LUMO of the three types of polyenes studied in this report. The levels were calculated from literature data of ionization potentials and ultraviolet spectra of the respective molecules. The appropriate metal d orbitals are not shown but are obviously situated somewhere between the two levels. They are closer to the LUMO level since there is both theoretical[30c,d] and experimental[31] evidence to support the view that in these compounds the $Fe(CO)_3$ fragment acts as an electron-donating moiety. We note that for 1,3-dienes the form of the HOMO and LUMO orbitals is such that participation of these MO's in the metal–diene bonding results in a weakening of the C(1)–C(2) and C(3)–C(4) bonds (original C–C double bonds) and a strengthening of the C(2)–C(3) bond (original C–C single bond). That is, in valence-bond terms of the structural extremes we have mentioned before, increased electron donation and acceptance by the diene moiety will favor form **1b**, or, as it is sometimes referred to, the $\sigma$–$\pi$ structure. A verification of the above argument comes from x-ray crystallographic studies of several ($\eta$-diene)$Fe(CO)_3$ complexes.[32] Defining $\Delta$ as the difference between the C(2)–C(3) and the average of C(1)–C(2) and

**Table II.** $^{13}C$ Chemical Shifts of the Diene Ligand in (1–4-$\eta$-diene)M(CO)$_3$ Complexes (M = Fe, Ru)[a]

| | $\delta$($^{13}C$ of free ligand)[b] | | | $\delta$($^{13}C$ of complexed ligand)[b] | | |
|---|---|---|---|---|---|---|
| Diene | Inner | Outer | Other | Inner | Outer | Other |
| 1 | 138.0[c] | 117.0[c] | | 86.4 | 41.5 | |
| 2 | 154.3 | 125.2 | 200.1 (C=O) | 103.7 | 82.5 | 169.9 (C=O) |
| 3 | 154.3 | 125.2 | 200.1 (C=O) | 107.1 | 81.9 | 173.7 (C=O) |
| 4 | *d* | *d* | *d* | 90.1[e] | 65.2[f] | 164.8 (C=O)<br>$\left\{\begin{matrix}122.6\\123.1\end{matrix}\right\}$ (CF$_3$) |
| 5 | *d* | *d* | *d* | 92.9[e] | 66.7[f] | 168.1 (C=O)<br>$\left\{\begin{matrix}122.1\\123.6\end{matrix}\right\}$ (CF$_3$) |
| 6 | 124.9[g] | 126.3[g] | 22.7 (CH$_2$) | 84.3 | 61.1 | 26.8 (CH$_2$) |
| 7 | 124.9[g] | 126.3[g] | 22.7 (CH$_2$) | 87.3 | 55.7 | 25.0 (CH$_2$) |
| 8 | 125.2[g] | 129.3[g] | 32.8 (CH)<br>27.9 (CH$_2$) | 87.7 | 71.6 | 38.2 (CH)<br>25.6 (CH$_2$) |
| 9 | 130.9 ($C_3$, $C_4$)<br>126.6 ($C_2$, $C_5$)<br>120.4 ($C_1$, $C_6$) | | 28.1 (CH$_2$) | $\left\{\begin{matrix}88.6\\93.7\end{matrix}\right\}$ | $\left\{\begin{matrix}56.2\\60.7\end{matrix}\right\}$ | 30.9 ($C_7$)<br>$\left\{\begin{matrix}125.6\\128.6\end{matrix}\right\}$ ($C_5$, $C_6$) |
| 10[j] | *d* | *d* | *d* | $\left\{\begin{matrix}91.8\\92.2\end{matrix}\right\}$ | $\left\{\begin{matrix}58.0\\62.4\end{matrix}\right\}$ | 208.1 (C=O)<br>$\left\{\begin{matrix}139.3\\136.0\end{matrix}\right\}$ ($C_5$, $C_6$) |
| 11[i] | 145.8 ($C_3$, $C_4$)[h]<br>142.4 ($C_2$, $C_5$)[h]<br>139.2 ($C_1$, $C_6$)[h] | | 189.1 (C=O) | $\left\{\begin{matrix}92.5\\97.5\end{matrix}\right\}$ | $\left\{\begin{matrix}52.9\\62.3\end{matrix}\right\}$ | 197.9 (C=O)<br>$\left\{\begin{matrix}148.8\\122.7\end{matrix}\right\}$ ($C_5$, $C_6$) |
| 12[k] | 126.5[g] | 131.3[g] | $\left\{\begin{matrix}23.7\\28.5\end{matrix}\right\}$ $\begin{matrix}(C_5, C_8)\\(C_6, C_7)\end{matrix}$ | 91.8 | 63.2 | $\left\{\begin{matrix}25.6\\29.2\end{matrix}\right\}$ $\begin{matrix}(C_5, C_8)\\(C_6, C_7)\end{matrix}$ |
| 13[k] | 135.4 ($C_3$, $C_4$)[h]<br>126.9 ($C_2$, $C_5$)[h]<br>126.2 ($C_1$, $C_6$)[h] | | 28.3 ($C_7$, $C_8$) | $\left\{\begin{matrix}89.0\\89.3\end{matrix}\right\}$ | $\left\{\begin{matrix}59.0\\60.5\end{matrix}\right\}$ | $\left\{\begin{matrix}122.3\\132.0\end{matrix}\right\}$ ($C_5$, $C_6$)<br>$\left\{\begin{matrix}22.0\\24.7\end{matrix}\right\}$ ($C_7$, $C_8$) |

[a] Chemical shifts in ppm relative to TMS. [b] "Inner" and "outer" refer to the carbon atoms that belong to the closed and open end of the 1,3-dienes, respectively. [c] H. Spiesecke and W. G. Schneider, *Tetrahedron Lett.*, **14**, 468 (1961). [d] Isolated as complexed ligand only. [e] Poorly resolved multiplet. [f] Well-resolved quartet: $^2J_{^{13}C-^{19}F}$ = 35 Hz. [g] Assignment based on some six-membered ring dienes in which "outer" carbon atoms resonate to low field of the "inner" ones: H. Gunther, H. Schmickler, and G. Jikeli, *J. Magn. Reson.*, 11, 344 (1973). [h] Based on cycloheptatriene assignment by H. Gunther and T. Keller, *Chem. Ber.*, **106**, 1863 (1973). [i] The room-temperature $^{13}C$ spectrum of this compound was also recorded by B. F. G. Johnson, J. Lewis, P. McArdle, and J. R. Norton, *J. Chem. Soc., Dalton Trans.*, 1253 (1974).

[j] Numbering of seven-membererd ring system



[k] Numbering of eight-membered ring system

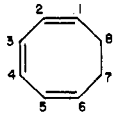


**Table III.** $^{13}C$ Chemical Shifts of Some Nonconjugated (diene)Fe(CO)$_3$ Complexes[a]

| | | $\delta$($^{13}C$ of ligand) | | | |
|---|---|---|---|---|---|
| Diene | $\delta$($^{13}CO$) (°C[b]) | Type | Free ligand | Complexed ligand | $\Delta$[c] |
| Cycloocta-1,5-diene | 218.8<br>(−130) | C=C<br>CH$_2$ | 129.0<br>28.7 | 83.7<br>33.8 | 45.3<br>−5.1 |
| Norbornadiene | 218.2<br>(−100)[d] | C=C<br>CH$_2$<br>CH | 145.0<br>51.7<br>76.4 | 38.3<br>43.3<br>59.3 | 106.7<br>8.4<br>17.1 |
| Tetrafluorobenzobicyclo-[2.2.2]octatriene | 217.2<br>(−70) | C=C<br>C-H<br>C[e]<br>C-F[f] | 140.4<br>42.0<br>131.6<br>142.1 | 43.8<br>34.4<br>130.7<br>140.5 | 96.6<br>7.6<br>0.9<br>1.6 |

[a] Chemical shifts in ppm relative to TMS. [b] A single sharp line is observed at this temperature. [c] $\delta$(free ligand) − $\delta$(complexed ligand) = $\Delta$. [d] Reported previously to show "no structural interconversion" down to −100 °C: O. A. Gansow, A. R. Burke, and W. D. Vernon, *J. Am. Chem. Soc.*, 94, 2550 (1972). [e] 1:1:1 triplet due to long-range $^{19}F$ coupling. [f] Broad doublet, $J_{^{13}C-^{19}F}$ ≈ 245 Hz.

C(3)–C(4) bond lengths of a 1,3-diene,[32a] it is observed that the value of ca. 0.09 Å of a free diene decreases and is in the range of 0.0 to −0.07 Å once the diene has been coordinated to the iron atom. It should be pointed out that a one to one correlation between the crystallographically observed $\Delta$ and

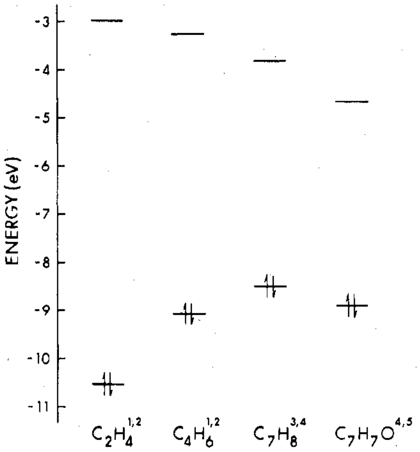


**Figure 3.** Diagram illustrating the energy of the HOMO and LUMO orbitals in representative diene ligands utilized in the present study. References: (1) M. J. S. Dewar, "The Molecular Orbital Theory for Organic Chemistry", McGraw-Hill, New York, N.Y., 1969, p 274; (2) C. Sandorfy, "Electronic Spectra and Quantum Chemistry", Prentice-Hall, Englewood Cliffs, N.J., 1964, p 341; (3) W. von E. Doering and L. H. Knox, *J. Am. Chem. Soc.*, 79, 352 (1957); (4) C. Müller, A. Schweig, and H. Verneer, *Angew. Chem., Int. Ed. Engl.*, 13, 273 (1974); (5) K. Inuzuka and T. Yokota, *J. Chem. Phys.*, 4, 911 (1966).

the donor–acceptor properties of the diene does not exist. This may reflect the inherent insensitivity of the method to what are undoubtedly small and subtle changes from diene to diene. We, of course, realize that the valence-bond description of the bonding in these molecules is an oversimplification and that there is a smooth transition from **1a** to **1b** which is best accounted for by molecular orbital arguments.[30,33] Nevertheless, we believe that it is this departure from pure five-coordination and the mixing of "six-coordinate character", with its associated reluctance to undergo isomerization and rearrangements by unimolecular processes, which are responsible for the unexpectedly high rearrangement barriers in (1–4-$\eta$-diene)-$Fe(CO)_3$ complexes.[34] However we should also add at this junction that experimental evidence suggests that the barriers are controlled more closely by variations in the LUMO level of the ligands. This is not surprising since, as mentioned before, this MO is closer to the metal d orbitals than the corresponding HOMO and thus interacts with the transition metal more strongly.

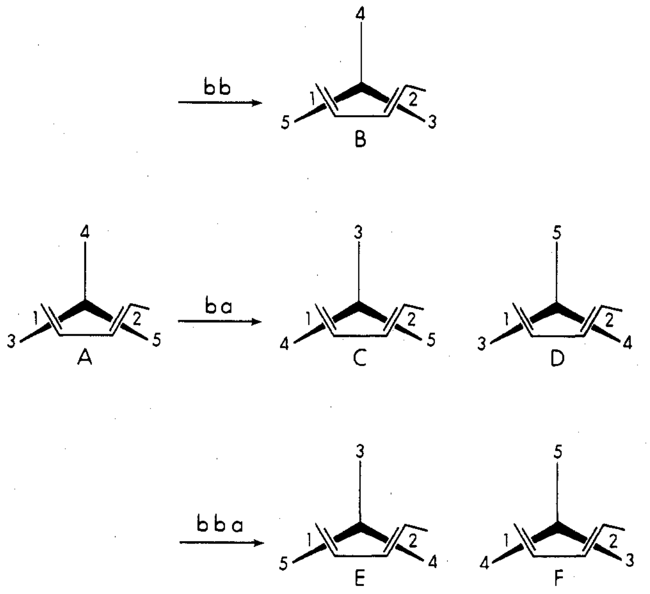
Proof for the at least qualitative correctness of the above argument concerning the electronic origin of the rearrangement barriers comes from the observed trend in the latter. As can be seen in Table I, $\Delta G^{\ddagger}_{298}$ increases roughly in the order diene < triene < dienone < trienone,[36] which is the order predicted from their acceptor abilities (Figure 3) and our argument based on the corresponding importance of the $\sigma$–$\pi$ structure or "six-coordinate character". It is interesting to note that ($\eta$-3,5-heptadiene-2-one)tricarbonyliron is reported by Kreiter et al.[13] to have a coalescence temperature of 260 K, a value intermediate between ($\eta^4$-tropone)tricarbonyliron and ($\eta^4$-cycloheptadienone)tricarbonyliron. Although structurally dissimilar, all three compounds possess the electron-withdrawing keto group in an outer position of the diene, implicating again the importance of the electronic effect. A comparison, admittedly limited and resting on only two dienes (diene = tetrakis(trifluoromethyl)cyclopentadienone and cyclohexa-1,3-diene[38]), between iron and ruthenium complexes is also in accord with the above conclusion. Indeed, on going from iron to ruthenium we expect the metal d orbitals to increase in energy (i.e., to become destabilized), a factor which should promote the electron-donating ability of the $Ru(CO)_3$ moiety with respect to its $Fe(CO)_3$ counterpart. Consequently, it is expected that the six-coordinate character of ($\eta$-1,3-diene)$Ru(CO)_3$ would increase[39] together with the rearrangement barrier when compared to its iron analogue. The $\Delta G^{\ddagger}_{298}$ nicely bears this out.

There are undoubtedly other factors (steric effect, nonplanarity of the 1,3-diene fragment, etc.) that contribute to the observed barriers and this is evidenced by the less than regular increase in $\Delta G^{\ddagger}_{298}$ as one proceeds from ($\eta$-1,3-cyclohexadiene)tricarbonyliron to ($\eta^4$-tropone)tricarbonyliron. Possible candiates for the steric acceleration of the carbonyl-scrambling process are the $\eta$-tetrakis(trifluoromethyl)-cyclopentadienone and $\eta$-tetraphenylcyclopentadieneone derivatives of $M(CO)_3$ (M = Fe, Ru). The latter complexes apparently remain fluxional down to the lowest accessible temperatures (although vide supra) whereas the former compounds exhibit activation parmeters that are somewhat lower than naively anticipated from the expected $\pi$ acidity of the diene moiety. In the trifluoromethyl-substituted complexes electronic factors, in addition to the steric effect of the $CF_3$ groups, could also be operating. The presence of the electron-withdrawing $CF_3$ groups will result in a stabilization of both LUMO and HOMO orbitals of the diene; this in turn will cause an increase in the $\pi$-acceptor ability of the diene and a decrease in its electron-donating power, and the net result could be a potentially much reduced six-coordinate character than the $\pi$-acidity consideration alone would have predicted. The smaller then expected activation parameters for these compounds could be a reflection of such an electronic effect.[41] In this regard we wish to mention the observed $\Delta G_c^{\ddagger}$ of 7.3 kcal mol$^{-1}$ for ($\eta$-1-methoxy-1,3-cyclohexadiene)tricarbonyliron.[16] Laszlo et al,[16] on the basis of the similarity of their value with our previously published $E_a$ for ($\eta$-1,3-cyclohexadiene)tricarbonyliron, concluded that "making a diene a better donor *and* a better acceptor towards backdonation from the metal (since introduction of the methoxy group shifts both the HOMO and LUMO by *ca.* 0.8 eV from the INDO calculation) has a mutually-cancelling effect, and the overall lability is little affected". Since our original spectra for ($\eta$-1,3-cyclohexadiene)tricarbonyliron suffered seriously from noise problems which resulted in the appearance of unrealistic entropy of activation, the reported $E_a$ value was suspect. The variable-temperature work was carefully retaken and the values appearing in Table I pertain to this new run. It is evident that carbonyl scrambling is not just comparable but indeed faster in the methoxy-substituted derivative. Thus the role of the HOMO level in this particular compound seems to be the opposite of what we assumed to be happening in [$\eta$-tetrakis(trifluoromethyl)cyclopentadienone]metal tricarbonyls. It is puzzling for us to see why increased electron donation from the ligand should result in greater fluxionality of the molecule, and before rejecting our assumption about the effect of the HOMO on metal scrambling, we wish to mention the following about the influence of the methoxy substituent. The methoxy group acts as an electron-withdrawing group through the $\sigma$ framework and as a resonance donor by interacting with the $\pi$ levels of the diene. Indeed it is this latter function that results in the destabilization of the HOMO level and the calculated increased electron-donating ability of the diene. In the $Fe(CO)_3$ complex, however, as has been observed in many structural works on cyclic dienes,[32] the substituents on the 1–3 position bend out of the plane of the diene carbons. This could largely destroy the resonance contribution and favor the electron-withdrawing effect. That is, the HOMO of the above diene, existing in a configuration imposed by its coordination to the $Fe(CO)_3$ moiety, could in fact be stabilized with respect to the unsubstituted diene. Should this be the case, the increased lability of the molecule is no longer the result of the better electron-releasing power of the ligand. Nevertheless, we recognize the need for further experimentation to identify the exact role of the HOMO level upon the fluxionality of similar types of molecules.

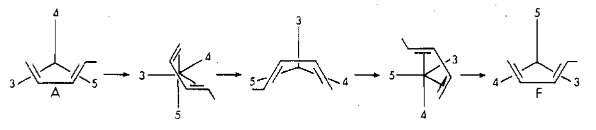
The above model also satisfactorily accounts for the fluxional behavior of (nonconjugated diene)$Fe(CO)_3$ complexes. Since, in these molecules, structure **1b** will not contribute to the bonding picture, the compounds can be considered as true five-coordinate species. The rapidity of carbonyl scambling, as witnessed by the observation of a single sharp line down to the lowest attainable temperature, therefore is not unlike previous findings with several other five-coordinate iron carbonyl derivatives.[6]

**Nature of the Intramolecular Process.** It is now generally well recognized that prior to any discussion about the mechanism of the intramolecular rearrangement the permutational nature of the exchange must be considered. In Chart I we summarize the results of such an analysis considering a generalized (asymmetric diene)$Fe(CO)_3$ complex and adopting the procedure of Musher.[43] Since the NMR method, in an achiral environment, does not distinguish between optical isomers, these, for the sake of clarity, have been omitted from the chart. The problem then, for an (asymmetric diene)$Fe(CO)_3$ complex with labeled CO groups and olefinic bonds, assuming for the present that each double bond occupies one coordination position, reduces to the generation of six distinct isomers of the tetragonal-pyramidal ground state. It is the generation of these isomers, by carbonyl group per-

**Chart I**



**Scheme I**



mutations, that is shown in the chart. An examination of the chart quickly reveals that, because the molecule has no symmetry, every permutation listed should give rise to a different temperature-dependent NMR line shape change or, according to Musher's nomenclature, to a distinct observable process (OP).[43] The observed symmetrical collapse of the three carbonyl resonances in the exchange region for these compounds and also for (heterodiene)Fe(CO)$_3$ type molecules[37] therefore identifies the bba processes that produce E or F isomers, as being responsible for the fluxional behavior. We note here that the situation with (symmetric diene)Fe(CO)$_3$ complexes is not as clear-cut. Indeed, due to $C_s$ symmetry the number of observable processes reduces from 6 for the above molecules to 2. These are

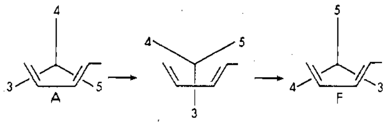
$OP_0$:I = bb

$OP_1$:ba(2) = bba(2)

(where I is the identity, the number in parentheses gives the number of rearrangements and the "equals" sign means "indistinguishable from") and the molecule rearranges via $OP_1$. However whether this involves the ba or bba processes or a combination of both cannot be resolved from the NMR experiment. We should also recognize that even with (asymmetric diene)Fe(CO)$_3$ compounds the permutational process is not as unambiguous as we indicated above. The low symmetry of the molecules results in activation energies that are different for every permutation listed in the chart. It follows that the possibility of a rearrangement proceeding by a stepwise sequence of permutations cannot be rigorously excluded.

Translating the permutational information gained from the above analysis into physical pathways for the rearrangement is very hazardous. Even if we concentrate on the favored bba process, we are faced with several alternatives. In particular the NMR experiment does not allow a distinction to be made between a one-step or a multistep process for carbonyl group permutations. For instance, as can be seen in Scheme I, the production of isomer F from A could involve three high-energy intermediates (two trigonal bipyramids and one of square-pyramidal geometry). On the other hand, Scheme II, synchronous rotation of the three carbonyl moieties about a pseudo $C_3$ axis,[44] would also convert A into F in one step and hence have the same permutational effect as the previous more involved process. It is also apparent that two mechanisms described above are related, within the limits imposed by the constraint of the diene moiety, to the well-known Berry pseudorotation and turnstile rotation, respectively, of five-coordinate molecules. Although, as mentioned before, a distinction between the two cannot be made, we wish to offer the following speculation concerning the possible ligand motions in the reported compounds. The first mechanism is attractive for explaining the greatly increased fluxional character of the 1,4- and 1,5-diene derivatives as compared to (η-1,3-diene)Fe(CO)$_3$ complexes. Indeed, as the ligand bite size decreases (1,5- > 1,4- > 1,3-diene) we anticipate a progressive destabilization of the required trigonal-bipyramidal intermediate and hence an increase in activation barrier, exactly as observed.[45] However, even though this mechanism might be operating for (η-1,4- and η-1,5-diene)Fe(CO)$_3$ molecules, the profound influence of the electronic structure of the 1,3-diene moiety on rearrangement rates is more difficult to account for in terms of the above model. For this reason we favor a physical pathway represented by Scheme II for the fluxionality of (η-1,3-diene)Fe(CO)$_3$ compounds. Indeed the "six-coordinate character" of the molecules which, as we discussed previously depends on the nature of the respective diene moiety, can easily be fitted into this model and account, therefore, for the trend observed in $\Delta G^{\ddagger}$ in the (η-1,3-diene)Fe(CO)$_3$ molecules. Should the actual mechanism be described as a turnstile rotation or a Bailar twist, due to the acquired "six-coordinate character", is a matter of semantics and need not be pursued any further.

**Scheme II**



We should also add that similar rotational motion to explain the exchange of carbonyl groups was assumed by both Clark[8,9,14] and Kreiter;[35] however our study seems to be the first to identify the importance and the role of the diene moiety in this regard.

**Carbonyl Group Chemical Shifts.** The interpretation of the $^{13}C$ NMR chemical shifts of carbon atoms directly bonded to transition metals has generated a great deal of interest and controversy. Restricting our attention to the carbonyl carbon atom in particular, it appears that the chemical shift moves to low field as the metal→carbonyl π-back-donation increases.[47] This experimental observation seems to have received some theoretical support.[48] However, in a recent publication Evans and Norton[49] cautioned against such a simplistic explanation and pointed out that the above correlation works only in closely related series. Although we fully subscribe to the advocated caution, we also believe that the identification of trends, albeit limited, is important since it should help to sort out the contributors and their importance to the chemical shift.

The averaged chemical shifts of the carbonyl groups of the reported complexes follow the π-back-bonding arguments. Conjugated 1,3-dienes, by virtue of their low-lying acceptor molecular orbital, are better π acids than nonconjugated dienes whose LUMO's are at higher energy. The extent of back-bonding into the carbonyl groups should therefore be conjugated dienes < nonconjugated dienes,[50] and, on the basis of the above model for the chemical shift, the carbonyl groups

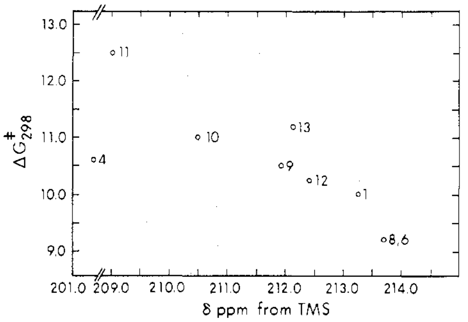


**Figure 4.** Carbonyl chemical shifts vs. $\Delta G^{\ddagger}_{298}$ for (1-4-η-diene)-tricarbonyliron complexes.

in (η-1,3-diene)$Fe(CO)_3$ should resonate at higher fields than in (η-1,4- and η-1,5-diene)$Fe(CO)_3$ complexes. The observed values in Tables I and III, 201.4–213.7 and 217.2–218.8 ppm, respectively, exactly mirror these expectations. Furthermore, even the variation of the averaged carbonyl chemical shifts within the conjugated diene series agrees with the predictions of the donor–acceptor model. It can be seen, Figure 3 and Table I, that as the π acidity of these ligands increases[51] in the order diene < triene < dienone < trienone, the chemical shift progressively moves to higher field, ca. 214–213, 212, 210, and 209 ppm, respectively. Indeed the reasonableness of the above correlation can be further tested with the present complexes. Since, to a first approximation, π acidity of the dienes also controls the activation barriers in these molecules, there should be a one to one correspondence between $\Delta G^{\ddagger}_{298}$ and $\delta_{CO}$. That this is the case can be seen in Figure 4. Although the correlation is far from linear, the increase in $\Delta G^{\ddagger}_{298}$ with upfield shifts in $\delta_{CO}$ is unmistakable. A notable exception to this is [η-tetrakis(trifluoromethyl)cyclopentadienone]tricarbonyliron, where the observed $\Delta G^{\ddagger}_{298}$ is very much smaller than the value expected from the above correlation. As discussed before, a change in the position of the HOMO level is believed to be responsible for this. So far in our discussion on carbonyl chemical shifts we have neglected the effect of the diene donor molecular orbital. This was a reasonable thing to do with most of the dienes, since the variations in these levels are less important than in the LUMO levels. This is because the iron d orbitals are closer to the LUMO than to the HOMO levels and therefore variations in these levels will affect less the electron distribution on iron. However, with a diene containing strongly electron-withdrawing groups both HOMO and LUMO levels are greatly stabilized. The result will be a much reduced back-bonding ability of iron to the carbonyl groups and a remarkably high-field carbonyl resonance. This, on the other hand, does not have to be followed by an increase in $\Delta G^{\ddagger}_{298}$ since the stabilization of the HOMO level works against the acquired "six-coordinate character" of the molecules. We note also that (1-methoxy-1,3-cyclohexadiene)tricarbonyliron does not seem to follow the regular trend either. The observed activation energy, 7.3 kcal $mol^{-1}$, is again much less than would be anticipated fromn the averaged $\delta_{CO}$ of 212 ppm. Stabilization of the diene donor molecular orbital *in the complex* is once more a plausible explanation for the apparent discrepancy. It is obvious that any prediction of fluxional behavior in these types of molecules from averaged carbonyl group chemical shifts must be done with extreme caution.

Although the so far mentioned chemical shifts could be accounted for in terms of back-bonding arguments, it is obvious that other factors are also important. The change of iron to ruthenium causes the carbonyl resonance to move upfield by approximately 14 ppm. Even though the concurrent increase in $\Delta G^{\ddagger}_{298}$ indicates that some of this shift is due to more effective electron removal by the diene, the generally observed high-field shift of the carbonyl resonances as one descends a transition metal triad[52] implicates some property of the central atom as instrumental for this observation.

Finally we wish to say a few words about the correlation between $^{13}C$ chemical shifts and carbonyl group force constants. In a careful study on (η-butadiene)-[8] and (η-1,3-cyclohexadiene)tricarbonyliron,[9] Clark concluded that whereas in the latter complex the $k_{basal}$ ($k$ is the force constant) and $k_{apical}$ were essentially identical, in the former molecule $k_{apical}$ was greater than $k_{basal}$. However, in the low-temperature limiting spectra of the present 1,3-diene complexes the basal carbonyl moieties invariably resonate to *high* field of the apical group. This is contrary to the usual observation of increased force constants resulting in high-field shifts.[47,53] Does this mean that we should abandon the metal→carbonyl π-back-bonding as a reasonable working framework to explain the chemical shift trends in an analogous series of metal carbonyls? We think not. In fact our ability to account for the averaged chemical shifts in the present complexes and in (olefin)$Fe(CO)_4$ molecules[54] in terms of this model and the correlation between $\delta_{CO}$ and $\Delta G^{\ddagger}$ for carbonyl scrambling can be cited as further corroborating evidence for its qualitiative success. On the other hand, the breakdown of the correlation between chemical shifts and force constants clearly shows that the expectation of a one to one correspondence between an experimentally measured quantity ($\delta_{CO}$), with all its contributors, and a calculated number ($k_{CO}$), from which some of these contributors might have been subtracted, is a fallacious one. The limited success of the correlation is therefore not unexpected.

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**Registry No. 1**, 12078-32-9; **2**, 33504-08-4; **3**, 12321-08-3; **4**, 12088-68-5; **5**, 54362-20-8; **6**, 12152-72-6; **7**, 12108-25-7; **8**, 34779-20-9; **9**, 36343-88-1; **10**, 34829-59-9; **11**, 12116-22-2; **12**, 33270-50-7; **13**, 53922-85-3; (cycloocta-1,5-diene)$Fe(CO)_3$, 12093-20-8; (norbornadiene)$Fe(CO)_3$, 12307-07-2; (tetrafluorobenzobicyclo[2.2.2]octatriene)$Fe(CO)_3$, 12130-08-4; $^{13}C$, 14762-74-4.

**Supplementary Material Available:** Table IV listing the rate data utilized to obtain the activation energies appearing in Table I (1 page). Ordering information is given in any current masthead page.

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(22) Programs used: (a) DNMR3 by G. Binsch—QCPE, Bloomington, Ind.; (b) ACTPAR by G. Binsch and EXCHSYS by G. M. Whitesides, Massachusetts Institute of Technology.

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(37) L. K. K. Li Shing Man, and J. Takats, in preparation.

(38) This compound has also been investigated by Whitesides et al.;[15] our values are in reasonable agreement with theirs.

(39) In agreement with this is the decrease in Δ on going from $(C_8H_8)Fe(CO)_3$ (0.00 Å) to $(C_8H_8)Ru(CO)_3$ (−0.05 Å).[40]

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# Two-Dimensional Magnetic Systems. Structural and Magnetic Characterization of Bis(propylene-1,3-diammonium) Tetrachlorocuprate(II)

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The crystal structure and magnetic properties of the compound bis(propylene-1,3-diammonium) tetrachlorocuprate, $[H_3NC_3H_6NH_3]CuCl_4$, have been determined. The material crystallizes in the orthorhombic space group *Pnma* ($D_{2h}{}^{16}$) with four formula units in a cell of dimensions $a = 7.200$ (2), $b = 18.246$ (6), and $c = 7.451$ (2) Å. Least-squares refinement of 1209 independent reflections has led to a final $R$ factor (on $F$) of 0.036. The structure consists of tetragonally distorted $[CuCl_6]^{2-}$ units which are chloro bridged to form a two-dimensional layer. Within the two-dimensional network there are two short copper–chloride bond distances of 2.275 (4) Å and two long Cu–Cl distances of 2.946 (4) Å. There are two copper–chloride bonds nearly perpendicular to the bridged network with distances of 2.314 (4) Å. The intralayer bond angles at copper are 87.70 (2) and 92.30 (2)° with the Cu–Cl–Cu bridging angle being 165.70 (4)°. The chlorocuprate sheet is puckered as a result of hydrogen bonding to the propylene-1,3-diammonium ions which lie between the layers. Magnetic susceptibility data collected on powdered and single-crystal samples revealed two-dimensional magnetic interactions with $J/k = 15.4$ K above the three-dimensional ordering temperature of 13.5 K. In the ordered state the preferred direction of the spins is along $c$ (perhaps with some canting) with the next preferred direction apparently perpendicular to the layer. This unusual result reflects the small interlayer separation of 9.123 (3) Å.

## Introduction

Compounds of the type $[H_3NC_nH_{2n+1}]_2MX_4$ ($n$ = 0, 1, 2, ...; M = Cu, Mn, Fe; X = Cl, Br) have been known for some time to exhibit two-dimensional magnetic behavior at temperatures above $T_c$,[1] a typical value of the ratio of interlayer $J'$ to intralayer exchange $J$ ($J'/J$) being less than $10^{-4}$ for $n$ greater than 2.[2] The pronounced two-dimensional properties arise by the separation of the $MX_4$ layers by the organic