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Localized and Internuclear Carbonyl Scrambling in Azulenepentacarbonyldiiron(*Fe–Fe*) and Its Ruthenium Analogue

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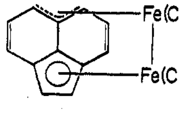
The molecules $(C_{10}H_8)Fe_2(CO)_5$ and $(C_{10}H_8)Ru_2(CO)_5$ have been shown to be fluxional by carbon-13 NMR. The slow-exchange spectrum for each molecule consists of five distinct carbonyl resonances. This is consistent with the crystallographically determined structure of $(C_{10}H_8)Fe_2(CO)_5$. On the basis of its NMR spectrum at −90 °C $(C_{10}H_8)Ru_2(CO)_5$ is assigned the same gross structure. Between −125 and −16 °C for the iron compound and between −90 and 29 °C for the ruthenium compound, three distinct carbonyl resonances of the $M(CO)_3$ groups are seen to collapse and form a single peak. From line shape analysis the activation energies for these processes are $E_a = 9.7 \pm 0.6$ and 11.5 ± 0.7 kcal mol^{-1} for the iron and ruthenium compounds, respectively, assuming $A = 10^{13.2}$ in each case. At higher temperatures all five carbonyl groups are observed to scramble. The observed line shape changes are well reproduced by calculated spectra based on a random-exchange matrix. Activation energies (again assuming $A = 10^{13.2}$) for these processes are $E_a = 15.4 \pm 1.0$ and 18.3 ± 1.1 kcal mol^{-1} for the iron and ruthenium compounds, respectively.

Introduction

Following our early studies of carbonyl scrambling in binuclear complexes of the type in which polyolefin ligands attached to the metal atoms were separate and unconnected for the two metal atoms, e.g., $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_4$ and its derivatives[1–5] and $(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_5(CNCH_3)$,[5,6] we have examined some systems in which each metal atom is attached to a different portion of one large polyolefin. A few that we have published include **1**,[7] **2**,[7], **3**,[8] **4**,[9] **5**,[9] and **6**.[10]



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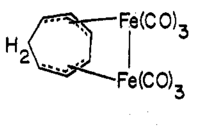

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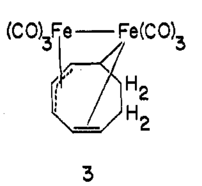

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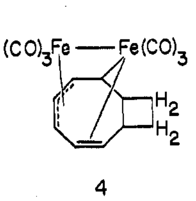

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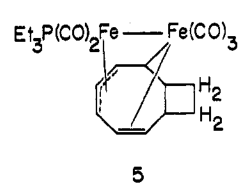

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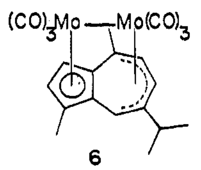

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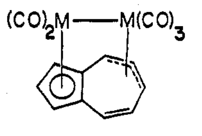

M = Fe 7
Ru 8

In the compounds with separate olefinic ligands on each metal atom mentioned above,[1–6] as well as $(\eta^5\text{-}C_5H_5)_2Rh_2(CO)_3$,[11] the characteristic process is *inter*nuclear exchange of CO groups; CO groups pass from one metal atom to the other, with bridged structures providing a low-energy pathway. Thus far, our studies of molecules with both metal atoms attached to the same large relatively rigid polyolefin have failed to reveal any indication of such *inter*nuclear exchange. For compounds **1** and **3–6**, the experimental results positively rule out the possibility of internuclear exchange. For structure **2**, the observations do not exclude it, but they can be fully and satisfactorily explained by assuming only local averaging, that is, scrambling of CO groups within each of the individual $Fe(CO)_3$ groups.

We report here the occurrence of internuclear scrambling in the case of (azulene)$Fe_2(CO)_5$ (**7**) and (azulene)$Ru_2(CO)_5$ (**8**). The structure of the iron compound was determined x-ray crystallographically some years ago by Churchill.[12]

Experimental Section

All samples were handled under nitrogen. Hexane and toluene were dried over Na–K alloy and distilled prior to use. CH_2Cl_2 was stored over molecular sieves and purged with nitrogen before use. Infrared spectra were recorded on a Perkin-Elmer 467 spectrometer. Carbon-13 NMR spectra were recorded on a Jeol-100/Nicolet 1080 FT system at 25.0352 MHz.

Azulenepentacarbonyldiiron, **7**, was prepared by reacting azulene (0.5 g, 3.9 mmol) with $Fe_2(CO)_9$ (3.6 g, 10 mmol) in 50 ml of hexane at room temperature for 40 h. After removal of the solvent at low pressure the residue was extracted with 1:1 CH_2Cl_2–hexane. Chromatography on 100–200 mesh Florisil using 1:1 CH_2Cl_2–hexane as eluent yielded **7** as a dark red band. The solution was concentrated and crystallized at −30 °C. The compound was identified by its IR spectrum in CS_2 (carbonyl bands at 2040, 1990, and 1970 cm^{-1}) and by the unit cell dimensions obtained for a single crystal, $a = 7.37$ Å, $b = 14.51$ Å, $c = 14.83$ Å, $\alpha = 116.0°$, $\beta = 92.9°$, and $\gamma = 92.2°$. These data agree with values previously reported in the literature.[12,13]

Attempts to prepare azulenepentacarbonyldiruthenium, **8**, by a literature procedure[14] in heptane yielded only $Ru_3(CO)_7(C_{10}H_8)$, as identified by IR spectroscopy. When toluene was used as the solvent, satisfactory yields of $(C_{10}H_8)Ru_2(CO)_5$ were obtained. Azulene (0.25 g, 1.95 mmol) and $Ru_3(CO)_{12}$ (0.5 g, 0.782 mmol) were refluxed in 250 ml of toluene for 24 h. After removal of solvent at low pressure, excess azulene was recovered by sublimation at room temperature and 10^{-3} Torr. The residue was extracted with CH_2Cl_2 and chromatographed on a 30 × 1.5 cm column packed with alumina, activity grade III, and using 1:4 CH_2Cl_2–hexane as eluent. The yellow band

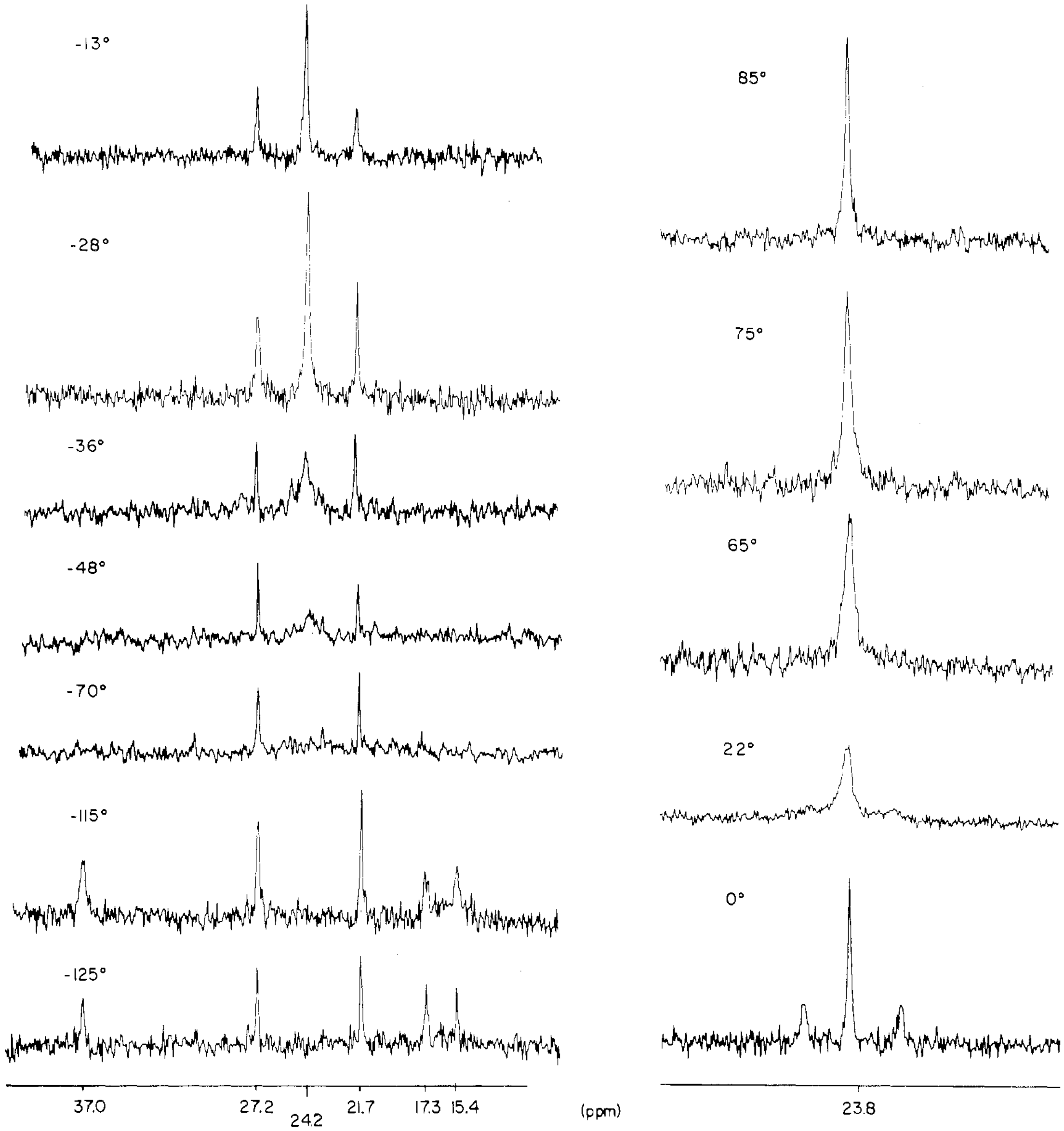

Figure 1. Spectra of $(C_{10}H_8)Fe_2(CO)_5$ from −125 to +85 °C in the carbonyl region. Chemical shifts are measured from internal CS_2.

containing $(C_{10}H_8)Ru_2(CO)_5$ yielded 0.3 g. The compound was identified by its infrared spectrum in hexane (carbonyl bands at 2060, 2007, 1992, and 1945 cm^{-1}) and by analysis. Anal. Calcd for $C_{15}H_8O_5Ru_2$: C, 38.3; H, 1.71. Found: C, 37.8; H, 1.6.

The temperatures were measured with a thermocouple inserted in the probe in an NMR tube containing solvent. The temperature was read from a Leeds and Northup 913 thermometer and remained constant within ±2 °C. $Cr(acac)_3$ (5 mg) was added to aid in the relaxation of the carbonyl carbon nuclei.

Solvents for the carbon-13 NMR spectra of **7** were 1:2 CH_2Cl_2–Freon 21 with 10% CD_2Cl_2 for spectra below −70 °C, 85% CH_2Cl_2–15% CD_2Cl_2 for spectra from −70 °C to room temperature, and 85% toluene–15% toluene-d_8 for spectra above room temperature; 5% CS_2 was added as a chemical shift standard.

Solvents for **8** were 40% $CDCl_3$–60% CH_2Cl_2 for spectra from −90 °C to room temperature and 20% C_6D_6–80% toluene for temperatures above 29 °C; 5% TMS was added as a reference; 5% CS_2 was used as a reference from 73 to 95 °C.

Computer-simulated spectra were prepared using a locally modified form of the program DNMR3 by D. A. Kleier and G. Binsch. In every case, the $M(CO)_3$ group in its own fast-exchange limit was treated as having three equivalent sites. Thus, the entire $M_2(CO)_5$ group was considered as an abc_3 system. The line shapes were calculated for four different permutation matrices, m_1–m_4.

$$\underset{m_1}{\begin{bmatrix} -1 & 0 & 1 \\ 1 & -1 & 0 \\ 0 & \frac{1}{3} & -\frac{1}{3} \end{bmatrix}} \qquad \underset{m_2}{\begin{bmatrix} -1 & 1 & 0 \\ 0 & -1 & 1 \\ \frac{1}{3} & 0 & -\frac{1}{3} \end{bmatrix}}$$

$$\underset{m_3}{\begin{bmatrix} -\frac{1}{2} & 0 & \frac{1}{2} \\ 0 & -\frac{1}{2} & \frac{1}{2} \\ \frac{1}{6} & \frac{1}{6} & -\frac{1}{3} \end{bmatrix}} \qquad \underset{m_4}{\begin{bmatrix} -1 & \frac{1}{2} & \frac{1}{2} \\ \frac{1}{2} & -1 & \frac{1}{2} \\ \frac{1}{6} & \frac{1}{6} & -\frac{1}{3} \end{bmatrix}}$$

In the Results section we shall designate the permutation represented by m_4 as "random exchange". A description of certain physical processes that these matrices represent will be found in the Discussion. The observed line shapes were about equally well reproduced by all four of the permutation schemes. Calculations using m_4 were carried out at close lifetime intervals in order to obtain the best fit for kinetic analysis.

Results

The carbon-13 NMR spectra of **7** in the carbonyl region from −125 to +85 °C are shown in Figure 1 Between −125 and −36 °C three resonances at 37.0, 17.3, and 15.4 ppm corresponding to the $Fe(CO)_3$ group are seen to collapse and form a single peak at 24.2 ppm. This peak lies almost exactly midway between the other two peaks which arise from the $Fe(CO)_2$ group. Thus, when the latter two peaks coalesce,

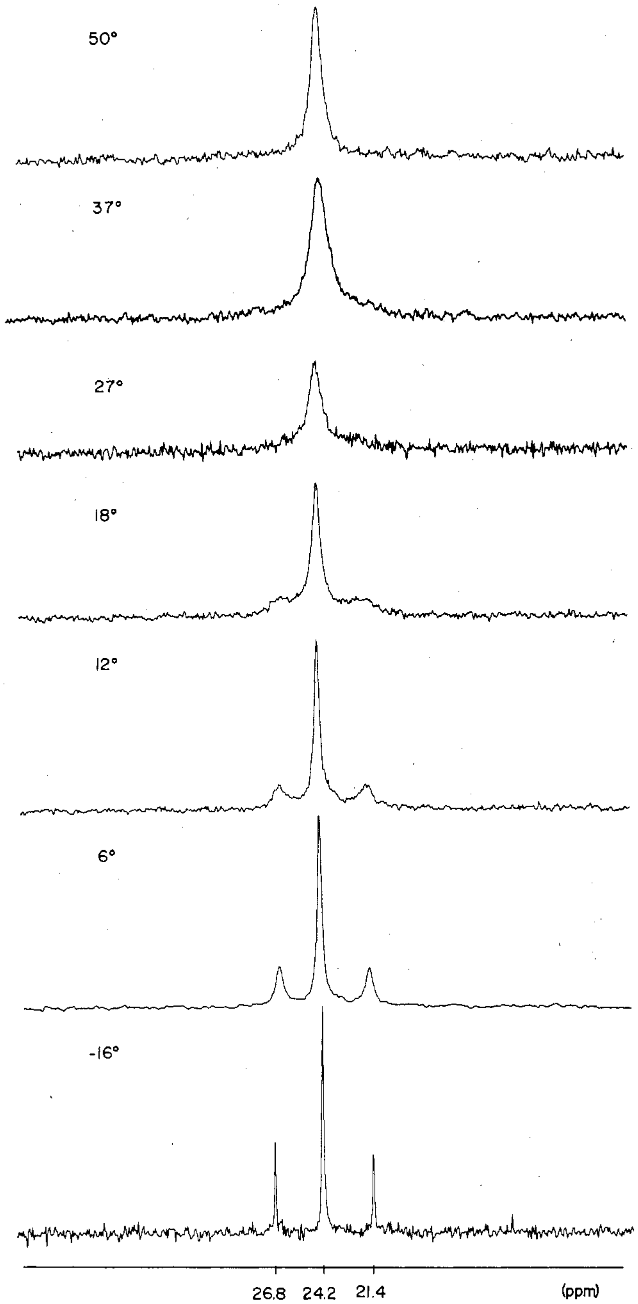

Figure 2. Spectra of $(C_{10}H_8)Fe_2(CO)_5$ from −16 to +50 °C. Recorded after accumulating 30 000–25 000 scans.

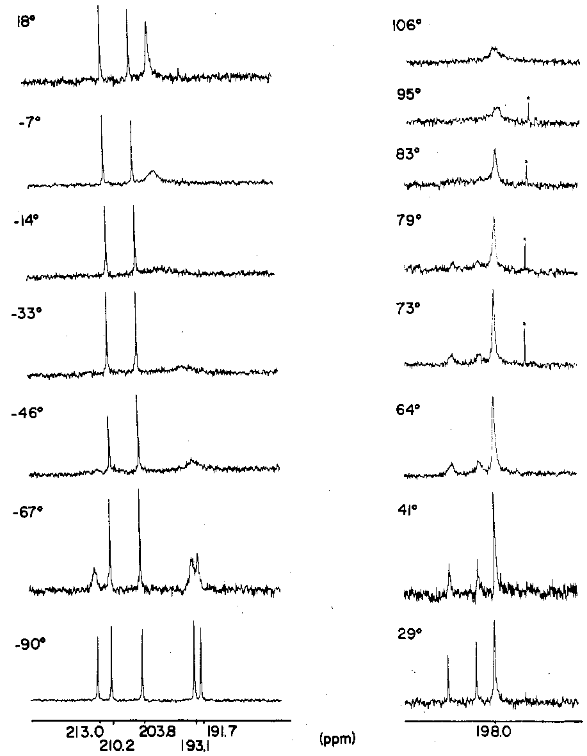

Figure 3. Spectra of $(C_{10}H_8)Ru_2(CO)_5$ in the carbonyl region. Chemical shifts are measured from internal TMS. The peak marked is due to CS_2.

the resultant peak of relative intensity 2 is expected to be superimposed upon the peak of relative intensity 3. However, the spectra between 0 and 65 °C, especially that at 22 °C, in Figure 1 suggest that we are dealing not with a case of simple superposition of peaks but with a coalescence of all three of the peaks. If this were not so, we should expect to see a persistent sharp spike of relative intensity 3 at or near the center of a much broader signal of relative intensity 2 in the 20–60 °C temperature range. Instead, once the two small, outer peaks have disappeared, there appears to be only one broadened signal that narrows with further increase in temperature.

The spectra in Figure 2 were recorded in order to cover the pertinent range of temperature at much closer intervals. They leave no doubt that the peaks of relative intensity 1 are coalescing not only with each other but also with the central peak of relative intensity 3. Moreover, the experimental spectra are consistent with simulated spectra computed using a random internuclear exchange matrix. From line shape analysis (vide infra) the activation energy for this process is found to be 15.4 ± 1.0 kcal mol^{-1}.

The spectra for **8** again provide unambiguous evidence for internuclear scrambling in that compound. In Figure 3 it can be seen that the 29 °C spectrum of **8** is analogous to the −16 °C spectrum of **7** (Figure 2). For the ruthenium compound, however, the peak due to the three carbonyl groups of the $M(CO)_3$ group lies upfield relative to the two peaks of the $M(CO)_2$ group. It is very clear that above 70 °C the peak of relative intensity 3 collapses. The experimental spectra of **8** from 29 to 106 °C were satisfactorily simulated using a random-exchange matrix, and the activation energy for the internuclear exchange process in **8** was found to be 18.3 ± 1.1 kcal mol^{-1}.

For both **7** and **8** line shape analysis was used to determine the activation energies for the localized scrambling of the CO groups in the $M(CO)_3$ units. The results are 9.7 ± 0.6 kcal mol^{-1} for $(C_{10}H_8)Fe_2(CO)_5$ and 11.5 ± 0.7 kcal mol^{-1} for $(C_{10}H_8)Ru_2(CO)_5$.

In all of the above evaluations of the Arrhenius activation energies, the conventional Arrhenius plots lead to doubtful values of log A, some as high as 16.0. This is not an uncommon situation and it may be caused by either systematic or random errors in the data, or by both. Binsch[15] has given a thorough discussion of the problem, in which he points out that $\Delta G^\ddagger$ is relatively insensitive to errors, even when $\Delta S^\ddagger$ and $\Delta H^\ddagger$ are seriously affected, because errors in the latter two generally compensate each other in the expression for $\Delta G^\ddagger$. However, $\Delta G^\ddagger$ is a function of temperature and is therefore a less desirable quantity than $\Delta H^\ddagger$ or the Arrhenius activation energy, E_a. We prefer to use the rates at several temperatures near the coalescence temperature and assume a frequency factor of $10^{13.2}$ (corresponding to $\Delta S^\ddagger = 0$) for each, since for a true unimolecular process the entropy of activation should be close to zero. The uncertainty intervals quoted for the E_a values are based on the scatter in the rates plus 0.50 to allow

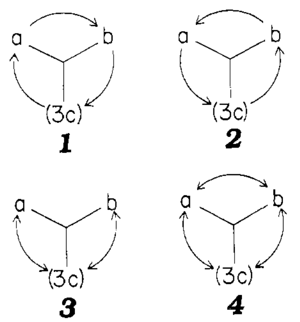

Figure 4. Some possible CO scrambling pathways which may be considered to explain the observed spectra.

for an interval of 2 cal mol^{-1} deg^{-1} in the assumed $\Delta S^{\ddagger} = 0$ value.

Discussion

The observations made on compounds **7** and **8** raise three points that we wish to discuss here.

Scrambling within the $M(CO)_3$ Groups. As noted in the Introduction, several molecules previously studied (**1**–**5**) have exhibited scrambling within individual $Fe(CO)_3$ groups. In addition to those mentioned there, other cases have been reported.[16–19] For the cases cited, activation energies range from about 7 to about 15 kcal mol^{-1} and coalescence temperatures from about 160 to 335 K. Thus, the coalescence temperature (ca. 200 K) and E_a (ca. 10 kcal mol^{-1}) for the $Fe(CO)_3$ group in **7** are quite ordinary.

Internal scrambling in the $Ru(CO)_3$ group of **8** has a coalescence temperature that is higher by about 50 K and an activation energy that is higher by about 2 kcal mol^{-1}. Increased hindrance to internal scrambling for $Ru(CO)_3$ as compared to an analogous $Fe(CO)_3$ has been observed in other cases[19,20] and is not, therefore, surprising.

Pathway for Internuclear Scrambling. The only new, important mechanistic fact that we have estabished with certainty is that all five CO groups are scrambled over the two iron nuclei in the high-temperature process. Unfortunately, we have not been able to identify the pathway by which this occurs or even to eliminate objectively any of a number of imaginable pathways.

Figure 4 shows some possible pathways. Those shown as *1* and *2* are similar to the mode of circulation of CO groups, via a doubly bridged intermediate structure, that is believed to take place in $[(\eta^5\text{-}C_5H_5)Mo(CO)_3]_2$. In the present case the two directions of circulation are not equivalent. The permutations of nuclei caused by these motions are described by the matrices m_1 and m_2 (see Experimental Section), while an equal mixture of both is described by the matrix m_4. The matrix m_4 represents what we have earlier designated random scrambling. The line shapes calculated using m_1, m_2, or m_4 differ so little from each other, and from the experimental spectra, that it was impossible to choose among them. We have also considered pathway *3*, in which a and b each independently exchange with the three c sites; for the special case where a and b exchange with c at the same rate, the matrix m_3 is applicable. In process *4* we have the added feature of direct a–b exchange. This might occur by rotation of the a–Fe–b group or, indirectly, by way of an intermediate in which one of the c type carbonyls passes temporarily to the other iron atom and there is rapid scrambling within this temporary $Fe(CO)_3$ group, followed by restoration of one CO group to a place on the other Fe atom. Process *4* is also represented by matrix m_4; that is, it is also a random-scrambling process, permutationally indistinguishable from the equal mixture of *1* and *2*. Once again, the line shapes obtained using the different matrices, m_3 and m_4, differ so little that no decision can be made as to which, if either, is correct.

Why Internuclear Scrambling Occurs. The question of why internuclear scrambling occurs in **7** but not, for example, in **1** merits attention. The Fe–Fe distances, 2.77[21] and 2.78 Å,[12] for **1** and **7**, respectively, are not significantly different. The most conspicuous difference is the orientation of the η^3-allyl group, but there are, of course, other differences with respect to conformational factors, rigidity of the polycyclic olefin ligand and possibly steric hindrance. At this time we cannot propose any specific explanation of the different degrees of CO scrambling in the two compounds. We are, however, actively studying a number of related systems in the hope of obtaining clues as to which factor or factors are critical.

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Registry No. 7, 12087-76-2; **8**, 57903-36-3; $Fe_2(CO)_9$, 15321-51-4; $Ru_3(CO)_{12}$, 15243-33-1.

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