A Fluxional Organometal Carbonyl Molecule with Several Scrambling Processes. Carbon-13 Nuclear Magnetic Resonance Study of (η^6-Cyclooctatriene)(hexacarbonyl)diiron(*Fe–Fe*)

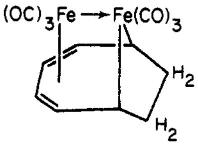
F. Albert Cotton,* Douglas L. Hunter, and Pascual Lahuerta

Contribution from the Department of Chemistry, Texas A&M University, College Station, Texas 77843. *Received September 3, 1974*

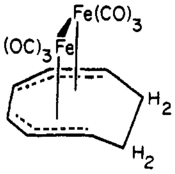
Abstract: The molecule $C_8H_{10}Fe_2(CO)_6$ (C_8H_{10} = 1,3,5-cyclooctatriene) had previously been shown to be fluxional to the extent that in the high temperature limit it has an nmr plane of symmetry according to its proton nmr spectrum, but the pathway for the rearrangement had not been ascertained. We have found by ^{13}C nmr that the fluxionality of the molecule is very extensive and consists of three processes, two of which occur in the same low-temperature range and the third much higher. At the lowest temperatures, (below −65°) the ^{13}C nmr spectrum is in complete accord with the skew structure observed in the crystal. There are eight separate ring carbon signals and six separate carbonyl carbon resonances. The first set of changes, observed, from −65° to about 8°, results from a "twitching" process in which the two enantiomorphous forms of the structure interconvert by the minimal movement of the $Fe_2(CO)_6$ group relative to the C_8H_{10} group, without interchanging the two ends of the $Fe_2(CO)_6$ group. Simultaneously, the three carbonyl groups on one of the iron atoms are scrambled among themselves. These two processes together cause the spectrum in the carbonyl region to collapse to a three-line (1:3:2) pattern. Above 8° the lines of intensity 1 and 2 collapse and coalesce giving a high-temperature spectrum consisting of two lines; this is caused by scrambling of the three CO groups on the other iron atom among themselves. The observations entirely rule out the occurrence of (1) a gliding motion of the $Fe_2(CO)_6$ group in which the iron atoms would change places and (2) any passage of CO groups from one metal atom to the other. Nevertheless there are three intimate mechanisms which qualitatively explain the observations. Reasons are given for preferring one of them, in which the twitching motion and internal scrambling of the three CO groups on the allyl-bound iron atom occur essentially simultaneously (−60 to 8°), while scrambling of CO groups on the other iron atom becomes rapid only at much higher temperatures (8-110°).

Since the first published mechanistic study of a fluxional molecule by nmr spectroscopy[1] in 1966, there has been a plethora of such investigations[2] particularly in the fields of organometallic and metal carbonyl compounds. The majority have been conducted using proton nmr spectroscopy, but in the last few years the advantages of ^{13}C nmr have been brought to bear on several such problems with marked success.[3-15]

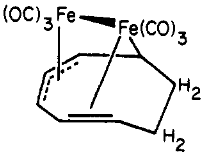
We have now applied ^{13}C nmr to a problem in which proton nmr had previously been used[16] but was recognized[17] to be incapable of providing a complete and unambiguous solution. The molecule in question is (η^6-cyclooctatriene)(hexacarbonyl)diiron(*Fe–Fe*), $C_8H_{10}Fe_2(CO)_6$. After two incorrect guesses, **1a** and **1b**, had been published, the correct structure of this molecule in the crystal was revealed by X-ray crystallography[18] to be **1c**. Since this unsymmetrical structure is incompatible, if rigid, with the apparent presence of a plane of symmetry, according to the proton nmr spectrum at ambient temperature, a study of the spectrum at lower temperatures was conducted.[16] It was found that a low-temperature limiting spectrum consistent with the unsymmetrical structure was exhibited at *ca.* −100° and that this underwent broadening and finally re-formed to give the spectrum indicative of a symmetrical structure, beginning at *ca.* 0°. At this juncture it seemed plausible to attribute these changes to the type of rearrangement shown in Scheme IA, which can be called the "twitching" process, although there was nothing in the experimental data to rule out the alternative "gliding" process shown in Scheme IB. For the two processes, twitching and gliding, the symmetrical intermediate configurations are those shown in Figure 1a and 1b, respectively. These are formally analogous to the previously postulated ground state structures, **1a** and **1b** for the molecule.



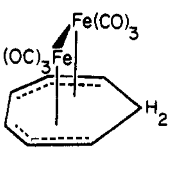
1a



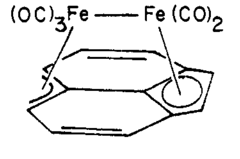
1b



1c

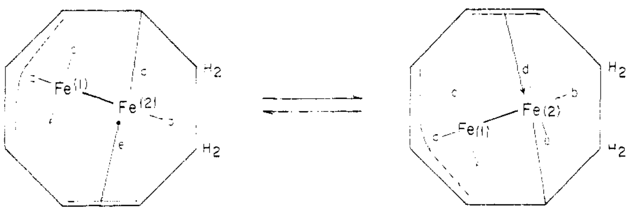


2

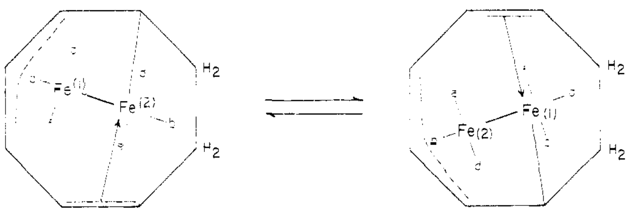


3

Scheme I

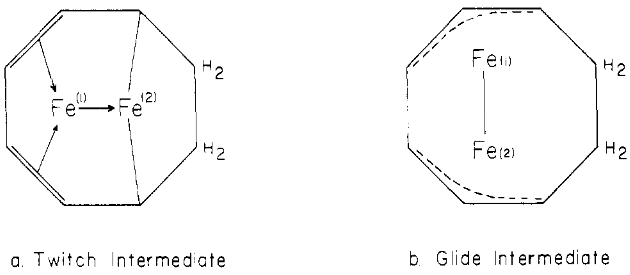


A. The Twitching Process



B. The Gliding Process

When it was later discovered[17] that the cycloheptatriene analog actually had the ground state structure shown as **2**, which is analogous to **1b**, the possibility of a gliding process gained considerably in plausibility. The type of structure



a. Twitch Intermediate

b. Glide Intermediate

Figure 1. Diagrams showing the relation of the pair of iron atoms to the C_8H_{10} ring at the midpoint of the motion for (a) the twitch process of rearrangment, and (b) the glide process of rearrangement.

exhibited in **2**, which takes the form **1b** in the cyclooctatriene case, would constitute an intermediate stage of the gliding process. Since it was now seen to be the preferred structure for a rather similar compound, the possibility of its lying at the midpoint of a low energy pathway for the interconversion of the enantiomorphs of **1c** had to be taken very seriously. Indeed, as emphasized by Figure 1, this type of intermediate with its resemblance to an observed structure, **2**, could perhaps have been considered even more plausible than the intermediate for the twitching mechanism since the latter type of structure, though once postulated[19] as the ground state structure for **1**, has not actually been observed in any closely similar molecule (see, however, the Discussion section).

It was recognized[17] that data capable of distinguishing between these two mechanisms should be obtainable from the behavior of Fe, C, or O nuclei of the $Fe_2(CO)_6$ moiety since in Scheme IA the two ends remain distinct, while in Scheme IB they interconvert. Thus, a study of the ^{13}C nmr spectrum of the compound was undertaken as soon as facilities became available. The results are reported and interpreted here.

Because of the vital role it will play in our analysis of the results to be presented here, we point out that the behavior of the carbonyl groups in **2** and **3**, which are both nonfluxional as far as ring-to-metal rearrangements are concerned, has been investigated recently by ^{13}C nmr.[15] It was found that in each case the nonequivalent carbonyl ligands within each $Fe(CO)_3$ group undergo exchange, presumably by a rotatory motion. Since the molecule under discussion in this paper also contains $Fe-Fe(CO)_3$ groups, such processes must be kept in mind when interpreting the spectra.

Experimental Section

The compound $C_8H_{10}Fe_2(CO)_6$ was prepared according to the method of King[19] and handled under nitrogen at all times. The solvents used were stored over Na-K alloy with benzophenone present and distilled just prior to use.

The carbon-13 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 a 10-mm diameter serum-stoppered nmr tube with a syringe. The spectra below ambient temperatures were obtained in CH_2Cl_2 with toluene-d_8 (15%) furnishing a deuterium lock and CS_2 (10%) as a reference. The spectra above −10° were recorded in *o*-dichlorobenzene or toluene with toluene-d_8 (15%) for an internal lock. To aid in the relaxation of the carbonyl carbon atoms, 35 mg of Cr(Acac)[4] was added to each tube. The variable temperature unit was calibrated by placing a copper-constantan thermocouple in an nmr tube inside the probe. The temperature was read from a Leeds and Northup Model 913 digital thermometer and was constant to ±2°.

Results

The carbon-13 spectra (proton decoupled) are shown in Figure 2 over the complete chemical shift range, with the CO carbon signals downfield (left) and the ring carbon signals upfield (right). There are three solvent signals in these spectra, easily recognized as such by their temperature invariance. In all eight traces, from −65 to +90°, there is a septet at the extreme right due to the methyl carbon atom of toluene-d_8. In the four spectra from −65 to −35° there is a sharp signal due to CS_2 observed just to the right of the signals from the carbonyl carbon atoms. Also in the four spectra from −65 to −35° there is an intense signal from CH_2Cl_2.

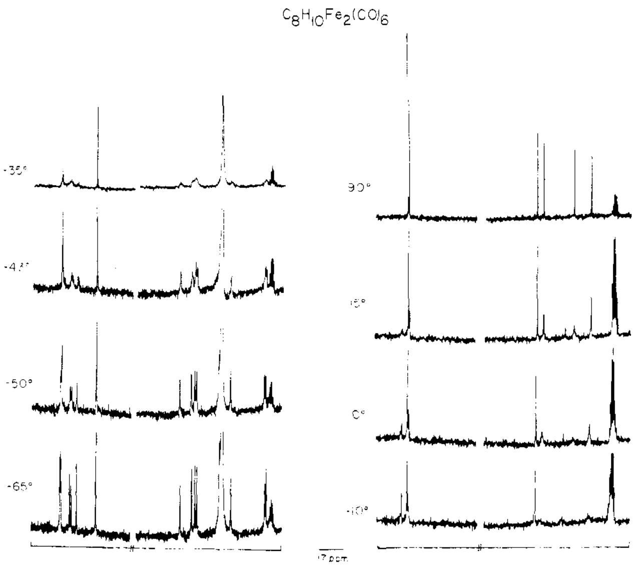


Figure 2. The ^{13}C nmr spectra of $C_8H_{10}Fe_2(CO)_6$ from −65 to 90°. Carbonyl carbon signals are at low field (left) and ring carbon resonances are at high field (right). For further details and assignments see text.

Ring Resonances. For the ring resonances, the chemical shifts are given in Table I, with the scale in parts per million from CS_2. Also suggested in Table I is a possible pairing of the eight low-temperature resonances to give the four-line spectrum observed in the fast-exchange limit. Some other slightly difference pairings, in which the 167.6 and 168.4 and/or the 119.4 and 120.7 ppm signals are interchanged might be correct, but we think a strong case can be made for those we have chosen. The main reason for pairing the 168.4 ppm signal rather than the 167.6 ppm signal with that at 144.2 ppm is that the former appears to be collapsing more rapidly, and this suggests that it is exchange-related to a closer resonance. The pairing of the 167.6 ppm signal with that at 120.7 ppm rather than either of those in the vicinity is that this choice gives the best agreement of observed with calculated chemical shifts for both the 118.4 and 144.0 ppm resonances at 90°. The pairing chosen to explain the 122.8 ppm signal at 90° is clearly the only possible one.

Table I. Chemical Shifts[a] for the Ring Carbon Atoms of $C_8H_{10}Fe_2(CO)_6$

−65°	+90° Obsd	Calcd
109.4		
117.2	118.4	118.3
119.4		
120.7	122.8	122.8
136.2		
144.2	144.0	144.2
	155.9	156.3
167.6		
168.4		

[a] Ppm upfield from CS_2, ±0.1 ppm.

It is not possible on the basis of the data at hand to suggest an assignment. The important conclusion, which follows unequivocally without any assignment, is that the eight-line spectrum expected for structure **1c** collapses and re-forms as a four-line spectrum thus showing that there is an increasingly rapid interconversion of the two enantiomorphs of **1c** with increasing temperature. The previous conclusion drawn from the proton spectra is therefore fully confirmed.

From the coalescence temperatures of three of the four pairs of averaging signals we estimate rates of 5.22×10^3 sec^{-1} at 263°K and 2.78×10^3 sec^{-1} at 248°K. From these rates, assuming a frequency factor of $10^{13.3}$ ($\Delta S^{\ddagger} = 0$) in the Arrhenius equation, the activation energy can be estimated to be about 11.7 ± 1.0 kcal mol^{-1}.

Carbonyl Resonances. We turn now to the behavior of the carbonyl carbon resonances, which are shown in more detail and over a slightly wider temperature range in Figure 3. The chemical shifts, measured downfield from CS_2 are indicated on the figure. The spectrum at −75° again confirms the structure **1c** which requires the presence of six signals of equal intensity, as observed.

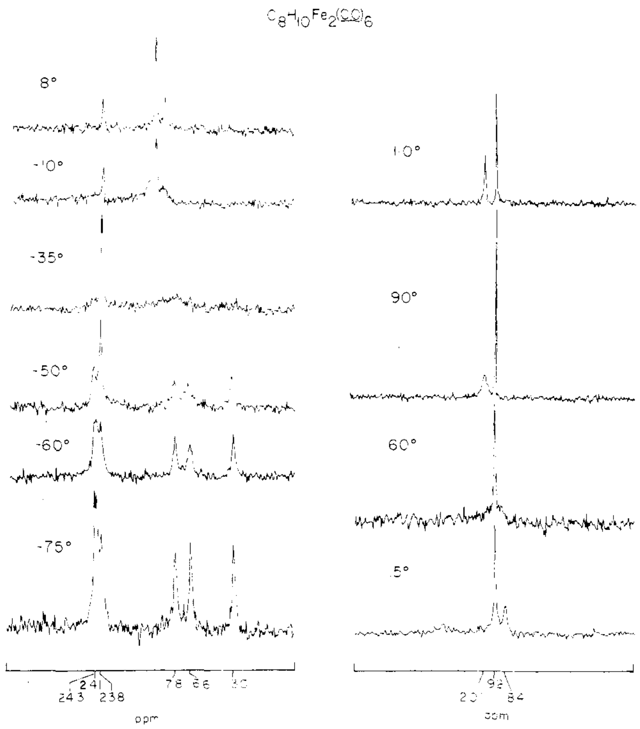


Figure 3. The carbon-13 nmr spectrum at various temperatures in the region of the carbonyl carbon resonances. Chemical shifts are in ppm downfield from CS_2.

The behavior of the carbonyl resonances as the temperature is raised is complex and shows several stages of selective line shape changes. As was first shown in the study[1] of (η^5-C_5H_5)Fe(CO)$_2$(η^1-C_5H_5), selective line shape changes provide mechanistic information if correctly interpreted. The changes observed here have the following critical features. (1) Between −75 and −35°, five of the six lines, the exception being one of those at low field, (23.8 ppm) collapse uniformly so that at −35° all that can be seen is the one sharp signal at *ca.* 24 ppm and a residual, broad signal at 18–19 ppm. (2) As the temperature is raised to about 0° a new resonance of relative intensity 3 appears at 19.2 ppm and another of intensity 2 at 18.3 ppm. (3) The resonance at 19.2 ppm is fully sharpened by about 8°, and remains sharp and distinct at all higher temperatures, whereas the resonance at 18.3 ppm never becomes fully narrowed before it begins to collapse again between 8 and 15°. Beginning at above −35° the signal at *ca.* 24 ppm which had remained sharp begins to broaden and has virtually collapsed at 15°. (4) At room temperature and up to about 80° the spectrum *appears* to consist of but one signal, as previously reported.[20] However, the isolated observation of a single line at about room temperature can be entirely misleading if it is taken to mean that all six CO groups have become time-average equivalent. The spectra at temperatures below this point show, of course, that this signal cannot represent all of the carbonyl groups. However, striking proof that it represents just three of them is obtained at higher temperatures. (5) As seen in the spectra at 90 and 110° (severe decomposition prevents measurements at any higher temperature) a second signal appears at 20.1 ppm. Its integrated intensity is equal to that of the signal at 19.2 ppm although even at 110° it does not become quite as narrow.

Discussion

The results just presented give a great deal of insight into the dynamical properties of this molecule. They allow us to draw several rigorous conclusions, but (at least) three intimate mechanisms are consistent with the pattern of line shape changes unless additional arguments based on assignments and analogies are also employed.

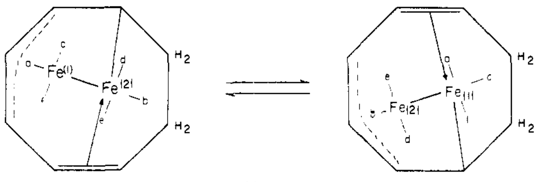
Rigorous Conclusions. From the fact that the high-temperature spectrum contains two resonances of equal intensity, we know that the two ends of the $(OC)_3Fe$–$Fe(CO)_3$ moiety are not exchanging environments, but that the two sets of three CO groups are each scrambling among themselves. It is also evident that one $Fe(CO)_3$ group engages in complete internal scrambling only at a much higher temperature than the other. When these firm conclusions are taken in conjunction with the independently established conclusion that the $Fe_2(CO)_6$ moiety as a whole is moving in such a way as to give the ring a time-average plane of symmetry, in a process which has a relatively low activation energy (<13 kcal mol^{-1}), we finally conclude that the twitch mechanism is operating and the glide mechanism is not.

The last conclusion follows from a consideration of those line shape changes which occur in the carbonyl CO resonances from −75 to about 8°. It is clear that by 8° the following three sets of permutations are occurring. (1) Three CO groups have become equivalent and are giving rise to a single line of intensity 3 at 19.2 ppm. (2) The remaining CO groups consist of one (time-average) equivalent pair and one which is still unique. (3) The molecule as a whole has a time average plane of symmetry. The glide alone or the twitch alone are insufficient to explain the 8° spectrum. From Scheme I it can be seen that the glide would cause a three-line spectrum but with three equally intense lines, due to (a, b), (c, d), and (e, f). The twitch would give a four-line spectrum with lines of relative intensities 1:1:2:2 due to (a), (b), (c, f), and (d, e), respectively.

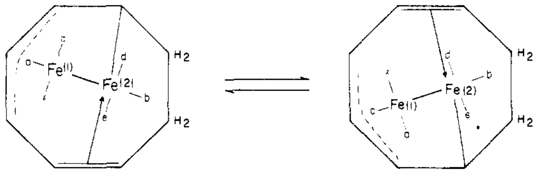
A combination of the twitch with the glide is unacceptable since this would lead to a two-line spectrum with one line of relative intensity 2 (a, b) and one line of relative intensity 4(c, d, e, f).

Some combination of either the twitch or the glide with local averaging within one $Fe(CO)_3$ moiety will be required to explain the observations. Scheme II shows several possibilities. In A we see the effect of the glide plus rotation of CO groups on Fe(1) about their local quasi-threefold axis. This can be ruled out with certainty since it scrambles the CO groups too extensively. It would lead to a single CO carbon resonance since the two ends of the $Fe_2(CO)_6$ group are permuted so that, in effect, local scrambling about both ends would occur, given that it occurs about either one.

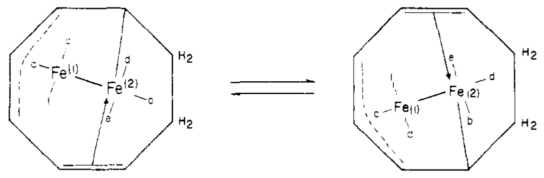
Scheme II



A Glide + Rotation around Fe(1)



B Twitch + Rotation around Fe(1)



C Twitch + Rotation around Fe(1) & Fe(2)

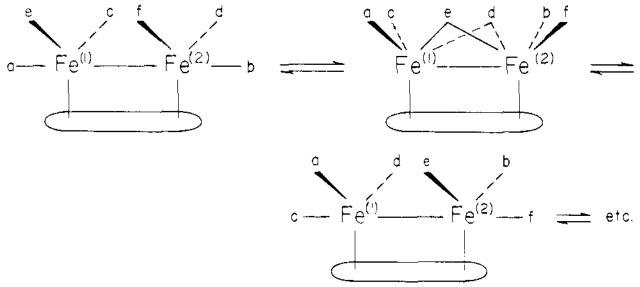
Thus there is no way in which the glide, alone or in combination, can lead to the spectrum observed at 8°.

In Scheme IIB is shown the combined effect of the twitch plus rotational scrambling within one set of CO groups. This leads to precisely the pattern observed at 8°. Assuming that it is the set of CO groups on Fe(1) which are locally scrambled, Scheme IIB predicts that there will be three resonances in the intensity ratio 1:2:3 due to (b), (d, e), and (a, c, f), respectively. We cannot be certain that the local scrambling is among the set on Fe(1). If it were among those on Fe(2), the assignment of the signals with intensities of 1:2:3 would instead be to (a), (c, f), and (b, d, e), respectively. Either way, however, only this particular combination, *i.e.*, twitch plus one local scrambling, leads to the type of spectrum observed at 8°.

In order to account for the further line shape changes which occur above 8° it is only necessary to add to Scheme IIB, either as shown or with local rotation of CO groups on Fe(2) instead of Fe(1) the additional localized scrambling on the other iron atom (Scheme IIC) to obtain the two-line pattern which is seen in the high-temperature limit.

One more rigorous conclusion we can draw is that no process involving a CO-bridged intermediate or transition state such as that depicted in Scheme III occurs rapidly here, even though such processes are well known in other cases.[21,22] Such a process would lead directly to time-average equivalence of all six CO groups, even in the absence of either the twitch or gliding motions.

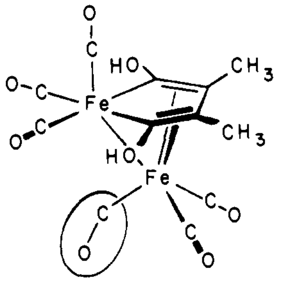
Scheme III



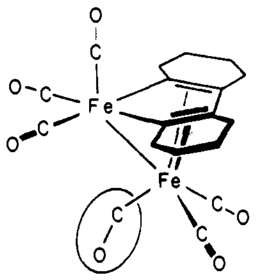
In the foregoing discussion and in Scheme II, the term "rotation" about an iron atom has been used. A rotation of the set of three CO groups relative to the rest of the molecule is only one way in which the local set of CO environments could be completely scrambled, and we do not have any direct evidence that this is the correct choice. The other intimate mechanism for this local scrambling would be a sequence of one-for-one exchanges, *e.g.*, [abc] ⇄ [acb] ⇄ [bca] ⇄ [cba], etc. We intuitively favor the rotatory process, however, and have for simplicity used the term rotation to describe the scrambling within one $Fe(CO)_3$ moiety even though we cannot objectively rule out the other possibility.

Three Possible Intimate Mechanisms. Apart from the problem just discussed, as to whether complete scrambling among the set of three CO groups on a given iron atom occurs by rotation or repeated one for one exchanges, there are three intimate mechanisms which can account qualitatively for the observed line shape changes at temperatures up to 8°. The first two have already been mentioned: (1) twitch plus rotation about Fe(1), (2) twitch plus rotation about Fe(2), (3) twitch plus rotation about Fe(2), plus partial rotation about Fe(1).

Mechanism 3 and the reason for considering it will now be explained in detail. The structure originally proposed, incorrectly as it turned out, by King[19] for the ground state of **1** was based on precedent. There are two compounds, **4** and **5**, closely related to each other, which have structures[23,24] of the same formal type as **1a.** The important points about such a structure are the fact that the Fe–Fe bond is formally a dative bond and that in order to avoid the unbalanced charge distribution which would result therefrom one CO ligand lies directly over the Fe→Fe band and serves as a semibridging carbonyl group.[25] This locks it into a position directly over the Fe–Fe bond. Now the transition state or intermediate for the twitch mechanism, Figure 1a, is the same as **1a, 4,** and **5** in having the dative Fe→Fe bond. It is possible, therefore, that it would be stabilized by the formation of a temporary semibridging carbonyl group. The positioning of the CO groups which is necessary for this to happen entails a partial rotation (roughly 60°).



4



5

As Figure 4 shows, when proper account is taken of microscopic reversibility, the process we are considering leads to site exchange of a and f, or, if rotation of the set a, c, f were in the opposite sense, to exchange of a and c. Thus, if a process of this nature occurs on Fe(1) while at the same time complete scrambling of the three CO groups on Fe(2) occurs, an intermediate spectrum with three lines of relative intensities 1:2:3 would be expected.

The conclusion drawn so far, namely, that only mechanisms 1, 2, or 3 are possible (barring the embarrassing possibility that there is some other mechanism besides these or any of the rejected ones), has been reached without recourse to any assignment of the carbonyl resonances. Obviously an assignment or even a partial assignment would allow a decision among (1), (2), and (3). Using only data from the unsubstituted molecule containing one ^{13}CO, there does not appear to be any way to make a rigorous assignment.

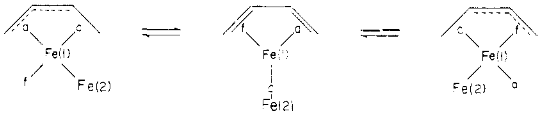


Figure 4. A diagram showing how partial rotation of the CO groups on Fe(1), induced by formation of a semibridging CO group in the twitch intermediate (Figure 1a), would lead to site exchange for only two of the three CO groups.

There is, however, one argument which favors mechanism 1. It is based on comparison with other molecules, Table II, in which localized scrambling in $Fe(CO)_3$ groups occurs. The temperature range in which the easiest rotational process occurs, *viz.*, −60 to 8° is very similar to the ranges for two other cases[15] in which $Fe-Fe(\eta^3\text{-allyl})(CO)_3$ are internally scrambling, namely (acenaphthylene)$Fe_2(CO)_5$ (**3**) (−60 to 20°) and $(C_7H_8)Fe_2(CO)_6$ (**2**) (−60 to 12°). There would appear to be no reason why the range should be a great deal higher here (8 to 110°) when the basic structural unit involving Fe(1) is the same. On the other hand the environment about Fe(2) is very different, with a more explicitly octahedral arrangement about Fe(2), involving one Fe–Fe bond, one Fe–C bond and one olefin–Fe bond. We feel that this might reasonably lead to a higher barrier to rotation since, in general, such rearrangements are less facile in truly octahedral complexes than in complexes which are in a sense five-coordinate, as Fe(1) is if the η^3-allyl group is considered to be a single ligand. A similar situation occurs with diene $Fe(CO)_3$ compounds[10] where those in which the diene is conjugated, and can thus be regarded as occupying three coordination sites, scramble less rapidly than those with nonconjugated, chelating dienes, where the iron atom is truly five-coordinated.

According to mechanism 1 the occurrence of twitching and internal rotation of $Fe(1)(CO)_3$ in the same temperature range is a coincidence, and not the result of any direct interrelation between them. Such a coincidence is not particularly unlikely and does not, in our opinion, detract from the plausibility of the mechanism. In any event, an entirely analogous coincidence must be assumed in each of the other mechanisms.

Table II. The Chemical Shift Values of Two Model Sawhorse Diiron Carbonyl Molecules[a]

	Trans	Average	Cis		Temp, °C	Ref
(acenaphthylene)$Fe_2(CO)_5$	26.5		17.2[b]		−60	15
		23.2			+40	
$(C_7H_8)Fe_2(CO)_6$	31.7		17.3	15.0	−60	15
		20.8			+40	

[a] ±0.1 ppm downfield from CS_2. [b] Structurally equivalent carbonyls.

Note Added in Proof. It has recently been shown, conclusively, that for the isoelectronic molecule $(C_8H_{10})Rh_2(\eta^5\text{-}C_5CH_5)_2$, the rearrangement pathway is also the twitching motion (*cf.* Evans, *et al.*[26]).

Acknowledgments. We thank the National Science Foundation for support of this work under Grant No. 33142X. P.L. acknowledges support from the Program of Cultural Cooperation between the United States of America and Spain during a leave of absence from the University of Zaragoza.

References and Notes

(1) M. J. Bennett, F. A. Cotton, A. Davison, J. W. Faller, S. J. Lippard, and S. M. Morehouse, *J. Amer. Chem. Soc.*, **88**, 4371 (1966).
(2) L. M. Jackman and F. A. Cotton, Ed., "Dynamic Nuclear Magnetic Resonance Spectroscopy," Academic Press, New York, N.Y., 1975.
(3) D. J. Ciappenelli, F. A. Cotton, and L. Kruczynski, *J. Organometal. Chem.*, **42**, 159 (1972).
(4) O. A. Gansow, A. R. Burke, and W. D. Vernon, *J. Amer. Chem. Soc.*, **94**, 2550 (1972).
(5) F. A. Cotton, L. Kruczynski, B. L. Shapiro, and L. F. Johnson, *J. Amer. Chem. Soc.*, **94**, 6191 (1972).
(6) G. Rigatti, G. Boccalon, A. Ceccon, and G. Giacometti, *J. Chem. Soc., Chem. Commun.*, 1165 (1972).
(7) J. Evans, B. F. G. Johnson, J. Lewis, and J. R. Norton, *J. Chem. Soc., Chem. Commun.*, 79 (1973).
(8) F. A. Cotton, L. Kruczynski, and A. J. White, *Inorg. Chem.*, **13**, 1402 (1974).
(9) J. Evans, B. F. G. Johnson, J. Lewis, J. R. Norton, and F. A. Cotton, *J. Chem. Soc., Chem. Commun.*, 807 (1974).
(10) L. Kruczynski and J. Takats, *J. Amer. Chem. Soc.*, **96**, 932 (1974).
(11) L. Kruczynski, L. K. K. LiShingMan, and J. Takats, *J. Amer. Chem. Soc.*, **96**, 4006 (1974).
(12) S. T. Wilson, N. J. Coville, J. R. Shapely, and J. A. Osborn, *J. Amer. Chem. Soc.*, **96**, 4038 (1974).
(13) B. F. G. Johnson, J. Lewis, and T. W. Matheson, *J. Chem. Soc., Chem. Commun.*, 441 (1974).
(14) F. A. Cotton, D. L. Hunter, and P. Lahuerta, *J. Amer. Chem. Soc.*, **96**, 4723 (1974).
(15) F. A. Cotton, D. L. Hunter, and P. Lahuerta, *Inorg. Chem.*, in press.
(16) F. A. Cotton and T. J. Marks, *J. Organometal. Chem.*, **19**, 237 (1969).
(17) F. A. Cotton, B. G. DeBoer, and T. J. Marks, *J. Amer. Chem. Soc.*, **93**, 5069 (1971).
(18) F. A. Cotton and W. T. Edwards, *J. Amer. Chem. Soc.*, **91**, 843 (1969).
(19) R. B. King, *Inorg. Chem.*, **2**, 807 (1963).
(20) G. Deganello, *J. Organometal. Chem.*, **59**, 329 (1973).
(21) R. D. Adams and F. A. Cotton, *J. Amer. Chem. Soc.*, **95**, 6589 (1973).
(22) R. D. Adams, M. D. Brice, and F. A. Cotton, *J. Amer. Chem. Soc.*, **95**, 6594 (1973).
(23) A. A. Hock and O. S. Mills, *Acta Crystallogr.*, **14**, 139 (1961).
(24) H. B. Chin and R. Bau, *J. Amer. Chem. Soc.*, **95**, 5068 (1973).
(25) F. A. Cotton and J. M. Troup, *J. Amer. Chem. Soc.*, **96**, 1233 (1974).
(26) J. Evans, B. F. G. Johnson, J. Lewis, and R. Watt, *J. Chem. Soc., Dalton Trans.*, 2368 (1974).