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# $^1$H AND $^{13}$C NMR INVESTIGATION OF THE FLUXIONAL BEHAVIOR OF $\eta^6$-(BICYCLO[6.1.0]NONA-2,4,6-TRIENE)HEXACARBONYLDIIRON-(*Fe—Fe*)

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## Summary

The variable temperature $^1$H and $^{13}$C NMR spectra of $(C_9H_{10})Fe_2(CO)_6$ have been recorded. The molecule is fluxional. The high temperature spectra indicate an apparent plane of symmetry bisecting the bound organic ligand, whereas the low temperature limiting spectra are entirely consistent with the asymmetric skew-type structure found in the crystal. Thus the molecule is also properly described in solution as $\mu$-(2-$\sigma$,6,7-$\eta$:3—5-$\eta$-bicyclo[6.1.0]nonatriene)hexacarbonyldiiron(*Fe—Fe*). Based on the observed line shape changes of the carbonyl resonances between —140 and —110° C, it is shown that the twitching and not the gliding process is responsible for the relative movement of the $Fe_2(CO)_6$ moiety with respect to the ring. The $\Delta G_c^{\neq}$ for this process is found to be 7.4 kcal mol$^{-1}$, a value smaller than those previously established for the related $(C_{10}H_{12})$-$Fe_2(CO)_6$ and $(C_8H_{10})Fe_2(CO)_6$ complexes. Further carbonyl line shape changes, at higher temperatures, are only consistent with the twitch followed by local scrambling of the carbonyl groups first on the allyl-bound and then on the other iron atom, assuming that the virtually identical chemical shifts of the carbonyl resonances of this and $(C_{10}H_{12})Fe_2(CO)_6$ molecules can be taken to imply a correspondingly identical assignment of the respective signals. Thus it is concluded that the dynamic properties of $(C_9H_{10})Fe_2(CO)_6$ are totally analogous to those reported for $(C_8H_{10})Fe_2(CO)_6$ and $(C_{10}H_{12})Fe_2(CO)_6$.

## Introduction

In a series of articles Cotton et al. have reported the results of an extensive investigation on the structural [1,2] and fluxional [2—5] behavior of ($\eta^6$-cyclooctatriene)(hexacarbonyl)diiron(*Fe—Fe*) and ($\eta^6$-bicyclo[6.2.0]deca-2,4,6-

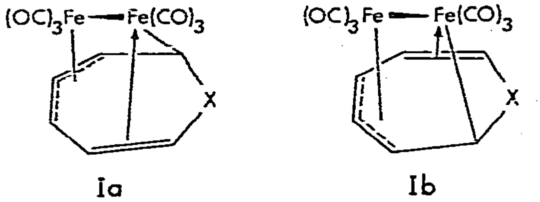
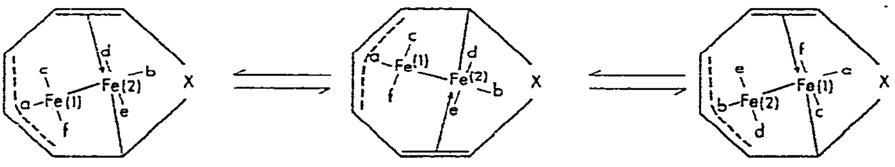


Fig. 1. Schematic representation of the enantiomeric skew structures found for $(C_8H_{10})Fe_2(CO)_6$, $(C_{10}H_{12})Fe_2(CO)_6$ and $(C_9H_{10})Fe_2(CO)_6$.

triene)(hexacarbonyldiiron)(*Fe—Fe*). The results of these studies can be summarized as follows. The solid state structure of the complexes was found to be of the skew-type shown in Fig. 1. However, in solution the molecules were found to be fluxional. By a very elegant combination of variable temperature $^1H$ and $^{13}C$ NMR spectroscopy Cotton et al. have shown that of two possible rearrangement pathways, Scheme 1, A and B, that could interconvert the two enantiomorphous structures Ia and Ib, only the twitching process was operating in these molecules. It was also shown that the enantiomerization process was accompanied by rapid carbonyl scrambling about each iron atom.

SCHEME 1



A. The Twitching Process

B. The Gliding Process

Recently one of us (J.T.) has reported [6] that the solid state structure of ($\eta^6$-bicyclo[6.1.0]nona-2,4,6-triene)hexacarbonyldiiron(*Fe—Fe*), $(C_9H_{10})Fe_2(CO)_5$, was also of the skew-type. To establish whether or not the solution behavior of the compound parallels that of Cotton's finding, a detailed variable temperature $^1H$ and $^{13}C$ NMR spectral study was undertaken. The results of this study are reported here.

## Experimental

The compound $(C_9H_{10})Fe_2(CO)_6$ was prepared as previously described [7].

Proton NMR spectra were recorded on a Varian HA-100 spectrometer fitted with a Varian 60H0 temperature control unit. The sample was prepared in a mixture of dry $CD_2Cl_2/CHF_2Cl$ (20/80 v/v) and sealed in an NMR tube under vacuum. The decoupling experiments were carried out on the same instrument, using standard decoupling techniques to arrive at the assignments described later.

The limited solubility of the compound prevented $^{13}C$ NMR spectra from being recorded at low temperatures. Therefore, a $^{13}CO$-enriched sample was prepared as follows. 50 mg of the complex were dissolved in 15 ml of dry and degassed hexane in a pyrex vessel. The vessel was evacuated and filled with one atmosphere of 90% $^{13}CO$. The solution was stirred magnetically and irradiated with a 100 Watt-mercury lamp for 45 minutes. Solvent was removed and sublimation onto a water-cooled probe at 50° C/$10^{-3}$ mmHg yielded bright orange-red crystals. A mass spectral analysis of the isotropic distribution indicated a 40% $^{13}CO$ enrichment. Using a mixture of $CD_2Cl_2/CHF_2Cl$ (20/80 v/v) and 20 mg of the enriched complex in a sealed 10 mm NMR tube allowed proton noise-decoupled carbon-13 spectra to be recorded down to −140° C on a deuterium-lock Bruker HFX-90/Nicolet 1085 FT spectrometer operating at 22.628 MHz. Temperature (±1° C) was controlled by a Bruker temperature unit, Model B-ST 100/700. High temperature runs were carried out in dry toluene-$d_8$ solution containing a small amount of $Cr(acac)_3$ as a relaxation reagent [8]. Pulse width was adjusted to give a tilt angle of 30—35° and 500 (low temperature) to 1000 scans (high temperature) were usually sufficient to give reasonably good spectra.

## Results and discussion

### *Variable temperature $^1H$ NMR study*

The proton NMR spectra of $(C_9H_{10})Fe_2(CO)_6$ are shown in Fig. 2. The spectrum at −30° C is similar to that previously reported by Deganello et al. [7] at room temperature. Since we have recorded our spectra at 100 MHz as opposed to 60 MHz of the previous study, the observed slight variations in the splitting patterns are hardly surprising. The spectrum consists of five sets of resonances in the ratio 2/2/2/3/1. The assignments of the protons which accompanies the spectrum has been verified by spin decoupling experiments. It differs from the original suggestion in that the resonance position of H(1,8) and H(2,7) have been reversed. The new assignment follows from the observation that irradiation of the H(3,6) position causes the collapse of the H(2,7) doublet to a sharp singlet whereas the H(1,8,9,9′) multiplet remains virtually unchanged. It should be noted that the chemical shift of H(2,7), with the new proposal, is also more in line with previous values found for the same type of protons in related complexes [2,3]. Of course, as pointed out before [7], this simple spectrum (i.e., pairwise equivalence of the olefinic protons) is not consistent with the asymmetric skew-type structure I found in the solid state for this molecule [6]. On the other hand, the temperature dependent spectral changes displayed in Fig. 2 clearly show that this is not the result of a symmetric configuration in solution but arises from some rapid fluxional motion which interconverts the enantiomorphous structures Ia and Ib and thereby imposes a time-average mirror plane upon the molecule.

The spectral changes which result upon lowering the temperature are akin to previous observations [2,3]. Doublet H(2,7) broadens out first and continues its collapse until −110° C where the coalescence is complete. At still lower temperatures two separate resonances, at 1.6 and 3.7 ppm, are seen to emerge. The assignment of these signals to protons 2 and 7, respectively is based on the following observation and assumption. Irradiation at −127° C of the H(2) peak caused the H(7) resonance to collapse and vice-versa, indicating that slow chemical exchange between these two sites is still occurring even at this temperature [9]. This clearly shows that the above resonances belong to protons H(2,7). The distinction between the two sites follows from the usual high field position of

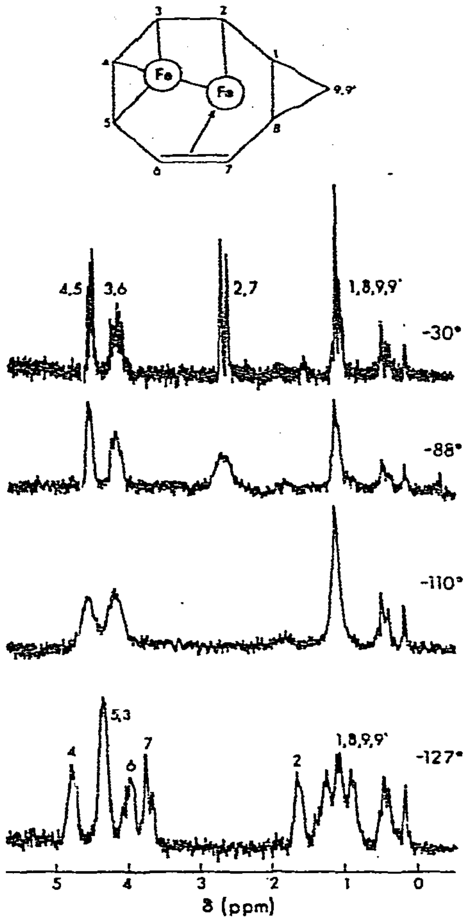


Fig. 2. 100 MHz $^1$H spectra of $(C_9H_{10})Fe_2(CO)_6$ at various temperatures. The assignment of the resonances corresponds to the numbering scheme shown at the top of the figure.

protons attached to carbon atoms that are bonded to transition metals by a σ bond [10a].

Figure 2 also shows that in the same temperature interval the other peaks also undergo line broadening. Although the changes are more subtle than those of the H(2,7) resonance, it is evident that by —127° C the averaged peaks H(4,5) and H(3,6) have separated into indivudual components, two of which are superimposed on one another. The tentative assignment of these resonances, which appear on the low temperature spectrum, is compatible with the experimental observation that the central proton of an allyl moiety usually resonates downfield from the outer proton positions [10a,b]. It also gives good agreement with the averaged chemical shifts of the high temperature spectrum.

The low temperature spectrum is clearly consistent with the asymmetric skew structure found in the crystalline state and demonstrates that, as was the case for all other related molecules, the solid state strucutre with the present molecule is still preferred in solution. Based on the chemical shift separation between protons 2 and 7, 208 Hz, and the coalescence temperature, —110° C, we estimate

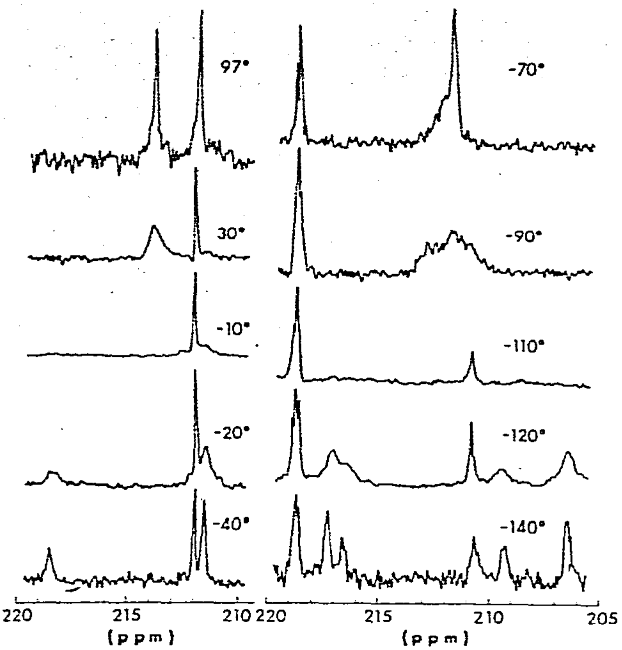


Fig. 3. $^{13}$C NMR spectra of $(C_9H_{10})Fe_2(CO)_6$ at various temperatures in the carbonyl region.

that the free energy of activation of the fluxional motion that interconverts the two enantiomorphous structures in solution is 7.4 kcal mol$^{-1}$ [11] at this temperature.

### *Variable tempeature $^{13}$C NMR study*

Although the variable temperature $^1$H NMR study clearly establishes that $(C_9H_{10})Fe_2(CO)_6$ is a fluxional molecule, the study provides no answer as to which process, twitch or glide, is responsible for this. Both types of motion impose a time-averaged plane of symmetry upon the molecule, and thus both processes would give the simplified PMR spectra observed above −30° C.

Reference to Scheme 1 shows that the difference between the twitching and the gliding processes resides in the fact that whereas the former motion maintains the distinction between the two $Fe(CO)_3$ moieties, the latter causes an averaging of the environments of the two iron atoms. Thus a study of the NMR behavior of the carbonyl groups should, in principle, resolve the above ambiguity *. For this reason we have recorded and presented in Fig. 3 the carbon-13 spectra of $(C_9H_{10})Fe_2(CO)_6$ in the carbonyl region at different temperatures. The chemical shift scale appearing on the figure is referenced to $Si(CH_3)_4$. The fine structures exhibited by some of the peaks in the low temperature spectra are presumably due to $^{13}C$—$^{13}C$ couplings.

The observation of six distinct carbonyl resonances at −140° C again demon-

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* This was recognised before [12] and was successfully applied to $(C_8H_{10})Fe_2(CO)_6$ [4] and $(C_{10}H_{12})Fe_2(CO)_6$ [5].

strates the persistence of the asymmetric skew structure 1 for this molecule in solution. As the temperature is raised from —140° C only four of the six resonances begin to broaden. Qualitatively it appears that the signals at 209.5 and 216.6 ppm collapse slightly faster than the peaks at 206.5 and 217.2 ppm. By —110° C, the coalescence of these peaks is complete and only the signals at 210.6 and 218.8 ppm remain. Above —110° C, and even somewhat below, the peak at 210.2 ppm also begins to collapse. Further increase of the temperature to —70° C causes the appearance of a new signal with relative intensity of two at 211.4 ppm. The low field shoulder flanking this new peak, continues to grow, becomes fully sharpened by —20° C and undergoes no further line shape changes at higher temperature. The signal at 211.4 ppm becomes slightly narrower at —60° C. However, above this temperature, this resonance and the line at 218.3 ppm broaden out, coalesce completely between —10 and 0° C and emerge as an averaged new peak above 30° C. The spectrum at 97° C consists only of two sharp resonances of equal intensity at 211.2 and 213.1 ppm. This of course indicates that each of these signals arises from the averaging of three carbonyl groups and further demonstrates that, although at no time is there the appearance of a spectrum where the relative intensity of the resonances is in the ratio of 1/3/2, the low field shoulder in the —70° C spectrum, which becomes the peak at 211.8 ppm in the —60° C and subsequent spectra *, represents three averaged carbonyl groups.

The results just presented are in good agreement with previous observations made by Cotton et al. [4,5] and mirror especially closely the line shape changes reported for $(C_{10}H_{12})Fe_2(CO)_6$ once an allowance of ca. 25° C is made for the increased fluxionality of the present molecule. This spectral analogy clearly implies equivalent mechanisms for the dynamical properties of the above three compounds. Since an excellent and thorough discussion of the mechanistic intricacies has already been given by Cotton [4,5], it would serve no purpose to repeat here much of the previous arguments. Thus in this article we will limit ourselves to show how the twitch, sometimes in combination with rotational averaging of the carbonyls on an iron atom, is entirely consistent with the spectral features shown in Fig. 3.

Reference to Scheme 1 quickly reveals that the twitching motion alone would only average the carbonyls (c,f) and (d,e). That is, at the inception of the process line broadening of only four of the six low temperature signals is expected. The coalescence pattern of the spectra between —140 and —110° C is evidently in accord with this and indicates that the twitch is responsible for the movement of the $Fe_2(CO)_6$ moiety relative to the ring. However, as the temperature is raised, the anticipated four line spectrum of the twitch is never obtained. Thus, additional processes, beside the twitch, must be operating to account for the line shape changes above this temperature. As shown before [4,5], the only supplement motions that will satisfactorily lead to the observed spectra are local averaging of the carbonyl groups within one and both sets of $Fe(CO)_3$ moieties **.

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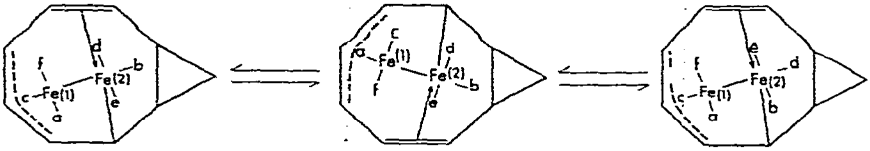
* The chemical shifts of the carbonyl groups are slightly temperature and solvent dependent. Thus the particular signal just mentioned instead of resonating at 211.8 ppm, is observed at 211.2 ppm in the 97° C spectrum.

** Of course internal scrambling of carbonyls is, by now, a well-recognized and often observed phenomenon with compounds containing the $M(CO)_3$ fragment [4,5,13 and refs. therein].

SCHEME 2

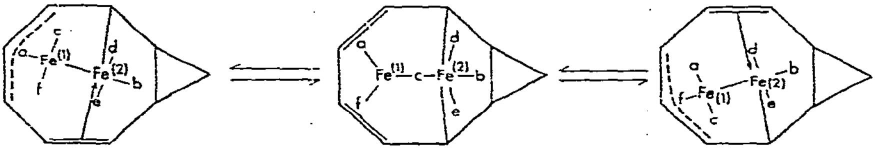


A. Twitch + Rotation around Fe(1) B. Twitch + Rotation around Fe(1) & Fe(2)

Scheme 2 shows the respective composite processes. Scheme 2A involves a combination of the twitch with carbonyl scrambling on Fe(1), it would result in a three line spectrum of relative intensities 1/2/3 due to the carbonyls b, d,e and a,c,f, respectively. An explanation for showing the rotational averaging of carbonyls on Fe(1) before it occurs on Fe(2) will be given later on. Of course it is immaterial which iron undergoes local scrambling first; as long as only one set of $Fe(CO)_3$ is averaged a three line spectrum is obtained. Only the pertinent resonances being averaged will be different. It is easy to see that the appearance of the spectra between −110 and −40° C follow the expectations based on this mechanism. The coalescence of the high field carbonyl resonance, which up until now remained essentially non-exchanged, signals the initiation of carbonyl rotation about Fe(1). By −70° C we observed that the twitch is sufficiently rapid to cause the equivalence of the d,e resonances and finally at −40° C the three line spectrum obtains (Scheme 2A). We note that the relative intensity of the signals is not 1/3/2 as anticipated. However, as we explained before, there is no doubt that the two high field peaks of the −40° C spectrum are the result of three and two averaged carbonyl groups respectively. The reason for this apparent discrepancy is that above this temperature local rotation of CO groups on Fe(2) has also begun. The mechanism 2B, twitch and internal scrambling of carbonyls about Fe(1) and Fe(2), is responsible for the line shape changes at high temperatures. Clearly such processes will maintain the environmental integrity of the two iron atoms and will give, at its fast exchange limit, two signals of equal intensity as observed in the 97° C spectrum. Although we have not considered alternate mechanisms, it should be easy for the reader to verify that the gliding process alone, in combination with the twitch, or with carbonyl scrambling, is incapable of yielding any of the spectrum presented in Fig. 3.

There are two additional fine points that need to be considered before we can conclude that there exists a one to one correspondence between the mechanistic details established for $(C_{10}H_{12})Fe_2(CO)_6$ and the present molecule. One question relates to the actual operation of the twitching process. As explained by Cotton [4], beside the simple process presented on Scheme 1, there is another one that is consistent with the low temperature spectral changes of Fig. 3. The process is shown in Scheme 3. Here it is assumed that the twitch,

SCHEME 3



Twitch + Partial Rotation around Fe(1)

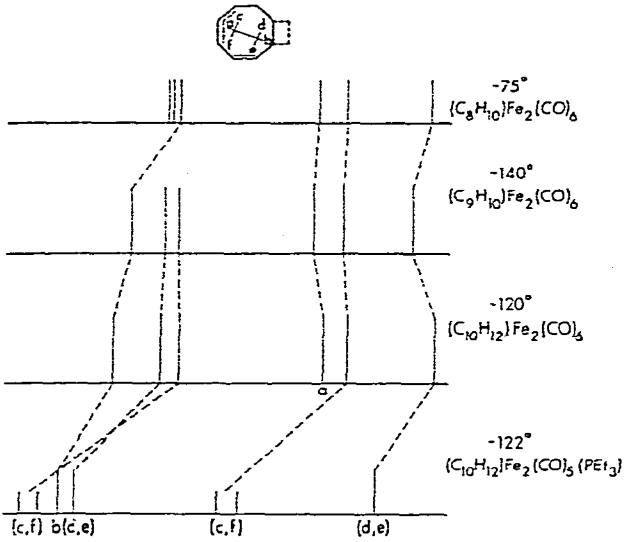


Fig. 4. Comparison of the chemical shift data of $(C_9H_{10})Fe_2(CO)_6$ with related molecules. The correlation between the spectra and the implied assignment are taken from ref. 5, see also text for discussion.

by going through an intermediate necessitating the presence of a semibridging carbonyl group, activates partial rotational exchange of two carbonyls on Fe(1). The result of this process is to average pairs a,f and d,e instead of c,f and d,e of Scheme 1, but coalescence of only four peaks would obtain from both. The second question pertains to the permutation of the carbonyl groups on the iron atoms and seeks to establish which $Fe(CO)_3$ set is more rapid in this regard. It is evident that answers to both of these questions are dependent on the assignment of the carbonyl resonances and that with the data at hand a rigorous assignment of the signals cannot be made. However, reference to Fig. 4 shows, that, not only the spectral changes of $(C_9H_{10})Fe_2(CO)_6$ resemble those of $(C_{10}H_{12})Fe_2(CO)_6$, but the chemical shift data of the two molecules are virtually identical, only the highest and lowest field resonances move by more than 0.2 ppm. Thus it would seem entirely reasonable to us that the assignment proposed by Cotton for $(C_{10}H_{12})Fe_2(CO)_6$ [5] would also apply to the present molecule. The correlation between the lines, presented in Fig. 4, is based on this assumption and one additional observation which will be dealt with shortly.

Having secured the assignment of the carbonyl resonances, answers to the previous two questions follow naturally. First, the identification of the resonances at 210.8 and 218.8 ppm as belonging to carbonyl groups a and b, respectively, clearly shows that carbonyl scrambling begins first on Fe(1), the allyl-bound iron atom. Second, since the signals a and b do not collapse between —140 and —110° C, the simple twitch, Scheme 1A, and not the composite movement shown in Scheme 3, is indicated. The coalescing resonances at low temperature are then due to pairs c,f and d,e. We have already noted that the peaks at 209.5 and 216.6 ppm seem to broaden out more quickly than the lines at 206.5 and 217.2 ppm. This is of course as expected based on the chemical shift differences between the signals provided that the resonances within each pair are exchange related. It is this argument and experimental observation that allows us to assign the former pair of peaks to the c,f, while the latter one to the d,e carbonyl groups respectively and to complete the assignments appearing in Fig. 4. We note that this additional piece of information appearing in the figure is in fact a corroboration of Cotton's intuitively preferred but not totally substantiated assignment [5]. According to this assignment, the following free energies of activation for the twitch can be estimated [11]; c,f, $\Delta\nu$ 160.7 Hz, $T_c$ −115°C, $\Delta G_c^\ddagger$ 7.4 kcal mol$^{-1}$; d,e, $\Delta\nu$ 242.1 Hz, $T_c$ 110°C, $\Delta G_c^\ddagger$ 7.3 kcal/mol. It is gratifying to see that these numbers are identical to the one obtained from the proton NMR data. It is also interesting to note that the energy barrier for the twitching process, which is in the order $(C_9H_{10})Fe_2(CO)_6 < (C_{10}H_{12})Fe_2(CO)_6 < (C_8H_{10})Fe_2(CO)_6$, is directly relatable to the degree of buckling of the cyclooctatrienyl portion of the ligand in each molecule [5].

## Conclusions

We have undertaken the present investigation in order to clarify the solution behavior of $(C_9H_{10})Fe_2(CO)_6$ and to compare it to that established for $(C_8H_{10})Fe_2(CO)_6$ [3,4] and $(C_{10}H_{12})Fe_2(CO)_6$ [2,5]. The molecule, like the other two related compounds, is fluxional and maintains, as its instantaneous structure, the asymmetric skew arrangement found in the solid state [6]. By making the reasonable assumption that the assignment of the carbonyl group resonances made for $(C_{10}H_{12})Fe_2(CO)_6$ is transferable to the present molecule, we have shown that only the simple twitch process, Scheme 1A, followed first by carbonyl scrambling about the allyl-bound iron atom and finally by scrambling of the CO groups on the other iron, Scheme 2A and B, respectively, is compatible with the temperature dependent line shape changes of the carbon-13 NMR spectra. Thus the dynamic properties of $(C_9H_{10})Fe_2(CO)_6$ are analogous, in every detail, to those reported by Cotton et al. for $(C_8H_{10})Fe_2(CO)_6$ and $(C_{10}H_{12})Fe_2(CO)_6$.

## Acknowledgements

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