A Carbon-13 Nuclear Magnetic Resonance Investigation of the Ring Exchange in (1—4-η^4-Cyclo-octatetraene)(1—6-η^6-cyclo-octatetraene)iron

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The site exchange between the η^4- and η^6-C_8H_8 rings in [Fe(η^4-C_8H_8)(η^6-C_8H_8)] is shown to occur *via* a mechanism where the transition state retains the differentiation between the four different types of CH groups in the η^6-C_8H_8 ring with $\Delta G_{300}^{\ddagger}$ = 10.9 kcal mol^{-1}. No evidence is found for any shifts within the η^6-C_8H_8 ring, while the shifts of the η^4-C_8H_8 ring have $\Delta G^{\ddagger} < 5.4$ kcal mol^{-1}, and the reasons for this are discussed.

THE observation of the scrambling of differently bonded rings in molecules is a relatively rare event. Examples have been found of exchange between differently bonded σ-cyclopentadienyl rings, *e.g.* between the σ- and η-bonded rings of [Ti(σ-C_5H_5)$_2$(η-C_5H_5)$_2$],[1] arene rings, *e.g.* between the η^4- and η^6-bonded rings of [Ru(η^4-C_6Me_6)(η^6-C_6Me_6)],[2] and cyclo-octatetraene rings, *e.g.* between the η^4- and η^6-bonded rings of [Fe(η^4-C_8H_8)(η^6-C_8H_8)].[3-5] In contrast, molecules such as [Fe(σ-C_5H_5)(η-C_5H_5)(CO)$_2$] [6,7] have not been shown to undergo scrambling of the differently bonded rings. For molecules such as [Ti(σ-C_5H_5)$_2$(η-C_5H_5)$_2$] [1] and [Mo(σ-C_5H_5)(η-C_5H_5)(NO)(S_2CNR_2)] [8] the variable-temperature n.m.r. spectra give no information on the mechanism of scrambling. At low temperatures both molecules show limiting spectra, but, on warming, coalescence of the σ-C_5H_5 signals occurs before the scrambling of differently bonded rings begins at a significant rate. All the mechanisms of scrambling result in the signals due to the σ-C_5H_5 and η-C_5H_5 rings broadening at the same rate. For molecules such as [Fe(η^4-C_6Me_6)(η^6-C_6Me_6)] [9] and [Fe(η^4-C_8H_8)(η^6-C_8H_8)] [3-5] the η^4-C_6Me_6 and η^6-C_8H_8 rings are static until scrambling commences and mechanistic information does become available. The complex [Fe(η^4-C_8H_8)(η^6-C_8H_8)] was chosen since the η^6-C_8H_8 ring in [Cr(η^6-C_8H_8)(CO)$_3$] has been shown to be fluxional *via* [Cr(η^4-C_8H_8)(CO)$_3$].[10] If the η^6-C_8H_8 ring in [Fe(η^4-C_8H_8)(η^6-C_8H_8)] were to behave similarly to give [Fe(η^4-C_8H_8)$_2$], then ring exchange would be achieved by the same mechanism. It was hoped that it would be possible to differentiate between this mechanism and an alternative one involving [Fe(η^5-C_8H_8)$_2$].[6]

EXPERIMENTAL

Cyclo-octatetraene was a gift from B.A.S.F. The complex [Fe(η^4-C_8H_8)(η^6-C_8H_8)] was prepared following the published procedure [11] and recrystallised twice from pentane before use.

The ^{13}C n.m.r. spectra were recorded using a JEOL PS-100 spectrometer at 25.15 MHz. The complex was dissolved in degassed $C_6D_5CD_3$ and transferred under a dinitrogen atmosphere to a 10-mm n.m.r. tube which was being flushed with dinitrogen. The spin-saturation method has been described previously.[8,12] Temperatures were measured using a Comark electronic thermometer connected to a thermocouple immersed in toluene in a 10-mm n.m.r. tube. At least 10 min were allowed for thermal equilibrium to be achieved.

Lineshape analysis was performed by analysis of the standard complex equations.[13] The rate matrices used are shown on p. 1762. These matrices are derived using the following assumptions. (*a*) The transition state has equal probability of reverting to the initial bonding situation without exchange of the η^4- and η^6-bonded rings or of going through to produce exchange of the η^4- and η^6-bounded rings. (*b*) The rate, *k*, is the rate at which the transition state goes through and produces exchange of the η^4- and η^6-bonded rings. This is half the rate of the ground state going to the transition state and is equivalent to using a transmission coefficient of 0.5. (*c*) For the specific 1,2, 1,3, and 1,4 shifts it is assumed that the transition state, on reversal,

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[1] J. L. Calderon, F. A. Cotton, B. G. DeBoer, and J. Takats, *J. Amer. Chem. Soc.*, 1970, **92**, 3801; 1971, **93**, 3592; J. L. Calderon, F. A. Cotton, and J. Takats, *ibid.*, 1971, **93**, 3587.

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[5] G. Allegra, A. Colombo, and E. R. Mognaschi, *Gazzetta*, 1972, **102**, 1060.

[6] F. A. Cotton, in 'Dynamic N.M.R. Spectroscopy,' eds. L. M. Jackman and F. A. Cotton, Academic Press, New York and London, 1975, p. 378 and refs. therein.

[7] D. J. Ciappenelli, F. A. Cotton, and L. Kruczynski, *J. Organometallic Chem.*, 1972, **42**, 159.

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[12] B. E. Mann, *J. Magnetic Resonance*, 1976, **21**, 18.

[13] R. A. Sack, *Mol. Phys.*, 1958, **1**, 163.

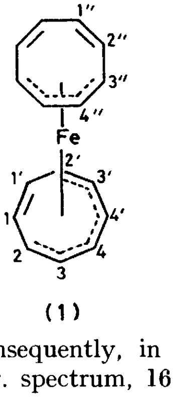
can only produce one of the two possible shifts or the original bonding situation.

	C(1)	C(2)	C(3)	C(4)	η^4-C_8H_8
(1) Direct exchange					
C(1)		0.0	0.0	0.0	*k*
C(2)	0.0		0.0	0.0	*k*
C(3)	0.0	0.0		0.0	*k*
C(4)	0.0	0.0	0.0		*k*
η^4-C_8H_8	0.25*k*	0.25*k*	0.25*k*	0.25*k*	
(2) Random shifts					
C(1)		0.25*k*	0.25*k*	0.25*k*	*k*
C(2)	0.25*k*		0.25*k*	0.25*k*	*k*
C(3)	0.25*k*	0.25*k*		0.25*k*	*k*
C(4)	0.25*k*	0.25*k*	0.25*k*		*k*
η^4-C_8H_8	0.25*k*	0.25*k*	0.25*k*	0.25*k*	
(3) 1,2 Shifts					
C(1)		0.25*k*	0.0	0.0	*k*
C(2)	0.25*k*		0.25*k*	0.0	*k*
C(3)	0.0	0.25*k*		0.25*k*	*k*
C(4)	0.0	0.0	0.25*k*		*k*
η^4-C_8H_8	0.25*k*	0.25*k*	0.25*k*	0.25*k*	
(4) 1,3 Shifts					
C(1)		0.25*k*	0.25*k*	0.0	*k*
C(2)	0.25*k*		0.0	0.25*k*	*k*
C(3)	0.25*k*	0.0		0.25*k*	*k*
C(4)	0.0	0.25*k*	0.25*k*		*k*
η^4-C_8H_8	0.25*k*	0.25*k*	0.25*k*	0.25*k*	
(5) 1,4 Shifts					
C(1)		0.0	0.25*k*	0.25*k*	*k*
C(2)	0.0		0.0	0.25*k*	*k*
C(3)	0.25*k*	0.0		0.0	*k*
C(4)	0.25*k*	0.25*k*	0.0		*k*
η^4-C_8H_8	0.25*k*	0.25*k*	0.25*k*	0.25*k*	
(6) 1,5 Shifts					
C(1)		0.0	0.0	0.5*k*	*k*
C(2)	0.0		0.5*k*	0.0	*k*
C(3)	0.0	0.5*k*		0.0	*k*
C(4)	0.5*k*	0.0	0.0		*k*
η^4-C_8H_8	0.25*k*	0.25*k*	0.25*k*	0.25*k*	

Visual comparison was used to obtain the best fit between the observed and computed spectra. The errors quoted are one standard deviation.

RESULTS AND DISCUSSION

The *X*-ray structure of [Fe(η^4-C_8H_8)(η^6-C_8H_8)] shows no plane of symmetry through the two C_8H_8 rings, which are twisted at an angle of 68° with respect to each other, see (1).[4,5] Consequently, in the limiting low-temperature ^{13}C n.m.r. spectrum, 16 signals are to be expected. At −85 °C the ^{13}C n.m.r. spectrum in [$^2H_8$]toluene shows five signals due to the four inequivalent pairs of carbon atoms in the η^6-C_8H_8 ring and the averaged carbon atoms of the η^4-C_8H_8 ring [see Figure 1(*a*)]. Thus, although ring exchange and migration within the η^6-C_8H_8 ring are frozen out on the n.m.r. time scale, there are further fluxional processes still occurring if the solution structure is the same as that found in the solid state. The η^4-C_8H_8 ring is still fluxional giving only one signal instead of the eight signals expected for a static system, and a twist process is creating an apparent plane of symmetry through the η^6-C_8H_8 ring.



(1)

Most of the ^{13}C n.m.r. signals may be unambiguously assigned. On the basis of intensity and position, the signal at δ 96.4 p.p.m. can be assigned to the exchange-averaged η^4-C_8H_8 ring The low-frequency shift compared to [Fe(η^4-C_8H_8)(CO)$_3$] [14] at δ 104.4 p.p.m. may be attributed to a weaker *trans* influence of the η^6-C_8H_8 ring compared to (CO)$_3$. The remaining four signals of equal intensity at δ 133.3, 98.8, 97.1, and 85.0 p.p.m. must be due to the static η^6-C_8H_8 ring. By comparison with the signals due to free cyclo-octatetraene [15] and [M(η^6-C_8H_8)(CO)$_3$] (M = Cr, Mo, or W),[10,16] the signals at δ 133.3 and 85.5 p.p.m. may be assigned to C(1) and C(2) respectively. The remaining two signals at δ 98.8 and 97.1 p.p.m. are then due to C(3) and C(4), but any argument based on the assignment of these two remaining signals must be suspect. At −85 °C the η^4-C_8H_8 ring is sharp in the ^{13}C n.m.r. spectrum, showing that the dynamic process is still fast. This permits an upper limit of 5.4 kcal mol^{-1} to be set for $\Delta G^\ddagger$ in contrast to the 6.8 kcal mol^{-1} reported for [Fe(η^4-C_8H_8)(CO)$_3$].[14,*]

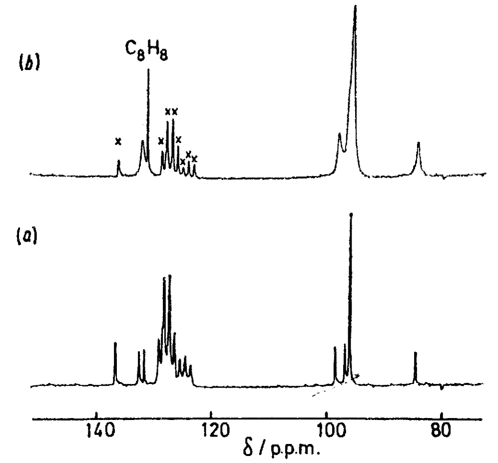


FIGURE 1 The ^{13}C n.m.r. spectrum of [Fe(η^4-C_8H_8)(η^6-C_8H_8)] in [$^2H_8$]toluene at (*a*) −85 and (*b*) −61.5 °C. There are extra signals due to [$^2H_8$]toluene (×) and a cyclo-octatetraene impurity

In order to attempt to clarify the mechanism of exchange, the Forsén–Hoffman spin-saturation method was applied.[8,10,12,17] Unfortunately, at the required

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[*] Throughout this paper: 1 cal = 4.184 J.

[14] F. A. Cotton and D. L. Hunter, *J. Amer. Chem. Soc.*, 1976, **98**, 1413 and refs. therein.

[15] E. Lippmaa, V. Sokolov, A. Olivson, J. Past, and O. Reutov, *Doklady Akad. Nauk S.S.S.R.*, 1967, **173**, 358.

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[17] J. A. Gibson and B. E. Mann, unpublished work.

temperature, crystallisation was relatively fast and quantitative measurements could not be performed. Qualitatively, a valuable observation was made. When either the signal at δ 133.3 [C(1)] or at 85.0 p.p.m. [C(2)] is irradiated the three remaining η^6-C_8H_8 resonances decrease *equally* in intensity. This observation immediately eliminates any transition state which permits specific exchange between C(1), C(2), C(3), and/or C(4). Thus only a mechanism where the transition state produces random or no shifts on reversal is permitted.

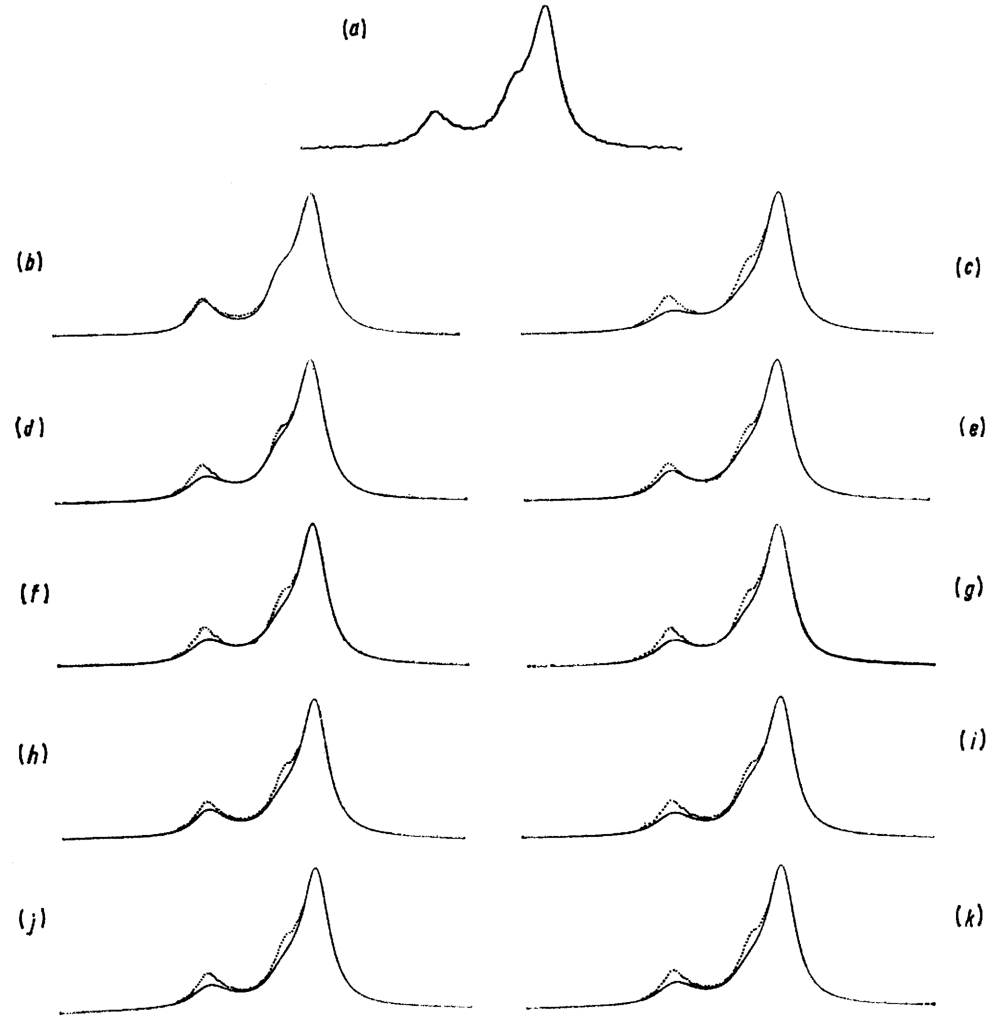


FIGURE 2 (*a*) An expansion of the 90—100 p.p.m. shift range of the ^{13}C n.m.r. spectrum of [Fe(η^4-C_8H_8)(η^6-C_8H_8)] in [$^2H_8$]-toluene at −61.5 °C. The other spectra are computer calculated at a rate constant of 44 s^{-1} from the η^4- to η^6-ring with the places where there are deviations from the experimental spectrum indicated with dots. The spectra were calculated on the basis of the rate matrices: (*b*) direct, (*c*) random, (*d*) 1,2 shifts with assignments of C(3) and C(4) at δ 98.8 and 97.1 p.p.m., (*e*) 1,2 shifts with reversed C(3) and C(4) assignments, (*f*) 1,3 shifts, (*g*) 1,3 shifts with reversed assignments, (*h*) 1,4 shifts, (*i*) 1,4 shifts with reversed assignments, (*j*) 1,5 shifts, and (*k*) 1,5 shifts with reversed assignments

At higher temperatures broadening becomes significant, with all the resonances broadening at the same rate, see Figures 1(*b*) and 2. From this observation it can be concluded that reversal of the transition state does not allow the η^6-C_8H_8 ring to undergo any shift, but that it merely returns to the original bonding situation. In order to confirm this deduction, lineshape calculations were performed for all the feasible behaviours of the η^6-C_8H_8, *i.e. via* a transition state which on reversal produces (*i*) no change in the η^6-C_8H_8 ring (direct), (*ii*) random shifts in the η^6-C_8H_8 ring, (*iii*) 1,2 shifts in the η^6-C_8H_8 ring, (*iv*) 1,3 shifts in the η^6-C_8H_8 ring, (*v*) 1,4 shifts in the η^6-C_8H_8 ring, or (*vi*) 1,5 shifts in the η^6-C_8H_8 ring, using the rate matrices given in the Experimental section. Since the assignment of C(3) and C(4) is uncertain, the calculations were performed for both assignments for cases (*iii*)—(*vi*) but not for (*i*) or (*ii*) where the assignment does not affect the lineshape at the relatively slow exchange rate (44 s^{-1}) found at −61.5 °C. Only (*i*), the direct mechanism, gave good agreement with the experimental observations, and this is illustrated in Figure 2 for C(3), C(4), and the η^4-C_8H_8 carbon atoms. Except for case (*i*), the signals due to C(3) and C(4) are broadened considerably more than that due to the carbon atoms of the η^4-C_8H_8 ring. Hence the direct mechanism, (*i*), which is in agreement with the spin-saturation transfer measurements, is the operative mechanism, and the experimental data (see Figure 3) were analysed on this basis. The results are given in the Table, and yield $\Delta G_{300}^{\ddagger} = 10.9$ kcal mol^{-1}, $\Delta H^{\ddagger} = 10.4 \pm 0.2$ kcal mol^{-1}, and $\Delta S^{\ddagger} = -1.7 \pm 0.9$ cal K^{-1} mol^{-1} for the rate from one carbon position of the η^6-C_8H_8 ring to the η^4-C_8H_8 ring.

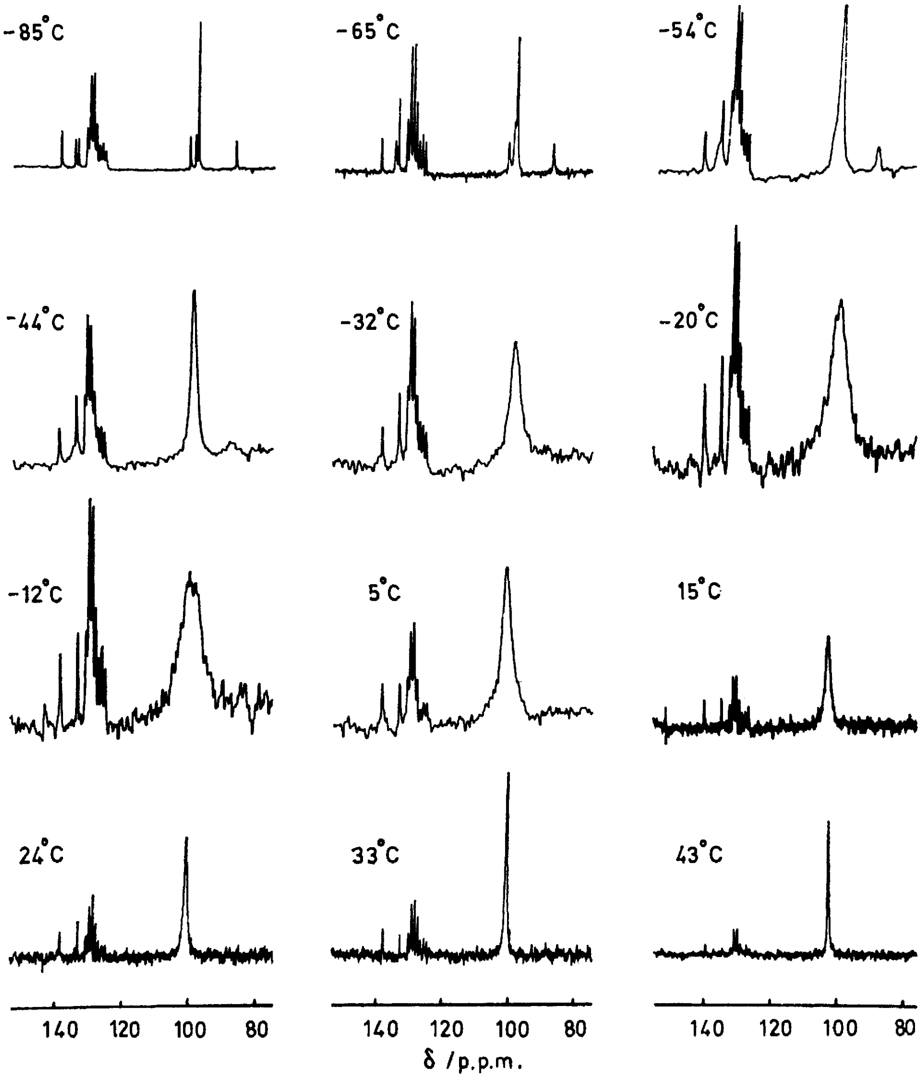
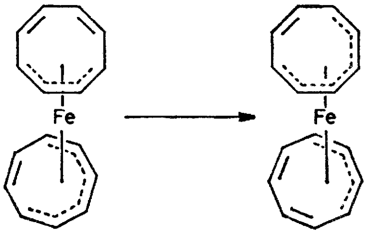


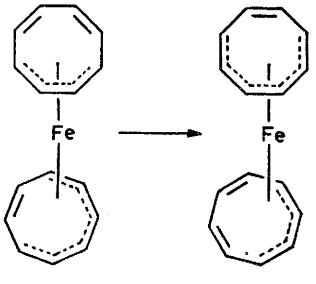
FIGURE 3 Variable-temperature ^{13}C n.m.r. spectra of [Fe(η^4-C_8H_8)(η^6-C_8H_8)] in [$^2H_8$]toluene

Exchange rate between the η^6- and η^4-cyclo-octatetraene rings in [Fe(η^4-C_8H_8)(η^6-C_8H_8)] as a function of temperature, calculated on the basis of direct exchange. The rates are from one carbon position on the η^6-C_8H_8 ring to the η^4-C_8H_8 ring

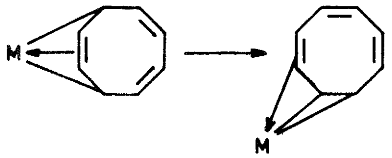
θ_c/°C	k/s^{-1}	θ_c/°C	k/s^{-1}	θ_c/°C	k/s^{-1}
−65	20	−32	670	15	33 000
−61.5	44	−20	1 440	24	57 000
−54	100	−12	4 500	33	100 000
−44	220	5	18 000	43	223 000

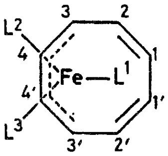
Although it has been possible to prove that the mechanism is one of six which are different for the n.m.r. experiments, no direct information has been obtained on the nature of the transition state or intermediate. All the transition states which exchange inequivalent carbon atoms on the η^6-C_8H_8 ring can be eliminated. Unfortunately this only eliminates a few very specific transition states. For example, following the suggestion of Cotton[6] for [Ti(σ-C_5H_5)$_2$(η-C_5H_5)$_2$], [Fe(η^5-C_8H_8)$_2$] may appear as the transition state to induce a 1,2 shift in the η^6-C_8H_8 ring on reversal, but this is only true if there is a plane of symmetry through the C_8H_8 ring in the transition state. That only occurs if the two rings are eclipsed or turned 180° with respect to each other. Since it is known that in [Fe(η^5-C_7H_7)(η^5-C_7H_9)] the two rings are twisted 60° relative to each other,[18] it is probable that ' Fe(η^5-C_8H_8)$_2$ ' would also have the two rings twisted relative to each other. There is then no plane of symmetry through the C_8H_8 ring in the transition state. Thus for the η^6-C_8H_8 ring in (1), if C(2) is removed from co-ordination on going to the transition state, C(2) does not become equivalent to C(1′), and microscopic reversibility requires that reversal of the transition state will give the original co-ordination rather than a 1,2 shift. An identical argument applies if C(2′) instead of C(2) is removed from co-ordination. Similar reservations apply to most other possible transition states, especially as the two rings start off twisted by 68° in the ground state [4,5] In the absence of bond shifts, this mutual twisting of the two π systems is relatively high in energy. Thus for $[\mathrm{Fe}(\eta^5\text{-}\mathrm{C_7H_7})(\eta^5\text{-}\mathrm{C_7H_9})]$ the free energy of activation is *ca.* 9.5 kcal mol^{-1} for the mutual twisting of the two π systems.[18] In addition to a mechanism involving $[\mathrm{Fe}(\eta^5\text{-}\mathrm{C_8H_8})_2]$ as the transition state, there are two other feasible mechanisms. Since it has been shown that $[\mathrm{Cr}(\eta^6\text{-}\mathrm{C_8H_8})(\mathrm{CO})_3]$,[10,16] $[\mathrm{Mo}(\eta\text{-}\mathrm{C_5H_5})(\eta^3\text{-}\mathrm{CH_2Ph})(\mathrm{CO})_2]_2$,[19] $[\mathrm{Fe}(\eta^4\text{-}\mathrm{C_7H_8})(\mathrm{CO})_3]$,[20,21] and probably $[\mathrm{Ru}(\eta^6\text{-}\mathrm{C_8H_8})(\mathrm{nbd})]$ (nbd = norbornadiene) [22] are fluxional *via* a 16-electron intermediate, $[\mathrm{Fe}(\eta^4\text{-}\mathrm{C_8H_8})_2]$ appears to be a feasible transition state, but comparison of activation energies, *e.g.* 14.1 ± 0.7 kcal mol^{-1} for $[\mathrm{Ru}(\eta^6\text{-}\mathrm{C_8H_8})(\mathrm{nbd})]$,[22] makes this mechanism unlikely. An additional mechanism is feasible for $[\mathrm{Fe}(\eta^4\text{-}\mathrm{C_8H_8})(\eta^6\text{-}\mathrm{C_8H_8})]$ where there is a concerted movement of the two rings. This movement may occur in one of two ways. A double bond on the η^4-$\mathrm{C_8H_8}$ ring may do an S_N2-style displacement of a double bond on the η^6-$\mathrm{C_8H_8}$ ring. Alternatively, the C(2) carbon atoms of the η^4-$\mathrm{C_8H_8}$ ring may co-ordinate to the metal as the C(2) carbon atoms of the η^6-$\mathrm{C_8H_8}$ ring are removed from co-ordination.





At present there is not the information available to differentiate between these mechanisms. The behaviours of the η^4- and η^6-$\mathrm{C_8H_8}$ rings are markedly different. For the η^4-$\mathrm{C_8H_8}$ ring the free energy of activation for migration, presumably by 1,2 shifts, is <5.4 kcal mol^{-1}. In contrast, the η^6-$\mathrm{C_8H_8}$ ring has a free energy of activation in excess of 10.9 kcal mol^{-1}, and, in $[\mathrm{Fe}(\eta\text{-}\mathrm{C_5H_5})(\eta^6\text{-}\mathrm{C_8H_8})]^+$, the η^6-$\mathrm{C_8H_8}$ ring is static.[23] Recently, Mingos [24] has shown how Hückel molecular-orbital (m.o.) theory, and hence the Woodward–Hoffmann rules,[25] can be applied to fluxional organometallic compounds. Thus a 1,2 shift in the η^4-$\mathrm{C_8H_8}$ ring may be interpreted as a thermal supraficial sigmatropic [1,5]-rearrangement. Consequently the 1,2 shifts of the η^4-$\mathrm{C_8H_8}$ ring are symmetry allowed. Further, this treatment permits the prediction of the movement of the other ligands on the metal. On the basis of the known structures of $[\mathrm{Fe}(\eta^4\text{-}\mathrm{C_8H_8})(\mathrm{CO})_3]$,[26] $[\mathrm{Fe}(\eta\text{-}\mathrm{C_4H_6})(\eta^4\text{-}\mathrm{C_8H_8})(\mathrm{CO})]$,[27] and $[\mathrm{Fe}(\eta^4\text{-}\mathrm{C_8H_8})(\eta^6\text{-}\mathrm{C_8H_8})]$,[4,5] the ligand arrangement may be represented by (2). On rotation of the M–C(3) bond to give a M–C(2′) bond, the whole group of ligands, L^1—L^3, rotate to give (3), with consequential exchange of L^1, L^2, and L^3, when the ligands are equivalent. Thus Cotton *et al.*[16] found that the 1,2 shift and CO scrambling





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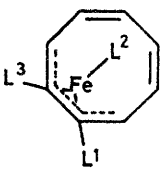

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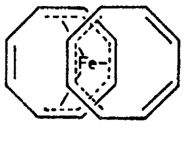

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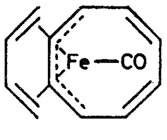

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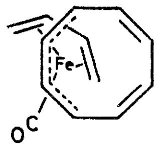

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in both $[Fe(\eta^4-C_8H_8)(CO)_3]$ and $[Ru(\eta^4-C_8H_8)(CO)_3]$ occur at very similar rates. In the case of $[Fe(\eta^4-C_8H_8)(\eta^6-C_8H_8)]$ this treatment would only produce one 1,2 shift. A second 1,2 shift would produce (4), rather than the 68°-twisted structure of the ground state. This will raise the activation energy for 1,2 shifts, but this rise can only be small since $\Delta G^\ddagger$ is <5.4 kcal mol^{-1}. The presence of the two rates may account for the anomalous results found in the solid-state n.m.r. spectra where the Arrhenius pre-exponential factor is only 6×10^7 s^{-1} rather than the *ca.* 10^{13} s^{-1} to be expected for an intramolecular process.[5,28,29] On this basis, $[Fe(\eta^4-C_8H_8)(CO)_3]$ would be expected to have a lower, and not a higher, activation energy, since the symmetry of the carbonyl ligands does not restrict the fluxionality. However, Cotton *et al.*[30] pointed out that $[\{Mo(\eta-C_5H_5)(CO)_2\}\{Fe(CO)_3\}(C_7H_7)]$ is fluxional while $[\{Fe(CO)_3\}_2(C_8H_8)]$ is static and attributed this behaviour to the angle between the two π systems, 119° for the former and 98° for the latter complex. A similar explanation may be given for $[Fe(\eta^4-C_8H_8)(\eta^6-C_8H_8)]$ and $[Fe(\eta^4-C_8H_8)(CO)_3]$. In the former the angle between the co-ordinated and unco-ordinated π systems is 147°, and 137.5° in the latter.[25] On going to $[Fe(\eta-C_4H_6)(\eta^4-C_8H_8)(CO)]$ the angle remains at 137°,[27] but the activation energy increases to *ca.* 12—14 kcal mol^{-1},[31] which is attributable to the energy required to go from the ground state (5), as found in the crystal structure,[26] to an intermediate, (6). This would imply that the $\eta^4-C_8H_8$ ring in $[Fe(\eta-C_4H_6)(\eta^4-C_8H_8)(CO)]$ will undergo 1,4 shifts. However, in practice 1,2 shifts are found,[32] which are attributable to rotation of butadiene and carbon monoxide being of lower energy than (6).

For the fluxionality of the $\eta^6-C_8H_8$ ring in $[Fe(\eta^4-C_8H_8)(\eta^6-C_8H_8)]$ the activation energy is >10.9 kcal mol^{-1}, which is the activation energy for ring exchange. In terms of the Woodward–Hoffman rules for sigmatropic thermal shifts, this is a [1,3]-shift and is symmetry allowed for an antarafacial shift, which is chemically impossible in this case. It is therefore not surprising that the $\eta^4-C_8H_8$ ring is far more fluxional than the $\eta^6-C_8H_8$ ring. This observation is not specific to $[Fe(\eta^4-C_8H_8)(\eta^6-C_8H_8)]$ but is general for all 1—4-η^4- and 1—6-η^6-cyclooctatetraene ring systems so far investigated, with the 1—6-$\eta^6-C_8H_8$ ring becoming fluxional *via* an $\eta^4-C_8H_8$ transition state or intermediate. Similarly, the $\eta^2-C_8H_8$ ring in $[Mn(\eta-C_5H_5)(\eta^2-C_8H_8)(CO)_2]$ is static,[33] as a symmetry-forbidden [1,7]-suprafacial shift is required for the molecule to be fluxional.

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