A Reinvestigation of the Fluxionality of Tricarbonyl(η^6-cyclo-octatetraene)-chromium and -tungsten using the Carbon-13 Forsén–Hoffman Spin-saturation Method †

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It is shown that the mechanism of metal migration in $[M(CO)_3(\eta^6\text{-}C_8H_8)]$ (M = Cr or W) is a combination of 1,2- and 1,3-shifts. The mechanisms of both this migration and also that found for $[Cr(CO)_3(\eta^6\text{-}C_8H_4Me_4\text{-}1,3,5,7)]$ are explained.

THE mechanism of metal migration in $[M(CO)_3(\eta^6\text{-}C_8H_8)]$ (M = Cr, Mo, or W) [1] and $[Ru(\eta^4\text{-}C_7H_8)(\eta^6\text{-}C_8H_8)]$ [2] was originally reported by Cotton as involving either 1,3- or random-shifts, with the latter mechanism being preferred. Subsequently, it was argued by Whitesides and Budnik [3] that random shifts *via* a 20-electron intermediate are unlikely while 1,3-shifts *via* a 16-electron intermediate are far more likely. Further confusion in this area is caused by the observation that $[Cr(CO)_3(\eta^6\text{-}C_8H_4Me_4\text{-}1,3,5,7)]$ undergoes 1,2-shifts,[1-4] as do the vast majority of other fluxional organometallic compounds. It is therefore pertinent to ask a number of questions. What is the mechanism, why are these compounds unusual, and why should methylation of $[Cr(CO)_3(\eta^6\text{-}C_8H_8)]$ change the mechanism?

For $M(\eta^6\text{-}C_8H_8)$ systems, lineshape analysis does not permit the separation of the 1,3- and random-shift mechanisms as both produce equal broadening of all four cyclo-octatetraene resonances. However, the Forsén–Hoffman spin-saturation method offers a technique to distinguish between these mechanisms.[5-7] As originally described, the method could only be applied with considerable difficulty to a problem involving more than two exchanging sites and has only once been applied to a three-site problem.[6] The analysis requires the exchanging nuclei to undergo no cross-relaxation, as would be expected for the ^1H nuclei in a C_8H_8 ring, and even if this condition was met five separate frequencies would be used: an observation, a lock, and three irradiating frequencies. These problems are removed by using Fourier-transform n.m.r. spectra of the magnetically dilute ^{13}C nuclei with ^1H decoupling, as has already been described for $[Mo(\sigma\text{-}C_5H_5)(\eta^5\text{-}C_5H_5)(NO)(S_2CNR_2)]$.[8] This method permits the determination of each individual rate. A preliminary report of this work has already appeared.[9]

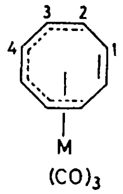
EXPERIMENTAL

Cyclo-octatetraene was a gift from B.A.S.F. The compounds $[Cr(CO)_3(\eta^6\text{-}C_8H_8)]$ and $[W(CO)_3(\eta^6\text{-}C_8H_8)]$ were prepared following the published procedures *via* the $[M(CO)_3(NCMe)_3]$ compounds.[10,11]

The ^1H n.m.r. spectra were recorded at 220 MHz using a Perkin-Elmer R34 spectrometer, and the ^{13}C n.m.r. spectra using a JEOL PS-100 spectrometer at 25.15 MHz. The compounds were dissolved in degassed CD_2Cl_2 (^1H) or CD_2Cl_2–CH_2Cl_2 (*ca.* 1 : 5) (^{13}C) and transferred to the n.m.r. tube under an atmosphere of dinitrogen. The spin-saturation method has been previously described.[7,8] Temperatures were measured using a Comark electronic thermometer connected to a thermocouple immersed in CH_2Cl_2 in an n.m.r. tube. At least 10 min were allowed for thermal equilibrium to be achieved.

RESULTS

The ^{13}C n.m.r. spectrum at −15 °C of $[Cr(CO)_3(\eta^6\text{-}C_8H_8)]$ in CD_2Cl_2–CH_2Cl_2 shows signals due to the cyclo-octatetraene ring at δ 130.6, 104.8, 102.5, and 93.2 p.p.m. The signal at δ 130.4 p.p.m. may be assigned to the free double bond, C^1, numbering as in (1) since it occurs close to that of free cyclo-octatetraene, 133 p.p.m.,[12] but the assignment, *a priori*, of the remaining signals is uncertain. By comparison with known compounds, it is probable that the signal at 93.2 p.p.m. is due to C^2. Similarly, the ^{13}C n.m.r. spectrum at 13 °C of $[W(CO)_3(\eta^6\text{-}C_8H_8)]$ in CD_2Cl_2–CH_2Cl_2 has the cyclo-octatetraene signals at δ 133.3 and 101.4 [$^1J(^{183}W\text{–}^{13}C)$ 3.9], 98.5 [$^1J(^{183}W\text{–}^{13}C)$ 3.2], and 82.2 p.p.m. [$^1J(^{183}W\text{–}^{13}C)$ 9.8 Hz], see Figure 1. Once again, the signal at 133.3 p.p.m. may be assigned to C^1. For both $[Cr(CO)_3(\eta^6\text{-}C_8H_8)]$ and $[W(CO)_3(\eta^6\text{-}C_8H_8)]$ the ^{13}C-{^1H} n.m.r. spectra were recorded in order to relate the ^{13}C chemical shift to the ^1H chemical shift for the same CH group,[13] see the Table and Figure 2. It was then possible to unambiguously assign the ^1H n.m.r. signal due to H^1. ^1H-{^1H} Decoupling experiments permit-



(1)

TABLE

Hydrogen and ^{13}C n.m.r. data (p.p.m.) for the cyclo-octatetraene ring of $[M(CO)_3(\eta^6\text{-}C_8H_8)]$ (M = Cr or W) in CD_2Cl_2 (^1H), or in CD_2Cl_2–CH_2Cl_2 (^{13}C)

δ(^{13}C)	δ(^1H)	*J*/Hz	Assignment
(*a*) $[Cr(CO)_3(\eta^6\text{-}C_8H_8)]$			
130.6	4.92		1
93.2	4.64	$^3J(^1H^2\text{–}^1H^3)$ 10	2
104.8	5.19	$^3J(^1H^2\text{–}^1H^3)$ 10	3
102.5	6.28	$\lvert ^3J(^1H^3\text{–}^1H^4) + {}^4J(^1H^3\text{–}^1H^{4'})\rvert$ 6	4
(*b*) $[W(CO)_3(\eta^6\text{-}C_8H_8)]$			
133.3	5.26	$\lvert ^3J(^1H^1\text{–}^1H^2) + {}^4J(^1H^1\text{–}^1H^{2'})\rvert$ 3	1
		$^3J(^1H^1\text{–}^1H^{1'})$ 8	
82.2	4.23	$^3J(^1H^2\text{–}^1H^3)$ 10	2
101.4	5.40	$^3J(^1H^2\text{–}^1H^3)$ 10	3
98.5	6.14	$^3J(^1H^4\text{–}^1H^{4'})$ 10	4
		$^3J(^1H^4\text{–}^1H^3)$ ±10	
		$^4J(^1H^4\text{–}^1H^{3'})$ ∓ 3	

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† No reprints available.

ted the unambiguous assignment of the remaining ^{1}H n.m.r. signals, see Figure 3, and hence, *via* the ^{13}C-{^{1}H} decoupling experiments, the ^{13}C n.m.r. signals as given in the Table. These assignments are in agreement with the probable assignment of C^2 noted above and the ^{1}H assignments previously published for $[Cr(CO)_3(\eta^6\text{-}C_8H_8)]$ and $[Mo(CO)_3(\eta^6\text{-}C_8H_8)]$,[14] but not with those for $[W(CO)_3(\eta^6\text{-}C_8H_8)]$ [11] which are believed to be in error.

In order to determine the mechanism of the fluxionality of $[Cr(CO)_3(\eta^6\text{-}C_8H_8)]$ and $[W(CO)_3(\eta^6\text{-}C_8H_8)]$, the Forsén–Hoffman spin-saturation method was used. As originally described, the method was only applicable to sensitive nuclei,[5,6] but it has recently been extended to become a very powerful tool in dynamic ^{13}C n.m.r. spectroscopy.[7,8] It should, however, be noted that this is only the case because natural-abundance ^{13}C nuclei are magnetically dilute. In the original work,[5,6] the method was correctly applied to ^{1}H n.m.r. *intermolecular* exchange. Subsequently, a number of workers have applied the method ' quantitatively ' to ^{1}H n.m.r. *intramolecular* exchange where significant errors may arise from cross-correlation effects, nuclear-Overhauser enhancements, and decoupling.

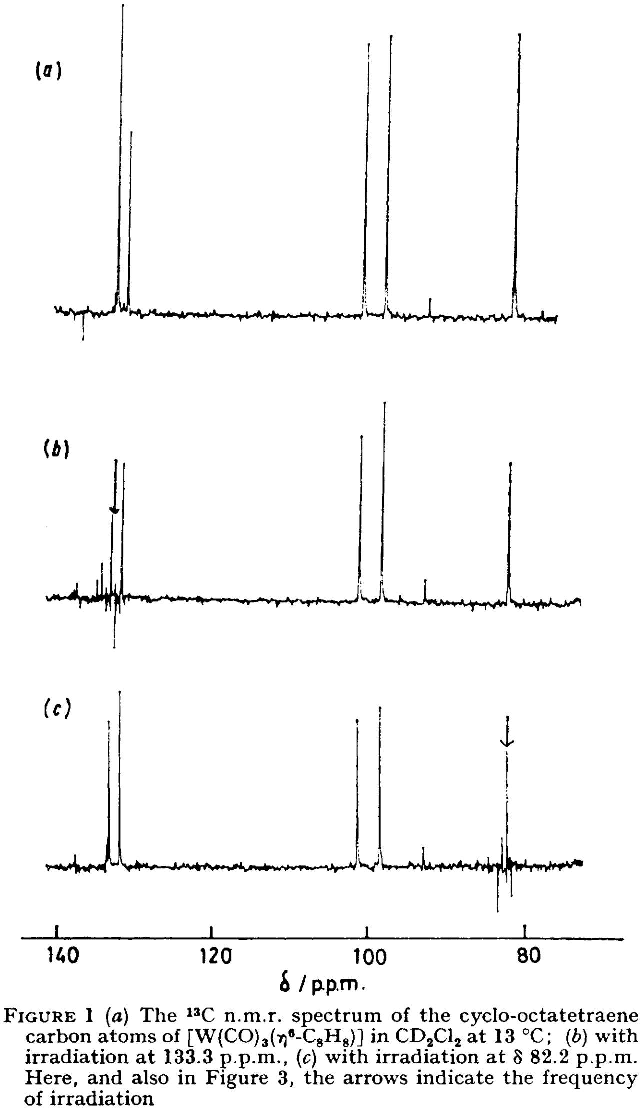


FIGURE 1 (*a*) The ^{13}C n.m.r. spectrum of the cyclo-octatetraene carbon atoms of $[W(CO)_3(\eta^6\text{-}C_8H_8)]$ in CD_2Cl_2 at 13 °C; (*b*) with irradiation at 133.3 p.p.m., (*c*) with irradiation at δ 82.2 p.p.m. Here, and also in Figure 3, the arrows indicate the frequency of irradiation

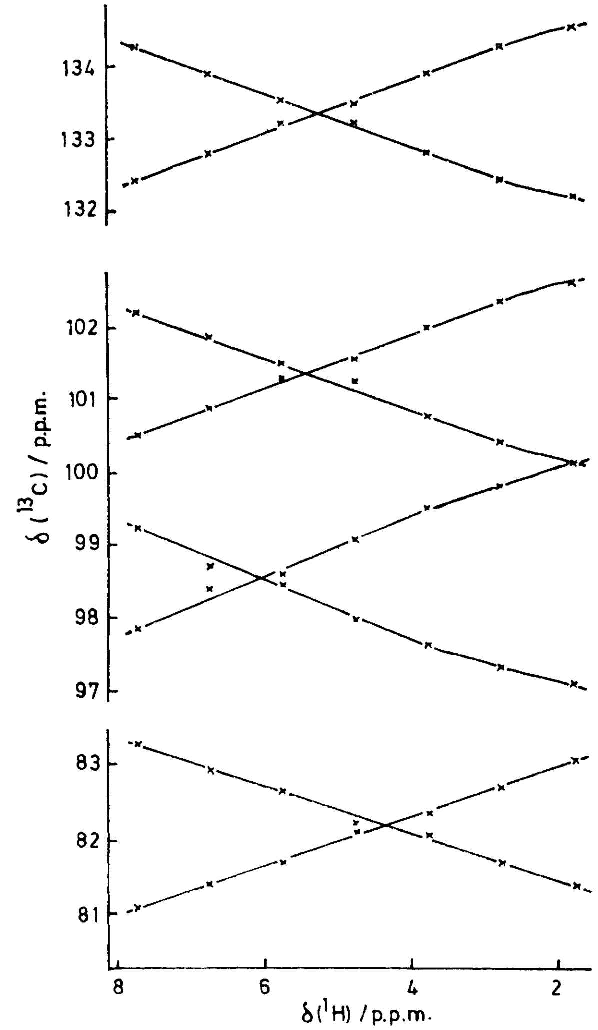


FIGURE 2 A plot of the ^{13}C chemical shifts of the partially proton-coupled spectra of $[W(CO)_3(\eta^6\text{-}C_8H_8)]$ in CD_2Cl_2 at 24.5 °C as a function of ^{1}H irradiation frequency (*cf.*, B. Birdsall, N. J. M. Birdsall, and J. Feeney, *J.C.S. Chem. Comm.*, 1972, **316**; J. W. Emsley, J. C. Lindon, and D. Shaw, *J. Magn. Resonance*, **1973**, **10**, 100)

In the original method,[6] in order to determine the exchange rate in an *n*-site problem, it was necessary to decouple *n* – 1 sites, a problem fraught with difficulties. When the method is applied to pulse Fourier-transform ^{13}C n.m.r. spectroscopy the difficulties vanish. It has been shown that if a pulse Fourier-transform ^{13}C n.m.r. spectrum is measured with at least 5 T_1 between each pulse, and in the presence and in the absence of a saturating decoupling field at one site, then, for the *K*th site, equation (1) holds, where M_0^K is the magnetisation of the *K*th site in the absence of

$$(M_0^K - M_z^K)/T_{1K} = M_z^K \sum_{K \neq \nu} \lambda_{K\nu} + \sum_{K \neq \nu} \lambda_{\nu K} M_z^{\nu} \quad (1)$$

irradiation, M_z^{ν} is the equilibrium magnetisation of the νth site in the presence of irradiation at one site, T_{1K} is the spin-lattice relaxation time of the *K*th site and $\lambda_{K\nu}$ is the exchange rate between the *K*th and νth sites.[8] It should be noted that λ_{12} is not the rate of a 1,2-shift since it arises from both the movement of C^1 to C^2 and to $C^{2'}$ in (1), *e.g.* if $k_{\alpha\beta}$ is the rate of the α,β-shift, then $\lambda_{1,2} = k_{1,2} + k_{1,3}$. A set of spectra is

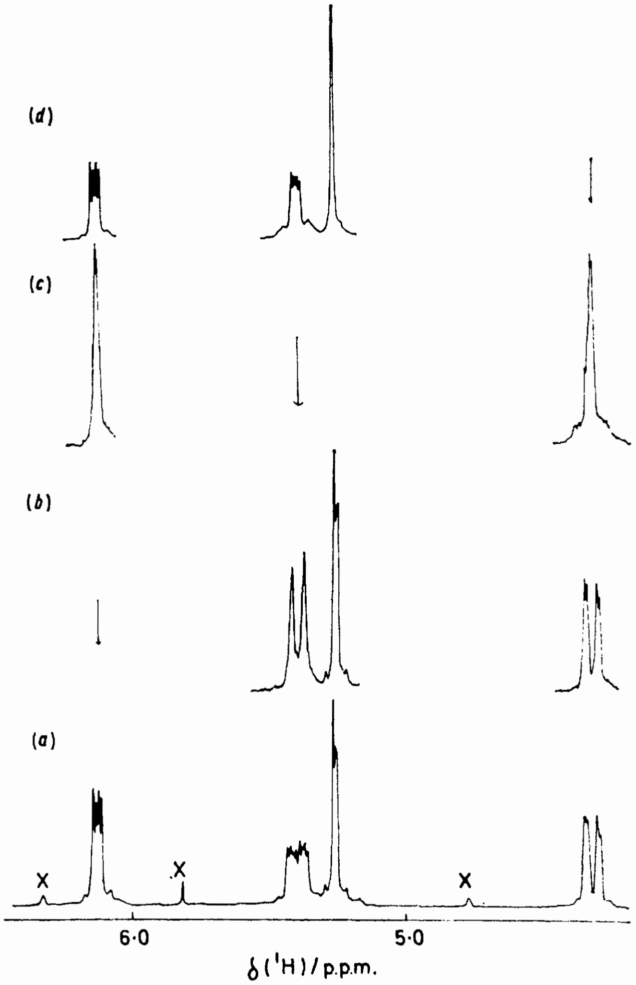
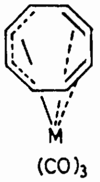


FIGURE 3 (*a*) The 220-MHz ^{1}H n.m.r. spectrum of $[\mathrm{W(CO)_3}(\eta^6\text{-}\mathrm{C_8H_8})]$ in $\mathrm{CDCl_3}$ at −20 °C; (*b*) with irradiation at δ 6.14 p.p.m., (*c*) with irradiation at 5.40 p.p.m., and (*d*) with irradiation at 4.23 p.p.m. Impurity signals (X) are present

shown in Figure 1. T_{1K} was measured using the usual $(\pi-\tau-\frac{\pi}{2}-5T_1)_n$ pulse sequence. This method is valid provided that all the exchanging sites have the same T_1,[15] which is true in this case. For $[\mathrm{Cr(CO)_3}(\eta^6\text{-}\mathrm{C_8H_8})]$ and $[\mathrm{W(CO)_3}(\eta^6\text{-}\mathrm{C_8H_8})]$ there are in principle 12 independent equations derivable and only four unknown rates. In practice, since the two resonances at δ 104.8 and 102.5 p.p.m. for $[\mathrm{Cr(CO)_3}(\eta^6\text{-}\mathrm{C_8H_8})]$, and at 101.4 and 98.5 p.p.m., for $[\mathrm{W(CO)_3}(\eta^6\text{-}\mathrm{C_8H_8})]$, are too close to saturate one without affecting the other, only six independent equations were derived. An inspection of the spectra for $[\mathrm{W(CO)_3}(\eta^6\text{-}\mathrm{C_8H_8})]$ in Figure 1 and for $[\mathrm{Cr(CO)_3}(\eta^6\text{-}\mathrm{C_8H_8})]$ * shows that saturation transfer is not random. Quantitative analysis of the spectra gave, for $[\mathrm{Cr(CO)_3}(\eta^6\text{-}\mathrm{C_8H_8})]$ at −22.5 °C, $k_{12} = 0.03 \pm 0.02\ \mathrm{s^{-1}}$ and $k_{13} = 0.29 \pm 0.03\ \mathrm{s^{-1}}$, and at −15 °C, $k_{12} = 0.12 \pm 0.06\ \mathrm{s^{-1}}$ and $k_{13} = 0.58 \pm 0.09\ \mathrm{s^{-1}}$, and, for $[\mathrm{W(CO)_3}(\eta^6\text{-}\mathrm{C_8H_8})]$ at 13 °C, $k_{12} = 0.44 \pm 0.08\ \mathrm{s^{-1}}$ and $k_{13} = 0.46 \pm 0.01\ \mathrm{s^{-1}}$. In each case, k_{14} and k_{15} were not significantly different from zero. Since k_{12} is not zero, then when the lines broaden by exchange the lines due to C^2 and C^3 should broaden faster than the lines due to C^1 and C^4. This behaviour was indeed found for $[\mathrm{Cr(CO)_3}(\eta^6\text{-}\mathrm{C_8H_8})]$ at 26.5 °C, see Figure 4. Lineshape analysis gave $k_{12} = 24\ \mathrm{s^{-1}}$ and $k_{13} = 48\ \mathrm{s^{-1}}$. Decomposition prevented similar measurements being made on $[\mathrm{W(CO)_3}(\eta^6\text{-}\mathrm{C_8H_8})]$. The compound $[\mathrm{W(CO)_3}(\eta^6\text{-}\mathrm{C_8H_8})]$ decomposes slowly even at room temperature to give a species with signals at δ 134.7 and 94.0 p.p.m. which may be $[\mathrm{W(CO)_4}(1\text{—}2:5\text{—}6\text{-}\eta^4\text{-}\mathrm{C_8H_8})]$ by analogy with the known reaction between $[\mathrm{Mo(CO)_3}(\eta^6\text{-}\mathrm{C_8H_8})]$ and CO to give $[\mathrm{Mo(CO)_4}(1\text{—}2:5\text{—}6\text{-}\eta^4\text{-}\mathrm{C_8H_8})]$.[16]

DISCUSSION

In the original work on $[\mathrm{M(CO)_3}(\eta^6\text{-}\mathrm{C_8H_8})]$ (M = Cr, Mo, or W) it was found that all the cyclo-octatetraene signals broaden at the same rate.[1] It was therefore concluded that 1,3- or random-shifts occur. Use of the Forsén–Hoffman spin-saturation method has shown the existence of 1,3-shifts, and, in contrast to the earlier work, 1,2-shifts. This work immediately eliminates the ' piano-stool ' mechanism proposed by Cotton involving the 20-electron intermediate, $[\mathrm{M(CO)_3}(\eta^8\text{-}\mathrm{C_8H_8})]$.[1] The simplest mechanism available to explain the fluxionality of $[\mathrm{M(CO)_3}(\eta^6\text{-}\mathrm{C_8H_8})]$ is *via* the 16-electron intermediate $[\mathrm{M(CO)_3}(1\text{—}4\text{-}\eta^4\text{-}\mathrm{C_8H_8})]$ as suggested by Whitesides and Budnik,[3] and found earlier by Cotton for $[\mathrm{Mo(CO)_2}(\eta\text{-}\mathrm{C_5H_5})(\eta^3\text{-}\mathrm{CH_2Ph})]$ which is fluxional *via* $[\mathrm{M(CO)_2}(\eta\text{-}\mathrm{C_5H_5})(\sigma\text{-}\mathrm{CH_2Ph})]$ (M = Mo or W).[17] There is an alternative mechanism available involving a concerted process where the free double bond displaces the co-ordinated double bond, *via* (2). However, this transition state must be very close in character to that for a 1,2-shift.



(2)

It is therefore possible that the transition state or intermediate lies between $[\mathrm{M(CO)_3}(1\text{—}4\text{-}\eta^4\text{-}\mathrm{C_8H_8})]$ and (2) in character, enabling both 1,2- and 1,3-shifts to occur.

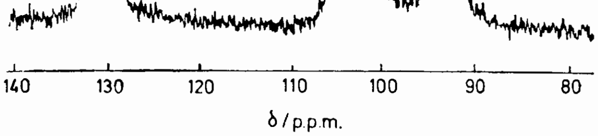


FIGURE 4 The ^{13}C n.m.r. spectrum of the cyclo-octatetraene-carbon atoms of $[\mathrm{Cr(CO)_3}(\eta^6\text{-}\mathrm{C_8H_8})]$ in $\mathrm{CD_2Cl_2}$–$\mathrm{CH_2Cl_2}$ at 26.5 °C

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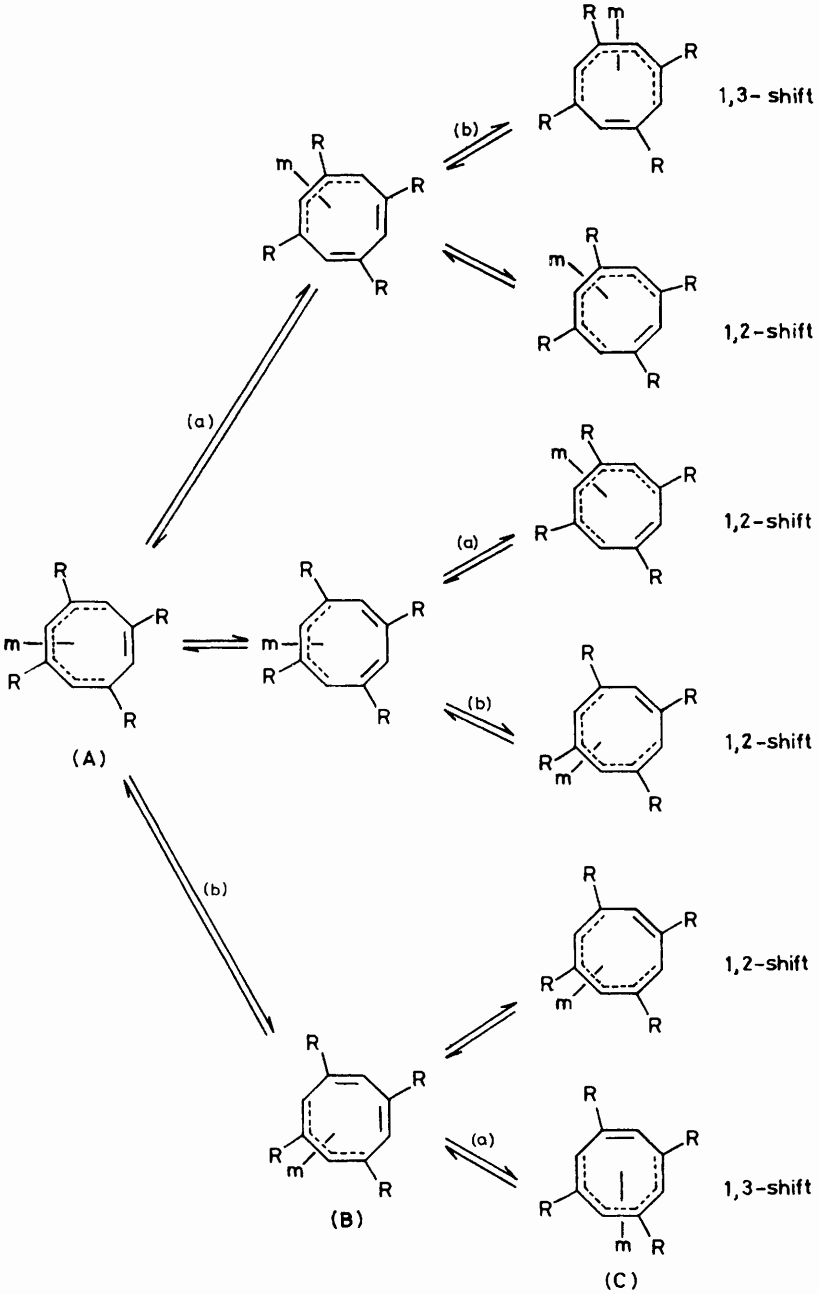
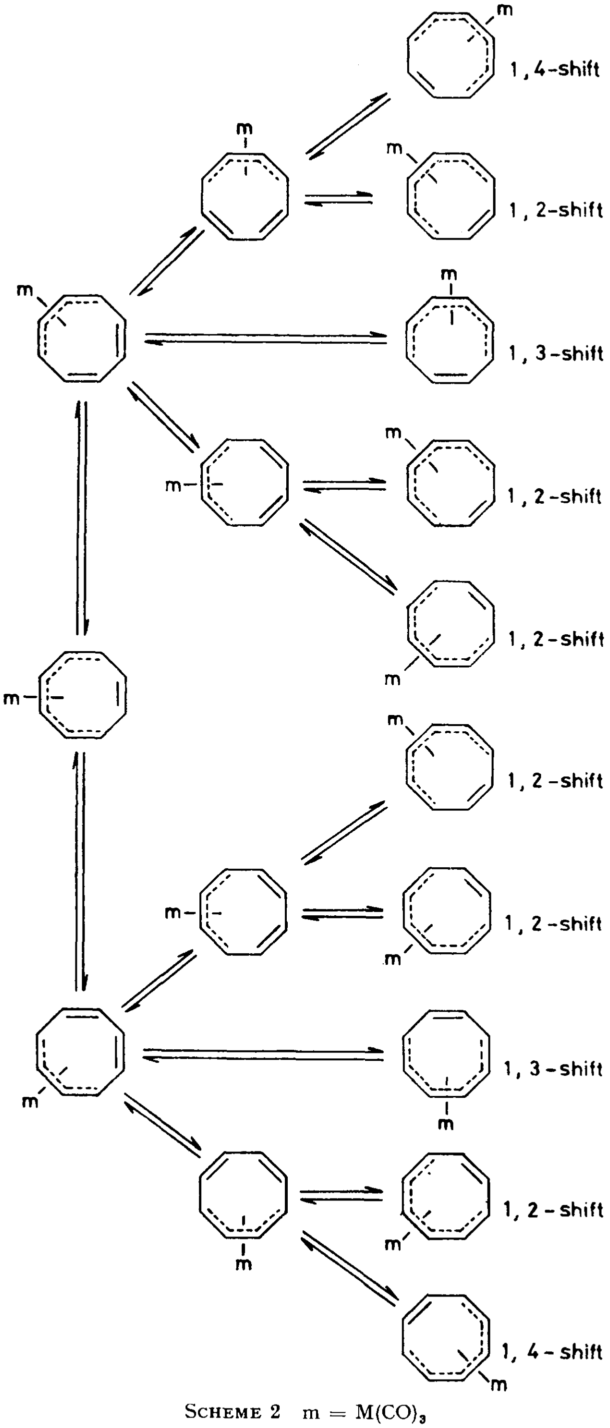
* See Figure in ref. 9.

If (2) can undergo a 1,2-shift, then, by the law of microscopic reversibility, we have to allow the reverse reaction to occur. Avoiding the complexity of including the extra bonding implicit in (2), then the complete reaction mechanism is given in Scheme 1 (R = H).

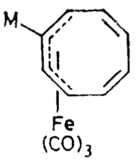


SCHEME 1 m = $M(CO)_3$

This is not the only way of producing 1,2-shifts in addition to the 1,3-shifts. It is known that, in general, $M(\eta^4-C_8H_8)$ complexes are highly fluxional. If the $[M(CO)_3(\eta^4-C_8H_8)]$ intermediate has a finite existence, long enough for one 1,2-shift to occur, then 1,2-, 1,3-, and 1,4-shifts will occur, with at least a 1,4-shift occurring for every three 1,2-shifts, see Scheme 2. More than one 1,2-shift in the $[M(CO)_3(\eta^4-C_8H_8)]$ intermediate leads to a greater probability of 1,4- and 1,5-shifts, producing random shifts in the limit of multiple 1,2-shifts in the $[M(CO)_3(\eta^4-C_8H_8)]$ intermediate. The spin-saturation data for $[W(CO)_3(\eta^6-C_8H_8)]$ make 1,4-shifts improbable since a rate of one third that of the 1,2-shifts is detectable. It is therefore probable that Scheme 1 represents the mechanism. Any mechanism should also be consistent with the observed 1,2-rock, followed by complete scrambling, found for $[Cr(CO)_3(\eta^6-C_8H_4Me_4-1,3,5,7)]$. The two terminal double bonds are not equivalent, and in order to explain the observations it is necessary to postulate that there is a considerable difference in the rates for their removal, although the resulting two [Cr(CO)$_3$(η^4-C$_8$H$_4$Me$_4$-1,3,5,7)] intermediates are identical, see reaction profile in Figure 5. Experimental evidence concerning the relative rates of removal of such bonds appears to be non-existent, and the only evidence is circumstantial. The most direct piece of evidence is that [Fe(CO)$_3$(η^4-C$_8$H$_7$Me)] adopts structure (3) as the most stable isomer.[18] This is consistent with the two requirements for Scheme 1 (R = Me) to fit the data, namely that methyl substitution stabilises the system, and hence increases the activation energy, and that the bonding to a double bond with a terminal methyl group is weaker than that to a double bond without a terminal methyl group. The ^{13}C co-ordination shifts are also consistent with this view. For [Cr(CO)$_3$(η^4-C$_8$H$_4$Me$_4$-1,3,5,7)] (4), the co-ordination shifts for C(2) and C(3) are between 24.3 and 26.5 p.p.m., while the co-ordination shifts for C(6) and C(7) are 39.1 and 23.9 or 21.9 p.p.m.[1] There appears to be a crude relationship between co-ordination shift and bond strength in closely related species.[19] Thus, in Scheme 1 (R = Me) there are two independent routes, (a) and (b) depending on the methyl-substitution pattern of the leaving double bond. If only one mechanism is operative, then there is no nett migration. It is when two mechanisms become operational that shifts occur. A combination of mechanism (a) and a 1,2-shift produces the lower-energy 1,2-rock. It is necessary to involve mechanism (b) before complete fluxionality is achieved. A reversal of the relative energies of mechanisms (a) and (b) would produce the reverse 1,2-rock to that observed.



SCHEME 2 m = M(CO)$_3$



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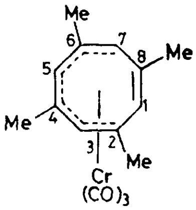

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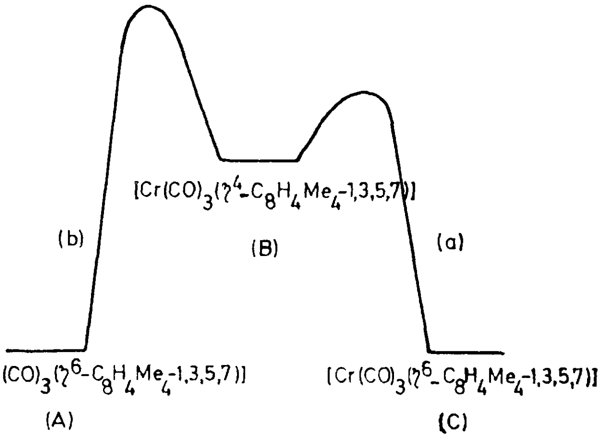
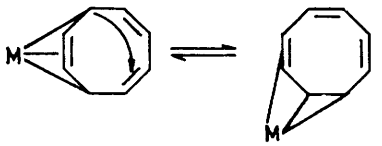


FIGURE 5 Reaction profile for [Cr(CO)$_3$(η^6-C$_8$H$_4$Me$_4$-1,3,5,7)]; (a) and (b) refer to the two mechanisms, and (A), (B), and (C) refer to the three compounds indicated in Scheme 1

The observation of 1,3-shifts in [M(CO)$_3$(η^6-C$_8$H$_8$)] compounds is anomalous since the vast majority of related compounds undergo 1,2-shifts. Even the very similar compound [Mn(CO)$_3$(η^5-C$_7$H$_7$)] undergoes 1,2-shifts. Recently, Mingos[20] has drawn attention to the ease of shifts in the η^4-C$_8$H$_8$, η^3-C$_7$H$_7$, η^2-C$_6$H$_6$, and σ-C$_5$H$_5$ systems and has interpreted this in terms of a symmetry-allowed thermal suprafacial [1,5]-shift, *e.g.*:



In contrast, in 18-electron compounds, the η^6-C_8H_8, η^5-C_7H_7, and η^4-C_6H_6 ring systems generally have high activation energies for fluxionality. In each case, the required thermal suprafacial [1,3]-shift is symmetry forbidden and either requires considerable energy or results in an alternative mechanism being adopted. In the case of the C_8H_8 ring the thermal suprafacial [1,3]-shift or the 1,2-shift, indicated in Scheme 1, is more difficult than for the smaller ring systems since the metal has to move a greater distance. In contrast, as the ring becomes larger, it becomes more difficult to bring the required number of carbon atoms into a plane to co-ordinate to the metal, an idea already expressed in terms of the 'elplacarnet tree.'[21] Consequently, the strain in the cyclo-octatetraene ring favours the removal of one double bond to give a 16-electron intermediate, and consequently 1,3-shifts. On going from the chromium atom, in [$Cr(CO)_3$(η^6-C_8H_8)], to the larger tungsten atom, in [$W(CO)_3$(η^6-C_8H_8)], it becomes easier to bond all six carbon atoms to the metal and 1,3-shifts are discouraged with the corresponding increase in 1,2-shifts.

The mechanism *via* [$M(CO)_3$(1—4-η^4-C_8H_8)] raises the possibility of 1,5-shifts *via* [$M(CO)_3$(1—2 : 5—6-η^4-C_8H_8)]. While there is no experimental evidence for the occurrence of such shifts, [$Mo(CO)_3$(1—6-η^6-C_8H_8)] reacts with carbon monoxide to give [$Mo(CO)_4$(1—2 : 5—6-η^4-C_8H_8)] [16] and it appears from the present work that [$W(CO)_3$(1—6-η^6-C_8H_8)] decomposes to give [$W(CO)_4$(1—2 : 5—6-η^4-C_8H_8)] rather than the corresponding [$M(CO)_4$(1—4-η^4-C_8H_8)] isomers. The explanation may arise from the fact that [$M(CO)_4$(1—2 : 5—6-η^4-C_8H_8)] (M = Mo or W) are six-co-ordinate. In the five-co-ordinate [$Fe(CO)_3$(η^4-C_8H_8)],[22] the cyclo-octatetraene is co-ordinated in the 1—4-η^4 mode rather than the 1—2 : 5—6-η^4 mode. It is therefore suggested that the fluxionality of [$M(CO)_3$(η^6-C_8H_8)] *via* [$M(CO)_3$(1—4-η^4-C_8H_8)] rather than [$M(CO)_3$(1—2 : 5—6-η^4-C_8H_8)] arises from the greater stability of the 1—4-η^4-C_8H_8 co-ordination in the five-co-ordinate intermediate. However, a mechanism *via* the 18-electron intermediate, (2), may provide the explanation.

At present there are only a few fluxional compounds which show the 18- to 16- to 18-electron change for fluxionality, namely [$Mo(CO)_2$(η-C_5H_5)(η^3-CH_2Ph)],[13] [$Fe(CO)_3$(η^4-C_7H_8)],[23] and [$M(\eta^6$-$C_8H_8)$] [M = $Cr(CO)_3$, $Mo(CO)_3$, $W(CO)_3$, and probably Ru(η^4-C_7H_8) [2]]. The reverse 16- to 18- to 16-electron mechanism has been shown for [$Pd(\eta^3$-$C_7H_9)L_2]^+$ and related compounds.[24] It is to be anticipated that this mechanism of fluxionality will be found more commonly in the future.

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