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Fluxionality of Polyene and Polyenyl Metal Complexes

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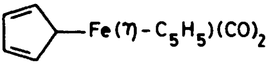
1 Introduction

Since the discovery of the fluxionality of $Fe(\eta^1\text{-}C_5H_5)(\eta^5\text{-}C_5H_5)(CO)_2$ (1) there has been considerable interest in the dynamic behaviour of polyenes and polyenyls attached to metals.[1] In part, interest was raised from the realization that the mechanism could be determined from the observation of differential line broadening during the onset of fluxionality. During the initial investigations, the mechanism was controversial because of ambiguities of assignment of the signals of σ-cyclopentadienyl groups. Several ingenious approaches were adopted to solve this problem, and by the early seventies it appeared that the dynamic behaviour of polyene and polyenyl metal complexes could be interpreted in terms of the least motion model with the metal undergoing [1,2]-shifts. An excellent review of this stage of development appeared in 1975 and the reader is referred to it for further information.[2] Subsequently a number of awkward observations were made which were very difficult to explain using this approach. Thus, $(\eta^4\text{-}C_8H_8)Fe(CO)_3$ is highly fluxional with $\Delta G^\ddagger = 28.5$ kJ mol^{-1} while $[(\eta^2\text{-}C_8H_8)Fe(\eta^5\text{-}C_5H_5)(CO)_2]^+$, $(\eta^2\text{-}C_8H_8)Mn(\eta^5\text{-}C_5H_5)(CO)_2$, and $[(\eta^6\text{-}C_8H_8)Fe(\eta^5\text{-}C_5H_5)]^+$ have $\Delta G^\ddagger > 90$ kJ mol^{-1}.[3–6] Over the same period, the work of Hoffmann[7] especially led to a greater understanding of the bonding in these compounds and enabled Mingos[8] to develop a theoretical model for the dynamic behaviour of these systems based on



(1)

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[1] T. S. Piper and G. Wilkinson, *J. Inorg. Nucl. Chem.*, 1956, **3**, 104.

[2] F. A. Cotton, in 'Dynamic Nuclear Magnetic Resonance Spectroscopy', ed. L. M. Jackman and F. A. Cotton, Academic Press, New York, 1975, p. 377

[3] F. A. Cotton and D. L. Hunter, *J. Am. Chem. Soc.*, 1976, **98**, 1413.

[4] A. Cutler, D. Ehntholt, W. P. Giering, P. Lennon, S. Raghu, A. Rosan, M. Rosenblum, J. Tancrede, and D. Wells, *J. Am. Chem. Soc.*, 1976, **98**, 3495.

[5] I. B. Benson, S. A. R. Knox, R. F. D. Stansfield, and P. Woodward, *J. Chem. Soc., Chem. Commun.*, 1977, 404.

[6] D. L. Reger and C. Coleman, *J. Organomet. Chem.*, 1977, **131**, 153.

[7] R. Hoffmann, *Science*, 1981, **211**, 995.

[8] D. M. P. Mingos, *J. Chem. Soc., Dalton Trans.*, 1977, 1; D. M. P. Mingos, in 'Comprehensive Organometallic Chemistry', ed. E. W. Abel, F. G. A. Stone, and G. Wilkinson, Pergamon Press, Oxford, 1982, Vol. 3, p. 1.

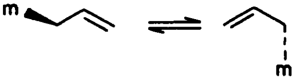
the Woodward–Hoffmann rules of organic chemistry.[9] This review will examine the application of these rules to fluxional organometallic systems, the evidence for the applicability of these rules, the mechanisms available to systems where these rules prohibit dynamic behaviour, and the problem molecules which do not appear to fit into these mechanisms. A review of this treatment appeared in 1982, but is now somewhat out of date.[10]

It is convenient to divide the fluxional polyene and polyenyl metal complexes into those with a σ-polyenyl ligand and the rest.

2 Molecules Containing σ-Polyenyl Ligands

A. Theoretical Background.—Those complexes with a σ-polyenyl ligand can be expected to follow the same rules as found for organic migration reactions involving polyenyl groups. Thus a hydrogen atom undergoes sigmatropic shifts, subject to strict rules which derive from the conservation of orbital symmetry.[9] For the purposes of this review, the relevant rules are that:

(a) A 1,3-sigmatropic shift occurs antarafacially, *i.e.*, the migrating group moves from one side of the ligand to the other (see Scheme 1).



Scheme 1

Although this process is theoretically allowed, it is very difficult for the migrating group to be bonded to both ends of the ligand in the transition state because of the large distances involved. As a consequence this process has not been detected in organometallic compounds.

(b) A 1,5-sigmatropic shift occurs suprafacially, *i.e.*, the migrating group remains on the same side of the ligand (see Scheme 2).

Scheme 2

As it is easy to bring both ends of the ligand close together in a *cis*-pentadienyl or cyclopentadienyl group, the migrating group can easily move between the two ends of the ligand, and there are many examples of this process. However, for a *trans*-pentadienyl ligand, a large distance separates the two ends of the ligand making it very difficult for the metal group to migrate, and this process has not been observed.

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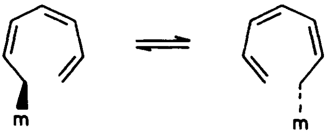
[9] R. B. Woodward and R. Hoffmann, 'The Conservation of Orbital Symmetry', Academic Press, New York, 1970.

[10] B. E. Mann, in 'Comprehensive Organometallic Chemistry', ed. E. W. Abel, F. G. A. Stone, and G. Wilkinson, Pergamon Press, Oxford, 1982, Vol. 3, p. 90.

(c) A 1,7-sigmatropic shift occurs antarafacially, *i.e.*, the migrating group moves from one side of the ligand to the other (see Scheme 3).



Scheme 3

This process is in theory facile when the ligand is *cis,cis*-heptatrienyl, but no metal complexes of this ligand are at present known. Complexes are known of the cycloheptatrienyl ligand, but it would be very difficult for a concerted reaction to occur with the metal group moving from one side of the ligand to the other.

(d) A 1,9-sigmatropic shift occurs suprafacially, *i.e.*, the migrating group remains on the same side of the ligand (see Scheme 4).

Scheme 4

Although there are no metal complexes of the nona-tetraenyl ligand known, the fluxionality of one complex containing the σ-cyclononatetraenyl group has been observed.

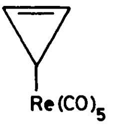
In all these cases, if the migrating group is chiral, the migration will occur with retention of chirality.

Problems occur when the orbital being used by the migrating metal atom is *p* or *d* in character. It has been shown that for a *p*-orbital, the above rules are reversed. This means that if it is not known whether the orbital is *s* or *p*, there is in effect no rule as the correct orbital can be selected to fit the facts. However, it will be shown that the vast majority of complexes behave in a way consistent with the orbital used to bond the metal to the polyenyl ligand being normally hydrogen-like and can therefore be treated using the rules outlined above for *s*-orbitals. The few exceptions may arise from the involvement of *p*- and/or *d*-orbitals.

A second problem occurs in that the above rules were established in organic chemistry, where the carbon–carbon and carbon–hydrogen bond strengths are substantial. Processes involving the loss of orbital symmetry require energy comparable with the bond strength. As metal–carbon bond strengths are considerably weaker than carbon–carbon and carbon–hydrogen bond strengths, 'forbidden' fluxional processes requiring close to the metal–carbon bond strength are to be expected.

B. Experimental Evidence.—The evidence will be examined by ligand type over as wide a range of compounds as possible, but the coverage is not intended to be exhaustive.

(a) σ-Cyclopropenyl derivatives should be 'static' on the above arguments. Only two such organometallic compounds appear to have been reported, namely $Re(\eta^1\text{-}C_3H_3)(CO)_5$,[11] (2) and the two isomers of $Re(\eta^1\text{-}C_3HDBu^t)(CO)_5$, (3) and (4).[12]



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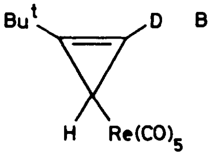

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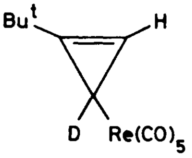

(4)

Both compounds are static, and (3) and (4) do not interconvert! Consequently, the activation energy for the forbidden [1,3]-shifts must be greater than 100 kJ mol^{-1}.

(b) σ-Allyl derivatives should also be 'static' and where no other fluxional pathway is feasible, experiment supports the rules. Thus $Mn(\eta^1\text{-}C_3H_5)(CO)_5$ and $Sn(\eta^1\text{-}C_3H_5)_4$ are static[13,14] as no alternative mechanism is energetically available. However, many alternative mechanisms are available and some can be identified. $Ti(\eta^1\text{-}C_3H_5)(NMe_2)_3$ (5) and $Pd(\eta^1\text{-}C_3H_5)(PMe_2Ph)(O_2CC_5H_4N)$ are highly fluxional[15,16] but as the central atoms have less than 18 electrons in the co-ordination sphere, the metal can expand its co-ordination sphere to give an $\eta^3\text{-}C_3H_5$ intermediate for the reaction pathway (see Scheme 5). A variation on this mechanism involves the initial loss of a ligand. Thus, for $Co(dmgH)_2(\eta^1\text{-}C_3H_5)(OH_2)$, water is lost to give $Co(dmgH)_2(\eta^3\text{-}C_3H_5)$ as an intermediate.[17] It has been shown that exchange occurs between the η^1- and η^2-bonded ends in $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(\eta^1,\eta^2\text{-}CH_2CH{=}CH_2)Fe(\eta^5\text{-}C_5H_5)(CO)_2]^+$ (6) and $Pt_2(acac)_2(\eta^1,\eta^2\text{-}C_3H_5)_2$[18,19] (see Scheme 6). This mechanism has only been demonstrated for these two intramolecular processes, but can, in principle, provide a mechanism for intermolecular exchange. This mechanism could be operative in allyl exchange on $Hg(\eta^1\text{-}C_3H_5)X$ where the process is catalysed by the presence of

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[11] D. M. DeSimone, P. J. Desrosiers, and R. P. Hughes, *J. Am. Chem. Soc.*, 1982, **104**, 4842.

[12] P. J. Desrosiers and R. P. Hughes, *J. Am. Chem. Soc.*, 1981, **103**, 5593.

[13] H. L. Clarke and N. J. Fitzpatrick, *J. Organomet. Chem.*, 1972, **40**, 379.

[14] M. Fishwick and M. G. H. Wallbridge, *J. Organomet. Chem.*, 1970, **25**, 69.

[15] H. J. Neese and H. Bürger, *J. Organomet. Chem.*, 1971, **32**, 213.

[16] J. Powell and A. W. L. Chan, *J. Organomet. Chem.*, 1972, **35**, 203.

[17] C. J. Cooksey, D. Dodd, M. F. Johnson, and B. L. Lockman, *J. Chem. Soc., Dalton Trans.*, 1978, 1814.

[18] G. E. Jackson, J. R. Moss, and L. G. Scott, *S.-Afr. Tydskr. Chem.*, 1983, **36**, 69.

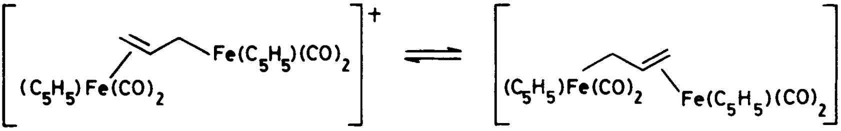
[19] B. P. Gracey, B. E. Mann, and C. M. Spencer, *J. Organomet. Chem.*, 1985.

Hg^{2+}.[20] Even radical mechanisms can occur, as have been observed in the dynamic behaviour of $(\eta^5\text{-}C_5H_5)Fe(CO)\{P(OCH_2)_3CMe\}(\eta^1\text{-}C_3H_5)$.[21]

(5)

Scheme 5

(c) σ-Cyclopentadienyl groups are generally fluxional, as predicted by the Woodward–Hoffmann rules, undergoing the required [1,5]-suprafacial shifts. The activation energy may range from *ca.* 30 kJ mol^{-1} in $Sn(\eta^1\text{-}C_5H_5)Me_3$, upwards.[22] The activation energy appears to reflect the strength of the metal–carbon bond. This is why in $Sn(5\text{-}\eta^1\text{-}C_5H_5)Me_3$, the tin migration is far more facile than hydrogen migration to give isomers, $Sn(1\text{-}\eta^1\text{-}C_5H_5)Me_3$ and $Sn(2\text{-}\eta^1\text{-}C_5H_5)Me_3$. This is a problem for the analogous silicon compound, where isomerization occurs at a comparable rate to silicon migration.[23]



(6)

Scheme 6

The Woodward–Hoffmann rules predict that the dynamic behaviour occurs with retention of configuration at the metal. This effect has been observed for $Mo(\eta^1\text{-}C_5H_5)(\eta^5\text{-}C_5H_5)(NO)(S_2CNBu^n{}_2)$,[24] and $Fe(\eta^1\text{-}C_5H_5)(\eta^5\text{-}C_5H_5)(CO)L$.[25]

(d) There are only two examples of covalent complexes containing the σ-pentadienyl group: $Ph_3SnC_5H_7$ and $Ph_3SnC_7H_9$.[26,27] In both cases, the tin undergoes [1,5]-suprafacial shifts. In addition there are examples of beryllium, magnesium, and zinc complexes, but it is probable, that these complexes are

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[20] W. Kitching, M. L. Bullpitt, P. D. Sleezer, S. Winstein, and W. G. Young, *J. Organomet. Chem.*, 1972, **34**, 233.

[21] M. Rosenblum and P. Waterman, *J. Organomet. Chem.*, 1981, **206**, 197.

[22] Yu. K. Grishin, Y. M. Sergeyev, and Yu. A. Ustynyuk, *Org. Magn. Reson.*, 1972, **4**, 377.

[23] A. V. Kisin, V. A. Korenevsky, N. M. Sergeyev, and Yu. A. Ustynyuk, *J. Organomet. Chem.*, 1972, **34**, 93.

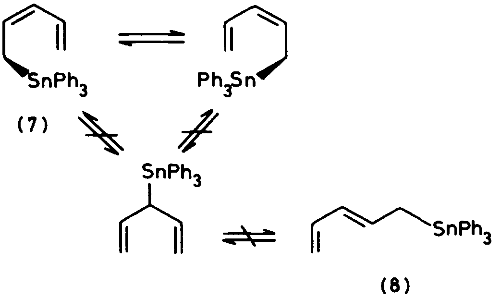
[24] N. M. Hunt, W. G. Kita, B. E. Mann, and J. A. McCleverty, *J. Chem. Soc., Dalton Trans.*, 1978, 467.

[25] B. D. Fabian and J. A. Labinger, *J. Organomet. Chem.*, 1980, **204**, 387.

[26] M. H. Hails, B. E. Mann, and C. M. Spencer, *J. Chem. Soc., Dalton Trans.*, 1983, 729.

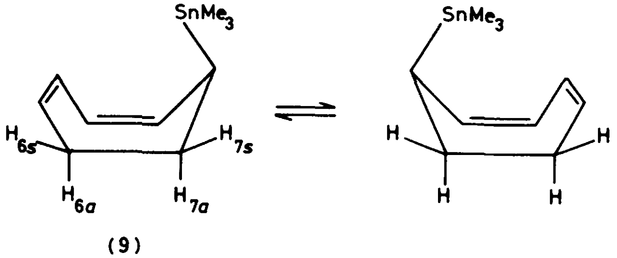
[27] B. E. Mann, B. F. Taylor, N. A. Taylor, and R. Wood, *J. Organomet. Chem.*, 1978, **162**, 137.

significantly ionic and could undergo a mechanism involving ion pairs.[28] The *cis*-isomer of $Ph_3SnC_5H_7$ (7) is fluxional while the *trans*-isomer (8) is static. This observation is consistent with a [1,5]-shift mechanism, where geometric constraints prevent the shift in the *trans*-isomer. The absence of dynamic behaviour in the *trans*-isomer also eliminates the possibility of the mechanism being two sequential [1,3]-shifts, as both the *cis*- and *trans*-isomers would give the same intermediate (see Scheme 7).



Scheme 7

The suprafacial nature of the [1,5]-shift has been demonstrated in $Me_3SnC_7H_9$ (9) where ^1H magnetization transfer measurements clearly show the pairwise exchange of the protons H_{6s} and H_{7s} and H_{6a} and H_{7a}[29] (see Scheme 8).



Scheme 8

(e) There are a number of examples of complexes containing the σ-cycloheptatrienyl group. Unfortunately, unlike the classes of compounds discussed earlier, the results are conflicting, and at least two mechanisms appear to be operative. For $R_3SnC_7H_7$, R = Me or Ph, both ^1H and ^{13}C n.m.r. spectra have

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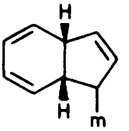
[28] H. Yasuda, Y. Ohnuma, A. Nakamura, Y. Kai, N. Yasuoka, and N. Kasai, *Bull. Chem. Soc. Jpn.*, 1980, 53, 1101.

[29] B. P. Gracey and B. E. Mann, unpublished results.

been used to show the shifts are [1,5].[27,30] The mechanism is facilitated by the conformation, as demonstrated by the X-ray structure.[31] The seven-membered ring adopts a 'boat' conformation with the Ph_3Sn substituent axial, and close to carbon to which it migrates.

Problems arise with the σ-cycloheptatrienyl derivatives of the transition metals. A detailed investigation of $Re(\sigma\text{-}C_7H_7)(CO)_5$ has shown that [1,2]-shifts occur,[32] despite the X-ray structure[32] showing the molecule to have the same 'boat'-structure with axial $Re(CO)_5$ as observed for $Ph_3SnC_7H_7$.[31] An ambivalent behaviour has been found for $(\eta^5\text{-}C_5H_5)Ru(CO)_2(\sigma\text{-}C_7H_7)$, where spin saturation transfer measurements have shown that both [1,2]-and [1,5]-shifts occur.[33] At present the cause of the [1,2]-shifts is far from clear. It could arise from the breakdown of the Woodward–Hoffmann rules due to the participation of the metal p- and/or d-orbitals. Alternatively, the activation energy is not far removed from the homolytic fission energy of the metal–carbon bond, as estimated from the decomposition rate. It follows from the Woodward–Hoffmann treatment, that the symmetry forbidden mechanism should have an activation energy comparable with the bond fission energy.[9]

(f) Due to the facile rearrangement of σ-cyclononatetrenyl ligands to (10), only one such complex has been shown to be fluxional, namely $H_3Sn(C_9H_9)$ where $\Delta G^\ddagger = ca.\ 38$ kJ mol^{-1}.[34] [1,9]-shifts occur as predicted by the Woodward–Hoffmann rules.



(10)

3 Molecules Containing π-Polyenyl Ligands

A. Theoretical Background.—The real breakthrough in establishing the value of the Woodward–Hoffmann rules to fluxional organometallic compounds came when Mingos showed how they can be applied to π-bonded ligands.[8] This is illustrated best by considering complexes of cyclo-octatetraene. When the cyclo-octatetraene ligand is η^4-bonded, then a valence bond representation of the bonding is (11). This representation is consistent with the changes in diene bond lengths on η^4-co-ordination to a metal, when the middle carbon–carbon bond shortens and the terminal ones lengthen.[8] The least-motion shift of the metal can then be represented

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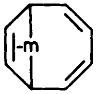
[30] R. B. Larrabee, *J. Am. Chem. Soc.*, 1971, **93**, 1510.

[31] J. E. Weidenborner, R. B. Larrabee, and A. L. Bednowitz, *J. Am. Chem. Soc.*, 1972, **94**, 4140.

[32] D. M. Heinekey and W. A. G. Graham, *J. Am. Chem. Soc.*, 1979, **101**, 6115; D. M. Heinekey and W. A. G. Graham, *J. Organomet. Chem.*, 1982, **232**, 335.

[33] D. M. Heinekey and W. A. G. Graham, *J. Am. Chem. Soc.*, 1982, **104**, 915.

[34] A. Bonny and S. R. Stobart, *J. Chem. Soc., Dalton Trans.*, 1979, 786.



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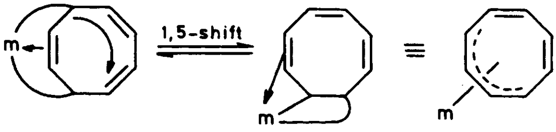
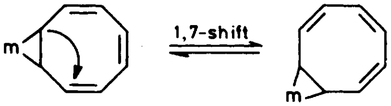


Scheme 9

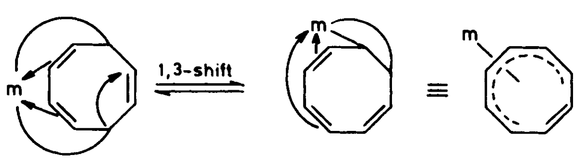
as a [1,5]-suprafacial sigmatropic shift of one of the metal–cyclo-octatetraene bonds (see Scheme 9). This is a fully allowed process and consequently is facile.

When the same treatment is applied to the η^2-cyclo-octatetraene ligand, then a [1,7]-suprafacial sigmatropic shift is required, which is forbidden (see Scheme 10).



Scheme 10

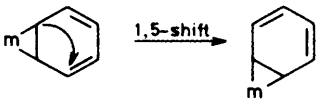
Similarly, the same treatment can be applied to the η^6-cyclo-octatetraene ligand, where a [1,3]-suprafacial shift is required. This is also forbidden (see Scheme 11).



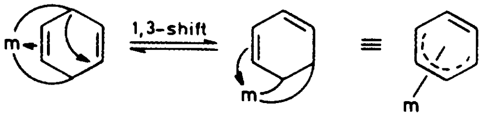
Scheme 11

This approach works equally well for arenes, correctly predicting the high fluxionality of the (η^2-C_6R_6) system. In a valence bond analysis of the system, an allowed [1,5]-sigmatropic shift is required (see Scheme 12).

The dynamic behaviour of an η^4-arene ring requires a forbidden [1,3]-sigmatropic shift (see Scheme 13), and such systems generally have very high activation energies.

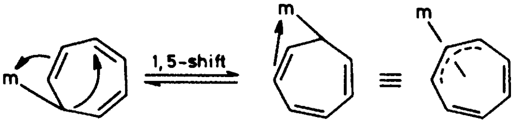


Scheme 12



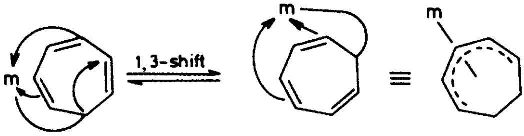
Scheme 13

Problems arise with the cycloheptatrienyl ring. The η^3-C_7H_7 system is predicted as being highly fluxional as [1,5]-shifts are required (see Scheme 14). Systems



Scheme 14

containing the (η^5-C_7H_7) ring are predicted as being 'static' or highly hindered due to the forbidden [1,3]-shift (see Scheme 15), but these systems are frequently highly fluxional.



Scheme 15

This treatment based on the Woodward–Hoffmann rules represents a significant increase in the predictive understanding of these fluxional compounds, but does not make further predictions that can then be tested by experiment. Consequently, the treatment has been further extended[35] to predict the resulting motion of the other ligands on the metal when the metal is undergoing shifts on the polyene or polyenyl ring. For η^4-cyclo-octatetraene complexes of iron, using the valence bond treatment outlined above, the coordination at the iron can be viewed as remaining constant during the bond shift (see Scheme 16). Thus, as the iron moves around the ring, there are consequential movements of the other ligands on the metal. If this migration causes the population of a higher energy isomer, then the activation

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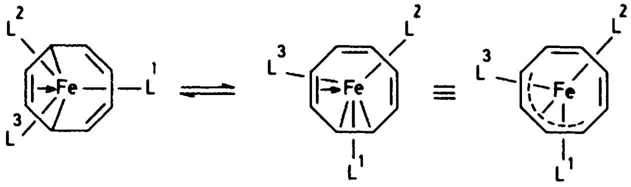
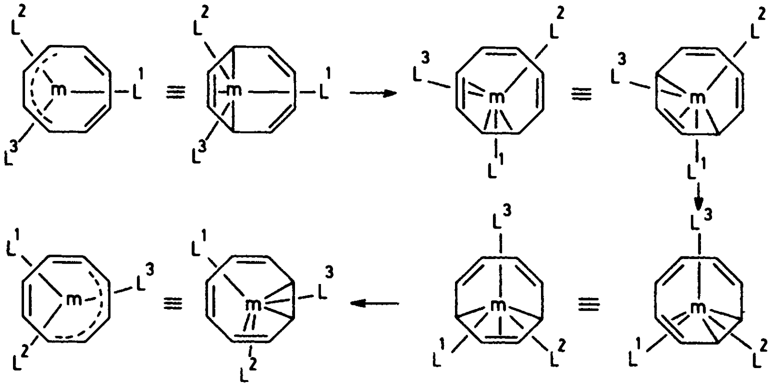
[35] M. H. Hails, B. E. Mann, and C. M. Spencer, *J. Chem. Soc., Dalton Trans.*, 1985, 693.



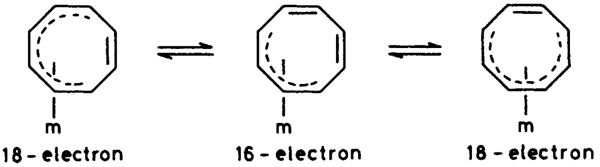
Scheme 16

energy will increase, and possibly give the impression of longer range shifts, *e.g.*, [1,4]-shifts as a result of the required three consecutive [1,2]-shifts to get back to the ground state (see Scheme 17).



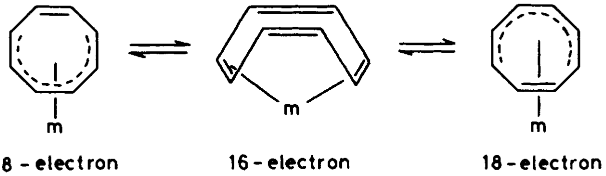
Scheme 17

Although fluxionality permitted by the Woodward–Hoffmann rules is the dominant mechanism in all systems so far investigated, a major alternate mechanism has been discovered, based on a change in the number of valence electrons. Thus, an 18-electron η^6-C_8H_8 complex can undergo [1,3]-shifts by one double bond lifting away from the metal to give an η^4-C_8H_8 complex, and then the other double bond co-ordinates (see Scheme 18).



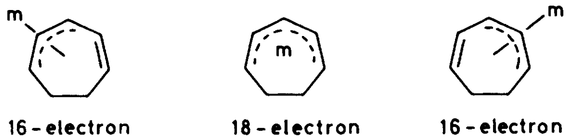
Scheme 18

Alternatively, [1,5]-shifts can be achieved similarly (see Scheme 19).



Scheme 19

When the ground state is a 16-electron complex, then the reverse mechanism can occur, with an 18-electron intermediate (see Scheme 20).



Scheme 20

A number of other less-well defined mechanisms exist and will be discussed later.

B. Experimental Evidence for Sigmatropic Shifts.—The initial evidence was circumstantial and will be examined from the nature of the ligand.

(a) The best and most extensive evidence comes from complexes of the cyclooctatetraene ligand. Considerable work has been done on η^4-complexes, and it had been demonstrated that this ligand is highly fluxional due to the allowed [1,5]-sigmatropic shifts, resulting in the observed [1,2]-metal shifts (see Scheme 9). Thus $Fe(\eta^4\text{-}C_8H_8)(CO)_3$ is extremely fluxional with $\Delta G^{\ddagger} = 28.5$ kJ mol^{-1}.[3] The *X*-ray structure shows that there are two types of carbonyl groups. The metal migration in Scheme 16 results in the two types of carbonyl groups exchanging at the same rate as the [1,2]-shifts. This behaviour has been observed by ^{13}C n.m.r. spectroscopy,[3] but does not prove the mechanism. It is possible that the two fluxional processes are not connected, but are accidentally degenerate. It is known that the carbonyl groups in the complexes $Fe(\eta^4$-butadiene$)(CO)_3$ scramble with $\Delta G^{\ddagger} = 44$ kJ mol^{-1}.[36,37] In order to differentiate between these two possibilities $Fe(\eta^4\text{-}C_8H_8)(CO)_2(CNPr^i)$ was examined.[35] The application of the Woodward–Hoffmann rules and the local ligand movements outlined above in Scheme 16, predicts the very specific ligand movements as given in Scheme 21. $Fe(\eta^4\text{-}C_8H_8)(CO)_2(CNPr^i)$ exists in solution at −118 °C as mixture of two isomers, (12) and (13). The existence of these ligand movements was proved to occur by use of

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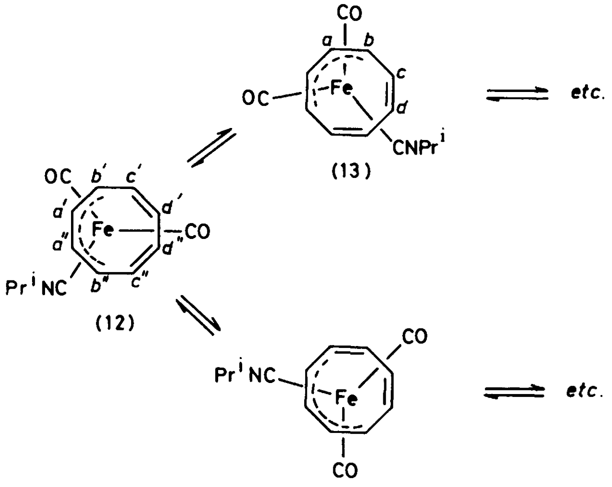
[36] L. Kruczynski and J. Takats, *Inorg. Chem.*, 1976, **15**, 3140.

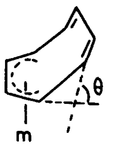
[37] D. Leibfritz and H. tom Dieck, *J. Organomet. Chem.*, 1976, **105**, 255.

selective population inversion in the ^{13}C n.m.r. spectrum to label one specific carbon atom, *b′*, and to demonstrate that it moves initially to positions *a and c″*. This observation is completely consistent with the predictions in Scheme 21 and inconsistent with all other possible mechanisms.



Scheme 21

Using this approach, it is then possible to explain qualitatively the relative activation energies for the dynamic behaviour of η^4-C_8H_8 complexes for a given metal. For complexes of the type $M(\eta^4\text{-}C_8H_8)L_n$, the distance between the metal and the nearest uncoordinated carbon atoms of the cyclo-octatetraene ring will determine the ease of the [1,5]-sigmatropic shift shown in Scheme 9. An equivalent statement of this approach was made by Cotton in 1971, when he used the angle between the plane of the four coordinated carbon atoms and the plane of the four non-bonded carbon atoms to explain the relative ease of fluxionality,[38] as in (14).



(14)

For complexes of the type $M(\eta^4\text{-}C_8H_8)L_nL'_{3-n}$, the presence of the two different ligands results in the interconversion of isomers, as shown in Scheme 21. In the case of $Fe(\eta^4\text{-}C_8H_8)(CO)_2(CNPr^i)$ discussed above, there is little or no difference in

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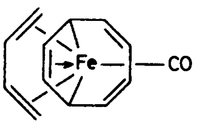
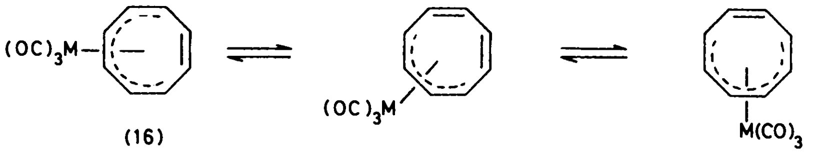
[38] F. A. Cotton, B. F. DeBoer, and M. D. LaPrade, *23rd. Int. Congr. Pure Appl. Chem., 1971 Spec. Lect.*, vol. 6, p. 1.



(15)

energy between the two isomers, but, for Fe(η^4-C_4H_6)(η^4-C_8H_8)(CO) (15), there is a marked difference in energy so that only one isomer is detected. When dynamic behaviour occurs, then at first sight, a [1,4]-shift might be expected resulting from three sequential [1,2]-shifts (see Scheme 22). However, it would appear that the



Scheme 22

disfavoured isomer is of such high energy, that instead of taking three sequential [1,2]-shifts, enough energy is supplied to scramble the ligands on the metal. The activation energy increases from 28.5 kJ mol^{-1} in Fe(η^4-C_8H_8)$(CO)_3$ or <22.6 kJ mol^{-1} in Fe(η^4-C_8H_8)(η^6-C_8H_8) to *ca.* 55 kJ mol^{-1}. Hence the molecule is fluxional by [1,2]-shifts. As yet no molecule has been discovered where the disfavoured isomer lies only 5 to 20 kJ mol^{-1} above the favoured isomer so that apparent [1,4]-shifts occur.

In contrast, complexes containing the η^2-C_8H_8 ligand are predicted to be static. Only two such complexes are known, (η^2-C_8H_8)(η^5-C_5H_5)Mn$(CO)_2$ and [(η^5-C_5H_5)Fe(η^2-C_8H_8)$(CO)_2$]$^+$ and both are reported as being 'static',[4,5] which means $\Delta G^\ddagger > 90$ kJ mol^{-1}. According to the Woodward–Hoffmann rules, complexes containing the η^6-C_8H_8 ligand should also be static or have a high activation energy. In many cases, these complexes are fluxional, but $\Delta G^\ddagger > 60$ kJ mol^{-1}, and the shifts are mainly either [1,3]- or [1,5]-shifts. Cr(η^6-C_8H_8)$(CO)_3$ (16), M = Cr, and W(η^6-C_8H_8)$(CO)_3$ (16), M = W, have been shown to undergo predominantly [1,3]-shifts, *via* a 16-electron η^4-C_8H_8 intermediate (see Scheme 23).[39]

Both these molecules also undergo [1,2]- and [1,4]-shifts. This behaviour is attributed to the η^4-C_8H_8 intermediate having a long enough lifetime to undergo a facile [1,2]-shift, allowed by the Woodward–Hoffmann rules (see Scheme 24). When a substituted cyclo-octatetraene is used as in Cr(η^6-1,3,5,7-$Me_4C_8H_4$)$(CO)_3$ (17),[40] then the two departing double bonds are different. Thus it is the same bond that departs that re-enters the coordination sphere resulting in no net change (see Scheme 24). In the 16-electron η^4-intermediate, an allowed [1,2]-shift occurs (see Scheme 25). At higher energy, complete scrambling occurs, presumably *via* [1,3]-

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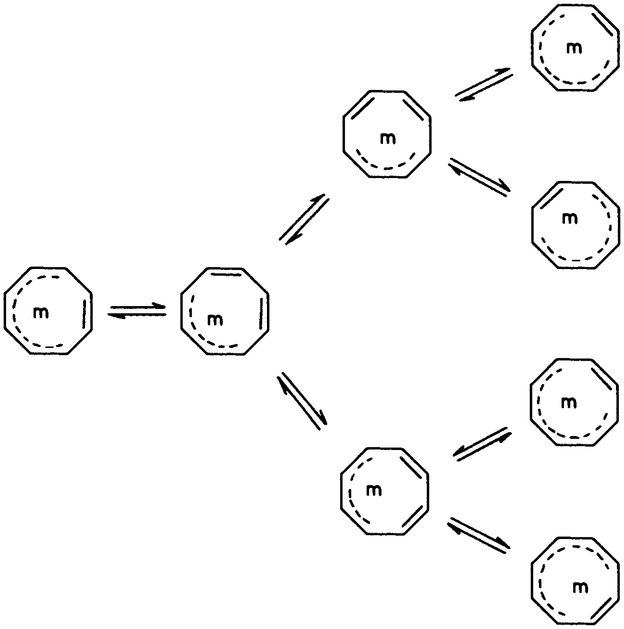
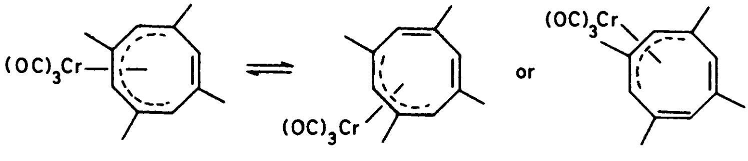
[39] J. A. Gibson and B. E. Mann, *J. Chem. Soc., Dalton Trans.*, 1979, 1021.
[40] F. A. Cotton, J. Faller, and A. Musco, *J. Am. Chem. Soc.*, 1968, **90**, 1438.



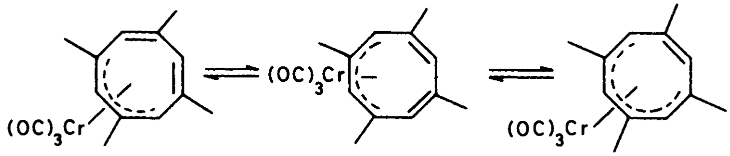
Scheme 23

shifts when there is sufficient energy to overcome the differentiation between the two types of double bond in Scheme 24.



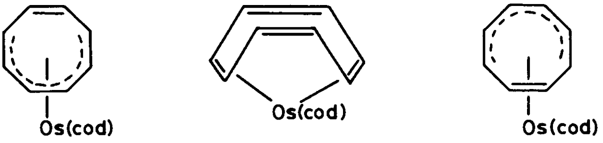
(17)

Scheme 24



Scheme 25

Very recently, an example of [1,5]-shifts in an η^6-C_8H_8 system has been discovered for Os(η^6-C_8H_8)(η^4-1,5-cyclo-octadiene) (18).[41] Spin saturation transfer measurements, at room temperature, have clearly demonstrated pairwise exchange of the cyclo-octatetraene protons, consistent only with a [1,5]-shift mechanism (see Scheme 26). At higher temperature, complete scrambling occurs, presumably with [1,3]-shifts analogous to Cr(η^6-C_8H_8)$(CO)_3$.[39]



(18)

Scheme 26

(b) Arenes co-ordinated to a metal are fairly well behaved, when allowance is made for the uncertainty of the structure of some of the molecules involved. According to the Woodward–Hoffmann rules, complexes containing η^2-arenes should be highly fluxional. Only one well defined η^2-arene complex has been investigated, Pt{η^2-$C_6(CF_3)_6$}$(PEt_3)_2$, where [1,2]-shifts occur with $\Delta G^\ddagger$ = *ca.* 45 kJ mol^{-1}.[42] A series of complexes, Ni{$C_6(CF_3)_6$}L_2, have been reported as being highly fluxional with $\Delta G^\ddagger < 40$ kJ mol^{-1}.[43] At the time of publication of this paper the compounds were believed to be η^4, but on the basis of the evidence, they could equally well be η^2.

All well characterized η^4-arene complexes have high activation energies for metal shifts, and such fluxionality has only been observed for Rh{η^4-$C^6(CO_2Me)_6$}(η^5-C_5Me_5),[44] with $\Delta G^\ddagger$ = 85 kJ mol^{-1} for [1,2]-shifts. A number of other related compounds exhibit dynamic behaviour, but *via* role exchange of two differently bonded arene rings, *e.g.*, in Ru(η^4-C_6Me_6)(η^6-C_6Me_6).[45]

(c) Cycloheptatrienyl complexes are more problematic. As predicted by the Woodward–Hoffmann rules, complexes containing the η^3-C_7H_7 group are highly fluxional. Thus $\Delta G^\ddagger$ for Co(η^3-C_7H_7)$(CO)_3$ is *ca.* 30 kJ mol^{-1}.[46] All other cases have more than one type of other ligand, and ligand effects could be raising $\Delta G^\ddagger$. Thus, Mo(η^3-C_7H_7)(η^5-C_5H_5)$(CO)_2$ has $\Delta G^\ddagger$ = *ca.* 40 kJ mol^{-1},[46,47] and Fe(η^3-C_7H_7)(η^5-C_5H_5)(CO) has $\Delta G^\ddagger$ = *ca.* 55 kJ mol^{-1}.[48]

Complexes containing the η^5-C_7H_7 ligand are predicted to be static or fluxional

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[41] M. Grassi, B. E. Mann, and C. M. Spencer, *J. Chem. Soc., Chem. Commun.*, 1985, 1169.

[42] J. Browning, M. Green, B. R. Penfold, J. L. Spencer, and F. G. A. Stone, *J. Chem. Soc., Chem. Commun.*, 1973, 31.

[43] J. Browning, C. S. Cundy, M. Green, and F. G. A. Stone, *J. Chem. Soc. (A)*, 1971, 448.

[44] J. W. Kang, R. F. Childs, and P. M. Maitlis, *J. Am. Chem. Soc.*, 1970, **92**, 720.

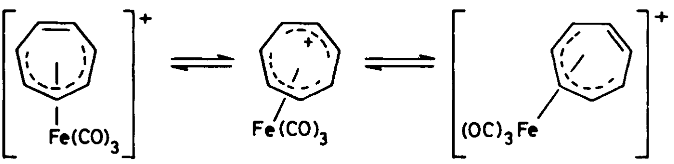
[45] E. O. Fischer and C. Elschenbroich, *Chem. Ber.*, 1970, **103**, 162.

[46] M. A. Bennett, R. Bramley, and R. Watt, *J. Am. Chem. Soc.*, 1969, **91**, 3089.

[47] J. W. Faller, *Inorg. Chem.*, 1969, **8**, 767.

[48] D. Ciappennelli and M. Rosenblum, *J. Am. Chem. Soc.*, 1969, **91**, 6876.

with a high activation energy, but the predictions are questionable. For neutral compounds, $\Delta G^{\ddagger}$ is somewhat larger, but not as large as might be expected on the basis of the behaviour of η^6-C_8H_8 and η^4-C_6R_6 systems. Thus for Mn(η^5-C_7H_7)(CO)$_3$, $\Delta G^{\ddagger}$ = *ca.* 60 kJ mol^{-1},[49,50] but [Fe(η^5-C_7H_7)(CO)$_3$]$^+$ (19) has $\Delta G^{\ddagger}$ of only 46 kJ mol^{-1}.[49,50] This charge dependence is also found in that $\Delta G^{\ddagger}$ for Fe(η^5-C_7H_7)(CO)$_2$(SnR$_3$) is *ca.* 60 kJ mol^{-1},[51] but ligand effects could also be responsible. In view of the success of the Woodward–Hoffmann theory for all other η^n-systems, it is tempting to invoke an alternative mechanism. In view of the charge dependence, then the formation of a charge-separated intermediate can be suggested (see Scheme 27).



(19)

Scheme 27

(d) η^3-Benzylic derivatives are generally highly fluxional, and this can readily be explained. Using the valence bond representation in Scheme 28, the dynamic behaviour can be explained as an allowed [1,5]-sigmatropic suprafacial shift. Thus Pd(η^3-CPh$_3$)(acac) is highly fluxional with $\Delta G^{\ddagger} < 20$ kJ mol^{-1}.[52] The two inequivalent methyl groups of the acetylacetonate remain inequivalent, consistent with this interpretation. There are no examples of this process being stopped on the n.m.r. timescale, although broadening of signals in the Pt(η^3-CPh$_3$)(acac) has yielded an approximate $\Delta G^{\ddagger}$ of 27 kJ mol^{-1}.[52]

Scheme 28

An apparent exception is Mo(η^3-CH$_2$Ar)(η^5-C_5H_5)(CO)$_2$ (20) and related compounds where the activation energy for exchange across the benzyl ligand *via*

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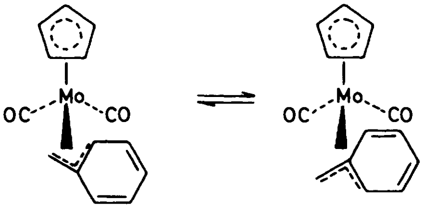
[49] T. H. Whitesides and R. A. Budnik, *J. Chem. Soc., Chem. Commun.*, 1971, 1514.
[50] T. H. Whitesides and R. A. Budnik, *Inorg. Chem.*, 1976, 15, 874.
[51] J. Takats, personal communication.
[52] B. E. Mann, A. Keasey, A. Sonoda, and P. M. Maitlis, *J. Chem. Soc., Dalton Trans.*, 1979, 338.

$Mo(\eta^1\text{-}CH_2Ar)(\eta^5\text{-}C_5H_5)(CO)_2$ is *ca.* 80 kJ mol^{-1}.[53] However, the shift in Scheme 28 will result in the formation of a second isomer (21) (see Scheme 29). It is probable that this process is occurring and is extremely fast. The i.r. spectrum of $Mo(\eta^3\text{-}CH_2Ph)(\eta^5\text{-}C_5H_5)(CO)_2$ shows the presence of two sets of signals, consistent with the presence of two isomers.[54] The ^{13}C n.m.r. spectrum shows a marked temperature dependence for the *o*-carbon atoms, consistent with a fast equilibrium between the isomers in Scheme 29, and a temperature-dependent equilibrium constant.

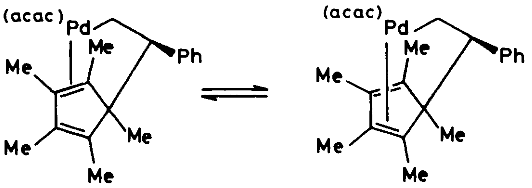


(20) (21)

Scheme 29

C. Experimental Evidence for an Associative/Dissociative Mechanism.—There are a large number of fluxional systems involving the change in the coordination sphere of the metal. One example has already been discussed, the dynamic behaviour of σ-allyl groups, *via* a η^3-allyl intermediate (see Scheme 5).

(a) The η^2-diene ligand can be fluxional on 16-electron metals *via* an η^4-intermediate. This behaviour has been found for $Pd(C_5Me_5CHPhCH_2)(acac)$ (22) (see Scheme 30).[55]



(22)

Scheme 30

(b) The η^3-dienyl ligand should be static, but when the metal is 16-electron a fluxional mechanism is available *via* an 18-electron intermediate. A series of

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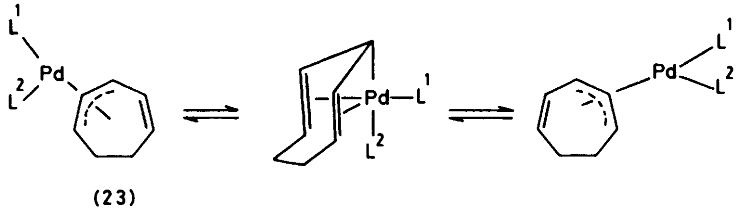
[53] F. A. Cotton and T. J. Marks, *J. Am. Chem. Soc.*, 1969, **91**, 1339.

[54] T. Gauntlett, B. E. Mann, and M. Winter, unpublished results.

[55] T. Hosokawa, C. Calva, H. B. Lee, and P. M. Maitlis, *J. Am. Chem. Soc.*, 1973, **100**, 7425.

$[Pd(\eta^3\text{-}C_7H_9)L_2]^+$ (23) complexes have been synthesized.[56] The fluxional mechanism does not result in exchange of the two inequivalent L groups. Consequently, the mechanism shown in Scheme 31 has been proposed. The activation energy is markedly dependent on L, ranging from 28.5 kJ mol^{-1}, when $L_2 = \eta^4$-1,5-cyclooctadiene, to 69.5 kJ mol^{-1}, when $L_2 = [acac]^-$. The activation energy and ^{13}C chemical shifts follow the order of *trans*-influence. Similar processes have been observed for $Pd(\eta^3\text{-}CPh_3)(acac)$,[52] $Pd\{\eta^3\text{-}PhCHCHC(OAc)CHCHPh\}(acac)$,[57] $[Pd(C_6H_3Bu^t{}_3Cl)Cl]_2$,[58] and $Rh(\eta^3\text{-}C_7H_9)(\eta^4\text{-}1,5\text{-cod})$.[59] The activation energy increases markedly in $[Pd(\eta^3\text{-}C_8H_{11})Cl]_2$.[56] This is attributable to the twist of the ring,[60] making it difficult for the formation of the $\eta^5\text{-}C_8H_{11}$ 18-electron intermediate.



(23)

Scheme 31

The 18-electron $Co(\eta^3\text{-}C_7H_9)(CO)_2(PPh_3)$ is fluxional, with $\Delta G^\ddagger = 74$ kJ mol^{-1}.[61] Although, a 20-electron intermediate, $Co(\eta^5\text{-}C_7H_9)(CO)_2(PPh_3)$, cannot be ruled out, it is far more likely that fluxionality occurs *via* the 16-electron intermediate $Co(\eta^1\text{-}C_7H_9)(CO)_2(PPh_3)$, analogous to that proposed to explain the fluxionality of $Fe(\eta^3\text{-}C_3H_5)(\eta^5\text{-}C_5H_5)(CO)$.[62]

(c) A number of η^4-triene complexes are fluxional. The system based on $Fe(\eta^4\text{-}C_7H_8)(CO)_3$ (24) has received considerable attention. It is fluxional *via* $Fe(\eta^2\text{-}C_7H_8)(CO)_3$ (25), a 16-electron intermediate (see Scheme 32).[63,64] An alternative pathway *via* $Fe(\eta^4\text{-norcaradiene})(CO)_3$ (26) was eliminated by the synthesis of $Fe\{\eta^4\text{-}7\text{-}Ph(EtO_2C)C_7H_6\}(CO)_3$ where it is known that in the free organic compound, the norcaradiene isomer is considerably favoured, but the activation energy was not significantly changed.[64]

A novel mechanism has been proposed for $Fe(\eta^4\text{-}C_5H_6N_2)(CO)_3$ (27) *via* a protonated form[65] (see Scheme 33).

D. Miscellaneous Mechanisms.—There are a number of systems undergoing one-off mechanisms, and these are included here for completeness. As more and more

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[56] B. E. Mann and P. M. Maitlis, *J. Chem. Soc., Chem. Commun.*, 1976, 1058.

[57] A. Sonoda, B. E. Mann, and P. M. Maitlis, *J. Organomet. Chem.*, 1975, **96**, C16.

[58] P. M. Bailey, B. E. Mann, A. Segnitz, K. L. Kaiser, and P. M. Maitlis, *J. Chem. Soc., Chem. Commun.*, 1974, 567.

[59] J. Müller, H.-O. Stühler, and W. Goll, *Chem. Ber.*, 1975, **108**, 1074.

[60] M. R. Churchill, *Inorg. Chem.*, 1966, **5**, 1608.

[61] P. V. Rinze, *J. Organomet. Chem.*, 1975, **90**, 343.

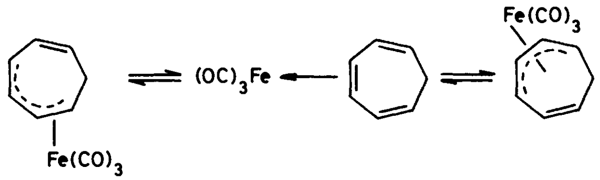
[62] R. W. Fish, W. P. Giering, D. Marten, and M. Rosenblum, *J. Organomet. Chem.*, 1976, **105**, 101.

[63] B. E. Mann, *J. Organomet. Chem.*, 1977, **141**, C33.

[64] K. J. Karel and M. Brookhart, *J. Am. Chem. Soc.*, 1978, **100**, 1619.

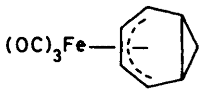
fluxional processes are found, these compounds may be found to fit into a pattern. These processes involve two processes occurring concurrently.

(a) In $Ru(C_8H_8SiMe_3)(SiMe_3)(CO)_2$ (28), the ruthenium oscillates between two positions, with great facility, $\Delta G^{\ddagger} = 52.7 \pm 0.8$ kJ mol^{-1} (see Scheme 34).[66]

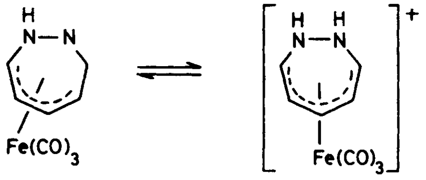


(24) (25)

Scheme 32

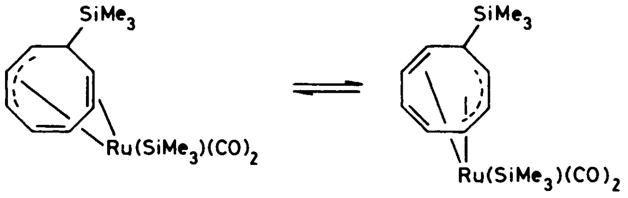


(26)



(27)

Scheme 33



(28)

Scheme 34

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[65] P. J. Harris, J. A. K. Howard, S. A. R. Knox, R. J. McKinney, R. P. Phillips, F. G. A. Stone, and P. Woodward, *J. Chem. Soc., Dalton Trans.*, 1978, 403.

[66] A. J. Carty, C. R. Jablonski, and V. Snieckus, *Inorg. Chem.*, 1976, 15, 601; A. J. Carty, R. F. Hobson, H. A. Patel, and V. Snieckus, *J. Am. Chem. Soc.*, 1973, 95, 6835.

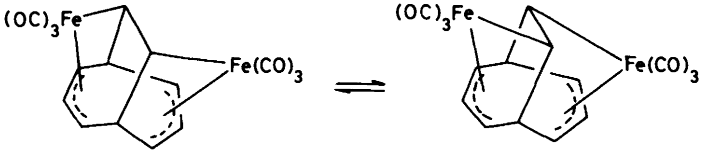
(b) $Fe(C_8H_{10})(CO)_3$ (29) is fluxional as in Scheme 35, but the activation energy is

(29)

Scheme 35

very high at 133 kJ mol^{-1}.[67] The mechanism can be considered to be a [1,5]-shift of the metal, combined with a [1,5]-shift of the C–C bond in the reverse sense.

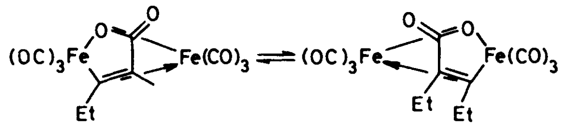
(c) The fluxionality of $Fe_2(CO)_6(C_{10}H_{10})$ (30) requires two concomitant [1,2]-shifts of the metal–carbon bonds (see Scheme 36).[68]



(30)

Scheme 36

(d) The fluxionality of $Fe_2(CO)_6(CEt{=}CEtCO_2)$ (31) involves only a minor movement of the atoms, but still has an activation energy of *ca.* 55 kJ mol^{-1} (see Scheme 37).[69]



(31)

Scheme 37

(e) A similar fluxional mechanism is observed for $Fe_2(CO)_6(C_{10}H_{10})$ (32) with $\Delta G^{\ddagger} = 66.9 \pm 0.8$ kJ mol^{-1} (see Scheme 38).[68]

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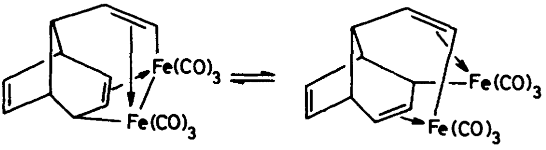
[67] R. Aumann, *Chem. Ber.*, 1976, **109**, 168.

[68] R. Aumann, *Chem. Ber.*, 1975, **108**, 1974.

[69] S. Aime, L. Milone, E. Sappa, A. Tiripicchio, and M. T. Camellini, *J. Chem. Soc., Dalton Trans.*, 1979, 1155.



(32)

Scheme 38

(f) The interchange of metal between the ends of allyl groups has already been noted in Scheme 6 for $[Fe_2(C_5H_5)_2(CO)_4(C_3H_5)]^+$ (5) and $Pt_2(acac)_2(C_3H_5)_2$.[19,20]

4 Conclusions

The dynamic behaviour of polyene and polyenyl metal complexes occurs principally by one of two mechanisms: the Woodward–Hoffmann symmetry-allowed sigmatropic shifts of changes in the coordination sphere of the metal involving the removal or addition of ligands. Organometallic compounds are highly versatile in the reactions which they can undergo. As a result, there are exceptions to this generalization but fortunately these are uncommon. The above generalizations are valuable in aiding the understanding of these types of fluxional systems.