A Topological Hückel Model for Organometallic Complexes. Part III.† The Perturbation Molecular-orbital Method

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The perturbation molecular-orbital method (PMO) is used to define the 18-electron rule for organometallic π complexes with alternant-bonding networks. Situations where the rule does not hold are also discussed. The PMO method is also used to distinguish possible 18-electron rule isomers and to account for the fluxional behaviour of η^4 and η^2 metal complexes.

THE perturbation molecular orbital (PMO) method developed by Coulson, Longuet-Higgins, and Dewar[1-5] has been used to provide elegant solutions to many bonding and reactivity problems in organic chemistry. The simplicity of this method arises from the special quantum-mechanical properties of alternant conjugated hydrocarbons within the Hückel molecular-orbital (m.o.) approximation. In a previous paper[6] it was demonstrated that the essential bonding features of η^3 and η^4 organometallic complexes could also be represented by alternant bonding networks and can be adequately described within the Hückel approximation. Therefore these complexes should also be amenable to a simple PMO analysis. The PMO method is based on two fundamental rules derived from first-order perturbation theory.[1-5]

Rule (1) *for Intramolecular Union.*—The energy change, δE, on intramolecular union between pairs of orbitals i and j of an alternant-bonding network is given by equation (1), where p_{ij} is the bond order between

$$\delta E = 2p_{ij}\delta\beta_{ij} \qquad (1)$$

orbitals i and j calculated according to the Hückel approximation and $\delta\beta_{ij}$ is the change in the i–j resonance integral which accompanies union. For alternant-bonding networks the bond order between pairs of orbitals can be calculated very easily from the pairing theorem. For alternant networks which have the same number of valence electrons as the number of basis-set orbitals the bond order p_{ij} is zero if the orbitals i and j have the same parity.

For odd-alternant networks which have one less electron than the number of basis-set orbitals (*i.e.* the non-bonding m.o. is empty) the bond order between orbitals i and j of like parity is given by equation (2),

$$p_{ij} = -c_{0i}c_{0j} \qquad (2)$$

where c_{0i} and c_{0j} are the atomic-orbital coefficients of the orbitals i and j in the non-bonding m.o. If the odd-alternant network has one more electron than the number of basis-set orbitals then the bond order is given by equation (3).

$$p_{ij} = c_{0i}c_{0j} \qquad (3)$$

Rule (2) *for Intermolecular Union.*—It has been shown that the union of two odd-alternant bonding networks R and S has little affect on the bonding m.o.s of the two networks. The change in delocalization energy which accompanies union arises primarily from a first-order interaction between the non-bonding m.o.s. This interaction is shown schematically in Figure 1. The non-bonding m.o.s of R and S give rise to two new m.o.s and the magnitude of the stabilization δe reflects the interaction between these m.o.s and depends on the non-bonding m.o. coefficients at the points of union. If the two bonding networks R and S each have a single electron in their non-bonding m.o.s the change in energy, δE, which accompanies their union to form an even bonding network RS is given by equation (4), where the sum-

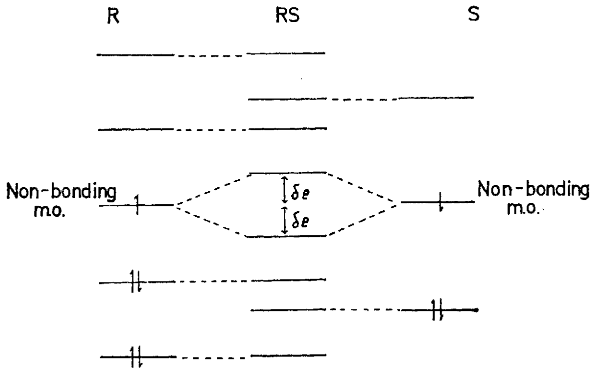

FIGURE 1 First-order perturbation-theory interaction of two odd-alternant bonding networks R and S to form an even network RS

$$\delta E = 2\sum_{rs} c_{0r}c_{0s}\beta \qquad (4)$$

mation is made over all points of union and c_{0r} and c_{0s} are the atomic-orbital coefficients of the non-bonding m.o.s of R and S. It also follows from Figure 1 that if the two bonding networks R and S each have two electrons occupying the non-bonding m.o.s the change in energy on union is zero.

I will now demonstrate how the PMO rules can be used to elucidate certain bonding problems in organometallic chemistry. The analysis will be based on hypothetical bonding networks whose basis-set orbitals

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† Part II, preceding paper.

[1] C. A. Coulson and H. C. Longuet-Higgins, *Proc. Roy. Soc.*, 1947, **A191**, 39; **A192**, 16; 1948, **A193**, 447, 456.

[2] H. C. Longuet-Higgins, *J. Chem. Phys.*, 1950, **18**, 265, 275, 283.

[3] M. J. S. Dewar, *J. Amer. Chem. Soc.*, 1952, **74**, 3345, 3350, 353, 3357.

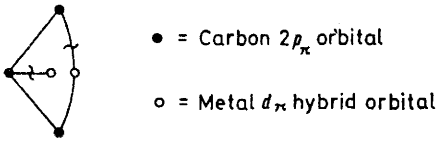
[4] M. J. S. Dewar, 'The Molecular Orbital Theory of Organic Chemistry,' McGraw-Hill, New York, 1969.

[5] W. B. Smith, 'Molecular Orbital Methods in Organic Chemistry, HMO and PMO—An Introduction,' Marcel Dekker, New York, 1974.

have equal Coulomb integrals, α, and the interactions between adjacent orbitals will be assumed to be equal. I have demonstrated previously that these assumptions lead to a reasonable account of the bond lengths in complexes of conjugated olefins.[6] For alternant-bonding networks the effects of differences in atomic-orbital electronegativities can be simply dealt with by use of perturbation theory[4-6] and will be discussed in detail later.

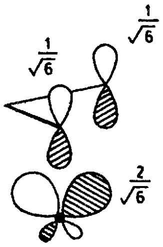
RESULTS AND DISCUSSION

The 18-*Electron Rule.*—The PMO method provides a simple rationalization for the adherence to the 18-electron rule in [M(olefin)(CO)$_n$] complexes because the bonding networks for a wide range of organometallic complexes can be generated by intermolecular union of a metal-allyl fragment with a hydrocarbon radical, *e.g.* $CH_3\cdot$ of the allyl radical. The metal–allyl bonding in the complex [Fe(η-allyl)(CO)$_3$] can be represented by the bonding network shown in (I).[7] The symbol ~ is used to indicate the phase dislocations in the metal–allyl bonding network, introduced by the nodal characteristics of the metal d_π orbitals.[8] This allyl complex has a non-bonding m.o. which is singly occupied and has the orbital coefficients shown in (II).



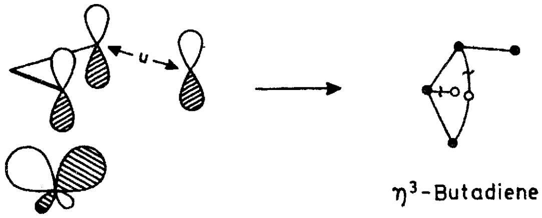
(I)

The allyl complex could be converted into a butadiene complex by union with a methyl radical. This union, which is represented by the symbol ←u→, involves the breaking and making of carbon–hydrogen and carbon–carbon σ bonds as well as changes in π bonding. However, if the changes in π-electron energy are of importance, the Hückel m.o.s form a satisfactory basis for the calculation. The methyl radical can be considered as the simplest case of an odd-alternant hydrocarbon radical, the electron being in a normalized atomic orbital of energy α and with a coefficient of unity. The first-order energy change in π-delocalization energy which accompanies intermolecular union can be calculated from rule (2) above.

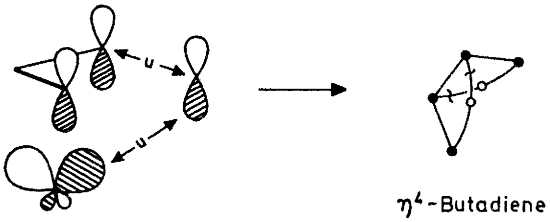


(II)

The union of (II) with the methyl radical to generate a metal–butadiene complex can occur in two distinct ways: one retains the η^3 co-ordination mode by a single union [see (III)] and the other generates an η^4 co-ordination mode by a multiple union [see (IV)]. According to rule (2) the π-delocalization energy resulting from single union [(III)] is $2/\sqrt{6}\beta$ and that from double union [(IV)] is $6/\sqrt{6}\beta$. Therefore, an η^4 co-ordination mode is energetically preferred for an iron tricarbonyl–butadiene complex. An even larger π-delocalization energy results from triple union to generate a cyclobutadiene complex; in this case $\delta E = 8/\sqrt{6}\beta$.

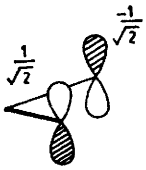


(III)



(IV)

Union of the metal–allyl bonding network to an allyl radical, which has the non-bonding m.o. coefficients shown in (V), gives a basis for calculating the relative stabilizations for η^4, η^5, and η^6 co-ordination. Figure 2 illustrates the types of union which would generate these geometries and application of rule (2) suggests the following first-order perturbation-theory energy changes: η^4, $3/\sqrt{3}\beta$; η^5, $1/\sqrt{3}\beta$; and η^6, $1/\sqrt{3}\beta$. For the η^5 and η^6 co-ordination modes the additional unions involve inactive positions either on the metal–allyl or allyl non-bonding m.o.s and therefore the stabilizations are smaller. The above analysis therefore demonstrates very simply why an iron-tricarbonyl fragment prefers and indeed often seeks out a η^4 co-ordination mode.[9]



(V)

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[6] D. M. P. Mingos, *J.C.S. Dalton*, 1977, 20.

[7] D. M. P. Mingos, *J.C.S. Dalton*, preceding paper.

[8] The topological bonding networks in mononuclear complexes have been discussed by E. A. Magnusson, *Nature Phys. Sci.*, 1971, **229**, 167.

[9] For a more detailed discussion of η^4-olefin complexes see M. Elian and R. Hoffmann, *Inorg. Chem.*, 1975, **14**, 1058.

From Figure 1 it is apparent that, if the non-bonding m.o.s of the fragments undergoing union are each doubly occupied by electrons, the first-order energy change, δE, is equal to zero. Therefore, union of $[\mathrm{Fe}(\eta\text{-allyl})(\mathrm{CO})_3]^-$ with $\mathrm{CH_3}^-$ (or allyl$^-$) results in a zero value for δE and such a complex will retain a strong preference for the η^3-co-ordination geometry.

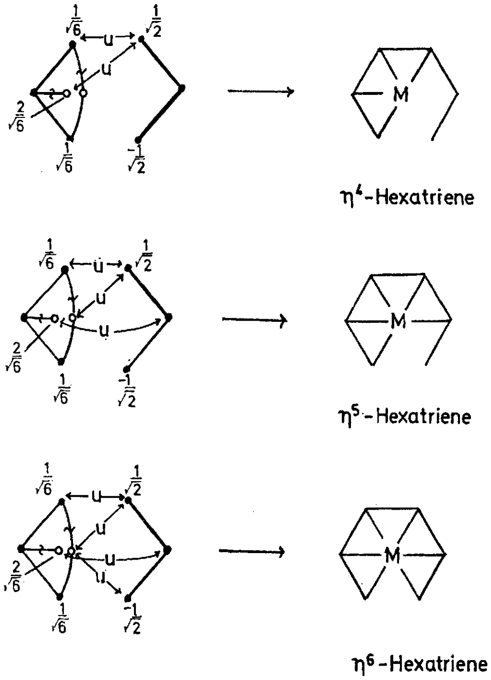
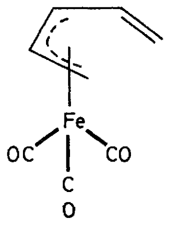
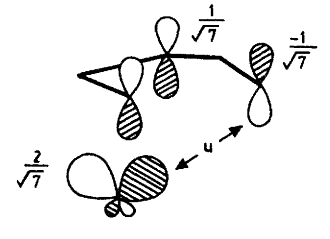


FIGURE 2 Interactions between $[\mathrm{Fe}(\eta\text{-allyl})(\mathrm{CO})_3]$ and the allyl radical to generate η^4-, η^5-, and η^6-hexatriene complexes

The tricarbonyl(η^3-pentadienyl)iron complex (VI) also has an odd-alternant bonding network and the orbital coefficients of the non-bonding m.o. of this radical are shown in (VII). According to the pairing theorem the bond orders between atoms of like parity are zero for the neutral molecule and consequently the intramolecular interaction shown in (VII) between the non-bonded carbon $2p_\pi$ orbital and the metal d_π orbital will not be associated with a first-order stabilization [see rule (1)]. For the related cationic and anionic complexes the bond orders between these orbitals are respectively $\frac{2}{7}$ and $-\frac{2}{7}$ (*i.e.* the products of the non-bonding m.o. atomic-orbital coefficients). Rule (1) suggests that the following energy changes will be associated with the intramolecular interaction indicated above: $[\mathrm{Fe}(\mathrm{C_5H_7})(\mathrm{CO})_3]^+$, $\delta E = \frac{4}{7}\delta\beta$; $[\mathrm{Fe}(\mathrm{C_5H_7})(\mathrm{CO})_3]^-$, $\delta E = -\frac{4}{7}\delta\beta$. Therefore for the cationic complex there is a positive driving force for increasing the co-ordination mode from η^3 to η^5. This driving force will be increased by a multiple union which generates a cyclopentadienyl metal complex.



(VI)



(VII)

A similar analysis for the $[\mathrm{Fe}(\mathrm{CO})_3]^{2+}$ fragment based on calculated partial bond orders indicates that the maximum stabilization is gained for η^6 co-ordination. The geometrical preferences for metal tricarbonyl fragments may be summarized as $[\mathrm{Fe}(\mathrm{CO})_3]^-$ (η^3), $\mathrm{Fe}(\mathrm{CO})_3$ (η^4), $[\mathrm{Fe}(\mathrm{CO})_3]^+$ (η^5), and $[\mathrm{Fe}(\mathrm{CO})_3]^{2+}$ (η^6), and are represented by equation (5), where h = hapto co-ordination mode, d is the number of valence electrons of the central metal atom, and z the total charge on the complex.

$$h + d - z = 12 \qquad (5)$$

The axially symmetric $\mathrm{Cr}(\mathrm{CO})_4$ fragment will have identical co-ordination preferences because it also has a pair of electrons in outpointing d–p hybrid orbitals.[9] This equivalence arises because this fragment has one fewer non-bonding m.o. than $\mathrm{Fe}(\mathrm{CO})_3$. Therefore, for $[\mathrm{M}(\text{olefin})(\mathrm{CO})_4]$ complexes, equation (6) will hold.

$$h + d - z = 10 \qquad (6)$$

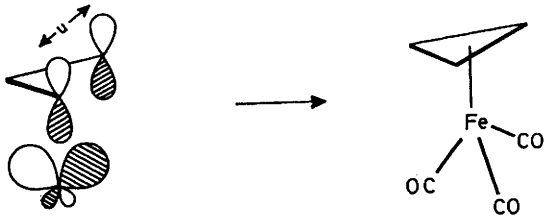
Clearly (5) and (6) are specific examples of a more general equation which is applicable to all $[\mathrm{M}(\text{conjugated olefin})\text{-}\mathrm{L}_n]$ complexes, *viz.* (7) where n is the number of two-electron donor ligands L. Clearly equation (7) is a statement of the 18-electron rule, for complexes with axially symmetric ML_n components.

$$h + d - z + 2n = 18 \qquad (7)$$

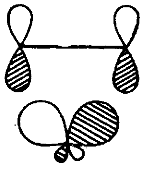
From the laborious analysis above it is evident that adherence to the 18-electron rule depends on two critical factors: (*a*) that the metal and carbon $2p_\pi$ orbitals generate a three-dimensional polycyclic bonding network with Hückel topology (*i.e.* an even number of phase dislocations); and (*b*) that the non-bonding orbitals localized on the metal are fully occupied. The 18-electron rule is frequently unfulfilled because the non-bonding orbitals are incompletely occupied, and the sandwich complexes of the lighter elements provide many illustrations of this limitation. The bonding networks for η^3-allyl and η^2-olefin complexes are monocyclic and therefore have Möbius topology (*i.e.* only a single phase dislocation). Such complexes therefore do not satisfy condition (*a*) above and provide many examples where the 18-electron rule is not adhered to.

We have previously noted that the metal–allyl bonding network in $[\mathrm{M}(\eta\text{-allyl})(\mathrm{CO})_3]$ is odd-alternant and therefore 16-, 17-, and 18-electron complexes will have approximately the same delocalization[7] energies within the Hückel approximation. This provision does not extend to the related cyclopropenyl complexes because the intramolecular union shown in (VIII) which generates the ring compound will only have a first-order stabilization for the anionic complex {*i.e.* the 18-electron [Fe(η-C_3H_3)$(CO)_3$]$^-$ complex}.[10]

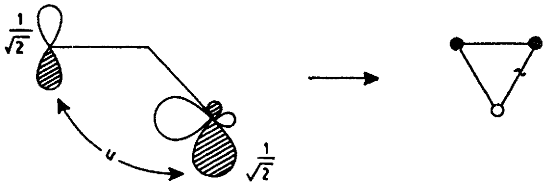
The bonding network for a simple η^2 metal–olefin complex is also monocyclic and has Möbius topology. This network, which is shown in (IX), may be generated by the intramolecular union of the odd-alternant network (X). The first-order energy changes associated with intramolecular union are $-\beta$ for two, 0 for three, and $+\beta$ for four electrons. Consequently the η^2 geometry will only be stabilized in those complexes with a doubly occupied d_π orbital. This conclusion is of course in complete agreement with the Chatt–Dewar suggestions that back donation from a filled d_π orbital stabilizes the metal–olefin bond. The $M(CO)_3$ fragment has an additional d_π hybrid orbital which is orthogonal to the metal–olefin plane and consequently cannot enter into metal–olefin bonding. The population of this orbital does have some interesting geometrical and chemical consequences, however. If M has a d^8 electronic configuration then this orbital is empty and suitably hybridized to interact well with the σ-donor orbital of an incoming two-electron ligand. The wide range of d^8-[M(olefin)L_4] complexes which have been isolated reflect this co-ordinative unsaturation. In a d^{10}-[M(olefin)L_3] complex this orbital, which is somewhat antibonding between the metal and the ligands (see XI), is doubly occupied. The antibonding character of this orbital can be effectively removed (without destabilizing the metal–olefin bonding) by the loss of one of the ligands, L, as shown in (XII).



(VIII)

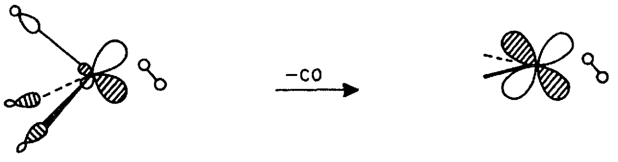


(IX)



(X)

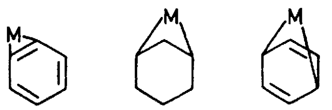
The concomitant dehybridization of the metal orbital also contributes a stabilizing effect. Therefore for d^{10} metal–olefin complexes, 18-electron [M(olefin)L_3] and 16-electron [M(olefin)L_2] species are anticipated. For the platinum metals the latter species predominate especially with unidentate phosphine ligands. With the tripodal ligand $MeC(CH_2PPh_2)_3$ the 18-electron complex has been isolated.[11]



(XI) (XII)

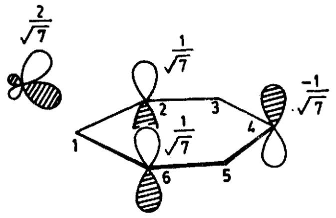
The PMO method outlined above therefore provides a simple rationalization in m.o. terms of the 18-electron rule. In addition it indicates situations, *e.g.* η-allyl and η-olefin complexes, where 16- and 17-electron complexes may also exist.

Eighteen- and Sixteen-electron Isomers.—This PMO technique may also be used to distinguish alternative modes of hapto co-ordination for a particular complex. For example, a d^{10} metal–benzene complex has the three possible η^2 isomers shown in (XIII), but only the 1—2-η^2 geometry has been established by crystallographic studies.[12] A metal η^1-benzene conjugated network has a non-bonding m.o. with the atomic coefficients shown in (XIV). In a d^{10} complex this non-bonding m.o. is doubly occupied and therefore according to rule (1) the first-order energy changes for the possible modes of intramolecular union are:



(a) (b) (c)

(XIII)



(XIV)

1,2-η $\delta E = \frac{4}{7}\beta$

1,3-η $\delta E = 0$

1,4-η $\delta E = -\frac{4}{7}\beta$

Therefore the 1,2-η isomer is energetically preferred.

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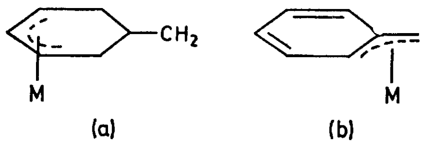
[10] M. D. Rausch, R. M. Tuggle, and D. L. Weaver, *J. Amer. Chem. Soc.*, 1970, **92**, 4981.

[11] F. G. A. Stone, *J. Organometallic Chem.*, 1975, **100**, 257.

[12] W. Silverthorn, *Adv. Organometallic Chem.*, 1975, **13**, 48.

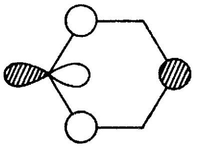
A similar analysis of the bonding in η^3-benzyl complexes indicates that the following geometries may be distinguished:



(XV)

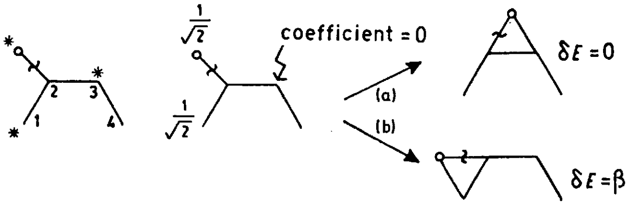
The intermolecular union energy for (XVb) is found to be $\frac{2}{7}\beta$ greater than that for (XVa). La Prade and Cotton[13] established the geometry (XVb) for the complexes [M(η^3-benzyl)(η^5-C_5H_5)$(CO)_2$] (M = Mo or W) but no examples of co-ordination mode (XVa) have been found. This method has also been used to verify that the 1—4-η co-ordination mode is the most stable one for benzene and cyclo-octatraene complexes of $Fe(CO)_3$.[14]

Fluxional π-Complexes.—The PMO analysis of the bonding in d^{10} metal–benzene complexes indicates an additional feature which may have a bearing on the fluxional behaviour of these molecules. The non-bonding m.o. shown in (XIV) has a mirror plane of symmetry and therefore the metal orbital can undergo intramolecular union in two ways to generate equivalent metal η^2-benzene complexes, *i.e.* to atoms 2 and 6 of the benzene ring. Therefore the metal atom has two equivalent bonding sites related by a 1,2 shift of the metal atom. Furthermore, the activation energy for the metal migration is expected to be low because in the transition state the metal *dp* hybrid retains a stabilizing interaction with both sites as shown in (XVI).



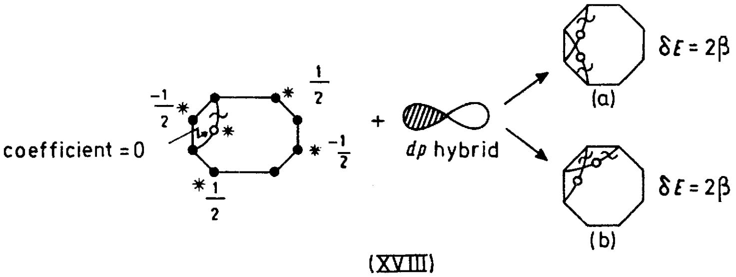
(XVI)

Stone and his co-workers[15] have shown by ^{19}F n.m.r. studies that [Pt{1—2-η-$C_6(CF_3)_6$}$(PPh_3)_2$] does indeed show fluxional behaviour at room temperature. At −90 °C the n.m.r. spectrum shows two multiplets of relative intensity 1 : 2, but the spectrum is not sufficiently well resolved for an assignment of an unambiguous mechanism to the migratory process. A similar 1,2 metal shift is not anticipated for a metal η^2-butadiene complex because the non-bonding m.o. for the bonding network in this instance does not have two equivalent sites for intramolecular union [see (XVII)]. The p_π orbital at carbon atom 3 of butadiene does not contribute to the non-bonding m.o. and therefore the first-order energy change for the intramolecular union shown in (a) is zero. ^{19}F N.m.r. studies have demonstrated that [Pt(1—2-η-C_4F_6)$(PEt_3)_2$] is indeed stereochemically rigid at room temperature.[11,16]



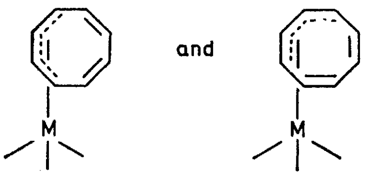
(XVII)

A similar analysis can be proposed for η^4 metal tricarbonyl complexes of cyclo-octatetraene and benzene. The bonding network for the former case can be simply constructed by the following intermolecular unions:



(XVIII)

The alternative modes of intermolecular union shown in (XVIII) generate two η^4 metal–olefin configurations with equal stabilization energies and which are related by a 1,2 shift of the metal atom around the octatetraene ring, *i.e.* as follows:



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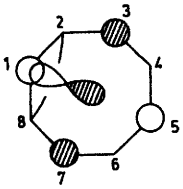
[13] M. D. La Prade and F. A. Cotton, *J. Amer. Chem. Soc.*, 1968, **90**, 5418.

[14] M. L. H. Green, 'Organometallic Compounds,' vol. 2, 'The Transition Elements,' Methuen, London, 1968.

[15] J. Browning, M. Green, J. L. Spencer, and F. G. A. Stone, *J.C.S. Dalton*, 1974, 97.

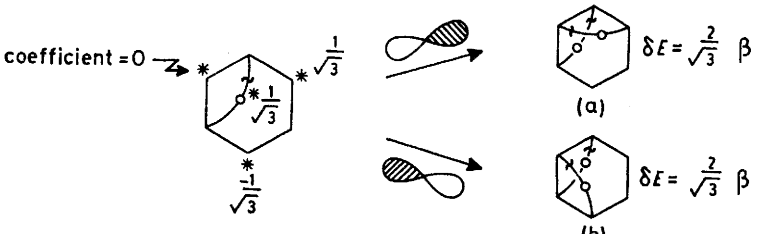
[16] P. K. Maples, M. Green, and F. G. A. Stone, *J.C.S. Dalton*, 1974, 1194.

The transition state for metal migration may be constructed in such a way that one of the metal *dp* hybrid orbitals lies in a position between the two extremes shown in (XVIII, [(a) and (b)]). Such a transition state would be expected to have a low activation energy because the *d–p* hybrid which is largely responsible for the migration process retains its interaction with the carbon p_π orbital at carbon atom 1 and at the same time will gain an additional stabilization from simultaneous positive overlaps with the orbitals at carbon atoms 3 and 7, *i.e.* the orbitals which are at the termini of the migration movement. These orbital interactions are illustrated in (XIX).



(XIX)

The bonding network for a benzene complex of iron tricarbonyl can be generated in an analogous fashion by the following intermolecular unions:

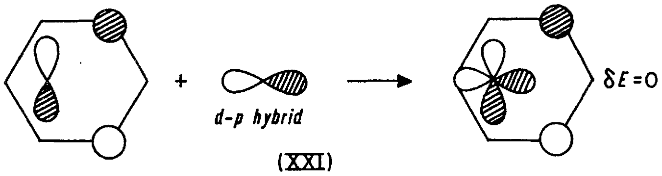


(a) (b)

(XX)

The metal atom in this example also has two equivalent binding sites related by a 1,2 shift of the metal around the ring; however, the removal of a C_2H_2 fragment from cyclo-octatetraene to form a benzene ring changes the nodal characteristics of the non-bonding m.o. in (XX). In particular, this non-bonding m.o. has zero contribution from the p_π orbital at carbon atom 1 and the orbitals at the termini of the migration process have different signs. The transition state for this process is therefore not as favourable, because the stabilization energy for the transition state is zero. The intermolecular union which generates the transition state is shown in (XXI).

The experimental evidence is in reasonable agreement with the above theoretical analysis. The cyclo-octatetraene complexes $[M(1—4\text{-}\eta\text{-}C_8H_8)(CO)_3]$ (M = Fe or Ru) are fluxional and the elegant n.m.r. experiments of Cotton [17] have shown that the metal undergoes a series of 1,2 shifts around the double bonds of the carbocyclic ring. The activation energies for these complexes are particularly low and limiting n.m.r. spectra are only observed below −140 °C. In contrast, the substituted benzene complexes $[Rh(\eta\text{-}C_5H_5)\{1—4\text{-}\eta\text{-}C_6(CF_3)_6\}]$ [18] and $[Ru\{1—4\text{-}\eta\text{-}C_6(CF_3)_6\}(CO)_2\{P(OMe)_3\}]$ [19] are stereochemically rigid at room temperature and $[Rh(\eta\text{-}C_5H_5)\{1—4\text{-}\eta\text{-}C_6(CO_2Me)_6\}]$ [20] is only fluxional at high temperature (155 °C). The bis(hexamethylbenzene) complex $[Ru(\eta\text{-}C_6Me_6)(1—4\text{-}\eta\text{-}C_6Me_6)]$ has an n.m.r. spectrum at 5 °C which is consistent with the molecular structure found in the solid state.[21] At 30 °C this spectrum has collapsed to give a broad singlet overlapping a sharp one; however, it has not been established whether 1,2 or 1,3 metal shifts are involved.



(XXI)

Although the results above are generally consistent with the theoretical ideas presented in this paper, further work, especially on unsubstituted olefin complexes, is necessary to really test the validity of the bonding-network approach.

It should be emphasized that the present choice of basis-set orbitals and analysis in terms of bonding networks has reduced the problem of metal migrations to a simple sigmatropic shift in Woodward–Hoffmann terms.[22] Clearly the interconversion of the cyclo-octatetraene isomers (XVIIIa) and (XVIIIb) is topologically related to a suprafacial 1,5 sigmatropic shift which is symmetry allowed, and the interconversion of the benzene isomers (XXa) and (XXb) is topologically related to a symmetry-forbidden 1,3 sigmatropic shift. Using Woodward–

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

[18] M. R. Churchill and R. Mason, *Proc. Roy. Soc.*, 1966, **A292**, 61.

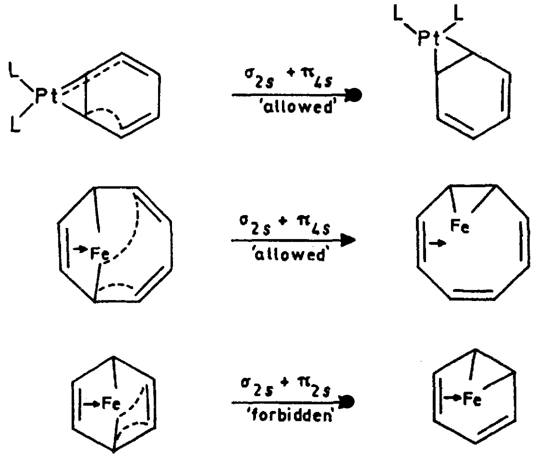
[19] R. Burt, M. Cooke, and M. Green, *J. Chem. Soc. (A)*, 1970, 2981.

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

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

[22] R. B. Woodward and R. Hoffmann, 'The Conservation of Orbital Symmetry,' Verlag Chemie–Academic Press, New York, 1969.

Hoffmann notations, the metal migrations can be classified in the following manner: †



I note that the fluxional behaviour of certain η^3-allyl and η^2-allene complexes can also be analysed simply by using the PMO method and the generalized Woodward–Hoffmann rule as described above.

In a subsequent paper it will be demonstrated that the PMO method can also be used to analyze other sorts of pericyclic reactions of organometallic complexes, notably electrocyclic ring closures and cycloaddition reactions. The Woodward–Hoffmann type of topological analysis is applicable to strongly bound 16- and 18-electron olefin complexes because they conform to the same general rules for effective cyclic delocalization as do planar organic molecules.

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† The use of resonance structures shown here follows from the alternant properties of the metal–olefin bonding network.