# A Topological Hückel Model for Organometallic Complexes. Part I. Bond Lengths in Complexes of Conjugated Olefins

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A simplified molecular-orbital (m.o.) model is developed which accounts simply for the bond lengths of a wide range of metal $\eta^4$-olefin complexes. The calculations reproduce the two most important geometric features associated with metal $\eta^4$-polyene complexes, *i.e.* the relative insensitivity of the carbon–carbon bond lengths of the co-ordinated butadiene moiety to the number of phenyl rings fused to it and the fixation of one double bond in the phenyl ring which is adjacent to the butadiene moiety.

THE rapid development of transition-metal organometallic chemistry during the last 20 years has taken place within the framework of two important concepts: the Chatt–Dewar–Duncanson [1,2] $\pi$-bonding model and the 18-electron (or inert-gas) rule.[3] The Chatt–Dewar–Duncanson approach is a symmetry-based molecular-orbital (m.o.) model derived from perturbation-theory arguments. As such it is most suitable for describing the bonding in weakly interacting metal–olefin systems, and indeed was originally proposed to explain the geometries of olefin complexes of platinum(II) and silver(I) where the metal ions and hydrocarbon ligands retain their essential characteristics on complex formation. In more strongly bound complexes, *e.g.* of $Pt^0$, the geometries and reactions of the co-ordinated olefin can be rationalized within the Chatt–Dewar–Duncanson scheme if it is assumed that the back donation of electron density from filled metal orbitals to empty ligand antibonding orbitals is of much greater importance than the forward donation of electron density from the ligand $\pi$ orbitals to the metal.[4,5]

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[1] M. J. S. Dewar, *Bull. Soc. chim. France*, **1951**, **18**, C71.

[2] J. Chatt and L. A. Duncanson, *J. Chem. Soc.*, **1953**, **2939**.

[3] C. A. Tollman, *Chem. Soc. Rev.*, **1972**, **1**, 337.

[4] R. Mason, *Proc. 13th Internat. Congr. Pure Appl. Chem.*, I.U.P.A.C., Boston, **1971**, vol. **6**, p. 31.

[5] R. Mason, D. M. P. Mingos, G. Rucci, and J. A. Connor, *J.C.S. Dalton*, **1972**, 1729.

The Chatt–Dewar–Duncanson approach has been less successfully used to account for the bond lengths in transition-metal complexes of conjugated olefins, largely because the symmetry arguments which are an essential feature of the model are less decisive for these complexes of low symmetry. Only for butadiene has it been possible to construct symmetry arguments which account qualitatively for the observed bond lengths of the co-ordinated ligand.[6,7]

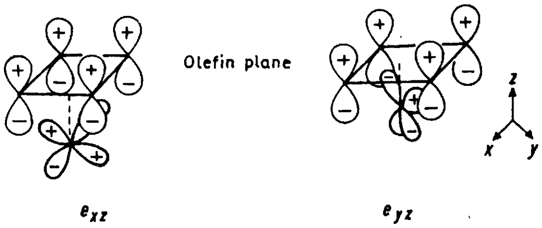
In complexes of conjugated olefins it appears that the metal interacts rather strongly with the olefin π orbitals.[8] For example, the cyclobutadiene and cyclo-octatetraene complexes of tricarbonyliron, $[Fe(\eta\text{-}C_4H_4)(CO)_3]$ and $[Fe(1\text{—}4\text{-}\eta\text{-}C_8H_8)(CO)_3]$ have ligand geometries and reactivities which are completely different from those of the free ligands. The free hydrocarbon ligands are anti-aromatic (and, in the case of $C_4H_4$, very unstable as a consequence),[9] yet when they are co-ordinated to the $Fe(CO)_3$ moiety they exhibit chemical and geometric properties which are characteristic of aromatic hydrocarbons, *viz.* an equalization of carbon–carbon bond lengths,[10,11] distortions towards planarity for the organic ligand, a propensity for electrophilic substitution,[12] and a lack of reactivity towards Diels–Alder reagents.[13] These grossly modified properties are indicative of a major reorganization of π-electron density when the ligand co-ordinates to the metal and the suitability of perturbation-theory arguments to such systems is questionable.

Although the metal atom interacts rather strongly with the olefin π system, the organometallic complex which is formed retains the characteristics of a conjugated π system, *viz.* a transmission of electronic effects over several atoms, high reactivity towards nucleophiles and electrophiles, and low-energy electronic transitions.[14] It is my view that the metal and organic-ligand orbitals in the π complex combine to form a unique three-dimensional π system which is effectively delocalized over the metal and carbon atoms. The geometric properties and reactions of the organometallic π complex are governed primarily by the topology and nodal characteristics of this three-dimensional π framework. In this paper, it is demonstrated that, once the topology of this π system is defined, the bond lengths in a wide variety of $\eta^4$-complexes can be rationalized. In subsequent papers it will be demonstrated that the reactions and sigmatropic rearrangements of these complexes can also be rationalized according to this bonding model.

RESULTS AND DISCUSSION

Recent experience in organic chemistry has shown that the Hückel approximation of m.o. theory is a reliable technique for defining the basic topology of the π network in conjugated organic molecules and transition states involving these molecules, and therefore I have attempted to develop an analogous three-dimensional model for complexes of olefins.[15-17] The model is based on the following assumptions and simplifications.

(1) The basis-set orbitals for the π-electron calculation are the olefin $p_\pi$ orbitals and two orthogonal metal valence orbitals which have π symmetry with respect to the perpendicular line connecting the olefin plane to the metal atom, *i.e.* $e_{xz}$ and $e_{yz}$ in (I).* In the Chatt–Dewar–



(I)

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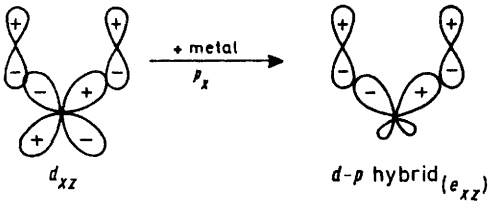
* If there are additional ligands, L, co-ordinated to the metal, *e.g.* CO, and the $ML_n$ fragment has axial symmetry, then $e_{xz}$ and $e_{yz}$ are degenerate. The calculations of Elian and Hoffmann [18] have shown that, for axially symmetric $M(CO)_3$ and $M(CO)_4$ fragments, $e_{xz}$ and $e_{yz}$ are *d*–*p* hybrids which have the correct radial characteristics to interact strongly with the olefin $p_\pi$ orbitals as shown below. (The Hückel calculations can easily be extended to deal with situations where the $ML_n$ fragment does not have axial symmetry. This is done by assigning different resonance and coulomb integrals to the two orbitals $e_{xz}$ and $e_{yz}$.) The metal $d_{z^2}$, $d_{x^2-y^2}$, and $d_{xy}$ orbitals in an $M(CO)_3$ fragment remain essentially non-bonding with respect to the metal–olefin π system and are therefore excluded from the calculations discussed in this paper. Numerous calculations and photoelectron (p.e.) spectral studies on metal sandwich and metal tricarbonyl olefin complexes have confirmed that these orbitals are essentially non-bonding.[19-23]



[6] M. R. Churchill and R. Mason, *Adv. Organometallic Chem.*, 1967, **5**, 93.

[7] F. A. Cotton and G. Wilkinson, 'Advanced Inorganic Chemistry,' 3rd edn., Wiley–Interscience, New York, 1972, pp. 731—733.

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

[9] L. Watts, J. D. Fitzpatrick, and R. Petit, *J. Amer. Chem. Soc.*, 1965, **87**, 3253.

[10] B. Dickens and W. N. Lipscomb, *J. Chem. Phys.*, 1962, **37**, 2084.

[11] J. D. Dunitz, H. C. Mez, O. S. Nills, P. Pauling, and H. M. Shearer, *Angew. Chem.*, 1960, **72**, 755.

[12] B. F. G. Johnson, J. Lewis, and G. L. P. Randall, *J. Chem. Soc.* (*A*), 1971, 422.

[13] M. Green and D. C. Wood, *J. Chem. Soc.* (*A*), 1969, **1172**.

[14] L. Salem, ' Molecular Orbital Theory of Conjugated Systems,' W. A. Benjamin, New York, 1966.

[15] H. E. Zimmerman, *Accounts Chem. Res.*, 1971, **4**, 272.

[16] M. J. S. Dewar, *Angew. Chem. Internat. Edn.*, 1971, **10**, 761.

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

[18] M. Elian and R. Hoffmann, *Inorg. Chem.*, 1975, **14**, 1058.

[19] R. Prins, *Mol. Phys.*, 1970, **19**, 603; *J. Chem. Phys.*, 1969, **50**, 4804.

[20] C. B. Harris, *Inorg. Chem.*, 1968, **7**, 1517.

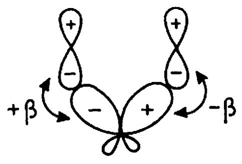
[21] M. D. Fayer and C. B. Harris, *Inorg. Chem.*, 1970, **8**, 2792.

[22] M. F. Guest, I. H. Hiller, B. R. Higginson, and D. R. Lloyd, *Mol. Phys.*, 1975, **29**, 113.

[23] J. A. Connor, L. M. R. Derrick, M. B. Hall, I. H. Hillier, M. F. Guest, B. R. Higginson, and D. R. Lloyd, *Mol. Phys.*, 1974, **28**, 1193.

Duncanson model this approximation is equivalent to the suggestion that the back-donation component from the metal to the ligand is of paramount importance in strongly bound complexes.

(2) The carbon–carbon $2p_\pi$–$2p_\pi$ overlap integrals in these co-ordinated-olefin complexes are comparable to the metal hybrid–$2p_\pi$ overlap integrals [10] and therefore, to a first approximation, all the resonance integrals (β) in the three-dimensional bonding network are taken to be equal.



(II)

(3) The metal and carbon Coulomb integrals (α) are initially taken to be equal (*i.e.* the basis-set orbitals are assumed to have the same electronegativities). The effects of electronegativity differences can be introduced as an additional refinement to the model either by modifying the Hückel parameters [24] or by using perturbation-theory arguments [25] (see Appendix).

(4) The signs of the metal–carbon resonance integrals (β) are chosen in a way which reflects the phase changes in the chosen set of basis orbitals: +β is associated with no phase change and −β with a phase change. This convention is illustrated in (II). Craig first recognised that the nodal characteristics of *d* orbitals could influence the bonding properties of phosphorus- and sulphur-containing ring compounds.[26] The present work extends this idea to complexes of conjugated olefins.

Figure 1 illustrates the six basis-set orbitals for the Hückel calculation on a metal–butadiene complex. The metallahydrocarbon π network is characterized by the seven resonance integrals and six Coulomb integrals shown in Figure 1(c). Five of the resonance integrals have a positive sign and two have a negative sign, reflecting the phase changes which result from the nodal characteristics and positions of the metal *e* orbitals relative to the carbon $2p_\pi$ orbitals. The Hückel calculation demonstrates that these basis-set orbitals combine to form three bonding and three antibonding molecular orbitals. The energies and coefficients of these m.o.s are given in the Appendix and the results are compared with those calculated by more sophisticated methods.

The $Fe(CO)_3$ fragment is characterized by the electronic configuration $(e_{xz})^1(e_{yz})^1$ because six of the eight valence electrons of the iron atom occupy the non-bonding orbitals $a_1(d_{z^2})$, and $e(d_{x^2-y^2}, d_{xy})$.[18] Therefore the $Fe(CO)_3$ moiety contributes two electrons for metal–butadiene bonding. These together with the four carbon $2p_\pi$ electrons fill the three bonding m.o.s of the metal–butadiene bonding network.

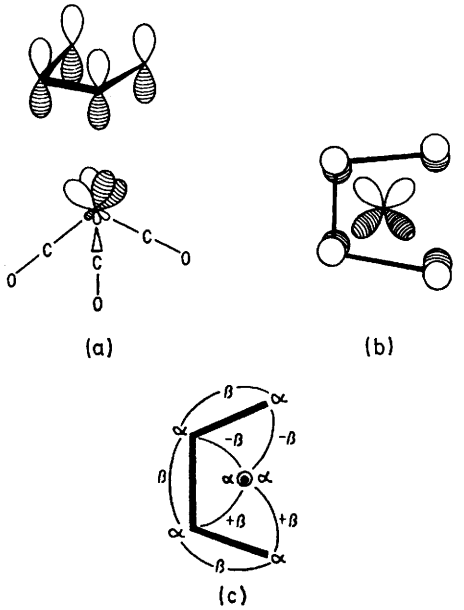


FIGURE 1 (a) And (b) illustrate the basis-set orbitals for the calculation on [Fe($\eta$-$C_4H_6$)$(CO)_3$]. (c) Demonstrates the bonding network for metal–butadiene bonding and gives the Hückel parameters used in the calculation

TABLE 1

Bond lengths (Å) in co-ordinated-butadiene complexes

| Complex | | $C^1$–$C^2$ [a] | $C^2$–$C^3$ [a] | $C^3C^4$ [a] | C–C (av.) | Δ [b]/Å | Ref. |
|---|---|---|---|---|---|---|---|
| [Fe($C_{11}H_{14}$)$(CO)_3$] | | 1.412(4) | 1.411(3) | 1.417(3) | 1.413 | 0.004(5) | 28 |
| [{Fe$(CO)_3$}$_2$($C_{11}H_{12}O$)] | Fe(1) | 1.424(4) | 1.392(4) | 1.427(4) | 1.414 | 0.034(5) | 29 |
| | Fe(2) | 1.413(4) | 1.399(4) | 1.416(3) | 1.407 | 0.016(5) | |
| [{Fe$(CO)_3$}$_2$($C_{12}H_{12}O$)] | | 1.413(6) | 1.401(6) | 1.422(6) | 1.415 | 0.017(7) | 30 |

[a] See (III) for numbering. [b] Δ is the difference between $C^2$–$C^3$ and the average of $C^1$–$C^2$ and $C^3$–$C^4$ [see (III) and ref. 28].

The π-bonding orders which result from the Hückel calculation on [Fe($C_4H_6$)$(CO)_3$] can be used to estimate the carbon–carbon bond lengths of the co-ordinated olefin through the Coulson–Golebiewski expression (1),[27]

$$\tau = 1.517 - 0.18\,p \qquad (1)$$

where τ is the calculated C–C bond length in Å and $p$ is the Hückel π-bond order. For co-ordinated butadiene,

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[24] A. Streitweiser, 'Molecular Orbital Theory for Organic Chemists,' Wiley, New York, 1961.

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

[26] D. P. Craig, 'Theoretical Organic Chemistry (Kekulé Symposium),' Butterworths, London, 1959, vol. 20.

[27] C. A. Coulson and A. Golebiewski, *Proc. Phys. Soc.*, 1961, **78**, 1310.

the Hückel calculation leads to the following calculated bond orders and lengths:

| Hückel ($\alpha_{Fe} = \alpha_C - 1.00$) | | Population analysis (%) | | |
|---|---|---|---|---|
| Orbital | Energy | metal | terminal carbons | central carbons |
| $2a_1$ | $\alpha + 0.54\beta$ | 40 | 55 | 5 |
| $1a''$ | $\alpha + 1.41\beta$ | 25 | 50 | 25 |
| $1a'$ | $\alpha + 1.68\beta$ | 13 | 18 | 69 |

(a) Calculated π-bond orders (b) Calculated bond length (Å)

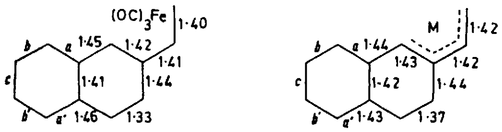
(III)

For the co-ordinated butadiene ligand the calculations suggest that the carbon–carbon bonds are equal in strength and the calculated bond length is 1.413 Å. These results agree surprisingly well with the C–C bond lengths determined by the most accurate crystallographic studies [28-30] to date for iron tricarbonyl–butadiene complexes (see Table 1).

These studies have shown that the three independent C–C bonds of the co-ordinated butadiene fragment have very similar bond lengths. In each case a slightly shorter central C–C bond is observed, but the difference in length between the central and average of the terminal C–C bond lengths (Δ) is only statistically significant for one of the structural determinations. The average C–C bond length for the co-ordinated butadiene ligand in these complexes agrees closely with that computed by my simple model. If the electronegativity difference between iron and carbon is taken into account, the central C–C bond is computed to have a slightly higher π-bond order in agreement with the structural results (see Appendix).

The main advantage of the Hückel model is that it can be simply extended to more complex molecules which have very little symmetry. It is also possible to evaluate the effect of co-ordinating more than one metal atom to a conjugated ligand. The observed and calculated bond lengths for two such complexes are illustrated in (IV) and (V). Considering the assumptions associated with this simple Hückel model, the agreement between calculated and observed bond lengths is remarkably good. However, in view of the relatively large standard deviations associated with individual C–C bond lengths (*i.e. ca.* ±0.01 Å),[31] it is, perhaps, better to emphasize the fact that the model reproduces the correct trends in the observed bond lengths rather than placing too much emphasis on the absolute values for the C–C bond lengths.

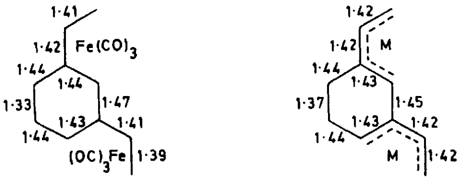
The calculations also reproduce the two most important geometric features associated with these and related molecules, *i.e.* the relative insensitivity of the carbon–carbon bond lengths of the co-ordinated butadiene moiety to the number of phenyl rings which are fused to it and the fixation of one double bond in the phenyl ring which is adjacent to the butadiene moiety. The calculated value for this short bond (1.37 Å) is consistently larger by 0.04 Å than the observed bond length (1.33 Å). It is a common feature of Hückel calculations that differences in C–C bond lengths are underestimated (see ref. 14 for a fuller discussion of this point). This deficiency arises from the assumption of equal β values for all the C–C bonds in the Hückel calculation and can be simply overcome by a self-consistent procedure first suggested by Coulson and Golebiewski.[27] The Hückel procedure suggested in this paper has also been applied to many other $\eta^4$ complexes of this type and the agreement between observed and calculated bond lengths has been consistently good.



Average of *a*, *b*, *c*, *b'*, and *a'* = 1·39 Å Average of *a*, *b*, *c*, *b'*, and *a'* = 1·40 Å

Observed[31] Calculated

(IV)



Observed[31] Calculated.

(V)

Even for non-planar olefins co-ordinated to metal atoms, the Hückel model gives a reasonable account of the trends in observed bond lengths [see (VI) and (VII)],

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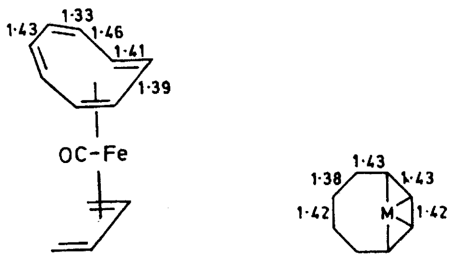
[28] F. A. Cotton, V. W. Day, B. A. Frenz, K. I. Hardcastle, and J. M. Troup, *J. Amer. Chem. Soc.*, 1973, **95**, 4522.

[29] G. I. Birnbaum, *J. Amer. Chem. Soc.*, 1972, **94**, 2455.

[30] K. B. Birnbaum, *Acta Cryst.*, 1972, **B28**, 161.

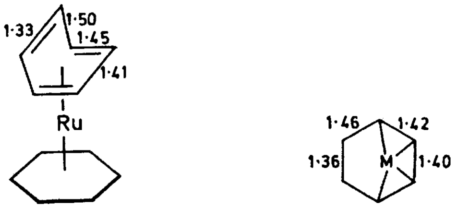
[31] R. E. Davies and R. Petit, *J. Amer. Chem. Soc.*, 1970, **92**, 716.

although, of course, the absolute agreement between observed and calculated values is less good. These co-ordinated olefins generally have dihedral angles of *ca.* 40° associated with a folding of the carbon skeleton, and therefore the trends calculated assuming a planar olefin geometry underestimate the degree of bond-length alternation. The agreement between observed and calculated values could be improved by weighting the carbon–carbon resonance integrals according to the relative $2p_\pi$–$2p_\pi$ overlap integrals for adjacent carbon atoms, but in my opinion this procedure would over-parameterize the model and destroy its essential simplicity. The calculations do suggest one important trend for the carbon–carbon bond lengths of the co-ordinated butadiene fragment in these polyene metal complexes. The $C^2$–$C^3$ bond [see (III)] in each case is calculated to be marginally shorter than the $C^1$–$C^2$ and $C^3$–$C^4$ bonds. This result is reproduced experimentally in the examples shown in (VI) and (VII) and is supported by the statistical analysis of the bond lengths in $\eta^4$-polyene complexes of iron tricarbonyl.[28]



Observed[32] Calculated

(VI)

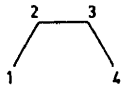


Observed[33] Calculated

(VII)

Bond-fixation effects have been noted for $\eta^2$ and $\eta^3$ organometallic complexes, *e.g.* [Pt{1—2-$\eta$-$C_6(CF_3)_6$}-$(PPh_3)_2$] [34] and [Mo($\eta$-$C_5H_5$)(1—3-$\eta$-$CH_2Ph$)$(CO)_2$],[35] and may be similarly rationalized using the Hückel m.o. model outlined above.

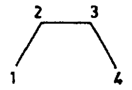
These calculations also present rather simple explanations for other geometric features of these co-ordinated ligands. For example, the free butadiene ligand has a negative $\pi$-bond order associated with the $C^1$–$C^4$ vector [see (VIIIa)] but the co-ordinated butadienes in all the molecules discussed above have a positive $C^1$–$C^4$ $\pi$-bond order [see (VIIIb) for example]. Therefore, some shortening of the $C^1$–$C^4$ distance would be anticipated for this co-ordinated ligand moiety and indeed is observed.[4,36]



$p_{1,4} = -0{\cdot}44$

free butadiene

(VIIIa)



$p_{1,4} = 0{\cdot}21$

co-ordinated butadiene

(VIIIb)

The observed folding of the co-ordinated polyene ligands in (VI) and (VII) for example can also be rationalized in terms of the calculated metal–carbon bond orders. This geometrical aspect will be discussed in more detail elsewhere.[37]

From the above discussion, it is clear that the topology of the metal–ligand $\pi$ system plays an important role in influencing the bond lengths in these organometallic systems. The presence of an even number of phase dislocations (*ie.* two) noted for the metal–butadiene $\pi$ system characterizes it as a Hückel $\pi$ system, and therefore, the six valence electrons contributed by the carbon and metal atoms constitute a Hückel sextet and occupy three very stable m.o.s which are effectively delocalized over the metal and the ligand.[15,17] The aromatic properties of this co-ordinated ligand and the related cyclobutadiene ligand can be related directly to the presence of this three-dimensional $\pi$ system.

## APPENDIX

*Hückel Molecular Orbitals for* [Fe($\eta$-$C_4H_6$)$(CO)_3$].—The coefficients and energies of the Hückel m.o.s calculated on the basis of the orbital interactions illustrated in Figure 1 are shown in Figure 2. The six basis-set orbitals give rise to bonding and antibonding m.o.s which are paired (in terms of energies and coefficients). This type of symmetry arises directly from the alternant properties of the metal–butadiene bonding network and will be discussed in subsequent papers in more detail.[37] For the [Fe($\eta$-$C_4H_6$)$(CO)_3$] complex the bonding m.o.s will be filled by the six valence electrons contributed by the butadiene and $Fe(CO)_3$ fragments.

The m.o.s have been classified according to whether they are symmetric ($a'$) or antisymmetric ($a''$) with respect to the mirror-plane symmetry operation of the $C_s$ point group. It is pertinent to note that the metal basis-set orbitals reflect this symmetry by forming the linear combinations $(1/2^{\frac{1}{2}})/(e_{xz} \pm e_{yz})$. The precise form of the m.o.s shown in Figure 2 can be related to the orbital characteristics of the $Fe(CO)_3$ and butadiene fragments using perturbation-theory arguments.[38] The orbitals $1a'$ and $1a''$ are clearly related to the $a'$ and $a''$ bonding $p_\pi$ m.o.s of the free butadiene ligand. The central m.o.s which are noded at carbon atoms 2 and 3 arise from the out-of-phase mixing of the bonding and antibonding ligand $\pi$ m.o.s which is induced by concomitant

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[32] I. W. Bassi and R. Scordamaglia, *J. Organometallic Chem.*, 1972, **37**, 353.

[33] G. Hutner, L. Lange, and E. O. Fischer, *Angew. Chem. Internat. Edn.*, 1971, **10**, 556.

[34] J. Browning, M. Green, J. L. Spencer, and B. R. Penfold, *J.C.S. Chem. Comm.*, 1973, 31.

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

[36] R. Mason, *Discuss. Faraday Soc.*, 1969, **47**, 21.

[37] D. M. P. Mingos, unpublished work.

[38] The methodology is described in R. Hoffmann, *Accounts Chem. Res.*, 1971, **4**, 1; L. Libit and R. Hoffmann, *J. Amer. Chem. Soc.*, 1974, **96**, 1370.

TABLE 2

Comparison of orbital occupations for $[Fe(\eta\text{-}C_4H_6)(CO)_3]$ according to SCF and Hückel calculations

| SCF [23] | | | | | Hückel ($\alpha_{Fe} = \alpha_C$) | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | Population analysis (%) | | | | | Population analysis (%) | | |
| Orbital | Energy (eV) | metal | terminal carbons | central carbons | Orbital | Energy | metal | terminal carbons | central carbons |
| 31*a′* | −8.07 | 42 | 34 | 9 | 2*a′* | $\alpha + \beta$ | 50 | 50 | 0 |
| 18*a″* | −10.78 | 13 | 61 | 21 | 1*a″* | $\alpha + 1.73\beta$ | 39 | 39 | 22 |
| 29*a′* | −14.09 | 35 | 12 | 47 | 1*a′* | $\alpha + 1.73\beta$ | 10 | 10 | 79 |

overlap with the metal $d_\pi$-orbital combinations. Alternatively the symmetry-adapted linear combinations $(1/2^{\frac{1}{2}})/(\phi_1 \pm \phi_2)$, $(1/2^{\frac{1}{2}})/(\phi_2 \pm \phi_3)$, and $(1/2^{\frac{1}{2}})/(e_{xz} \pm e_{yz})$ ($\phi_i$ represent the carbon $p_\pi$ orbitals) can be regarded as constituting a pseudo-allylic (or cyclopropyl) three-orbital problem with the combinations $(1/2^{\frac{1}{2}})/(\phi_2 \pm \phi_3)$ as the central components.

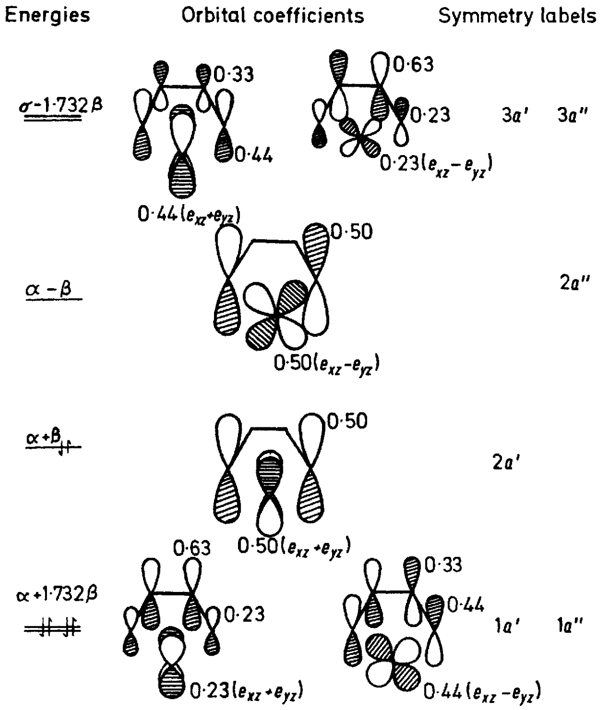


FIGURE 2 Hückel m.o.s. for $[Fe(\eta\text{-}C_4H_6)(CO)_3]$ using the parameters $\alpha_{Fe} = \alpha_C$

This analogy accounts rather simply for the noded characteristics of the m.o.s 2*a′* and 2*a″* shown in Figure 2.[15]

The *ab initio* SCF caculations on $[Fe(\eta\text{-}C_4H_6)(CO)_3]$ [23] indicate that the metal–butadiene bonding is localized predominantly in three m.o.s (29*a′*, 31*a′*, and 18*a″* using the notation in ref. 23). The composition of these orbitals is shown in Table 2 and compared with those calculated by the simple Hückel method. The latter method clearly reproduces the correct trends in the orbital populations of the butadiene $p_\pi$ orbitals, although the agreement is less satisfactory for the metal contributions in the lower-lying m.o.s. The noded characteristic of the highest-occupied m.o. is clearly an exaggeration of the Hückel model and arises largely from the assumption of equal α values for all the basis-set orbitals. If the Coulomb integral of iron is taken to be equal to $\alpha_C - 1.00$ then the noded characteristic of this orbital is lost and it resembles more closely the lowest-lying antibonding m.o. of butadiene. With these parameters the Hückel model gives a satisfactory account of the charge distribution in the metal–butadiene moiety (see Table 3).

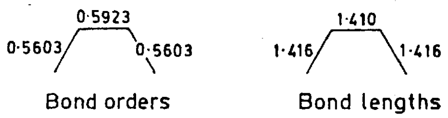
TABLE 3

Comparison of charge distributions for $[Fe(\eta\text{-}C_4H_6)(CO)_3]$ according to Hückel and SCF calculations

| | SCF [23] | Hückel [a] |
|---|---|---|
| $Fe(CO)_3$ | 0.87 | 0.64 |
| Terminal carbon | −0.23 [b] | −0.23 |
| Central carbon | −0.02 [b] | −0.09 |
| Total charge on butadiene ligand | −0.88 | −0.64 |

[a] With $\alpha_{Fe} = \alpha_C - 1.00$. [b] Net increase in electron density on butadiene $p_\pi$ orbitals on complex formation.

The π-bond orders and bond lengths calculated for the modified iron parameters are shown below. There is a slight shortening of the central C–C bond in agreement with experimental observations, but the effects are rather marginal. The calculated bond lengths discussed in the paper are not affected significantly by these changes in parameters.



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