A Topological Hückel Model for Organometallic Complexes. Part II.[†] Alternant Bonding Networks in η^3- and η^4-Olefin Complexes

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Within the Hückel approximation, metal η^3- and η^4-olefin complexes are shown to have alternant bonding networks. Application of the pairing theorem to such systems indicates the electronic origins of the 18-electron rule and provides some insight into the chemical properties of these molecules. The topological implications of the bonding network in η-allyl complexes are also discussed.

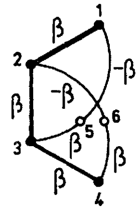
THE 18-electron rule has played an important role in rationalizing the structures and reactivities of a wide range of organotransition-metal complexes.[1,2] However, its simplicity and aura of numerological certainty have obscured the fact that it has little quantum-mechanical justification. Craig and Doggett,[3] in a rare theoretical analysis of the problem, concluded that the rule will be followed when the metal-to-ligand charge transfer supplements electron donation from the ligand, for it is then that the radial and angular dependence of the potential experienced by the metal '*d*' orbitals approaches that in the rare-gas element. Other workers have noted that the rule reflects a full utilization of metal valence orbitals.[1,2]

The 18-electron rule has a numerical form reminiscent of the Hückel ($4n + 2$) rule of organic chemistry [4,5] and therefore I have attempted to develop a justification for it using techniques which have proved successful for planar conjugated olefin pericycles. Coulson, Longuet-Higgins, and Dewar have elegantly demonstrated [6-8] that for alternant conjugated hydrocarbons [‡] the Hückel rule can be derived simply by using perturbation molecular-orbital (PMO) theory. Therefore, if the bonding networks of metal–olefin complexes could be shown to have this alternant property a similar proof of the 18-electron rule should be accessible. In this paper it is demonstrated that a wide range of η^3 and η^4 complexes can be described by alternant bonding networks and the chemical and theoretical significance of this observation are indicated.

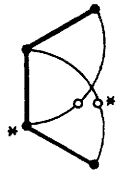
RESULTS AND DISCUSSION

Within the Hückel approximation the bonding in a metal–butadiene complex can be represented by the interaction diagram (or graph) in (I) and (II). The six valence orbitals involved in metal–ligand bonding shown in Figure 1 are represented by the six vertices of the graph. The connections of the graph represent the interactions between the orbitals. The sign of the β values in (I) reflect the signs of the orbital–adjacent orbital interactions shown in Figure 1.[9]

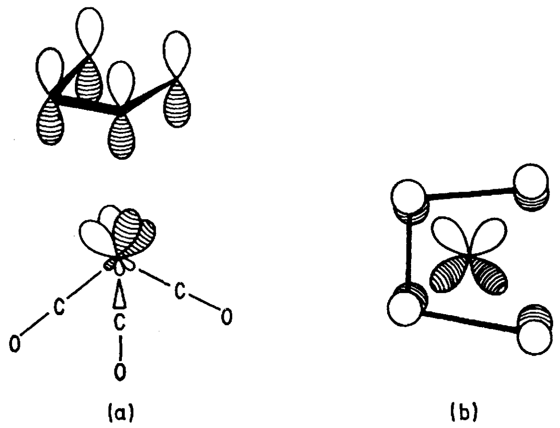
The bonding network (I) has one very important and useful feature: it is an alternant network, *i.e.* the constituent atomic orbitals can be divided into two groups starred and unstarred in such a way that no two orbitals of like parity overlap directly. It is, perhaps, important to emphasize that, although the two metal d_π orbitals have the same origin (*i.e.* at the metal atom), the overlap between them is zero because they are orthogonal.



(I)



(II)



(a) (b)

FIGURE 1 Basis-set orbital of sheet metal–butadiene alternant bonding networks

Consequently in the network (I) these orbitals are represented by the unconnected vertices 5 and 6. The alternant property of the network is illustrated in (II). It is, furthermore, an even-alternant network because the number of starred and unstarred vertices (orbitals) are equal. In an odd-alternant network the number of

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[†] Part 1, preceding paper.

[‡] An alternant conjugated hydrocarbon is one in which the carbon atoms can be divided into two groups, starred and unstarred, in such a way that no two atoms of like parity are linked.

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

[2] R. Mason, *Proc. 13th Internat. Congr. Pure Appl. Chem.*, Boston, 1971, vol. 6, p. 31.

[3] D. P. Craig and G. Doggett, *J. Chem. Soc.*, 1963, 4189.

[4] E. Hückel, *Z. Physik*, 1931, **70**, 204.

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

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

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

[8] M. J. S. Dewar, *J. Amer. Chem. Soc.*, 1952, **74**, 3345, 3350, 3353, 3357.

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

starred vertices exceeds the number of unstarred vertices by one.

In the Hückel approximation a set of atomic orbitals which can be represented by the vertices of an alternant graph have well defined and useful properties.[6-8,10] The m.o.s formed from linear combinations of these atomic orbitals conform to a set of rules described collectively as the Pairing Theorem, full details of which can be found in ref. 11. Briefly, the following results of this theorem are important to the present discussion.

(*a*) An even-alternant basis set of atomic orbitals forms m.o.s whose Hückel energy levels occur in pairs. Thus for every molecular orbital with energy $\alpha + n\beta$ there is a corresponding orbital with energy $\alpha - n\beta$.

(*b*) The pairing property described in (*a*) above is also present in odd-alternant basis sets of atomic orbitals, but in addition there is a non-bonding m.o. of energy α.

(*c*) Using a method developed by Longuet-Higgins,[7] the coefficients of the non-bonding m.o. in an odd-alternant system may be easily obtained without solving the relevant secular equations. He showed that for this m.o. the coefficients of the unstarred orbitals are zero and that the coefficients of the starred orbitals, c^*, conform to the simple equation (1). In the Hückel approximation

$$\sum_{k\neq i} c_k{}^*\beta_{ik} = 0 \qquad (1)$$

β_{ik} is assumed to vanish unless the atomic orbitals i and k are interacting directly, therefore all the terms in (1) vanish except those where k is an atom directly linked to i.

For the metal–butadiene network, which has six basis-set orbitals, the pairing theorem immediately suggests that there are three bonding and three antibonding m.o.s whose energies are paired.[9] The pairing theorem permits alternative solutions with an even number of non-bonding m.o.s but these may be discounted for the organometallic bonding networks discussed in this paper which have non-zero algebraic structure counts (a.s.c.) (see ref. 10 for a detailed discussion of structure counts and 'supernumerary' non-bonding m.o.s). Furthermore, Hückel calculations on all the even-bonding networks discussed herein have confirmed the absence of non-bonding m.o.s and the paired property of bonding and antibonding m.o.s.[9] Therefore a stable closed-shell electron configuration for [M(butadiene)(CO)$_3$] will result if the metal-tricarbonyl fragment contributes two valence electrons, *i.e.* if the fragment is Fe(CO)$_3$ or an isoelectronic species, *e.g.* Co(η-C$_5$H$_5$) or Mn(CO)$_2$(NO). Metal-carbonyl fragments which contribute more than two electrons for metal–butadiene bonding will lead to the population of antibonding m.o.s and therefore such complexes are unlikely to be stable. Consequently the pairing theorem gives a simple quantum-mechanical rationalization for the stabilities of [Fe(butadiene)(CO)$_3$] complexes and an insight into the electronic origins of the 18-electron rule. In addition, it demonstrates the importance of considering the topological properties of the complete bonding network which is generated when the metal and butadiene orbitals interact strongly.

A major advantage of classifying organometallic complexes as alternant can be appreciated when more complex molecules are considered. Figure 2 indicates that a wide range of η^4 complexes of conjugated olefins have alternant bonding networks and therefore the conclusions of the pairing theorem are applicable to these molecules.[12] The pairing theorem suggests that each of the networks shown in this Figure will have a closed-shell electronic configuration if the metal-carbonyl fragments bonded to the olefin are two-electron donors, *i.e.* Fe(CO)$_3$ or isoelectronic fragments. All the ligands shown in Figure 2, or substituted derivatives of them, do indeed form stable complexes when co-ordinated to this fragment.[13-15]

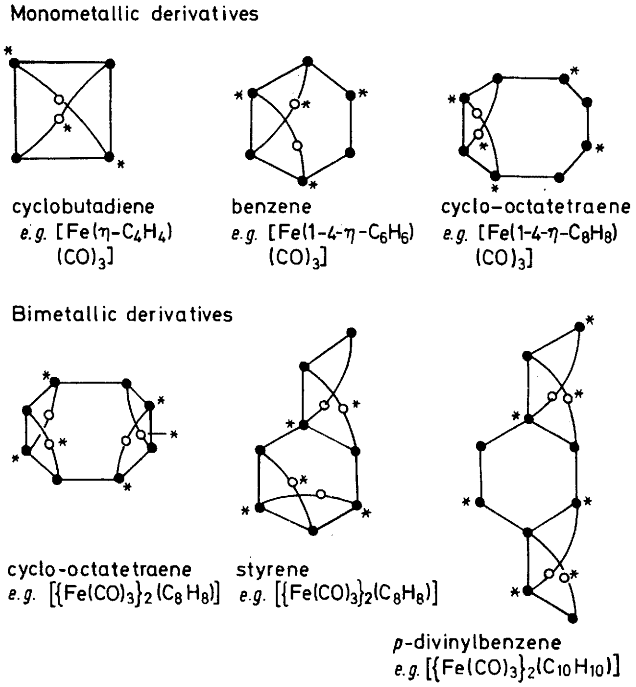

FIGURE 2 Alternant bonding networks in mono- and bimetallic metal η^4 complexes

Transition-metal organo-derivatives also provide examples of odd-alternant bonding networks. For example, the cation (IIIa)[16,17] has five carbon $2p_\pi$ and two

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[10] W. B. Smith, 'Molecular Orbital Methods in Organic Chemistry, HMO and PMO—An Introduction,' Marcel Dekker, New York, 1974, pp. 91—102.

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

[12] The bonding in such complexes has also been discussed by R. Hoffmann and M. Elian, *Inorg. Chem.*, 1975, **14**, 1058.

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

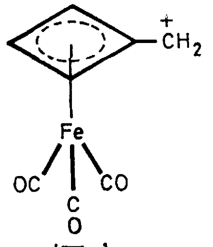
[14] J. Powell, *M.T.P. Internat. Rev. Sci.*, Ser. 1, Inorg. Chem., 1972, **6**, 309.

[15] M. A. Bennett, *Specialist Periodical Reports*, 'Organometallic Chemistry,' The Chemical Society, 1973, vol. 2, p. 305.

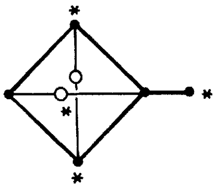
[16] J. D. Fitzpatrick, L. Watts, and R. Petit, *Tetrahedron Letters*, 1966, 1299.

[17] R. E. Davis, H. D. Simpson, N. Grice, and R. Petit, *J. Amer. Chem. Soc.*, 1971, **93**, 6688.

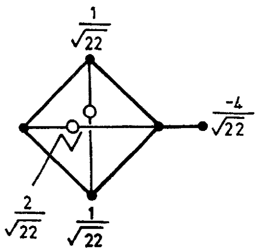
metal d_π orbitals which can be represented by the odd-alternant network shown in (IIIb). According to proposition (*b*) of the pairing theorem the seven basis-set orbitals of this system generate three bonding and three antibonding m.o.s with paired energies, and in addition a non-bonding m.o. localized exclusively on the starred atoms shown in (IIIb). The form of this non-bonding m.o. can be calculated from proposition (*c*) of the pairing theorem if the correct signs for the β values are introduced into equation (1). The calculated coefficients of the m.o. are shown in (IVa) and the m.o. is illustrated in (IVb). In order to confirm that the Hückel model was giving a reliable bonding picture for these organometallic complexes, a complete extended-Hückel self-consistent charge calculation was made on this iron cation. This calculation showed that the lowest virtual orbital of this ion closely resembles that shown in (IV). (A detailed comparison of the two types of calculation is given in the Appendix.)



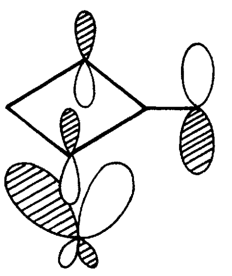
(IIIa)



(IIIb)

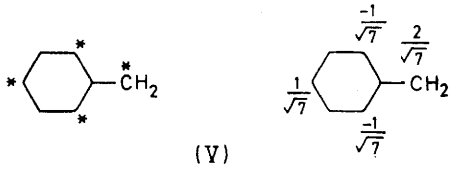


(IVa)



(IVb)

The form of this non-bonding m.o., which is empty in the cation (IIIa), is similar to that of the non-bonding m.o. of the isoelectronic benzyl cation, which is also an odd-alternant ion [see (V)]. Furthermore, both species have an exocyclic CH_2 group attached to a Hückel aromatic cyclic network [polycyclic in the case of (IIIa)] [9] and therefore the two ions are expected to show similar properties. This is found to be the case: both are remarkably stable carbonium ions and undergo nucleophilic addition at the exocyclic carbon atom [16,17] (*i.e.* the position where the non-bonding m.o.s have their greatest amplitudes).[18] A more sophisticated treatment which takes into account the different electronegativities of the basis-set orbitals [*i.e.* which reflects the electron-donating properties of the $Fe(CO)_3$ group] is able to account for the greater rate of hydrolysis of $[Fe\{\eta\text{-}C_4H_3\text{-}(CH_2Cl)\}(CO)_3]$ compared with benzyl chloride.[17,*]



(V)

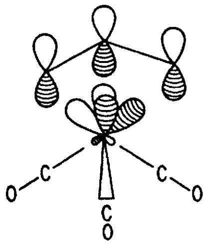
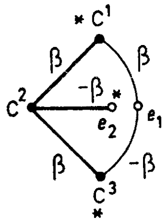
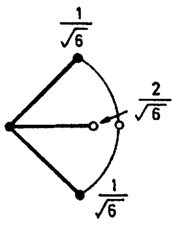


FIGURE 3 The basis-set orbitals for the alternant bonding network in $[M(\eta\text{-allyl})(CO)_3]$

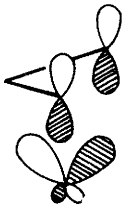
The metal η-allyl moiety presents the most important and ubiquitous odd-alternant bonding network in organometallic chemistry. The five basis-set orbitals for the complexed η-allyl ligand are shown in Figure 3, and the bonding network which represents the orbital interactions is shown in (VI). If the metal lies below the midpoint of the C^1–C^3 vector and the allyl plane is at right angles to the C^1–C^3–metal plane then the C^1 e_2 and C_3 e_2 † resonance integrals are exactly zero because the C^2 and C^3 $2p_\pi$ orbitals lie in the nodal plane of the metal e_2 orbital. The C^2 e_2 resonance integral has been assigned a negative value of β for convenience; a positive assignment does not alter the form of the non-bonding m.o. (VI). According to the pairing theorem the non-bonding m.o. of this network will have the form shown in (VII).



(VI)



(VIIa)



(VIIb)

This bonding network also generates two bonding and two antibonding m.o.s with paired energies in addition

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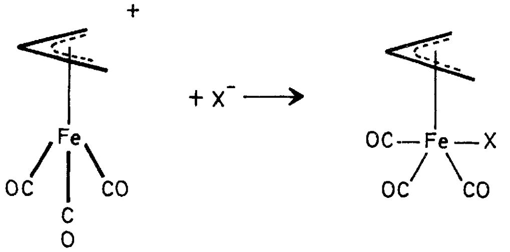
[18] K. Fukui, *Accounts Chem. Res.*, 1971, **4**, 57.

* D. M. P. Mingos, unpublished work.

† e_1 and e_2 represent the two metal *d–p* hybrid orbitals.

to the non-bonding m.o. Therefore, metal-carbonyl fragments which donate three electrons for metal–allyl bonding [*e.g.* $Co(CO)_3$, $Ni(\eta-C_5H_5)$, and $Rh(PF_3)_3$] will result in a closed-shell electronic configuration for the complex. Such complexes conform to the 18-electron rule. As the highest-occupied m.o. in this scheme is non-bonding, 16- and 17-electron η-allyl complexes which have the same delocalization energies are also predicted to be thermodynamically stable.* These complexes may be kinetically labile, however, because they have a low-lying empty or half-empty m.o.

The 16-electron $[Fe(\eta\text{-allyl})(CO)_3]^+$ ions, which have been well characterized,[20] are indeed labile to nucleophilic attack forming 18-electron complexes according to equation (2). It is significant that nucleophilic addition occurs at the position which has the largest orbital coefficient in the empty non-bonding m.o. (VIIb), *i.e.* the metal e_2 orbital. This preference for the metal contrasts with that noted above for the cyclobutadiene cation (IIIa).



(2)

Electrophilic additions to 18-electron allylic complexes will be governed by similar orbital considerations. The report that $[Rh(\eta\text{-allyl})(PF_3)_3]$ reacts with HCl at —75 °C to give an (η-allyl)hydridorhodium complex confirms this suggestion. Furthermore, on warming, propene is produced and the corresponding reaction with DCl showed that deuteriation occurred exclusively at the C^1 and C^3 positions of the resulting propene.[21] The nodal characteristics of the non-bonding m.o. (VIIb) would encourage the transfer of a proton from the metal to the C^1 and C^3 positions but not to the C^2 position of the complexed allyl ligand.

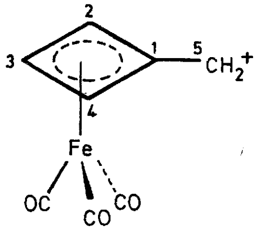
The 17-electron complex $[Fe(\eta\text{-allyl})(CO)_3]$ has been characterized in solution by e.s.r. spectroscopy.[22] This monomer is in equilibrium with a dimer which has an iron–iron bond, *i.e.* coupling occurs through the most active position. The isolation of these 17- and 16-electron complexes underlines the limitations of the 18-electron approach, and the above analysis indicates how the topological Hückel model can be used to give a more flexible and useful account of the chemical properties of these complexes.

The metal–allyl network shown in (VII) has only a single closed cycle which connects four of the five vertices and is therefore topologically distinct from those discussed above for butadiene and cyclobutadiene. Furthermore, this cycle has Möbius topology because it has an odd number of phase dislocations (*i.e.* only one $-\beta$). Möbius π networks are characterized by a $4n$ rule for aromaticity, in contrast to the more common $4n + 2$ Hückel rule.[11] Therefore, the η-allyl metal-bonding network represents a Möbius analogue of the benzyl radical (V). In the former there is an exocyclic metal d_π orbital in conjugation with a four-orbital Möbius aromatic system, and in the latter there is an exocyclic carbon p_π orbital in conjugation with a Hückel aromatic ring. Both topologies give rise to a non-bonding orbital, and therefore within the Hückel approximation equal resonance stabilization will be associated with the cationic, radical, and anionic forms. It is this topological feature which makes the η-allyl moiety such a versatile and important ingredient of organometallic reactions and catalytic processes.[13]

In a subsequent paper the properties of alternant bonding networks will be used to define more precisely the topological and electronic requirements for cyclic delocalization in organometallic π complexes.

APPENDIX

In order to verify that the PMO method was faithfully reproducing the bonding in organometallic π complexes, a self-consistent charge m.o. calculation was made on the iron cation (I). C_s Symmetry was assumed and the molecular dimensions were taken from the *X*-ray analysis of the related complex $[\{Fe(CO)_3\}(C_4H_3CPhC_4H_3)]$.[17] Initially a planar geometry was assumed for the hydrocarbon moiety with C–C distances equal to 1.443 Å and C–H 1.08 Å. The iron atom was assumed to lie below the centre of the ring at a distance of 1.79 Å. The iron-tricarbonyl fragment was assigned C_{3v} symmetry and the dimensions Fe–C 1.90 Å and C–O 1.19 Å.



(VIII)

The calculations were made using the extended-Hückel method with off-diagonal elements estimated by expression (3).[23] The metal orbital energies H_{ii} were obtained from self-consistent charge iterative calculations using Professor

$$H_{ij} = 1.75\, S_{ij}(H_{ii} + H_{jj})/2 \qquad (3)$$

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* The non-bonding m.o. can become slightly bonding if the metal moves away from the midpoint of the C^1–C^3 vector towards C^2. The C^3 e_2 and C^1 e_2 resonance integrals are then no longer zero on symmetry grounds and a small stabilization results. This conclusion is supported by extended-Hückel calculations on $[Fe(\eta\text{-allyl})(CO)_3]$.[19]

[19] R. Hoffmann and K. Haraiki, personal communication.

[20] G. F. Emerson, J. E. Mahler, and R. Petit, *Chem. Ind.*, 1964, 836.

[21] J. F. Nixon and B. Wilkins, *J. Organometallic Chem.*, 1972, **44**, C25.

[22] H. D. Murdoch and E. A. Lucken, *Helv. Chim. Acta*, 1964, **47**, 1517.

[23] R. Hoffmann, *J. Chem. Phys.*, 1963, **39**, 1397.

Hoffmann's programs at Cornell University.[24] The final metal and main-group atom orbital parameters were:

Orbital		H_{ii} [a]/eV	Exponent(s)[25]	Coefficients [b]
Fe	3*d*	−13.940	5.350	0.5369
			1.800	0.66799
	4*s*	−9.456	1.5750	
	4*p*	−4.529	0.9750	
C	2*s*	−21.400	1.625	
	2*p*	−11.400	1.625	
O	2*s*	−32.300	2.275	
	2*p*	−14.800	2.275	

[a] H. Basch and H. B. Gray, *Theor. Chim. Acta*, 1967, **4**, 367. [b] J. W. Richardson, W. C. Niewpoort, R. R. Powell, and W. F. Edgell, *J. Chem. Phys.*, 1962, **36**, 1057.

Double-ξ wavefunctions were used for the metal 3*d* orbitals.

The final charge distribution and overlap populations for the cation are given in the Table and compared with those calculated by the PMO method. The correct trend is observed for the starred atoms of the alternant-bonding network, *i.e.* Fe, C^2, C^4, and C^5, although the charge differences are somewhat overestimated by the PMO method. For the unstarred atoms, *i.e.* C^1 and C^3, the agreement is less satisfactory. The carbon–carbon bond-overlap populations calculated by the extended-Hückel method, and the π-bond orders derived from PMO method are also shown in the Table together with the bond lengths in the cation $[\{Fe(CO)_3\}(C_4H_3CPhC_4H_3)]$.[17]

Bond-overlap populations and charges for $[Fe(C_4H_3CH_2)(CO)_3]^+$

(*a*) Charges

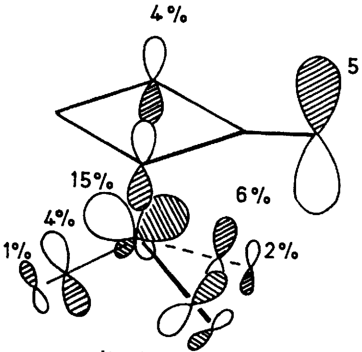
Atom	Extended [a] Hückel	PMO
Fe	0.1234	0.1818
C^1 [b]	0.1344	0.000
C^2	0.0372	0.0455
C^3	0.0779	0.000
C^4	0.0372	0.0455
C^5	0.265	0.7273

(*b*) Overlap populations

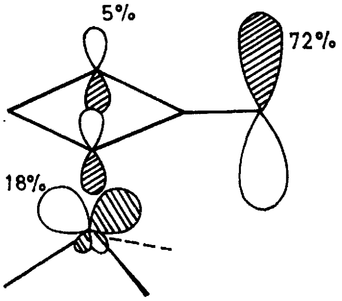
Bond	Extended Hückel	PMO π-bond orders	Corresponding bond lengths (Å) in $[(OC)_3Fe(C_4H_3CPhC_4H_3)Fe(CO)_3]^+$
C^1–C^2	0.8928	0.4342	1.47
C^1–C^5	1.0602	0.5158	1.40
C^2–C^3	0.9476	0.5158	1.42

[a] Calculated on the basis of a Mulliken population analysis (R. S. Mulliken, *J. Chem. Phys.*, 1955, **23**, 1833). [b] See (I) for numbering.

The lowest-lying virtual orbital of $[Fe(C_4H_3CH_2)(CO)_3]^+$ lies at −10.661 eV according to the extended-Hückel calculation and is schematically represented as in (IX).* The percentage character of the contributing orbitals is also shown in (IX). The agreement between (IX) and that estimated by the PMO method, (X), without the use of any computational aids is remarkably good. The symmetry and important nodal characteristics of this orbital are reproduced and in particular the non-involvement of the carbon p_π orbitals at carbon atoms 1 and 5 (the extended-Hückel calculation indicates only a 0.5% contribution from these atoms). The only major deficiency of the PMO method arises from the neglect of the carbonyl-orbital contributions which contribute *ca.* 20% to the total wavefunction.



(IX)



(X)

I thank Professor R. Hoffmann for his generous hospitality at Cornell University and many useful discussions. The stay at Cornell was made possible by a grant from the N.A.T.O. Scientific Affairs Division.

[5/2464 *Received*, 17*th December*, 1975]

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* 1 eV ≈ 1.60 × 10^{-19} J.

[24] P. J. Hay, J. C. Thibeault, and R. Hoffmann, *J. Amer. Chem. Soc.*, 1975, **97**, 4884.

[25] E. Clementi, *J. Chem. Phys.*, 1964, **40**, 1944.