A Theoretical Study of Three-centre M–H–C Interactions†

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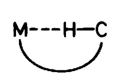
The results of extended-Hückel calculations on some complexes of general formula $[M(\text{cycloalkenyl})L_3]^n$, which are known to possess agostic M–H–C interactions, are presented. The effects of changes in M and L are investigated and compared with experimental observations. It is found that the M–H–C interaction is best considered electronically as a highly bent open system rather than as a three-membered ring. Examination of the complex $[Cr(C_8H_{11})H(PF_3)_3]$ shows that it possesses several features in common with the alkenyl compounds, and hence should be considered as a weakly agostic system rather than a metal hydride.

The activation of aliphatic C–H bonds by transition-metal systems is currently attracting great chemical interest, due mainly to the industrial importance of developing catalytic systems for functionalising hydrocarbons.[1,2] Interaction between a transition-metal atom or group of atoms and an aliphatic C–H bond may occur intermolecularly or, more commonly, intramolecularly,[3] yielding structures which have been termed agostic by Brookhart and Green.[4]

A unique group of complexes exhibiting intramolecular behaviour is that in which interaction occurs between an electron-deficient metal centre and an adjacent C–H bond. Usually the metal co-ordinates non-classically to the hydrogen to share the sigma electrons and move towards an 18-electron configuration, although some agostic systems do not obey this rule, *e.g.* $[TiRCl_3(dmpe)]$ (R = Me or Et, dmpe = $Me_2PCH_2PMe_2$).[5,6] This M–H–C interaction has been known for many years in the open form (**1**) in compounds containing *ortho*-hydrogen–metal interactions, *e.g.* $[Ru(PPh_3)_3Cl_2]$[7] (**3**) and $[PdI_2(PMe_2Ph)_2]$[8] (**4**), and also in the pyrazolyl complexes discovered by Trofimenko,[9–11] such as $[Ni\{Et_2B(pz)_2\}_2]$ (**5**). Recently, however, complexes of type (**6**) have been characterised which appear to contain a closed M–H–C interaction (**2**). In these complexes, as in the open structures, the metal attempts to reach an 18-electron configuration by sharing the sigma electrons in the C–H bond to form a two-electron, three-centre bond. Spectroscopic and structural studies of these complexes[12–19] have shown that they possess a number of features in common.

(*i*) On the n.m.r. time-scale, independent fluxional processes are observed which correspond to: (*a*) *endo*-exchange of the hydrogen atoms at opposing ends of the η^3-alkenyl system [Scheme (*a*)]; (*b*) migration of the ML_3 group around the ring *via* a series of hydride transfers from the ring to the metal, creating a diene system, and 1,2 shifts [Scheme (*b*)]; (*c*) equivalencing of the L groups by rotation either while the M–H–C interaction is still intact, or during the transition state for process (*a*) [Scheme (*c*)].

(*ii*) In cases where structural determinations have been carried out it is found that the agostic hydrogen atom occupies a near-octahedral site on the metal atom, producing a three-centre system in which both the M–C and M–H distances are very short. Evidence for co-ordination is also provided by the lengthening of the C–H bond, presumably as electrons are withdrawn into the three-centre system. However, Ittel and co-workers[12] have suggested that the short M–C distance may simply be incidental, being constrained thus if the hydrogen atom is to occupy the octahedral co-ordination site.



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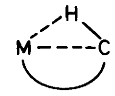

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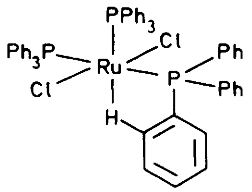

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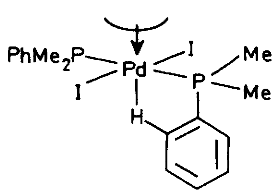

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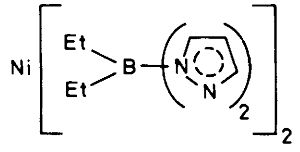

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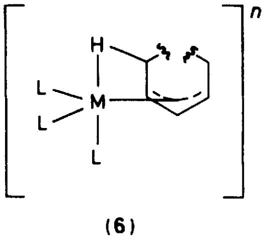

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This group[12] performed modified extended-Hückel calculations[20] on the model system $[Co(\eta^3\text{-}C_4H_7)(PH_3)_3]^{0,1+,2+}$ (**7**), and were able to simulate the breakdown of the M–H–C interaction in moving from the dication (a 16-electron system) to the neutral species (18 electrons), due to the filling of the lowest unoccupied molecular orbital (l.u.m.o.), which has an antibonding M–H–C contribution. They also found that, despite the closed M–H–C spatial geometry, the M–C interaction was very weak, apparently the result of antibonding C–H contributions from filled orbitals involving metal–allyl bonding. Hoffmann and Saillard[21] mention a similar result from a calculation on the isoelectronic iron complex.

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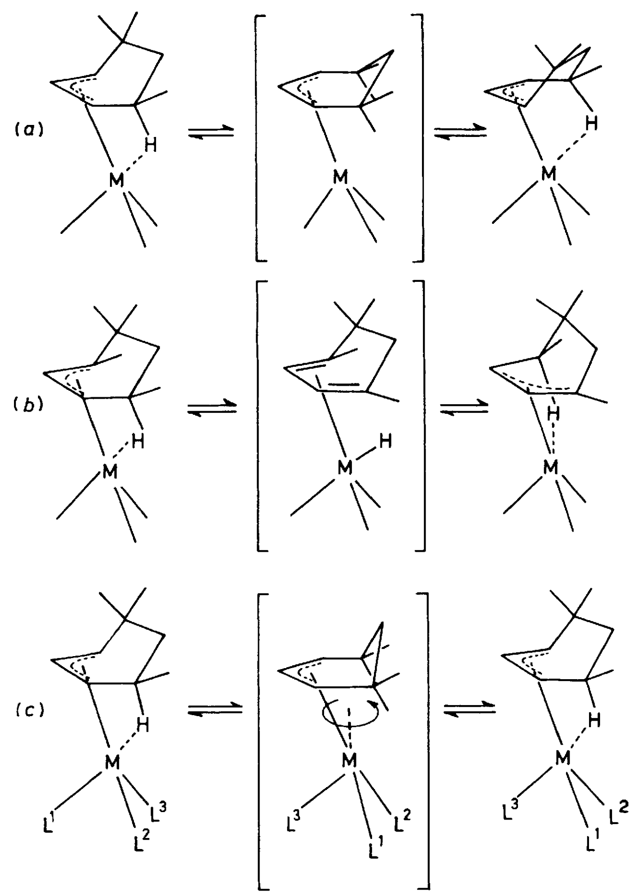
† *Non-S.I. units employed:* cal = 4.184 J, eV ≈ 1.60 × 10^{-19} J.

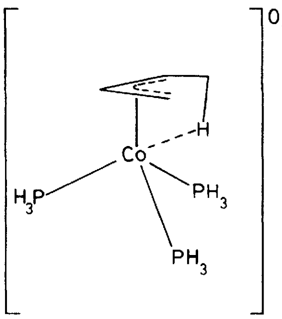


Scheme. Fluxional processes observed on the n.m.r. time-scale in η^3-cycloalkenyl–ML_3 complexes: (*a*) *endo*-exchange; (*b*) hydride transfer; and (*c*) ligand equivalencing

In this paper we present the results of the first comparative theoretical study of alkenyl–ML_3 complexes, using experimentally determined geometries. The complexes selected for investigation are **(8)**—**(10)**. The question of whether the M–H–C system should be viewed as open or closed is considered, and the effects of changes in M and L examined. Also, the study is extended to the complex $[Cr(C_8H_{11})H(PF_3)_3]$ to determine whether or not it may be considered agostic. This system has hitherto been regarded as a metal hydride.

Calculations

The *X*-ray crystal structure of $[Mn(C_6H_8CH_3)(CO)_3]$ determined by Brookhart and co-workers[19] served as a basis for the geometries of the six-membered ring complexes. A neutron-diffraction study of this complex has also been published.[22] The structures of $[M(C_6H_9)(CO)_3]^n$ (M = Mn, *n* = 0; M = Fe, *n* = 1+) were obtained by replacement of the *endo*-methyl group with a hydrogen atom at a distance of 1.03 Å. Geometries for $[Fe(C_8H_{13})L_3]^+$ (L = CO or PH_3) were derived from the neutron-diffraction structure determined by Williams and co-workers.[14] The structure of $[Cr(C_8H_{11})H(PF_3)_3]$ was taken from the *X*-ray study of Von Gustorf and co-workers.[23] The structures are shown in Figure 1.



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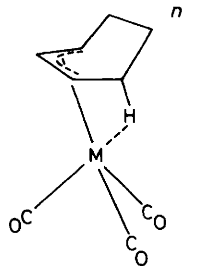

M = Mn, *n* = 0
M = Fe, *n* = 1

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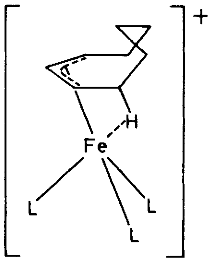

L = CO or PH_3

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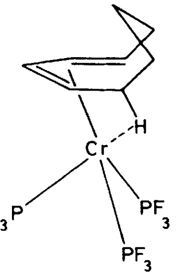

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Calculations on the complexes were performed using the self-consistent charge and configuration (SCCC) method. The basis set for the metal atoms consisted of valence Slater-type 3*d*, 4*s*, and 4*p* atomic orbitals (a.o.s), and for the first-row atoms 2*s* and 2*p* a.o.s were used, 3*s* and 3*p* a.o.s were included on phosphorus and 1*s* orbitals on the hydrogen atoms. The radial wave-functions computed by Fitzpatrick and Murphy[24] as a best least-squares fit to the SCF functions of Herman and Skillman[25] were chosen (double-zeta functions were used to represent the *d* orbitals). A value of 1.3 was used as the exponent for the hydrogen 1*s* orbital. Valence orbital ionisation potentials for nine configurations of the metal atom and two configurations of the first-row atoms were taken from the work of Basch *et al.*[26] as approximations to the diagonal elements of the Coulomb matrix. These parameters are summarised in Table 1.

Calculations on fragments were performed using the non-

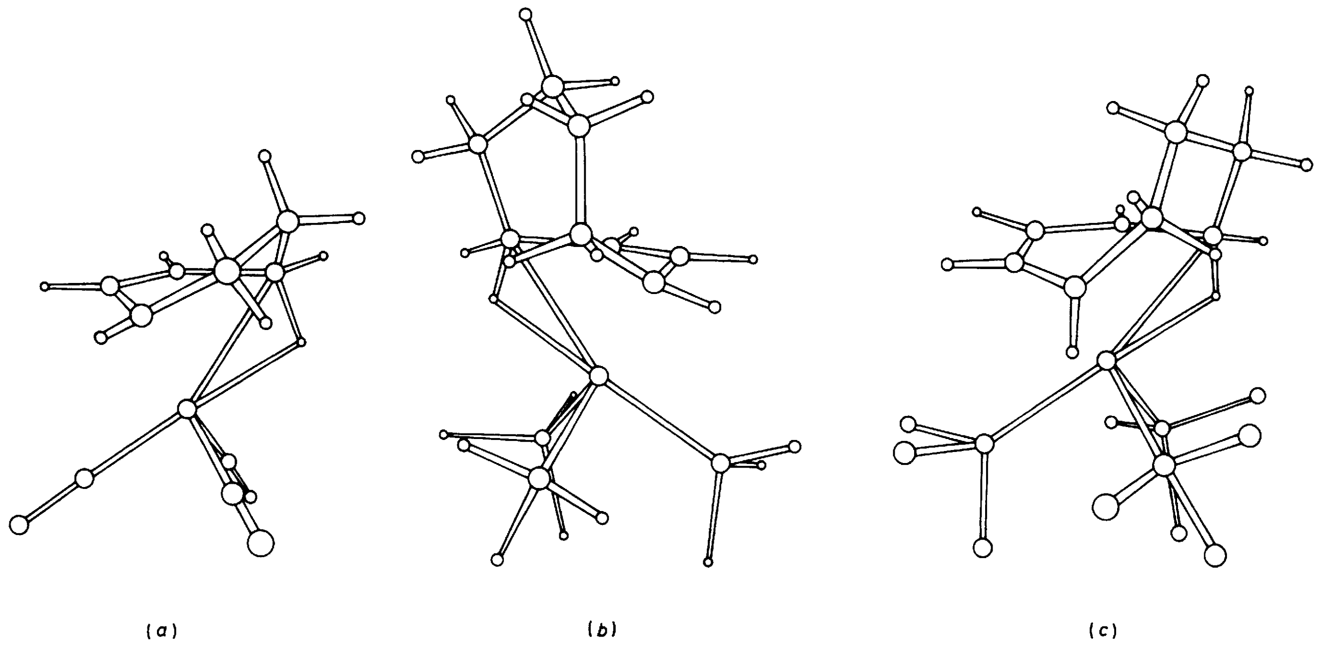


Figure 1. Perspective diagrams of: (a) $[Fe(C_6H_9)(CO)_3]^+$; (b) $[Fe(C_8H_{13})(PH_3)_3]^+$; and (c) $[Cr(C_8H_{11})H(PF_3)_3]$, showing the conformation adopted by the organic moiety

Table 1. Semiempirical parameters used in the SCCC calculations

	Exponent				Coefficient		Valence orbital ionisation potential (eV)		
Atom	s	p	d_1	d_2	c_1	c_2	s	p	d
Cr	1.3153	0.9239	4.9782	2.0222	0.4752	0.6727	−6.590	−3.520	−7.780
Mn	1.3738	0.9493	5.3176	2.1758	0.4807	0.6659	−6.860	−3.620	−8.580
Fe	1.4296	0.9717	5.6528	2.3246	0.4847	0.6610	−7.104	−3.707	−9.390
C	1.5533	1.4500					−20.31	−10.71	
O	2.1632	2.1739					−32.34	−15.80	
F	2.4652	2.5173					−40.12	−18.65	
P	1.8086	1.4535					−18.77	−10.12	
H	1.3000						−13.60		

iterative extended-Hückel scheme using the same basis sets and diagonal Coulomb terms obtained from the SCCC calculations on the appropriate parent complexes. Small changes in any of the parameters or geometries used in this study do not significantly alter the conclusions.

The calculations were carried out using the FORTICON 8 computer program of Hoffmann and co-workers.[27] The weighted Wolfsberg–Helmholz parameterisation[28] was used to calculate the off-diagonal elements of the Coulomb matrix, with $k = 1.75$. Calculations typically required 10—15 min of computing time (depending on molecular size and rate of convergence) using an IBM 4341 computer with the VM/CMS operating system. In most cases approximately 50 iterations were required to reach self-consistency.

Contour plots were executed on a CALCOMP 1012 drum plotter using programs developed in this laboratory. Perspective diagrams were obtained using the program NAMOD available from the Quantum Chemistry Program Exchange.[29] For the contour plots, all distances are in Å. Positive contours are described by solid lines and negative ones by dashed lines. A plan of the ML_3 and MHC systems has been superimposed on each plot. Contours were drawn corresponding to the following values of the wavefunction: −2.80, −2.20, −1.60, −1.00, −0.50, −0.30, −0.25, −0.20, −0.16, −0.12, −0.08, −0.04, −0.02, −0.01, 0.00, 0.01, 0.02, 0.04, 0.08, 0.12, 0.16, 0.20, 0.25, 0.30, 0.50, 1.00, 1.60, 2.20, and 2.80.

Results and Discussion

The energy-level diagram for $[Fe(C_6H_9)(CO)_3]^+$ is shown in Figure 2. The levels have been traced to show their parentage in the molecular orbitals of the ring and ML_3 fragments by appropriate transformations of the basis sets. Only the highest-occupied and lowest-unoccupied energy levels of the complex are appreciably different in energy from those calculated for the isolated fragments, hence for simplicity only these have been drawn. The general pattern is similar for all complexes. The shape of the frontier orbitals of the ML_3 and allyl fragments has been the subject of previous discussion[30,31] and will not be reiterated here.

In all the complexes the principal bonding interaction occurs between the π-character highest-occupied molecular orbital (h.o.m.o.) of the ring fragment and the metal-dominated l.u.m.o.s of the ML_3 group. This suggests that the force holding the complexes together is the polyenyl–ML_3 interaction rather than the M–H–C interaction, in agreement with the results of

Table 2. Overlap populations for M–H–C occupied bonding m.o.s

Complex	m.o.[a]	Σc_i^2 M	Σc_i^2 C	Σc_i^2 H	Overlap population C–H	Overlap population C–M	Overlap population M–H
$[Fe(C_6H_9)(CO)_3]^+$	MCH (a)	0.284	0.066	0.045	0.017	0.019	0.014
	MCH (b)	0.248	0.196	0.033	0.016	0.016	0.019
$[Mn(C_6H_9)(CO)_3]$	MCH	0.082	0.037	0.028	0.012	0.012	0.009
$[Fe(C_8H_{13})(CO)_3]^+$	MCH (a)	0.039	0.023	0.018	0.008	0.001	0.007
	MCH (b)	0.090	0.104	0.122	0.097	0.011	0.024
$[Fe(C_8H_{13})(PH_3)_3]^+$	MCH	0.190	0.044	0.019	0.009	0.006	0.004
$[Cr(C_8H_{11})H(PF_3)_3]$	MCH	0.173	0.067	0.022	0.019	0.001	0.004

[a] (a), (b) refer to labelled levels in Figure 2.

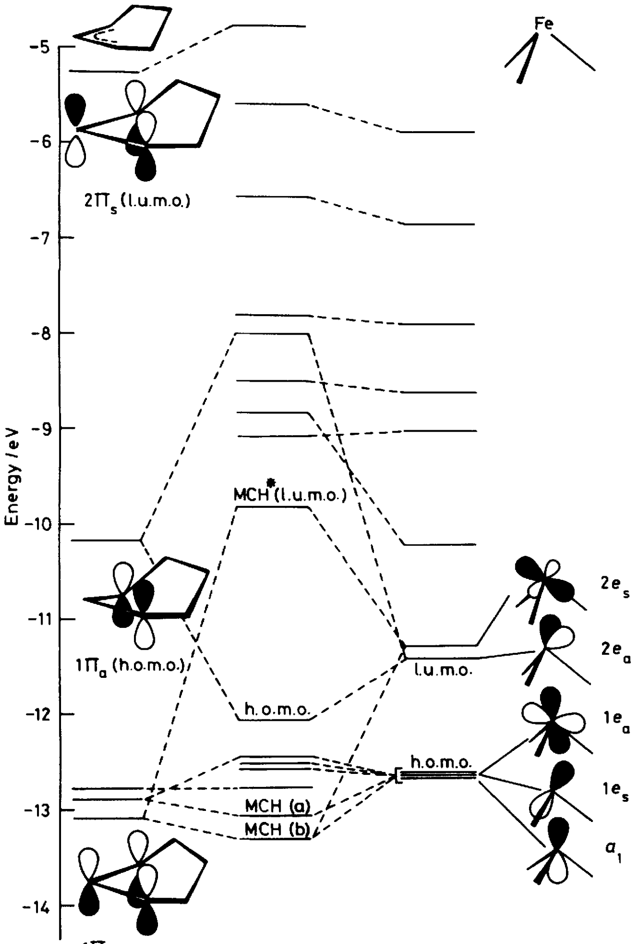


Figure 2. Fragment molecular orbital interaction diagram for $[Fe(C_6H_9)(CO)_3]^+$

the previous study of Ittel and co-workers.[12] The stabilisation due to the interaction of the ring h.o.m.o. and the ML_3 l.u.m.o. is independent of the nature of the organic moiety, the metal, and the ligand groups. However, if the h.o.m.o.–l.u.m.o. group of orbitals on the ML_3 fragment lies sufficiently low in energy relative to the h.o.m.o. of the ring, further stabilisations, due to interactions with low-lying occupied ring m.o.s are possible. Thus, in the case of the complexes $[Fe(C_6H_9)(CO)_3]^+$ and $[Fe(C_8H_{13})(CO)_3]^+$ the metal fragment m.o.s have dropped in energy relative to the organic m.o.s, and additional

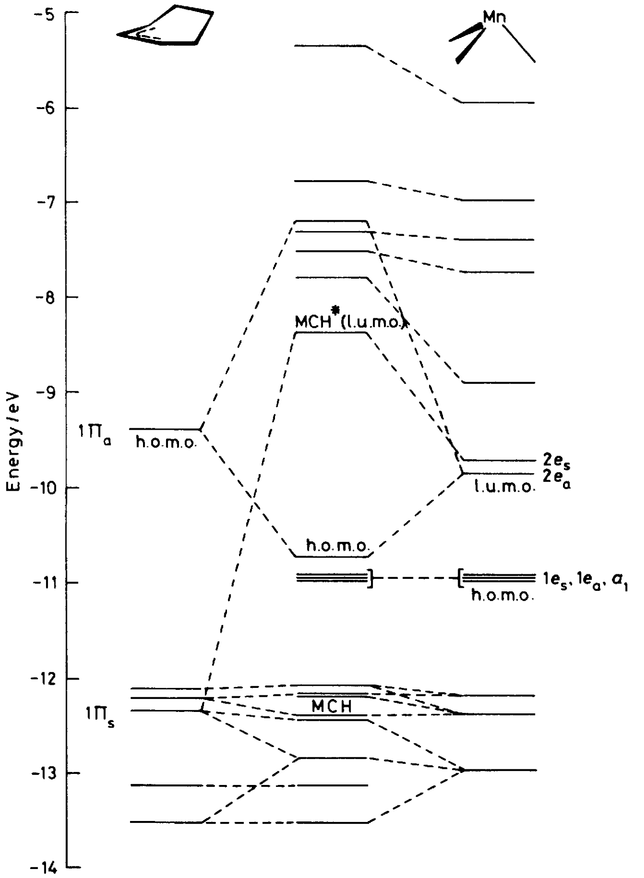
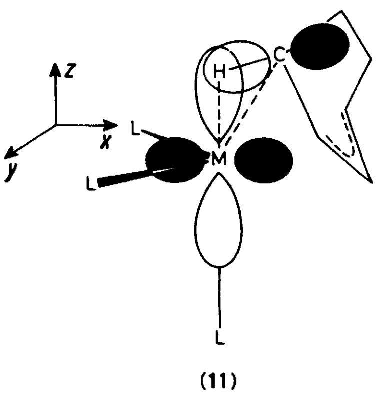


Figure 3. Fragment molecular orbital interaction diagram for $[Mn(C_6H_9)(CO)_3]$



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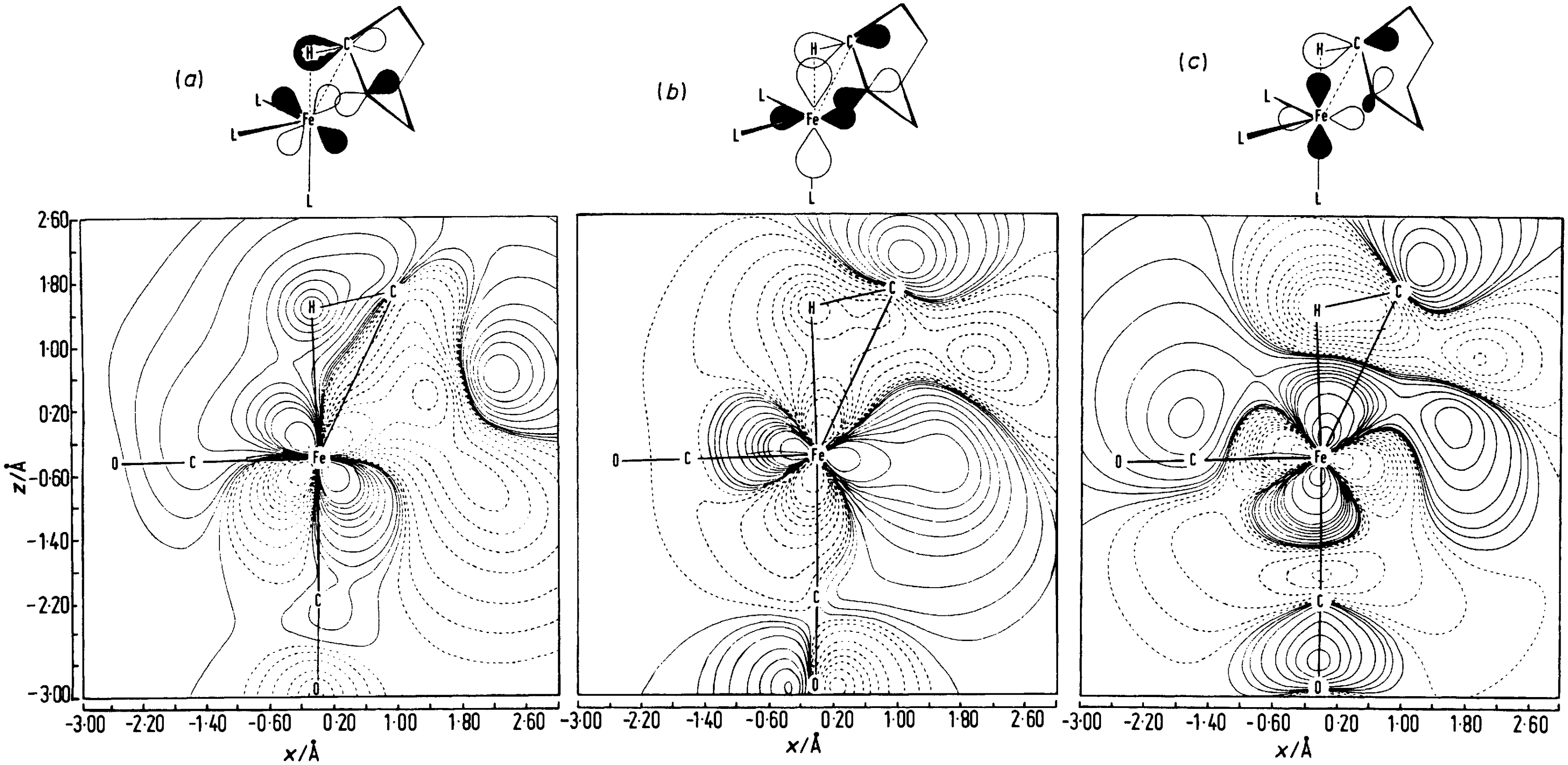

Figure 4. Contour plots of the M–H–C bonding and antibonding m.o.s of $[Fe(C_6H_9)(CO)_3]^+$, sliced in the plane of the M–H–C system. Energies: (*a*) MCH m.o., −13.10; (*b*) MCH m.o., −13.38; (*c*) MCH* l.u.m.o., −9.85 eV

Table 3. Total M–H, C–H, and C–M overlap populations

Complex	C–H of isolated ring	C–H in complex	C–M	M–H	Decrease on complexation
$[Fe(C_6H_9)(CO)_3]^+$	0.836	0.773	−0.103	0.061	0.063
$[Mn(C_6H_9)(CO)_3]$	0.835	0.796	−0.120	0.050	0.039
$[Fe(C_8H_{13})(CO)_3]^+$	0.795	0.740	−0.099	0.064	0.055
$[Fe(C_8H_{13})(PH_3)_3]^+$	0.795	0.785	−0.148	0.023	0.010
$[Cr(C_8H_{11})H(PF_3)_3]$	0.861	0.858	−0.161	−0.002	0.003

Table 4. Overlap populations in the principal polyenyl–ML_3 bonding m.o.

Complex	M–C	M–H	C–H
$[Fe(C_6H_9)(CO)_3]^+$	−0.009	0.004	0.001
$[Mn(C_6H_9)(CO)_3]$	−0.004	−0.001	0.017
$[Fe(C_8H_{13})(CO)_3]^+$	−0.021	0.004	0.000
$[Fe(C_8H_{13})(PH_3)_3]^+$	−0.013	0.005	−0.001
$[Cr(C_8H_{11})H(PF_3)_3]$	−0.010	0.004	−0.004

stabilisations can occur. This effect is strongly dependent on M and L. In the case of $[Mn(C_6H_9)(CO)_3]$, the energy gap between the l.u.m.o.s of $Mn(CO)_3$ and the low-lying filled ring m.o.s is large and the interactions are consequently poor (Figure 3). This is also true in the iron–phosphine and chromium complexes.

From this discussion it is clear that the M–H–C interaction plays a secondary role in the bonding in these complexes. To determine which m.o.s are the principal contributors to the three-centre system, the electron density (the sum of the squares of the m.o. coefficients for each orbital, normalised to two electrons) was computed for the M, C, and H atoms for each m.o. The l.u.m.o. and one or more h.o.m.o.s in each complex showed appreciable contributions from all three atoms. Detailed population analyses for these orbitals are given in Table 2, which show that: (*a*) the l.u.m.o. represents a strong antibonding M–H–C interaction, in agreement with the previous study; (*b*) in all cases, independent of ring size, metal, or co-ordinating ligand, there are usually one or two filled m.o.s which exhibit appreciable bonding interactions between all three atoms in the three-centre system, these levels are always relatively low-lying.

The M–H–C bonding m.o., shown schematically in (**11**), results from stabilisation of filled m.o.s on the ring (donor orbitals), which have appreciable C–H bonding contribution, by the $2e_g$ l.u.m.o. of the ML_3 group. The strength of the M–H–C system is therefore governed to a large extent by the strength of this interaction. The M–H–C bonding and antibonding m.o.s of $[Fe(C_6H_9)(CO)_3]^+$, sliced in the plane of the M–H–C system, are illustrated in Figure 4. Plots for the other complexes are similar. With the complexes oriented so that the H–M–L^1 group lies approximately along the z axis and the L^2–M–L^3 system occupying the xy plane, the $2e_g$ acceptor l.u.m.o. is composed mainly of metal p_z and d_{z^2} contributions, and is hence well directed to overlap with a bonding C–H orbital, if the two lie close enough in energy.

For the $[Mn(C_6H_9)(CO)_3]$ complex (Figure 3) the energy gap between the bonding η^3-allyl m.o., which has a significant C–H content, and the $Mn(CO)_3$ acceptor l.u.m.o. is large, and interaction is weak. In the analogous iron complex (Figure 2), due to the stabilisation described above, much greater interaction occurs, and we would expect the M–H–C system to be stronger. This is actually the case: the overlap populations for the M–H–C system are greater in the iron compound than in the manganese one. A greater free energy of activation is predicted for *endo* exchange in the case of the iron complex, since during such an exchange the M–H–C system must be disrupted, and the stronger the interaction the more energy will be needed. In fact the measured energies are very similar, 8.3 kcal mol^{-1} for the manganese and 10.6 kcal mol^{-1} for the iron complex.

A similar effect is observed upon changing the ligand groups. For $[Fe(C_8H_{13})(PH_3)_3]^+$ the larger gap between the donor and acceptor m.o.s weakens the interaction relative to that observed for $[Fe(C_8H_{13})(CO)_3]^+$, where the gap is small, allowing better stabilisation. Hence we would expect that the energy required to permit *endo*-exchange should be greater in the carbonyl than the phosphine complexes, as is found experimentally to be the case. In theory it is possible to envisage an interaction of the type described by Hoffmann and Saillard in which an unoccupied m.o. incorporating an antibonding C–H contribution is stabilised by interaction with metal-dominated ML_3 h.o.m.o.s. In fact this does not seem to occur, possibly due to the large energy gap between the h.o.m.o. and l.u.m.o. on all the ring systems except in the chromium complex, which places the unoccupied ring m.o.s at too high an energy to interact with the metal orbitals. In the case of the chromium complex, the h.o.m.o.–l.u.m.o. gap on the ring fragment is much smaller, and good interactions occur between the h.o.m.o.s of the $Cr(PF_3)_3$ fragment and the ring l.u.m.o., but the latter has no large C–H contribution and no M–H–C orbital results.

The total M–C, M–H, and C–H overlap populations for each complex are given in Table 3. The C–M population is negative, in contrast to the situation found in the M–H–C bonding m.o., for each system. There are two senses in which the M–H–C system may be regarded as 'closed,' geometrically or electronically. Geometrically, for the manganese complex, the M–H–C angle is 100° and the M–C distance of 2.34 Å is within bonding limits, thus on spatial grounds the system is closed. Electronically, however, it is more correct to regard the system as a bent 'open' structure, with, at best, only a weak interaction between the carbon and metal atoms, since the M–C overlap population is negative. The reason for this changeover is, as suggested by the previous workers,[12,21] that the strong stabilising interactions between the unsaturated portion of the ring and the frontier ML_3 orbitals set up an antibonding interaction between the adjacent C–H bond and the metal, which cancels out the C–M bonding effect in the M–H–C m.o. This is seen by examining the overlap populations in the h.o.m.o. of each complex, which represent, in general, the strongest stabilisation (Table 4). In every case the M–C population is negative, and the accumulated effect over a number of such m.o.s overcomes the bonding effects. However, the relative strengths of the M–H interactions as discussed above are not affected by this weakening factor. In fact, the destabilisation of the M–C bond in the manganese complex is greater than in the analogous iron compound, and the destabilisation of the Fe–C bond in the phosphine complex is greater than that in the analogous carbonyl one, so that the points made are in fact reinforced. The chromium complex is the only one to show a negative overall M–H population, which indicates that the M–H–C system in this molecule is very weak.

Thus, in conclusion, this study shows that bonding in the alkenyl–ML_3 complexes studied here is, in all cases, dominated by the interaction of the h.o.m.o. of the allyl group with the frontier orbitals of the ML_3 fragment. The M–H–C interaction plays a secondary role. In each case there exists a relatively low-lying orbital in which the M–C, M–H, and C–H interactions are all bonding. This orbital is produced by the stabilisation of a filled donor m.o. ring incorporating a bonding C–H contribution by the $2e_g$ l.u.m.o. on ML_3, the vacant acceptor m.o. The strength of this interaction depends on how close in energy the donor and acceptor orbitals are. In $[Mn(C_6H_9)(CO)_3]$ and $[Fe(C_8H_{13})(PH_3)_3]^+$ they are far apart and we would hence expect a weaker M–H–C interaction. This correlates with the known free energies of activation for *endo*-exchange in these complexes. The bonding C–M interaction is cancelled out, in every case, by an antibonding effect caused by the allyl–metal interaction, suggesting that the M–H–C system should be regarded as open.

If the h.o.m.o.–l.u.m.o. gap in the ring fragment were smaller, it is possible that the h.o.m.o.s of the ML_3 fragment could stabilise an antibonding C–H orbital to produce further M–H–C bonding m.o.s.

The chromium complex possesses several features which show an M–H–C interaction: (1) predominant diene–metal bonding; (2) a low-lying filled M–H–C bonding m.o.; and (3) a l.u.m.o. with antibonding M–H–C character. However, the overall overlap populations are unfavourable for the formation of an M–H–C system. Against this, the plot of the l.u.m.o. does not show as marked an antibonding character as do the other complexes. This suggests a weak agostic interaction.

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