Molecular Orbital Calculations on Transition Metal Complexes

XVII. The π-Cyclopentadienyl-π-cycloheptatrienyl Complexes of Ti, V, and Cr

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INDO SCF MO calculations are reported for the complexes $(C_5H_5)M(C_7H_7)$ (M = Ti, V and Cr), and for the corresponding V and Cr cations. The results correctly predict $^1A_1$ ground states for the V^+ and the neutral Ti and Cr species, and for the neutral V and Cr^+ complexes confirm the $^2A_1$ ground levels. The formally metal d-levels followed the H^{core} sequence $e_2 < a_1 < e_1$, and the most important interactions were those between the metal e_2 level and the ligand C_7H_7 π-orbitals, and between the metal e_1 level and the ligand C_5H_5 π-orbitals. Calculations also satisfactorily reproduced other experimental quantities, and the results indicate that the e_2 ligand interaction becomes more important, and the e_1 ligand interaction less important, with increasing size of the ligand ring.

Key words: Mixed sandwich complexes of Ti, V, and Cr, INDO SCF MO calculations on ∼

1. Introduction

Recent INDO SCF MO calculations [1–3] have largely vindicated the traditionally held view of the bonding in metallocene, MCp_2, systems ($Cp = C_5H_5$), in which the metal 3d orbitals of a_1 and e_2 symmetry are regarded as essentially non-bonding, whilst the e_1 level becomes strongly anti-bonding by virtue of its interaction with the lower lying ligand π-orbital of that symmetry. Thus the metal coefficients of presence for the a_1 and e_2 levels are both of the order of 0.95, whilst for the formally 3d e_1 level it may be as little as 0.60 to 0.70. For the bis-benzene (MBz_2) metal complexes however, a somewhat different situation obtains because of the appreciable metal → ligand back-bonding involving the e_2 level, so that for these systems only the a_1 3d level is approximately non-bonding. Here the metal

$3d$ level of e_2 symmetry is significantly bonding in character, with a metal co-efficient of about 0.75 to 0.80, and the degree of mixing is in fact comparable to that in the anti-bonding e_1 level, for which the metal presence coefficient is again of the order of 0.80.

These observations may nevertheless be rationalized in terms of the simple molecular orbital calculations of Fischer [4], which show that the energies of the π-ligand e_1 and e_2 combinations should decrease progressively with increasing size of the ligand ring. Thus, as the ring size becomes greater, the ligand e_2 level (which for MCp$_2$ and MBz$_2$ systems lies above the metal $3d$ level) should approach more closely to the metal $3d$ level, thereby increasing the bonding interaction, whilst at the same time the ligand e_1 level will drop further below the metal $3d$ orbital, thus reducing the extent of the anti-bonding interaction.

It therefore appeared desirable to test this hypothesis further by carrying out calculations on systems containing seven membered ligand rings, Ch or π-cyclo-heptatrienyl (Ch$=$C$_7$H$_7$), and since MCh$_2$ systems are virtually unknown the CpMCh complexes of the $3d$ series constitute the most extensive group of com-pounds available for this purpose. Thus the neutral systems are known for M$=$Ti, V, and Cr, and the corresponding cations for M$=$V and Cr. Consequently we have made full basis set INDO SCF molecular orbital calculations (including both σ- and π-contributions from the rings) for these systems, using a technique [5] already well tested for a wide variety of transition metal complexes, including MCp$_2$ and MBz$_2$ systems.

As an initial test of our approach we established that our calculations yielded ground states for the CpMCh systems which agreed with those found experi-mentally, and suggested by the ligand field model, and as a further check we have compared experimental data for g values, proton hyperfine coupling constants, and ionisation potentials, with the relevant calculated quantities. The rather satisfactory agreement thus obtained encouraged us to believe that our calculations do give a reasonable account of the bonding in these CpMCh systems, and we have accordingly used them as a basis from which to draw more general conclusions concerning the effect of ligand ring size on the bonding in transition metal sand-wich complexes.

2. Method

The calculations employ the all valence electron INDO SCF MO method pre-viously developed in these laboratories [5]. The molecular orbitals are described by linear combinations derived from the metal $3d$, $4s$, and $4p$, the carbon $2s$ and $2p$, and the hydrogen $1s$ orbitals.

The molecular structure for CpTiCh was taken from the recent X-ray measure-ments by Zeinstra and De Boer [6], but initial calculations on the ground state of CpVCh, using the metal-carbon distances of an earlier structural determination [7], led to computed ring hydrogen hyperfine coupling constants, A_H, which were in rather poor agreement with the experimental values. Consequently it was decided

to obtain the equilibrium V–Cp and V–Ch metal-carbon distances by minimizing the total energy: these values, V–C (Cp) = 2.32 Å and V–C (Ch) = 2.16 Å, whilst differing significantly from the older X-ray values, yielded much more reasonable proton transferred spin densities, and were therefore used for all the other calculations on this molecule and on its cation. For the [CpCrCh]$^+$ cation, for which no structural data are available, we similarly optimized both the Cr–C (Cp) and the Cr–C (Ch) distances, and the resulting values (Cr–C (Cp) = 2.18 Å and Cr–C (Ch) = 2.16 Å) in fact agree exactly with the recently measured distances for the neutral CpCrCh molecule [8]. Consequently these values were again used throughout for all calculations on the Cr species. Finally it may be noted that the variations in total energy encountered during the optimization of the bond lengths were always small by comparison with the differences in state energies listed in Table 1, and thus in no way call into question the ground states similarly determined on the basis of total energies.

3. Results and Discussion

3.1. Ground States

When the neutral CpMCh complexes of the $3d$ series are treated by the ligand field formalism [9, 10], assuming the ligands to act as Cp$^-$ and Ch$^+$, a formal zero oxidation state necessarily results for the metal, M. Thus, on this picture, the Ti, V, and Cr species will respectively correspond to d^4, d^5, and d^6 configurations, although precisely which d-orbitals will be occupied depends largely upon the magnitude of the splitting of the $3d$ set produced by the effectively pseudo-axial ligand field. As for the MCp$_2$ and MBz$_2$ series the model predicts a one-electron energy ordering of $e_2 < a_1 < e_1$ for the mainly metal $3d$ levels, (using the D_5 and D_7 symmetry labels – see Fig. 1) so that although by analogy with FeCp$_2$ and CrBz$_2$ a diamagnetic, $^1A_1$ ($e_2^4 a_1^2$), ground level may confidently be expected for the d^6 CpCrCh, a number of possibilities need to be considered in the d^4 and d^5 cases.

Thus, for the d^4 configuration a $^3E_2(e_2^3 a_1)$ ground level is found [11, 12] for CrCp$_2$ (although the $^3A_2(e_2^2 a_1^2)$ state lies only slightly higher), but when the difference between the H^{core} terms for the e_2 and a_1 levels becomes large, a diamagnetic, $^1A_1(e_2^4)$ level is more likely to be the ground state, as is probable for example in TiBz$_2$ [13]. Similarly, for the d^5 situation the MCp$_2$ systems display either a $^6A_1(e_2^2 a_1 e_1^2)$ or a $^2E_2(e_2^3 a_1^2)$ ground state [1, 10], but in the MBz$_2$ series, for which the separation between the e_2 and a_1 levels is larger, only the $^2A_1(e_2^4 a_1)$ level is found as the lowest state [2, 10].

Moreover, in the CpMCh series the ground states follow the pattern of the MBz$_2$ systems, and experimentally the neutral Ti and Cr species and the [CpVCh]$^+$ cation are found to be diamagnetic [14, 15] (and therefore presumably to have $^1A_1$ ground states), whilst for both CpVCh and [CpCrCh]$^+$ ESR data [16, 17] clearly show the ground state to be $^2A_1$. Consequently, as a first check of our procedure we calculated the energies of the lowest lying states of the various d^x configurations

Table 1. Excited state energies and metal mixing coefficients for CpMCh systems

State	ΔE(a.u.)	Metal mixing coefficients	ΔE(a.u.)	Metal mixing coefficients
$3d^4$		CpTiCh		$[\text{CpVCh}]^+$
$^3A_2(e_2^2 a_1^2)$	0.132_4	$c_0=0.948$, $c_2=0.574(2)$, $0.526(1)^a$	0.175_1	$c_0=0.957$, $c_2=0.736(2)$, $0.716(1)^a$
$^3E_2(e_2^3 a_1)$	0.144_3		0.169_7	$c_2=0.739$
$^1A_1(e_2^4)$	0.000	$c_2=0.674$	0.000	
$3d^5$		CpVCh		$[\text{CpCrCh}]^+$
$^2E_1(e_2^4 e_1)$	0.071_0	$c_1=0.740$, $c_2=0.680$	0.105_0	$c_1=0.655$, $c_2=0.786$
$^2E_2(e_2^3 a_1^2)$	0.079_8	$c_0=0.960$, $c_2=0.537(2)$, $0.561(1)^a$	0.059_0	$c_0=0.965$, $c_2=0.726(2)$, $0.735(1)^a$
$^2A_1(e_2^4 a_1)$	0.000	$c_0=0.958$, $c_2=0.680$	0.000	$c_0=0.958$, $c_2=0.786$
$3d^6$		CpCrCh		
$^1A_1(e_2^4 a_1^2)$	0.000	$c_0=0.965$, $c_2=0.654$		

I.P. $^1A_1 \rightarrow {}^2A_1(e_2^4 a_1)=8.46$ eV, I.P. $^1A_1 \rightarrow {}^2E_2(e_2^3 a_1^2)=10.04$ eV

[a] The metal coefficients for the a_1, e_1, and e_2 levels are denoted by c_0, c_1, and c_2 respectively; for e_2^3 configurations the coefficients for the doubly and singly occupied orbitals are shown by (2) and (1) respectively
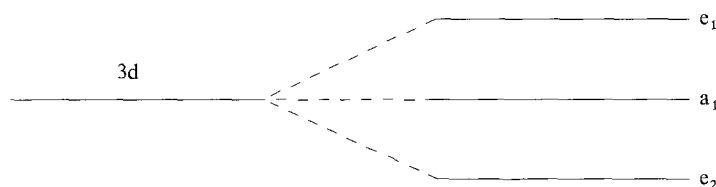
Fig. 1. One-electron splitting of the $3d$ manifold in pseudo-axial symmetry

represented, and as shown in Table 1 the experimentally indicated ground levels are in each case reproduced by the INDO SCF technique. Furthermore, the results also seem to indicate that the one-electron contribution for the e_2 $3d$ level is always appreciably more negative than that for the a_1 level; thus in the two d^4 systems the lowest excited states lie some 30 000 to 35 000 cm^{-1} above the $^1A_1(e_2^4)$ ground state, whilst for the d^5 complexes the corresponding value is of the order of 12 000 to 18 000 cm^{-1} above $^2A_1(e_2^4a_1)$. In Table 1 are also shown values of the metal d-orbital mixing coefficients for the occupied, formally d, levels of the various states considered: from these results it is apparent that although the a_1 level is once more essentially non-bonding, as in the MCp$_2$ and MBz$_2$ systems, the e_2 orbital shows appreciably more ligand character even than in the MBz$_2$ series, and may indeed actually be more strongly mixed than the e_1 level. These results will be treated in more detail later, but it here suffices to note that the e_2 interaction involves mainly the Ch ring, whereas that for the e_1 level arises mainly from Cp ring contributions.

3.2. Ionisation Energies

As is already well known, it is not possible to predict ionisation sequences for the loss of formally d-electrons from transition metal sandwich complexes simply from the ordering of the SCF orbital energies; thus in these systems Koopmans' theorem is far from reliable because of the extensive reorganisation effects which occur following the loss of an electron from the metal, and it is necessary instead to determine ionisation potentials from differences in total energy between the neutral species and the corresponding cation. However, for the closed-shell (d^6) system, CpCrCh, our results (Table 1) clearly show that an electron is more readily lost from the a_1 than from the e_2 metal orbital, in agreement with the interpretation of the photoelectron spectra, and although our values for the ionisation $^1A_1 \rightarrow \, ^2A_1$, and $^1A_1 \rightarrow \, ^2E_2$, are rather larger than the observed results (5.59 and 7.19 eV, respectively) [18], the difference between the two ionisation energies is rather well reproduced. Similarly, for the d^5 complex, CpVCh, our calculations again predict that the a_1 electron should be lost more readily than that in the e_2 level, which is also in agreement with the photoelectron spectral data, but for the d^4 complex, CpTiCh, all the formally d-electrons reside in the e_2 level, so that no estimate of the ease of removal from the a_1 level can be made. Thus for the two CpMCh species which can be studied we find the ionisation sequence $a_1 < e_2$, as observed experimentally [19] for the MBz$_2$ systems, but contrary to that found [20] for FeCp$_2$. Thus for the MBz$_2$ and CpMCh systems the *effective* SCF orbital energies (as

reflected by the ease of ionisation) follow the same sequence as the one-electron H^{core} terms, thus paralleling the much larger difference in the H^{core} terms for the e_2 and a_1 levels in these complexes by comparison with that found in the metallocenes. Moreover, this observation is again in accordance with the substantial bonding character indicated by the metal coefficients of presence for the e_2 levels, due (*vide infra* and Fig. 2) mainly to interaction with the Ch ring.
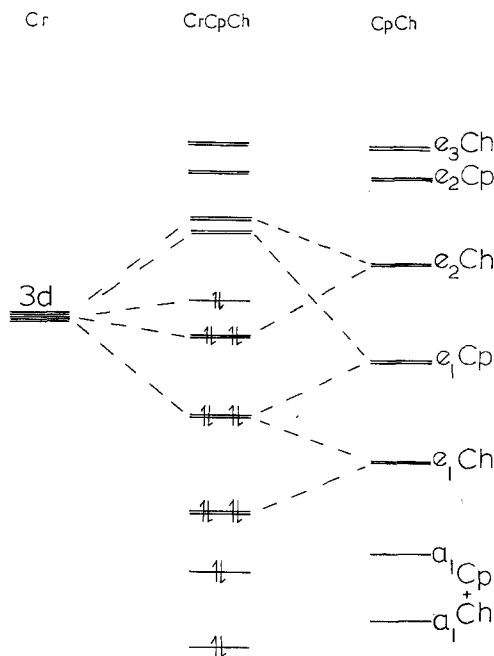

Fig. 2. H^{core} diagram for 3d – ligand-π interaction in CpCrCh

As far as ionisations from the ligands are concerned, our experience with the present method indicates that the SCF orbital energies do here provide a fairly reliable sequence, since reorganisation effects consequent upon ionisation normally affect the metal much more strongly than the ligands. Thus in all the cases studied here the highest lying filled, mainly ligand, level is that of e_1 symmetry which arises predominantly from the π-system of the five-membered ring; the expected order of ligand ionisations is therefore $e_1(\pi\text{-Cp}) < e_1(\pi\text{-Ch})$.

3.3. ESR Parameters

For the two formally d^5 systems, CpVCh and $[CpCrCh]^+$, quite detailed ESR data are available [16, 17] with which to compare the calculated quantities. Moreover, for a d^5 system in pseudo-axial symmetry one finds [10], to the first order, $g_{\parallel} = 2.0023$ and $g_{\perp} = 2.0023 - 6\xi_{eff}/\Delta E$, assuming a $^2A_1(e_2^4a_1)$ ground state, where ΔE is the energy of the $^2E_1(e_2^4e_1)$ excited state above the ground level. Thus, approximating ξ_{eff} as $c_0c_1\xi$, where c_0 and c_1 are the metal coefficients of presence

in the a_1 and e_1 orbitals respectively, it is possible from the data of Table 1, to calculate values from the spin-orbit coupling constants of both V^0 and Cr^1, and to compare these with the results deduced from experimental measurements. Thus, for CpVCh($g_\perp = 1.978$) one finds $\xi(V^0) = 90$ cm^{-1}, as against the value of 95 cm^{-1} given by Garrett and Cole [21], whilst for [CpCrCh]$^+$ ($g_\perp = 1.9797$) there results $\xi(Cr^1) = 130$ cm^{-1}, compared with the value of 135 cm^{-1} deduced [21] from experimental data.

Furthermore, for both systems the hyperfine coupling constants of the hydrogen atoms of the two different rings have been determined, and these provide an additional test of the quality of the calculations. In fact, although the calculated A_H values are quite sensitive to changes in the metal-carbon distances (*vide supra*), the values determined at the distances corresponding to the energy minima well reflect the spin densities found experimentally on the two rings. Thus, for CpVCh the calculated quantities are $A_H(Ch) = 2.6$ G and $A_H(Cp) = 1.55$ G, as against the experimental values of 4.8 G and 1.8 G respectively, whilst for [CpCrCh]$^+$ we find $A_H(Ch) = 1.95$ G and $A_H(Cp) = 1.72$ G, compared with the experimental values of 3.62 G and 2.16 G. Clearly therefore the agreement is not impressive in absolute terms, but the theoretical quantities do correctly indicate which ring bears the major share of the spin density, and also succeed in indicating that the spin density is more evenly distributed in [CpCrCh]$^+$ than in CpVCh. Moreover, the calculated A_H values also rule out the possibility of a $^2E_2(e_2^3 a_1^2)$ ground state; thus for CpVCh one finds $A_H(Ch) = 0$ and $A_H(Cp) = 0.10$, and for [CpCrCh]$^+$ $A_H(Ch) = -0.52$ and $A_H(Cp) = 0$ G, in total disagreement with the measured values.

3.4. One-Electron 3d H^{core} Energies

For CpVCh and [CpCrCh]$^+$ the calculated energies of the $^2E_2(e_2^3 a_1^2)$ and $^2E_1(e_2^4 e_1)$ levels above the $^2A_1(e_2^4 a_1)$ ground state are shown in Table 1, and for the former compound the measured electronic spectrum [22] shows a broad, rather weak, band at 17 800 cm^{-1} which may be attributed to one or more d-d excitations. Furthermore, although ligand field theory [10, 23] indicates that there should be numerous other one-electron d-d excitations in this region, the calculated energies for the $^2A_1 \rightarrow {}^2E_1$ and $^2A_1 \rightarrow {}^2E_2$ transitions (15 580 and 17 510 cm^{-1} respectively) are in good agreement with this observation, and thus encourage us to believe that the calculated energies of these two excited states may be useful for estimating the one-electron 3d H^{core} terms in the ligand field model for these CpMCh species, thereby enabling comparisons to be made with other sandwich systems such as MCp_2 and MBz_2.

Using the ligand field model [10], the energies of the $^2A_1 \rightarrow {}^2E_1$ and $^2A_1 \rightarrow {}^2E_2$ transitions are, to the first order, given by the expressions, $\Delta E({}^2A_1 \rightarrow {}^2E_1) = \Delta E_1 + 10\ B$, and $\Delta E({}^2A_1 \rightarrow {}^2E_2) = \Delta E_2 - 20\ B$, where $\Delta E_1 = H_{e_1}^{core} - H_{a_1}^{core}$, $\Delta E_2 = H_{a_1}^{core} - H_{e_2}^{core}$, and B is the familiar Racah repulsion parameter; thus, if a value can be obtained for B, the one-electron splittings of the 3d manifold may be estimated. However, from the photoelectron spectrum of the neutral CpVCh a B value of

about 250 cm^{-1} may be deduced [10] for the cation, $[CpVCh]^+$, and for the neutral species B will if anything be smaller, assuming a comparable degree of metal-ligand mixing. Thus, for B lying within the range 150–250 cm^{-1}, one finds $\Delta E_1 = 14\,000$–13 000 cm^{-1} and $\Delta E_2 = 20\,500$–22 500 cm^{-1} respectively, whilst for the cationic system, $[CpCrCh]^+$, for which a somewhat larger B value would be anticipated, the calculated $^2E_1$ and $^2E_2$ energies lead to the results $\Delta E_1 = 21\,000$–20 000 cm^{-1} and $\Delta E_2 = 17\,000$–19 000 cm^{-1}, taking B to lie within the range 200–300 cm^{-1}.

It is moreover of interest to compare these values with those derived from experimental data for other sandwich systems. Thus, for MCp_2 complexes ΔE_2 is commonly [10] only of the order of 3000 to 7000 cm^{-1}, suggesting a much smaller e_2 bonding involvement than for the CpMCh species, whilst ΔE_1 ranges between about 14 000 and 24 000 cm^{-1}, indicating an e_1 interaction comparable to that here found for the CpMCh series. This latter observation is not however especially surprising since our results show the e_1 involvement to be due almost entirely to the Cp ring, and since ΔE_2 is probably of the order of 11 000–15 000 cm^{-1} for MBz_2 complexes, the magnitude of this parameter shows a progressive increase with the size of the ligand ring, bearing in mind that for the CpMCh compounds the e_2 bonding is due predominantly to the Ch ring.

3.5. Charge Distribution

In Table 2 are compared the carbon and hydrogen orbital occupancies of the cyclopentadienyl and cycloheptatrienyl rings before and after formation of the neutral CpCrCh complex. The eigenfunctions for the uncomplexed ring systems (placed at the same internuclear separation as in the Cr complex) reveal little interaction between the two separate rings, but interestingly this diamagnetic sixty electron ring combination leaves *exactly* six π electrons on both the Cp and Ch moieties, in accordance with the formal unit negative and positive charges respectively attributed to these two rings for the manifestation of aromatic character. This excess of π electrons for the Cp ring (6 instead of 5 for neutral Cp)

Table 2. Electronic populations for the free CpCh system and the complex CpCrCh

	Free CpCh	Complex CpCrCh
$Cp(\pi)$, C, $2p_z$	6.00	5.35
$Ch(\pi)$, C, $2p_z$	6.00	7.65
$Cp(\sigma)$, C, $2s, 2p_{x,y}$	2.904 ($\times 5$)	2.885 ($\times 5$)
$Ch(\sigma)$, C, $2s, 2p_{x,y}$	3.027 ($\times 7$)	2.855 ($\times 7$)
Cp, H, $1s$	1.095 ($\times 5$)	1.018 ($\times 5$)
Ch, H, $1s$	0.974 ($\times 7$)	1.033 ($\times 7$)
Cr, $3d$, a_1	—	1.95
Cr, $3d$, e_1	—	0.56
Cr, $3d$, e_2	—	1.86
Cr, $4s$	—	0.45
Cr, $4p$	—	1.44

leads to a polarization of the σ-electron framework, with approximately 0.1 electron drifting from each carbon atom to its attached hydrogen, whilst conversely the deficiency of π electrons for the Ch ring pulls a small amount of σ-electron density from the hydrogen atoms towards the ring carbons.

Formation of the chromium complex however restores the charges on all these atoms to more like electroneutrality, and the considerable negative charges on the Cp carbon atoms (ca. -0.1) become small positive charges due to π electron donation to the metal through bonding via the e_1 orbital. In contrast, a substantial amount of electronic charge is drawn *into* the Ch π-orbitals by considerable mixing of the filled metal e_2 orbitals with the vacant e_2^* orbitals of the Ch ring (see Fig. 2). Thus electrons are effectively channelled from the formally negatively charged Cp ring via the metal onto the formally positively charged Ch ring.

For the σ-framework of the rings significant bonding to the metal $4s$ and $4p$ orbitals removes electron density from the carbon $2s$, $2p_x$, and $2p_y$ ring orbitals. For the Cp ring most of this density derives from the hydrogen atoms so that the carbon $2s$, $2p_x$, and $2p_y$ occupations remain almost unaltered, but their counterparts on the Ch ring lose a total of 1.2 electrons, compared with the uncomplexed $[Ch]^+$ system, as a consequence of the large amount of π-electron density attracted into the $2p_\pi$ orbitals of the Ch ring through the back-bonding interaction with the metal.

In view of the fact that the $3d_{z^2}$ orbital is essentially non-bonding, the occupation of this a_1 orbital is, as expected, close to two electrons. However, the $3d_{x^2-y^2}$ and $3d_{xy}(e_2)$ pair of orbitals lose more than half of their formal occupation of four electrons because of the back-donation to the Ch ring, whilst the $3d_{xz}$, $3d_{yz}(e_1)$ set acquire about half an electron, mainly through interaction with the Cp ring. The overall $3d$ occupancy therefore corresponds to 4.37 electrons with a further 1.9 electrons residing in the metal $4s$ and $4p$ orbitals.

3.6. General Bonding Considerations

Although, as noted above, the σ-frameworks of the rings are significantly involved in the bonding, especially with the metal $4s$ and $4p$ orbitals, our results clearly show that the dominant contribution arises from the interaction between the metal $3d$ orbitals and the π-systems of the rings. Thus in Fig. 2 we represent this interaction for the CpCrCh complex in terms of the appropriate H^{core} quantities, and it is apparent that the formally $3d\,e_2$ level is quite strongly bonding whilst the mainly $3d\,e_1$ level is markedly anti-bonding. In the former case the bonding takes place mainly to the Ch ring, as would be expected from the proximity of the metal $3d$ and the π-ligand Ch e_2 level, whereas the interaction between the $3d$ level and the π-ligand e_1 orbitals is similarly predominantly due to involvement of the Cp ring. The $3d\,a_1$ level remains however virtually non-bonding, largely by reason of unfavourable overlap.

Thus Fig. 2 and the results of Table 1 show the metal-π-ligand e_2 interaction for the Ch ring to be much stronger than that for the Cp ring, as for example in the MCp_2

series. Consequently the data are consistent with the simple molecular orbital picture which predicts an increasing e_2 interaction (and a decreasing e_1 involvement) as the size of the ligand ring is increased, by virtue of a progressively decreasing (more negative) H^{core} term for both the e_1 and e_2 π-ligand levels. Moreover, the metal mixing coefficients for the formally $3d\ e_2$ level in the CpMCh systems are all appreciably less than the corresponding values for metallocenes (MCp_2), and also smaller than generally found for the MBz_2 species, indicating as expected a greater metal-ligand mixing.

This interpretation of our results is also borne out by a comparison of the two iso-electronic pairs, CpVCh and $[CpCrCh]^+$, and CpTiCh and $[CpVCh]^+$. Thus the $3d\ H^{core}$ term for vanadium (formally V^+) in $[CpVCh]^+$ should be rather more negative than for titanium (formally Ti^0) in CpTiCh, so that in the former the metal $3d$ and the π-ligand $e_2\ H^{core}$ levels should lie further apart than in the latter, and should thereby interact less. Similarly, the metal $3d$–e_2 π-ligand interaction would be predicted to be smaller in $[CpCrCh]^+$ than in CpVCh, and in both cases this expectation is fulfilled since the metal e_2 mixing coefficients are greater in the cationic than in the neutral species, thus demonstrating a smaller extent of metal-ligand mixing. Conversely, the metal H^{core} term (by becoming more negative) should approach more closely to the π-ligand e_1 level, and one would therefore anticipate a greater extent of metal-ligand interaction for the e_1 level on passing from CpVCh to $[CpCrCh]^+$; in accordance with this expectation the metal mixing coefficient for the e_1 level of the $^2E_1(e_2^4 e_1)$ state is significantly smaller for the cationic species, thereby confirming a greater degree of metal-ligand mixing for the e_1 level. For the e_2 level the trends discussed above are followed both for the ground states and for the excited levels ($^2E_2$ and $^3E_2$ for the d^5 and d^4 systems respectively); however, where the e_2 level is only partially filled (i.e. e_2^3) the increase in the metal coefficient on passing from neutral to cationic species is even more marked than for the ground states, again reflecting the marked diminution in metal-ligand mixing.

Finally, it is useful briefly to consider the measured bond lengths for the CpMCh compounds. Thus, using the effective metal radii as a guide one would expect the metal-carbon distance for either ring to decrease somewhat on passing from Ti to Cr, and this prediction is fulfilled as far as the M–Cp distance is concerned, the bond length reducing from 2.32 to 2.18 Å. However, although the measured M–Ch bond length has been reported to decrease between vanadium and chromium, the bond length for CpTiCh (M–Ch = 2.19 Å) is extraordinarily short for a titanium complex. Nevertheless, these tendencies can be rationalized on the basis of the bonding picture described above. Thus, for the Cp ring which interacts mainly via the e_1 level, the metal $3d$ and ligand $e_1\ H^{core}$ levels become closer on passing from Ti to Cr, thereby leading to stronger bonding and the prediction of a shorter bond length – i.e. the bonding trends parallel the tendency expected on size considerations. However, for the Ch ring, for which the e_2 level is mostly involved, the extent of metal-ligand bonding should increase from Cr to Ti, so that for the M–Ch bond length the resulting prediction of a reducing distance is in opposition to the trend to increasing bond length based on metal radii considerations. Thus it is

not too surprising that the outcome is that the M–Ch lengths should be almost the same in CpTiCh as in CpCrCh, and that therefore the Ti–Ch distance should appear to be anomalously short.

To summarize therefore we conclude that our calculations give a reasonable account of the observed properties of the CpMCh complexes, and that the bonding scheme which emerges is fully consistent with the dependence of the ligand π-orbital energies on ring size suggested by one-electron type calculations.

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