

MOLECULAR ORBITAL CALCULATIONS ON TRANSITION METAL COMPLEXES

XX. THE π -CYCLOPENTADIENYL- π -BENZENE COMPLEXES OF CHROMIUM AND MANGANESE

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Summary

INDO SCF MO calculations are reported for the complexes $(C_5H_5)M(C_6H_6)$ ($M = Cr$ and Mn) and for the corresponding cations. A 2A_1 ground state is correctly predicted for the neutral Cr system, and other experimental quantities are satisfactorily reproduced. The dominantly metal d -levels yield the H^{core} sequence $e_2 < a_1 < e_1$ and the principal interactions were found to be those between the metal e_1 level and the π -orbitals of the C_5H_5 ligand, and between the metal e_2 level and the ligand C_6H_6 π -orbitals. From the state energies of the formally $3d^5$ species estimates were made of the one-electron $3d$ splittings in the ligand field model, and comparisons made with similar results for $M(C_5H_5)_2$, $M(C_6H_6)_2$, and $(C_5H_5)M(C_7H_7)$ systems: these indicated the general validity of the bonding scheme in which the extent of the metal–ligand interaction via the e_1 and e_2 $3d$ levels varied systematically with the sizes of the ligand rings.

Introduction

From the results of our recent INDO SCF MO calculations on CpMCh systems [1] ($Cp = \pi-C_5H_5$, $Ch = \pi-C_7H_7$) we were able to make comparisons between the mode of bonding in such molecules and that found for other sandwich systems such as MCp_2 and MBz_2 derivatives [2–4] ($Bz = \pi-C_6H_6$). Thus in the metallocene, MCp_2 , series the metal $3d$ a_1 (d_{z^2}) and e_2 ($d_{x^2-y^2}$, d_{xy}) orbitals are little involved in the bonding and the dominant interaction is that between the metal $3d$ e_1 (d_{xz} , d_{yz}) level and the lower lying ligand π -orbital of the same symmetry. However, in systems containing the Bz and Ch moieties the ligand- π e_1 and e_2 symmetry orbitals become progressively lower in energy with increasing ring size, and our findings confirmed that this was accompanied by the

expected decrease in the importance of the metal e_1 interaction, and a corresponding increase in the extent of the metal e_2 -ligand bonding. We have now therefore carried out similar calculations for CpMBz systems, completing our coverage of the known sandwich and mixed sandwich systems of the $3d$ series, and thus providing a further test of the hypothesis advanced earlier [1] concerning the bonding mechanism.

Unfortunately, the known CpMBz systems do not constitute such an extensive series of compounds as for the MCp_2 , MBz_2 and CpMCh species, and of the neutral complexes only the Cr and Mn compounds are well established. We have accordingly treated the ground and certain excited states of these systems and their corresponding cations, finding general agreement with the predictions of the ligand field model [5,6] and with experimental data relating to such quantities as ionisation potentials, g values, and proton hyperfine coupling constants. The good concordance found gives rise therefore to some confidence in the present description of the bonding in CpMBz systems, and we have consequently used our results as a basis for comparison with other sandwich molecules, from which a consistent picture of the one-electron $3d$ splitting pattern for all sandwich complexes may be deduced.

Method

The all valence electron INDO SCF MO method previously described [7] was employed. The basis set spanned the metal $3d$, $4s$, and $4p$, the carbon $2s$ and $2p$, and the hydrogen $1s$ orbitals.

Lacking X-ray structural data for CpCrBz we were nevertheless able to fix the Cr—C(Cp) and Cr—C(Bz) distances by minimisation of the total energy, as described earlier [1] for CpMCh systems. The Cr—C(Cp) and Cr—C(Bz) distances found were 2.17 Å and 2.07 Å respectively, and these were used for all further calculations on CpCrBz and its cation. Encouragingly, almost the best calculated proton transferred spin densities obtained for CpCrBz were those relating to the structure of minimum energy. For CpMnBz there is no doubt that the $^1A_1(e_2^4a_1^2)$ level lies lowest, and the same internuclear distances were therefore assumed.

Results and discussion

Ground states and bonding considerations

If the neutral $3d$ CpMBz complexes are considered on the basis of the ligand field approach [5,6], treating the ligands as Cp^- and Bz^0 , a formal M^I oxidation state clearly results for the metal, M . Thus the Cr and Mn species respectively represent $3d^5$ and $3d^6$ configurations. In the effectively pseudo-axial ligand field a one-electron energy sequence of $e_2 < a_1 < e_1$ is predicted for the dominantly metal $3d$ levels (using the D_5 and D_6 symmetry labels, see Fig. 1), as in the MCp_2 , MBz_2 , and CpMCh series, so that for the d^6 CpMnBz a diamagnetic $^1A_1(e_2^4a_1^2)$ ground state is obviously to be anticipated.

However, $3d^5$ metal sandwich systems are known to display a variety of ground states, including $^6A_1(e_2^2a_1e_1^2)$ in MnCp_2 , $^2E_2(e_2^3a_1^2)$ in $[\text{FeCp}_2]^+$, and $^2A_1(e_2^4a_1)$ in VBz_2 , $[\text{CrBz}_2]^+$, CpVCh , and $[\text{CpCrCh}]^+$, and ESR evidence [8]

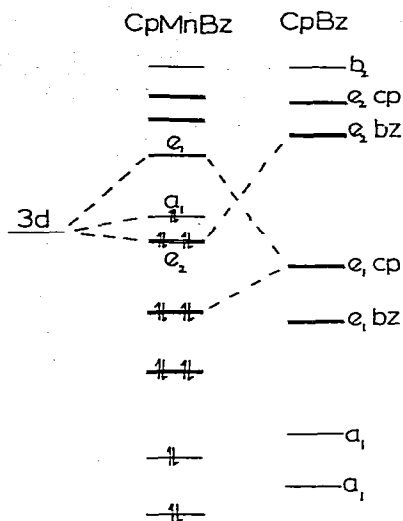


Fig. 1. H core diagram for $3d$ -ligand- π interaction in CpMnBz.

clearly indicates a 2A_1 ground state for CpCrBz too. Since the cationic $3d^5$ system, $[\text{CpMnBz}]^+$, is not unfortunately known experimentally, a check of our procedure for the correct ground state prediction is only possible for the CpCrBz molecule, but calculations of the energies of the lowest lying states of the various d^x systems, as shown in Table 1, do yield the required 2A_1 ground state for this system.

The results of Table 1 also confirm that the one-electron contribution for the e_2 $3d$ level is in fact more negative than that for the a_1 level. Thus, consider-

TABLE 1
EXCITED STATE ENERGIES AND METAL MIXING COEFFICIENTS FOR CpMBz SYSTEMS

State	ΔE (a.u.)	Metal mixing coefficients	ΔE (a.u.)	Metal mixing coefficients
$3d^4$				$[\text{CpCrBz}]^+$
${}^3E_2(e_2^3 a_1)$			0.055(7)	$c_0 = 0.961, c_2 = 0.906$ (2), 0.905 (1) ^a
${}^1A_1(e_2^4)$			0.000	$c_2 = 0.898$
$3d^5$		$[\text{CpCrBz}]$		$[\text{CpMnBz}]^+$
${}^2E_1(e_2^4 e_1)$	0.101(8)	$c_1 = 0.749, c_2 = 0.860$	0.109(5)	$c_1 = 0.634, c_2 = 0.914$
${}^2E_2(e_2^3 a_1^2)$	0.024(4)	$c_0 = 0.958, c_2 = 0.830$ (2), 0.841 (1) ^a	0.000	$c_0 = 0.969, c_2 = 0.912$ (2), 0.913 (1) ^a
${}^2A_1(e_2^4 a_1)$	0.000	$c_0 = 0.961, c_2 = 0.864$	0.000	$c_0 = 0.965, c_2 = 0.915$
$3d^6$		$[\text{CpMnBz}]$		
${}^1A_1(e_2^4 a_1^2)$	0.000	$c_0 = 0.967, c_2 = 0.856$		
I.P. ${}^1A_1 \rightarrow {}^2A_1(e_2^4 a_1)$		\approx I.P. ${}^1A_1 \rightarrow {}^2E_2(e_2^3 a_1^2) = 6.43$ 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.

ing the two $3d^5$ systems, the ${}^2E_2(e_2^3a_1^2)$ state of CpCrBz is calculated to lie some 5350 cm^{-1} above the ${}^2A_1(e_2^4a_1)$ ground level, and although for [CpMnBz]⁺ the 2A_1 and 2E_2 levels are almost coincident, simple ligand field considerations (vide infra) show that the value of the quantity $H_a^{\text{core}} - H_e^{\text{core}}$ is always appreciably more positive than $E({}^2E_2) - E({}^2A_1)$. It is however qualitatively evident that the one-electron separation between the a_1 and e_2 levels is appreciably smaller than in the CpMCh series [1], and this and other comparisons will be discussed later.

For the $3d^6$ CpMnBz the ${}^1A_1(e_2^4a_1^2)$ ground state was never in serious doubt, but it is possible to compare the calculated ionisation potentials for this closed shell system with those deduced from measurements of photoelectron spectra. Because of the extensive reorganisation effects which accompany electron loss in sandwich molecules, it is not possible to obtain ionisation energies from the SCF orbital energies by the application of Koopmans' theorem, but these values are nevertheless obtainable by comparison of the total energies of the neutral molecules and the various cationic species. In the event, within the accuracy of our calculations, we derive the same energy of 6.43 eV for both ionisations, ${}^1A_1 \rightarrow {}^2A_1(e_2^4a_1)$ and ${}^1A_1 \rightarrow {}^2E_2(e_2^3a_1^2)$; however, the experimental results [9] show the two peaks to be closely juxtaposed, with loss of the a_1 and e_2 electrons at 6.36 and 6.72 eV respectively, and the numerical agreement between the experimental and theoretical results is quite gratifying.

For the $3d^4$ cation, [CpCrBz]⁺, our results indicate that the ${}^1A_1(e_2^4)$ level should lie some 1.5 eV below ${}^3E_2(e_2^3a_1)$. However, although there is some uncertainty from the photoelectron spectrum of CpCrBz [9,10] whether the 1A_1 level of the cation is coincident with, or lies above, the 3E_2 level, it is clear that the calculations place the 1A_1 state too low in energy, and we have noted some tendency for our method to overestimate the stability of the e_2^4 closed shell in d^4 species. Thus, although TiBz₂ is known to be diamagnetic [11], the d^4 [V(Mes)₂]⁺ system (Mes = π -(CH₃)₃C₆H₃) is certainly paramagnetic [12], as is CrCp₂ [13,14], and both the photoelectron spectrum of MnCp₂ [15] and INDO SCF MO calculations on its cation [2] indicate the latter to be paramagnetic (5E_1), thus strongly suggesting that [CpCrBz]⁺ should also be paramagnetic, with a 3E_2 ground state.

For the d^5 CpCrBz ESR results have been reported [8], with which the calculated quantities may be compared. Thus, for a ${}^2A_1(e_2^4a_1)$ system in pseudo-axial symmetry ligand field theory [6] predicts $g_{\parallel} = 2.0023$ and $g_{\perp} = 2.0023 - 6 \xi_{\text{eff}}/\Delta E$, where ΔE is the energy of the ${}^2E_1(e_2^4e_1)$ level above the ground state, and ξ_{eff} the effective spin-orbit coupling constant. Allowing for metal-ligand mixing, and writing c_0 and c_1 for the metal coefficients of presence in the a_1 and e_1 orbitals respectively, leads to the approximation $g_{\perp} = 2.0023 - 6c_0^2c_1^2 \xi/\Delta E$, from which it is possible, using the data of Table 1, to calculate a value for the spin-orbit coupling constant of Cr^I in CpCrBz. (We had previously simply approximated ξ_{eff} as c_0c_1 , but the Zeeman contributions will naturally be reduced by the same factor, and we are grateful to Ammeter [16] for drawing our attention to this inaccuracy: our previous similar calculations for CpTiCot [17] (Cot = π -C₈H₈) and for the CpMCh systems [1] should therefore yield larger ξ values which somewhat exceed those listed by Garrett and Cole [18], but are still in reasonable agreement with other compilations such as that of

Griffith [19].) In the present case we calculate, from $g_{\perp} = 1.9787$, $\xi = 177 \text{ cm}^{-1}$, which lies close to the value of Garrett and Cole (190 cm^{-1}) although somewhat below that of Griffith (222 cm^{-1}).

As well as the g values the hyperfine coupling constants for the hydrogen atoms of the two different rings have also been reported, and these may be compared with the values calculated from the theoretical spin densities. Thus the ESR data yield the results $A_H(\text{Cp}) = 2.35 \text{ G}$ and $A_H(\text{Bz}) = 4.65 \text{ G}$, as against the calculated values of $+2.60 \text{ G}$ and $+3.80 \text{ G}$ respectively. The two sets of values are thus in reasonably good agreement, with the calculations correctly indicating the greater free spin density to lie on the six-membered ring. For the $[\text{CpMnBz}]^+$ cation, assuming a 2A_1 ground state, we find $A_H = +1.56 \text{ G}$ and $A_H(\text{Bz}) = +2.12 \text{ G}$, so that as for the CpMCh series [1] the spin density is predicted to be both reduced in magnitude and more evenly distributed on passing from the neutral to the cationic d^5 system.

Although the σ -frameworks of the ligand rings are, as is usual for sandwich species, appreciably involved in the bonding, particularly with the metal $4s$ and $4p$ orbitals, our results demonstrate the familiar dominant contribution due to the interaction between the metal $3d$ orbitals and the π -orbitals of the rings. This is illustrated in Fig. 1 for the d^6 system, CpMnBz, using the appropriate H^{core} levels, from which it is evident that the formally $3d e_2$ molecular orbital is significantly bonding in character whilst the mainly $3d e_1$ level is quite markedly anti-bonding. For the metal e_2 level the bonding chiefly involves the Bz ring, as would be predicted since the π -ligand e_2 Bz level is the closest lying orbital above the metal $3d$ level, whilst the interaction of the metal e_1 level mainly involves the lower lying e_1 π -ligand orbitals of the Cp ring. As usual though unfavourable overlap leaves the $3d a_1$ level as essentially non-bonding.

The changes that the bonding to the metal described above impose on the electronic populations on the two rings are illustrated in Table 2. Thus, interaction of the σ -framework with the metal $4s$ and $4p$ orbitals results in a small loss of density from both ring σ -orbitals. Moreover, a substantial amount of electronic population (0.63) is lost from the Cp ring π -system, in contrast to the small net increase in π -occupation (0.29) on the benzene ring, which reflects the respective electron donating and electron accepting properties of the two

TABLE 2
ELECTRONIC POPULATIONS FOR THE FREE CpBz SYSTEM AND THE COMPLEX CpMnBz

	Free CpBz	Complex CpMnBz
Cp(π), C, $2p_z$	6.000	5.370
Bz(π), C, $2p_z$	6.000	6.288
Cp(σ), C, $2s$, $2p_{x,y}$	2.894 (X5)	2.867 (X5)
Bz(σ), C, $2s$, $2p_{x,y}$	2.962 (X6)	2.854 (X6)
Cp, H, $1s$	1.104 (X5)	1.026 (X5)
Bz, H, $1s$	1.036 (X6)	1.028 (X6)
Mn, $3d, a_1$		1.938
Mn, $3d, e_1$		0.536
Mn, $3d, e_2$		3.029
Mn, $4s$		0.498
Mn, $4p$		1.580

ligands. In fact, for the benzene ring, the changes in electron population which occur on complexation are almost identical to those calculated previously [4] for the Bz ring in CrBz₂, whilst the charge migrations from the Cp ring parallel those found [1] in the CpMCh series of complexes.

A closer examination of the results for CpMnBz shows that the formally 3d *a*₁ level is almost completely localised on the metal (93.5%), but that the mainly 3d *e*₂ molecular orbital has only about 73.3% metal character, the remaining admixture being almost entirely *e*₂ π-Bz in origin. Similarly, the highest occupied formally ligand level, which is dominantly *e*₁ π-Cp in composition, reflects its anti-bonding interaction with the metal 3d *e*₁ level by admixing some 8.2% of the latter contribution. In total these covalencies produce the metal electronic configuration of 3d (*e*₂)^{3.029}(*a*₁)^{1.938}(*e*₁)^{0.536}; the 4s and 4p levels contain 0.498 and 1.580 electrons respectively, and the overall charge on the metal is -0.583.

On passing to the 3d⁵ CpCrBz system the *a*₁ and *e*₂ 3d contributions to the dominantly metal orbitals remain at very much the same values as for CpMnBz in both the ²A₁ and the ²E₂ states. The results for the ²E₁ state however enable us to determine the extent of metal-ligand mixing for an occupied *e*₁ orbital, for which the metal character amounts to only 56.1%.

Comparison with the corresponding 3d⁵ and 3d⁶ CpVCh and CpCrCh systems is however very illuminating. Thus the mostly 3d *a*₁ level again remains essentially localised, but the 3d *e*₂ level is significantly more delocalised, mostly into the *e*₂ π-Ch orbitals, showing only 42.8% metal character in CpCrCh, and slightly more (46.2%) in the ²A₁ ground state of CpVCh. On the other hand, in the ²E₁ state of CpVCh the coefficient of the singly occupied *e*₁ level, which interacts in an anti-bonding sense with the ligand π-Cp *e*₁ orbital, is almost the same (0.740) as in CpCrBz, indicating a comparable degree of metal-ligand interaction for the Cp ring in both systems. This similar bonding behaviour of the Cp ring (in CpCrBz and CpVCh) is moreover also exhibited when comparison is made between the d⁶ CpMnBz and CpCrCh as regards the composition of the highest filled, formally ligand, level, which is mostly *e*₁ π-Cp in character. For CpMnBz the metal 3d contribution was some 8.2%, and significantly an almost identical admixture, 8.4%, is found for CpCrCh. Thus one may conclude that the bonding of the Cp ligand to the metal is essentially similar in both series, involving only the metal 3d *e*₁ level to any significant extent. In contrast the degree of involvement of the 3d *e*₂ level diminishes markedly in passing from the CpMCh to the CpMBz series.

This is however by no means unexpected since the simple molecular orbital scheme proposed by Fischer [20] in 1963 makes it clear that the one-electron energies of the π-ligand *e*₁ and *e*₂ symmetry orbitals become appreciably higher (less negative) with decrease in the size of the ligand ring. Thus, on moving from a Ch to a Bz ligand the *e*₂ π-orbitals, which lie above the metal 3d level, will become higher in energy, thereby interacting less strongly with the metal, as is in fact observed. The similar raising of the *e*₁ π-levels, on passing from CpMCh to CpMBz, is however of little consequence since the effectively constant *e*₁ π-Cp orbitals lie appreciably higher than either the *e*₁ π-Bz or π-Ch levels, and in either case dominate the interaction with the 3d *e*₁ level.

A very similar picture also emerges when comparison is made between the cationic d⁵ species, [CpMnBz]⁺ and [CpCrCh]⁺: once again the metal coefficients

of presence for the e_1 orbital in the ${}^2E_1(e_2^4e_1)$ states are of very similar magnitude (0.634 and 0.655 respectively), but the e_2 level is much more strongly mixed in the CpMCh system, just as was found for the neutral species. Furthermore, a comparison between the CpCrBz and [CpMnBz]⁺ results also accords with the bonding scheme proposed. Thus in changing the metal from Cr to Mn the H^{core} term becomes more negative by some 0.01 a.u. which should therefore reduce the extent of the metal e_2 - π -ligand interaction, but increase that involving the metal and the e_1 π -ligand orbitals. This energy change is appreciably smaller than that in the π ligand e levels with change of ring size, but the calculated results nevertheless fulfil our predictions, just as in the CpMCh series. Thus the e_1 metal coefficient becomes smaller in [CpMnBz]⁺ (larger mixing) whilst the e_2 coefficient increases (smaller mixing), as compared with CpCrBz. Finally, a comparison of the present results for CpMBz systems with earlier data [2-4,21] for MCp₂ and MBz₂ species indicates that the metal coefficients of presence for occupied e_1 levels are very comparable with those found in MCp₂ systems, whilst those for the e_2 orbitals are similar to the values obtained for MBz₂ complexes. The conclusion that the e_1 and e_2 interactions in the present series are almost entirely directed towards the Cp and Bz rings respectively is thus further reinforced.

As discussed above the ionisation energies for electron loss from a_1 and e_2 orbitals in CpMBz systems are of quite comparable magnitude, although the one-electron H^{core} sequence is unequivocally $e_2 < a_1 < e_1$. For ionisations from mainly ligand levels the SCF orbital energy sequence has generally proved reliable (in contrast to the results for the mainly metal levels), and here the highest filled mainly ligand level is of chiefly e_1 π -Cp character, the dominantly e_1 π -Bz level lying somewhat lower. The expected order of ligand ionisations (of higher energy than the d -ionisations) is therefore $e_1(\pi\text{-Cp}) < e_1(\pi\text{-Bz})$.

One-electron 3d H^{core} energies

We have previously shown [1] that by use of the ligand field model [6] estimates of the effective one-electron H^{core} splittings of the 3d manifold could be obtained for CpVCh and [CpCrCh]⁺ from the state energies of the $3d^5$ 2A_1 , 2E_2 , and 2E_1 levels. Thus, to the first order, the ligand field treatment yields the expressions $\Delta E({}^2A_1 \rightarrow {}^2E_1) = \Delta E_1 + 10B$, and $\Delta E({}^2A_1 \rightarrow {}^2E_2) = \Delta E_2 - 20B$, where B is the well known Racah parameter and $\Delta E_1 = H_{e_1}^{\text{core}} - H_{a_1}^{\text{core}}$, with $\Delta E_2 = H_{a_1}^{\text{core}} - H_{e_2}^{\text{core}}$. As demonstrated before [1], estimates of the appropriate B values can usually be derived from photoelectron spectra and electronic spectra [6] so that values for ΔE_1 and ΔE_2 can in principle be obtained once the $3d^5$ state energies have been calculated. In Table 3 therefore we collect together the calculated $3d^5$ state energies for all the sandwich systems so far studied, together with the assumed B values (cf. [6]) and the ΔE_1 and ΔE_2 parameters thence derived. If the B values are only accurate to ± 100 cm⁻¹ (which is probably a cautious estimate) ΔE_1 will have a fiducial limit of $\mp 1,000$ cm⁻¹, and ΔE_2 a similar limit of $\pm 2,000$ cm⁻¹.

In Table 3 results are given both for low-spin and for high-spin MnCp₂, but it now seems clear [6] that the latter (6A_1) is the actual ground level, so that these latter results are later used in making comparisons between the various sandwich systems. It may also be noted that the results of Table 3 correctly

TABLE 3

EFFECTIVE ONE-ELECTRON H^{core} 3d SPLITTINGS FOR MCp_2 , CpMBz , CpMCh , AND MBz_2 SYSTEMS ^a

Complex	Calculated energy ${}^2A_1 \rightarrow {}^2E_1$ ^b	Calculated energy ${}^2A_1 \rightarrow {}^2E_2$ ^b	Assumed value of B ^b	Derived ΔE_1 ^b	Derived ΔE_2 ^b
MnCp_2 ^c	22,300	-7,600	700	16,300	6,400
$[\text{FeCp}_2]^+$	33,800	-7,900	500	28,800	2,100
CpCrBz	22,300	5,350	400	18,300	13,400
$[\text{CpMnBz}]^+$	26,350	0	500	21,400	9,900
CpVCh	15,600	17,500	200	13,600	21,500
$[\text{CpCrCh}]^+$	23,000	12,950	300	20,000	19,000
VBz_2	19,600	12,900	250	17,100	17,900
$[\text{CrBz}_2]^+$	24,100	8,600	400	20,100	16,600

^a Data from references [1-4,21]. ^b In cm^{-1} . ^c For high-spin MnCp_2 [2] the state energies yield directly the splitting parameters $\Delta E_1 = 24,300 \text{ cm}^{-1}$ and $\Delta E_2 = 5,000 \text{ cm}^{-1}$.

indicate that FeCp_2 more readily loses an electron from the e_2 than from the a_1 level (${}^2E_2 < {}^2A_1$), the ionisation energies being calculated as 7.53 and 8.53 eV respectively (cf. experimental values of 6.88 and 7.23 eV), but nevertheless yields a positive ΔE_2 for $[\text{FeCp}_2]^+$, i.e. $H_{e_2}^{\text{core}} < H_{a_1}^{\text{core}}$.

From the results two sets of comparisons may be made: firstly between CpMBz and MBz_2 systems, and in addition along the series CpMCh , CpMBz , and MCp_2 , these being shown in Fig. 2. In the first case we may compare CpCrBz with VBz_2 and $[\text{CpMnBz}]^+$ with $[\text{CrBz}_2]^+$ for which a marked increase in ΔE_2 from CpMBz to MBz_2 is found for both pairs, with a smaller corresponding decrease in ΔE_1 . The latter feature presumably arises partly because the replacement of Cp by Bz weakens the e_1 interaction, and partly because passage from Cr to V or from Mn to Cr raises the metal 3d levels, again weakening the e_1 interaction and reducing ΔE_1 . The contrary increase in ΔE_2 may thus similarly be attributed partly to the replacement of a Cp by a more strongly e_2

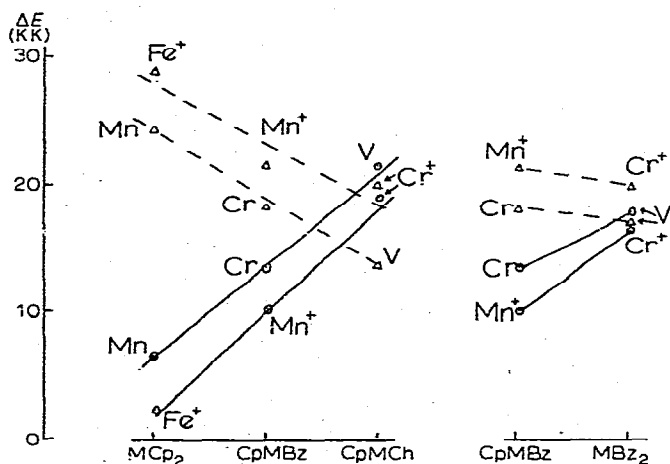


Fig. 2. Effective one-electron H^{core} splittings for 3d sandwich systems, --- ΔE_1 , — ΔE_2 .

interacting Bz group, and partly to the substitution of Cr by V or of Mn by Cr, raising the metal $3d$ levels and strengthening the e_2 interaction, both of which would tend to increase ΔE_2 .

Similarly, the trends in ΔE_1 and ΔE_2 within the MCp_2 , CpMBz , and CpMCh sequence may be rationalised. Thus, the decrease in ΔE_1 observed therein is clearly associated with the progressive replacement of a Cp group by a larger and more weakly e_1 interacting ligand ring, together with a raising of the metal $3d$ level (Mn to V or Fe to Cr), which would also tend to reduce the e_1 interaction and lower ΔE_1 . Conversely, the more marked increase in ΔE_2 on passing from MCp_2 to CpMBz to CpMCh may be attributed partly to the progressive replacement of Cp by the more strongly e_2 interacting Bz and Ch ligands, and partly to the increasing energy of the metal $3d$ levels on passing from Mn to V or Fe to Cr, which would bring the metal $3d$ and the π -ligand e_2 interaction and increasing ΔE_2 .

Thus the trends in the derived one-electron H^{core} splittings for all the accessible sandwich systems can be interpreted using the simple bonding scheme outlined above. Moreover, the description of the bonding mainly in terms of the metal $3d$ -ligand- π e_1 and e_2 interactions, depending for their relative importance upon the sizes of the ligand rings involved, appears satisfactorily to represent the situation for all the sandwich species of the $3d$ series.

References

- 1 D.W. Clack and K.D. Warren, *Theoret. Chim. Acta*, 46 (1977) 313.
- 2 D.W. Clack, *Theoret. Chim. Acta*, 35 (1974) 157.
- 3 D.W. Clack and M. Monshi, *J. Organometal. Chem.*, 116 (1976) C41.
- 4 D.W. Clack and W. Smith, *Inorg. Chim. Acta*, 20 (1976) 93.
- 5 K.D. Warren, *J. Phys. Chem.*, 77 (1973) 1681.
- 6 K.D. Warren, *Structure and Bonding*, 27 (1976) 45.
- 7 D.W. Clack, *Mol. Phys.*, 27 (1974) 1513.
- 8 C. Elschenbroich and F. Gerson, *J. Organometal. Chem.*, 49 (1973) 445.
- 9 S. Evans, J.C. Green and S.E. Jackson, *J. Chem. Soc. Faraday II*, 68 (1972) 249.
- 10 S. Evans, J.C. Green, S.E. Jackson and B. Higginson, *J. Chem. Soc. Dalton*, (1974) 304.
- 11 M.T. Anthony, M.L.H. Green and D. Young, *J. Chem. Soc. Dalton*, (1975) 1419.
- 12 E.O. Fischer, G. Joos and W. Meer, *Z Naturforsch.*, 13B (1958) 456.
- 13 F. Englemann, *Z. Naturforsch.*, 8B (1953) 775.
- 14 K.R. Gordon and K.D. Warren, *J. Organometal. Chem.*, 117 (1976) C27.
- 15 S. Evans, M.L.H. Green, B. Jewitt, G.H. King and A.F. Orchard, *J. Chem. Soc. Faraday II*, 70 (1974) 356.
- 16 J.H. Ammeter, private communication.
- 17 D.W. Clack and K.D. Warren, *Inorg. Chim. Acta*, 24 (1977) 35.
- 18 G.M. Cole and B.B. Garrett, *Inorg. Chem.*, 9 (1970) 1898.
- 19 J.S. Griffith, *The Theory of Transition Metal Ions*, Cambridge University Press, London, 1964.
- 20 R.D. Fischer, *Theoret. Chim. Acta*, 1 (1963) 418.
- 21 D.W. Clack and W. Smith, unpublished results.