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Molecular Orbital Calculations on Transition Metal Complexes. Part XXI. The Influence of Ring Size on Metal–Ligand Interactions in 3d Sandwich Compounds

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INDO SCF MO calculations have been carried out for the neutral metallocenes, MCp_2 (M = Ti–Cu) and bis-benzene complexes, MBz_2 (M = Sc–Co) of the 3d series, and for certain mixed sandwich, CpMBz and CpMCh (Ch = C_7H_7), species. The results indicate that in all of these systems interactions between the metal orbitals and the π-orbitals of the ligand rings make the dominant contribution to the metal–ligand bonding, the most strongly involved levels being the metal $3d_{xz}$, $3d_{yz}$ (e_1), $3d_{x^2-y^2}$, $3d_{xy}$ (e_2), and $4p_x$, $4p_y$ (e_1) orbitals. In addition significant, but generally smaller, interactions also take place between the metal 3d, 4s, and 4p orbitals and the carbon 2s and $2p_x$, $2p_y$ orbitals of the σ-frameworks of the rings.

Of the metal 3d orbitals the d_{z^2} (a_1) level is in all cases only very weakly concerned in the bonding, but the d_{xz}, d_{yz} (e_1) and $d_{x^2-y^2}$, d_{xy} (e_2) orbitals both interact strongly with the ligand π-orbitals. Moreover, calculations of the appropriate bond orders and overlap densities show the e_1 bonding to decrease and the e_2 interaction to increase systematically with increasing size of the ligand rings, as predicted qualitatively by simple molecular orbital arguments. Thus in the MCp_2 series the bonding occurs almost entirely via the e_1 interaction, with a much smaller e_2 involvement, whilst for the MBz_2 systems the e_2 bonding is dominant and appreciably greater than the e_1 contribution. For the CpMBz systems the bonding of the Cp and Bz ligands similarly takes place primarily via the e_1 and e_2 orbitals respectively, whilst for the CpMCh complexes the Cp and Ch ligands again bond essentially via the e_1 and e_2 levels respectively, but the metal 3d–e_2Ch interaction is here even stronger than the e_2 bonding in the MBz_2 species. Consequently the splitting patterns of the metal 3d levels in all these compounds, and hence many of the spectroscopic and magnetic properties, are determined almost exclusively by the dependence of the e_1 and e_2 interactions on the size of the ligand rings.

In the MCp_2 series the bond orders for both the e_1 and e_2 interactions show a maximum at ferrocene, in accordance with the known exceptional stability of this system, but for the MBz_2 compounds no clear maximum occurs, thus reflecting the experimental absence of any especially stable bis-arene derivative. Finally, the very low bond orders predicted for cuprocene correctly mirror the failure of attempts to obtain that system, whereas for $CoBz_2$ the calculated e_2 bond order is sufficiently great to offset the low e_1 value due to the high population of that antibonding metal level, thus according with the experimental accessibility of a bis-arene cobalt(0) compound.

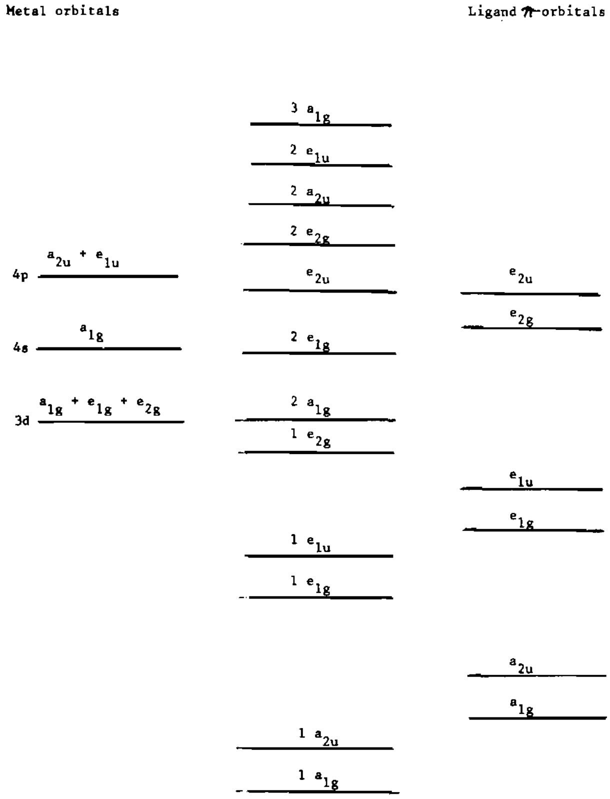

Figure 1. Simplified molecular orbital scheme for 3d metallocene (MCp_2) systems.

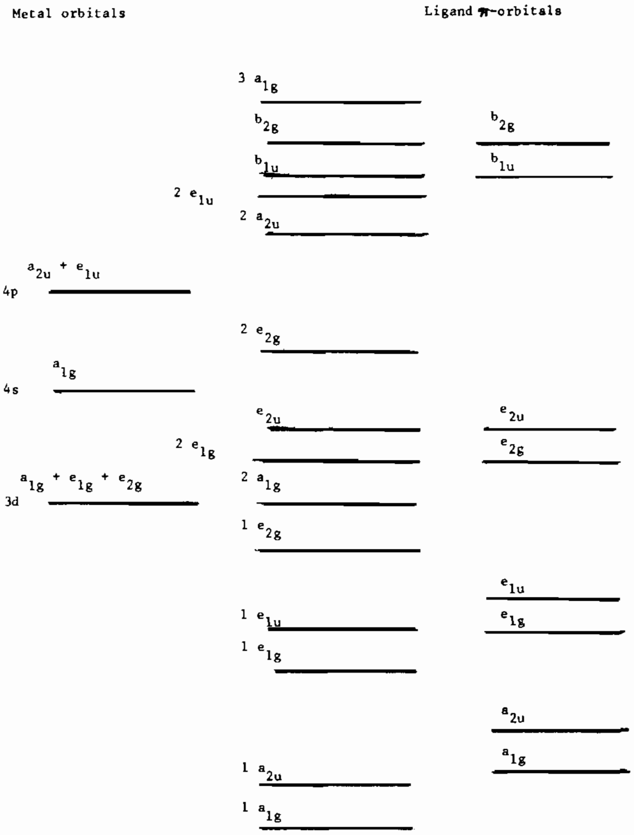

Figure 2. Simplified molecular orbital scheme for 3d bis-benzene (MBz_2) systems.

Introduction

Since the synthesis of transition metal sandwich complexes in the 1950s ideas concerning the nature of the bonding in such species have tended to concentrate upon the interactions between the metal d-orbitals and the π-orbitals of the conjugated ring systems. Thus for metallocene, MCp_2, systems the ligand π-orbitals give rise to the D_{5d} symmetry combinations a_{1g}, a_{2u} < e_{1g}, e_{1u} < e_{2g}, e_{2u}, in order of ascending energy, as shown in Figure 1 and an elementary molecular orbital approach indicates that the metal 3d levels should lie above the e_{1g} but below the e_{2g} ligand orbitals. Similarly, for the metal bis-benzene, MBz_2, derivatives the ligand π-orbitals yield the D_{6h} combinations a_{1g}, a_{2u} < e_{1g}, e_{1u} < e_{2g}, e_{2u} < b_{1u}, b_{2g} (Figure 2), with the metal 3d orbitals again disposed between the e_{1g} and e_{2g} ligand levels.

In principle therefore the mainly metal 3d e_{2g} level ($1e_{2g}$) should be bonding in character, and the dominantly metal a_{1g} ($2a_{1g}$) and e_{1g} ($2e_{1g}$) levels antibonding, although the very small group overlap integrals which usually result for the a_{1g} orbital ensure that this level remains essentially non-bonding. However, it was pointed out by Fischer [1] in 1963 that the energies of the e_1 and e_2 π-levels of the conjugated ligand rings should become progressively more negative with increasing size of the ligand rings. Thus the e_2 interaction should be strengthened (increasing the H^{core} separation between the mainly metal a_1 and e_2 levels (ΔE_2)) and the e_1 interaction weakened (decreasing the separation between the e_1 and a_1 levels (ΔE_1)).

Nevertheless, this simple molecular orbital picture disregarded the possible contributions to the bonding from the σ-frameworks of the ligand rings and also discounted the participation of the metal 4s and 4p levels, and for this reason INDO SCF molecular orbital calculations have recently been carried out [2–5] on a variety of 3d sandwich and mixed sandwich species, so as to ascertain whether or not the naive model outlined above was of general validity. These results were sufficiently encouraging for us to carry out similar calculations for all the known (and some unknown) neutral species of the MCp_2 and MBz_2 series, and for some mixed sandwich systems, and we now discuss these results, especially the calculated bond orders, in order to present a comprehensive picture of the bonding in these systems.

We therefore consider initially the relative contributions to the bonding of the σ- and π-frameworks of the ligand rings, together with the respective importance of the metal 3d, 4s, and 4p interactions. Since it transpires that the metal 3d e_1 and e_2 interactions with the ligand π-orbitals play a dominant role in the bonding process (and determine the magnitudes of the d-orbital splitting parameters, ΔE_1 and ΔE_2) we have examined these effects more closely, so as to determine both the variation in bonding with orbital occupations within a given series, and more particularly the changes in bonding characteristics due to the respective sizes of the ligand rings. Finally, we consider more specifically the phenomenon of the exceptional stability of ferrocene in the MCp_2 series, and the absence of any comparable outstanding stability amongst the MBz_2 species, together with the problems of what factors determine the stability limits of the sandwich series (*e.g.* the existence of a d^9 Co(0) bis-arene complex, but the non-existence of the d^9 $CuCp_2$).

Method

The INDO SCF molecular orbital method previously described [6] was employed throughout. The basis set used spanned the metal 3d, 4s, and 4p orbitals, together with the carbon 2s, $2p_x$, $2p_y$, and $2p_z$ and the hydrogen 1s orbitals, so that both σ- and π-bonding effects of the ligands were included. In all cases the values reported relate to the equilibrium metal–ligand distances, these being obtained by minimisation of the total energy as described earlier [4].

TABLE I. Comparison of Bond Orders and Orbital Compositions for Typical Metallocene and Bis-Benzene Complexes.

FeCp$_2$: Bond Orders

Metal Orbitals	Ligand Orbitals		
	2s	2p$_x$ + 2p$_y$	2p$_z$
3d a$_1$ (z^2)	0.015	0.127	0.042
3d e$_1$ (xz + yz)	0.297	0.506	0.958
3d e$_2$ (x^2 − y^2 + xy)	0.134	0.066	0.696
4s a$_1$	0.456	0.153	0.367
4p a$_2$ (z)	0.496	0.336	0.234
4p e$_1$ (x + y)	0.681	0.597	0.984

FeCp$_2$: Orbital Compositions for Dominantly 3d Levels

	3d	2s	4s	2p$_x$	2p$_y$	2p$_z$	H
3d a$_1$	93.70	0.17	0.99	0.61	0.61	0	4.01
3d e$_2$	91.01	0	0	1.23	1.26	6.49	0
3d e$_1$[a]	40.44	1.59	0	1.19	1.55	53.51	1.72

CrBz$_2$: Bond Orders

Metal Orbitals	Ligand Orbitals		
	2s	2p$_x$ + 2p$_y$	2p$_z$
3d a$_1$ (z^2)	0.010	0.167	0.053
3d e$_1$ (xz + yz)	0.282	0.463	0.684
3d e$_2$ (x^2 − y^2 + xy)	0.119	0.045	1.380
4s a$_1$	0.414	0.184	0.355
4p a$_2$ (z)	0.445	0.353	0.222
4p e$_1$ (x + y)	0.647	0.508	0.944

CrBz$_2$: Orbital Compositions for Dominantly 3d Levels

	3d	2s	4s	2p$_x$	2p$_y$	2p$_z$	H
3d a$_1$	93.30	0.17	1.78	0.13	0.13	0.14	3.72
3d e$_2$	56.90	0	0	0.75	0.44	41.87	0
3d e$_1$[b]	71.61	3.00	0	1.29	0.79	19.15	4.13

[a] For CoCp$_2$. [b] For MnBz$_2$.

Results and Discussion

In Table I we list the calculated bond orders per ring for the metal–ligand interactions in FeCp$_2$ and CrBz$_2$: these compounds, both formally 3d^6 systems on a ligand field approach [7, 8], each show (e$_2^4$ a$_1^2$) d-orbital occupations and were chosen as typical of the MCp$_2$ and MBz$_2$ series respectively. We consider in both cases the interactions between the metal 3d (a$_1$, e$_1$, and e$_2$), 4s(a$_1$), and 4p(a$_2$ and e$_1$) orbitals, and the σ-(carbon 2s and 2p$_x$, 2p$_y$) and π-frameworks (carbon 2p$_z$) of the ligand rings; from these results it is evident that the strongest bonding processes in both series are those involving the ring π-orbitals, particularly the interactions with the metal 3d(e$_1$ and e$_2$) and 4p (e$_1$) levels, but that the only values differing appreciably between the MCp$_2$ and MBz$_2$ systems are those describing the bonding in the former two levels – 3d e$_1$ and e$_2$.

In addition in Tables II and III we present selected results for the complete MCp$_2$ (M = Ti–Cu) and MBz$_2$ (M = Sc–Co) series, the values listed including the metal-π-ligand bond orders per ring for the a$_1$, e$_1$, and e$_2$ 3d levels, the corresponding overlap integrals, and the appropriate d-orbital occupations, together with the total 3d, 4s and 4p populations and the overall net charge on the metal. In Table IV we give similar data for the CpMBz and CpMCh mixed sandwich species. For the MCp$_2$ series data are given for two low lying states of TiCp$_2$, ^{3}A$_2$ (e$_2^2$) and ^{3}E$_2$ (e$_2$a$_1$), of which the latter proves to lie lower, whilst for MnCp$_2$ we consider both the gas phase ground state, ^{6}A$_1$(e$_2^2$a$_1$e$_1^2$) and the very slightly higher ^{2}E$_2$(e$_2^3$a$_1^2$) level. Furthermore, we list also the

TABLE II. Bonding Properties of MCp_2 Systems[a].

Complex	$TiCp_2$	$TiCp_2$	VCp_2	$CrCp_2$	$MnCp_2$	$MnCp_2$	$MnCp_2$	$FeCp_2$	$CoCp_2$	$NiCp_2$	$CuCp_2$
Ground State	$^3E_2$	$^3A_2$	$^4A_2$	$^3E_2$	$^6A_1$	$^2E_2$	$^2A_1$	$^1A_1$	$^2E_1$	$^3A_2$	$^2E_1$
Configuration	e_2a_1	e_2^2	$e_2^2a_1$	$e_2^3a_1$	$e_2^2a_1e_1^2$	$e_2^3a_1^2$	$e_2^4a_1$	$e_2^4a_1^2$	$e_2^4a_1^2e_1$	$e_2^4a_1^2e_1^2$	$e_2^4a_1^2e_1^3$
$P_{ij}3d\ a_1\ \pi$	0.110	0.093	0.084	0.064	0.053	0.058	0.055	0.042	0.035	0.031	0.026
$P_{ij}3d\ e_1\ \pi$	0.917	0.918	0.914	0.918	0.422	0.874	0.907	0.958	0.744	0.471	0.295
$P_{ij}3d\ e_2\ \pi$	0.132	0.305	0.286	0.467	0.186	0.397	0.603	0.696	0.626	0.472	0.382
$P_{\mu\mu}3d\ a_1$	0.908	0.044	0.963	0.985	0.997	1.951	0.955	1.958	1.967	1.980	1.986
$P_{\mu\mu}3d\ e_1$	0.594	0.594	0.596	0.602	2.242	0.533	0.578	0.692	1.556	2.314	3.191
$P_{\mu\mu}3d\ e_2$	0.978	1.907	1.920	2.841	1.971	2.889	3.799	3.728	3.782	3.878	3.920
$P_{\mu\mu}4s$	0.412	0.309	0.423	0.458	0.499	0.516	0.496	0.536	0.556	0.578	0.598
$P_{\mu\mu}4p$	1.178	1.168	1.345	1.497	1.642	1.622	1.618	1.726	1.806	1.876	1.918
d^x	2.480	2.545	3.479	4.428	5.210	5.373	5.372	6.378	7.305	8.172	9.097
Net Charge	−0.069	−0.021	−0.247	−0.383	−0.352	−0.510	−0.486	−0.640	−0.666	−0.626	−0.613
$S_{ij}3d, a_1 - p_z$	0.082	0.082	0.064	0.061	0.056	0.056	0.056	0.037	0.029	0.028	0.026
$S_{ij}3d, e_1 - p_z$	0.157	0.157	0.147	0.138	0.123	0.123	0.123	0.130	0.124	0.110	0.099
$S_{ij}3d, e_2 - p_z$	0.066	0.066	0.071	0.062	0.055	0.055	0.055	0.065	0.065	0.057	0.051

[a] P_{ij}, bond order, $P_{\mu\mu}$ electronic population, S_{ij} overlap integral.

results for the $^2A_1$ ($e_2^4a_1$) state since in the MBz_2, CpMBz, and CpMCh series this always constitutes the ground level for formally $3d^5$ systems. In all other cases results are only given for the known (or assumed) ground states and formal orbital occupations.

From the results given in the Tables it is apparent that, although the metal 4s and 4p orbitals are significantly involved in the bonding in all sandwich systems, these levels tend in general to interact more strongly with the σ-frameworks of the rings than with the delocalised π-orbitals, this behaviour being common to all the metals across both the metallocene and bis-benzene series of complexes. The extent of 4s and 4p involvement is reflected in the electronic populations given in Tables II and III which show electron density to be attracted into these formally vacant metal orbitals by bonding with the ligands. It is clear however that the amounts of 4s and 4p participation varies monotonically across the series Ti–Cu (MCp_2) and Sc–Co (MBz_2), the degree of this involvement being very similar in both series, and is greatest for the heavier metals simply by virtue of their more negative H^{core} terms.

It is therefore evident that it is not possible to explain the differences in ground states, in stabilities, or in the limits of existence of the two series of compounds in terms of any differing extents of 4s and 4p contributions, and similarly we must look elsewhere for an explanation of differences in the pattern of the d-orbital splitting parameters. Likewise any anomalous features in the two series are not readily rationalised in terms of the overall d-electron densities. Thus Tables II and III show that there is a fairly smooth change in this quantity across both series. For the MCp_2 systems the values change from an excess of about 0.5 electrons (Ti) over that expected [8] for a formal metal oxidation state of II to only a small surplus (*ca.* 0.1 electrons) at Cu. Moreover, for the bis-benzene series the change, from Sc to Co, is even less pronounced and although more than one electron is lost from the metal due to back-bonding, the difference in calculated metal 3d occupation from that anticipated for a formal M^0 configuration varies very little across the whole series. Thus it may be concluded that any differences in bonding between the metallocene and bis-arene series, and between these systems and the mixed sandwich species, must be attributed to differing metal 3d e_1 and e_2 interactions with the π-orbitals of the ligand rings. Clearly such effects would be expected to exert a substantial influence upon the magnitudes of the splitting parameters, ΔE_1 and ΔE_2, and thereby also in some cases to lead to differing ground states for systems of different sandwich series but the same formal d^x configurations.

However, in considering more closely the metal 3d interactions with the π-orbitals of the ligand rings we

TABLE III. Bonding Properties of MBz_2 Systems.

Complex	$ScBz_2$	$TiBz_2$	VBz_2	$CrBz_2$	$MnBz_2$	$FeBz_2$	$CoBz_2$
Ground State	$^2E_2$	$^1A_1$	$^2A_1$	$^1A_1$	$^2E_1$	$^3A_2$	$^2E_1$
Configuration	e_2^3	e_2^4	$e_2^4a_1$	$e_2^4a_1^2$	$e_2^4a_1^2e_1$	$e_2^4a_1^2e_1^2$	$e_2^4a_1^2e_1^3$
P_{ij} 3d a_1 π	0.035	0.020	0.034	0.053	0.036	0.023	0.021
P_{ij} 3d e_1 π	0.725	0.776	0.747	0.684	0.566	0.379	0.207
P_{ij} 3d e_2 π	1.053	1.398	1.377	1.380	1.369	1.342	1.311
$P_{\mu\mu}$ 3d a_1	0.033	0.034	0.965	1.925	1.920	1.928	1.942
$P_{\mu\mu}$ 3d e_1	0.401	0.466	0.445	0.365	1.295	2.150	2.995
$P_{\mu\mu}$ 3d e_2	1.443	2.206	2.270	2.381	2.426	2.541	2.700
$P_{\mu\mu}$ 4s	0.230	0.304	0.395	0.455	0.485	0.507	0.529
$P_{\mu\mu}$ 4p	0.821	1.047	1.232	1.381	1.530	1.630	1.697
d^x	1.877	2.706	3.680	4.671	5.641	6.619	7.637
Net Charge	+0.071	−0.055	−0.307	−0.508	−0.656	−0.756	−0.863
S_{ij} 3d, $a_1 - p_z$	0.043	0.032	0.021	0.021	0.004	0.013	0.010
S_{ij} 3d, $e_1 - p_z$	0.177	0.165	0.154	0.137	0.133	0.126	0.114
S_{ij} 3d, $e_2 - p_z$	0.093	0.090	0.088	0.078	0.082	0.086	0.078

TABLE IV. Bonding Properties of CpMBz and CpMCh Systems.

Complex	CpCrBz	CpMnBz	CpTiCh	CpVCh	CpCrCh
Ground State and Configuration	$^2A_1e_2^4a_1$	$^1A_1e_2^4a_1^2$	$^1A_1e_2^4$	$^2A_1e_2^4a_1$	$^1A_1e_2^4a_1^2$
P_{ij} 3d a_1 π (Cp)	0.066	0.053	0.129	0.088	0.051
P_{ij} 3d e_1 π (Cp)	0.959	0.921	0.998	0.969	0.994
P_{ij} 3d e_2 π (Cp)	0.566	0.548	0.255	0.243	0.345
P_{ij} 3d a_1 π (Bz or Ch)	0.051	0.037	0.153	0.093	0.027
P_{ij} 3d e_1 π (Bz or Ch)	0.788	0.745	0.667	0.626	0.617
P_{ij} 3d e_2 π (Bz or Ch)	1.661	1.610	1.928	1.919	1.930
$P_{\mu\mu}$ 3d a_1	0.988	1.938	0.051	0.999	1.954
$P_{\mu\mu}$ 3d e_1	0.608	0.536	0.591	0.546	0.557
$P_{\mu\mu}$ 3d e_2	2.900	3.029	1.741	1.810	1.863
$P_{\mu\mu}$ 4s	0.444	0.499	0.320	0.393	0.451
$P_{\mu\mu}$ 4p	1.455	1.581	1.103	1.279	1.441
d^x	4.496	5.503	2.383	3.355	4.374
Net Charge	−0.395	−0.583	+0.194	−0.027	−0.265
S_{ij} 3d, $a_1 - p_z$ (Cp)	0.061	0.056	0.087	0.079	0.062
S_{ij} 3d, $e_1 - p_z$ (Cp)	0.138	0.123	0.143	0.126	0.137
S_{ij} 3d, $e_2 - p_z$ (Cp)	0.062	0.055	0.057	0.050	0.061
S_{ij} 3d, $a_1 - p_z$ (Bz or Ch)	0.013	0.008	0.067	0.067	0.056
S_{ij} 3d, $e_1 - p_z$ (Bz or Ch)	0.153	0.137	0.146	0.130	0.117
S_{ij} 3d, $e_2 - p_z$ (Bz or Ch)	0.102	0.091	0.130	0.122	0.107

may first effectively discount any significant contribution from the d_{z^2} (a_1) level. As our calculations show this level remains essentially non-bonding throughout all the series of sandwich complexes, and this is at least partly due to the large energetic separation between the 3d a_1 level and the ligand π-level of the same symmetry (see Figures 1 and 2). Furthermore, by virtue of the non-coaxial overlap between the metal 3d levels and the π-orbitals of the rings the group overlap expressions contain both S_σ and S_π

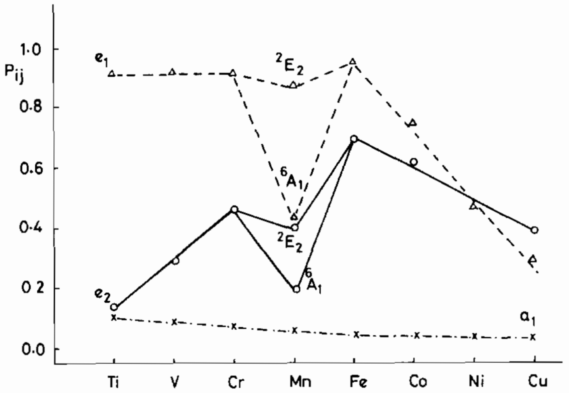

Figure 3. Variation of the metal 3d–ligand-π bond orders within the MCp_2 series.

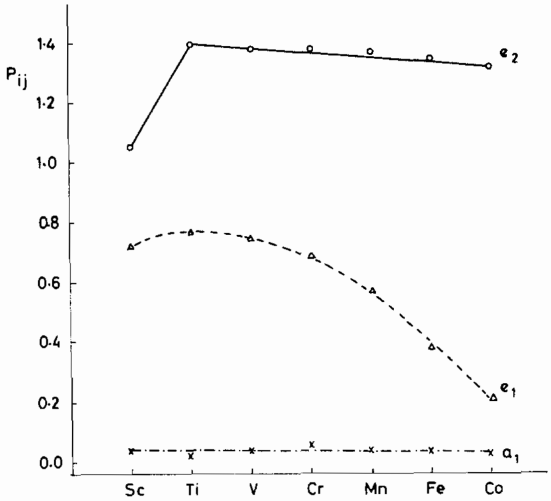

Figure 4. Variation of the metal 3d–ligand-π bond orders within the MBz_2 series.

contributions which for the d_{z^2} level are of opposite sign, leading to rather small resultant values for the group overlap per ring. For the d_{xz}, d_{yz} (e_1) and $d_{x^2-y^2}$, d_{xy} (e_2) orbitals the group overlap values are appreciably larger, and although the π-ligand e_1 levels lie much further below the metal 3d levels than the ligand e_2 set, this greater energetic separation is compensated by the fact that the group overlap for the e_1 set is roughly twice as large as for the e_2 orbitals. Nevertheless, the magnitudes of the respective a_1, e_1, and e_2 group overlaps show relatively little variation between the different series of sandwich compounds, although the e_1 and e_2 values are slightly larger in the MBz_2 than in the MCp_2 series.

The major difference in the bonding between the metallocene and bis-arene series arises however from the lower ligand H^{core} terms for the e_1 and e_2 levels in the larger ring system. Thus in the MBz_2 complexes the π-ligand e_2 level lies closer to the metal 3d levels and the ligand e_1 further away, than in the MCp_2 systems. Consequently, as shown by the appropriate P_{ij} values, the metal 3d–ligand e_1 interaction is greater than the e_2 interaction for the metallocenes whilst the converse situation obtains for the bis-benzene species. In Figures 3 and 4 therefore we present these results diagramatically and the dependence of the P_{ij} values on the formal orbital occupations may readily be rationalised bearing in mind that the dominantly metal e_2 orbitals are always bonding in character, whilst the mainly metal e_1 levels are anti-bonding. Thus the progressive filling of the e_2 levels should tend to increase the corresponding P_{ij}, whilst a similar filling of the e_1 levels should have the opposite effect.

In general the results of Figures 3 and 4 show these predictions to be rather well fulfilled, although there are certain features which merit further comment. Thus for $MnCp_2$ we have shown the results for both the high-spin, $^6A_1$, ground state, and for the low lying excited state, $^2E_2$ (*cf.* [9]). In the former case the P_{ij} plots show large discontinuities at Mn, because of the formal ($e_2^2a_1e_1^2$) orbital occupation, whilst for the $^2E_2$ level, which has a formal ($e_2^3a_1^2$) configuration, the discontinuity, although smaller, is still evident. In this latter case however, as compared with the $^3E_2$ ($e_2^3a_1$) $CrCp_2$, no further electrons have been formally added to the bonding e_2 level, so that no increase in the e_2 P_{ij} value would be anticipated, whilst the addition of an extra electron to the non-bonding a_1 level would not be expected significantly to affect the bonding. Nevertheless, with the exception of Mn the e_2 bond order shows a steady increase from Ti to Fe as the bonding mainly metal e_2 level is filled, whilst the e_1 bond order, arising essentially from the completely filled mainly ligand e_1 level, remains effectively constant. In the case of $TiCp_2$ our calculations indicated that the $^3E_2(e_2a_1)$ level should be significantly more stable than the $^3A_2$ (e_2^2) state which had [10] been assumed to be the ground level, but the e_2 bond order is extremely small and may not be unconnected with the extreme lability of the $TiCp_2$ system, which is not known as a stable monomer [11].

It is of course always somewhat hazardous to attempt to predict stabilities on the basis of theoretical quantities such as bond orders, since stability may well be an artifact of both kinetic and thermodynamic effects. Nevertheless, it is striking that the maxima in P_{ij} for both the e_1 and e_2 interactions occur at Fe, in keeping with the well known exceptional stability of ferrocene. The decrease in the e_1 bond order after Fe is naturally expected, since the mainly metal anti-bonding e_1 level is now being filled, but the reason for the marked decrease in the e_2 bond order in the same region is less obvious. However, as shown in Table I, the metal e_2 level is in $FeCp_2$ only rather weakly involved in bonding with the ligand π-system, the mainly metal level containing some 91% 3d and 6.5% π-ligand contribution. Furthermore, on passing from Fe to Co to Ni to Cu, the metal H^{core} term becomes progressively more negative, thus increasing its separation from the π-ligand e_2 level, and diminishing the admixture of the latter to the bonding e_2 level, as confirmed by inspection of the eigenvectors. Thus, since the π-ligand contribution to this level was quite small, even at Fe, its further reduction should markedly reduce the e_2 P_{ij} value, as is indeed found. As suggested by the P_{ij} values the 3d e_1 orbitals are much more strongly mixed with the π-ligand orbitals than are the metal e_2 3d levels. Thus, although it constitutes the molecular orbital containing the largest metal 3d e_1 contribution, the formally metal anti-bonding e_1 level contains (Table I) only just over 40% metal character in $CoCp_2$ (formally $e_2^4a_1^2e_1$) with some 53.5% of ligand-π. Finally, for the MCp_2 series, mention may be made of the as yet unknown cuprocene, $CuCp_2$, molecule for which both the e_1 and e_2 calculated bond orders are extremely small and which may therefore account for its inaccessibility. Presumably, in this system there does not exist any sufficiently strong bonding mechanism to offset the effects of three electrons formally situated ($e_2^4a_1^2e_1^3$) in the e_1 anti-bonding level.

It is however noteworthy that in the bis-arene series there does exist a formally $d^9(e_2^4a_1^2e_1^3)$ system, $Co(HMBz)_2$ (HMBz = hexamethylbenzene) which, although not particularly stable is nevertheless well characterised and established [12]. Inspection of Figure 4 does though show that this result is not altogether surprising. Thus the P_{ij} values show that for the bis-benzene complexes the 3d e_2 interaction is much stronger than for the metallocenes, whilst the e_1 involvement in the bonding is now weaker than that of the e_2 level and appreciably smaller than the e_1 interactions in the MCp_2 series. In fact the only discontinuity in the P_{ij} plot for the MBz_2 systems lies at Sc, for which a $^2E_2$ (e_2^3) ground state is calculated; thus it is the only system not to exhibit the maximum e_2 bonding with a filled (e_2^4) shell, and this is therefore consistent with it being at present unknown. Moreover, the bond orders from Ti to Co show no very well defined maximum in either the e_1 or the e_2 interactions. The e_1 P_{ij} value remains essentially constant as far as $CrBz_2$, thereafter declining sharply as the anti-bonding, mainly metal 3d, level is filled, but the e_2 bond order shows only a small and gradual decrease from Ti to Co. In this latter case the e_2 bond order declines across the series, even though all the systems from Ti to Co possess the filled (e_2^4) shell, for much the same reason as in the metallocenes – by virtue of the decreasing (more negative) H^{core} term for the metal, which causes a larger energetic separation between the ligand-π e_2 level and the metal 3d levels. However, in the bis-benzene series the degree of metal–ligand mixing for the e_2 interaction is much greater than for the metallocenes. Thus, as shown in Table I, In $CrBz_2$ the bonding e_2 level is only 56.9% 3d, with 41.9% ligand-π whilst the ligand admixture into the anti-bonding e_1 level in $MnBz_2$ – some 19.2% with 71.6% 3d – is appreciably less than for $CoCp_2$ in the metallocenes. Consequently, as far as the e_2 bond order is concerned, small decreases in the amount of ligand-π contribution to the bonding e_2 level, although diminishing the P_{ij} value, will have a much smaller influence than in the MCp_2 series. Thus it may be concluded that in the formally d^9 $CoBz_2$, although the e_1 bond order is small by virtue of the three electrons formally located in the antibonding level, the e_2 bond order, being much greater than in the corresponding $CuCp_2$ system, is sufficiently large to sustain the stability of the system. It should also here be pointed out that of the MBz_2 species considered, apart from $ScBz_2$, the $MnBz_2$ entity is at present not known, and our calculations [13] suggest that it should not in fact be stable; however in this case other considerations obtained than those discussed here, which we shall treat separately in a general description of the stabilities of d^7 species.

Finally, it is appropriate briefly to discuss the bond orders resulting for the mixed sandwich, CpMBz and CpMCh, species (Table IV). Considering first the CpMBz series it is apparent that the two ligand rings, Cp and Bz, behave essentially in the same way as in the MCp_2 and MBz_2 series respectively. Thus for the Cp ring the e_1 bond order appreciably exceeds that for the e_2 interaction whilst for the Bz ring the opposite is true. It is however interesting to compare the e_1 and e_2 bond orders per ring obtained for the formally $3d^6$ $FeCp_2$ and $CrBz_2$ systems with those found for the individual rings in the isoelectronic CpMnBz. Thus, on passing from $FeCp_2$ to CpMnBz the Cp e_1 bond order is almost unaffected (0.921 as against 0.958), but the Cp e_2 value is noticeably reduced from 0.696 to 0.548. Conversely, when the Bz bond orders are examined by comparing $CrBz_2$ with CpMnBz the Bz e_1 value is but little affected (0.745 as against 0.684), but the e_2 bond order is now sharply increased, from 1.380 to 1.610. Clearly, in the mixed sandwich species the situation differs from that in the symmetrical systems since for any given interaction (e_1 or e_2) a particular ring (Cp or Bz) is competing not against an identical ligand but against a ligand which may bond either more strongly or more weakly via the 3d orbitals in question. It thus appears that when a Bz ligand is bonding via the metal 3d e_2 levels it is able to dominate the more weakly interacting Cp ligand, thereby increasing the Bz e_2 bond order at the expense of the Cp e_2 bonding, but that the converse situation as regards the e_1 interaction – stronger in the Cp ligand – does not result. It should however be borne in mind that the e_2 bond order results essentially from the occupation of the mainly metal 3d level which is bonding in character, the metal 3d and the π-ligand e_2 levels lying relatively close together, whereas the e_1 bond order arises from the occupation of the lower lying, mainly ligand e_1 bonding level, the metal 3d and the π-ligand e_1 levels being much more widely separated.

Similarly, the e_2 bond order proves to be much more sensitive to changes in ring size when comparison is made between the bond orders resulting for the series MCp_2, CpMnBz, and CpCrCh, *i.e.* one ring Cp, is kept constant and the other varied from Cp to Bz to Ch. Thus in these systems the e_2 bond order increases with ring size from 0.696 to 1.610 to 1.930, but the e_1 value only decreases from 0.958 to 0.745 to 0.617. It is however clear that the e_1 and e_2 bond orders do in fact respectively decrease and increase with increasing size of the ligand ring, as predicted by the simple molecular model and confirmed by more sophisticated calculations [2–5]. Thus a firm theoretical foundation has been established for the assumption used in the ligand field treatment [7, 8] of sandwich and mixed sandwich species that the d-orbital splitting parameters, ΔE_1 and ΔE_2, should respectively decrease and increase with increasing ring size of ligand. Consequently the preference of MBz_2 and mixed sandwich systems for ground states showing the maximum e_2 orbital occupation is readily understood, for example in d^4 and d^5 species showing respectively the $^1A_1$ (e_2^4) and $^2A_1$ $(e_2^4a_1)$ ground levels, rather than the $^3E_2$ $(e_2^3a_1)$ and $^6A_1$ $(e_2^2a_1e_1^2)$ or $^2E_2(e_2^3a_1^2)$ states exhibited by the metallocenes.

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