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Preliminary communication

THE ELECTRONIC STRUCTURES OF FORMALLY d^7 TRANSITION METAL SANDWICH COMPLEXES

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Summary

INDO SCF calculations have been carried out for the d^6 sandwich species $FeCp_2$, $CrBz_2$, CpCrCh, CpMnBz, $[CoCp_2]^+$, $[MnBz_2]^+$, $[CpMnCh]^+$, and $[CpFeBz]^+$ (Cp = π-C_5H_5, Bz = π-C_6H_6, Ch = π-C_7H_7), and for systems obtained therefrom by the addition of one further electron. For all complexes except $CoCp_2$ the extra electron is predicted to lie in a dominantly ligand level and the species generated to be less stable than the corresponding d^6 systems.

Amongst the sandwich and mixed sandwich complexes of the 3d series the only well established neutral d^7 system is that exemplified by cobaltocene, $CoCp_2$ (Cp = π-C_5H_5) [1, 2]; similarly it has proved extremely difficult to obtain anionic species by the reduction of neutral d^6 complexes, only $[CpCrCh]^-$ (Ch = π-C_7H_7) yet being known [3]. However, although all these systems exhibit pseudo-axial symmetry and show a one-electron d-orbital splitting pattern $e_2(d_{x^2-y^2}, d_{xy}) < a_1(d_{z^2}) < e_1(d_{xz}, d_{yz})$, the magnitudes of the splitting parameters, $\Delta E_1(H^{core}_{e_1} - H^{core}_{a_1})$ and $\Delta E_2(H^{core}_{a_1} - H^{core}_{e_2})$, are known [4, 5] to depend significantly upon the sizes of the ligand rings involved, ΔE_1 decreasing and ΔE_2 increasing with increasing ring size. Consequently it is by no means clear whether the addition of an electron to a d^6 system should take place at the metal atom (giving a d^7 species) or at the ligand (yielding a d^6 ligand configuration), and we have therefore carried out INDO SCF-MO calculations [6] for the d^6 systems $FeCp_2$, $CrBz_2$ (Bz = π-C_6H_6), CpCrCh, CpMnBz, $[CoCp_2]^+$, $[MnBz_2]^+$, $[CpMnCh]^+$, and $[CpFeBz]^+$, and for the corresponding complexes containing one extra electron.

Qualitatively the d-orbital splitting arises as shown in Fig. 1 by the interaction of the metal 3d levels with the π-orbitals of the ligand rings. For the symmetrical sandwich species this interaction involves only the even (g) ligand combinations, and the resulting e_{2g}, a_{1g}, and e_{1g} levels are respectively bonding, essentially nonbonding, and anti-bonding in character. However, increasing size of the ligand

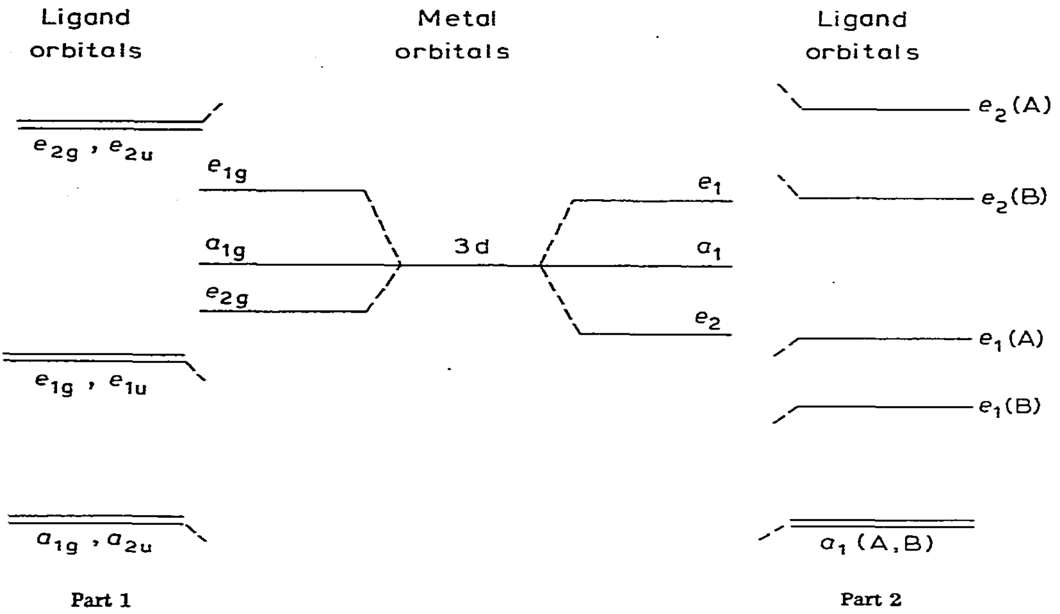

Fig. 1. Simplified molecular orbital diagrams for metal sandwich species. Part 1. M(Ligand)$_2$ systems. Part 2. Ligand A—M—Ligand B systems (Ring B larger than Ring A).

rings lowers the energies of the e_1 and e_2 ligand combinations, increasing ΔE_2 and decreasing ΔE_1, but this also renders it more probable that addition of an extra electron to a d^6 system will take place on the ligand rather than at the metal. Moreover, other things being equal, electron addition to the ligand should be more facile for the earlier members of the *3d* series since the *3d* $\mathrm{H^{core}}$ term becomes more negative with increasing atomic number.

For mixed sandwich species, Ligand A—M—Ligand B, a similar situation obtains. As Ring B becomes larger than Ring A, its e_1 and e_2 levels will move progressively to lower energies than those of Ring A. Thus the e_2 interaction will take place primarily via Ring B, increasing ΔE_2, whilst the e_1 involvement remains predominantly with Ring A. Nevertheless, as the e_2 Ring B level becomes lower in energy it is clear that the d^6 ligand arrangement will be more favoured as opposed to the d^7 configuration.

In fact our calculations vindicate these arguments to a remarkable degree. Thus, of all the systems studied only $\mathrm{CoCp_2}$ shows d^7 more stable than d^6 ligand, in accordance with experiment: $[\mathrm{FeCp_2}]^-$ on the other hand is predicted to be d^6 ligand, essentially by virtue of the higher (less negative) metal *3d* $\mathrm{H^{core}}$ term. Moreover, the d^7 arrangement becomes successively less stable with respect to d^6 ligand as the size of the ligand rings increases; thus, as expected, the quantity $E(d^7) - E(d^6$ ligand) follows the sequence $\mathrm{MCp_2} < \mathrm{CpMBz} < \mathrm{MBz_2} < \mathrm{CpMCh}$.

Unfortunately all attempts to synthesise the anionic species $[\mathrm{FeCp_2}]^-$ and $[\mathrm{CrBz_2}]^-$ have as yet been unsuccessful, but the system $[\mathrm{CpCrCh}]^-$ has been obtained and characterised by ESR measurements [3]. Moreover, despite a superficial resemblance of its ESR parameters to those of the corresponding d^5 cation, $[\mathrm{CpCrCh}]^+$, the spectrum of $[\mathrm{CpCrCh}]^-$ was shown conclusively to be due to a species bearing the unpaired electron essentially on the ligand Ch ring, with which finding our calculations are in full accord.

Finally, all the anionic systems, $[FeCp_2]^-$, $[CrBz_2]^-$, $[CpCrCh]^-$, and $[CpMnBz]^-$ are found to be of higher energy than the neutral d^6 compounds, whilst of the neutral systems only $CoCp_2$ is calculated to be more stable than the corresponding cation: CpMnCh and CpFeBz are nearly equienergetic with their cations whilst $MnBz_2$ is appreciably less stable. The stability of $CoCp_2$ and the instability of $MnBz_2$ (which is as yet unknown) may readily be understood since increasing ring size leads to a diminution of the e_1 interaction. Thus in $MnBz_2$ the metal e_1 level is less delocalised than in $CoCp_2$, leading to increased one-centre metal repulsion terms for the d^7 system. The neutral complex CpMnCh is also not known and although CpFeBz has been obtained [7] it has not been unequivocably characterised and its ESR g values are not obviously indicative of either a d^7 or a d^6 ligand ground level.

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