

## MOLECULAR ORBITAL CALCULATIONS ON TRANSITION METAL COMPLEXES

### XXV \*. SOME $d^5$ METALLOCENE AND BIS-BORABENZENE SYSTEMS

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(Received September 16th, 1980)

#### Summary

INDO SCF MO calculations have been carried out for the formally  $d^5$  species  $M(C_5H_5)_2$  and  $M(C_5H_5BH)_2$  ( $M = Cr^-, Mn, Fe^+$ ) in order to make further comparison between the bonding characteristics of the cyclopentadienyl,  $C_5H_5$  (Cp), and borabenzene,  $C_5H_5BH$  (BBz), ligands in transition metal sandwich systems. The calculations suggest that differences in ground states may be observed both within and between the two series of compounds, and comparison is also made with results for unsubstituted bis-benzenemetal complexes. The findings are discussed and rationalised in terms of the simple ligand field model.

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#### Introduction

Recently, we reported [1] the results of INDO SCF MO calculations for various bis-borabenzene,  $M(BBz)_2$ , systems of the  $3d$  series ( $M = Cr, Mn, Fe, Co$ ). Initially, these calculations were designed to investigate the magnitudes of the splittings of the dominantly metal  $3d$  orbitals of  $e_1$  and  $e_2$  symmetry produced by the boron heteroatoms (which in the event proves to be small), but the results also showed that the borabenzene (BBz) ligand should be intermediate in behaviour between the cyclopentadienyl (Cp) and benzene (Bz) ligands when bonding to a transition metal in a sandwich complex. The BBz ligand should however be more closely akin to the Cp than to the Bz moiety.

Further experimental data relating to the BBz ligand have moreover lately been recorded by Koelle [2,3], who has carried out an electrochemical study of a number of *B*-methyl and *B*-phenyl substituted bis-borabenzene systems ( $M =$

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\* For part XXIV see ref. 7.

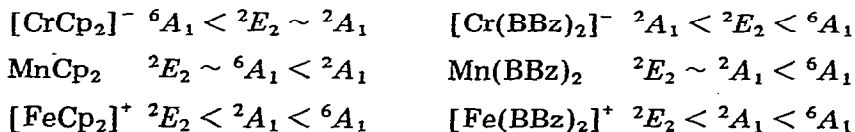
V, Cr, Fe, Co), and their respective anions and cations, making comparisons with similar results for the corresponding metallocenes, and concluding that the borabenzene ligand was generally more easily able to accept electrons than the Cp ligand. In the course of his investigations a number of hitherto unknown or little studied metallocene and bis-borabenzene species were obtained electrolytically, and since no ground state electronic structure could be assigned to these systems we have applied our INDO SCF MO procedure to the formally  $d^5$  species amongst them, for which our method has hitherto proved to yield some of its most reliable results. Thus we now report results for these  $M(\text{BBz})_2$  ( $M = \text{Cr}^-, \text{Mn}, \text{Fe}^+$ ) systems, and for the corresponding metallocenes, paying particular attention to the various ground states thereby predicted. Comparisons are made both within and between the two series, and with the cognate unsubstituted bis-benzene compounds, and the conclusions are surveyed in the light of simple ligand field considerations.

### Method

The all valence INDO SCF MO method previously described [4] was used. The basis set employed spanned the metal  $3d$ ,  $4s$ , and  $4p$ , the carbon and boron  $2s$  and  $2p$ , and the hydrogen  $1s$  orbitals. The geometry of the borabenzene ring was taken as before [1], and the total energies were in each case minimised with respect to the metal to ligand distance.

### Results and discussion

Of the metallocene species studied the iron and manganese complexes are both well known, and the  $[\text{CrCp}_2]^-$  anion was obtained electrochemically by Koelle [3]. For the bis-borabenzenes the iron cation is again well characterised, and the chromium anion similarly accessible electrolytically; the bis-borabenzene manganese complex is not as yet known, although the V, Cr, Fe, and Co compounds have all been prepared, and it is therefore included in our comparisons. For each system therefore calculations were made for the three states which could conceivably constitute the ground level for a transition metal sandwich complex with a  $d^5$  configuration, namely  ${}^2A_1$  ( $a_1e_2^4$ ),  ${}^2E_2$  ( $a_1^2e_2^3$ ), and  ${}^6A_1$  ( $a_1e_1^2e_2^2$ ). The energies of each state, relative to the ground level, are given in Table 1, and within the limit of reliability of the method imply the stability sequences:



There are therefore a number of fairly striking differences between the two series since although the Mn and  $\text{Fe}^+$  compounds each yield  ${}^2E_2$  ground levels in both series, the  $\text{Cr}^-$  complexes are predicted to show a  ${}^6A_1$  ground state for  $[\text{CrCp}_2]^-$  but a  ${}^2A_1$  ground level for  $[\text{Cr}(\text{BBz})_2]^-$ . Moreover, although the  ${}^6A_1$  state is the ground level for  $[\text{CrCp}_2]^-$  and virtually equienergetic with the

TABLE 1

RELATIVE ENERGIES OF ELECTRONIC STATES OF  $d^5$  METALLOCENE AND BIS-BORABENZENE SYSTEMS <sup>a</sup>

Metalloenes	$^2A_1$	$^6A_1$	$^2E_2$	
[CrCp <sub>2</sub> ] <sup>-</sup>	4200	0	4000	
MnCp <sub>2</sub>	4800	1500	0	
[FeCp <sub>2</sub> ] <sup>+</sup>	5300	21100	0	
Bis-borabenzenes	$^2A_1$	$^6A_1$	$^2E_2$	$\Delta^b$
[Cr(BBz) <sub>2</sub> ] <sup>-</sup>	0	13200	6800	2000
Mn(BBz) <sub>2</sub>	1100	2600	0	900
[Fe(BBz) <sub>2</sub> ] <sup>+</sup>	3300	18200	0	1100

<sup>a</sup> Energies in cm<sup>-1</sup>. <sup>b</sup> Splittings of  $^2E_2$  level due to boron heteroatoms.

ground level for MnCp<sub>2</sub>, this sextet always lies highest of the three possible electronic states in the BBz series. In order to make further comparisons within and between the two series it is convenient now to consider the energy differences  $E(^2E_2 - ^2A_1)$  and  $E(^6A_1 - ^2A_1)$ . In the former case the two configurations differ by the transfer of one electron between the  $e_2$  and  $a_1$  levels (thus depending upon  $\Delta E_2$  of Figure 1) and in the other by the interchange of two electrons from the  $e_2$  to the  $e_1$  level (thus depending upon  $\Delta E_1 + \Delta E_2$  of Figure 1), the use of ligand field arguments [5] being thereby facilitated.

Initially, however, it is appropriate to consider the general bonding behaviour of the Cp, BBz, and Bz ligands. Thus, it is now well established [6] that the dominant bonding interactions in transition metal sandwich complexes are those between the  $\pi$ -orbitals of the ligand rings and the metal 3d orbitals. Moreover, the one-electron energies of the ligand  $\pi$ -orbital combinations of two-fold degeneracy ( $e$  symmetry) decrease progressively with increasing ring size (Figure 2), so that the interaction involving the ligand- $\pi e_1$  levels should thereby diminish, and that involving the ligand- $\pi e_2$  levels increase in importance. The ligand- $\pi a_1$  level is however essentially invariant to change in ring size, and in any case interacts only very slightly with the corresponding metal 3d level by virtue of unfavourable overlap. Thus, since the metal 3d level is usually intermediate in energy between the ligand- $\pi e_1$  and  $e_2$  combinations, a splitting pattern of the type shown in Figure 1 normally arises for sandwich complexes of pseudo-axial symmetry.

On a ligand field model the Cp ligand may be formally considered as the 6  $\pi$  electron system, [C<sub>5</sub>H<sub>5</sub>]<sup>-</sup>, so that MnCp<sub>2</sub> for example, regarded as Mn<sup>2+</sup> 2 Cp<sup>-</sup>, would represent a formally  $d^5$  system. Similarly, the borabenzene ligand, C<sub>5</sub>H<sub>5</sub>BR (or BBz) (R = H, CH<sub>3</sub>, C<sub>6</sub>H<sub>5</sub>) is also a formally anionic 6  $\pi$  electron system, [C<sub>5</sub>H<sub>5</sub>BR]<sup>-</sup>, so that Mn(BBz)<sub>2</sub> will also be  $d^5$  and iso-electronic with MnCp<sub>2</sub>. In the bis-benzene complexes, however, the 6  $\pi$  electron ligand is formally neutral (Bz<sup>0</sup>), so that here VBz<sub>2</sub> would constitute the  $d^5$  species.

Moreover, the introduction of the more electropositive heteroatom, boron, into the benzene ring will not only alter the formal valency of the metal, but will also lift somewhat the two-fold degeneracies of the  $e_1$  and  $e_2$   $\pi$ -ligand levels (Figure 3), raising one component in energy in each case. Thus it would be anti-

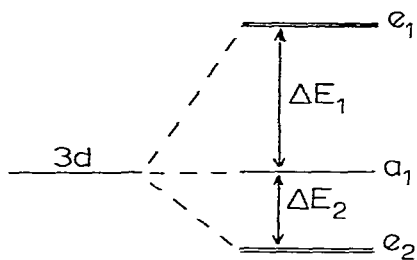


Fig. 1. One-electron  $d$ -orbital splitting pattern for pseudo-axial symmetry.

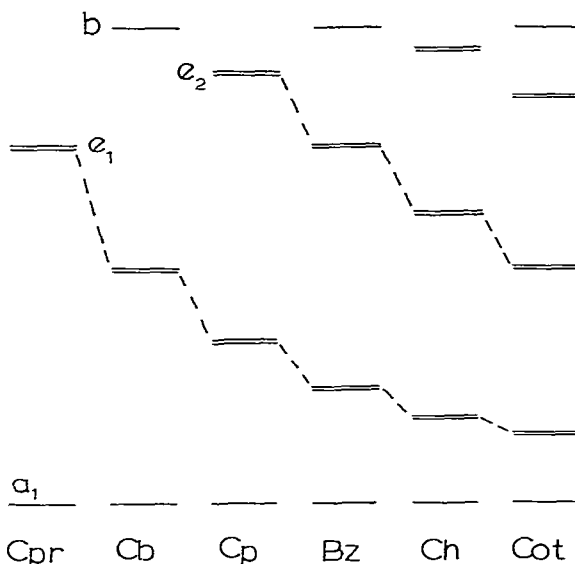


Fig. 2. Dependence of ligand  $\pi$ -orbital energies on ring size (schematic).

anticipated that the rather large  $e_1$   $\pi$ -interaction in  $M(\text{BBz})_2$  systems should be somewhat stronger than for  $M\text{Bz}_2$  species, but weaker than for  $M\text{Cp}_2$  compounds, whilst the rather smaller  $e_2$   $\pi$ -involvement should be weaker than in  $M\text{Bz}_2$  but stronger than for  $M\text{Cp}_2$ .

Returning now to the values of the quantity  $E(^2E_2 - ^2A_1)$ , which may be deduced from the results of Table 1, it is found that for both the Cp and the BBz series this quantity becomes smaller (more negative) in the sense  $\text{Cr}^- > \text{Mn} > \text{Fe}^+$ , and is always larger (more positive) for the BBz complexes than for

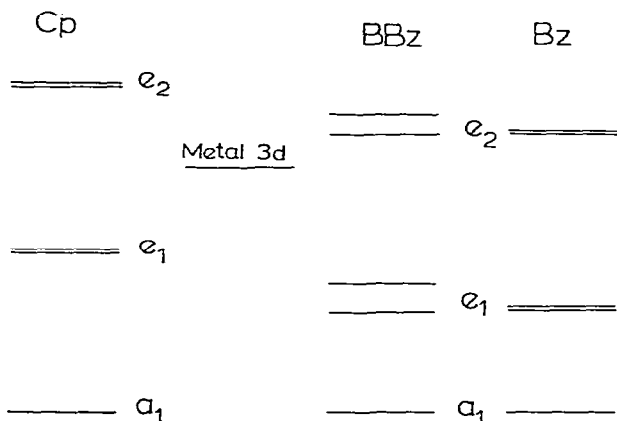


Fig. 3. Metal  $3d$ -ligand- $\pi$  interaction for Cp, BBz, and Bz ligands.

the corresponding metallocenes. However, since this energy difference largely reflects changes in the value of  $\Delta E_2$  it is not surprising that it should become smaller in the sense found; thus one would expect that the metal  $3d H^{\text{core}}$  term would become lower (more negative) in energy in the order  $\text{Cr}^- > \text{Mn} > \text{Fe}^+$ , so that the metal  $e_2$ -ligand- $\pi$  interaction should decrease from  $\text{Cr}^-$  to  $\text{Fe}^+$ . Consequently  $\Delta E_2$  should become smaller and the maximum occupation of the  $e_2$  level (i.e. the  ${}^2A_1$  state) less favoured as against  ${}^2E_2$ , as is in fact found. On the other hand the values of  $E({}^2E_2 - {}^2A_1)$  for the BBz species, being all greater than for their Cp analogues, clearly imply that  $\Delta E_2$  is larger for the BBz series than for the Cp compounds. This therefore is consistent with a stronger metal  $3d$ -ligand- $\pi$   $e_2$  involvement, making the mainly metal molecular orbital more bonding, as is predicted by the simple scheme of Figure 3. In fact, of course, the energy difference between the  ${}^2E_2$  and the  ${}^2A_1$  states is readily found by the ligand field model [5] to be dependent not only on  $\Delta E_2$  but also upon the Racah parameter,  $B$ , since  $E({}^2E_2 - {}^2A_1) = \Delta E_2 - 20B$ . Nevertheless, the above conclusions remain valid since one would anticipate an increase in  $B$  from  $\text{Cr}^-$  to  $\text{Fe}^+$ , accompanying the decrease in  $\Delta E_2$ , whilst on passing from the Cp to the BBz series the greater  $e_2$  interaction for the latter should lead to more metal-ligand mixing and thus smaller  $B$  values in conjunction with the anticipated increase in  $\Delta E_2$ . This, moreover, is consistent with the derivation [1] of smaller nephelauxetic ratios for  $\text{Fe}(\text{BBz})_2$  than for  $\text{FeCp}_2$ , using the available spectroscopic data.

It is however more difficult to rationalise the trends found for the relative energies of the  ${}^6A_1$  states, and we therefore largely report our findings without comment. Thus, simple ligand theory [5] gives  $E({}^6A_1 - {}^2A_1) = 2(\Delta E_1 + \Delta E_2) - 35B - 10C$ , so that if comparison is made between the BBz and the Cp series the effects of the change of ligand upon both the  $e_1$  and  $e_2$  interactions must be taken into account, bearing in mind that these will be reflected not only in  $\Delta E_1$  and  $\Delta E_2$ , but also in the appropriate  $B$  and  $C$  values. The simple ligand field picture outlined above would indicate that with a change of ligand from Cp to BBz the metal  $e_1$  and  $e_2$  interactions with the ligand- $\pi$  system should respectively be decreased ( $e_1$ ) or increased ( $e_2$ ), as reflected in the bond order per ring calculated [1] for  $\text{FeCp}_2$  and for  $\text{Fe}(\text{BBz})_2$  [ $e_1$ : 0.958 and 0.916,  $e_2$ : 0.696 and 0.905]. Comparison with the iso-electronic  $\text{CrBz}_2$  also indicates that, as expected, this displays a smaller  $e_1$  but a larger  $e_2$  ligand- $\pi$  interaction than  $\text{Fe}(\text{BBz})_2$ , the bond orders per ring being 0.684 and 1.380 for the  $e_1$  and  $e_2$  levels, respectively.

Nevertheless, analysis [1] of the available electronic spectral data for  $\text{FeCp}_2$  and for  $\text{Fe}(\text{BBz})_2$  reveals that  $\Delta E_1$  for the latter is, in fact, calculated to be the larger by about  $5000 \text{ cm}^{-1}$ , contrary to the above expectations. However, the introduction of the more electropositive boron heteroatom into the carbocyclic ring would be expected to move the ring- $\sigma$ -levels to higher energies, and thus to increase their participation in bonding to the metal, and calculations [1] of the appropriate metal-ring- $\sigma$ -bond orders indicate that, although both the  $e_1$  and the  $e_2$   $\sigma$ -interactions are larger in  $\text{Fe}(\text{BBz})_2$  than in either  $\text{FeCp}_2$  or in  $\text{CrBz}_2$ , the  $e_1$  involvement is much more markedly increased than the  $e_2$ , thus affording a rationalisation of the larger  $\Delta E_1$  value deduced.

Thus, considering the calculated values of the quantity  $E({}^6A_1 - {}^2A_1)$ , one

would anticipate that this should generally be larger for the  $M(\text{BBz})_2$  systems than for the  $\text{MCp}_2$  species. For two of the three cases this is indeed found by our calculations to be so (in the other case the quantities are almost the same) but in view of the numerous factors determining this energy difference further comment would necessarily be speculative. Of the newly studied species, therefore, our results predict a  ${}^6A_1$  ground state for  $[\text{CrCp}_2]^-$ , a  ${}^2E_2$  ground level for  $[\text{Fe}(\text{BBz})_2]^+$  and  $\text{Mn}(\text{BBz})_2$ , and a  ${}^2A_1$  ground state for  $[\text{Cr}(\text{BBz})_2]^-$ , thus suggesting that ESR investigations, for example, might be of interest. Of the corresponding  $\text{MBz}_2$  systems  $[\text{CrBz}_2]^+$  and  $\text{VBz}_2$  are both well known to display the expected  ${}^2A_1$  ground level, and our present calculations indicate that for  $[\text{TiBz}_2]^-$  also this state should easily constitute the ground level.

Thus, our calculations are again fully consistent with the expectation that the values of  $\Delta E_2$  should increase progressively along the series  $\text{MCp}_2 < M(\text{BBz})_2 < \text{MBz}_2$ , largely by virtue of the increasing metal  $3d$ -ligand- $\pi$   $e_2$  interaction. This is also in accordance with the findings of Koelle [2,3] whose electrochemical investigations showed the BBz ligand to be a more facile electron acceptor than the Cp moiety, the stronger  $e_2$  metal-ligand- $\pi$  interaction in the former case permitting a greater degree of electron delocalisation onto the ligands. Finally, our previous results [1] for  $\text{FeCp}_2$ ,  $\text{Fe}(\text{BBz})_2$ , and  $\text{CrBz}_2$  indicated that on complexation to the transition metal the Cp, BBz, and Bz ligand should respectively show an electron loss from their  $\pi$ -systems of 0.630 (Cp) and 0.409 (BBz) electrons, whilst the Bz ligand should actually gain 0.323 electrons. Clearly therefore the ease of electron acceptance via this mechanism would, as here found, be expected to increase from Cp to BBz to Bz.

## References

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