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Preliminary communication

MOLECULAR ORBITAL ANALYSIS OF THE "SLIP" DISTORTION IN ELECTRON RICH
 SANDWICH COMPLEXES DERIVED FROM THE $1,2-C_2B_9H_{11}^{2-}$ LIGAND.

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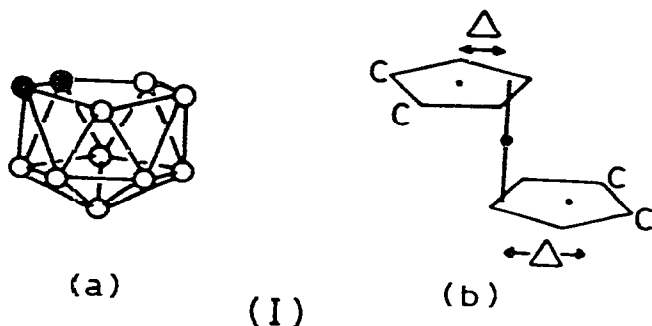
Summary

Extended Hückel molecular orbital calculations on $[Cu(B_{11}H_{11})_2]^{n-}$ and related carbaborane complexes have indicated that the electronic configuration of the metal and the substituents in the borane cage influence the extent of the "slip" distortion. The conclusions of the analysis are shown to account for the results of x-ray structural analyses on these complexes.

The "slip" distortion in electron rich metallocarboranes was first recognised almost a decade ago as a result of an extensive investigation of sandwich complexes derived from the nido-icosahedral carbaborane ligand $1,2-C_2B_9H_{11}^{2-}$ (Ia). These early structural studies defined the "slip" distortion in terms of a lateral displacement Δ , of the dicarbollide ligands as illustrated in (Ib)*. More recently it has been noted that the "slip" is also accompanied

* For reasons of clarity only the bonded pentagonal face of the $C_2B_9H_{11}^{2-}$ ligand is illustrated in this and subsequent illustrations.

by a slight folding of the C_2B_3 face away from the metal atom in such a way that the C_{2h} symmetry of the molecule is maintained.²



Several qualitative bonding models have been proposed to account for these distortions³⁻⁷. In this paper we report the first molecular orbital calculations on these systems, calculations which are based on the extended Hückel approximation, which has previously been used with some success to account for the conformations of platinacarbaboranes.^{8,9}

Figure 1 illustrates the Walsh diagram for the lateral "slip" distortion in the hypothetical $[Cu(B_{11}H_{11})_2]^{n-}$ ion. For an 18 electron complex the highest occupied level is $5e_{1u}$, and results from the bonding combination of the metal x, y orbitals and the antisymmetric component of the ligand $5e_1$ set. (For illustrations of these orbitals see reference 8). The molecular orbitals $a_{1g}(z^2)$ and $e_{2g}(x^2-y^2, xy)$, which are commonly the highest occupied levels in metallocenes¹⁰ lie at the lower energies because of the lower electronegativity of boron relative to carbon and the choice of copper as the central metal atom. The lowest unoccupied level is $5e_{1g}(xz, yz)^*$ which is the antibonding combination of the metal xz, yz orbitals with symmetric component of the ligand $5e_1$ set.

The slip distortion is unfavourable for such an 18 electron complex because the reduced metal-ligand overlaps which accompany the distortion reduce the bonding characteristics of the a_u and b_u components of the $5e_{1u}$ set, shown in Figure 1, and the lower lying bonding $5e_{1g}(xz, yz)$ orbitals not shown in the Figure. In contrast the higher lying and antibonding $5e_{1g}(xz, yz)^*$ levels (and in particular the a_g component) are stabilised by the loss of

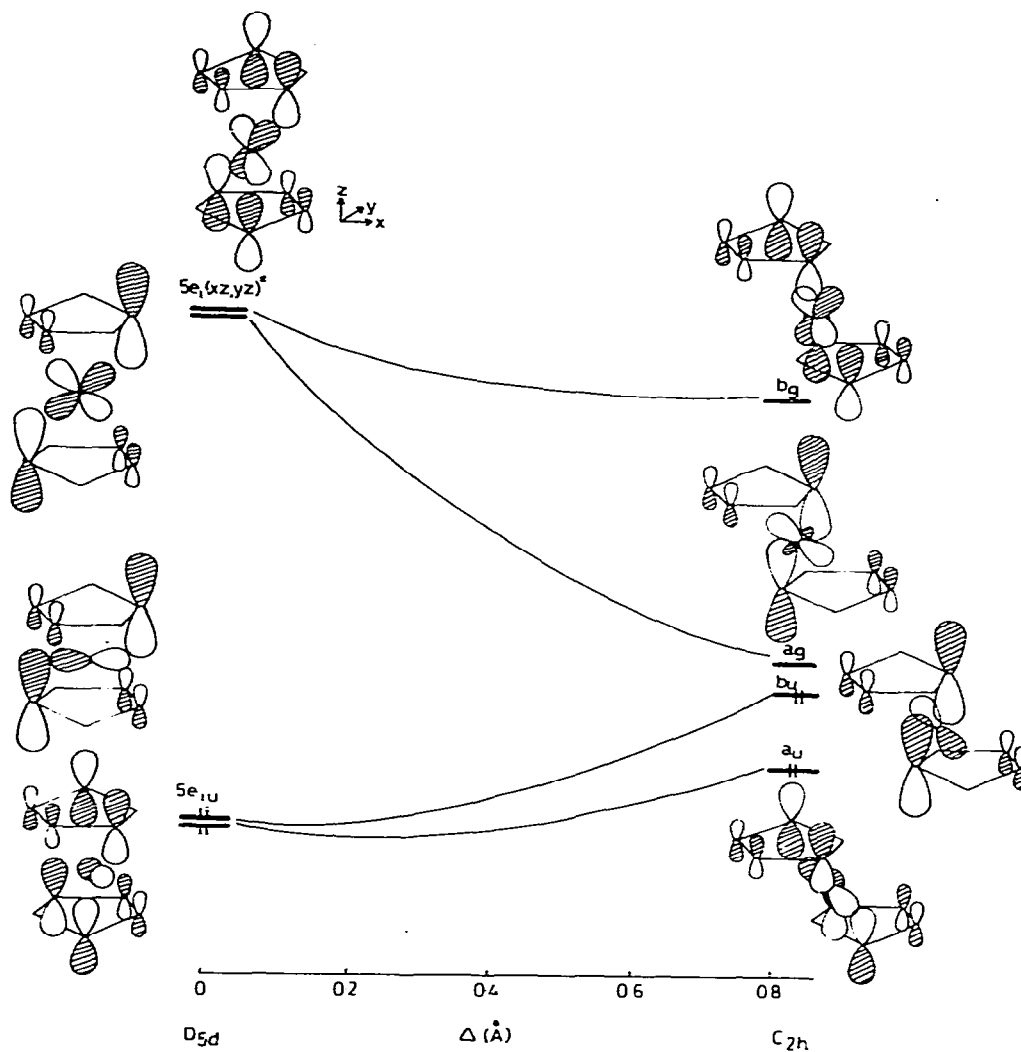
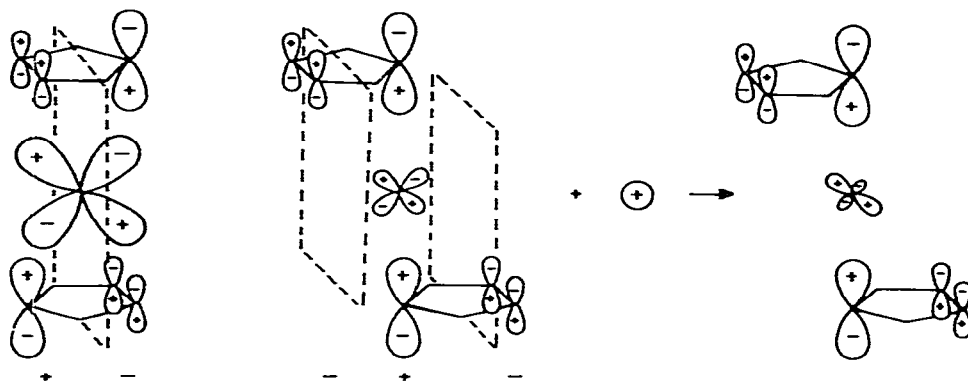


Fig. 1. Walsh diagram for the "slip" distortion in $[\text{Cu}(\text{B}_{11}\text{H}_{11})_2]^{n-}$.

The energy levels occupied correspond to an 18 electron situation.

overlap and provide a driving force for the distortion when the electron count exceeds 18. The "slip" distortion most effectively changes the pseudosymmetry of the a_g component from π to σ and thereby transforms the antibonding $xz-5e_1$ interaction into a non-bonding one. At the same time this transformation permits a bonding interaction between the metal s orbital which is empty and the filled

p_{π} - orbitals of the adjacent boron atoms (see II below).



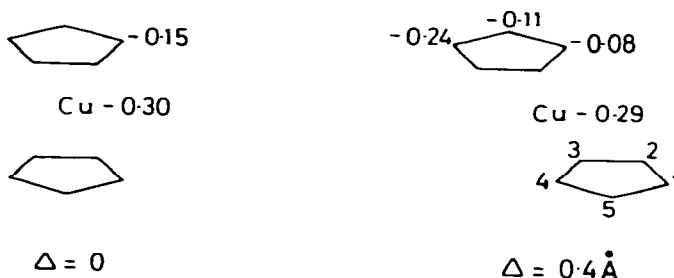
(II)

The interaction between s and the non-adjacent boron atoms is slightly antibonding, but this effect is diminished by the slight folding distortion observed in the "slipped" dicarbollide complexes.² The stabilisation of the b_g component of the $5e_{1g}(xz,xy)^*$ set is much smaller than that described for a_g above, because the nodal plane of this orbital is coincident with the direction of slip and consequently reasonable overlap is maintained (see Figure 1).

The computed Walsh diagram for $[\text{Cu}(\text{B}_{11}\text{H}_{11})_2]^{n-}$ and the isoelectronic dicarbollide complexes suggests that single electron occupation of the component a_g of $5e_{1g}(xz,yz)^*$ in a 19 electron complex provides an insufficient driving force for the distortion, and only in 20-22 electron complexes does the stabilisation associated with the a_g and b_g levels exceed the destabilisation of a_u , b_u and the lower lying molecular orbitals. X-ray crystallographic studies on 19, 20 and 21 electron 1,2-dicarbollide complexes have demonstrated that the "slip" distortion is only observed when the electron count exceeds 19,^{3,11,12} in complete agreement with the above theoretical analysis.

The calculated atomic charges for the unslipped and slipped $[\text{Cu}(\text{B}_{11}\text{H}_{11})_2]^{3-}$ complex shown in (III), indicate a build up of electron density at those boron atoms which lie farthest from the metal atom (i.e. 1,2) and a loss of electron

density at the other positions (i.e. 3,4 and 5). This suggests that electro-negative substituents at the 1,2 positions will encourage, and substituents at the 3,4 and 5 positions will discourage, the "slip" distortion. It is significant in this regard that the "slip" distortion has only been observed in electron rich 1,2-dicarbollide complexes, and that a 20 electron dicarbollide complex with the carbon atoms at the 3,5 positions shows only a very small slip distortion ($\Delta < 0.15 \text{ \AA}$).³



(III)

Similar substituent effects have been reported for "slipped" $\text{Pt}(\text{PR}_3)_2(\text{C}_n\text{B}_{11-n}\text{H}_{11})$ complexes⁹ and have been rationalised using analogous theoretical arguments¹³.

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