CHAPTER 3

STABILITY OF MACROPOLYHEDRAL BORANES - A MOLECULAR ORBITAL STUDY ON THE CAP-CAP (INTERPOLYHEDRAL) INTERACTIONS
3.0. INTRODUCTION

The development of polyhedral borane chemistry has often involved isoelectronic and isolobal relationships with carbon and metals connecting it to hydrocarbons and to organometallics.\textsuperscript{1,2} Various attempts to merge organometallics with boranes are carried out mostly through the intermediacy of metallaboranes and metallocenes.\textsuperscript{3} Here the examples known in organometallic chemistry is used to have a better understanding on bonding in isolobally related and structurally similar polyhedral boranes. The interaction between the non-bonded atoms on adjacent polyhedra in a condensed skeleton is assumed to be one of the major factors that hinder the stabilities of macropolyhedral systems as they are thought to be repulsive. The nature of these intrapolyhedral interactions in the macropolyhedral boranes are explored first followed by the impact due to the presence of hetero atoms.

In sandwich complexes involving boron as the bridging atom, the interaction between non-bonded atoms tend to be antibonding, but a closer analysis of various condensed systems shows that this cannot be generalized. The interactions between proximate atoms in adjacent units of macropolyhedral boranes are studied taking B\textsubscript{10}H\textsubscript{14} and isolobal [C\textsubscript{6}H\textsubscript{4}(Ru(CO)\textsubscript{2}GeMe\textsubscript{3})\textsubscript{2}] as prototype. In general single-atom bridging with main group elements leads to antibonding interactions between two formally non-bonded pairs of atoms, whereas higher fusions show greater inclination to have bonding interactions. Models to comprehend the nature of cap-cap interactions in heteroboranes were restricted to single vertex and edge shared systems, as all higher fusions are found to share the same trends.
3.1. CONDENSED POLYHEDRAL BORANES

Steric interactions induced between two adjacent vertices of an icosahedron by replacing terminal hydrogen atoms with bulky substituents have been studied previously; a representative example is shown in 1, Figure 1. In these molecules, mostly metallacarboranes, the phenyl groups on two neighboring carbon atoms result in repulsive interactions leading to the cleavage of the C-C bond. The ligands on the metal are mostly Cp or C₆H₆ which makes the molecule a two-cluster system fused through a transition metal vertex. Macropolyhedral boranes formed by the condensation of two or more polyhedral clusters through one or more boron atoms bring additional complexity as the non-bonding interactions are suspected to influence their stability. The nature of these interactions is the subject of the current study. Though there are many ways of fusing polyhedral boranes starting with single vertex to four-atom sharing, mixing the various fusions, alleviating the charges of opened cages by adding bridging hydrogens and so on, progress appears to be hindered due to the suspected steric interactions. The existence of pentalene complexes of metals with both cis and trans orientations prompted us to have a detailed analysis of such interactions. Taking the same B₁₂ skeleton, Figure 1 shows the various condensations (2, 4-6) known in polyhedral borane chemistry. Here the dotted lines indicate the interactions between atoms from two adjacent subclusters, which are linked to the same shared atoms. These atoms are called as caps and the interactions between them as cap-cap interactions (Figure 1).
All the fusion modes starting from single vertex to four-atom sharing is shown taking a B_{12} unit: [B(B_{11}H_{11})_2]^{+} (2), [B_{22}H_{20}]^{-} (4), [B_{22}H_{18}]^{+} (5) and B_{20}H_{16} (6). The cap-cap interactions due to condensation are depicted as dotted lines. [C_{2}R_{2}B_{9}H_{9}RuC_{6}H_{6}] (1) corresponds to the monopolyhedral system where such interactions are induced between the vertices of the B_{12} cage. [B(B_{6}H_{6})]^{+} (3) corresponds to a sandwich system based on pentagonal bipyramidal skeleton. Structures 2, 3 and 4 are hypothetical examples. 5 and 6 corresponds to the minimized geometries on the PES. 6 is also known experimentally.

Structure 2 with all boron atoms does not exist in an isolated form. Molecular Orbital (MO) studies on sandwich compounds involving octahedral aluminium clusters by Hoffmann et al have shown that the cap-cap distance and hence their interactions are
major factors in determining the stability of sandwich complexes. A similar approach has been used in studying hypothetical borane clusters based on pentagonal bipyramid, $[B(B_6H_6)_2]$ (3). Structure 4 where two $B_{12}$ skeletons share an edge is not realizable due to the very close distance between the caps (1.5 Å with the experimental B-B distances of 1.5 Å). All the experimentally known structures with edge sharing exhibits either bisnido patterns with open faces opposite to each other or the skeleton has been slightly rearranged. Realizable models are taken in edge shared systems from closo ($B_{12}H_{10}^2$, 7, $B_{10}H_8^2$, 8), nido ($B_{11}H_{13}$ 9), and bisnido ($B_{10}H_{14}$ 10, 11) forms where there is the possibility of cap-cap interactions. A comparison across two fusions is possible through 8 which has a nido face shared isomer (12). The closo form of the face condensation product of two $B_{12}$ skeletons, $B_{21}H_{18}$ (5), discussed earlier and which is a subject of many theoretical studies is yet to be isolated. 5 along with its nido form, $B_{20}H_{18}^2$ (13) is considered in the studies. Structure 13 is derived from the known $B_{20}H_{16}(NCMe)_2$ by the replacement of NCMe$_2$ groups by H$_2$. After the experimental isolation and structural characterization of this molecule by Lipscomb et al., the existence of the closo $B_{21}H_{18}$ (5) was predicted. According to Lipscomb, the steric interactions between atoms on adjacent clusters in 5 will be larger in relation to that in 6; the non-bonded distance is less than the sum of the van der waal's radii. The only known closo form among condensed clusters, $B_{20}H_{16}$ (6) involving four-atom fusion was isolated in the early 1960s. The extent of steric interactions that occur in the different condensation modes and how it affects the stability of these molecules has been studied here.
The geometries of the optimized structures used for the study. Structures [B_{13}H_{18}]^{2-} (7), [B_{19}H_{18}]^{2-} (8 and 12), B_{13}H_{13} (9), Cis-B_{10}H_{14} (10), Trans-B_{10}H_{14} (11), [B_{20}H_{18}]^{2-} (13), B_{10}H_{14} (14) are calculated at B3LYP/6-31g* level. All are minima on the PES.

Most of the molecules which have m+n number of skeletal electron pairs are inclined to show the same trend in the nature of Overlap Population (OP). A simplified and realistic model of the isomers of B_{10}H_{14} is taken as representative examples for our detailed MO study. Such a system (10 and 11) can be reduced from the experimentally
isolated pentalene complexes of metals by isolobal replacement. While *cis* \( \text{B}_{10} \text{H}_{14} \) has its equivalent in \([\text{C}_8\text{H}_6(\text{Ru}(\text{CO})_2\text{GeMe}_3)_2]\) and \([\text{C}_8\text{H}_6(\text{Re}(\text{CO})_3)_2]\), *trans* form has many isolobal organometallic molecules; one among them is \([\text{Ni}(\text{C}_3\text{H}_5)_2(\text{C}_8\text{H}_6)]\). This also enables to compare several classes of isomers ranging from a condensed system with either the presence or absence of the cap-cap interactions (*cis* and *trans* bisnido, 10 and 11) and the known monopolyhedral system (14). The single vertex sandwiches, which have m+n+o skeletal electron pairs has a greater tendency towards antibonding interactions between the caps depending on the nature and size of the central atom.

Mülliken Overlap Population (OP)\(^1\) at both *ab initio* and Extended Hückel (EH)\(^1\) levels on the *ab initio* optimized geometries of selected structures are used to study the nature of the cap-cap interactions. The OP is a rough and ready indicator of bonding and antibonding interactions, especially useful when comparisons involve analogous bonding situations.\(^1\) Hence its use is restricted in similar contexts and expect the conclusions on cap-cap interactions to be qualitatively correct. Wiberg Bond Index (WBI)\(^1\) between the caps in the *cis* arrangements is also computed as a further verification of the quantitative results obtained. The values of OP at both *ab initio* and EH levels, the WBI, total energies and the non-bonding B-B distance and the dihedral angles wherever possible along the shared atoms are given in Table 1. The relative energies of the isomers whenever applicable are given in Table 1. The EH studies have also been used in understanding the bonding and energetics of MOs of some selected systems, which are minima on the PES.
3.1.1. Sandwich complexes involving five-membered rings

Sandwich complexes with all boron atoms are not known so far experimentally, except as a part of β-rhombohedral boron.\(^{19}\) Let us consider the hypothetical closo-\([\text{B(B}_5\text{H}_6)_{2}]^{5+}\) (3) with the charge of 5- from the mno rule. With boron as the sandwiched atom, the two B5H5 rings are too close with each other and the OP between the caps is -0.138 (cap-cap distance of 2.577 Å at B-B bonding distance of 1.786 Å). The nature of the cap-cap interaction in 3 is maintained even at a B-B distance found in the experimentally isolated sandwich complexes with heavy atom at the shared site (-0.07 at cap-cap distance of 3.143 Å).

The MOs contributing to this antibonding interaction between the caps is shown in Figure 3. In the hypothetical structure obtained from (3) by removing four electrons, \([\text{B(B}_3\text{H}_3)_{2}]^{1+}\), where this degenerate pairs of MOs are vacant, the non-bonded interactions become favorable (0.035 and 0.007 at cap-cap distances of 2.577 Å and 3.143 Å respectively). A sandwich structure involving Si3H3 rings and central boron atom. \([(\text{Si}_3\text{H}_3)_{2}\text{B}]^{1+}\), has been characterized as minima on the PES. This follows the mno rule if the tetrahedron is treated as a closed polyhedron.\(^{20}\)

![Figure 3](image)

The degenerate \(e_g\) MO which is responsible for the antibonding interactions between the caps in a sandwiched complex with a bridging main group atom.
Table 1. The Total energies (T.E.) of 5-16 (B3LYP/6-31g*) and 17, 18 B3LYP/LANL2DZ, Overlap Populations (OP) between the caps calculated using wave functions obtained at the \textit{ab initio} and EH MO levels and WBI at \textit{ab initio} level of all molecules, corresponding cap-cap distances (D (in \AA)) and the dihedral angles (\( \Phi \) (in °)) between the caps along the shared atoms. The relative energies (R.E. in kcal mol\(^{-1}\)) when isomers are present are given with roman numbers within brackets representing each species with a given molecular formula.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>T.E. (a.u.)</th>
<th>R.E. (kcal mol(^{-1}))</th>
<th>WBI</th>
<th>OP</th>
<th>D (\AA)</th>
<th>A (°)</th>
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<tr>
<td>B_{21}H_{18}(^{1-}) (5)</td>
<td>-533.12037</td>
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<td>0.0514</td>
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<td>0.0258</td>
<td>-0.001</td>
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<tr>
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<td>0.0397</td>
<td>0.053</td>
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<tr>
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<td>0.0</td>
<td>0.1112</td>
<td>0.213</td>
<td>2.11</td>
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<tr>
<td>B_{11}H_{13} (9)</td>
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<td>0.024</td>
<td>0.0226</td>
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<td>Cis-B_{10}H_{14} (10)</td>
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<td>66.9 (II)</td>
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<td>0.0596</td>
<td>0.042</td>
<td>2.49</td>
</tr>
<tr>
<td>Trans-B_{10}H_{14} (11)</td>
<td>-256.95059</td>
<td>30.7 (II)</td>
<td>0.233</td>
<td>0.1445</td>
<td>0.152</td>
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<tr>
<td>B_{10}H_{8}(^{2-}) (12)</td>
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<td>B_{20}H_{18}(^{2-}) (13)</td>
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<tr>
<td>B_{10}H_{14} (14)</td>
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<td>0.0 (II)</td>
<td>0.060</td>
<td>0.0485</td>
<td>0.039</td>
<td>2.44</td>
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3.1.2. Macropolyhedral \textit{boranes} involving higher fusions

The edge shared \textit{closo} structures considered are B_{12}H_{10}\(^{2-}\) (7) and B_{10}H_{8}\(^{2-}\) (8). The OP between the caps of the optimized structures of 7 and 8 is positive at both \textit{ab initio} and EH level. The \textit{nido} (9) as well as the \textit{cis bisnido} (10) form derived from B_{12}H_{10}\(^{2-}\) has weak bonding interactions between the caps (Table 1). The OP of -0.002 for B_{11}H_{13} at EH level is small. Though \textit{cis} (10) and \textit{trans}-B_{10}H_{14} (11) can exist in many isomeric forms depending on the positions of the bridging hydrogen atoms, 10 and 11 are found to be the most stable ones and are discussed. A comparison of the relative energies of 10 and 11 with its monopyhedral isomer (14) shows that 14 is the most stable form. The \textit{trans} (11) and the \textit{cis} (10) isomers of B_{10}H_{14} are higher in energy than the monopyhedral (14) by 30.7 kcal mol\(^{-1}\) and 66.9 kcal mol\(^{-1}\) respectively. The relative energy shows that the condensation reduces the stability, probably due to the involvement
of larger number of boron atoms at the open area and lesser number of bridging hydrogen atoms to be placed on the open face of the monopolyhedron against 10 or 11. Structure 14 also has the advantage of being a fragment of an inherently stable icosahedron whereas 10 and 11 are derived from pentagonal bipyramids. The trend in the calculated energies at a first sight appears to favor Lipscomb's suggestion about the role of cap-cap interactions in the stability of condensed systems.\textsuperscript{5}

The next isomers considered are of B\textsubscript{10}H\textsubscript{8} which, exist in a \textit{closo} edge shared form (8) and a \textit{nido} face shared form (12). The cap-cap OPs of these two systems indicate bonding (Table 1). A symmetric form of 12 with an \textit{endo} hydrogen falls back to the C\textsubscript{1} structure, 12 with hydrogen bridging two non-shared boron atoms. Another starting structure where the hydrogen bridges a shared and a non-shared atom (15a, Figure 4) converge to a totally different isomer, which is more like an edge shared system (15b, Figure 4). The energetics show that 12 is less stable than the \textit{closo} edge shared system 8 by 36.8 kcalmol\textsuperscript{-1}, despite the closer cap-cap distance in 8 (Table 1). Structure 15b is found to be less stable than 8 by 19.1 kcalmol\textsuperscript{-1}. Thus short non-bonded distances is not a decisive factor that destabilizes a system.\textsuperscript{3} The trend in relative energies of condensed boranes is explained taking B\textsubscript{10}H\textsubscript{14} isomers as a model in the next section. Condensed boranes involving three or four atom fusion show similar trends in the nature of OP.
The structure of nido face-shared $\text{B}_{10}\text{H}_{14}^2$ (15a, LHS) with the bridging hydrogen between a shared and a non-shared atom converges to structure 15b on the RHS on optimization. 15b corresponds to the geometry at B3LYP/6-31g* level of theory.

### 3.1.3. An MO Theoretical Explanation for cap-cap bonding in higher fusions

The bonding between the caps is studied using the hypothetical $\text{B}_{10}\text{H}_{14}$ molecule, a model edge shared system. The *cis* and *trans* isomers of $\text{B}_{10}\text{H}_{14}$ (10 and 11) is analyzed by a ring-cap fragmentation, emphasizing the differences in the two isomers. The discussion is restricted to those MOs involving combinations of the ring $\pi$ MOs and various combinations of the cap FMOs.$^{21}$

Figure 5 shows an interaction diagram between the ring FMOs ($\text{B}_8\text{H}_6^6$, center) and the cap FMOs ($((\text{BH}^3)^2$; LHS *trans*, RHS *cis*) to give $\text{B}_{10}\text{H}_8^6$. The skeletons are derived from *closo*-B$_{12}$H$_{10}^2$ (7) and have point group symmetries of C$_{2h}$ and C$_{2v}$ for *trans* and *cis* respectively. From the diagram it is clear that in the *cis* isomer there is no occupied MO which has an antibonding interaction between the caps resulting from an end-on-overlap between them. On the other hand there are occupied MOs with bonding interactions between the caps explaining the positive OP between the caps. The cap OP value for *cis*-B$_{10}$H$_8^6$ with C$_{2v}$ symmetry is 0.036, which is less than that in *closo*-B$_{12}$H$_{10}^2$ (0.053). The bending of the five-membered rings in the optimized form of *cis*-B$_{10}$H$_{14}$
increases the cap-cap overlap to 0.042. The cap-cap OP in B_{10}H_{14} is greater than that in B_{12}H_{10}^{2-} though WBI between caps is smaller for B_{10}H_{14} according to the \textit{ab initio} results (Table 1).

\begin{center}
\begin{figure}
\centering
\includegraphics[width=\textwidth]{image.png}
\caption{The MOs of \textit{cis} and \textit{trans} B_{10}H_{14} (RHS and LHS respectively) obtained by an interaction between an edge shared B_8 ring and two BH groups. Only the MOs involving p orbitals perpendicular to the ring are considered. The magnitude of stabilization of the ring FMOs due to the caps is given in brackets in eVs. The dotted lines correspond to secondary interactions.}
\label{fig:mo}
\end{figure}
\end{center}

The \textit{trans} form of B_{10}H_{14} is found to be more stable than \textit{cis} by 36.3 kcalmol\textsuperscript{-1}. In the absence of the cap-cap interaction as a factor in explaining the stability between the two isomers, the MOs are analyzed in detail to describe their relative stability. Figure 5 gives a comparison of the stabilization of the ring FMOs due to capping on the same sides or either sides of the two five-membered rings fused through an edge. Energies of
additional ring FMOs are depicted in Figure 5. These are FMOs involving in-plane orbitals of the ring boron atoms, which influence the energetics of the concerned MOs, by second order interactions. The stabilization energies of the ring FMO due to the cap is given in brackets at appropriate places.

While there are many interactions of varying importance shown in Figure 5, only the strongest among these are considered. These involve the $b_{3g}$, $2b_{1u}$ and $a_u$ FMOs of the ring. The ring FMO $b_{3g}$ finds its equivalent cap FMO with matching symmetry in $b_g$ of the trans arrangement and in $b_2$ of the cis arrangement. $b_g$ (LHS) corresponds to an antibonding cap FMO whereas $b_2$ (RHS) is a bonding cap FMO. The in-plane ring FMOs which can interact with these cap FMOs will be different in cis and trans. Thus while in trans, $b_{3g}$ is more stabilized due to a second order interaction from $b_{1g}$, in cis form $b_{3g}$ stabilization due to caps is reduced by the second order interaction from $b_{2u}$. In a similar way, the next ring FMO, $2b_{1u}$ has a second order interaction in both trans and cis; trans being affected by $b_{3u}$ and cis by nearer $2a_g$. The two levels being farther apart in trans than in cis, the destabilization is less in trans than in cis. The highest level, $a_u$ of the ring has a lesser stabilization due to caps in cis than in trans despite the closer interacting levels in cis than in trans. The symmetry matching cap FMO $a_2$ in the cis form for the ring FMO $a_u$ has antibonding character between the caps which explains the lesser stabilization in cis than in trans. The analysis show the lower stability of cis over trans as due to the lesser stabilization of the ring on capping caused by the resulting second order interactions from lower lying levels competing for the same cap FMO. In general it is observed that destabilizing second order interactions are prominent in cis, which reduces its stability over the trans from.
A correlation diagram between the $C_{2h}$ and $C_1$ geometries of trans $B_{10}H_{16}^6$ (LHS) and between $C_{2v}$ and $C_2$ geometries of cis $B_{10}H_{16}^6$ (RHS) is given. Only the MOs involving $p$ orbitals perpendicular to the ring are shown.

An EH analysis on cis-$B_{10}H_{16}^6$ correlating the initial $C_{2v}$ and the final $C_2$ geometries (Figure 6) show a decrease in the total one electron energies of the skeleton; $C_2$ being the optimized geometry of cis $B_{10}H_{14}$. The trans form has a net destabilization when the one electron energies are correlated between the $C_{2h}$ and the optimized $C_1$ geometries (Figure 6), though the trend in relative energies between cis and trans remains the same. The two five-membered rings deviates from planarity and subtends an angle of 159.0° instead of 180°.
According to the ring-cap matching principle, the out-of-plane bending of substituents in a ring is to increase its overlap with the cap. Here both the caps benefit from the non-planarity of the two rings. As a consequence the cap-cap distance decreases. There is also a contribution from the cap-cap bonding interaction towards the final geometry. The MOs which are greatly affected in the cis form are 2a1 and a2 (Figure 6), with stabilization energy of 0.485 eV and 0.283 eV respectively. In 2a1 the bonding between the caps helps in a greater stabilization of the MO when compared to a2 which has antibonding nature between the caps. Thus the bending of the ring can be partly attributed to the enhancement of cap-cap overlap in addition to the increase in ring-cap overlap. This is also reflected in the shortened cap-cap distance in cis-B10H14 (10) compared to that of the closo-B12H102 (7) (2.491 Å vs. 2.537 Å; Table 1).

3.2. CONDENSED POLYHEDRAL HETEROBORANES AND ANALOGOUS ORGANOMETALLIC CLUSTERS

The impact of the hetero atoms on the nature of the cap-cap interactions in macropolyhedral boranes is explored. The various examples used for the qualitative MO study are substantiated with higher level theoretical calculations. Since the condensed polyhedral boranes show striking difference between single vertex and higher fused systems, studies on heteroboranes are done on sandwich systems and edge shared systems representing the higher fusions to inquire the nature of the interactions.

The magnitude and nature of the interactions in single vertex sandwiches is found to depend on the size and nature of the central atom. Single vertex shared complexes always exist in the sandwich form as observed for [Al(C2B6H6)2] (1, Figure 7), and has been selected for our study. Usually they are known with some bulky groups like –SiMe3
on the carbon atoms.\textsuperscript{23} The Overlap Populations calculated for $[\text{Al}(C_2B_4H_6)_2]^+$ (1) optimized at B3LYP/6-31g* level indicate antibonding interactions between the caps. The skeletal atoms in 1 can also form a different polyhedron as shown in 2(a and b), Figure 1. Though there can be many more isomers for $[\text{Al}(C_2B_4H_6)_2]^+$, depending on the position of carbon in both skeletal frameworks discussed (1 and 2), only the experimentally isolated one and its corresponding isomer in the second arrangement are selected for the study. The effect due to transition metals at the sandwich position on the nature of the cap-cap interactions is analyzed taking $[\text{Co}(C_2B_4H_6)_2]^+$ (3) as the model.

Analogous organometallic clusters of $\text{B}_{10}H_{14}$ is found in $[\text{C}_8H_6(\text{Ru}(\text{CO})_2\text{GeMe}_3)_2]$ and $[\text{C}_8H_6(\text{Re}(\text{CO})_3)_2]$ for the cis form and $[\text{Ni}(\text{C}_3\text{H}_5)_2(\text{C}_8\text{H}_6)]$ for the trans form.\textsuperscript{6} Thus the cis and trans forms of $[\text{C}_8H_6(\text{Ru}(\text{CO})_2\text{Me})_2]$ (4, 5) are also considered. The large GeMe$_3$ group is replaced by Me for computational ease. $[\text{C}_8H_6(\text{Ru}(\text{CO})_2\text{Me})_2]$ (4), studied at B3LYP/LANL2DZ level\textsuperscript{24,25} have weak Ru-Ru interactions. DFT calculations using Double Zeta functional without polarization (DZ) and Triple Zeta functional with Polarization (TZP) are also carried out on the transition metal complexes at Becke Perdew level using Amsterdam Density Functional (ADF) package version 2002.03.\textsuperscript{26} Taking the same skeleton the isoelectronic borane-transition metal systems $[\text{B}_8\text{H}_{12}(\text{Ru}(\text{CO})_2\text{Me})_2]$ (6, 7) and isolobal carbon-boron systems $[\text{C}_8\text{H}_6(\text{BH})_2]^{2+}$ (8, 9) are also optimized to understand how the nature of the cap-cap interactions varies with different substitutions. The nature of cap-cap interactions in transition metal systems is substantiated by a detailed Extended Hückel$^{16}$ based MO study taking 4 and 5 as the model. $\text{C}_2\text{B}_8\text{H}_{12}$ (10) which is topologically equivalent and isoelectronic to the edge shared $\text{B}_{10}H_{14}$ is also considered for the study, the nature of the cap-cap interactions of
which can also be compared with 8 as 10 is just an interchange of the ring and cap atoms, except for the bridging hydrogens in 10. The negative OP between the carbon atoms in 10 is substantiated by a Fragment Molecular Orbital (FMO) analysis. The values of OP at both \textit{ab initio} and EH levels, the Weiberg Bond Index (WBI),\textsuperscript{18} total energies and the non-bonding B-B distance and the dihedral angles wherever possible along the shared atoms are given in Table 2. The relative energies of the isomers are also given in Table 2.

3.2.1. Sandwich Complexes involving heteroatoms at the shared position

A well characterized structure is available where four boron atoms of two pentagonal rings shared by a vertex are replaced by carbon and the sandwiched boron atom by a larger atom Al. The optimized geometry of this structure, [Al(C\textsubscript{2}B\textsubscript{4}H\textsubscript{6})\textsubscript{2}]\textsuperscript{-1}(1), Figure 7, is close to that of the experimental geometry.\textsuperscript{23} The non-boned B-B distances are much larger (3.65 Å) but the OP is negative, though small in magnitude (Table 2). The e\textsubscript{g} set of [B(B\textsubscript{5}H\textsubscript{5})\textsubscript{2}] loses its degeneracy in 1 due to the lack of symmetry, but still remains at the frontier region and is responsible for the antibonding interactions between the caps.

The other isomer 2a, on optimization converges to 2b. The relative energy of 2b when compared to 1 is 71.04 kca\textsubscript{mol}\textsuperscript{-1}. The higher stability of 1 is quite obvious from the ring-cap matching principle.\textsuperscript{21} In 2, aluminum caps a four membered ring, which is less favorable for a bulky atom with more diffused orbitals. On optimization the coplanarity of the two rings are lost; one ring makes an angle of 88° with the other. This may be to reduce the antibonding cap-cap interactions that are greater in magnitude in 2 compared to that in 1 since both the ring atoms and cap atoms are proximate.
Figure 7

The geometries of the optimized structures used for the study. Structures [(C$_2$B$_3$H$_4$)$_2$Al]$^+$ (1, 2), [(C$_2$B$_3$H$_4$)$_2$Co]$^+$ (3), [(C$_8$H$_6$(Ru(CO)$_2$Me)$_2$] (4, 5), [(B$_8$H$_{12}$)(Ru(CO)$_2$Me)$_2$] (6, 7), [(C$_8$H$_6$(BH)$_2$] (8, 9), C$_2$B$_3$H$_4$ (10); compounds involving transition metals are calculated at B3LYP/LANL2DZ level and others at B3LYP/6-31g* level. All are minima on the PES.
Transition metals are also observed at the sandwich site, instead of larger main group elements. Such an optimized structure of \([\text{Co(C}_2\text{B}_4\text{H}_6)_2]\)^{1-} (3) at B3LYP/LANL2DZ has a positive OP between the caps. This is not surprising as the MO involving antibonding interactions between the caps, which remain as the HOMO and HOM0-1 in 1, is stabilized by the symmetry equivalent d orbitals of the transition metal and becomes a low lying MO. These MOs which are split from \(e_g\) of the more symmetric D\(_{5d}\) form into \(b\) and \(a\) of C\(_2\) symmetry in 1 and 3 are shown in Figure 8, A and B respectively.

Table 2. The Total energies (T.E.) of 1-10, Overlap Populations (OP) between the caps calculated using wave functions obtained at the \textit{ab initio} and EH MO levels and WBI at \textit{ab initio} level of all molecules, corresponding cap-cap distances (D (in Å)) and the dihedral angles (A (in °)) between the caps along the shared atoms. The relative energies (R.E. in kcalmol\(^{-1}\)) when isomers are present are given with roman numbers within brackets representing each species with a given molecular formula.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>T.E. (a.u.)</th>
<th>R.E. (kcalmol(^{-1}))</th>
<th>WBI</th>
<th>OP</th>
<th>D (Å)</th>
<th>A (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>([\text{Al(C}_2\text{B}_4\text{H}_6)_2])^{1-} (1)</td>
<td>-601.05742</td>
<td>0.0 (I)</td>
<td>0.001</td>
<td>-0.0068</td>
<td>-0.012</td>
<td>3.72</td>
</tr>
<tr>
<td>([\text{Al(C}_2\text{B}_4\text{H}_6)_2])^{1-} (2b)</td>
<td>-600.94421</td>
<td>71.0 (I)</td>
<td>0.003</td>
<td>-0.0053</td>
<td>-0.015</td>
<td>3.90</td>
</tr>
<tr>
<td>([\text{Co(C}_2\text{B}_4\text{H}_6)_2])^{1-} (3)</td>
<td>-503.55700</td>
<td>0.0444</td>
<td>0.0216</td>
<td>0.020</td>
<td>3.27</td>
<td></td>
</tr>
<tr>
<td>Cis[\text{C}_8\text{H}_6(\text{Ru(CO)}_2\text{M})_2] (4)</td>
<td>-1029.31659</td>
<td>0.0 (II)</td>
<td>0.058</td>
<td>-0.1592</td>
<td>0.048</td>
<td>3.27</td>
</tr>
<tr>
<td>Trans[\text{C}_8\text{H}_6(\text{Ru(CO)}_2\text{M})_2] (5)</td>
<td>-1029.31420</td>
<td>1.5 (II)</td>
<td>0.050</td>
<td>-0.1657</td>
<td>0.048</td>
<td>3.27</td>
</tr>
<tr>
<td>Cis[\text{B}<em>9\text{H}</em>{12}(\text{Ru(CO)}_2\text{M})_2] (6)</td>
<td>-926.89733</td>
<td>26.5 (III)</td>
<td>0.0</td>
<td>-0.1657</td>
<td>0.048</td>
<td>3.27</td>
</tr>
<tr>
<td>Trans[\text{B}<em>9\text{H}</em>{12}(\text{Ru(CO)}_2\text{M})_2] (7)</td>
<td>-926.93916</td>
<td>0.0 (III)</td>
<td>0.073</td>
<td>0.0410</td>
<td>0.019</td>
<td>2.59</td>
</tr>
<tr>
<td>Cis[\text{C}_8\text{H}_6(\text{BH})_2] (8)</td>
<td>-358.58476</td>
<td>7.6 (IV)</td>
<td>0.0</td>
<td>0.0410</td>
<td>0.019</td>
<td>2.59</td>
</tr>
<tr>
<td>Trans[\text{C}_8\text{H}_6(\text{BH})_2] (9)</td>
<td>-358.59692</td>
<td>0.0 (IV)</td>
<td>0.0</td>
<td>0.0410</td>
<td>0.019</td>
<td>2.59</td>
</tr>
<tr>
<td>\text{C}_2\text{B}<em>8\text{H}</em>{12} (10)</td>
<td>-282.11141</td>
<td>0.029</td>
<td>-0.0104</td>
<td>-0.041</td>
<td>2.55</td>
<td>63.6</td>
</tr>
</tbody>
</table>
Figure 8

The MOs corresponding to the Mulliken's symbol b and a of 1 and 3 are shown in A and B respectively. While 1 has these MOs as HOMO and H0M0-1, in 3 they are low lying MOs.

3.2.2. Higher Fusions involving Hetero atoms

A comparison is attempted between B$_{10}$H$_{14}$ and its isolobal analog, the pentalene-Ru complex which is known in its cis form (4). The experimental report on the cis form suggests the presence of a bond between the two Ru atoms at a distance of 3.0 Å. A bond between the metals is presumed based on the 18 electron rule (Ru$^{2+}$ have 6 electrons, 2 COs donate 4 electrons, Me$^{1+}$ - 2, C$_{8}$H$_{6}^{2-}$ - 10/2 = 5; leading to the 17 electron count); the M-M a bond completes the 18 electron. The trans orientation of 4 is also predicted on the basis of reported geometries of isoelectronic molecules like trans-[Ni(C$_{3}$H$_{5}$)$_{2}$(C$_{6}$H$_{6}$)]. The trans arrangement is explained as a structure resonating between two forms with one of the metal having 16 and the other 18 electrons around it. The understanding of the bonding in these systems can be simplified by the application of mno rule where one considers the entire cluster to be delocalized. Thus according to the mno rule, m = 2, n = 10, o = 0 and there are two nido faces which predicts a total of 14 (2 + 10 + 2) skeletal electron pairs for stability. This is achieved from 6 CH (9 electron pairs), two carbons (4) and two d$^{7}$ ML$_{3}$ fragments isolobal to BH$^{+}$ (1). Thus cluster electron count remains the same for the cis and trans structures. The metal as well as the
cluster attains its stable electron count without invoking resonance in the \textit{trans} structure alone. Thus the \textit{mno} rule is more preferred for complexes with condensed ligands.

On optimization of $[C_8H_6(Ru(CO)_2Me)_2]$ at \textit{cis} (4) and \textit{trans} (5) orientations, the \textit{cis} is found to be more stable than \textit{trans} by 1.5 kcal/mol$^{-1}$ at B3LYP/LANL2DZ level and by 1.3 kcal/mol$^{-1}$ at Becke Perdew level using DZ basis set. The optimized structure of 4 has a somewhat longer metal-metal distance of 3.27 Å and 3.20 Å at B3LYP/LANL2DZ and BP86/DZ levels respectively. Inclusion of polarization functions, (a triple zeta basis (BP86/TZP)), changes the M-M bond distance marginally to 3.21 Å. Some of the important structural parameters of 4 at the experimental geometry and at various levels of theory are given in Table 3 for comparison. The dihedral angle $C_m$-$C_s$-$C_s$-$C_m$ (Table 3) in 4 is the angle subtended by the two planar five membered rings and is bent away from the caps. While the calculated value in all the three levels is around 174°, the experimental structure has an average value of 176.6° (values varying from 173° to 178°). The bending of the ring away from the caps in contrast to that observed in \textit{cis-B}_{10}H_{14} is due to the more diffused metal orbitals with a smaller carbon ring.$^{21}$ The OP between the metals in the experimental and the LANL2DZ optimized geometry is found to be positive at EH with a value of 0.041 and 0.048 respectively. But a higher \textit{ab initio} level show antibonding interaction with an OP of -0.1592. The repulsive nature between the metals identified at higher levels of theory is an added reason for bending of the five membered rings in pentalene than that observed in the experimental geometry. This helps in increasing the M-M distance thereby overcoming the possible repulsion between them. The NBO studies$^{18}$ on the optimized geometry suggest that there is no bond between the

95
two metals. Further, the near equal stability of the trans form leads us to conclude that there is practically no bonding interaction between the two metals in the cis form.

Table 3: Some important parameters of Cis - \( \text{C}_{8}\text{H}_{6}(\text{Ru(CO)}_{2}\text{Me})_{2} \) at the experimental and theoretical geometries at B3LYP/LANL2DZ, BP86/DZ and BP86/TZP. \( C_{s} \) is the shared carbon. \( C_{m} \) connects \( C_{s} \) and a non shared carbon. \( C \) bonds two \( C_{m} \). R.E. is the relative energy with its trans isomer. Distances are in \( \text{Å} \), dihedral angles in (°) and R.E. in kcalmol\(^{-1}\). The distances and dihedrals are averaged in the experimental geometry.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Expt.al</th>
<th>B3LYP/LANL2DZ</th>
<th>BP86/DZ</th>
<th>BP86/TZP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ru-Ru</td>
<td>3.06</td>
<td>3.27</td>
<td>3.20</td>
<td>3.21</td>
</tr>
<tr>
<td>Ru-( C_{s} )</td>
<td>2.52</td>
<td>2.65</td>
<td>2.64</td>
<td>2.61</td>
</tr>
<tr>
<td>Ru-( C_{m} )</td>
<td>2.22</td>
<td>2.37</td>
<td>2.37</td>
<td>2.33</td>
</tr>
<tr>
<td>Ru-( C_{t} )</td>
<td>2.17</td>
<td>2.27</td>
<td>2.30</td>
<td>2.24</td>
</tr>
<tr>
<td>( C_{s}-C_{s} )</td>
<td>1.43</td>
<td>1.46</td>
<td>1.46</td>
<td>1.45</td>
</tr>
<tr>
<td>( C_{s}-C_{m} )</td>
<td>1.44</td>
<td>1.45</td>
<td>1.45</td>
<td>1.44</td>
</tr>
<tr>
<td>( C_{m}-C_{t} )</td>
<td>1.35</td>
<td>1.45</td>
<td>1.45</td>
<td>1.43</td>
</tr>
<tr>
<td>( C_{m}-C_{s}-C_{s}-C_{m} )</td>
<td>176.3</td>
<td>174.5</td>
<td>173.5</td>
<td>174.3</td>
</tr>
<tr>
<td>R.E.</td>
<td></td>
<td>1.5</td>
<td>1.4</td>
<td>1.8</td>
</tr>
</tbody>
</table>

A boron ring with the transition metal as caps also produces similar results as the pentalene complex. Here bridging hydrogens are added to compensate for the electronic requirement of the skeleton which results in the molecular formula of \( \text{B}_{8}\text{H}_{12}((\text{Ru(CO)}_{2}\text{Me})_{2}) \). The relative stabilities between the cis (6) and trans (7) isomers is found to be very high. The trans form (7) is found to be more stable than the cis (6) by 26.5 kcalmol\(^{-1}\) at B3LYP/LANL2DZ level. Since pure DFT studies with and without polarization gave almost similar results for 4 and 5, the calculations for 6 and 7 are carried out only at B3LYP/LANL2DZ level. The Ru-Ru distance of 6 are almost identical to 4 with a value of 3.27 Å, but the two B5 rings are bend towards the caps as in \( \text{B}_{10}\text{H}_{14} \) making an average angle of 172° between each other.
A detailed FMO analysis is done on 4 and 5 to account for the observations in transition metal capped edge shared cluster compounds. An FMO analysis is done on the optimized geometries of both cis and trans forms by following the fragmentation of rings and caps. Similar EH studies have been done for sandwich complexes of pentalene \([M_2(C_8H_6)_2]; (M=Co, Ni)\), where the OP between metals is found to be zero.\(^{28}\) The important interactions in the cis and trans form (4 and 5) which leads to the stabilization of the ring FMOs are shown in Figures 9 and 10 respectively.

The Mulliken symbols assigned to the orbitals are based on the symmetry of the resultant molecule and assuming similar coordinate system in the fragments. The \(d^7L3M-d^7ML_3\) bimetallic part with three ligands arranged in a conical manner on each metal has its octahedral remnants, the bonding and antibonding contribution of the \(t_{2g}\) sets; \((t_{2g}+t_{2g})\) and \((t_{2g}-t_{2g})\), occupied. The remaining two electrons will occupy the most bonding FMO \((a_1, \text{Figure 9})\) between the metals. In Figure 9, \(a_1\) is shown to be empty as the binuclear metal fragment is considered to be dicaticionic donating the two electrons to the \(C_8H_6\) ligand. The \(2b_2\) and \(a_2\) orbitals of the cis structure stabilize the ring FMOs (Figure 9). The \((t_{2g}-t_{2g})\) remains almost non-bonding here, while the \((t_{2g}+t_{2g})\) participates in two orbital - four electron interactions. One such combination is depicted in Figure 9, where two \(1b_2\) fragments interact. Here the antibonding combination is stabilized by the high lying \(2b_2\) level on the metal side. The HOMO \((a_1)\) of the molecule has bonding interaction between the metals. Removal of two electrons from this MO results in zero OP between the metals by EH studies.
The interaction diagram between the ring and caps of the cis isomer of $[\text{C}_8\text{H}_6(\text{Ru}(\text{CO})_2\text{Me})_2]$. All the stabilizing interactions and one representative 2o-4e interaction are shown. Here $(t_{2g}+t_{2g})$ remains almost non-bonding and $(t_{2g}+t_{2g})$ is involved in 2o-4e interactions. The geometry of cis-$[\text{C}_8\text{H}_6(\text{Ru}(\text{CO})_2\text{Me})_2]$ corresponds to the optimized one at B3LYP/LANL2DZ.

In the trans form (5) the stabilizing interactions are decreased (Figure 10). Here the $(t_{2g}+t_{2g})$ set remains almost non-bonding whereas the $(t_{2g}-t_{2g})$ is involved in two orbital - four electron interactions. The HOMO of 5 is one such antibonding level resulting from the interaction between two $1b_u$ orbitals. The HOMO is stabilized by a higher lying $2b_u$ FMO on the metal fragment. Only one level ($a_u$) is involved in a two
orbital - two electron interaction. Though the second order stabilizing interactions are present even in the \textit{trans} structure, its magnitude is less because interactions comes from MOs with antibonding character between the metals and are high in energy.

An isolobal replacement of the metal fragment of 4 and 5 to BH$^+$ to give [C$_8$H$_6$(BH)$_2$]$^{2+}$ (8 and 9) reduces the relative stability to 7.6 kcalmol$^{-1}$; \textit{trans} being more
stable than the *cis* form. The plane of the two C5 rings are shifted towards the BH caps subtending an angle of 171° with each other. The nature of the cap-cap interaction is also similar to that of B_{10}H_{14}. 8 and 9 are optimized at B3LYP/6-31g* level of theory and the results can be comparable more with B_{10}H_{14}. Hence the MO justifications of B_{10}H_{14} are equally valid for 8.

When the two cap BH groups of *cis*-B_{10}H_{14} are replaced by CH groups, the molecular formula becomes C_{2}B_{8}H_{12} and structure 10 results. Such a system differs from 8 in the interchange of the atom types between the ring and cap, except for the bridging hydrogens in 10. The special case of C_{2}B_{8}H_{12} (10) which has anitbonding interactions between the caps is analyzed comparing the FMO interactions with B_{10}H_{14}. In 10, where the caps are CH groups, the OP is found to be negative (Table 2). This suggests that the MOs responsible for the negative OP in 10 corresponds to the in plane FMOs of the ring, rather than the perpendicular set which is common for all higher fusions. Among the various isomers possible for C_{2}B_{8}H_{12} depending on the position of bridging hydrogens, 10 is the most stable one where the *cis* arrangement is retained, others converging to a skeleton where one of the carbon occupies a lesser coordination site. A comparative analysis between the interaction diagrams when CH and BH caps show that the difference lies in an MO with contribution from an in plane ring FMO. The interaction that results in this MO is shown in Figure 11 which clearly illustrates the higher contribution of the antibonding cap FMO when CH becomes the caps. The reason is obviously the greater electronegative nature of carbon which brings down the energy levels. Thus the cap FMO shown in Figure 11, which is responsible for the antibonding nature between the caps is very close to the ring FMO and has strong interaction resulting
in the greater stabilization of the ring FMO. This is clear from the percentage contribution of the cap FMOs to this particular MO in the two compounds. While in B$_{10}$H$_{8}^6$, there is only 12% contribution, C$_2$B$_8$H$_{6}^4$ has 43% contribution from the cap FMO to the resultant MO as shown in Figure 5.

3.3. CONCLUSIONS

The common belief that the interactions between two non-bonded proximate atoms are repulsive in polycondensed boranes is not found to be generally true. This problem is analyzed using B$_{10}$H$_{14}$ as the model system. This enabled a further analysis among various isomers of B$_{10}$H$_{14}$. The energy changes involved due to the condensation
of open polyhedral boranes has thus been explored using $\text{B}_{10}\text{H}_{14}$ as the model. The relative stability between the two isomers of $\text{B}_{10}\text{H}_{14}$ has been explained based on a detailed FMO approach. The difference in the nature of OP between the caps in sandwich and higher fusions involving borons has been understood by MO study. The nature of bonding between the caps is attributed to the absence of cap-cap end on overlap which is antibonding, unlike in sandwich complexes. The additional MO in sandwich compounds has predominant antibonding character between the caps, which result in a negative OP in these systems. The results of the study demonstrate the significance of cap-cap interactions in the stability of higher fusions, regardless of the experimental abundance of only trans isomers in edge shared systems. The higher stability of closo edge shared $\text{B}_{10}\text{H}_{8}^{2-}$ over its nido face shared isomer is a further support for this argument.

Single vertex sandwiches with main group hetero-atoms retain the antibonding nature between the caps as in boranes despite the longer nonbonding distances. Transition metal sandwiched systems on the other hand reverse the cap-cap nature by stabilizing the MOs responsible for the antibonding interactions with its symmetry equivalent d orbitals. Heteroboranes as caps in edge shared systems tend to be antibonding unlike in boranes. The negative OP in edge shared dicarbaboranes with two CH as caps is due to the greater contribution of the cap-cap antibonding FMO to one of the in plane ring FMO. This arises from the greater electronegativity of carbon which brings down the cap FMO closer to the interacting ring FMO. Interchange of the boron and carbon atoms between the ring and caps results in positive OP between the BH caps making it similar to boranes. The positive OP at EH between ruthenium atoms in the
transition metal capped pentalene and borane complexes reflects weak bonding interactions between them; this becomes slightly antibonding at higher levels. It is therefore better to treat the pentalene complex under the mno rule rather than the 18 electron rule where a localized concept of M-M bond has to be considered. The almost equal stability of cis and trans forms of \([C_8H_6(Ru(CO)_2GeMe_3)_2]\) supports this conclusion. Appropriate macropolyhedral borane equivalents await experimental scrutiny.
REFERENCES


24. B3LYP is Becke’s three parameter hybrid method with LYP correlation functional:

