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## The Relation Between Polymorphs of Elements and Their Compounds: The Story of Boron

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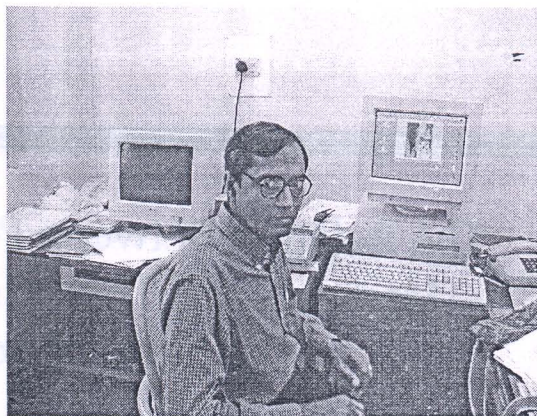
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### About the Author

Eluvathingal Devassy Jemmis was born in Chevoor, Kerala. After schooling at the village, Jemmis obtained BSc (Calicut Univ.), MSc (IIT, Kanpur) and PhD (Princeton Univ.) degrees, the latter while working with Professors Paul Schleyer, Leland Allen and John Pople. A two year postdoctoral



stint at Cornell (Professor Roald Hoffmann) followed. In 1980, Jemmis joined the School of Chemistry, University of Hyderabad. The research interests of Jemmis span a range of areas in the application of theory in the structure and reactivity problems of real life molecules, clusters and solids. He works with small and large systems using theoretical techniques ranging from the simplest of molecular orbital methods to the most sophisticated electronic structure theory depending on the system at hand and the type of questions to be answered. A constant attempt is made by Jemmis to find common threads between problems in one area to another, e.g. between organic and organometallic chemistry, amongst the chemistry of various main group elements, between polymorphs of elements and their compounds, and so on. This talk presents a solution to a problem that has puzzled Jemmis from the undergraduate days, viz. the relation between boranes, macropolyhedral boranes, elemental boron and boron-rich solids. The strategy used here lends itself to obvious extensions.

## The Relation Between Polymorphs of Elements and Their Compounds: The Story of Boron

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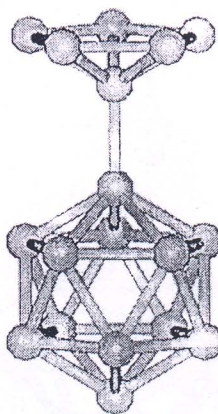
Boron is an unusual element<sup>1</sup>. Its most stable polymorph,  $\beta$ -rhombohedral boron, is harder than steel, lighter than Al and is also an intrinsic semi-conductor. Doping of carbon to  $\beta$ -rhombohedral boron results in a steady increase of microhardness, up to 6% by weight. The remarkable physical properties and chemical inertness of  $\beta$ -B<sub>105</sub> presage diverse range of industrial applications. Though polymorphs of elemental boron are recognised as covalent solids, their electronic structure is far more complex than that of the adjacent element, carbon. The relation between benzene, polycondensed aromatics and graphite is obvious. Similarly, tetracoordinate tetrahedral carbon with its  $sp^3$  hybridization is the building principle for all of saturated carbon chemistry and of diamond. In contrast, the relation between the polymorphs of elemental boron and compounds of boron is not clear at all, despite the fact that elemental boron is a covalent solid and compounds of boron, especially the boranes, are all covalent compounds. There is no general principle equivalent to the  $sp$ ,  $sp^2$  and  $sp^3$  hybridization that can be used to construct the element in a systematic fashion from the compounds of boron. Here we present the dominant building principles in the structural chemistry of boranes and use it to construct the structure of complex polymorphs of elemental boron.

One of the often-repeated structural unit in the chemistry of boranes is the icosahedral B<sub>12</sub><sup>2</sup>. However, construction of the element from the equivalent of the most stable borane B<sub>12</sub>H<sub>12</sub><sup>-2</sup> has many problems. The five-fold rotational symmetry associated with icosahedral point group is

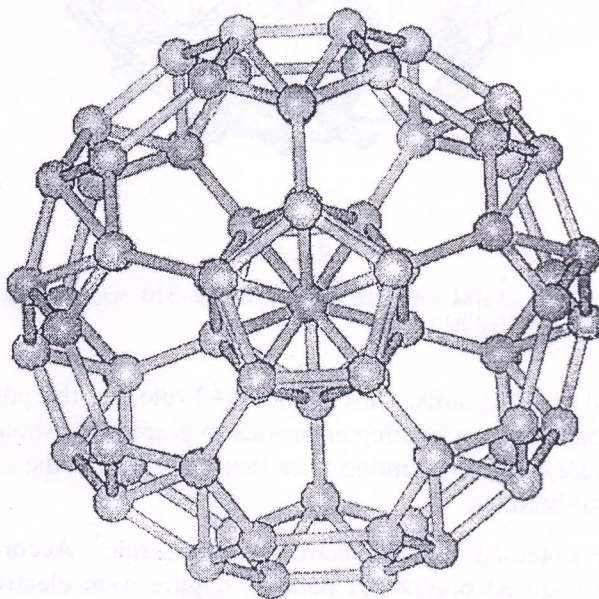
incompatible with lattice periodicity. Besides, unlike methane and benzene which are neutral building blocks of diamond and graphite,  $B_{12}H_{12}$  requires 2-electrons for stability<sup>3</sup>. Hence, its employment in a covalent network will accumulate negative charge. Obviously, the B12 based polymorphs of elemental boron should be electron deficient. The stability then should depend on the extent and the mechanism by which electron sufficiency is achieved in the lattice. We first present the structure of the thermodynamically most favorable polymorph,  $\beta$ -rhombohedral boron. The possible building blocks of the element and the borane equivalents will be discussed next. The new rules necessary to put these building blocks together will be developed. This process brings in a deeper understanding of the structural and electronic structural requirements of boron and should help in the design of novel boranes and boron rich solids.

The idealized structure of the  $\beta$ -rhombohedral boron has 105 atoms in the unit cell<sup>4</sup>. Eightyfour of them form a part of the spheroidal structure which can be best described as B12@B12@B60 (Figure 1). The structure begins with a B12 icosahedron. A pentagonal pyramidal group is attached to each of these boron atoms. The 12 five-membered rings of the pentagonal pyramids form the outer B60 skeleton similar to C60 in this B84 structure. When two such B84 units come close to each other, yet another icosahedral B12 unit emerges. However, around one B84 unit of the  $\beta$ -rhombohedral boron, only six B84 units can be brought. The remaining six five-membered rings of the B84 unit also form an icosahedral arrangement using the 21 atoms left in the unit cell (Figure 2). These B21 units are arranged as two B10 units connected by one boron atom (B10-B-B10). These B10 units have three five-membered faces each of which provides the equivalent of a pentagonal pyramidal arrangement to a different B84. In the process the B10 units have added three B6 units out of B84 to itself so that these can be separately represented as B28 (Figure 3). Two of these units are attached through the single atom completing the B10-B-B10 (B21) part of the unit cell.

We had provided an overlap and symmetry-based explanation for the unusual preference of icosahedron for boranes, in comparison to all known  $B_nH_n^{-2}$  (ref. 1). However, as mentioned above, the construction of the  $\beta$ -rhombohedral boron by assembling B12 units is not straightforward. If these building blocks were stand-alone B12 units, each such unit requires two additional electrons, which is not possible for neutral elemental boron. Obviously, new strategies have to be found for the condensation of

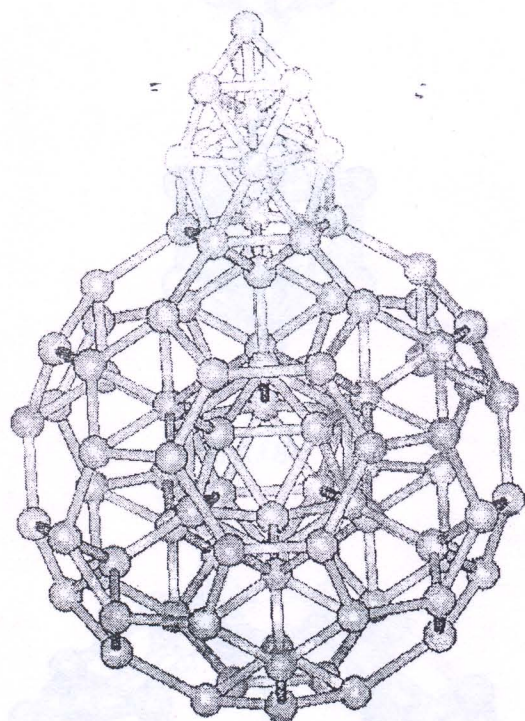


B12-B6



B84

Figure 1. The structure of B12, and the construction of B84 by attaching 12 pentagonal pyramidal units around B12.

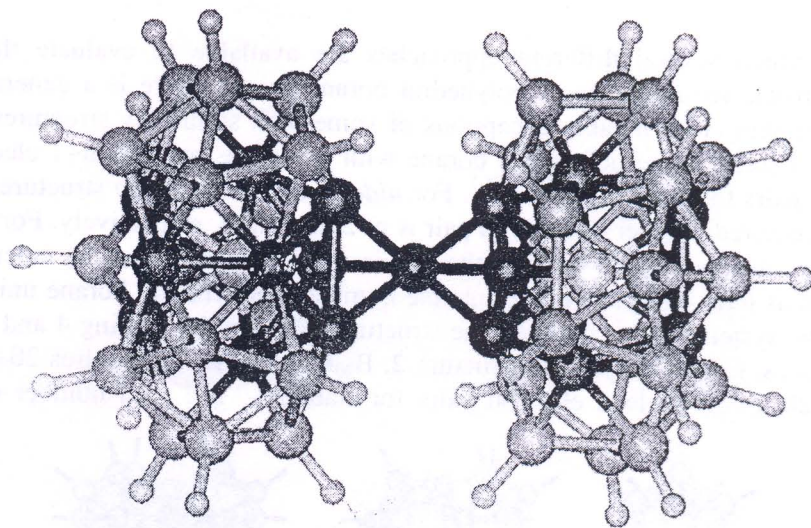


B10-B84

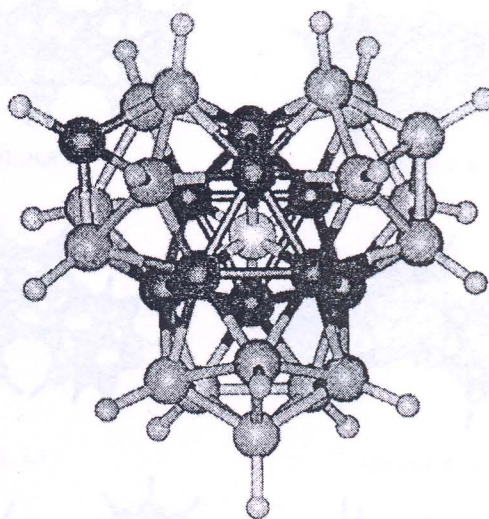
**Figure 2.** Interaction of B84 with B10 from the B10-B-B10 segment leading to the formation of new icosahedral B12 motif.

the icosahedral B12 units. Just as the  $4n+2$  rule and the polycondensation of benzene help in relating aromatics to graphite, it should be possible to generate electron counting rules that would allow the condensation of polyhedral boranes.

We have obtained such a electron counting rule<sup>5</sup>. According to this rule, polycondensed polyhedral boranes require  $n+m$  electron pairs for stability where  $n$  is the number of vertices and  $m$  is the number of polyhedra that are condensed. These results also show that the condensation of polyhedral boranes leads to the overall reduction in the electron deficiency of the system. It is impossible to extend the conventional fusion to infinity due to the accumulation of positive charge. The rule is best explained by following the existing electron count for single polyhedral borane anions.



B28-B-B28



B28

**Figure 3.** A B10 unit along with the three pentagonal pyramidal B6 units taken from three B84 structures ( below, B28). The dangling valencies are satisfied by B-H bonds. Two such units connected through the unique B atom (above B28-B-B28).

Though several different approaches are available to evaluate the electronic requirements of polyhedral borane anions, there is a general agreement (with notable exceptions of some high symmetry structures) that a stable *closo* polyhedral borane with  $n$  vertices requires  $n+1$  electron pairs to bind the skeleton<sup>6,7</sup>. For *nido*, *arachno* and *hypo* structures, the required number of electron pair is  $n+2$ ,  $n+3$ ,  $n+4$ , respectively. For a poly-condensed *closo*-borane, the required electron pairs can be calculated as  $n+m$ , where  $m$  represents the number of polyhedral borane units in the system. Let us consider the structures obtained by sharing 4 and 3 vertices, respectively. The structure 2,  $B_{20}H_{16}$  (Figure 4) requires  $20+2$  ( $n=20$ ,  $m=2$ ) skeletal electron pairs for stability. The total number of

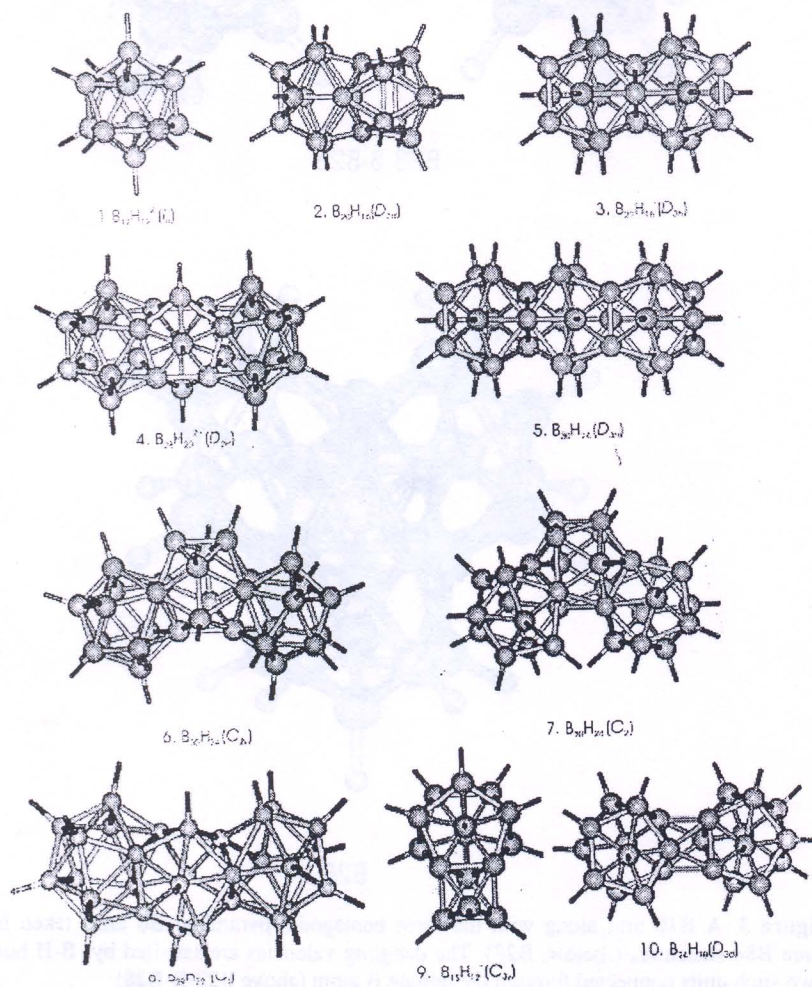


Figure 4. Polycondensed polyhedral boranes 1-10 demonstrating the electron counting rules



electron pairs available is also 22, (one electron pair from each of the 16 B-H groups and 6 electron pairs from the four shared boron atoms), so that **2** is neutral in accordance with the experimental finding. The structure **3** ( $B_{21}H_{18}$ ), obtained by sharing three vertices between two icosahedra, has 21 vertices and two polyhedral units. So the number of skeletal electron pair required is 23 (i.e.,  $21+2$ ). The total number available is only 22.5 (18 from the B-H group and 4.5 from the three shared boron atoms). Thus structure, **3** requires a negative charge, so that  $B_{21}H_{18}^{-1}$  is a stable species as predicted earlier.

A triple-polyhedral system,  $B_{28}H_{20}$  (**4**,  $D_{3h}$ ), is obtained by the condensation of another unit to **2** by sharing four vertices. By the  $n+m$  rule, it requires 31 electron pairs ( $28+3$ ).  $B_{28}H_{20}$  has 32 electron pairs. Thus, the dication  $B_{28}H_{20}^{2+}$  should be the stable species. Extension of **3** in a similar fashion leads to  $B_{30}H_{24}$  (**5**). The  $n+m$  electron pair rule gives 36 electron pairs for **5**. The molecular formula provides the same number so that **5** should be neutral as was intuitively expected by Lipscomb. The next higher member in the series 1, 3, 5 is  $B_{39}H_{30}^{+1}$ . This homologous series can be represented by the molecular formula  $B_{9x+12}H_{6x+12}^{x-2}$  ( $x = 0, 1, 2$  etc). Obviously, the positive charge increases quickly so that higher members will be unfavorable without appropriate substitutions such as Be in the place of B. Similarly, the series 1, 2, 4 has the molecular formula  $B_{8x+12}H_{4x+12}^{2x-2}$  ( $p = 0, 1, 2 \dots$ , etc). Here the charge increases by two with unit increase in  $m$ , so that the higher members will be unfavorable. Condensation of more than two polyhedra brings in isomerism akin to those of anthracene and phenanthrene. For example, **6** ( $C_{2v}$ ) and **7** ( $C_2$ ) are isomers of **5** ( $D_{3h}$ ).

A variety of mixing and matching is possible in poly-condensed polyhedral boranes. Structure **2** can be condensed with icosahedral  $B_{12}H_{12}^{-2}$  by sharing three vertices to give  $B_{29}H_{22}^{+}$  (**8**). Obviously, several isomers are possible. It is not necessary to limit the condensation among identical polyhedra. For example, condensation of an octahedron with an icosahedron by sharing three vertices leads to  $B_{15}H_{12}^{-1}$  (**9**). Condensation with another icosahedral  $B_{12}$  symmetrically, leads to the neutral  $B_{24}H_{18}$  (**10**). The possibilities are endless. Amongst these structures  $B_{20}H_{16}$  (**2**) has been known for a long time<sup>3</sup>. The  $B_{21}$  skeleton of **3** is shown to be a part of the tetragonal boron polymorph.

The  $n+m$  electron count can be extended to include common polyhedral fragments such as the *nido*, *arachno* and *hypo* variety by adding the appropriate number of electron pairs. Thus, the condensation of one *nido* and one *closo* polyhedron requires  $n+m+1$  electron pairs. For example,

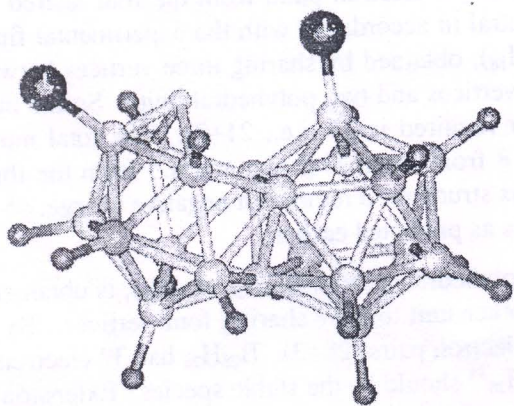
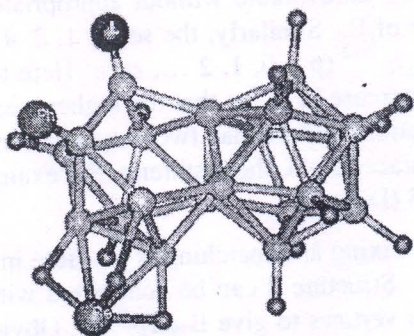
11.  $B_{20}H_{16}L_2$  (C.)12.  $(PMe_2Ph)_2HR_eB_{20}H_{16}Ph(PHMe_2)$  (C.)

Figure 5. Two examples of nido-hetero-boranes that follow the new electron count.

$B_{20}H_{16}$  (2) is found to add with bases to form stable molecules of the type  $B_{20}H_{16}L_2$  viz.,  $B_{20}H_{16}(NCCH_3)_2$ ,  $B_{20}H_{16}(S(CH_3)_2)_2$ ,  $B_{20}H_{16}(N(CH_3)_3)_2$ ,  $B_{20}H_{16}(P(C_6H_5)_3)_2$ ,  $B_{20}H_{16}(OC_2H_5)_2$  without any release of hydrogen<sup>9</sup>. The structure of  $B_{20}H_{16}(CH_3CN)_2$  has been characterized experimentally (11, Figure 5). This structure can be formally derived from 3 by removing a B-H vertex. With the condensation of a *closo* and a *nido* fragment the skeleton represented by 11 requires 23 ( $n=20$ ,  $m=2$  and one for *nido*) electron pairs. In the  $B_{20}H_{16}(CH_3CN)_2$ , the 15 B-H groups provide 15 electron pairs. Three shared borons provide 4.5 lone pairs. Since the lone

pair on the nitrogen is involved in the  $N^+ \rightarrow B^-$  dative bond, these two boron atoms have an extra electron for skeletal bonding. This adds up to 22.5 electron pairs. The remaining one electron is obtained from the bridging hydrogen. Since the primary motif for these reactions is to form *nido*- $B_{20}H_{16}L_2$  skeleton with the L having its own lone pair for B-L bond, all the other unresolved structures should be similar though the position of L-substitution may differ.  $B_{20}H_{16}$  reacts with water to form a strong acidic solution forming a product of unknown structure with the characteristics of a diprotic acid<sup>9</sup>. The molecular structure is not resolved but the composition is found to be  $[B_{20}H_{16}(OH)_2]^{2-} \cdot 2[H_3O]^+$ . The electron count rule helps to visualise the structure of this compound. The polyhedral skeleton may remain the same as that of **11** but here, the nature of the O-B bond requires one electron from boron, similar to that of the *exo*-B-H bond. This makes the skeleton electron deficient and hence requires two more electrons to attain stability. Other adducts like  $[B_{20}H_{16}(OH)_2]^{2-} [N(CH_3)_4]^{2+}$  and  $[Cs^+]_2 [B_{20}H_{16}(OC_2H_5)_2]^{2-}$  can be deduced in a similar way.

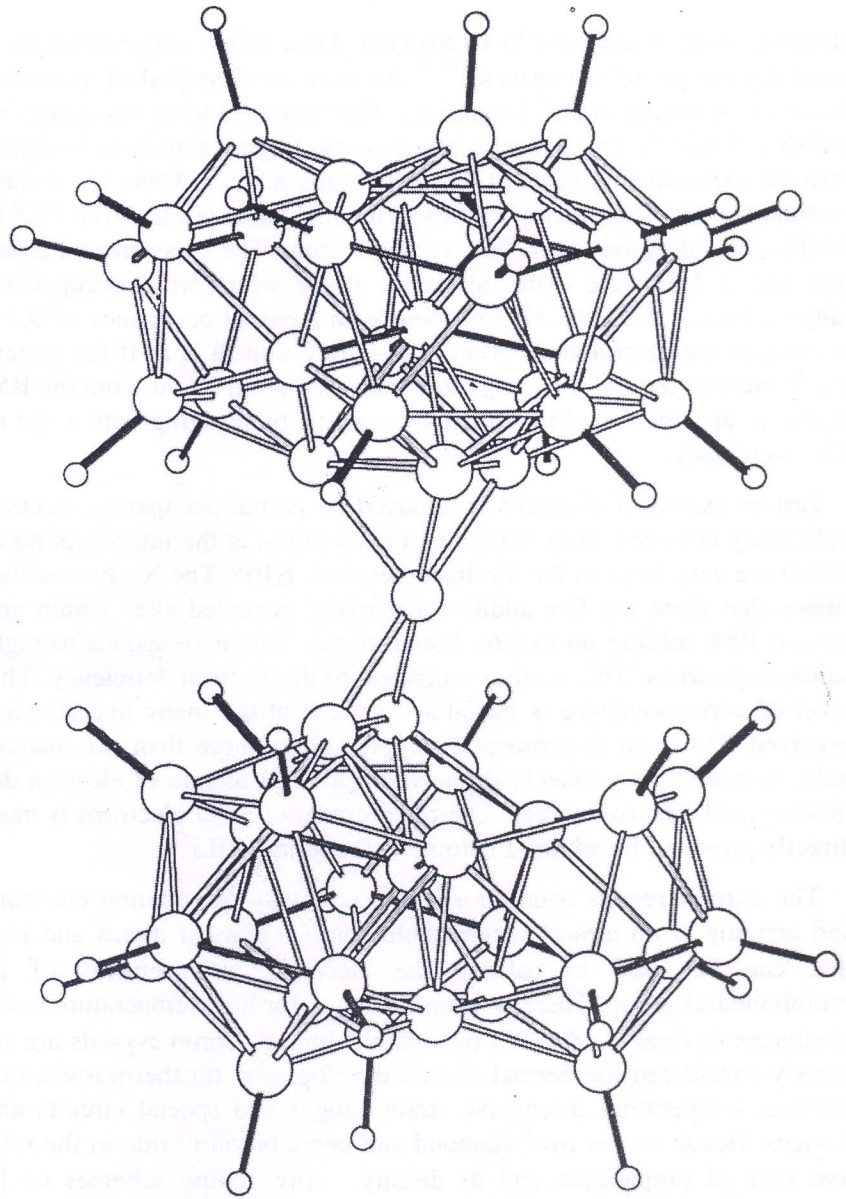
Even hetero-boranes follow the electron count. For example, the electronic requirements of the recently reported metalloborane  $[(PMe_2Ph)_3HReB_{20}H_{15}Ph(PHMe_2)]$  **12** (Figure 5), can be understood in this way. The number of skeletal electron pairs required by the rule remains 23, same as that of **11**. The 15 B-H groups and one B-Ph in **12** give 16 electron pairs. The  $Me_2HP \rightarrow B$  vertex contributes 1.5 electron pairs. The three shared borons contribute 4.5 electron pairs, making a total of 22 electron pairs so far. The remaining two electrons are obtained by an equally ingenious transition metal bridge.  $Re(PMe_3)_3H$  requires 4 electrons to satisfy the 18 electrons rule of the metal. This is achieved by accepting two B-H bond pairs as ligands, so that two 3c-2e bridge involving Re, B and H are formed. This would however leave the B<sub>20</sub> skeleton without its share of two electrons. Re becomes more generous by sharing an additional B-H bond so that the extra electrons can be put to the boron skeleton. There are hundreds of examples that can be explained by this rule. Just about all methods used in justifying the  $n+1$  electron pair rule of polyhedral boranes can be used in the  $n+m$  electron count rule as well.

The  $n+m$  rule does not include single vertex bridging as in the central atom of the B<sub>5</sub>-B-B<sub>5</sub> unit. Without going into the theoretical justification, we present that the single vertex bridging compounds require an additional electron pair for skeletal bonding. Thus, the new electron counting rule—the *mno* rule—has the third variable “o” representing

the number of single-vertex bridging<sup>11</sup>. This rule helps in bringing polycondensed polyhedral boranes, metalloboranes and metallocenes under the same umbrella. For example,  $\text{Al}(\text{C}_2\text{B}_9\text{H}_{11})_2^{-1}$ , with one single-vertex bridging Al atom, must have 26 electron pairs ( $m=23$ ,  $n=2$  and  $o=1$ )<sup>12</sup>. The total number available is also 26 (18BH, 6C-H, 1.5Al and .5 from the negative charge). Ferrocene ( $\text{C}_5\text{H}_5$ )<sub>2</sub>Fe can be considered as a combination of *nido* structures connected through a single atom bridge, Fe. Thus, according to the mno rule, there must be 16 electron pairs ( $m=2$ ,  $n=11$ ,  $o=1$ , and an additional two for the two *nido* arrangements). The total number is also 16 [15 from 10CH, 1 from Fe(II)].

Armed with these electron counting rules, let us get to the structure of  $\beta$ -rhombohedral boron. The B84 unit could be divided into 4B12 units and the B28-B-B28 units. The latter may be disconnected from the solid by breaking 36 B-B bonds, much the same way a naphthalene frame may be cut out from graphite. The dangling valencies can be saturated to give  $\text{B}_{57}\text{H}_{36}$  (Figure 3) just as naphthalene,  $\text{C}_{10}\text{H}_8$ . The application of the mno rule shows that there has to be 66 electron pairs ( $m=8$ ,  $n=57$ ,  $o=1$ ). The number of electron pairs available is 67.5 (36 from 36BH, 31.5 from B21). Thus  $\text{B}_{57}\text{H}_{36}$  must have +3 charge, contrary to the expectations of electron deficiency. Calculations indicate that  $\text{B}_{57}\text{H}_{36}^{+3}$  has all characteristics of a highly delocalized aromatic system<sup>13</sup>. B48 on the other hand is electron deficient. The two negative charge of the stable  $\text{B}_{12}\text{H}_{12}^{-2}$  implies that the B48 part needs 8 electrons. In an idealized structure three out of these eight could be obtained from the B57 part. Thus, the B105 unit cell of  $\beta$ -rhombohedral boron is deficient by 5 electrons. This electron count is in tune with the band structure calculations carried out by Bullet as early as 1982. The properties of elemental boron do not, however, fit with this description of the electronic structure. Nature finds an ingenious way to salvage the situation, taking lessons from boranes again.

The *nido*, *arachno*, and *hypo* boranes are polyhedral boranes which have one two and three missing vertices, but which require the same number of skeletal bonding electrons. For example,  $\text{C}_2\text{B}_9\text{H}_{13}$  is a stable icosahedral structure where one vertex is missing, but has the same number of skeletal bonding electrons<sup>14</sup>. The easiest way of alleviating the excess electrons in the B57 region is to knock off an atom so that three valence electrons are decreased. Figure 6 shows the B56 structure where a boron atom is deleted, with least disturbance to the structure. The  $\text{B}_{56}\text{H}_{36}$  structure that is left behind requires 66 electron pairs ( $8+56+1+1$ , the last one to account for a *nido* corner that is generated). The actual



B56

Figure 6. The B56 structure with the partial occupancy demanded by the electron count and observed in the  $\beta$ -rhombohedral structure.

dental or to be ignored, but is to be traced to the electronic structural requirements.

The process of finding the mode of understanding to connect boranes to the  $\beta$ -rhombohedral boron also brings about several structural possibilities for novel boranes. The nature of B57 has prompted the series of stuffed boranes<sup>18</sup>. The family of YB66 structures have led to the unusual possibility of a benzyne equivalent B12H10 structure<sup>19</sup>. The larger polyhedral structures that are possible with polycondensation should help in designing better candidates for boron neutron capture therapy of cancer. Story of boron and boranes is only beginning to be written. The process brings in new modalities of understanding in chemistry.

### Acknowledgements

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