Inorg. Chem. **2001,** *40,* 6369−6374

Defective Vertices in *closo*- and *nido*-Borane Polyhedra

R. B. King

Department of Chemistry, University of Georgia, Athens, Georgia 30602

Received June 11, 2001

Boron polyhedra can be described in terms of the deviation of their local vertex environments from the degree 5 vertices found in ideal icosahedra. Vertices of degrees other than 5 can be considered to be defective vertices. The most favorable structures for borane polyhedra are those in which the defective vertices are isolated as much as possible, similar to the Frank−Kasper polyhedra found in metal alloy structures. Using this criterion, the 9- and 10-vertex borane deltahedra are seen to be more favorable than the other nonicosahedral deltahedra in the boranes $B_nH_n^{2-}$ ($6 \leq n \leq 12$) in accord with experimental observations. Extension of such ideas to neutral boron hydrides of the type B_nH_{n+4} accounts for the relatively high stability of $B_{10}H_{14}$, the formation of metal complexes of B_6H_{10}, and the stability of $B_{18}H_{22}$. In addition, the borane $B_{12}H_{16}$ is predicted to form stable transition-metal complexes.

1. Introduction

The most stable molecular boron cages, such as $B_{12}H_{12}^{2-}$ and $C_2B_{10}H_{12}$, are based on icosahedral structures.[1,2] In addition, icosahedral cages are found in the stable allotropes of boron and many of the most stable metal borides.[3,4] This paper presents a new approach to the description of boron polyhedra in terms of the deviation of their local vertex environments from those found in ideal icosahedra. This method complements other methods for the study of borane structures, including the topological methods of Lipscomb[5] leading to localized bonding models as well as methods based on graph theory[6] or tensor surface harmonics[7] for the study of three-dimensional aromaticity.[8]

A preliminary discussion of this method as applied to deltahedral boranes was presented at the 10th International Conference on Boron Chemistry in 1999.[9] This paper extends this work to *nido*-boranes of the general formula B_nH_{n+4}. Such *nido*-boranes for $n = 10$ are derived from a single deltahedron by the removal of a highest-degree vertex. The *nido*-boranes for $12 \leq n \leq 18$ are derived from a pair of edge-sharing deltahedra by removing one vertex from each deltahedron.

2. Background

The characteristic feature of the geometry of a regular icosahedron is the presence of 12 equivalent vertices of degree 5, where the degree of a vertex is defined as the number of edges meeting at that vertex. If the unusual stability of borane icosahedra can be attributed to the special stability of degree 5 boron vertices, then vertices of degrees other than 5 can be considered to be defects in the deltahedral borane structure. The most favorable borane polyhedra are those with the minimum number of such defective vertices and with the defective vertices as widely spaced as possible. Conversely, the defective vertices are potential sites of chemical reactivity in borane deltahedra.

Computational studies on boranes during the past 2 decades support the assumption of a special stability for degree 5 boron vertices. Thus, Jemmis and Pavankumar[10] use MINDO calculations on pyramidal boron units in borane structures to show that pentagonal-pyramidal B_6 units corresponding to degree 5 vertices for the central (apical) boron atoms are energetically more favorable than square-pyramidal B_5 units corresponding to degree 4 vertices for the apical boron atoms. In addition, Boustani[11] has shown, by ab initio computations, that pentagonal-pyramidal B_6 units are favorable building blocks for bare boron clusters. Also, in theoretical papers spanning more than 20 years,[12−14] Williams has recognized the special stability of degree 5 boron vertices. He refers to vertices of degrees 3−6 as hot, warm, cool, and frozen, respectively, and designates them by black hexagons, open squares, solid dots, and open triangles, respectively. This designation will be used for the figures in this paper.

The idea of defective vertices is not original but was used by Frank and Kasper more than 40 years ago to study polyhedra found in metal alloy structures.[15] In such Frank−Kasper polyhedra, the defective vertices are vertices of degree 6. Frank and Kasper showed that there are only four polyhedra (Figure 1) having only degree 5 and 6 vertices and with isolated degree 6 vertices (i.e., no pair of degree 6 vertices is connected by an edge).

---

(1) *Boron Hydride Chemistry*; Muetterties, E. L., Ed.; Academic Press: New York, 1975.
(2) Grimes, R. N. *Carboranes*; Academic Press: New York, 1970.
(3) Hoard, J. L.; Hughes, R. E. In *Chemistry of Boron and its Compounds*; Muetterties, E. L., Ed.; Wiley & Sons: New York, 1967; pp 25−154.
(4) *Boron-Rich Solids*; American Institute of Physics Conference Proceedings 140; Emin, D., Aselage, T., Beckel, C. L., Howard, I. A., Woods, C., Eds.; American Institute of Physics: Melville, NY, 1986.
(5) Lipscomb, W. N. *Boron Hydrides*; Benjamin: New York, 1963; Chapter 2.
(6) King, R. B.; Rouvray, D. H. *J. Am. Chem. Soc.* **1977**, *99*, 7834.
(7) Stone, A. J.; Alderton, M. J. *Inorg. Chem.* **1982**, *21*, 2297.
(8) King, R. B. *Chem. Rev.* **2001**, *101*, 1119.
(9) King, R. B. In *Contemporary Boron Chemistry*; Davidson, M., Hughes, A. K., Marder, T. B., Wade, K., Eds.; Royal Society of Chemistry: Cambridge, U.K., 2000; p 506.
(10) Jemmis, E. D.; Pavankumar, P. N. V. *Proc.—Indian Acad. Sci., Chem. Sci.* **1984**, *93*, 479.
(11) Boustani, I. *J. Solid State Chem.* **1997**, *133*, 182.
(12) Williams, R. E. *Inorg. Chem.* **1971**, *10*, 210.
(13) Williams, R. E. *Adv. Inorg. Chem. Radiochem.* **1976**, *18*, 67.
(14) Williams, R. E. *Chem. Rev.* **1992**, *92*, 177.
(15) Frank, F. C.; Kasper, J. S. *Acta Crystallogr.* **1958**, *11*, 184.

10.1021/ic0106165 CCC: $20.00

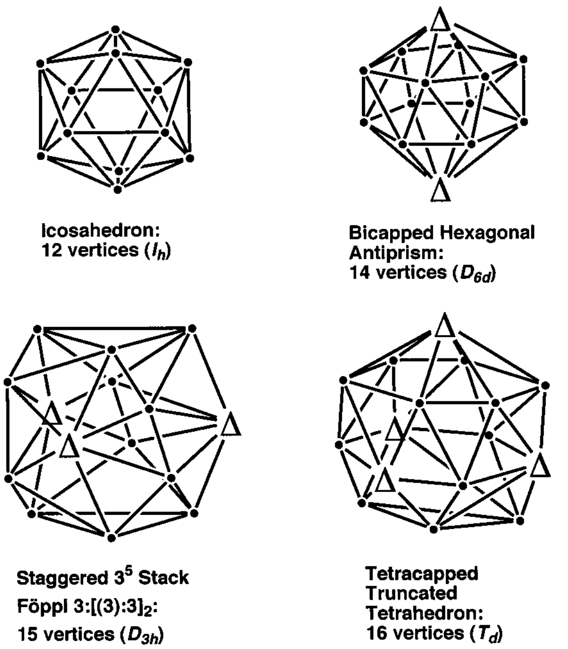


Figure 1. Four Frank–Kasper polyhedra. Vertices of degrees 4–6 are indicated by □, ●, and △, respectively, in accord with the practice of Williams.[14]

The deltahedra for the stable cage boranes (i.e., $B_nH_n^{2-}$ and their carborane analogues with $6 \leq n \leq 12$) are characterized by having no degree 3 vertices and having only degree 4 or 5 vertices (Figure 2) except for the $B_{11}H_{11}^{2-}$ polyhedron, which is topologically required to have at least one degree 6 vertex.[16] In such boranes, the defective vertices can be considered to be the vertices of degree 4. Among borane deltahedra other than the icosahedron, only the bicapped square antiprism of $B_{10}H_{10}^{2-}$ and the tricapped trigonal prism of $B_9H_9^{2-}$ are seen to meet a Frank–Kasper-like criterion of isolated degree 4 vertices (Figure 2).

Equations of balance, similar to those used by Lipscomb and Dickerson[5,17,18] for orbital and electron balance in polyhedral boranes, can also be applied to the balance of their vertex degrees. For a regular deltahedron with v vertices, e edges, and f faces, consider Euler's theorem (eq 1), the presence of only triangular faces, and the sharing of each edge by exactly two faces (eq 2) so that

$$v - e + f = 2 \tag{1}$$

and

$$3f = 2e \tag{2}$$

Combining eqs 1 and 2 gives

$$e = 3v - 6 \tag{3}$$

Now consider a deltahedron in which all of the vertices have the ideal degree of 5 so that

$$5v = 2e \tag{4}$$

Solving eqs 3 and 4 simultaneously leads to $v = 12$, in accord with the fact that the regular icosahedron is the unique deltahedron where all of the vertices are of degree 5.

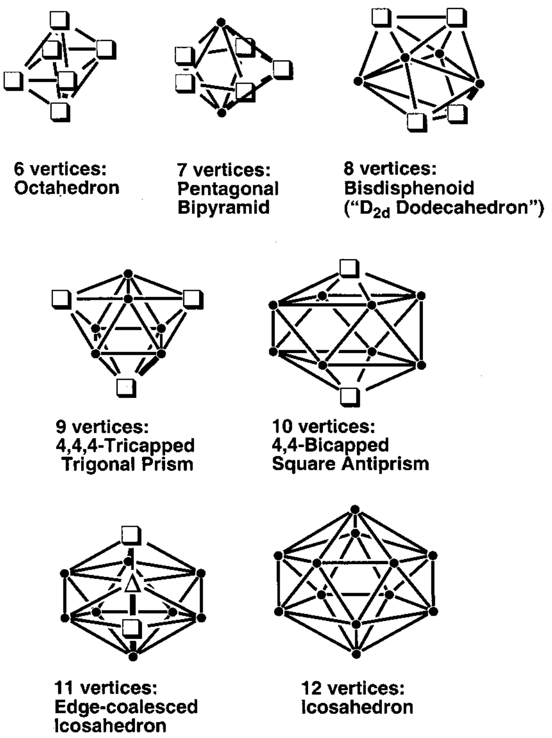


Figure 2. Deltahedra found in boranes $B_nH_n^{2-}$ ($6 \leq n \leq 12$). Each vertex in this and subsequent figures is a BH group unless otherwise indicated.

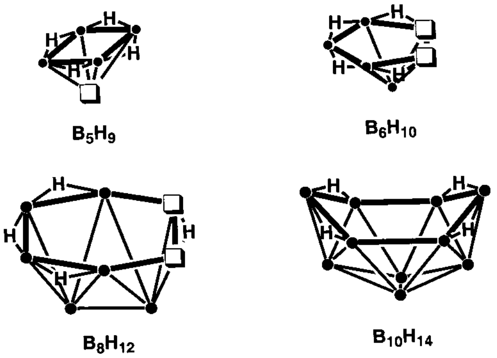


Figure 3. Known *nido*-boranes B_nH_{n+4} ($n = 5, 6, 8, 10$) showing the four bridging hydrogen atoms in each structure. In this and subsequent figures, the edges of the open face(s) are shown as bold lines.

Now, let us apply similar reasoning to *nido*-boranes of the general formula B_nH_{n+4}. Such boranes have structures based on a polyhedral fragment obtained by the removal of one vertex and its associated edges from a closed deltahedron with $n + 1$ vertices (Figure 3). An open face or hole is generated having h edges (i.e., a polygonal hole with h sides), where h corresponds to the degree of the vertex deleted from the $n + 1$ vertex closed deltahedron. Now, assume that each boron atom has an external terminal hydrogen atom, thereby accounting for all except four of the hydrogen atoms in the B_nH_{n+4} structure. These four extra hydrogen atoms generally appear as bridges across the pairs of boron atoms bordering the open face. The degrees of the border boron atoms are equal to the sums of the numbers of their edges to the other boron atoms and their additional edges to the bridging hydrogen atoms.

The $n + 1$ vertex closed deltahedra, from which the *nido*-B_nH_{n+4} boranes are derived, have $3(n + 1) - 6$ edges, in accord with eq 3 where $v = n + 1$. Removal of a vertex of degree h from such an $n + 1$ vertex deltahedron leads to $3(n + 1) - 6 - h$ edges in the resulting B_nH_{n+4} borane framework. To this

---

(16) King, R. B.; Duijvestijn, A. J. W. *Inorg. Chim. Acta* **1990**, *178*, 55.
(17) Dickerson, R. E.; Lipscomb, W. N. *J. Chem. Phys.* **1957**, *27*, 212.
(18) Lipscomb, W. N. In *Boron Hydride Chemistry*; Muetterties, E. L., Ed.; Academic Press: New York, 1975; pp 30–78.

must be added the additional edges provided by the hydrogen atoms bridging the open face. For the B_nH_{n+4} derivatives based on a single boron polyhedron, there are necessarily four bridging hydrogen atoms leading to four such additional edges. Combining this information leads to the following equation for B_nH_{n+4} boranes in which all of the vertices are of degree 5:

$$3(n + 1) - 6 - h + 4 = 3n - h - 1 = {}^5\!/_2 n \qquad (5a)$$

$$\Rightarrow n = 2h - 2 \qquad (5b)$$

Substituting $h = 6$ corresponding to a hexagonal open face into eq 5b leads to $n = 10$ corresponding to decaborane $B_{10}H_{14}$, which is the most stable of the *nido*-B_nH_{n+4} boranes.

Now, consider a B_nH_{n+4} derivative with a tetragonal open face so that $h = 4$ in eq 5b. This leads to a solution of $n = 6$, implying the possibility of a B_6H_{10} hexaborane with a tetragonal open face and with all degree 5 vertices, including the bridging hydrogen atoms. Such a hexaborane would need to be derived from a six-vertex polyhedron having one quadrilateral face and six triangular faces. The four vertices of the quadrilateral face are all required to have a degree of 3 in order to accommodate two bonds (edges) each to the bridging hydrogen atoms, whereas the remaining two vertices, which are not part of the quadrilateral face, are required to have a degree of 5. Such a polyhedron is topologically impossible.[19,20] In fact, the hexaborane B_6H_{10} has a pentagonal-pyramidal structure with a pentagonal open face and two adjacent degree 4 basal vertices. The presence of these two adjacent degree 4 basal vertices makes B_6H_{10} significantly less stable than B_5H_9, with only a single degree 4 vertex, or $B_{10}H_{14}$, with only degree 5 vertices.

Now, consider a B_nH_{n+4} derivative with a pentagonal open face so that $h = 5$ in eq 5b. This leads to a solution of $n = 8$, suggesting the possibility of a B_8H_{12} octaborane with a pentagonal open face with all degree 5 vertices, considering the bridging hydrogen atoms. Such a structure would be derived from an eight-vertex polyhedron having one pentagonal face and nine triangular faces, with three vertices of the pentagonal face having a degree of 3 and the other two vertices of the pentagonal face having a degree of 4. This pattern of vertex degrees on the pentagonal face can accommodate the four required bridging hydrogen atoms to give all degree 5 vertices in the B_8H_{12} structure, including the bridging hydrogen atoms. Inspection of a listing of all 257 topologically distinct polyhedra with eight vertices[19] or of the corresponding listing of the 257 dual polyhedra with eight faces[20] reveals 13 topologically distinct polyhedra with the required three vertices of degree 5, two vertices of degree 4, and three vertices of degree 3. Among these 13 polyhedra, seven meet the requirement of the three degree 5 vertices forming a triangular face. However, among these seven polyhedra, none meet the requirement of the two degree 4 vertices and the three degree 3 vertices forming the single pentagonal face. Thus, a *nido*-B_8H_{12} with a pentagonal open face with all degree 5 vertices (including the four bridging hydrogen atoms) is topologically impossible, even though $n = 8$ is the solution of eq 5b for $h = 5$. In fact, the known *nido*-B_8H_{12} has a structure with a hexagonal open face and two adjacent degree 4 vertices.

3. Deltahedral Boranes

The idea that vertices of degree 4 are defective vertices and are sites of potential reactivity is consistent with experimental observations on the deltahedral borane anions $B_nH_n^{2-}$ ($6 \leq n \leq 12$). For example, their hydrolytic stability decreases in the approximate sequence[21]

$$B_{12}H_{12}^{2-} > B_{10}H_{10}^{2-} > B_{11}H_{11}^{2-} > B_9H_9^{2-} \sim B_8H_8^{2-} \sim B_6H_6^{2-} > B_7H_7^{2-}$$

Thus, the most hydrolytically stable borane anions are those in which there are no adjacent degree 4 vertices, notably $B_{10}H_{10}^{2-}$ and $B_9H_9^{2-}$ as well as $B_{11}H_{11}^{2-}$. In addition, the generation of $B_nH_n^{2-}$ by the pyrolysis of CsB_3H_8 is known to lead only to $B_{12}H_{12}^{2-}$, $B_{10}H_{10}^{2-}$, and $B_9H_9^{2-}$, which are the only deltahedral boranes without adjacent degree 4 vertices.[22]

The pentagonal-bipyramidal $B_7H_7^{2-}$, which has an equatorial pentagon of degree 4 vertices but no triangular faces containing exclusively degree 4 vertices (Figure 2), is the most reactive toward hydrolysis. In $B_7H_7^{2-}$, a proton can attack an equatorial edge, converting the degree 4 vertices of this edge to degree 5 vertices. This can ultimately lead to neutral B_7H_9 with two such protonated equatorial edges. A neutral borane of this type, like the known neutral boranes, is likely to be much more reactive toward hydrolytic degradation than the deltahedral boranes, thereby providing a plausible mechanistic pathway for the hydrolysis of $B_7H_7^{2-}$.

The octahedral borane $B_6H_6^{2-}$ is unique among the known deltahedral boranes not only in having all degree 4 vertices but also necessarily in having (triangular) faces composed exclusively of degree 4 vertices (Figure 2). In this connection, $B_6H_6^{2-}$, although highly symmetrical, is only obtainable in relatively low yield in cage borane syntheses.[23,24] Furthermore, $B_6H_6^{2-}$ may be regarded as an unsaturated deltahedral borane, because it is unusually reactive toward addition reactions in which its degree 4 vertices effectively become degree 5 vertices.[25] For example, protonation of $B_6H_6^{2-}$ to give $B_6H_7^-$ occurs much more readily ($pK_a = 7.00$)[26] than the protonations of other $B_nH_n^{2-}$ ions to give the corresponding $B_nH_{n+1}^-$ ions so that the aqueous solutions of alkali-metal salts of $B_6H_6^{2-}$ are significantly basic owing to the equilibrium $B_6H_6^{2-} + H_2O = B_6H_7^- + OH^-$. In $B_6H_7^-$, the extra hydrogen atom caps one of the triangular faces of the $B_6H_6^{2-}$ octahedron so that three of the degree 4 vertices become degree 5 vertices through multicenter bonding with this extra hydrogen atom. Similarly, $B_6H_6^{2-}$ acts as a tridentate ligand in metal complexes such as $[n\text{Bu}_4\text{N}][(\eta^3\text{-}B_6H_6)_2\text{Cd}]$,[27] $(\text{Ph}_3\text{P})_2\text{M}(\eta^3\text{-}B_6H_6)$ (M = Cu and Au),[28] and $[n\text{Bu}_4\text{N}][\text{Ni}(\eta^5\text{-}C_5H_5)(\eta^3\text{-}B_6H_6)]$.[24]

4. *nido*-Boranes B_nH_{n+4} ($5 \leq n \leq 11$)

The *nido*-boranes B_nH_{n+4} are derived from $n + 1$ vertex deltahedra by the removal of a vertex, usually a vertex of the highest degree. The removal of such a vertex of degree *h* gives a nontriangular face or a hole consisting of a polygon with *h* edges. Each boron in a *nido*-borane has a single terminal hydrogen. The extra four hydrogens in B_nH_{n+4} appear as bridges across the edges of the open face. The degrees of the boron vertices bordering the open face include edges representing links

---

(19) Britton, D.; Dunitz, J. D. *Acta Crystallogr.* **1973**, *A29*, 362.

(20) Federico, P. J. *Geom. Ded.* **1975**, *3*, 469.

(21) Middaugh, R. L. In *Boron Hydride Chemistry*; Muetterties, E. L., Ed.; Academic Press: New York, 1975; p 283.

(22) Klanberg, F.; Muetterties, E. L. In *Inorganic Syntheses*; Jolly, W. L., Ed.; McGraw-Hill: New York, 1968; Vol. 11, p 27.

(23) Boone, J. L. *J. Am. Chem. Soc.* **1964**, *86*, 5036.

(24) Kabbani, R. M. *Polyhedron* **1996**, *15*, 1951.

(25) Preetz, W.; Peters, G. *Eur. J. Inorg. Chem.* **1999**, 1831.

(26) Preetz, W.; Heinrich, A.; Thesing, J. *Z. Naturforsch.* **1988**, *43B*, 1319.

(27) Schaper, T.; Preetz, W. *Inorg. Chem.* **1998**, *37*, 363.

(28) Schaper, T.; Preetz, W. *Chem. Ber. Recl.* **1997**, *130*, 405.

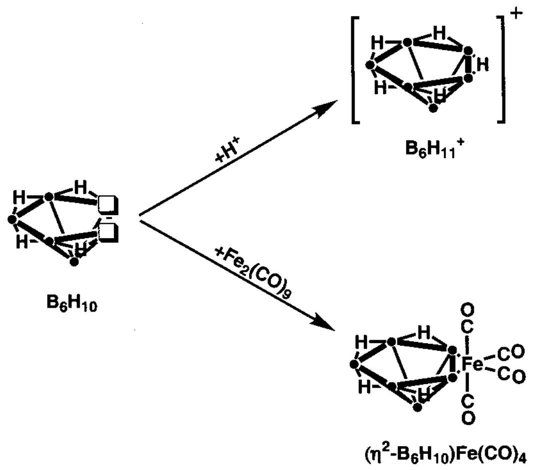


Figure 4. Reactivity of B_6H_{10} toward H^+ and $Fe_2(CO)_9$.

to the nearest-neighbor boron atoms as well as edges representing links to the bridging hydrogen atoms. The structures of the known *nido*-boranes B_nH_{n+4} are depicted in Figure 3, with the edges of the open face designated by bold lines. The defective vertices in these structures are indicated by the same symbols as those used for the deltahedra in Figure 2.

The most stable and readily formed of the *nido*-boranes is decaborane ($B_{10}H_{14}$), which is an air-stable solid obtained by the pyrolysis of diborane.[29] Decaborane has a nido structure with a hexagonal open face and with all of the boron vertices of degree 5 (i.e., no defective vertices; Figure 3). All of the other *nido*-boranes have structures with defective vertices. Thus, the known structures of hexaborane (B_6H_{10})[30] and octaborane (B_8H_{12})[31] have pentagonal and hexagonal open faces, respectively, with two adjacent degree 4 vertices in each case (Figure 3). The presence of two adjacent degree 4 vertices in B_6H_{10} is related to the following aspects of its chemical reactivity (Figure 4): (1) protonation[32] to give $B_6H_{11}^+$ isolated at low temperatures as the salt $[B_6H_{11}][BCl_4]$ and (2) formation of transition-metal complexes[33] such as $(\eta^2\text{-}B_6H_{10})Fe(CO)_4$, *trans*-$(\eta^2\text{-}B_6H_{10})_2PtCl_2$, and $[(\eta^2\text{-}B_6H_{10})MCl]_2$ (M = Rh, Ir).

The two adjacent degree 4 vertices in B_8H_{12} are not analogous to the two adjacent degree 4 vertices in B_6H_{10}, because they are of degree 4 even after being bridged by a hydrogen atom (Figure 3). The presence of two adjacent hydrogen-bridged vertices in B_8H_{12} of such low degrees may account for the low thermal stability of B_8H_{12}. Thus, the reported[31] decomposition temperature of B_8H_{12} is -20 °C.

The chemistry of *nido*-boranes B_nH_{n+4} with odd numbers of boron atoms is much more limited except for pentaborane (B_5H_9), a spontaneously flammable liquid that, like $B_{10}H_{14}$, is a pyrolysis product of diborane.[34] Pentaborane has a square-pyramidal structure with its four bridging hydrogen atoms around the base so that the basal vertices become degree 5 vertices. The only defective vertex in B_5H_9 is the apex, which has a degree of 4. The presence of only one defective degree 4 vertex may account for the fact that B_5H_9 is the most stable B_nH_{n+4} borane except for $B_{10}H_{14}$, which has only degree 5 vertices.

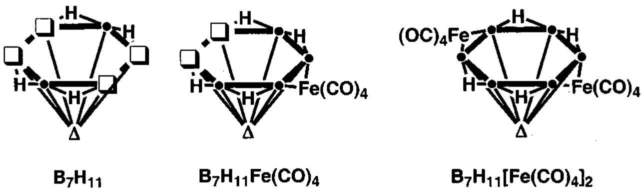


Figure 5. Hexagonal-pyramidal structures for the hypothetical B_7H_{11}, the known $B_7H_{11}Fe(CO)_4$, and the currently unknown $B_7H_{11}[Fe(CO)_4]_2$.

The next *nido*-borane with an odd number of boron atoms is B_7H_{11}, which is unknown except in an iron carbonyl complex[35] $B_7H_{11}Fe(CO)_4$, whose structure has apparently never been determined by X-ray diffraction. A hexagonal-pyramidal structure with four bridging hydrogen atoms around the hexagonal open face appears feasible for B_7H_{11} (Figure 5). This structure has a degree 6 vertex as the apex of the hexagonal pyramid and two pairs of adjacent degree 4 vertices around the hexagonal base. One of these pairs of adjacent basal degree 4 vertices could bond to the $Fe(CO)_4$ group in much the same manner as the pair of adjacent degree 4 vertices in the B_6H_{10} bonds to the $Fe(CO)_4$ group in $(\eta^2\text{-}B_6H_{10})Fe(CO)_4$. The hexagonal-pyramidal structure suggested for $B_7H_{11}Fe(CO)_4$ in Figure 5 has four different types of boron atoms in the ratio of 1:2:2:2. This is consistent with its reported ^{11}B NMR spectrum[35] that exhibits a high-field resonance and three low-field resonances. Note that the structure suggested for $B_7H_{11}Fe(CO)_4$ still has a pair of adjacent degree 4 vertices. This suggests the possible chemical reactivity of $B_7H_{11}Fe(CO)_4$ toward additional $Fe_2(CO)_9$ to form a binuclear complex $B_7H_{11}[Fe(CO)_4]_2$ (Figure 5). The structure proposed for B_7H_{11} in Figure 5 has only two vertices of the favored degree of 5 among its seven vertices, which may indicate why uncomplexed B_7H_{11} has never been observed.

The other possible *nido*-boranes B_nH_{n+4} with odd numbers of boron atoms, namely, B_9H_{13} and $B_{11}H_{15}$, are unstable under ambient conditions, even in the absence of air. In both cases, placing the required four bridging hydrogen atoms around the open face boron atoms is impossible without having one or more degree 6 boron atoms. Alternatively, the presence of degree 6 vertices can be avoided by converting one bridging hydrogen atom per degree 6 vertex into an extra terminal hydrogen atom, namely, a so-called *endo*-hydrogen atom. This process eliminates one boron vertex degree but generates a BH_2 group in the structure. Such BH_2 groups appear to be unfavorable in the structures of *nido*-boranes, probably because of steric congestion around the open faces.

Bridging hydrogens on degree 6 boron atoms are so acidic that *nido*-boranes with this structural feature readily ionize to give the corresponding $B_nH_{n+3}^-$ anions. Thus, B_9H_{13} appears to be too unstable to be isolated because it has only been detected by mass spectrometry as an unstable intermediate from the pyrolysis of $B_9H_{13}L$ compounds (e.g., L = $(CH_3)_2S$).[36] A plausible structure for B_9H_{13} has a hexagonal open face with adjacent degree 6 and degree 4 vertices (Figure 6a). Alternative structures for B_9H_{13} with a pentagonal open face obtained by the removal of a degree 5 vertex from the bicapped square antiprism (Figure 2) necessarily have at least one unfavorable feature such as the following (Figure 7): (1) one of the four

---

(29) Parry, R. W.; Walter, M. K. In *Preparative Inorganic Reactions*; Jolly, W., Ed.; Interscience: New York, 1968; Vol. 5, pp 45−102.

(30) Hirschfeld, F. L.; Eriks, K.; Dickerson, R. E.; Lippert, E. L., Jr.; Lipscomb, W. N. *J. Chem. Phys.* **1958**, *28*, 56.

(31) Enrione, R. E.; Boer, F. P.; Lipscomb, W. N. *Inorg. Chem.* **1964**, *3*, 1659.

(32) Johnson, H. D.; Brice, H. V. T.; Brubaker, G. L.; Shore, S. G. *J. Am. Chem. Soc.* **1972**, *94*, 6711.

(33) Davison, A.; Traficante, D. D.; Wreford, S. S. *J. Am. Chem. Soc.* **1974**, *96*, 2802.

(34) McCarty, L. V.; Di Giorgio, P. A. *J. Am. Chem. Soc.* **1951**, *73*, 3138.

(35) Hollander, O.; Clayton, W. R.; Shore, S. G. *J. Chem. Soc., Chem. Commun.* **1974**, 604.

(36) Ardini, L. C.; Fehlner, T. P. *Inorg. Chem.* **1973**, *12*, 798.

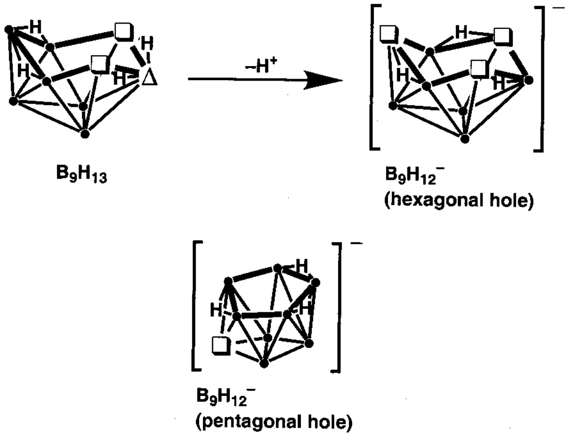


Figure 6. (a) Structures for B_9H_{13} and $B_9H_{12}^-$ with hexagonal open faces and (b) the known[37] structure of $B_9H_{12}^-$ with a pentagonal open face.

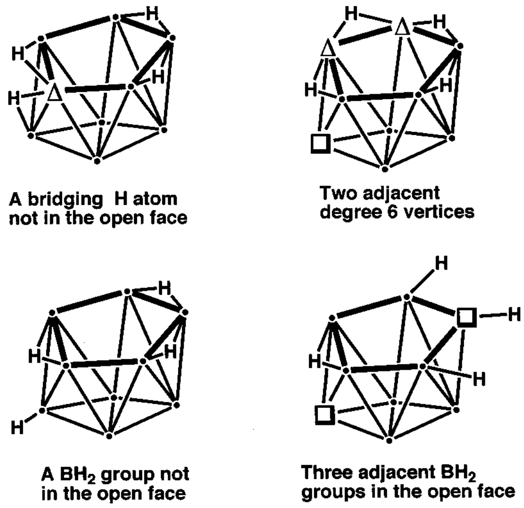


Figure 7. Examples of unfavorable structural features arising when a structure for B_9H_{13} is constructed with a pentagonal open face. Note that each boron atom is assumed to have one external (terminal) hydrogen atom so that an explicitly shown terminal hydrogen is part of a BH_2 group.

bridging hydrogens not bridging an edge of the open face but instead an edge inside the polyhedral fragment, (2) two adjacent degree 6 vertices on the open face, (3) a BH_2 group not in the open face, or (4) three adjacent BH_2 vertices in the open face. Note that, in Figure 7, only the extra hydrogen atom of each BH_2 group is shown (i.e., one hydrogen atom is assumed to be located on every vertex and is not shown explicitly).

Deprotonation of the hypothetical B_9H_{13} with a hexagonal open face (Figure 6a) to give $B_9H_{12}^-$ with the redistribution of the remaining three bridging hydrogen atoms leads to a structure having a C_3 axis with alternating degree 4 and degree 5 vertices around the hexagonal open face. In this structure, the Frank−Kasper requirement of isolated degree 4 vertices is met. However, an alternative structure for $B_9H_{12}^-$, having only degree 5 vertices except for a single degree 4 vertex, can be constructed if a pentagonal rather than a hexagonal open face is used (Figure 6b). This structure is found by X-ray diffraction in the salts of the $B_9H_{12}^-$ anion that have been isolated.[37]

The removal of a single vertex from an icosahedron generates plausible structures for 11-vertex *nido*-boranes. However, the placement of four bridging hydrogens around the pentagonal open face obtained by removal of a BH vertex from $B_{12}H_{12}^{2-}$ to give a $B_{11}H_{15}$ structure necessarily leads to three adjacent degree 6 vertices (Figure 8), which is very unfavorable. Thermally unstable and very acidic $B_{11}H_{15}$ has been isolated by the low-temperature protonation of $KB_{11}H_{14}$ with HCl.[38] Deprotonation of $B_{11}H_{15}$ gives the ion $B_{11}H_{14}^-$. The $B_{11}H_{14}^-$ ion is also readily prepared directly from $B_{10}H_{14}$,[39] B_5H_9,[40] or even BH_4^-.[41] Determination of the structure of $[(CH_3)_3PH]^+[B_{11}H_{14}]^-$ by X-ray diffraction indicates that only two of the three extra hydrogen atoms bridge the edges of the pentagonal open face.[42] The third extra hydrogen atom forms a BH_2 vertex using the open face boron atom not bonded to a bridging hydrogen atom (Figure 8). In this way, the presence of a degree 6 vertex in $B_{11}H_{14}^-$ is avoided. Further deprotonation of $B_{11}H_{14}^-$ gives the stable dianion $B_{11}H_{13}^{2-}$, shown by X-ray diffraction[43] to have the expected structure with two bridging hydrogens across the nonadjacent edges of the pentagonal open face and with a single degree 4 vertex (Figure 8).

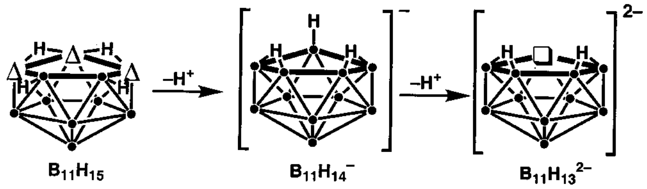


Figure 8. Deprotonation of $B_{11}H_{15}$ to $B_{11}H_{14}^-$ and $B_{11}H_{13}^{2-}$. The indicated structures for $B_{11}H_{14}^-$ and $B_{11}H_{13}^{2-}$ have been confirmed by X-ray diffraction.[42,43]

5. Fused Polyhedral Boranes B_nH_{n+4} ($12 \le n \le 18$)

Polyhedral boranes B_nH_{n+4} containing 12 or more boron atoms no longer have structures generated by removal of a vertex from a single deltahedron. Instead, their structures consist of two *nido*-borane units sharing an edge (Figure 9). The two boron atoms common to both of the nido units (indicated as B in Figure 9) do not have any terminal hydrogen atoms so that six bridging hydrogen atoms are required for the B_nH_{n+4} stoichiometry. However, two open faces are available in these fused B_nH_{n+4} structures as sites for these six bridging hydrogen atoms. The two open faces in these structures share the same B−B edge as the two nido building blocks. Such fused polyhedral *nido*-boranes B_nH_{n+4} are only known with even numbers of boron atoms consistent with the fact that the isolable monopolyhedral neutral *nido*-boranes of similar stoichiometries (section 4) have even numbers of boron atoms except for B_5H_9. Skeletal electron counting in these fused polyhedral boranes has recently been discussed by Jemmis and co-workers.[44,45]

The most stable and readily available of the fused polyhedral boranes is $B_{18}H_{22}$, which forms two isomers. The structures of both isomers[46,47] consist of two edge-sharing $B_{10}H_{14}$ units (Figure 9) and differ only by the locations of the edges of the $B_{10}H_{14}$ units involved in the sharing. In both isomers, all 16 of

---

(37) Jacobsen, G. B.; Meina, D. G.; Morris, J. H.; Thomson, C.; Andrews, S. J.; Reed, D.; Welch, A. J.; Gaines, D. F. *J. Chem. Soc., Dalton Trans.* **1985**, 1645.

(38) Getman, T. D.; Krause, J. A.; Shore, S. G. *Inorg. Chem.* **1988**, *27*, 2398.

(39) Aftandilian, V. D.; Miller, H. C.; Parshall, G. W.; Muetterties, E. L. *Inorg. Chem.* **1962**, *1*, 734.

(40) Hosmane, N. S.; Wermer, J. R.; Hong, Z.; Getman, T. D.; Shore, S. G. *Inorg. Chem.* **1987**, *26*, 3638.

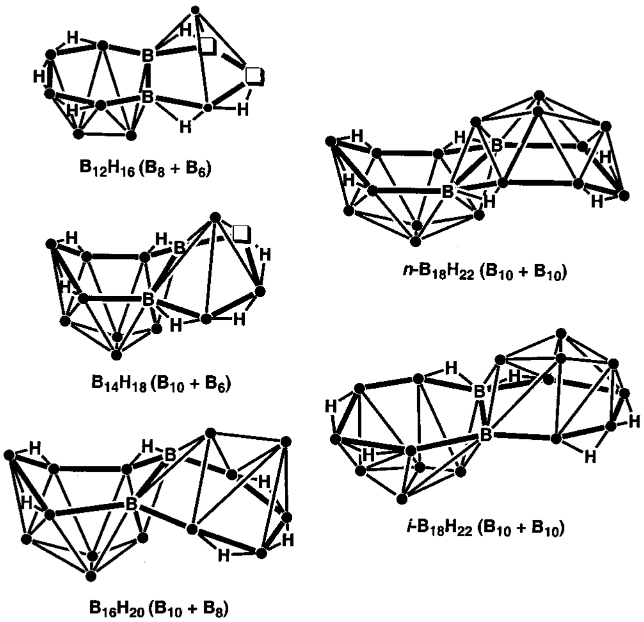
(41) Dunks, G. R.; Ordonez, K. P. *Inorg. Chem.* **1978**, *17*, 1514.

(42) McGrath, T. D.; Welch, A. J. *Acta Crystallogr.* **1997**, *C53*, 229.

(43) Fritchie, C. J., Jr. *Inorg. Chem.* **1967**, *6*, 1199.

(44) Balakrishnarajan, M. M.; Jemmis, E. D. *J. Am. Chem. Soc.* **2000**, *122*, 4516.

(45) Jemmis, E. D.; Balakrishnarajan, M. M.; Pancharatna, P. D. *J. Am. Chem. Soc.* **2001**, *123*, 4313.



$B_{12}H_{16}$ (B_8 + B_6)

n-$B_{18}H_{22}$ (B_{10} + B_{10})

$B_{14}H_{18}$ (B_{10} + B_6)

i-$B_{18}H_{22}$ (B_{10} + B_{10})

$B_{16}H_{20}$ (B_{10} + B_8)

Figure 9. Structures of the fused polyhedral boranes B_nH_{n+4} ($n = 12$, 14, 16, and 18) showing the two known isomers of $B_{18}H_{22}$. These structures are formed by the edge-sharing fusion of the indicated B_6, B_8, and B_{10} *nido*-borane fragments (Figure 3). The vertices in the shared edge (indicated by B) do not have terminal hydrogen atoms.

the boron vertices unique to a single B_{10} unit have the favored degree of 5. The two hydrogen-free boron atoms in the edge common to both B_{10} units in $B_{18}H_{22}$ have a degree of 7, but they use all four of their valence orbitals for skeletal bonding.

The smallest *nido*-borane of the type B_nH_{n+4} consisting of two edge-fused polyhedra is colorless air-stable $B_{12}H_{16}$, which is synthesized by oxidative coupling of $B_6H_9^-$.[48] Its structure consists of edge-sharing B_8H_{12} and B_6H_{10} units (Figure 9). The arrangement of the six bridging hydrogens across the fused hexagonal and pentagonal open faces in $B_{12}H_{16}$ leads to degree 5 vertices for all of the boron atoms unique to a single B_8 or B_6 unit except for an adjacent pair of degree 4 vertices in the pentagonal open face. The two hydrogen-free boron atoms in the edge common to the B_8 and B_6 units in $B_{12}H_{16}$ have degrees of 5 and 6. The location of defective vertices in $B_{12}H_{16}$ is similar to that in B_6H_{10} in that there is a pair of adjacent degree 4 boron vertices potentially reactive toward protonation or metal complexation. Thus, metal complexes of $B_{12}H_{16}$, such as (η^2-$B_{12}H_{16}$)Fe(CO)$_4$, are predicted to be stable.

The other structurally characterized fused polyhedral *nido*-borane of the type B_nH_{n+4} is $B_{16}H_{20}$, which is obtained by the pyrolysis of $B_9H_{13}S(CH_3)_2$.[49] The structural pattern of $B_{16}H_{20}$ is similar to fused *nido*-boranes discussed above except, in this case, a $B_{10}H_{14}$ unit is fused to a B_8H_{12} unit (Figure 9). This structure, like that of $B_{18}H_{22}$, has no defective vertices and thus, unlike B_6H_{10} and presumably $B_{12}H_{16}$, is predicted not to form η^2-metal complexes such as (η^2-$B_{16}H_{20}$)Fe(CO)$_4$.

The remaining member of this series is $B_{14}H_{18}$, which is a viscous liquid that has been obtained by the hydrolytic degradation of $B_{16}H_{20}$.[50] This borane has not been structurally characterized, apparently because it could not be crystallized. Its NMR spectra (^{1}H and ^{11}B) are consistent with a structure consisting of edge-sharing $B_{10}H_{14}$ and B_6H_{10} units (Figure 9). Unlike its B_6H_{10} building block, this structure of $B_{14}H_{18}$ has only a single degree 4 vertex, suggesting that it is not likely to complex with transition metals or undergo ready protonation. This structural feature probably explains why $B_{14}H_{18}$ could be isolated in reasonable yield (~30%) from a hydrolytic reaction.[50]

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research.

IC0106165

---

(46) Simpson, P. G.; Lipscomb, W. N. *J. Chem. Phys.* **1963**, *39*, 26.

(47) Simpson, P. G.; Folting, K.; Lipscomb, W. N. *J. Am. Chem. Soc.* **1963**, *85*, 1879.

(48) Brewer, C. T.; Swisher, R. G.; Sinn, E.; Grimes, R. N. *J. Am. Chem. Soc.* **1985**, *107*, 3558.

(49) Friedman, L. B.; Cook, R. E.; Glick, M. D. *Inorg. Chem.* **1970**, *9*, 1452.

(50) Heřmánek, S.; Fetter, K.; Pleek, J.; Todd, L. J.; Garber, A. R. *Inorg. Chem.* **1975**, *14*, 2250.