Inorg. Chem. **2006**, *45*, 6996–7003

Inorganic Chemistry
Article

Which *nido*:*nido*-Macropolyhedral Boranes are Most Stable?

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Received April 7, 2006

A comparison of the relative stabilities computed at RB3LYP/6-311+G(d,p)//RB3LYP/6-31G(d)+ZPE of the neutral *nido*-single clusters and two vertex-sharing macropolyhedral *nido:nido*-clusters shows single-cluster *nido*-boranes with up to 11 vertexes to be energetically more favorable than isomeric macropolyhedral boranes. Extra hydrogen atoms at the open face have a significant influence on the relative stabilities of the single cluster *nido*-boranes vs *nido*:*nido*-macropolyhedral boranes. For anionic species, a clear-cut turning point for macropolyhedral preference is shifted to no less than 17 vertexes. Thermodynamically most stable neutral and anionic *nido:nido*-macropolyhedral boranes usually consist of a *nido*-10-vertex and a *nido*-11-vertex unit, respectively. The relative stabilities of isomeric neutral macropolyhedra reflect the patterns exhibited by the sum of thermodynamic stabilities of the individual clusters.

1. Introduction

Single-cluster boranes and macropolyhedral boranes have attracted a quite different attention with respect to theoretical treatment. Single-cluster boranes are now well-understood. The principles that govern the stabilities of macropolyhedral boranes, however, are mostly unknown, and experimental research is largely exploratory.[1] Single clusters are either most spherical deltahedra, i.e., *closo*-boranes, or are derived by the removal of one, two, or three vertexes from *closo*-structures to give *nido*-, *arachno*-[2] and *hypho*-boranes,[3] respectively. A number of theoretical efforts, e.g., Wade's skeletal electron count principle,[4] Williams' heteroatom placement rules,[2,5] Jemmis and Schleyer's ring cap principle,[6] Ott-Gimarc's charge preference,[7] and structural[8] and connection[9] increment systems provide insight into the structural patterns of single clusters.

Large structures are composed of smaller clusters with two different modes of combining individual single clusters: (i) a two-center, two-electron[10] or three-center, two-electron bond[11] connects two independent units, or (ii) one,[12] two,[13] three,[14] or four[15] vertexes are shared by two individual units. The resulting clusters of fused polyhedral units have been termed macropolyhedra (see Scheme 1). The first case, i.e., joined clusters, is not special, as one cluster is just a substituent to another one and the individual clusters remain separate entities. In the second case, the more intimate fusion of clusters results in one new and different cluster. Except

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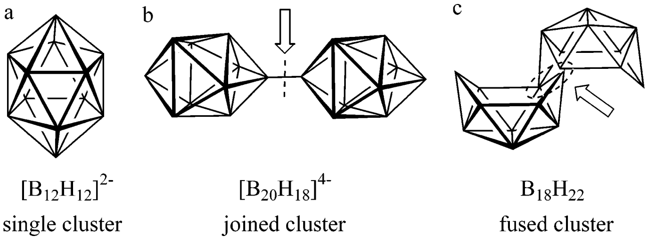
Scheme 1. Different Types of Polyhedral Boranes



(a) $[B_{12}H_{12}]^{2-}$ represents a single cluster; (b) two single clusters may share a two-center, two-electron bond, as in $[B_{20}H_{18}]^{4-}$; and (c) two cluster units may fuse to become a macropolyhedra, like two 10-vertex *nido* units share two vertexes in *nido*(10):*nido*(10)-$B_{18}H_{22}$. Arrows point to the mode of cluster connections.

for the skeletal electron count rule for macropolyhedral borane clusters,[16] no further theoretical consideration has been paid to macropolyhedral boranes. Jemmis' *mno* rule, a skeletal electron count principle,[16] can be easily and correctly employed to any macropolyhedral borane. In short, the sum of the number of single-cluster fragments (m), the number of vertexes in the macropolyhedron (n), the number of single-vertex-sharing junctions (o), and the number of missing vertexes (p) equals the number of skeletal electron pairs of a macropolyhedral borane.

But unlike Wade's[4] skeletal electron count principle for single clusters, which associates the number of skeletal electron with definite cluster shapes, the *mno* rule does not specify architectures or cluster shapes on the basis of the given number of skeletal electrons. It rather has to be known to do the *mno* counting. Therefore, it is impossible to determine the thermodynamically most stable structure out of a large number of possibilities for a given molecular formula. Here, we present a detailed study in order to explore the architectural patterns behind macropolyhedral boranes.

In the present paper, the relative stabilities of the various possible isomers of *nido*:*nido*-macropolyhedral boranes are compared with each other and also with the isomeric *nido* single clusters, each with the general formula B_nH_{n+4} ($n = 4-19$). We try to find computationally the turning point from *nido* single cluster to *nido*:*nido*-macropolyhedral preference in neutral and anionic clusters. We further explore the preferred fragment for each neutral and anionic macropolyhedral boranes in the thermodynamically most stable isomers.

2. Computational Details

2.1. Construction of *nido* Single Clusters. Basic skeletons for single *nido*-polyhedral borane clusters with the number of vertexes $n = 4-19$ were obtained by removing one highest-coordinate vertex[17] from *closo*-deltahedra with 5−20 vertexes. The structures for 5−12-vertex *closo*-clusters are most spherical deltahedra and are well-known from experiments.[18] For 13−17 vertexes, the optimized *closo*-geometries reported by Schleyer, Najafian, and Mebel were used.[19] Metal-free 13-[20] and 14-vertex[21] *closo*-carboranes have been recently synthesized. The *closo*-structures with 14 and 15 vertexes correspond to the deltahedra proposed by Frank and Kasper.[22] For 16 vertexes, we used the *closo*-polyhedron with two squares proposed in ref 19, which is thermodynamically more stable than that proposed by Frank and Kasper[22] or by Brown and Lipscomb.[26a] For 18−20 vertexes, we computed various *closo*-clusters, and the *nido*-structures were obtained by removal of the highest-coordinate vertex from the most stable *closo*-deltahedra. The skeleton of a 19-vertex *nido*-deltahedron was obtained by optimizing a D_{6d} symmetric *closo*-$[B_{20}H_{20}]^{2-}$ structure, as proposed by Brown and Lipscomb.[26a] The addition of four hydrogen atoms to edges of the open face of these basic skeletons resulted in numerous *nido*-B_nH_{n+4} isomers. The energy of each most stable *nido*-B_nH_{n+4} ($n = 4-19$) structure was compared with the most stable isomeric *nido*:*nido*-macropolyhedral borane. A representation of the optimized geometries of various B_nH_{n+4} *nido*-clusters with $n = 3-19$ is provided as Supporting Information (Appendix I).

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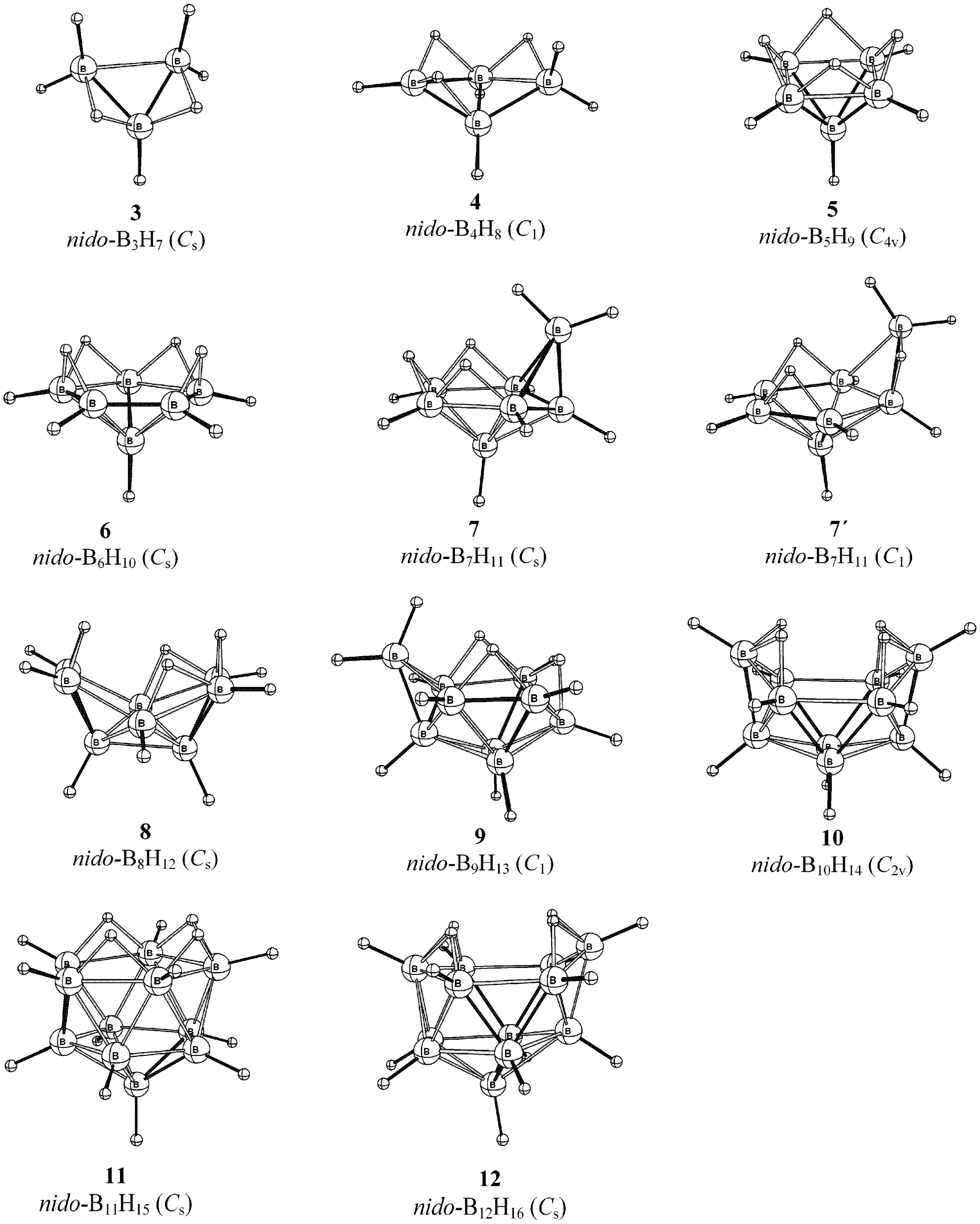


3
nido-B_3H_7 (C_s)

4
nido-B_4H_8 (C_1)

5
nido-B_5H_9 (C_{4v})

6
nido-B_6H_{10} (C_s)

7
nido-B_7H_{11} (C_s)

7′
nido-B_7H_{11} (C_1)

8
nido-B_8H_{12} (C_s)

9
nido-B_9H_{13} (C_1)

10
nido-$B_{10}H_{14}$ (C_{2v})

11
nido-$B_{11}H_{15}$ (C_s)

12
nido-$B_{12}H_{16}$ (C_s)

Figure 1. Single *nido*-clusters as building blocks of *nido:nido*-macropolyhedra.

2.2. Construction of *nido*:*nido*-Macropolyhedral Borane Clusters.

Different *nido* single cluster boranes were used as building blocks for two vertex-sharing *nido*:*nido*-macropolyhedral boranes; *nido*-B_3H_7 (**3**), *nido*-B_4H_8 (**4**), *nido*-B_5H_9 (**5**), *nido*-B_6H_{10} (**6**), *nido*-B_7H_{11} (**7**, C_s and **7′**, C_1), *nido*-B_8H_{12} (**8**), *nido*-B_9H_{13} (**9**), *nido*-$B_{10}H_{14}$ (**10**), *nido*-$B_{11}H_{15}$ (**11**), and *nido*-$B_{12}H_{16}$ (**12**) are shown in Figure 1. Formally, two vertex-sharing *nido*:*nido*-macropolyhedra result from the condensation reaction of two *nido*-boranes releasing B_2H_6. Hence, the number of vertexes of a given macropolyhedron is always two less than the sum of number of vertexes of the two *nido*-clusters that build it. Sharing of two vertexes between any two *nido* single clusters (**3**−**12**) results in a number of possible *nido:nido*-macropolyhedral combinations for each B_nH_{n+4} formula. For example, for *nido:nido*-$B_{14}H_{18}$, the following combinations are possible: *nido*(8):*nido*(8)-, *nido*(7):*nido*(9)-, *nido*(7′)-*nido*(9′)-, *nido*(6):*nido*(10)-, *nido*(5):*nido*(11)-, *nido*(4):*nido*(12)-$B_{14}H_{18}$ (Figure 2). For any of these options, there is more than one choice of connecting site and different bridging hydrogen positions on the open face. Hence, a large number of structural isomers are possible. As illustrated, two *nido*(4):*nido*(12)-$B_{14}H_{18}$ structures (**4**:**12a** and **4**:**12b**) are shown in Figure 2. The optimized geometries of various macropolyhedra B_nH_{n+4} for $n = 4-13$ and $15-19$ are shown in Appendix II of the Supporting Information.

Starting *nido*-geometries derived from *closo* clusters were initially optimized with density functional theory methods at the RB3LYP/3-21G level using the Gaussian 03 program.[23] Further geometry optimization as well as frequency calculations for the most stable RB3LYP/3-21G optimized *nido*-geometries as well as isomeric *nido:nido*-macropolyhedral starting geometries (see section 2.1) were performed at RB3LYP/6-31G(d) with symmetry restrictions, where applicable. Only a few macropolyhedral *nido*:*nido*-structures belong to symmetry point groups higher than C_1. Finally, single-point energies were computed at RB3LYP/6-311+G(d,p). All the structures presented in this paper are local minima at RB3LYP/6-31G(d). Relative energies reported for all the B_nH_{n+4} and $[B_nH_{n+3}]^-$ isomers considered for $n = 4-19$ correspond to the RB3LYP/6-311+G(d,p)//RB3LYP/6-31G(d)+ZPE level of theory.

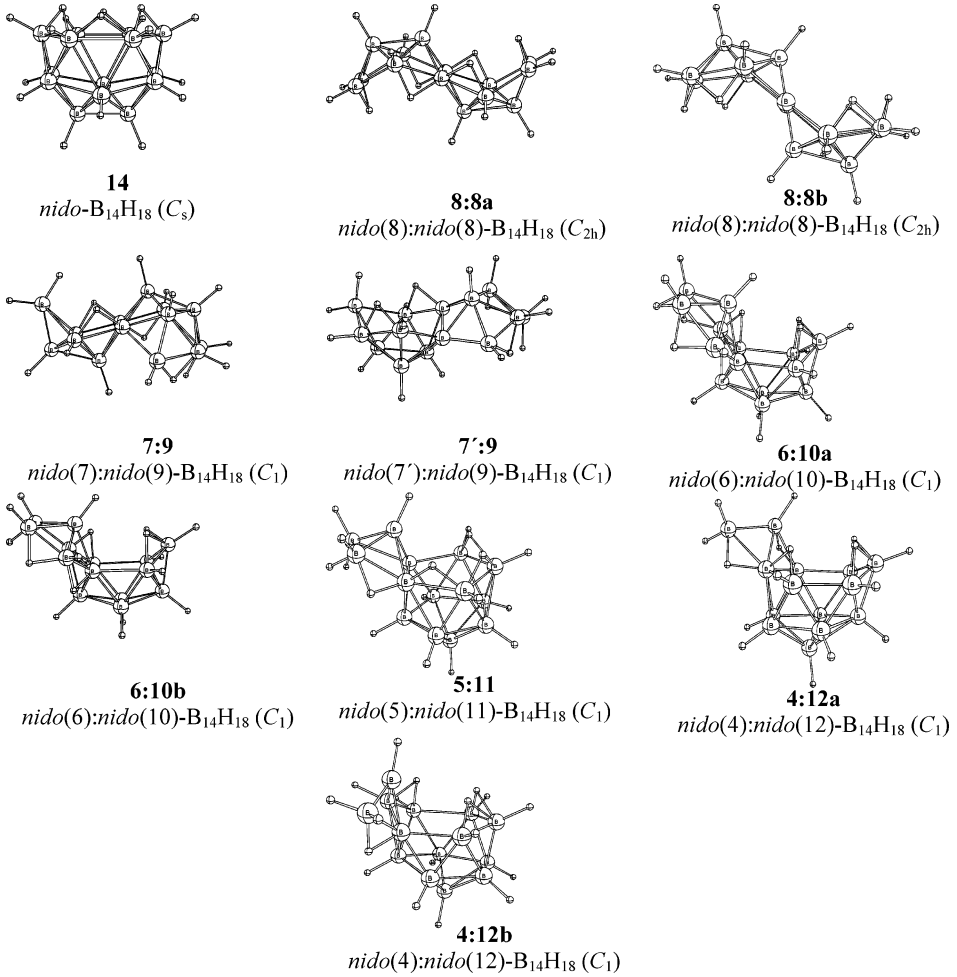


Figure 2. Single cluster (**14**) and macropolyhedral structures for $B_{14}H_{18}$.

3. Results and Discussion

3.1. Fusion Mode of *nido*:*nido*-Macropolyhedral Boranes. A large number of known macropolyhedral boranes with the general formula B_nH_{n+4} consist of two *nido* units sharing two vertexes. For the sake of convenience, we call them *nido*(x):*nido*(y)-macropolyhedral boranes in this paper, where x and y indicate the size of the cluster units that share two vertexes, i.e., $x + y = n + 2$. B_nH_{n+4} macropolyhedra with one or three vertexes shared between two *nido*-units do not obey the *mno* rule[16] and are experimentally unknown. To estimate the energetic influence of different fusion modes between two *nido*-clusters on the relative stability of isomeric structures, we computed one- and three-vertex-sharing $B_{18}H_{22}$ structures. They are 62.7 and 52.7 kcal mol^{-1} less stable, respectively, than the experimentally known two-vertex-sharing C_i symmetric *nido*(10):*nido*(10)-$B_{18}H_{22}$ structure.[13d−f] We conclude that there is a large preference (>50 kcal mol^{-1}) for two-vertex-sharing in *nido*:*nido*-macropolyhedral boranes.

3.2. Turning Point from *nido*-B_nH_{n+4} Single Cluster to *nido:nido*-B_nH_{n+4} Macropolyhedral Preference. The largest experimentally known homonuclear *nido* single cluster is $B_{11}H_{15}$,[24] whereas the smallest experimentally known homonuclear *nido*:*nido*-macropolyhedral borane is $B_{12}H_{16}$ (Scheme 2).[25] The latter consists of one eight-vertex *nido* unit sharing two vertexes with another six-vertex *nido* fragment. It is unclear if this also represents the turning point from *nido* single cluster to macropolyhedral borane preference in terms of thermodynamic stability. Computation of the experimentally known *nido*(6):*nido*(8)-$B_{12}H_{16}$ and the isomeric *nido*-$B_{12}H_{16}$ indicates that the former is 3.9 kcal mol^{-1} less stable than the *nido*-$B_{12}H_{16}$ single cluster. However, we found the *nido*(3):*nido*(11)-$B_{12}H_{16}$ isomer (**3**:**11**, Appendix II, part i, in the Supporting Information; also see Figure 3) to be 4.5 kcal mol^{-1} more stable than the *nido*-$B_{12}H_{16}$ (**12**) cluster. The former structure, i.e., *nido*(3):*nido*(11)-$B_{12}H_{16}$, is also 8.3 kcal mol^{-1} more stable than the experimentally known *nido*(6):*nido*(8)-$B_{12}H_{16}$.

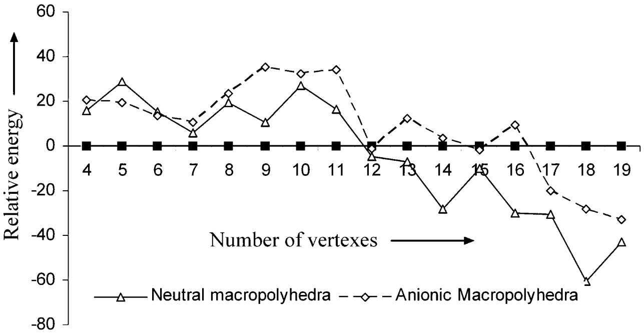
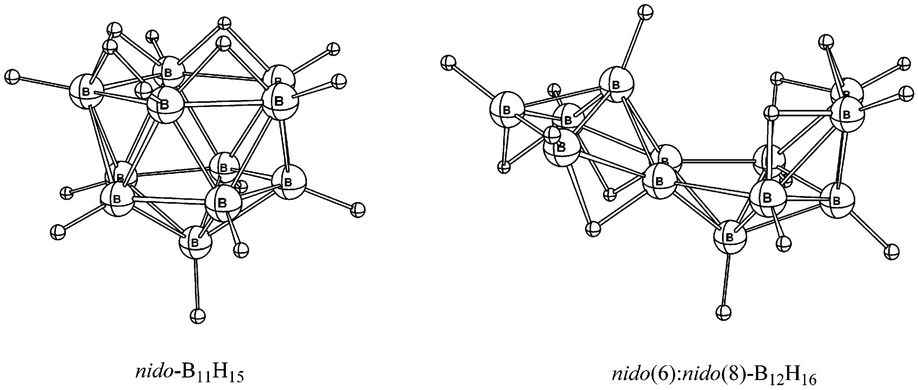


Figure 3. Relative energies (kcal mol^{-1}) of the most stable *nido*:*nido*-edge-sharing macropolyhedra relative to isomeric single-cluster polyhedra.

Scheme 2. Optimized Geometries of the Largest Experimentally Known Homonuclear Single *nido*-Cluster (*nido*-$B_{11}H_{15}$[24]) and Smallest Experimentally Known Homonuclear *nido*:*nido*-Macropolyhedral Borane Cluster (*nido*(6):*nido*(8)-$B_{12}H_{16}$[25]).



The thermodynamic stabilities of various *nido*:*nido*-B_nH_{n+4} macropolyhedral borane clusters with respect to the isomeric *nido*-B_nH_{n+4} single clusters are compared in Figure 3 (also see Appendices I−III in the Supporting Information). Any neutral *nido*:*nido*-macropolyhedral borane is less stable than the corresponding *nido* single-cluster borane as long as the total number of vertexes is equal to or less than 11. For 12 or more vertexes, i.e., for $n = 12-19$, macropolyhedra exist that are energetically preferred (Figure 3) over the single-cluster alternatives. For example, the most stable macropolyhedral $B_{10}H_{14}$, i.e., *nido*(6):*nido*(6)-$B_{10}H_{14}$ (**6**:**6a**, Appendix II, part g, in the Supporting Information) is 27.2 kcal mol^{-1} less stable than single-cluster *nido*-$B_{10}H_{14}$ (**10**). Similarly, the most stable *nido*(5):*nido*(8)-$B_{11}H_{15}$ is 16.7 kcal mol^{-1} less stable than the single *nido*-$B_{11}H_{15}$ (**11**) cluster. Twelve is the smallest number of vertexes for which a macropolyhedron exists that is lower in energy than its *nido* isomer. Figure 3 displays an obvious trend for macropolyhedra to become more and more favored over single-cluster isomers as the total number of vertexes increases.

The increase in the stability of *nido*:*nido*-macropolyhedral boranes can be explained on the basis of the connectivity of boron vertexes. Five-coordinate vertexes are especially favorable,[26] as indicated by the high stability of icosahedral *closo*-$[B_{12}H_{12}]^{2-}$.[27] Large-sized *nido* single-cluster boranes usually possess more highly connected vertexes in addition. Isomeric *nido*:*nido*-macropolyhedral boranes, on the other hand, are built from smaller cluster fragments and have a smaller number of highly connected vertexes (usually more five-coordinate vertexes), and therefore get enhanced stability.

Hydrogen atoms at the open face prefer to bridge vertexes of least connectivity. Vertexes at the open face of *nido*:*nido*-macropolyhedral boranes are usually less connected as compared to vertexes at the open face of corresponding single *nido* clusters. The reduced thermodynamic stability of neutral *nido* clusters may therefore be at least in part due to the high connectivity of open-face vertexes.

3.3. The Effect of Open-Face Hydrogen Atoms on the Relative Stabilities of *nido* Single-Cluster Boranes vs *nido*:*nido*-Macropolyhedral Boranes. Optimization of a *nido*(3):*nido*(10)-$B_{11}H_{15}$ starting geometry resulted in a structure that is 1.7 kcal mol^{-1} more stable than the experimentally known *nido*-$B_{11}H_{15}$ (**11**) single cluster. It has a BH_2 unit occupying the position of a hydrogen bridge of a regular 10-vertex *nido* fragment (**X**, Figure 4). This geometry can also be considered as being a distorted 11-vertex *nido* single cluster rather than a macropolyhedral borane. The presence of four open-face hydrogen atoms destabilizes the *nido*-$B_{11}H_{15}$ (**11**) cluster; adjacent hydrogen bridges on the open face of the 11-vertex *nido*-cluster represent a high-energy structural feature with an energy penalty of 25.9 kcal mol^{-1}.[8a] This might be responsible for the fact that distorted **X** with only two adjacent hydrogen atoms on the less-connected vertexes can compete energetically with **11**. The latter suffers from four adjacent hydrogen bridges.

It is also known from experiments that *nido*-$B_{11}H_{15}$ (**11**) is easily deprotonated to give *nido*-$[B_{11}H_{14}]^-$.[24] The deprotonated *nido*-$[B_{11}H_{14}]^-$ has three hydrogen atoms on the open face, only two of them adjacent to each other. Thus, *nido*-$[B_{11}H_{14}]^-$ has two fewer adjacent hydrogen bridges as compared to *nido*-$B_{11}H_{15}$ and should have enhanced thermodynamic stability. To confirm the effect of open-face hydrogen atoms, we computed *nido*-$[B_{11}H_{14}]^-$ and corresponding *nido*:*nido*-$[B_{11}H_{14}]^-$ structures. The *nido*-$[B_{11}H_{14}]^-$ is found to be 34.3 kcal mol^{-1} more stable than the most stable macropolyhedral $[B_{11}H_{14}]^-$, whereas the neutral *nido*-$B_{11}H_{15}$ structure is 16.7 kcal mol^{-1} more stable than the corresponding most stable macropolyhedral $B_{11}H_{15}$. Thus, the removal of one open-face hydrogen atom enhances the energetic preference for the regular *nido* cluster by 17.6 kcal mol^{-1}. The presence of heteroatoms in the 11-vertex *nido* cluster also results in a reduced number of extra open-face hydrogen atoms (e.g., *nido*-$CB_{10}H_{14}$ and *nido*-$HPB_{10}H_{12}$ have three and two open-face hydrogen atoms, respectively). Therefore, heteroatom-substituted single-cluster boranes suffer less from open-face hydrogen atom repulsion. As a consequence, heteroatom-substituted single-cluster isomers should be more competitive as compared to corresponding macropolyhedral boranes.

To determine the effect of open face hydrogen atoms on the relative stabilities (as in the case of $B_{11}H_{15}$ and $[B_{11}H_{14}]^-$),

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(27) Schleyer, Najafian, and Mebel computed various *closo*-$[B_nH_n]^{2-}$ clusters ($n = 5-17$) and found the least energy per vertex for $n = 12$. We extended the study up to 20 vertexes and found the progressive decrease in energy per vertex from $[B_{15}H_{15}]^{2-}$ to $[B_{17}H_{17}]^{2-}$, which was reported in ref 19 as not continuing for $n = 18-20$.

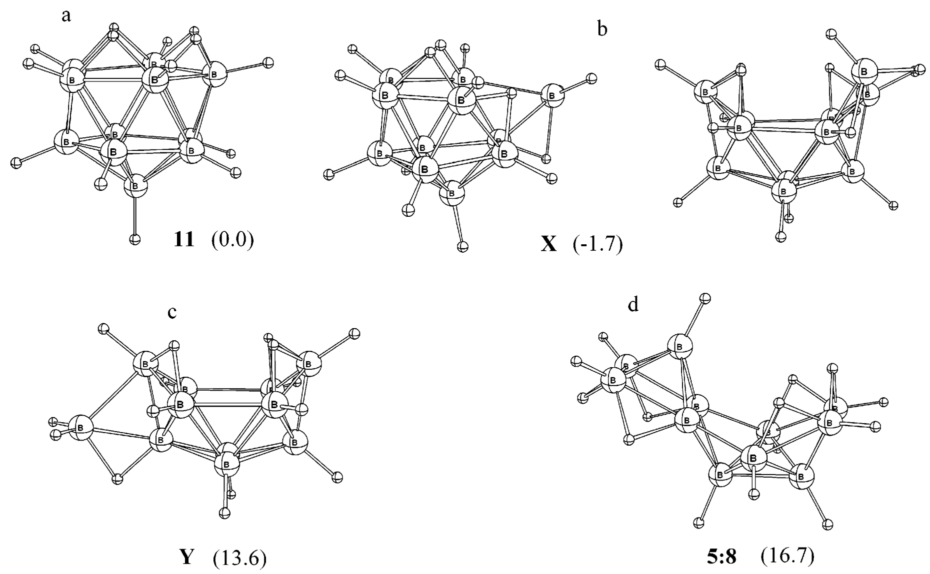


Figure 4. (a) Optimized geometry of *nido*-$B_{11}H_{15}$ (**11**, *C*s) with four adjacent hydrogen bridges. (b) Different views of **X** to show its relationship with the 11- and 10-vertex *nido*-clusters. (c) A *nido*(4):*nido*(9)-$B_{11}H_{15}$ starting geometry optimized to this distorted geometry (**Y**). (d) The most stable macropolyhedral $B_{11}H_{15}$ borane has a five-vertex *nido*-cluster that shares two vertexes with another eight-vertex *nido*-cluster (**5**:**8**). Relative energies in kcal mol^{-1} are given in parentheses.

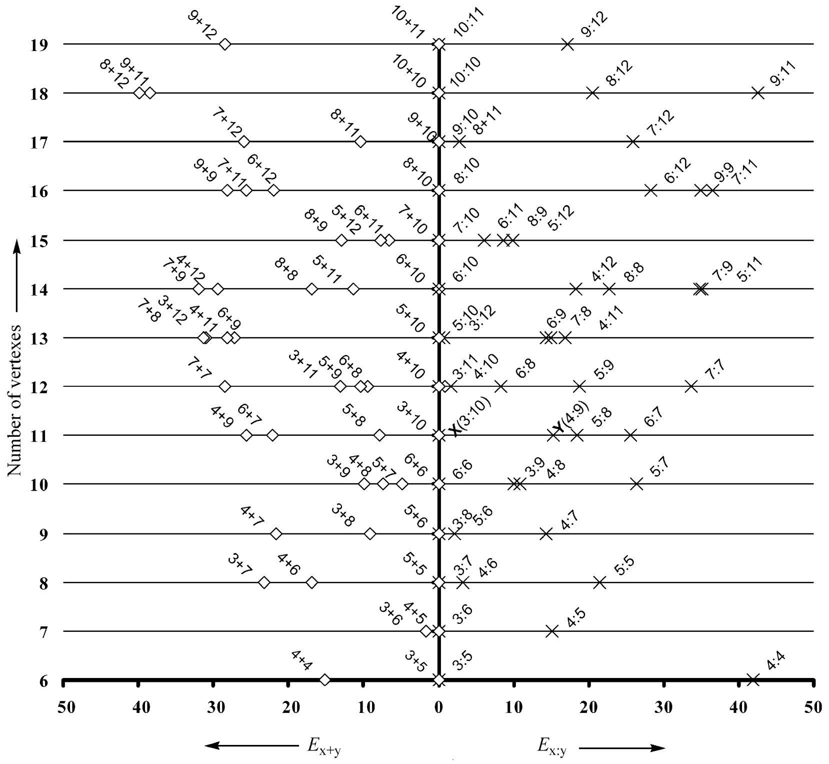
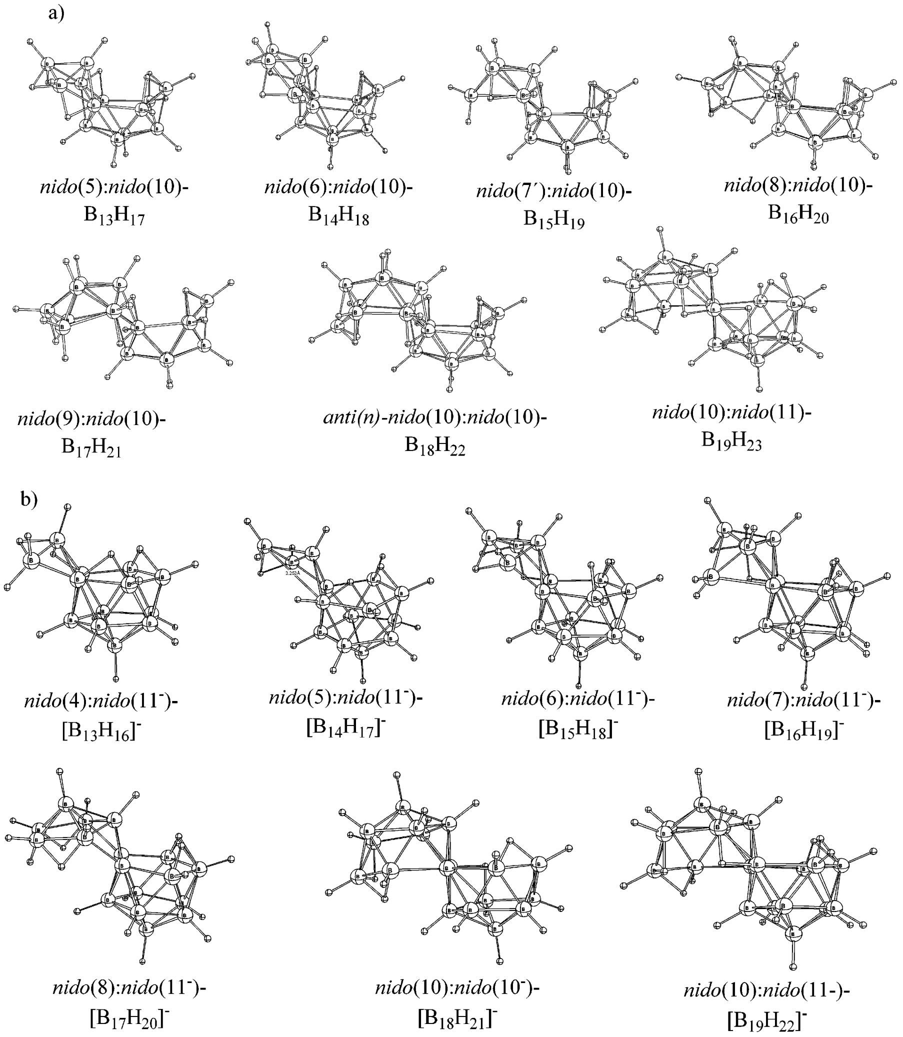


Figure 5. Comparison of relative energies (kcal mol^{-1}) of macropolyhedral *nido*:*nido*-B_nH_{n+4} boranes (labeled *x*:*y*, right half) with the relative energies E_{x+y} that result from the sum of energies computed for *nido*-boranes corresponding to the building units $E(B_xH_{x+4}) + E(B_yH_{y+4})$ (labeled *x*+*y*, left half). *x* and *y* indicate the size of the two clusters that make a macropolyhedron. **3**:**10** (**X**) can also be considered as being a distorted *nido*-$B_{11}H_{15}$ structure. The *nido*(4):*nido*(9)-macropolyhedra with one four-vertex *nido*-unit and the other 9-vertex *nido*-unit rearranged to a distorted geometry **Y** (for details, see Figure 4).

we computed the anionic single clusters as well as macropolyhedra of general formula $[B_nH_{n+3}]^-$ ($n = 4-19$). The stabilities of the most stable neutral macropolyhedra relative to the corresponding isomeric most stable neutral single clusters is usually higher (solid line in Figure 3) than that of the most stable anionic macropolyhedra relative to the corresponding most stable anionic *nido* single clusters (broken line in Figure 3). This shift can be explained on the basis of the presence of bridged hydrogen atoms on the open face. Neutral *nido* clusters with a single open face possess four extra open-face bridging hydrogen atoms, whereas neutral macropolyhedral boranes with two open faces possess six extra open-face bridging hydrogen atoms. Thus, hydrogen atoms exert more stress on the open face of single *nido*



nido(5):*nido*(10)-$B_{13}H_{17}$
nido(6):*nido*(10)-$B_{14}H_{18}$
nido(7′):*nido*(10)-$B_{15}H_{19}$
nido(8):*nido*(10)-$B_{16}H_{20}$
nido(9):*nido*(10)-$B_{17}H_{21}$
anti(n)-nido(10):*nido*(10)-$B_{18}H_{22}$
nido(10):*nido*(11)-$B_{19}H_{23}$

nido(4):*nido*(11^-)-$[B_{13}H_{16}]^-$
nido(5):*nido*(11^-)-$[B_{14}H_{17}]^-$
nido(6):*nido*(11^-)-$[B_{15}H_{18}]^-$
nido(7):*nido*(11^-)-$[B_{16}H_{19}]^-$
nido(8):*nido*(11^-)-$[B_{17}H_{20}]^-$
nido(10):*nido*(10^-)-$[B_{18}H_{21}]^-$
nido(10):*nido*(11-)-$[B_{19}H_{22}]^-$

Figure 6. Structures of the most stable 13−19-vertex-containing (a) macropolyhedral boranes and (b) borates.

clusters (four hydrogen atoms per open face) as compared to that of macropolyhedral boranes (three hydrogen atoms per open face). Monoanionic clusters have one open-face bridging hydrogen atom less in both cases (i.e., single *nido* clusters as well as *nido*:*nido*-macropolyhedral clusters), but more stress is released in single *nido* clusters as compared to macropolyhedral boranes and hence anionic *nido* clusters gain larger stability. As a consequence, the turning point from single *nido* cluster to macropolyhedral preference is shifted to a higher number of vertexes for anionic clusters. Anionic $[B_nH_{n+3}]^-$ macropolyhedral borates are clearly less stable than corresponding *nido* clusters for $n \leq 11$ (Figure 3). The relative stabilities of 12−16-vertex anionic macropolyhedral clusters are close to those of the most stable single *nido* clusters. For 17 vertexes or more, macropolyhedral borates are clearly preferred over anionic single *nido* clusters. We note that a more stable anionic macropolyhedral borate structure is obtained when the larger cluster unit is deprotonated.

3.4. Preferred Units for *nido*:*nido*-Macropolyhedral Boranes and Borates with 12−19 Vertexes. We further explored which *nido* clusters are best suited for the construction of macropolyhedral boranes and borates. The thermodynamic stabilities ($E_{x:y}$) of various *nido*:*nido*-B_nH_{n+4} macropolyhedra are indicated in the right half of Figure 5 relative to the most stable isomer for each number of vertexes (n). The energy range spanned by the isomers considered is always larger for even n than for the neighboring odd case of n+1 and $n - 1$. For even n larger than 12, the energetic separation of the most stable and the second most stable isomer is also more pronounced than for the neighboring odd $n + 1$ or $n - 1$. Obviously, among macropolyhedra with an even number of vertexes, a clearer preference exists for the most favorable distribution of vertexes among the two building blocks. Furthermore, whereas isomers with a 7-vertex unit are usually energetically disfavored, the thermodynamically most stable isomer for 13−19 vertexes contains at least one 10-vertex *nido* unit (Figure 6a).

The thermodynamically most stable *nido*:*nido*-macropolyhedral borates for $n = 12-17$ and 19 contain one deprotonated 11-vertex *nido* unit (Figure 6b, also see Appendix II, parts a−o, in the Supporting Information). For 18 vertexes, however, *nido*(10):*nido*(10)-$[B_{18}H_{21}]^-$ is 5.0 kcal mol^{-1} more stable than *nido*(9):*nido*(11)-$[B_{18}H_{21}]^-$.

The 11-vertex *nido* unit can be expected to be the most favorable *nido* unit, as it is obtained by the removal of one vertex from the highly stable icosahedral 12-vertex *closo* cluster.[19] However, the presence of three additional open-face hydrogen atoms on the five-membered open face of the 11-vertex *nido* cluster is unfavorable. Hence, the structure with a *nido*-10-vertex unit, which has a larger six-membered open face with adjacent hydrogen bridges sharing vertexes with cluster connectivity 3 rather than 4, enjoys greater thermodynamic stability in the case of neutral clusters. The loss of one extra open face hydrogen atom results in the release of stress in the 11-vertex *nido* unit; hence, anionic clusters with an 11-vertex deprotonated unit become more favorable.

3.5. Relative Energies ($E_{x:y}$) of Macropolyhedral Boranes in Comparison to Relative Energies (E_{x+y}) from Summation of Individual Clusters Making the Macropolyhedra. Does the observed stability order of isomeric two vertex-sharing macropolyhedra reflect that of the building units or is it different? In other words, are some *nido* clusters better than others in forming macropolyhedra? The right half of Figure 5 gives a comparison of relative stabilities of various B_nH_{n+4} macropolyhedral boranes ($E_{x:y}$) for $n = 6-19$, whereas the left half of Figure 5 gives relative energies that result from the sum of energies of individual clusters making the macropolyhedron (E_{x+y}).

For example, the most stable 19-vertex *nido*:*nido*-macropolyhedra ($B_{19}H_{23}$) is a 10-vertex *nido* unit sharing two vertexes with an 11-vertex *nido* unit ($E_{10:11}$ is smaller than $E_{9:12}$ for $n = 19$, right half of Figure 5). The sum of the energies of a 10-vertex ($B_{10}H_{14}$) and an 11-vertex ($B_{11}H_{15}$) *nido* cluster (E_{10+11}, left half of Figure 5) is also smaller than that of the nine-vertex (B_9H_{13}) and 12-vertex ($B_{12}H_{16}$) *nido* clusters (E_{9+12}). Although the stability order is the same in these cases, the numbers are different: $E_{9:12} = 17.2$ kcal mol^{-1} and $E_{9+12} = 28.4$ kcal mol^{-1}. The nine- and 12-vertex cluster combination seems to gain some stability with respect to the 10 plus 11 alternative, when incorporated into a macropolyhedron.

One 7-vertex unit usually results in a quite unfavorable distribution of vertexes in a macropolyhedra, whereas one 10-vertex usually means the best possible choice. The same is true for the sum of energies of two individual single *nido* clusters (E_{x+y}, listed in the left half of Figure 5). The sum of energies of the two units (E_{x+y}) for 11−19 vertexes is least when one component is a 10-vertex *nido* cluster, and E_{x+y} is usually large for the sum of energies of two single clusters with at least one 7-vertex *nido* unit.

For $n = 6$, 10−11, and 13−19, the thermodynamically most stable macropolyhedra, i.e., 3:5, 6:6, 3:10, 5:10, 6:10, 7:10, 8:10, 9:10, 10:10, and 10:11, are composed from the most stable choice of the individual clusters, i.e., 3+5, 6+6, 3+10, 5+10, 6+10, 7+10, 8+10, 9+10, 10+10, and 10+11 (Figure 5). As an example, the thermodynamically most stable 17-vertex macropolyhedron is a *nido*(9):*nido*(10)-$B_{17}H_{21}$, as $E_{9:10}$ gives the smallest value, just as E_{9+10} is smallest.

For the clusters with smaller sizes, the sum of energies of the individual clusters may not match the energies exhibited by the macropolyhedra. Moreover, the most stable isomer for smaller macropolyhedral boranes apparently contains one three-vertex *nido* unit. Such clusters resemble single-cluster boranes in the sense that both may be constructed by replacement of one hydrogen bridge by a BH_2 unit. Placement of a BH_2 unit to a bridging hydrogen atom position in a convex fashion gives another single cluster, whereas a concave orientation results in a *nido*(3):*nido*(x)-macropolyhedra.

The larger relative energy splitting for an even number of boron atoms is not special to the macropolyhedra but is inherent to the subclusters fused to a macropolyhedron. This conclusion is on the basis of the similar trends of relative stabilities of separated *nido* clusters (E_{x+y}), which are displayed in the left part of Figure 5 in comparison with $E_{x:y}$.

4. Conclusion

Neutral macropolyhedral boranes enjoy greater thermodynamic stability than single-cluster isomers for 12 or more vertexes. The loss of extra open-face hydrogen atoms results in the enhanced stability of *nido* clusters as compared to macropolyhedra. Hence, anionic macropolyhedra are less stable with respect to anionic single clusters than in the neutral case. The same should be true for suitably substituted heteroboranes. Usually, the thermodynamically most stable neutral macropolyhedral boranes have at least one 10-vertex *nido* single-cluster unit, whereas the anionic macropolyhedral clusters usually possess one deprotonated 11-vertex *nido* unit. The relative energies of the neutral macropolyhedra mostly reflect the stability patterns exhibited by the sum of the energies of two single-cluster units making a given macropolyhedra (E_{x+y}).

Acknowledgment. Financial support by DFG is gratefully acknowledged.

Supporting Information Available: Graphical display of optimized geometries of various isomers of 4−19 vertex *nido* clusters (Appendix I); optimized geometries of various B_nH_{n+4} macropolyhedra for $n = 4-13$ and 15−19 (Appendix II); thermodynamic stabilities of various *nido*:*nido*-B_nH_{n+4} clusters with respect to isomeric *nido*-B_nH_{n+4} clusters for $n = 4-19$ (Appendices IIIa−p, respectively); thermodynamic stabilities of various *nido*:*nido*-$[B_nH_{n+3}]^-$ clusters with respect to isomeric *nido* clusters for $n = 4-19$ (Appendices IVa−p, respectively); the optimized geometries of various $[B_nH_{n+3}]^-$ ($n = 4-19$) *nido* single clusters (Appendix V) and *nido*:*nido*-$[B_nH_{n+3}]^-$ macropolyhedral borates (Appendix VI); Tables with corresponding E_{x+y} computed at RB3LYP/6-311+G(d,p) for different *nido-x* and *nido-y* clusters (Appendix VII); Cartesian coordinates from optimized geometries of neutral *nido* clusters (Appendix VIII), neutral *nido*:*nido* macropolyhedral borane clusters (Appendix IX), anionic *nido* clusters (Appendix X), and anionic *nido*:*nido* clusters (Appendix-XI). This material is available free of charge via the Internet at http://pubs.acs.org.

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