Structural Paradigms in Macropolyhedral Boranes

Farooq Ahmad Kiani and Matthias Hofmann*[a]

Abstract: Macropolyhedral borane clusters are concave polyhedra constituting fused convex simple polyhedra. They are formally obtained by condensation of simple polyhedral boranes under elimination of between one and four BH_3 or isoelectronic units. The number of eliminated vertexes from simple polyhedra equals the number of shared vertexes in macropolyhedral boranes. For each of the eight classes with general formulae ranging from B_nH_{n-4} to B_nH_{n+10}, more than one structure type is possible, differing in the number of shared vertexes and in the types of the two combined cluster fragments. However, only one type of "potential structures" is represented by experimentally known examples and is found to be favored by theoretical calculations. A sophisticated system exists among the favored macropolyhedral borane structures. For each class of macropolyhedral boranes, the number of skeletal electron pairs is directly related to the general formula, the number of shared vertexes and the type of fused cluster fragments. In order to predict the distribution of vertexes among the fused fragments, we propose the concept of preferred fragments. Preferred fragments are those usually present in the thermodynamically most stable structure of a given class of macropolyhedral boranes and are also frequently observed in the experimentally known structures. This allows us to completely predict the cluster framework of the thermodynamically most stable macropolyhedral borane isomers.

Keywords: boranes · borates · density functional calculations · macropolyhedra · thermodynamics

Introduction

For a long time chemists have used generalized rules that relate the number of electrons[1] to the structures and properties of molecules. The octet rule,[2] the 18-electron rule,[3] Hückel's $4n+2$ π-electron rule for planar cyclic aromatic systems[4] and the $2(N+1)^2$ rule for three-dimensional aromatic systems[5] all make use of numbers of electrons to predict the structure or properties of molecules. Skeletal-electron-counting rules set by Wade[6] and Mingos[7] for simple polyhedral boron hydride clusters also relate the number of

[a] Dr. F. A. Kiani, Dr. M. Hofmann
Anorganisch-Chemisches Institut
Ruprecht-Karls-Universität Heidelberg
Im Neuenheimer Feld 270, 69120 Heidelberg (Germany)
Fax: (+49) 6221-548451
E-mail: matthias.hofmann@aci.uni-heidelberg.de

skeletal electrons to definite cluster shapes. Studies by Williams,[8] Jemmis and Schleyer,[9] Ott and Gimarc,[10] and Kiani and Hofmann,[11] provide further insight into the structural patterns of various simple polyhedral boranes. Clusters composed of fused polyhedra representing a concave curvature have been called macropolyhedra.[12] Macropolyhedra are realizable only for larger numbers of cluster atoms. A variety of homonuclear as well as heteronuclear boranes with more than one joint cluster unit are experimentally known and exhibit varying architectural patterns, for example, those with cluster units joined by a two-center–two-electron,[13] or by a three-center–two-electron bond,[13d,14] as well as those in which cluster units share one vertex, for example, $B_{14}H_{22}$,[15] two vertexes, for example, $B_{18}H_{22}$,[16,17] three vertexes, for example, $B_{20}H_{18}^{2-}$ dianion[18] or $B_{20}H_{16}L_2$ compounds,[19] or even four vertexes, for example, $B_{20}H_{16}$.[20] The underlying principles that govern the stabilities of macropolyhedral boranes are mostly unknown.[21–23] Except for Jemmis' skeletal-electron-counting rule ("*mno* rule"),[12d,24] no general theoretical consideration has been given to macropolyhedral boranes. According to the *mno* rule, 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 miss-

ing vertexes (p) equals the number of skeletal electron pairs (SEP) of a macropolyhedral borane, that is, $m+n+o+p = n(SEP)$. In order to perform this calculation, the molecular structure of the cluster has to be known. This procedure works as a test for a viable structure. Thus, unlike Wade's skeletal-electron-counting principle[6] for single clusters, the *mno* rule[24] does not specify architectures or cluster shapes based on the given number of skeletal electrons. Therefore, it is not necessarily possible to determine which structure out of a large number of possibilities is the thermodynamically most stable one corresponding to the expected cluster shape.[25] To give an example, the *mno* rule is in accordance with the three $B_{18}H_{22}$[16,17] isomers shown in Figure 1. These differ in the number of shared vertexes (i.e., one, two, or three), the types (i.e., *closo*-, *nido*-, and *arachno*-), and the size (i.e., nine, ten, or eleven vertexes) of the fused cluster fragments. In each case, isomers with the same number of shared vertexes but a different distribution of vertexes to the cluster fragments (e.g., *nido*-9-[2]-*nido*-11 rather than *nido*-10-[2]-*nido*-10 etc.; for nomenclature see below) would also follow the *mno* rule. However, the *mno* rule does not indicate which isomer is the thermodynamically most stable one! According to computations,[26] one-vertex-sharing *closo*(10)-[1]-*nido*(9)-$B_{18}H_{22}$ (B) and the three-vertex-sharing *arachno*(10)-[3]-*nido*(11)-$B_{18}H_{22}$ (C) are 65.0 and 61.7 kcal mol^{-1}, respectively, less stable than the two-vertex-sharing *nido*(10)-[2]-*nido*(10)-$B_{18}H_{22}$ isomer (A). The question arises of how to predict the "best" structure among various possibilities for $B_{18}H_{22}$ and for other macropolyhedral boranes without performing computations. Is there any relationship between the number of skeletal electrons and structures of macropolyhedral boranes akin to simple polyhedral clusters? Moreover, how are different classes of macropolyhedral boranes related to each other structurally as well as in terms of the number of skeletal electrons? Here, on the basis of our systematic survey of various experimentally known macropolyhedral boranes, assisted by suitable computations and our previously published results,[25] we present a generalized scheme that relates the number of skeletal electrons to the general formula, types of fused clusters or cluster fragments, the fusion modes between two or more individual clusters or cluster fragments, and the distribution of vertexes to the fused cluster fragments and hence, the structure of the thermodynamically most stable isomers for various classes of macropolyhedral boranes.

Results and Discussion

Nomenclature used for macropolyhedral boranes: In this paper, a nomenclature scheme is used for macropolyhedral boranes, according to the type and size of two cluster fragments and the number of shared vertexes. Names of types of each cluster fragment are italicized, with the number of vertexes of each cluster fragment in parenthesis. For two different cluster fragments, the names along with the cluster size are written in alphabetic order, regardless of the cluster size. For a macropolyhedral borane with two cluster fragments of the same type, the smaller cluster is given first. The number of shared vertexes between two cluster fragments is given in brackets between the cluster fragment specification, thus "-[1]-", "-[2]-", "-[3]-", and "-[4]-" indicate one, two, three, and four shared vertexes, respectively. The formula for the macropolyhedral boranes is written at the end, separated by a hyphen. As an example, *closo*(12)-[4]-*closo*(12)-$B_{20}H_{16}$ denotes the $B_{20}H_{16}$ structure that consists of two 12-vertex *closo*-cluster fragments, sharing four vertexes with each other, whereas *arachno*(8)-[1]-*nido*(7)-$B_{14}H_{22}$ has an architecture composed of an *arachno*-8- and a *nido*-7-vertex cluster fragment, sharing one vertex.

Various possible combinations of macropolyhedral boranes with different numbers of shared vertexes: All experimentally known macropolyhedral boranes sharing x vertexes can be formally constructed by the intimate fusion of simple polyhedral boranes eliminating a $(BH_3)_x$ (or isoelectronic) unit (Scheme 1). The topology of simple convex polyhedral borane clusters allows sharing of one to four vertexes ($x = 1$–4), when two clusters are fused to become a macropolyhedron. For example, in *nido*(6)-[2]-*nido*(8)-$B_{12}H_{16}$[27] two vertexes are shared between a *nido*-6-vertex and a *nido*-8-vertex fragment and, therefore, it is formally obtained by condensation of *nido*-B_6H_{10} and *nido*-B_8H_{12} under elimination of a B_2H_6 unit. Similarly, each of the experimentally known two-vertex-sharing *arachno*(9)-[2]-*nido*(6)-$B_{13}H_{19}$,[28] *nido*(6)-[2]-*nido*(10)-$B_{14}H_{18}$,[29] *nido*(8)-[2]-*nido*(10)-$B_{16}H_{20}$,[30] *nido*(10)-[2]-*nido*(10)-$B_{18}H_{22}$,[16] *nido*(10)-[2]-*nido*(11)-$B_{19}H_{22}^{-}$,[31] and *closo*(12)-[2]-*nido*(12)-$[B_{22}H_{22}]^{2-}$ dianion[32] may be derived from two cor-
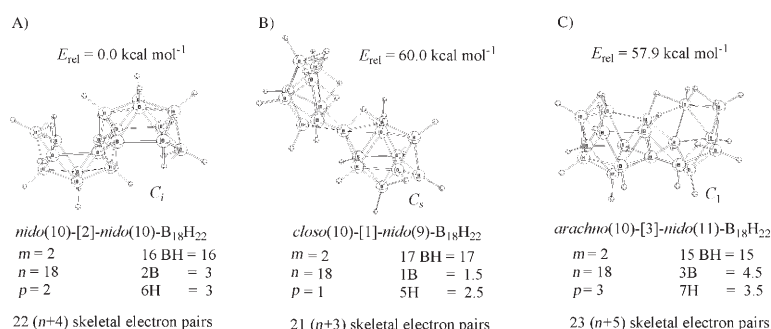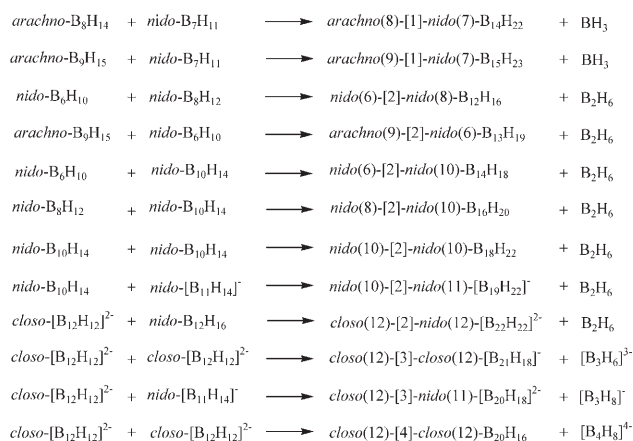

Figure 1. Optimized geometries and relative stabilities of various isomeric $B_{18}H_{22}$ structures differing with respect to the degree of vertex sharing. The number of required skeletal electron pairs according to the *mno* rule (left) equals the number of available skeletal electron pairs (right) for each structure. Notations *m*, *n*, and *p* stand for the number of cluster fragments, the total number of vertexes, and the number of missing vertexes, respectively (for nomenclature, see text).

A)

$E_{rel} = 0.0$ kcal mol^{-1}

C_i

nido(10)-[2]-*nido*(10)-$B_{18}H_{22}$

$m = 2$	16 BH = 16
$n = 18$	2B = 3
$p = 2$	6H = 3

22 ($n+4$) skeletal electron pairs

B)

$E_{rel} = 60.0$ kcal mol^{-1}

C_s

closo(10)-[1]-*nido*(9)-$B_{18}H_{22}$

$m = 2$	17 BH = 17
$n = 18$	1B = 1.5
$p = 1$	5H = 2.5

21 ($n+3$) skeletal electron pairs

C)

$E_{rel} = 57.9$ kcal mol^{-1}

C_1

arachno(10)-[3]-*nido*(11)-$B_{18}H_{22}$

$m = 2$	15 BH = 15
$n = 18$	3B = 4.5
$p = 3$	7H = 3.5

23 ($n+5$) skeletal electron pairs

responding clusters releasing a B_2H_6 unit. Single-vertex-sharing *arachno*(8)-[1]-*nido*(7)-$B_{14}H_{22}$ and *arachno*(9)-[1]-*nido*(7)-$B_{15}H_{23}$[15] are formally obtained by the removal of a single BH_3 unit from the corresponding clusters. Similarly, the three-vertex-sharing *closo*(12)-[3]-*nido*(11)-$B_{20}H_{18}^{2-}$ dianion[18] can be considered as obtained by the removal of a $[B_3H_8]^-$ unit from a 12-vertex *closo*-$[B_{12}H_{12}]^{2-}$ and an 11-vertex *nido*-$B_{11}H_{14}^-$. The unique four-vertex-sharing *closo*(12)-[4]-*closo*(12)-$B_{20}H_{16}$[20] is a formal condensation product of two $[B_{12}H_{12}]^{2-}$ units releasing a $[B_4H_8]^{4-}$ unit isoelectronic to B_4H_{12}.

Scheme 2. Classes of macropolyhedra according to general formulae, and possible types of structures according to incorporated cluster fragment types and fusion mode (i.e., sharing of one to four vertexes). Entries in grey boxes represent the cases for which experimentally known macropolyhedral boranes or borates exist. For nomenclature, see text. SEP = skeletal electron pairs. For two-vertex-sharing B_nH_{n+4}, only *nido*-[2]-*nido*-macropolyhedra are experimentally known.

$$arachno\text{-}B_8H_{14} + nido\text{-}B_7H_{11} \longrightarrow arachno(8)\text{-}[1]\text{-}nido(7)\text{-}B_{14}H_{22} + BH_3$$
$$arachno\text{-}B_9H_{15} + nido\text{-}B_7H_{11} \longrightarrow arachno(9)\text{-}[1]\text{-}nido(7)\text{-}B_{15}H_{23} + BH_3$$
$$nido\text{-}B_6H_{10} + nido\text{-}B_8H_{12} \longrightarrow nido(6)\text{-}[2]\text{-}nido(8)\text{-}B_{12}H_{16} + B_2H_6$$
$$arachno\text{-}B_9H_{15} + nido\text{-}B_6H_{10} \longrightarrow arachno(9)\text{-}[2]\text{-}nido(6)\text{-}B_{13}H_{19} + B_2H_6$$
$$nido\text{-}B_6H_{10} + nido\text{-}B_{10}H_{14} \longrightarrow nido(6)\text{-}[2]\text{-}nido(10)\text{-}B_{14}H_{18} + B_2H_6$$
$$nido\text{-}B_8H_{12} + nido\text{-}B_{10}H_{14} \longrightarrow nido(8)\text{-}[2]\text{-}nido(10)\text{-}B_{16}H_{20} + B_2H_6$$
$$nido\text{-}B_{10}H_{14} + nido\text{-}B_{10}H_{14} \longrightarrow nido(10)\text{-}[2]\text{-}nido(10)\text{-}B_{18}H_{22} + B_2H_6$$
$$nido\text{-}B_{10}H_{14} + nido\text{-}[B_{11}H_{14}]^- \longrightarrow nido(10)\text{-}[2]\text{-}nido(11)\text{-}[B_{19}H_{22}]^- + B_2H_6$$
$$closo\text{-}[B_{12}H_{12}]^{2-} + nido\text{-}B_{12}H_{16} \longrightarrow closo(12)\text{-}[2]\text{-}nido(12)\text{-}[B_{22}H_{22}]^{2-} + B_2H_6$$
$$closo\text{-}[B_{12}H_{12}]^{2-} + closo\text{-}[B_{12}H_{12}]^{2-} \longrightarrow closo(12)\text{-}[3]\text{-}closo(12)\text{-}[B_{21}H_{18}]^{2-} + [B_3H_6]^{3-}$$
$$closo\text{-}[B_{12}H_{12}]^{2-} + nido\text{-}[B_{11}H_{14}]^- \longrightarrow closo(12)\text{-}[3]\text{-}nido(11)\text{-}[B_{20}H_{18}]^{2-} + [B_3H_8]^-$$
$$closo\text{-}[B_{12}H_{12}]^{2-} + closo\text{-}[B_{12}H_{12}]^{2-} \longrightarrow closo(12)\text{-}[4]\text{-}closo(12)\text{-}B_{20}H_{16} + [B_4H_8]^{4-}$$

Scheme 1. Experimentally known homonuclear macropolyhedral boranes and borates can be formally obtained as condensation products of two simple polyhedral fragments eliminating as many BH_3 or isoelectronic units as there are vertexes shared (for nomenclature, see text).

All possible macropolyhedral borane types that result from condensation under elimination of one to four BH_3 or isoelectronic units (and share one to four vertexes between two clusters) are listed in Scheme 2. It is clear that among experimentally known structures (highlighted by gray boxes), more effective sharing (larger number of shared vertexes) is found for macropolyhedra with two *closo*-clusters (four-vertex-sharing B_nH_{n-4} macropolyhedra), whereas less pronounced sharing (least number of shared vertexes) is observed for more open *nido*- and *arachno*-clusters (one-vertex-sharing B_nH_{n+8} and B_nH_{n+10} macropolyhedra). In other words, the number of shared vertexes gradually decreases from four when two *closo*-clusters are fused to one in more open *arachno*-[1]-*nido*-clusters. The systematic relationships derived here for macropolyhedral boranes of course also hold true for corresponding main-group heteroboranes.

Number of skeletal electrons and the structure of macropolyhedral boranes: Let us consider the number of skeletal electron pairs, n(SEP), for various classes of macropolyhedral boranes listed in Scheme 2. In horizontal rows, the general formula for macropolyhedral boranes remains the same, while the number of shared vertexes increases. In the case of macropolyhedral boranes, the increase in the number of

shared vertexes for a given formula means the transformation of an exo-substituted BH unit (that contributes one SEP) into a bare boron atom (that contributes 1.5 SEP) and an endo-hydrogen atom (that contributes 0.5 SEP). In summary, per shared vertex the number of skeletal electron pairs increases by one.

As an example, a B_nH_n simple polyhedron has n skeletal electron pairs when each vertex is occupied by a BH unit contributing one SEP each. A *closo* compound, however, needs one SEP more ($n+1$). A hypothetical one-vertex-sharing B_nH_n macropolyhedral borane has ($n+1$) SEP, but for two cluster fragments at least ($n+2$) SEP are needed (i.e., in the case of two *closo* cluster fragments). At least two vertexes need to be shared (between two *closo* cluster fragments) to generate sufficient skeletal electrons, that is, a *closo*-[2]-*closo* macropolyhedron is the first viable structure for B_nH_n. More intimate fusion (e.g., three-vertex-sharing) increases n(SEP) further, which is accommodated by the opening of cluster fragments (e.g., *closo*-[3]-*nido*-B_nH_n with n(SEP) = $n+3$). Thus, along the horizontal rows, each additional shared vertex results in an increase in n(SEP) by one that results in the opening of one cluster fragment and the accommodation one more hydrogen atom on the open face.

For geometrical reasons, four-vertex sharing is the most intimate fusion possible for a stable macropolyhedral borane. When two *closo*-clusters are combined in such a

way, the required n(SEP) is $n+2$, which is realized for a formula of B_nH_{n-4}.[33]

Along the columns in Scheme 2, the number of shared vertexes remains the same, however, each pair of additional hydrogen atoms increases the n(SEP) by one. This additional electron pair makes one cluster fragment more open (i.e., *closo* to *nido* or *nido* to *arachno*). Alternatively, the n(SEP), and as a consequence also the type of fused fragments, remains unchanged when the number of shared vertexes is reduced by one (diagonal step "down to the left" in Scheme 2). The fact that macropolyhedra may structurally react to an increase in skeletal electron pairs by either opening a subcluster or by reducing the intimacy of cluster fusion has already been recognized.[12b,c,34]

The polyhedral skeletal-electron-pair approach[7b] may be applied to calculate the number of skeletal electron pairs, $a+b-x$, for a given macropolyhedron. Here, a and b represent the number of skeletal electron pairs the two fragments would require individually, and x equals the number of shared vertexes. In the formal condensation reaction of two simple polyhedral boranes, as many BH_3 units are eliminated as shared vertexes are formed. Each BH_3 takes away two SEPs (":BH,·H,·H") and each shared vertex generates one additional SEP (:BH→·B:,·H). Taken together, a macropolyhedral structure has the n(SEP) of its fragments diminished by the number of shared vertexes (also see Figure 2). Hence, the entries in Scheme 2 represent structures that realize a viable number of skeletal electrons for a given formula.

Number of skeletal electrons for higher condensed macropolyhedral borane systems: Scheme 2 relates the number of skeletal electrons to the structure for a given general formula of a macropolyhedral borane with two fused clusters. The number of skeletal electrons for various viable macropolyhedral boranes with more than two fused clusters can also be easily conceived on the basis of the *abx* rule (see above). All structures that can be obtained by the formal condensation of simple clusters under elimination of x BH_3 moieties, in which x is the number of shared vertexes in the macropolyhedral cluster, are viable macropolyhedral boranes obeying the *abx* rule. Thus, a macropolyhedral borane consisting of three fused fragments will have a skeletal electron count of $a+b+c-x$, or in general $\Sigma s_i - x$ in which Σs_i equals the number of skeletal electrons of individual clusters and x is the total number of shared vertexes.[35]

Potential structures for various classes of macropolyhedral boranes: With the exception of B_nH_{n+10}, the general formulae listed in Scheme 2 have at least one experimentally known homonuclear macropolyhedral borane or borate representative (highlighted with gray boxes, compare also Scheme 1). Various p-block heteroatom-containing macropolyhedral boranes are also known.[36] For a given general formula, all experimentally known structures belong to only one structure type. We suppose that the structure types for which experimentally known examples exist should be considerably more stable thermodynamically than the classes for which no structures are known experimentally, as in the case of B_nH_{n+4} (Figure 1).[37] In the case of B_nH_{n-2}, two *closo*-clusters sharing three vertexes should be a better choice than one *closo*- sharing four vertexes with a *nido*-cluster. The only experimental example, $[B_{21}H_{18}]^-$, synthesized recently[18] but predicted as a possible synthetic target for more than 40 years,[38] consists of two 12-vertex *closo*-clusters with three shared vertexes (Figure 2E). The alternative is a 12-vertex *closo*-cluster sharing four vertexes with a 13-vertex *nido*-cluster, which is thermodynamically 94.7 kcal mol^{-1} less stable than the former. A systematic study of all classes of experimentally known macropolyhedral boranes from B_nH_{n-4} to B_nH_{n+8} results in the selection of seven macropolyhedral borane categories listed in Table 1. We find that the structures, the type of fused clusters or cluster fragments (i.e., *closo*-, *nido*-, or *arachno*-), and the number of shared vertexes (i.e., one, two, three, or four) for various macropolyhedral boranes are directly related to the required number of skeletal electron pairs. This systematic relationship has not been suggested until now.

For example, all experimentally known B_nH_{n+4} macropolyhedral boranes[24] possess two shared vertexes and thus have n(SEP)$=n+4$: n skeletal electron pairs would result from n BH groups, supplemented by four skeletal electrons due to four extra hydrogen atoms, but two shared boron atoms increase the number of SEP further by two. This implies that these structures have two *nido*-clusters.[39] Attempts to construct a B_nH_{n+4} macropolyhedral borane, for example, $B_{18}H_{22}$ (Figure 1), with one or three shared vertex-

D) *closo*(12)-[4]-*closo*(12)-$B_{20}H_{16}$

16 BH	= 16 sep
4 B	= 6 sep
total	= 22 sep

abx rule		*mno* rule	
a	= 13	m	= 2
b	= 13	n	= 20
x	= 4	o	= 0
total = 22 sep		total = 22 sep	

E) *closo*(12)-[3]-*closo*(12)-$[B_{21}H_{18}]^-$

18 BH	= 18 sep
3 B	= 4.5 sep
-ve charge	= 0.5 sep
total	= 23 sep

abx rule		*mno* rule	
a	= 13	m	= 2
b	= 13	n	= 21
x	= 3	o	= 0
total = 23 sep		total = 23 sep	

F) *arachno*(8)-[1]-*nido*(7)-$B_{14}H_{22}$

13 BH	= 13 sep
1 B	= 1.5 sep
9 H	= 4.5 sep
total	= 19 sep

abx rule		*mno* rule	
a	= 11	m	= 2
b	= 9	n	= 14
x	= 1	o	= 0
		p	= 3
total = 19 sep		total = 19 sep	

G) *arachno*(9)-[2]-*nido*(6)-$B_{13}H_{19}$

11 BH	= 11 sep
2 B	= 3 sep
8 H	= 4 sep
total	= 18 sep

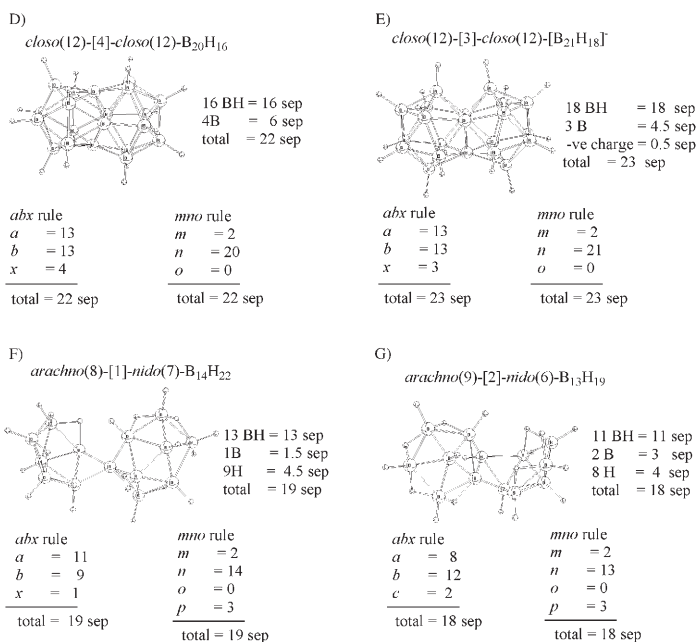| *abx* rule		*mno* rule	
a	= 8	m	= 2
b	= 12	n	= 13
c	= 2	o	= 0
		p	= 3
total = 18 sep		total = 18 sep	

Figure 2. Comparison of *abx* and *mno* approaches to obtain the number of skeletal electrons for various homonuclear macropolyhedral boranes. Notations m, n, and p stand for the number of cluster fragments, the total number of vertexes, and the number of missing vertexes, respectively, whereas a and b represent the number of skeletal electrons of the individual cluster fragments, and c is the number of shared vertexes (for nomenclature, see text).

Table 1. For each general formula, (i.e., class) of macropolyhedral boranes, a typical number of shared vertexes can be given and the corresponding number of skeletal electrons, the type of cluster fragments, as well as cluster-fragment sizes can be derived (for nomenclature, see text).

Formula	$x^{[a]}$	$n(\text{SEP})^{[b]}$	Structure	$F^{[c]}$	Proposed general formula	Experimental examples
B_nH_{n-4}	4	$n+2$	closo-[4]-closo	closo-12[d]	closo($n-8$)-[4]-closo(12)	closo(12)-[4]-closo(12)-$B_{20}H_{16}$
B_nH_{n-2}	3	$n+2$	closo-[3]-closo	closo-12[d]	closo($n-9$)-[3]-closo(12)	closo(12)-[3]-closo(12)-$B_{21}H_{18}^{-[e]}$
B_nH_n	3	$n+3$	closo-[3]-nido	closo-12[d]	nido($n-9$)-[3]-closo(12)	nido(11)-[3]-closo(12)-$B_{20}H_{16}L_2$
B_nH_{n+2}	2	$n+3$	closo-[2]-nido	closo-12[d]	nido($n-10$)-[2]-closo(12)	nido(12)-[2]-closo(12)-$[B_{22}H_{22}]^{2-}$
B_nH_{n+4}	2	$n+4$	nido-[2]-nido	nido-10[d, f]	nido($n-8$)-[2]-nido(10)	nido(10)-[2]-nido(10)-$B_{18}H_{22}$
B_nH_{n+6}	2	$n+5$	arachno-[2]-nido	nido-10[f]	arachno($n-8$)-[2]-nido(10)	arachno(10)-[2]-nido(10)-$[SB_{17}H_{20}]^{-[g]}$
B_nH_{n+8}	1	$n+5$	arachno-[1]-nido	nido-7	arachno($n-6$)-[1]-nido(7)	arachno(8)-[1]-nido(7)-$B_{14}H_{22}$

[a] Number of shared vertexes. [b] $n(\text{SEP})$ = number of skeletal electron pairs. [c] F = preferred fragment. [d] Preferred fragment as concluded from the occurrence in experimentally known structures. [e] See ref. [18]. [f] Preferred fragment based on known representatives and on a systematic computational study, see ref. [25]. [g] See ref. [36d].

es do not result in isomers with $n+4$ skeletal electron pairs. The closo(10)-[1]-nido(9)-$B_{18}H_{22}$ (Figure 1B) and arachno(10)-[3]-nido(11)-$B_{18}H_{22}$ (Figure 1C) have a total of $n+3$ (21) and $n+5$ (23) skeletal electron pairs, respectively, instead of $n+4$ (22).

Two less hydrogen atoms as in B_nH_{n+2} macropolyhedral boranes result in one skeletal electron pair less and one nido-fragment is oxidized to a closo-fragment to give B_nH_{n+2} macropolyhedral boranes with a closo-cluster sharing two vertexes with a nido-cluster. Like for B_nH_{n+4} macropolyhedral boranes, B_nH_{n+2} macropolyhedral boranes with a different number of shared vertexes will result in an undesired structure that has a different total number of skeletal electrons. Experimentally known[32] $[B_{22}H_{22}]^{2-}$ and its derivatives[40] correspond to this class of macropolyhedral boranes.

Macropolyhedral boranes of general formula B_nH_n contain $n+3$ skeletal electron pairs and the structures consist of a closo and a nido cluster sharing three vertexes. The $B_{20}H_{18}^{2-}$ dianion[18] and a series of $B_{20}H_{18}L_2$ compounds[19] in which a 12-vertex closo- and an 11-vertex nido-cluster share three vertexes are experimentally known.

Similarly, the correct macropolyhedral structure can also be predicted for other formulae. Each of the B_nH_{n-2} and B_nH_{n-4} macropolyhedral boranes has $n+2$ skeletal electron pairs. The B_nH_{n-2} macropolyhedral boranes (or the monoanionic $[B_nH_{n-3}]^-$, for example, $[B_{21}H_{18}]^-$ anion[18]) involve two closo-clusters sharing three vertexes with each other. The B_nH_{n-4} macropolyhedral boranes (e.g., $B_{20}H_{16}$[20]) share four vertexes between two closo-clusters. Any attempt to consider a B_nH_{n-4} or B_nH_{n-2} structure with a different number of shared vertexes or different type of fused clusters will result in discredited structures that do not fulfil the requirement of $n+2$ skeletal electron pairs.

B_nH_{n+6} macropolyhedral boranes have two shared vertexes and one additional skeletal electron pair ($n+5$ SEP), compared to the B_nH_{n+4} macropolyhedra. Opening of one cluster fragment from nido to arachno is the consequence. The predicted structures are arachno-[2]-nido-B_nH_{n+6}. Three more possible B_nH_{n+6} structure types (see Scheme 2) have different numbers of skeletal electron pairs and hence, different structures.

Two additional hydrogen atoms in B_nH_{n+8} structures result in decrease in the number of shared vertexes leaving the number of skeletal electrons unchanged, that is, n-

$(\text{SEP}) = n+5$. Such structures share one vertex between two highly open nido- and arachno-clusters. Experimentally known structures correspond to $B_{14}H_{22}$ and $B_{15}H_{23}$.[15]

Preferred fragments for macropolyhedral boranes: Computations of a large number of nido-[2]-nido-B_nH_{n+4} macropolyhedral borane isomers revealed that the thermodynamically most stable 13- to 19-vertex-containing macropolyhedra contain at least one 10-vertex nido-cluster fragment.[25] The size of the second nido-cluster fragment increases from five vertexes to eleven vertexes. Moreover, the structures of the experimentally known nido-[2]-nido-macropolyhedra usually represent the thermodynamically most stable framework, that is, contain a 10-vertex nido-fragment. Similarly, arachno-[2]-arachno-B_nH_{n+8} structures contain at least one nine-vertex arachno-cluster fragment, whereas arachno-[2]-nido-B_nH_{n+6} clusters usually contain a ten-vertex nido-cluster fragment (or a nine-vertex arachno-cluster fragment in the case of arachno(9)-[2]-nido(11)-$B_{18}H_{24}$). We note:

1) The thermodynamically most stable isomers of a given class of macropolyhedral boranes contain a unique preferred fragment.
2) These fragments are usually present in the experimentally known structures.

These two observations can be used to propose the structures of the thermodynamically most stable isomers of a given class of macropolyhedra. For example, all experimentally known macropolyhedral structures involving at least one closo-cluster have a 12-vertex closo-cluster. The 12-vertex closo-cluster alone is a highly symmetric and very stable structure with five-coordinate vertexes only. Its extraordinary stability[41] is also evident from its highest aromaticity and lowest energy-per-vertex values among closo-clusters.[42] Its presence in the experimentally known macropolyhedral structures recommends the 12-vertex closo-cluster as the preferred fragment for the thermodynamically most stable macropolyhedral boranes incorporating a closo-fragment. To confirm the high stability of macropolyhedral boranes containing at least one 12-vertex closo-cluster relative to other possible structures, we computed isomers of various classes of macropolyhedral boranes ranging from B_nH_{n-4} to $[B_nH_n]^{2-}$ (see Tables S1 to S4 in Supporting Information).

All macropolyhedral boranes that involve one 12-vertex *closo*-cluster are far more stable than corresponding isomers with other *closo*-clusters. This fact can be used to easily predict the general structures of the thermodynamically most stable macropolyhedral boranes involving at least one *closo*-cluster, that is, macropolyhedral boranes ranging from B_nH_{n-4} to B_nH_{n+2}.

The extent of preference for a specific size decreases as the fragment opens. There is a greater preference for the *nido*-10 (compared to other *nido*-cluster fragments) than for the *arachno*-9 (compared to other *arachno*-clusters).[25] The *nido*(10)-[2]-*nido*(10)-$B_{18}H_{22}$ is 42.5 kcal mol^{-1} more stable than the second most stable *nido*-[2]-*nido*-$B_{18}H_{22}$ isomer, but the *arachno*(9)-[2]-*arachno*(9)-$B_{16}H_{24}$ is only 7.5 kcal mol^{-1} more stable than the second most stable isomer.[25] Similarly, the *closo*-12 (compared to other *closo*-clusters) is preferred more than the *nido*-10 fragment (relative to other *nido*-fragments). The *closo*(12)-[4]-*closo*(12)-$B_{20}H_{16}$ is 110.5 kcal mol^{-1} more stable than the *closo*(11)-[4]-*closo*(13)-$B_{20}H_{16}$! As a consequence, in mixed *closo*-[3]-*nido*- or *closo*-[2]-*nido*-macropolyhedral boranes, always the *closo*-fragment determines the vertex distribution. Similarly, in the case of *nido*-[2]-*nido*- or *arachno*-[2]-*nido*-macropolyhedral boranes, almost always the *nido*-fragment determines the vertex distribution.

Two experimentally known one-vertex-sharing *arachno*-[1]-*nido*-B_nH_{n+8} structures, that is, *arachno*-[1]-*nido*-$B_{14}H_{22}$ and $B_{15}H_{23}$, each with one seven-vertex *nido*-fragment, are experimentally known.[15] Therefore, we suppose that the seven-vertex *nido*-cluster fragment might be the preferred fragment for the *arachno*-[1]-*nido*-B_nH_{n+8} macropolyhedra, although this preference is probably weak.

Preferred frameworks for different classes of macropolyhedral boranes: The idea of a given preferred fragment for each class of macropolyhedral boranes conveniently allows us to propose the complete framework for the thermodynamically most stable isomers of various macropolyhedral boranes. For example, for *nido*-[2]-*nido*-macropolyhedral boranes, the *nido*-10-vertex cluster is the preferred fragment and the thermodynamically most stable *nido*-[2]-*nido*-macropolyhedral isomers have the general formula *nido*$(n-8)$-[2]-*nido*(10)-B_nH_{n+4}. A similar general formula for the thermodynamically most stable *arachno*-[2]-*nido*-B_nH_{n+6} isomers was proposed to be *arachno*$(n-8)$-[2]-*nido*(10)-B_nH_{n+6}.[25b,c] As the 12-vertex *closo*-cluster is the preferred fragment for the thermodynamically most stable isomers of macropolyhedral boranes containing at least one *closo*-cluster, the cluster composition of various classes of macropolyhedral boranes ranging from B_nH_{n-4} to B_nH_{n+2} can be proposed (see Table S1). Similarly, the fragment sizes for the most stable one-vertex-sharing *arachno*-[1]-*nido*-B_nH_{n+8} structures are proposed to be *arachno*$(n-6)$ and *nido*(7).

Structures of all experimentally known homonuclear macropolyhedral boranes or borates can be derived on the basis of a general scheme provided in this paper. We note, however, that macropolyhedral metallaheteroboranes frequently possess structures that do not correspond to the structures preferred by boranes (see Scheme 2).[35]

Conclusion

All macropolyhedral borane clusters are formally obtained by intimate fusion of simple polyhedra resulting in the elimination of one to four BH$_3$ (or isoelectronic) units. The number of eliminated vertexes from simple polyhedra equals the number of shared vertexes in macropolyhedral boranes. The number of skeletal electrons of macropolyhedral boranes is simply $a+b-x$, in which a and b correspond to the number of skeletal electrons of individual cluster fragments, and x is the number of shared vertexes. All experimentally known (and some experimentally unknown) macropolyhedral boranes or borates can be divided into seven classes. For each class, the general formula is directly associated with the preferred number of shared vertexes. This allows the number of skeletal electron pairs and the types of fused clusters to be derived. The existence of a preferred fragment size for each cluster-fragment type allows us to predict the complete framework of the thermodynamically most stable macropolyhedral borane isomers.

[1] R. W. Rudolph, *Acc. Chem. Res.* **1976**, *9*, 446–452.

[2] G. N. Lewis, *J. Am. Chem. Soc.* **1916**, *38*, 762–785.

[3] N. V. Sidgwick, *Trans. Faraday Soc.* **1923**, *19*, 469.

[4] a) E. Hückel, *Z. Phys.* **1932**, *76*, 628–648; b) E. Hückel, *Z. Phys.* **1933**, *83*, 632–668.

[5] A. Hirsch, Z. Chen, H. Jiao, *Angew. Chem.* **2001**, *113*, 2916–2920; *Angew. Chem. Int. Ed.* **2001**, *40*, 2834–2838.

[6] a) K. Wade, *Adv. Inorg. Chem. Radiochem.* **1976**, *18*, 1–66; b) K. Wade in *Metal Interactions with Boron Clusters* (Ed.: R. N. Grimes), Plenum Press, New York, **1982**, Chapter 1, pp. 1–41.

[7] a) D. M. P. Mingos, *Nature Phys. Sci.* **1972**, *236*, 99–102; b) D. M. P. Mingos, *Acc. Chem. Res.* **1984**, *17*, 311–319.

[8] a) R. E. Williams, *J. Am. Chem. Soc.* **1965**, *87*, 3513–3515; b) R. E. Williams in *Progress in Boron Chemistry, Vol. 2* (Eds.: R. J. Brotherton, H. Steinberg), Pergamon Press, England, **1970**, Chapter 2, p. 57; c) R. E. Williams, *Chem. Rev.* **1992**, *92*, 177–207 and references therein.

[9] a) E. D. Jemmis, *J. Am. Chem. Soc.* **1982**, *104*, 7017–7020; b) E. D. Jemmis, P. v. R. Schleyer, *J. Am. Chem. Soc.* **1982**, *104*, 4781–4788.

[10] J. J. Ott, B. M. Gimarc, *J. Am. Chem. Soc.* **1986**, *108*, 4303–4308.

[11] a) F. A. Kiani, M. Hofmann, *Inorg. Chem.* **2004**, *43*, 8561–8571; b) F. A. Kiani, M. Hofmann, *Inorg. Chem.* **2005**, *44*, 3746–3754; c) F. A. Kiani, M. Hofmann, *Eur. J. Inorg. Chem.* **2005**, *12*, 2545–2553; d) F. A. Kiani, M. Hofmann, *J. Mol. Model.* **2006**, *12*, 597–609; e) F. A. Kiani, M. Hofmann, *Organometallics* **2006**, *25*, 485–490; f) F. A. Kiani, M. Hofmann, *Dalton Trans.* **2006**, 686–692.

[12] a) N. N. Greenwood, *Chem. Soc. Rev.* **1984**, *13*, 353–374; b) J. D. Kennedy in *Advances in Boron Chemistry* (Ed.: W. Siebert), Royal Society of Chemistry, Cambridge, **1997**, pp. 451–462; c) J. Bould, D. L. Ormsby, H.-J. Yao, C.-H. Hu, J. Sun, R.-S. Jin, S. L. Shea, W. Clegg, T. Jelinek, N. P. Rath, M. Thornton-Pett, R. Greatrex, P.-J. Zheng, L. Barton, B. Štíbr, J. D. Kennedy in *Contemporary Boron*

Chemistry (Eds.: M. Davidson, A. K. Hughes, T. B. Marder, K. Wade), Royal Society of Chemistry, Cambridge, **2000**, pp. 171–174; d) for a recent review, see: E. D. Jemmis, M. M. Balakrishnarajan, P. D. Pancharatna, *Chem. Rev.* **2002**, *102*, 93–144.

[13] See, for example, a) G. N. Srinivas, T. P. Hamilton, E. D. Jemmis, M. L. McKee, K. Lammertsma, *J. Am. Chem. Soc.* **2000**, *122*, 1725–1728; b) M. F. Hawthorne, R. L. Pilling, P. F. Stokely, P. M. Garrett, *J. Am. Chem. Soc.* **1963**, *85*, 3704–3705; c) M. F. Hawthorne, R. L. Pilling, P. F. Stokely, *J. Am. Chem. Soc.* **1965**, *87*, 1893–1899; d) R. A. Watson-Clark, C. B. Knobler, M. F. Hawthorne, *Inorg. Chem.* **1996**, *35*, 2963–2966.

[14] See, for example, M. F. Hawthorne, R. L. Pilling, *J. Am. Chem. Soc.* **1966**, *88*, 3873–3874.

[15] J. Rathke, R. Schaeffer, *Inorg. Chem.* **1974**, *13*, 3008–3011.

[16] Two isomers with C_i and C_2 symmetry, each incorporating two ten-vertex *nido*-cluster fragments with a two-vertex sharing pattern, are experimentally known. See a) P. G. Simpson, W. N. Lipscomb, *J. Chem. Phys.* **1963**, *39*, 26–34; b) A. R. Pitochelli, M. F. Hawthorne, *J. Am. Chem. Soc.* **1962**, *84*, 3218–3218; c) P. G. Simpson, W. N. Lipscomb, *Proc. Natl. Acad. Sci. USA* **1962**, *48*, 1490–1491; d) P. G. Simpson, K. Folting, R. D. Dobrott, W. N. Lipscomb, *J. Chem. Phys.* **1963**, *39*, 2339–2348; e) X. L. R. Fontaine, N. N. Greenwood, J. D. Kennedy, P. Mackinnon, *J. Chem. Soc. Dalton Trans.* **1988**, 1785–1793; f) P. G. Simpson, K. Folting, W. N. Lipscomb, *J. Am. Chem. Soc.* **1963**, *85*, 1879–1880.

[17] The C_i isomer (shown in Figure 1) is the most stable two-vertex-sharing $B_{18}H_{22}$ isomer and is also 1.2 kcal mol^{-1} more stable than the C_2 isomer. In Figure 1, the two-vertex-sharing C_i and two other possible isomers due to one- and three-vertex-sharing patterns are shown.

[18] E. Bernhardt, D. J. Brauer, M. Finze, H. Willner, *Angew. Chem.* **2007**, *119*, 2985–2988; *Angew. Chem. Int. Ed.* **2007**, *46*, 2927–2930.

[19] See, for example, a) J. H. Enemark, L. B. Friedman, W. N. Lipscomb, *Inorg. Chem.* **1966**, *5*, 2165–2173; b) Y. M. Cheek, N. N. Greenwood, J. D. Kennedy, W. S. McDonald, *J. Chem. Soc. Chem. Commun.* **1982**, 80–81.

[20] a) L. B. Friedman, R. D. Dobrott, W. N. Lipscomb, *J. Am. Chem. Soc.* **1963**, *85*, 3505–3506; b) N. E. Miller, E. L. Muetterties, *J. Am. Chem. Soc.* **1963**, *85*, 3506–3506.

[21] J. D. Kennedy in *Advances in Boron Chemistry* (Ed.: W. Siebert), Royal Society of Chemistry, Cambridge, **1997**, p. 451.

[22] R. N. Grimes, *Metal Interactions with Boron Clusters*, Plenum Press, New York, **1982**.

[23] T. D. McGrath, T. Jelinek, B. Štíbr, M. Thornton-Pett, J. D. Kennedy, *J. Chem. Soc. Dalton Trans.* **1997**, 2543–2545.

[24] E. D. Jemmis, M. M. Balakrishnarajan, P. D. Pancharatna, *J. Am. Chem. Soc.* **2001**, *123*, 4313–4323.

[25] a) F. A. Kiani, M. Hofmann, *Inorg. Chem.* **2006**, *45*, 6996–7003; b) F. A. Kiani, M. Hofmann, *Dalton Trans.* **2006**, 5515–5520; c) F. A. Kiani, M. Hofmann, *Dalton Trans.* **2007**, 1207–1213.

[26] All computations were carried out at RB3LYP/6-311+G(d,p)// RB3LYP/6-31G(d)+ZPE by using; Gaussian 03, Revision B.03, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, Gaussian, Inc., Wallingford CT, **2004**.

[27] a) C. T. Brewer, R. N. Grimes, *J. Am. Chem. Soc.* **1984**, *106*, 2722–2723; b) C. T. Brewer, R. G. Swisher, E. Sinn, R. N. Grimes, *J. Am. Chem. Soc.* **1985**, *107*, 3558–3564.

[28] J. C. Huffman, D. C. Moody, R. Schaffer, *Inorg. Chem.* **1976**, *15*, 227–232.

[29] S. Heřmánek, K. Fetter, J. Plešek, L. J. Todd, A. R. Garber, *Inorg. Chem.* **1975**, *14*, 2250–2253.

[30] a) J. Plešek, S. Heřmánek, F. Hanousek, *Collect. Czech. Chem. Commun.* **1967**, *32*, 699–705; b) L. B. Friedman, R. E. Cook, M. D. Glick, *J. Am. Chem. Soc.* **1968**, *90*, 6862–6863; c) L. B. Friedman, R. E. Cook, M. D. Glick, *Inorg. Chem.* **1970**, *9*, 1452–1458.

[31] The compound was reported as $B_{19}H_{20}^-$ anion in J. A. Dopke, D. R. Powell, D. F. Gaines, *Inorg. Chem.* **2000**, *39*, 463–467. The formula was corrected to be $B_{19}H_{22}^-$, because application of the *nmo* rule indicates missing electrons: E. D. Jemmis, M. M. Balakrishnarajan, P. D. Pancharatna, *Inorg. Chem.* **2001**, *40*, 1730–1731. Computed NMR chemical shifts also rule out $B_{19}H_{20}^-$ and are in support of $B_{19}H_{22}^-$ (see Supporting Information).

[32] N. S. Hosmane, A. Franken, G. Zhang, R. R. Srivastava, R. Y. Smith, B. F. Spielvogel, *Main Group Met. Chem.* **1998**, *21*, 319–324.

[33] More condensed species, that is, B_nH_m in which $m \ll n$, result from repeated condensation of polyhedral clusters. See, for example, E. D. Jemmis, E. G. Jayasree, *Acc. Chem. Res.* **2003**, *36*, 816–824.

[34] See, for example, a) S. L. Shea, T. Jelínek, B. Štíbr, M. Thornton-Pett, J. D. Kennedy, *Inorg. Chim. Acta* **2004**, *357*, 3119–3123; b) S. L. Shea, T. D. McGrath, T. Jelínek, B. Štíbr, M. Thornton-Pett, J. D. Kennedy, *Inorg. Chem. Commun.* **1998**, *1*, 97; c) S. L. Shea, T. Jelínek, B. Štíbr, M. Thornton-Pett, J. D. Kennedy, *Inorg. Chem. Commun.* **2000**, *3*, 169.

[35] Electronic requirements for macropolyhedral boranes depend upon the condensation mode (number of shared vertexes, x), between individual clusters, in which boron atoms occupy the shared vertexes. Macropolyhedral metallaboranes with shared metal atoms or fragments have a different condensation mode and can not be considered to be obtained by the removal of $(BH_3)_x$ units. Thus, they have different requirements of skeletal electron pairs. All macropolyhedral metallaboranes possess $\Sigma s_i + m - x$ skeletal electron pairs, in which m is the number of shared metal atoms or metal fragments.

[36] See, for example: a) T. Jelínek, I. Cisarova, B. Štíbr, J. D. Kennedy, *Dalton Trans.* **2007**, *42*, 4766–4768; b) P. K. Dosangh, J. Bould, M. G. S. Londesborough, T. Jelínek, M. Thornton-Pett, B. Štíbr, J. D. Kennedy, *J. Organomet. Chem.* **2003**, *680*, 312–322; c) M. Hofmann, S. K. Goll, *J. Organomet. Chem.* **2002**, *657*, 273–278; d) T. Jelínek, C. A. Kilner, S. A. Barrett, M. Thornton-Pett, J. D. Kennedy, *Chem. Commun.* **1999**, 1905–1906; e) T. Jelínek, I. Cisarova, B. Štíbr, J. D. Kennedy, M. Thornton-Pett, *J. Chem. Soc. Dalton Trans.* **1998**, 2965–2968; f) T. Jelínek, J. D. Kennedy, B. Štíbr, M. Thornton-Pett, *Inorg. Chem. Commun.* **1998**, *1*, 179–181; g) P. Kaur, J. Holub, N. P. Rath, J. Bould, L. Barton, B. Štíbr, J. D. Kennedy, *Chemical Commun.* **1996**, 273–275; h) T. Jelínek, J. D. Kennedy, B. Štíbr, M. Thornton-Pett, *J. Chem. Soc. Chem. Commun.* **1995**, 2407–2408; i) T. Jelínek, J. D. Kennedy, B. Štíbr, M. Thornton-Pett, *J. Chem. Soc. Chem. Commun.* **1995**, 1665–1666.

[37] One should keep in mind that any reaction product may be dictated by kinetics rather than thermodynamics. In the case of simple polyhedral boranes, usually the thermodynamically most stable isomers are obtained because rearrangements are typically facile. For macropolyhedral boranes, this is still less clear. From the structures we computed we find a remarkable preference for one typical fusion type, which was also found experimentally.

[38] a) J. H. Enemark, L. B. Friedman, W. N. Lipscomb, *Inorg. Chem.* **1966**, *5*, 2165–2173; b) J. H. Enemark, L. B. Friedman, J. A. Hartsuck, W. N. Lipscomb, *J. Am. Chem. Soc.* **1966**, *88*, 3659–3661; c) W. N. Lipscomb, *J. Less-Common Met.* **1981**, *82*, 1–20.

[39] Although a large number of *nido*:*nido*-macropolyhedral boranes have been reported, no example for the *closo*:*arachno*-alternative is experimentally known. This is probably because the difference in the excess skeletal electrons (one SEP for *closo* but three SEP for *arachno*) would be too large. *closo*(12):*aracho*(8) and *closo*(10):*ar*-

achno(10) isomers are computed to be less stable than C_i symmetric *nido*(10):*nido*(10)-$B_{18}H_{22}$ by 41.6 and 77.7 kcal mol^{-1}, respectively.

[40] O. Volkov, N. P. Rath, L. Barton, *J. Organomet. Chem.* **2003**, *680*, 212–217.

[41] a) L. D. Brown, W. N. Lipscomb, *Inorg. Chem.* **1977**, *16*, 2989; b) E. D. Jemmis, P. N. V. Pavankumar, *Proc. Indian Acad. Sci. Chem. Sci.* **1984**, *93*, 479; c) I. Boustani, *J. Solid State Chem.* **1997**, *133*, 182; d) R. B. King, *Inorg. Chem.* **2001**, *40*, 6369–6374.

[42] P. v. R. Schleyer, K. Najafian, A. M. Mebel, *Inorg. Chem.* **1998**, *37*, 6765–6772.