Boranes and Heteroboranes: A Paradigm for the Electron Requirements of Clusters?

Ralph W. Rudolph

Department of Chemistry, University of Michigan, Ann Arbor, Michigan 48109

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Chemists have long recognized that certain "magic numbers" of electrons are typically characteristic of certain chemical unions or classes of compounds. The "octet rule" for first-row elements,[1] the "rule of 18" for transition-metal complexes,[2] and the "Hückel rule" for aromatic molecules[3] are familiar to most chemists. Similar systematization schemes are now apparent for cluster compounds such as the polyhedral boranes, heteroboranes, and metalloboranes, which are often treated as classroom curiosities. The approach to be discussed below has become apparent over the last 15 years as the scope of borane chemistry has been revealed and numerous structures have been determined; we have chosen to call it the PERC approach (paradigm for the electron requirements of clusters). The ideas are conceptually simple and allow for surprisingly accurate predictions of possible molecules, their idealized geometries, their preferred isomeric forms, and their modes of interconversion. This Account will first focus on the boranes, heteroboranes, and their metal complexes, and then critically examine the adaptability to carbonium ions and metal clusters of the patterns evident in the boranes.

Formulation

The interest surrounding borane chemistry is at least in part due to their "electron deficiency". The subject systematics *need not* be concerned explicitly with how the various known polyhedral frameworks compensate for this deficiency in terms of the assignment of two-center and three-center bonds.[4] For instance, the lines depicting the skeletons of the illustrated structures are not electron-pair bonds. The lines merely join nearest neighbors and illustrate cluster geometry. However, exopolyhedral lines do represent the usual electron-pair bonds. The polyhedral skeletons described here can be termed quite descriptively as deltahedra (all faces triangular) or deltahedral fragments. The left-hand column[5] of Figure 1 shows the closo molecules (deltahedra) from which all the other idealized structures (deltahedral fragments) can be generated systematically.[6] Any nido or arachno cluster can be generated from the appropriate deltahedron by ascending a diagonal from left to right. This progression generates the nido structure (center column) by removing the most highly connected (highest order[5]) vertex of the deltahedron and the arachno structure (right column) by removal of the highest order[5] atom of the open (nontriangular) face of the nido cluster so as to generate the minimum number of vertices of order 2. The structural correlations shown in Figure 1 were first formulated by Williams[7] but are embellished here to present the new hypho class,[8] to emphasize the relationship between skeletal electron count and structure, and to anticipate exceptions. Theoretical bases for the empirically established trends of Figure 1 are discussed later.

Proposal of a structure from Figure 1 for a given borane or heteroborane proceeds by (1) selecting the row which corresponds to the framework atoms and (2) determining the number of electrons which can be reasonably assigned to the skeleton as opposed to exopolyhedral electrons (counts of $2n + 2$, $2n + 4$, and $2n + 6$ framework electrons give a closo, nido, or arachno classification, respectively, and suggest the structure corresponding to the appropriate column of Figure 1).

Other empirical rules, to be mentioned after some examples of each classification, speak to the preferred placement of heteroatoms and "extra" hydrogens. The systematics also emphasize the oxidation–reduction nature of closo–nido–arachno interconversions for frameworks of the same size.

Closo Molecules ($2n + 2$ Systems)

The usual assignment of valence electrons and factoring out of those in exopolyhedral bonds gives $2n$ framework electrons from n boron atoms, two electrons short of the $2n + 2$ closo count for a B_nH_n molecule. In fact, no neutral $B_n H_n$ molecules are known; however, the $B_nH_n^{2-}$ (n = 6–12) anions and the isoelectronic $C_2B_{n-2}H_n$ (n = 5–12) dicarbaboranes are the best-known examples of closo molecules. Thus, in these respective cases, the anion charge and the two carbon atoms, each with one more valence electron than boron, supply the 2 electrons in excess of the $2n$ count. In

Ralph W. Rudolph is Associate Professor of Chemistry at the University of Michigan, where he received the Ph.D. degree in 1966. He was born in Erie, Pa., and studied for the B.S. degree at The Pennsylvania State University. He served in the U.S. Air Force from 1966 to 1969, when he joined the faculty at the University of Michigan. Dr. Rudolph's research interests are in syntheses, structures, and reaction chemistry of heteroboranes, metalloheteroboranes, and organometallics.

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(1) G. N. Lewis, *J. Am. Chem. Soc.*, **38,** 762 (1916).

(2) N. V. Sidgwick, *Trans. Faraday Soc.*, **19,** 469 (1923). The original formulation was more concerned with the "effective atomic number" of the metal center than the 18 electrons in the valence shell.

(3) E. Hückel, *Z. Phys.*, **76,** 628 (1932); **83,** 632 (1933).

(4) For example, see (a) W. N. Lipscomb, "Boron Hydrides", W. A. Benjamin, New York, N.Y., 1963; (b) I. R. Epstein and W. N. Lipscomb, *Inorg. Chem.*, **10,** 1921 (1971).

(5) The deltahedra from n = 4–12 vertices are the: tetrahedron, trigonal bipyramid, octahedron, pentagonal bipyramid, bisdisphenoid, symmetrically tricapped trigonal prism, bicapped square antiprism, octadecahedron, and icosahedron. All of these idealized structures are convex (the plane of any face does not intersect the polyhedron) deltahedra except for the octadecahedron. The order of a vertex is given by the number of nearest-neighbor vertices within the framework.

(6) R. W. Rudolph and W. R. Pretzer, *Inorg. Chem.*, **11,** 1974 (1972).

(7) R. E. Williams, *Inorg. Chem.*, **10,** 210 (1971).

(8) The nomenclature closo, nido, arachno, and hypho is derived from the Greek and implies a closed, nestlike, weblike, and netlike structure, respectively.

general, the substitution of heteroatoms for boron alters the number of framework electrons contributed by a given vertex, but as long as the total amounts to $2n + 2$, the molecule is classified as closo.[6] Heteroatoms in the same group as boron contribute 2 framework electrons, those to the left in the periodic table contribute fewer, those to the right contribute more. As generalized in the form of an equation by Wade,[9] the number of framework electrons contributed by a main group element is equal to $(v + x - 2)$ where v = the number of valence-shell electrons and x = the number of electrons from ligands (e.g., for H, $x = 1$, and for Lewis bases, $x = 2$). Examples are given in Table I. Note that these considerations suggest an exodeltahedral lone pair in molecules such as $:SB_9H_9$ and $:PCB_{10}H_{11}$ as well as nominal bicapped square antiprism ($n = 10$) and icosahedral ($n = 12$) structures, respectively.

Nido Molecules (2*n* + 4 Systems)

A number of closo heteroboranes add the two electrons characteristic of a nido molecule and undergo a concomitant structural distortion from a deltahedron to a deltahedral fragment (horizontal progression in Figure 1). For instance, *closo*-$C_2B_9H_{11}$ ($2n + 2 = 24\ e^-$) is easily reduced to *nido*-$C_2B_9H_{11}^{2-}$ ($2n + 4 = 26\ e^-$),[10] and conversely, 7,9-$C_2B_9H_{11}^{2-}$ is readily oxidized to $C_2B_9H_{11}$.[11] Reduction also occurs in effect upon addition of donors to such molecules, i.e., the octahedron of the closo molecule $C_2B_4H_6$ opens to the nido pentagonal pyramid upon addition of $:NR_3 = L$ to give $C_2B_4H_6{\cdot}L$.[12] Such addition of donors formally can be regarded as addition of H^-, i.e., $C_2B_4H_6{\cdot}L$ is analogous to $C_2B_4H_7^-$. Other examples are given in Table I.

In molecules such as $C_2B_3H_7$ there are extra hydrogens, "extra" in the sense that there are more than necessary for an exopolyhedral hydrogen (substituent) per framework atom. Rationales for regarding extra hydrogens as contributing to framework electron count can be offered. "Extra" hydrogens usually are found on a nontrigonal face of the deltahedral-fragment skeleton in the form of bridging hydrogens or as the "second" hydrogen in a BH_2 group. These locations are reminiscent of framework positions in that the bridge positions usually are close to a spheroidal extension of the skeletal surface and in that one hydrogen of a BH_2 group is usually endo (close to a framework extension) and the other exo. Furthermore, extra hydrogens are generally acidic and can be removed to give anions without substantially altering framework geometry, i.e., extra hydrogens conceptually amount to protonated framework electrons. It follows that the addition of a lone-pair donor (conceptually H^-) to a framework adds two electrons and changes the molecule's classification accordingly.

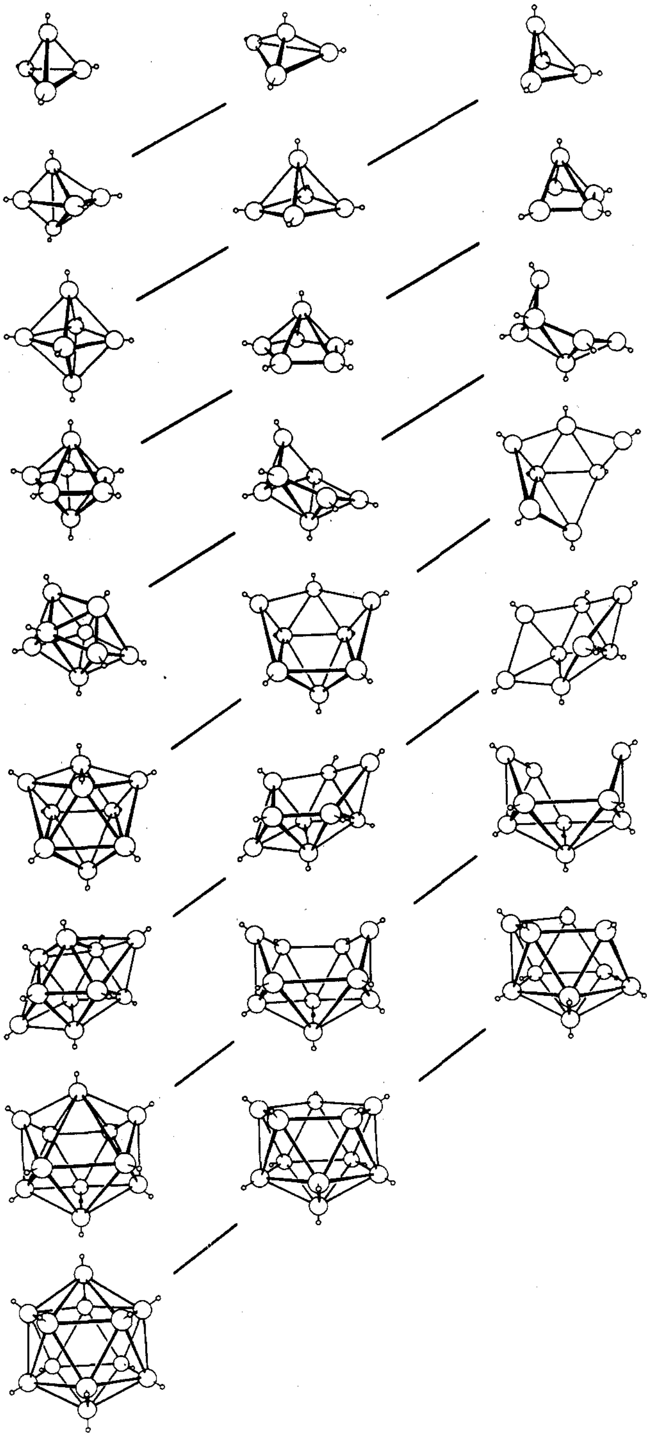

Figure 1. Idealized deltahedra and deltahedral fragments for closo, nido, and arachno boranes and heteroboranes. From left to right, the vertical columns give the basic closo, nido, and arachno frameworks; bridge hydrogens and BH_2 groups are not shown, but when appropriate they are placed around the open face of the framework (see text). The diagonal progression is described in the text as are the known members of the hypho class.

A recent topological approach to boron hydride reactivity gave no bases for the anticipation of framework rearrangement.[13] However, in light of the paradigm discussed above, we pointed out that major skeletal rearrangement would not be anticipated as long as the number of skeletal electrons remains unchanged, as would be the case for both associative and dissociative electrophilic mechanisms since H^+ is the model electrophile. For the model nucleophile H^-, associative and dissociative nucleophilic mechanisms would increase and decrease the framework electron count, respectively, and framework rearrangement is expected during the course of the reaction.[14]

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(9) K. Wade, *Chem. Brit.*, **11**, 177 (1975).

(10) W. J. Evans, G. B. Dunks, and M. F. Hawthorne, *J. Am. Chem. Soc.*, **95**, 4565 (1973).

(11) V. Chowdhry, W. R. Pretzer, D. N. Rai, and R. W. Rudolph, *J. Am. Chem. Soc.*, **95**, 4560 (1973).

(12) B. Lockman and T. Onak, *J. Am. Chem. Soc.*, **94**, 7923 (1972).

(13) I. R. Epstein, *Inorg. Chem.*, **12**, 709 (1973).

(14) R. W. Rudolph and D. A. Thompson, *Inorg. Chem.*, **13**, 2779 (1974).

Table I
Representative Examples of the $2n + 2$, $2n + 4$, and $2n + 6$ Rules

	Framework electron contributions				
Compound	Boron[a]	Carbon[a]	Other heteroatom[a]	Charge	Total
$2n + 2$ systems[c]					
$B_3C_2H_5$	3 (2)	2 (3)		0	12
$(B_6H_6)^{2-}$	6 (2)			2	14
$(CH_3)GaC_2B_4H_6$	4 (2)	2 (3)	1 (2)	0	16
$(B_8H_8)^{2-}$	8 (2)			2	18
$B_7C_2H_9$	7 (2)	2 (3)		0	20
$(B_9CH_{10})^-$	9 (2)	1 (3)		1	22
$B_9C_2H_{11}$	9 (2)	2 (3)		0	24
$B_{11}H_{11}S$	11 (2)		1 (4)	0	26
$B_9C_2H_{11}Sn$	9 (2)	2 (3)	1 (2)	0	26
$B_{10}CH_{11}P$	10 (2)	1 (3)	1 (3)	0	26
$2n + 4$ systems[c]					
$B_3C_2H_7$	3 (2)	2 (3)		2[b]	14
$B_3C_3H_7$	3 (2)	3 (3)		1[b]	16
$B_2C_4H_6$	2 (2)	4 (3)		0	16
$B_8H_{10}S$	8 (2)		1 (4)	2[b]	22
$B_9H_{11}S$	9 (2)		1 (4)	2[b]	24
$(B_9CH_{10}P)^{2-}$	9 (2)	1 (3)	1 (3)	2	26
$2n + 6$ systems[c]					
B_5H_{11}	5 (2)			6[b]	16
$B_7C_2H_{13}$	7 (2)	2 (3)		4[b]	24
$B_9H_{12}S$-	9 (2)		1 (4)	4[b]	26

[a] Number of atoms multiplied by number of electrons contributed to the framework. [b] In this case charge is used in only a formal sense. Actually the "charge" is balanced by protons, often resulting in bridge hydrogens and BH_2 groups in $2n + 4$ and $2n + 6$ systems as described in the text. [c] For the appropriate literature citation see ref 6.

Arachno Molecules ($2n + 6$ Systems)

In comparison to the number of known closo and nido boranes and heteroboranes, there are relatively few arachno counterparts. Therefore, some of the empirically founded structural types given in Figure 1 may become exceptions as more arachno molecules are discovered or, couched differently, arachno structures may prove to be less predictable than closo and nido. For example, two isomeric forms of B_9H_{15} are known, one with the arachno framework shown in Figure 1,[15a] the other with a framework more reminiscent of that shown for the 9-atom nido classification.[15b] The electron count for arachno molecules of course involves the recognition of even more "extra" hydrogens than for nido molecules. Typical examples are shown in Table I.

Hypho Molecules ($2n + 8$ Systems)

Shore has prepared and structurally characterized[16] $B_5H_9(PMe_3)_2$, $B_5H_{12}^-$, and $B_6H_{10}(PMe_3)_2$, three molecules which contain $2n + 8$ framework electrons and which represent the first well-established members of the hypho[14] class of boranes. This new class adopts structures which are as expected even more open than the arachno and nido counterparts. However, because of the embryonic nature of the hypho class, the two known structures have not been included in Figure 1. A complete range of hypho framework size eventually may be found. For instance, Kodama[16b] recently described $B_4H_8(PMe_3)_2$.

Theoretical Considerations

Various MO treatments show that the highest occupied MO (HOMO) is degenerate for most deltahedral B_nH_n molecules, but that a closed shell is obtained for $B_nH_n^{2-}$. We noted that the so-called Jahn–Teller criteria[17] for a good MO description [a large energy gap between HOMO and lowest unoccupied MO (LUMO) plus orbital degeneracy] are met by $B_5H_5^{2-}$ (D_{3h}), $B_6H_6^{2-}$ (O_h), $B_7H_7^{2-}$ (D_{5h}), $B_{10}H_{10}^{2-}$ (D_{4d}), and $B_{12}H_{12}^{2-}$ (I_h). Symmetry considerations also gave a basis for expecting rearrangement upon the *addition* of electrons to such closo clusters (vide infra).[6] Muetterties has extended these Jahn–Teller considerations to explain the stereochemical nonrigidity of $B_8H_8^{2-}$ where there is a small separation between HOMO and LUMO even in the deltahedral (D_{2d}) form of the molecule.[18]

The electron-counting scheme exemplified in Table I appears rather arbitrary for heteroelements where there is the possibility of lone pairs. For example, if two lone pairs are exodeltahedral in $SB_{11}H_{11}$ rather than one, the count of cluster electrons is an unprecedented $2n$. Our LCAO-MO calculations[6] on the heteroboranes SB_4H_4 (C_{3v} and C_{2v}), SB_9H_9 (C_{4v} and C_s), $PCB_{10}H_{11}$ (C_s), $C_3B_9H_{12}^+$ (C_{3v}), and $C_3B_9H_{11}$ (C_s) indicate that the counting scheme of Table I is justifiable. In all cases the energy level diagram showed a rather smooth progression until the entire set of valence electrons was accommodated and then a sizable gap (nominally 4–6 eV). In all cases the eigenvector matrix for those MO's below the energy gap showed the requisite number of

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[15] (a) R. E. Dickerson, P. J. Wheatley, P. A. Howell, and W. N. Lipscomb, *J. Chem. Phys.*, **27**, 200 (1957); (b) P. C. Keller, *Inorg. Chem.*, **9**, 75 (1970).

[16] (a) M. Mangion, R. K. Hertz, M. L. Denniston, J. R. Long, W. R. Clayton and S. G. Shore, *J. Am. Chem. Soc.*, **98**, 449 (1976); (b) G. Kodama and A. R. Dodds, *IMEBORON III*, Ettal, Germany, July 6, 1976.

[17] For example, see R. G. Pearson, *J. Am. Chem. Soc.*, **91**, 4947 (1969); L. S. Bartell, *J. Chem. Educ.*, **45**, 754 (1968).

[18] E. L. Muetterties and B. F. Beier, *Bull. Soc. Chim. Belg.*, **84**, 397 (1975).

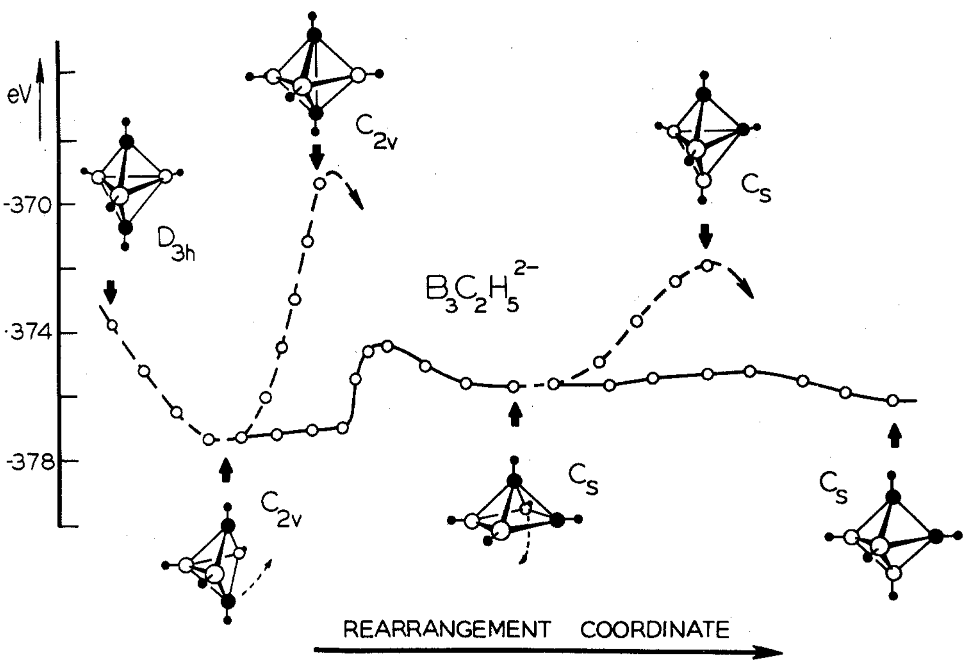

Figure 2. Energy as a function of geometry for $C_2B_3H_5^{2-}$. The solid line represents the interconversion of the isomeric forms of the molecule via symmetry-allowed arcing movements of the designated atoms. The broken line designates the interconversion via a dsd mechanism (see ref 20).

very low-lying B–H (C–H) bonding orbitals and a single, rather high-lying, exodeltahedral "sp hybrid" on the sulfur, phosphorus, or unique carbon in $C_3B_9H_{11}$. The remaining orbitals were best described as framework MO's and accounted for $2n + 2$ electrons.

The progressive opening of a given size cluster with the addition of electrons (movement across any row of Figure 1) might appear paradoxical for "electron-deficient" molecules. However, as alluded to above, the addition of two electrons to the LUMO's (e', t_{2u}, e_2'', e_3, and g_g, respectively) for the closo anions $B_nH_n^{2-}$ (n = 5–7, 10, 12) can result in orbital degeneracy and first-order Jahn–Teller instability. In those cases where degeneracy cannot be invoked (n = 8, 9, 11) there is reason to suspect instability and distortion from the closo in the second order for the reduced anion.[6,14,18] We examined these effects by mapping the energy of the B_5H_5 framework as a function of a symmetry-allowed deformation from the D_{3h} closo structure and as a function of electron count. Energy minima for the $2n + 2$, $2n + 4$, and $2n + 6$ count occur at closo, nido, and arachno clusters, respectively.

The disturbing feature of orbital degeneracy was noted previously for the D_{3h} isomer of $C_2B_3H_5^{2-}$ (nido electron count, closo geometry), but the new closo isomers obtained by permuting C-atom positions within the trigonal bipyramid were found to be "energetically inaccessible".[19] We found that when distortion to the nido structure is effected the energy drops and all three nominally square-pyramidal forms of $C_2B_3H_5^{2-}$ are lower in energy than the closo forms (Figure 2).[20] The nido structure has been suggested for the isoelectronic $C_5H_5^+$ carbonium ion on the basis of similar calculations.[21] We also found an implied instability for the nominally octahedral *trans*-$C_2B_4H_6^{2-}$, and even though other isomers such as the cis-octahedral and all the trigonal-prismatic forms are lower in energy, the nido pentagonal-pyramidal isomers are the most stable.[20]

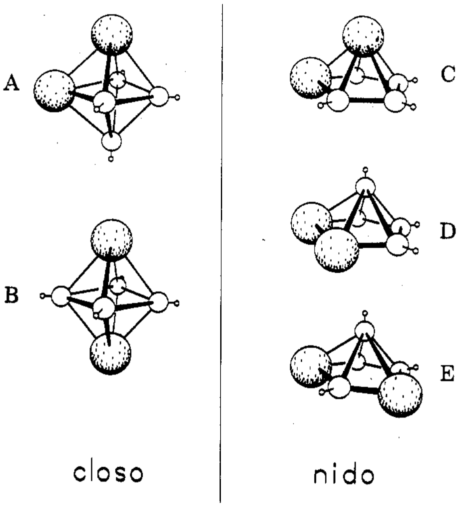

Figure 3. Closo and nido structures for $S_2B_4H_4$. The closo structures do not appear accessible for the neutral molecule. Isomer E is suggested to be most stable.

The correspondence of expected structure with electron count is also shown by known thiaboranes such as SB_9H_9.[22] Likewise, EHMO calculations for the yet to be isolated SB_4H_4 and SB_5H_5 show a lower total energy for the closo structures (C_{3v} and C_{2v} for SB_4H_4; C_{4v} for SB_5H_5) in comparison to nido when the count is $2n + 2$. However, when the count is $2n + 4$ the nido forms (C_{4v} and C_s for $SB_4H_4^{2-}$; C_{5v} and C_s for $SB_5H_5^{2-}$) are lower in energy.[22]

Neutral closo dithiaboranes should not exist if both sulfur atoms contribute four valence electrons to the framework. Again, EHMO results reinforce this predilection in that the three isomers of $S_2B_4H_4$ based on a pentagonal-pyramidal geometry (Figure 3, C–E) are lower in energy than the two based on an octahedron.[22]

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[19] R. Hoffman and W. N. Lipscomb, *Inorg. Chem.*, **2**, 231 (1963).
[20] B. J. Meneghelli and R. W. Rudolph, *Inorg. Chem.*, **14**, 1429 (1975).
[21] W. Stohrer and R. Hoffmann, *J. Am. Chem. Soc.*, **94**, 1661 (1972).
[22] R. W. Rudolph, unpublished results.

The anticipated nido geometry is observed for the tetracarbaborane $C_4B_2H_6$ isoelectronic with $S_2B_4H_4$.[23]

Exceptions

Although $C_4B_2H_6$ has a pyramidal nido geometry, the structural evidence favors a planar form for $C_4B_2F_2H_4$, where B–H has been replaced by B–F.[24] With fluorine and other halogens attached to boron there is, of course, the possibility of π bonding. It appears that the "electron deficiency" of boron can be ameliorated in some cases by back-donation rather than by the multicenter bonding afforded in a cage framework. Thus, we anticipate that the majority of exceptions to the systematics outlined here will occur where back-donation from the substituent to a cluster boron is possible. Salient examples are B_8Cl_8 and B_4Cl_4.[25,26]

B_4Cl_4 is not an exception in the same sense as the other halogenated boranes since the closo electron count for a tetrahedral cluster is unique ($2n$) among those considered here; *it is the only case where a closed-shell configuration is realized for the neutral deltahedral borane rather than the dianion.* The LUMO for B_4H_4 is degenerate (e), also suggesting $B_4H_4^{4-}$ and more feasibly C_4H_4 as tetrahedral molecules, but with nido electron counts. Protonation of $B_4H_4^{4-}$ can give C_{3v} $B_4H_7^-$ which has been proposed on the basis of simplified MO descriptions;[4,27] there is NMR evidence consistent with C_{3v} *nido*-$B_4H_7^-$.[28] Of course, the "butterfly" structure (C_{2v}) for *arachno*-B_4H_{10} has been well established.[29] With the expected electron count and structures of lower symmetry than the closo counterpart, the tetraborane cluster appears to return to "normalcy" for the nido and arachno classifications.

Heteroatom Placement

Obviously many of the deltahedra and deltahedral fragments of Figure 1 have two or more nonequivalent vertices. It does appear that heteroatoms exhibit a preference for certain of these positions which can be deduced on the basis of two variables: (1) the electron "richness" of the heteroatom relative to boron, and (2) the order of the polyhedral vertex.[5] "Rich" heteroatom groupings contribute more framework electrons than a :B–H moiety (2 framework electrons) and seem to prefer low-order vertices. For example, two of the three isomeric forms of $C_2B_8H_{10}$ can be isomerized thermally to the 1,10 isomer,[30] that molecule with the carbons at the lowest order vertices. The pyrolysis of 6-SB_9H_{11} gives 1-SB_9H_9 (sulfur axial at lowest order vertex) even though a least motion mechanism would predict 2-SB_9H_9.[31,32] When the heteroatom is in the same group as boron, it preferably adopts a high order vertex, e.g., $MeGaC_2B_4H_6$.[33] The most stable polyhedron with a heteroelement to the left of boron in the periodic chart presumably places that element at the highest order vertex, although no definitive examples are known (in $R_3NBeC_2B_9H_{11}$[34] all vertices are order five).

1,2-$C_2B_3H_7$ presents a notable exception to the predilection of carbon for low-order vertices. It has been suggested that this exception is in effect related to the placement of bridge hydrogens on the open face.[35]

Placement of Extra Hydrogens

It should be made clear at the outset that the placement of extra hydrogens is a moot point. In effect, their exact position sometimes appears to depend on the physical state of the molecule, e.g., different bridge hydrogen placements for $B_{10}H_{13}^-$ in the crystal[36] and solution[37] can be inferred from the experimental evidence, but the solution data are also consistent with a dynamic process of bridge-hydrogen tautomerism. A well-documented example of fluxionality for bridge hydrogens is provided by B_6H_{10}.[38] In spite of the polemics regarding hydrogen placement, some empirical rules are evident: (1) bridging occurs only between boron atoms, usually an adjacent pair on the open (nontriangular) face of the skeleton (an edge), and only rarely does a hydrogen bridge a triangular array of borons,[14,39,40] (2) when possible the bridge termini are the low-order vertices of the open face, and (3) there is only one bridge per edge. Generally BH_2 groups may be postulated as tautomeric intermediates in fluxional nido boranes, but they occur as ground-state moieties in arachno molecules and then at vertices of order three or lower.[41]

There is the contention that bridge-hydrogen placement is the most important variable in the determination of relative isomeric stability, outranking placement of the heteroatom.[35] It is true that in 1,2-$C_2B_3H_7$[42] one of the heteroatoms is at an unanticipated high-order vertex.[20] Williams[35] suggests that there are other similar cases where the heteroatoms will adopt high-order vertices in deference to bridge-hydrogen placement at low-order vertices. However, we feel that 1,2-$C_2B_3H_7$ is unique in that alternative C-atom placement *completely eliminates* the availability of a B–B edge suitable for a bridge hydrogen. Until there are sufficient thermodynamic data on the relative stabilities of isomeric heteroboranes, the question remains contestable.

Metalloboranes and Metalloheteroboranes

Metalloboranes formed from a main group metal and a borane or heteroborane merely can be treated as het-

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(23) J. P. Pasinski and R. A. Beaudet, *J. Chem. Soc., Chem. Commun.*, 928 (1973).

(24) P. L. Timms, *J. Am. Chem. Soc.*, **90**, 4585 (1968).

(25) R. A. Jacobson and W. N. Lipscomb, *J. Chem. Phys.*, **31**, 605 (1959).

(26) M. Atoji and W. N. Lipscomb, *J. Chem. Phys.*, **21**, 172 (1953).

(27) W. N. Lipscomb, *J. Chem. Phys.*, **28**, 170 (1958).

(28) G. Kodama, U. Englehardt, C. LaFrenz, and R. W. Parry, *J. Am. Chem. Soc.*, **94**, 407 (1972).

(29) C. E. Nordman and W. N. Lipscomb, *J. Chem. Phys.*, **21**, 1856 (1953).

(30) P. M. Garret, J. C. Smart, G. S. Ditta, and M. F. Hawthorne, *Inorg. Chem.*, **8**, 1907 (1969).

(31) W. R. Pretzer and R. W. Rudolph, *J. Am. Chem. Soc.*, **98**, 1441 (1976).

(32) W. R. Pretzer and R. W. Rudolph, *J. Am. Chem. Soc.*, **95**, 931 (1973).

(33) R. N. Grimes and W. J. Rademaker, *J. Am. Chem. Soc.*, **91**, 6498 (1969).

(34) G. Popp and M. F. Hawthorne, *Inorg. Chem.*, **10**, 391 (1971).

(35) R. E. Williams, *Adv. Inorg. Chem. Radiochem.*, **18**, 67 (1976).

(36) L. G. Sneedon, J. C. Huggman, R. Shaeffer, and W. E. Streib, *J. Chem. Soc., Chem. Commun.*, 474 (1972).

(37) A. R. Siedle, G. M. Bodner, and L. J. Todd, *J. Inorg. Nucl. Chem.*, **33**, 3671 (1971).

(38) V. T. Brice, H. D. Johnson, II, and S. G. Shore, *J. Am. Chem. Soc.*, **95**, 6629 (1973).

(39) G. L. McKown, B. P. Don, R. A. Beaudet, P. J. Vergamini, and L. H. Jones, *J. Chem. Soc., Chem. Commun.*, 765 (1974).

(40) This generalization does not hold for transition metal complexes where there are examples of M–H–B bridge bonds.

(41) When considering the balance between bridge hydrogens and BH_2 groups for arachno boranes, it is also prudent to investigate the allowed topological variants as outlined in ref 14 and 4. However, topological considerations have not been generalized yet to heteroboranes.

(42) D. A. Franz, V. R. Miller, and R. N. Grimes, *J. Am. Chem. Soc.*, **94**, 412 (1972).

eroboranes. For example, tricarbaborane analogs are found for $MC_2B_9H_{11}$ (M = Ge, Sn, Pb) species which appear to be carbenoid in that the metal is a "bare" vertex.[44,45] The lone pair on the metal appears to have largely ns^2 (n = 4, 5, 6) character[46] and contribute 2 electrons to the framework, giving a 26-electron closo icosahedron.

In addition to the framework electron requirements of the cage, transition-element metalloboranes and metalloheteroboranes generally adhere to the "rule of 18",[2] and therefore require a somewhat different treatment. If one rather arbitrarily assumes that the metal vertex uses only three orbitals in cluster bonding, then 12 of the 18 electrons at a metal vertex are not involved in cluster bonding. The d-electrons in effect are not included as framework electrons. Mingos[47] has generalized such premises to give the number of skeletal electrons per metal vertex as $v + x - 12$ where v = the number of valence electrons on the metal and x = the number of electrons donated by exocluster ligands and substituents. In this formalism moieties such as $Fe(CO)_3$ and $Co(\pi\text{-}C_5H_5)$ are analogous to a BH vertex while $Ni(\pi\text{-}C_5H_5)$ is effectively a CH vertex. There are numerous examples consistent with the latter analogies, e.g. (heteroborane analog given in brackets), closo: $(C_6H_5)_2C_2Fe_3(CO)_9$[48] [$C_2B_3H_5$], $C_2B_3H_5Fe(CO)_3$[49] [$C_2B_4H_6$], $C_2B_3H_5Fe_2(CO)_6$[49] [$C_2B_5H_7$], $(C_2B_6H_8Mn(CO)_3{}^-$ [50] [$C_2B_7H_9$], $(C_5H_5)CoC_2B_7H_9$[51] [$C_2B_8H_{10}$], $(C_5H_5)CoC_2B_8H_{10}$[52] [$C_2B_9H_{11}$], $(C_5H_5)_2Ni_2B_{10}H_{10}$[53] [$C_2B_{10}H_{12}$]; nido: $(Me_2(C_6H_5)P)_2PtB_3H_7$[54] [$B_4H_8$], $(C_5H_5)CoB_4H_8$[55] [B_5H_9], $(C_2B_3H_7)Fe(CO)_3$[56] [$C_2B_4H_8$], $((C_2H_5)_3P)_2PtB_8H_{12}$[57] [$B_9H_{13}$], $(CO)_3MnB_9H_{13}{}^-$ [58] [$B_{10}H_{14}$], $((C_2H_5)_3P)_2HPt(SB_9H_{10})$[57] [$SB_{10}H_{12}$]; arachno: $((C_6H_5)_3P)_2CuB_3H_8$[59] [B_4H_{10}] and $(B_3H_8Cr(CO)_4)^-$ [60] [B_4H_{10}]. Other examples have been discussed by Grimes.[43] The extension of these principles to organometallics is straightforward. $(C_5H_5)Mn(CO)_3$ and $(C_3H_5)Co(CO)_3$ are nido and arachno examples.[9]

As stated by Hawthorne, in terms of the number of electrons assigned to the framework, there are $2n + 14$, $2n + 16$, and $2n + 18$ for closo, nido, and arachno monometallic transition element complexes, respectively.[61] This alternative approach is sometimes inconvenient, as it requires a new sum as more metals are added to the cluster.

The "symmetrical sandwich" structure of the $((C_2B_9H_{11})_2M^{n+})^{n-4}$ complexes of d^6 metals M = Fe^{II}, Co^{III}, Ni^{IV}, and Pd^{IV} nicely fits the paradigm. The corresponding d^8 complexes with M = Cu^{III} and Ni^{II} could be expected to show an asymmetrically distorted nido–closo structure; however, a symmetrically "slipped sandwich" structure is observed, indicative of delocalization. Alternatively, the slipped structure can be explained in terms of a reduction of the closo molecule with concomitant distortion as observed for closo carboranes;[20] in accord with these notions, the d^9 copper complex is open slightly more than the d^8 complex[62] and the distortion can be rationalized with Jahn–Teller arguments.[63]

Since the electron counting paradigm incorporates the 18-electron rule when applied to transition-metal complexes, exceptions are expected just as is the case for classical coordination complexes. Relatively minor exceptions are found in $(C_5H_5)_2Fe_2C_2B_6H_8$[64] and $Ni(B_{10}H_{12})_2{}^{2-}$.[65] The former ($2n$ electrons) is noticeably distorted from an idealized structure, and the latter is reminiscent of the d^8 and d^9 complexes discussed above. However, the extremely deficient count obtained for $((C_2B_9H_{11})_2Cr^{III})^-$ presents a disconcerting situation in view of its clearly closo structural classification.[66] In some of these cases, it is more satisfying to consider the borane as a multidentate ligand, e.g., $B_{10}H_{12}{}^{2-}$ is effectively bidentate, giving square planar and tetrahedral complexes, $Ni(B_{10}H_{12})_2{}^{2-}$ and $Zn(B_{10}H_{12})_2{}^{2-}$, respectively.[65] Both the latter and the former are cases where the metal in effect occupies the position of a bridge hydrogen of the conjugate acid borane, a rather prevalent occurrence which gives rise to another classification for metalloboranes and metalloheteroboranes. Wegner[67a] and Lippard[67b] have discussed in more detail situations where the metal vertex is equivalent to an H^+, BH^{2+}, or $BH_2{}^+$ moiety; however, in the latter formalism the arachno molecules $(Ph_3P)_2CuB_3H_8$ and $[(OC)_4Cr(B_3H_8)]^-$ were incorrectly classified as nido.

Metal Clusters and Carbonium Ions

Just as for boranes, the triangle is the prevalent "building block" for metal clusters. However, in stark contrast to boranes, heteroboranes, and their metal complexes, there are few examples of metal clusters with more than six vertices. The octahedron was the largest structural unit until the recent discovery of the seven-atom capped octahedral clusters[68,69] $Rh_7(CO)_{16}{}^{3-}$ and $Os_7(CO)_{21}$. The deltahedra characteristic of *strictly metallic* clusters appear to be based on the tetrahedron, octahedron, and capped variants of these.[70] Thus, me-

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tallic clusters are quite reminiscent of sections of a closest packed array of metal atoms and are prototypal of a metal surface.

The known examples of deltahedral fragments are $Fe_5(CO)_{15}C$[71] and $Fe_3(CO)_9S_2$,[72] both of which are not strictly metallic clusters. Contrasting these observations with the plethora of deltahedra and deltahedral fragments found for boranes leads us to anticipate fewer frameworks in the PERC appropriate for metal clusters. Moreover, there is another important distinction between metal clusters and heteroboranes. Heteroboranes are electron deficient (fewer electron pairs than nearest neighbor interactions). However, octahedral metal cluster compounds such as $Rh_6(CO)_{16}$[73] and $H_2Ru_6(CO)_{18}$[74] have an excess of electron pairs over nearest neighbor interactions and moreover exceed the 18-electron rule.[73] A paradox arises in that Wade[9] and Mingos[47] nonetheless have rationalized these cluster shapes with the same paradigm used for boranes, e.g., if the $Ru(CO)_3$ vertex contributes 2 skeletal electrons,[75] then the closo count is obtained for $(Ru_6(CO)_{18})^{2-}$, the conjugate base of $H_2Ru_6(CO)_{18}$. The vast majority of known tetrahedral clusters are saturated clusters which conform to the 18-electron rule and are analogs of nido C_4H_4 (12 electrons). Examples include $Co_4(CO)_{12}$[76] and $Fe_4(C_5H_5)_4(CO)_4$.[77]

The modification of PERC appropriate for metal clusters is not clearly evident, although Mason has suggested recently that the capping of certain polyhedra does not alter the framework count, e.g., 12 electrons predict a tetrahedron, capped tetrahedron (trigonal bipyramid), and bicapped tetrahedron for four, five, and six atom clusters, respectively; 14 electrons predict an octahedron, capped octahedron, and bicapped octahedron for six, seven, and eight atom clusters, respectively.[69] Given[69] as examples are $Os_6(CO)_{18}$ and $Os_7(CO)_{21}$; in agreement with these ideas, a trigonal-bipyramidal cluster was recently found for $Os_5(CO)_{16}$.[78] However, we would suggest the addition of 8-electron tetrahedral clusters to the modified PERC in view of $H_4Re_4(CO)_{12}$[79] and its borane analog, *closo*-B_4H_4 (vide supra).

There is another embryonic (in the structurally characterized sense) class of strictly metallic clusters which appear to be very similar structurally to closo boranes, the homopolyatomic ions of the heavy post-transition elements. A vertex isoelectronic with BH is obtained for either a group IV metal or a group V metal monocation if an electron pair in the valence shell is considered as nonbonding, viz., $SnC_2B_9H_{11}$.[44–46] Thus, closo series like $M_n{}^{2-}$ and $M_n{}^{n-2}$ can be visualized for groups 4 and 5, respectively (the group 4 series would appear more accessible from charge considerations). Corbett has found a closo trigonal-bipyramidal structure[80a] for $Pb_5{}^{2-}$ and argues convincingly for the same[81] in $Bi_5{}^{3+}$. As might be anticipated, the $Sn_9{}^{4-}$ ion with a nido electron count has been found by both Corbett[80a] and Kummer[80b] to have a structure distorted from closo. Corbett has used MO results to explain the differences between his clusters and the boranes.[81,82]

In spite of the difficulties cited above regarding an unmodified PERC approach for metal clusters, the paradigm does find applicability in carbonium ion chemistry. Hogeveen[83] has recently discussed the experimental and theoretical evidence favoring nido structures for $(CH)_5{}^+$ and $(CH)_6{}^{2+}$ which have B_5H_9 and B_6H_{10}, respectively, as prototypes.

In summary, the paradigm certainly is most useful for boranes and heteroboranes, carbonium ions come under its pervasion, and metalloheteroboranes can be included by simultaneously incorporating the rule of 18 in the framework electron count. A modified PERC approach for strictly metallic clusters is evolving. It appears that the modification must account for the structures unprecedented by the boranes and different framework electron counts.

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(75) For accounting purposes, it is expedient to consider all carbonyls (ligands) as terminal since the change of a terminal carbonyl to a bridging carbonyl merely redistributes the $x = 2$ electrons of the terminal ligand over the number of metal centers bridged. Stated differently,

$$\left[\sum_{k=1}^{n} v_k + \sum_{l=1}^{m} x_l - 12n\right] = \text{framework count}$$

where n = the total number of metal atoms in the cluster and m = the total number of ligands in the cluster. Just as "extra hydrogens" are important to borane chemistry, the precise disposition of bridging and terminal ligands is of obvious interest here, but beyond the scope of this review.

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