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Electronic Requirements for Macropolyhedral Boranes

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I. Introduction

Among several theoretical tools available for investigating the molecular structure, there is always a balance between simplicity and reliability. While detailed electronic structure calculations are more accurate and reliable, the computed results are too hard to interpret owing to the higher complexity of the model and do not in general provide information that can be transferred from one molecule to another. Simple models such as Hückel and the extended Hückel theory—where the requirement is the topology or the geometrical arrangement—lead to an easy understanding of the concerned molecular system though quantitative reliability is lost. Even at this level, transferability of information is achieved by formulating electron-counting rules of general applicability. They give Boolean information, i.e., a true or false answer, to the most basic question, whether a molecule in a particular geometry with a given number of electrons is stable. In this review, we have attempted to answer this question for three- dimensional aromatic[1,2] macropolyhedral boranes, for which research is considered as largely exploratory and the underlying principles that govern their stability are mostly unknown.[3] The importance of electron counting, led by Wade's rule, is well realized, especially in the domain of monopolyhedral boranes.[4] Here, we will discuss the macropolyhedral molecules in a general context, using a recently developed generalized electron-counting scheme,[5,6] the *mno* rule. This rule is applicable to macropolyhedral boranes, heteroboranes, and metallaboranes and provides the borane chemist a new way to explain familiar macropolyhedral systems and predict new and interesting structures.

The need to include a new perspective in estimating the electronic requirements of a variety of experimentally characterized macropolyhedral boranes has forced us to restrict the discussion to the electron-counting rules applicable to the selected set of structures. In general, metallaboranes and heteroboranes are included in the discussion. We have omitted some transition-metal complexes containing boron in which the number of metals in the polyhedron exceeds the number of boron atoms. Similarly, we have dropped the section on monocage systems, as these were discussed in detail recently by King.[1b] Systems that contain only one polyhedral borane cage and large polycyclic hydrocarbon fragments are given only a cursory glance, but compounds containing multiple monocages that are connected by two-centered−two-electron (2c−2e) bonds are included for the sake of completeness.

This paper is organized as follows: In section II we give a very brief overview of various electron-counting rules used in chemistry for atoms, mono-

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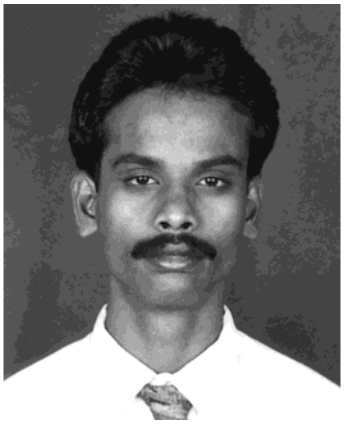

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meric systems, and polycondensed molecules. Special focus is given to the various topological possibilities that arise with macropolyhedral boranes and their varying electronic requirements. We also explore the relation between polyhedral boranes and annulenes. The recently introduced electron-counting rules for polycondensed polyhedral boranes are discussed in detail here. The origins of electron-counting rules are explained using fragment molecular orbital theory in section III. We will also explore the connection between polyhedral boranes and their equivalent annulenes, illustrating how the $4n + 2$ rule and consequently two-dimensional aromaticity naturally arise as a special case of the generalized *mno* rule[6] and three-dimensional aromaticity.

Section IV features the various possible topological patterns for extending simple polyhedral boranes to macropolyhedral systems. Unlike hydrocarbons, which can be extended in an infinite number of ways owing to the special catenation property of carbon, extension of polyhedral boranes to macropolyhedral boranes appears to be restrictive owing to the varying charge requirements. In this section we point out that, contrary to expectations, the number of isomers grows exponentially with respect to the number of vertexes and this combinatorial explosion occurs more rapidly with boranes than hydrocarbons. The primary requisites of the skeleton in extending the association of clusters to infinity are also discussed, which is critical for the synthesis of borane-based polymers.

In section V we address various problems that arise in extending the concepts/formalisms of simple polyhedral boranes to macropolyhedral boranes. Since the classification of boranes into *closo*, *nido*, *arachno*, etc., is inapplicable in the domain of macropolyhedral boranes without proper reformulations, we have attempted to follow a simplified definition based on the number of electrons that are involved in the polyhedron of interest. Polyhedral boranes that are composed of only one cage are referred to as “monopolyhedral” boranes, and those with multiple cages are referred to as “macropolyhedral” boranes.[3] We specifically refer to a class of macropolyhedral boranes that share one or more vertexes between two or more cages as “condensed” polyhedral boranes. These are also referred to as “*commo*” compounds in the literature. The term “sandwich complexes” has been exclusively used for single-vertex condensations. However, in a general context, we refer to both polycyclic aromatic hydrocarbons and macropolyhedral boranes as “macroaromatic” systems. This section also covers the special difficulties involved in dealing with metallaboranes. Finally, in section VI we have given the list of all the important macropolyhedral borane skeletons that are either experimentally characterized or predicted to be stable by high-level theoretical calculations. Straightforward examples such as the structures obtained by catenation involving 2c−2e bonds and polydecker sandwiches are given only token representations. In general, structures that differ in substituent atoms alone are represented by one or two examples. The list is not exhaustive but is chosen to give a unified understanding about the skeletal preferences and electronic requirements of macropolyhedral boranes. Even though the emphasis of this review is to catalog the macropolyhedral boranes and explain their electronic structure, section II also gives a brief summary of the electron-counting rules for a variety of systems that also includes the generalized *mno* rule. A reader who is only interested in applying the *mno* rule[5,6] for estimating the electronic requirements of a new polycondensed molecule may go to section VI directly.

II. Electron-Counting Rules

Electron-counting rules lead to a systematic expansion of knowledge concerning a set of molecules of interest, by permitting the incorporation of experimental and theoretical findings within a logically consistent and reasonably simple framework. Its most significant aspect is to reduce the complexity of the full problem of a large number of experimental observations, by presenting an abstract generalization in the concerned domain. The most prevalent conviction about electron-counting rules is to consider them as facts, and molecules that are not following these rules are termed as disobedient. On the contrary, an electron-counting rule is merely an unsubstantiated hypothesis or a speculation concerning reality, which will become useful only when appropriate confirmatory data have been obtained. Though exceptions occur in significant amounts for all these rules, they still represent a considerable step forward in chemical reasoning, and often these exceptions lead to further research and improved understanding. The counting rules described in this section share a central concern that they play a crucial role in the development of borane chemistry, even though most of these rules cannot be extended to the condensed polyhedral boranes.

Section A deals with the electron-counting rule for main group compounds and the simplest transition-metal complexes. The major role of the electron-counting rules in explaining the stability of mono-clusters of aromatic hydrocarbons, transition metals, and boranes is discussed in the next section. An extension of these rules to the respective polycondensed systems is explained in section C.

A. Atomic Electron-Counting Rules

Lewis’ octet rule[7] was developed in the early 1920s as the offspring of valence bond theory and Mosley’s modern periodic table. It is based on the assumption that most atoms utilize only their s- and p-orbitals. Therefore, each atom has a maximum of eight electrons in the valence shell, which is the sum of shared pairs and lone pairs. The octet rule enjoyed a major success in explaining the valences exhibited by atoms and in accounting for the nature of chemical bonds. The octet rule also indirectly dictates the nature of interactions by classifying them as covalent (or coordinate) or ionic depending on the number of electrons shared, given up, or accepted in reaching the octet. While LiCl or NaF on the ionic side and CH_4 on the covalent side were the prototypical examples of the eight-electron rule, B_2H_6 was an exception. The tendency of boron to form nonionic multicentered bonds is impossible to comprehend using the classical valence bond description of a 2c−2e bond. This multicentered bonding picture proposed for diborane (B_2H_6) was debated for a long time and acquired universal acceptance only after a decisive experimental verification.[8,9] The difficulty of boron to have four 2c−2e covalent bonds in a neutral hydride led to the concept of the electron deficiency of atoms. Multicenter bonding is exhibited by boron to reduce electron deficiency, by sharing electrons between many centers. This inherent tendency of boron to form nonclassical structures is also exhibited by other elements when they are placed in an electron-deficient environment.

The 18-electron rule is the transition-metal version of the octet rule formulated by Sidgwick[10] to evaluate the electronic requirements of complexes, as the basic assumption of the octet rule limits its applicability to main group elements. Also referred to as the EAN (effective atomic number) rule, it predicts that the sum of the number of electrons on the metals plus the number of electrons donated by the ligands should be equal to the atomic number of the nearest noble gas. As transition metals form a large number of complexes with main group elements, this rule is extremely powerful in traditional transition-metal organometallic chemistry even though its origins are recognized to be not as simple. The availability of the d-orbitals with their varied symmetry, the larger size of the transition-metal atom, and the varied nature of the ligands all lead to many exceptions. In many polyhedral borane−transition-metal complexes, the estimation of the number of electrons donated from the borane to the transition metal is not straightforward, except for the dicarbollide ligands, which are found to mimic hydrocarbyl ligands and stabilize transition-metal complexes.[11,12] This is especially true if the borane ligand is a macropolyhedral system.[3] It is increasingly felt that cluster electron-counting rules and isolobal relationships are much more reliable in assessing the electronic requirements,[12] which is the topic of the next section.

B. Molecular Electron-Counting Rules for Monomers

Just as attaining the noble gas configuration is the prime criterion for the above electron-counting rules, attaining aromatic character is the basic premise upon which the molecular electron-counting rules are formulated. Here, the counting rules are represented in the form of generating functions with one or more variables, which will give the number of delocalized electrons required for making a molecule aromatic. The dimensional attribute of aromaticity arises from the nature of delocalization; i.e., cyclic systems exhibit two-dimensional aromaticity, and spherical systems involve three-dimensional aromaticity.[2] Almost all of these counting rules are derived using molecular orbital theory and can be understood by analyzing the nature of interactions between the orbitals of the concerned fragments or groups.

1. Annulenes

Hückel's $4n + 2$ rule governs the two-dimensional aromaticity of planar monocyclic systems. This rule is derived from the simple Hückel molecular orbital (HMO) theory,[13−15] where the σ-framework is completely neglected. In this method, both the HOMO and LUMO are always doubly degenerate for cyclic systems except in a very few cases. Removal of an electron pair leaves the aromatic system with unpaired spins and makes it unstable ($4n$ systems, antiaromatic). The set of molecular orbitals obtained by the HMO analysis show that a closed-shell system is obtained only when there are $4n + 2$ electrons; i.e., the generating function is given by

$$F(e) = 4n + 2 \tag{1}$$

where $n = 0, 1, 2$, etc.

This rule is applicable if the molecular system under consideration has cyclic delocalization of π-electrons arising from the unhybridized p-orbitals that are perpendicular to the σ-framework. It is important to note that the only variable "n" in the generating function can be any positive integer and is completely independent of any system-specific attributes. Hence, any cyclic system with unhybridized perpendicular p-orbitals within overlapping distance can be aromatic provided the right number of electrons are available. This unrestricted nature of the rule made it applicable to a variety of structures, leading to different classes of aromaticity. The prototypical example is benzene, and its many variations have been dealt with extensively in the past.

2. Polyhedral Boranes

A systematic MO theoretical investigation on polyhedral boranes of higher symmetry ($B_{12}H_{12}^{2-}$ (I_h), $B_6H_6^{2-}$ (O_h)) was made in the early 1950s, much before the experimental characterization of these boranes. This revealed that these high-symmetry structures require two electrons in addition to what is available in the neutral skeleton and also that the $B_{10}H_{14}$ polyhedral skeleton can be viewed as an icosahedron with some missing vertexes.[16] However, recognition of the different bonding patterns[17,18] exhibited by boranes synthesized in the 1960s[19] and 1970s[20] led Wade to build on the styx formalism of Lipscomb, a generalized electron-counting rule for all simple polyhedral boranes. Generally referred to as Wade's rule,[18,21−25] it elegantly explains the electron counts for each structural motif. King has reviewed the development of these ideas in detail recently.[1b] On the basis of this revolutionary electron-counting rule, all of the available polyhedral boranes can be classified into discrete classes such as *closo*, *nido*, *arachno*, etc. Though exceptions to this rule are also found,[24,25] it is impossible to understand the several distinct patterns exhibited by polyhedral boranes without this rule.

According to Wade's rule, the number of skeletal bonding molecular orbitals of a polyhedral borane that is homeomorphic to a sphere (*closo*-borane) is just one more than the number of boron atoms in the cluster. The second important attribute is that this requirement of $n + 1$ electron pairs is not altered even if the *closo*-borane has defects by losing some vertexes to form *nido* or *arachno* structures or by having additional capping vertexes.[23,26,27] Hence, the generating function for the number of electron pairs required is given by

$$F(e) = n + p - q + 1 \tag{2}$$

where n is the number of vertexes in the polyhedral skeleton, p is the number of vertexes that are absent, and q is the number of capping vertexes.

This implies that the number of electron pairs required is $n + 1$ for a *closo*-borane, $n + 2$ for a *nido*-borane, and $n + 3$ for an *arachno*-borane. Among these, *closo*-boranes exist as charged species with high stability. Other forms generally have bridging hydrogen atoms on the surface of the open face, each of which will donate its electron to the cluster bonding, and such clusters are relatively more reactive. Thus, $B_{12}H_{12}^{2-}$ has an electron pair count of $n + 1$, whereas $B_{11}H_{15}$ has $n + p + 1$ ($p = 1$) electron pairs. $B_{13}H_{13}$ is an example in which an extra electron pair is obtained from a capped BH vertex on an icosahedron ($q = 1$) so that it is neutral rather than charged.[28]

Unlike Hückel's $4n + 2$ rule, Wade's rule is a function of two variables, the number of total vertexes of the polyhedra and the number of missing vertexes with respect to its *closo* form. Both of them are exclusively system specific. In several examples, the value of q is ambiguous, which can be attributed primarily to the lack of clear distinctive features in the open structures.[25] The perception of the number of missing vertexes in the parent *closo*-borane skeleton, by visual inspection of the open structure, allows room for arbitrary conclusions. This leads to considerable difficulty as illustrated later for some of the examples. Another feature of Wade's rule that has come under heavy critical usage involves the concept of isolobal analogy.[29] This has allowed the use of Wade's rule to connect seemingly different branches of chemistry, viz., boranes, transition-metal clusters, and even zintl-type clusters.[30] Metallaboranes furthered these implications by representing a hybrid between boranes and transition-metal clusters.[3b] However, these rules pertain to a single polyhedral system.

3. Transition-Metal Clusters

In polyhedral boranes, the electronic requirement is given by the skeletal electron count (SEC),[21] which is the number of electrons required to fill the bonding molecular orbitals involved in the skeletal bonding. In the case of transition-metal clusters, it is expressed in terms of the polyhedral electron count[23,31] (PEC), which is the sum of the number of electrons required for skeletal bonding and the number of electrons involved in the *exo* 2c−2e bond along with the number of nonbonding pairs.[32] A comparison of the calculated molecular orbital energies of the bare octahedral clusters of cobalt and boron[31] showed greater resemblance in the antibonding region. In addition to the molecular orbitals originating from s- and p-orbitals, the cobalt cluster has a narrow band of MOs derived from the d-orbitals[31,32] which render it difficult to have a sharp boundary for skeletal MOs. It can also result in a partial involvement of the metal “nonbonding” orbitals in the skeletal bonding. This necessitates the use of the polyhedral electron count rather than the skeletal electron count as a criterion for the determination of electronic requirements. Termed the polyhedral skeletal electron pair theory (PSEPT), it successfully explains the charges exhibited by several transition-metal carbonyl clusters.[23] Using this methodology, the number of electrons required for a *closo*-borane is $4n + 2$ (n = number of vertexes), which includes the electrons involved in the *exo* 2c−2e bonds. In the case of transition-metal carbonyls, this expression becomes $14n + 2$, which includes the additional contribution of five d-orbitals of the transition metals. $[Os_5(CO)_{15}]^{2-}$ has a trigonal bipyramidal structure and a PEC of 72 ($n = 5$). The osmium atoms and the carbonyl groups provide 70 electrons. This explains a charge of −2 for the compound. The straightforward extension of Wade’s rule through isolobal analogy is also used in naked metal clusters with or without *exo* 2c−2e bonds.[30]

In contrast to the polyhedral skeletal electron count theory, which extends Wade’s rule for main block elements through isolobal analogy, the topological electron count (TEC) theory[33,34] was developed as an alternative approach for electron counting. The basic assumption of this theory is that the cluster bonding molecular orbitals can be split into two independent sets, i.e., those involved in deltahedral bonding and the other low-lying orbitals.[35] It is to be noted that this is tacitly assumed in Wade’s rule for main block elements. The empirical upper limit for the bonding molecular orbitals was set at the p-level of the isolated metal atoms. An exhaustive extended Hückel study of different rhodium carbonyl clusters was made, and the $6M + X$ electron pair rule[36] was framed on the basis of the above assumptions. Here, M is the number of vertexes and the value of X is found to be in the range of 6−15, but for a majority of rhodium clusters it is 7. Unfortunately, no clear-cut relationship between the geometries and the values of X were deduced. Later, it was extended to other systems, and a generalized topology-based electron count rule[37] was deduced from Euler’s theorem for the polyhedra:

$$e = v + f - 2 \tag{3}$$

where e is the number of edges, v is the number of vertexes, and f is the number of faces.

Assuming that the 18-electron rule is satisfied for all the atoms in the metal cluster and all of the edges are 2c−2e bonds, the total number of electron pairs required for a transition-metal cluster is given by

$$F(e) = 9v - e \tag{4}$$

However, since all the edges in the polyhedron cannot be 2c−2e bonds, an adjustment parameter, x, is introduced into this equation. Substituting the values of e from eq 3, the exact electron pair requirement is

$$F(e) = 8v - f + 2 + x \tag{5}$$

Several empirical rules were framed to assess the values of x from experimental data and from extended Hückel calculations. x is interpreted as the number of false metal−metal bonds in valence bond (VB) terms or as the number of missing antibonding cluster orbitals in MO theoretic terms.

Though the two approaches, the PSEPT and the TEC theory, for electron counting are expressed in different terms, in many specific systems the justification for the value of x, given in the topological approach, enables the deduction of topological rules within the framework of polyhedral skeletal electron pair theory. This is because the following two common axiomatic bases exist for both these approaches:

(1) Every atom has the tendency to achieve noble gas configuration.

(2) Only three atomic orbitals are involved in the skeletal bonding.

These common assumptions reflect the similarity between the two approaches, but they are not exactly equivalent. Alternatively, the electronic requirement of the polyhedra, which involve both main block elements and transition metals, expressed in terms of the topological electron count rule is given by the equation[37]

$$F(e) = V_n + 6V_m + B \tag{6}$$

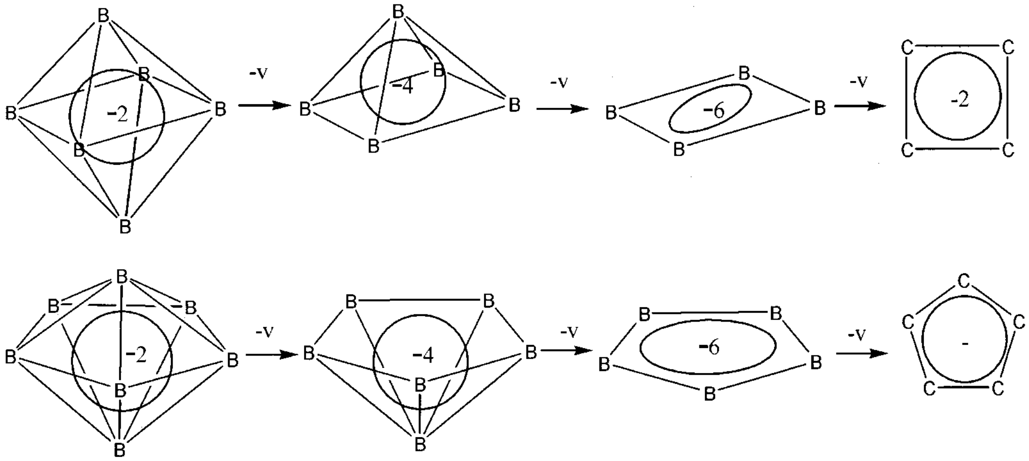
where $F(e)$ is the number of electron pairs required, V_n is the number of main group elements, V_m is the number of transition metals, and B is the number of electron pairs required for skeletal bonding (eq 2).

In summary, these are two alternative approaches for counting electrons, and each has its own strength and weakness depending upon the system under consideration.[38,39]

4. The Relation between Two and Three-Dimensional Aromaticity

The electron-counting rules of aromaticity formulated for cyclic systems such as annulenes and spherical systems such as polyhedral boranes, though nurtured individually, are intimately related to each

Scheme 1. 3D−2D Continuum of Aromaticity Depicted for Four- and Five-Membered Rings by Successive Removal of the Caps from the *closo* Polyhedral Borane, Leading to the Corresponding Aromatic Hydrocarbons[a]



[a] Exohedral hydrogens on each vertex are left out.

other. This can be easily visualized using the six-interstitial-electron rule.[40] This approach involves the conceptual division of three-dimensional aromatic *closo*-boranes such as $B_6H_6^{2-}$ and $B_7H_7^{2-}$ into two-dimensional rings and caps. If we consider all the boron atoms in the ring to be sp^2-hybridized, one of the sp^2-hybridized orbitals will be used in the *exo* B−H bond. The two remaining sp^2-hybrid orbitals form the σ-framework of the ring, which is equivalent to the σ-framework in annulenes. However, unlike annulenes, the unhybridized p-orbital of each boron atom that is perpendicular to the plane of the ring is empty. Three of these vacant molecular orbitals of the ring fragment are stabilized by the interaction with the orbitals of the two capping B−H groups on both sides of the ring, resulting in a complete spherical framework. Since each B−H cap has one electron pair that has to be delocalized, the total number of electrons involved is four. To fill the three stabilized MOs, two more electrons are required, which justifies the dianionic nature of these *closo*-boranes.

This can also be illustrated by the successive removal of the capping vertexes from the borane followed by the substitution of carbon atoms in the ring. Scheme 1 illustrate the effect of removing the capping atoms successively. Three-dimensional aromatic systems such as *closo*-$B_6H_6^{2-}$ and -$B_7H_7^{2-}$, upon transformation, will be reduced to two-dimensional aromatic systems with the proper charges. Here, the electronic requirement specified by Wade's rule smoothly converges to Hückel's rule when a polyhedral borane is reduced to a cyclic aromatic hydrocarbon.[41] It will be shown later that two-dimensional aromaticity is a subset of three-dimensional aromaticity. In polycondensed polyhedral boranes only one among the many possible condensation pathways can be reduced to two-dimensional aromatic systems.

Thus far, we have focused on electron-counting rules that govern the stability of an isolated aromatic unit. In the next section, we will suspend this restriction and consider the behavior of condensed systems where two or more aromatic units interact together to form macroaromatic systems.

C. Electron-Counting Rules for Macroaromatic Systems

Macroaromatic systems in general can be defined as molecules that possess two or more mutually interacting aromatic fragments, which enables delocalization to be extended to span the individual fragments. Three different topological modes of interaction are possible between two aromatic units:[6] (i) A condensed mode of interaction, in which the individual aromatic units share one or more edges. This pattern is ubiquitously found in both two-dimensional and three-dimensional aromatic compounds. Naphthalene is an example in the case of hydrocarbons, and $B_{20}H_{16}$ with a four-atom fusion is an example of a condensed polyhedron. (ii) A stacked mode of interaction, in which the individual aromatic units share a single vertex. This type of sharing is predominantly found among metallaboranes where the shared vertex position is preferentially occupied by bigger heteroatoms, though some transition-metal clusters do exhibit this pattern. Ferrocene and other metal−carborane sandwich complexes belong to this class of compounds. (iii) A linked mode of interaction, in which the two aromatic units are interconnected by 2c−2e/3c−2e bonds. Biphenyl forms a model of C−C linkage in two-dimensional aromatic systems. In three-dimensional structures, examples are known where two B_{10} (D_{4d}) units are joined by a 2c−2e bond between two boron atoms. Here, the electronic requirement is found to be additive; i.e., the total electron requirement is the sum of the electronic requirements of the individual aromatic units. Electron-counting rules that govern aromatic stability of different molecular systems were reported, and they all share some common characteristics. In this section, we will present some of these successful schemes.

1. Polycyclic Aromatic Hydrocarbons

The high and innate catenation tendency of carbon leads to a huge number of polycyclic aromatic hydrocarbons. All of them exhibit either a condensed mode or a linked mode of interaction. The stacked mode of interaction is completely absent owing to the smaller size and higher electronegativity. Most of the compounds contain hexagonal units as the dominant aromatic unit. Such hexagons are found even in the polymorphs of carbon, such as graphite and fullerenes.

Hückel's $4n + 2$ rule itself can be applied to the many polycyclic systems such as linear and catacondensed hydrocarbons where all the carbon atoms lie on the perimeter of the molecule. Unlike boranes, many of the polycyclic aromatic hydrocarbons are stable neutral species. Hence, the presence or absence of Kekulé valence structures is of critical importance,[42] and several generalized[43,44] or system-specific computer algorithms[45] are available to enumerate the number of Kekulé valence structures even for very large systems, which is found to be a fair indicator of stability. In condensed aromatic systems, it is found that the delocalized π-electrons are shared among the individual aromatic units.

2. Condensed Transition-Metal Clusters

There are numerous high-nuclearity transition-metal clusters in which two or more individual polyhedral units interact together to form the macroaromatic system. As bonding in simple transition-metal clusters can be understood by Wade's rule using the isolobal analogy, Mingos extended these ideas to cover the transition-metal clusters.[31,46] According to this rule, the overall electron requirement of a macropolyhedral cluster is the sum of the electronic requirements of the individual units minus the electron count characteristic of the atom, pair of atoms, or triangular face shared between them. The characteristic requirement of the shared atoms is defined as 18 electrons for vertex-sharing polyhedra, 34 for edge-sharing polyhedra, and 48 for face (triangle)-sharing polyhedra. It is to be noted here that the electronic requirement of an individual cluster is taken as the total number of electrons in the cluster including the *exo* 2c−2e bonds. This methodology gives $4n + 2$ electrons for (*closo*) borane clusters and $14n + 2$ electrons for (*closo*) transition-metal clusters.

Using this axiomatic basis, the generating function for the number of electron pairs in the condensed polyhedra having two interacting aromatic units can be expressed[31] as

$$F(e) = (7n + 1) + (7m + 1) - (9v - e) \qquad (7)$$

where n is the number of vertexes in the first fragment, m is the number of vertexes in the second fragment, v is the number of shared vertexes, and e is the number of shared edges.

This rule derives the electronic requirement of individual aromatic units by using Wade's rule. The second term $(9v - e)$ is referred to as the electronic characteristic of the shared fragment. An example to illustrate this rule is the complex $[Ru_{10}C_2(CO)_{24}]^{2-}$, which is essentially two octahedra fused by an edge. Equation 7 is derived on the basis of the assumption that the condensed polyhedron can be viewed as a complex between two individual polyhedra, with one polyhedron acting as a ligand, donating electrons to the second polyhedron. If the condensed system of two interacting units can be separated into individual fragments in such a way that one of the fragments retains the shared atom and the other fragment is without the shared atom, the second fragment acts as a ligand. The number of electrons donated from the "ligand" fragment is defined to be six for single-vertex-sharing systems owing to its *nido* framework. For an edge-sharing system, the ligand fragment is treated as a 10-electron donor owing to its *arachno* pattern. Using this axiomatic basis, the generating function for the number of electron pairs in the condensed polyhedron having two interacting aromatic units can be expressed as

$$F(e) = (7a + 1) + (7b + x + 1) - y \qquad (8)$$

where a is the number of vertexes in the (*closo*) first fragment, b is the number of vertexes in the second fragment, x is the number of shared vertices, and y is the number of electrons donated from the ligand fragment.

For vertex- and edge-shared systems this equation can be reduced to eq 7. Extending this implication further for a face-shared system, the ligand fragment should act as a 14-electron donor.[31] However, the electronic characteristic of the shared face becomes 25 electron pairs, which is one more than the value used by Mingo for a face-sharing system. Though an MO theoretic justification is still lacking, this rule explains the charges of several macropolyhedral transition-metal carbonyls successfully. It is interesting to note that bridging carbonyl groups of transition-metal clusters act like bridging hydrogens in boranes, donating two electrons to the skeletal bonding.

The topological electron count rule can also be extended to cover a macroaromatic system that shares a vertex, edge, or face. Using this model, the electronic requirement of the fused system is expressed by using the modified Euler equation depending on the nature of the fusion.[33,34] For edge- and vertex-shared systems, eq 3 is modified as

$$e = v + f - 2 - s \qquad (9)$$

where s is the number of shared vertexes or edges, respectively. For face-sharing systems (systems having three vertexes in common) it is

$$e = v + f - 2 + h \qquad (10)$$

where h is the number of hidden edges, i.e., the edges that are not on the external surface of the macroaromatic system. Similarly, while counting the number of faces f, only the peripheral faces are counted. Several attempts were made to extend this rule to explain the interactions of the parent borane clusters.[46,47] However, the nature of interaction between the individual borane fragments[48] and consequently their electronic requirements[5,6] are found to be very different from those of the transition-metal clusters, which is illustrated in the next section.

3. Macropolyhedral Boranes

Although the first experimental observation of macropolyhedral boranes dates back to the early 1960s,[19] the nature of interaction between two polyhedral borane units came into the limelight only in the last two decades, shortly after the formulation of electron-counting rules for condensed transition-metal clusters. So far, electron-counting rules for various systems have been uncovered progressively in increasing order of their complexity. However, both Teo's topological electron-counting schemes[47] and the polyhedral skeletal electron-counting rules of Mingos[49,50] were reformulated for condensed clusters of main block elements.

In place of the 18-electron rule, the octet rule was employed for clusters of main group elements, and eq 4 is modified to $F(e) = 4v - e$. The electronic characteristic for the shared fragment then is 8, 14, and 18, respectively, for vertex-, edge-, and face-sharing main block clusters. The resulting predictions were found to be inappropriate, even for characteristic structures. Later, these values were modified suitably to 4, 12, and 18, respectively. A clear justification for the choice of these numbers has yet to emerge.[46,50] The 6- and 10-electron-donation-based explanation, which works for vertex- and edge-shared transition-metal clusters, is also inapplicable in the domain of condensed clusters of main block elements. The topological electron-counting scheme also fails to predict the exact number of electrons required for condensed main block clusters.[48,51]

Looking for explanations, research on electron-counting rules took a regressive turn and studies were made exclusively on different modes of condensation of relatively simple individual aromatic clusters of main block elements in the 1990s.[48,52−54] These studies revealed the nature of the interaction between the bonding molecular orbitals in a systematic manner and successfully predicted the electronic requirements of the condensed main block clusters in specific instances. We have now made a systematic study on the nature of interaction between individual aromatic units of polyhedral boranes in all the possible modes.[5] This has resulted in a generalized electron-counting scheme, which is applicable to the whole range of main group elements. Despite the intricate structures exhibited by the individual aromatic units of the main group elements, this scheme offers a simple generating function for the requirement of electron pairs. Wade's $n + 1$ rule of polyhedral boranes and Hückel's $4n + 2$ rule for condensed aromatic hydrocarbons arise as the special case of the general scheme.[41] On the basis of the recent results, the interaction between individual aromatic units can be conveniently classified on the basis of their distinct electronic requirements.

Throughout this recent scheme, the electronic requirement can be conveniently expressed in terms of the total number of skeletal atoms n and the number of individual aromatic fragments (or polyhedra) m that constitute the macroaromatic system. For macroaromatic systems such as biphenyls and borane rods where the individual aromatic fragments are connected by a 2c−2e or 3c−2e bond and for condensed aromatic systems where at least one edge is shared between the individual aromatic units, the number of electron pairs required for aromatic stability is given by the equation

$$F(e) = n + m \tag{11}$$

With the exception of single-vertex sharing, this definition includes all the macroaromatic systems characterized so far, including "very condensed" systems[3] where more than two aromatic units are interacting with each other. The first *closo* macropolyhedral borane,[55−57] $B_{20}H_{16}$, stands as evidence for this rule. This kind of interaction results in the overall decrease in the charges when macropolyhedral boranes are concerned.

For systems involving single-vertex sharing, the nature of the interaction between the individual fragments is rather involved and several additional geometric factors affect the orbital overlap. The electronic requirements vary with respect to the nature of interaction between the atoms on either side of the shared atom. The distance between interacting groups depends on the size of the ring incident to the shared atom and the size of the shared atom.[40,52] When the size of the shared atom is comparatively larger than the size of the ring atoms and the size of the ring is very small, the atoms of the ring on both sides of the shared atom do not have any chemical interaction with each other. In this case, the number of electron pairs required for aromatic stability is found to be

$$F(e) = n + m + o \tag{12}$$

where the additional term "o" represents the number of single-vertex interactions in the macroaromatic system. All complexes of the general formula $[(C_2B_9H_{11})_2M]$, where M = Al, Si, Fe, Co, or Ni, obey the *mno* rule. The nonbonding interaction between the ring atoms at both sides of the shared atom becomes significant when the distance between the ring atoms is shortened. At this intermediate range the number of electron pairs required for aromatic stability is well studied[52,53] for vertex-sharing octahedral units of aluminum and is predicted to be similar for other main block octahedral vertex-sharing clusters.[52−54] Here, the two rings that exhibit nonbonding interactions are in the eclipsed orientation. No isolated molecule is experimentally characterized with this framework, though this pattern is observed in the solid state for aluminum clusters of the types AeM_2Al_9 (Ae = Ba, M = Fe, Co, Ni; Ae = Sr, M = Co; Ae = Ca, M = Co)[58−61] and $CaNiAl_9$.[58−61] When the distance between the two rings is reduced further so that they are within bonding distance, a staggered orientation is preferred which results in a giant single deltahedral cage with an atom at the center. The electronic requirement of this stuffed system is given by[62,63]

$$F(e) = n + m - r \tag{13}$$

It is to be noted that while the number of atoms n in the macropolyhedral system is enumerated, the stuffed atom is also included. This skeleton is ubiquitously present in transition-metal clusters[31] and characterized as minima by ab initio calculations for some selected stuffed polyhedral borane systems.[62,63]

To sum up, the electronic requirement of macropolyhedral borane requires the identification of the total number of vertexes, individual aromatic fragments, vertex-sharing junctions, missing vertexes in its pseudospherical surface, capping vertexes, and stuffed atoms. Hence, the generating function for the number of electron pairs can be evaluated in terms of six distinct variables as

$$F(e) = n + m + o + p - q - r \qquad (14)$$

where n is the number of vertexes in the polyhedron, m is the number of individual polyhedral fragments, o is the number of single-vertex-sharing junctions, p is the number of missing vertexes in the idealized *closo* skeleton, q is the number of capping vertexes, and r is the number of stuffed atoms.

III. Rationalization of Electron-Counting Rules in Polyhedral Boranes

In the scholarship of electron-counting rules, theories of rationalization play a crucial role in the construction of a symbolic model. Explanatory models increase the reliability of the rules by enabling their deduction within the framework and often account for the exceptions that occur while the rule is applied. The rationalization of various electron-counting rules described in this section deals with the nature of cluster bonding in the macropolyhedral boranes, though these results must be equally applicable to the macropolyhedral systems of other main block elements.

At the outset, various theories on monopolyhedral systems also receive attention if their main defining characteristic is the quest for generalized qualitative reasoning that can be used to rationalize the electronic requirement of all polyhedral boranes. The semantics of aromaticity advocated by these theories may seem entirely distinct, but each of these theories, in its own way, adopts the concept of molecular orbitals and treats all the experimentally isolated polyhedral boranes with an a priori assumption that they are aromatic. Each has been influential in advancing the conceptual understanding about the nature of polyhedral bonding. They are anchored on a series of assumptions and provide an appropriate position from which the rationalization of the macropolyhedral systems can be logically extended from the monomers. An important attribute shared by all these theories is the conceptual separation of the *exo* polyhedral bonds from the skeletal bonds, and all these assume localized 2c−2e nature for the *exo* bonds.

A. Monopolyhedral Boranes

Though molecules exhibiting polyhedral bonding have been known for a long time,[64] conclusive theoretical studies were made only in the latter half of the last century. Earlier, the localized 2c−2e bonding concept was successfully extended to include one more atom, resulting in 3c−2e bonds,[65] and is sufficient to explain the structural pattern exhibited by diborane[66] and similar structures. Attempts were made to extend this approach to cover polyhedral bonding exhibited by several low-symmetry structures, classifying polyhedral faces and edges as distinct 2c−2e and 3c−2e bonds. Lipscomb and coworkers made the initial attempts to give such a generalized perspective for all the open *nido* and *arachno* polyhedral varieties characterized earlier.[64] Before *closo* structures were discovered, they successfully predicted the electronic requirements of B_6H_6 and $B_{12}H_{12}$ motivated by the existence of such skeletal frameworks in borides, boron carbide, and elemental boron.[65] Shortly after that, the stability of B_6H_6 (O_h) and $B_{12}H_{12}$ (I_h) as dianions was confirmed by Longuet-Higgins and co-workers by an elegant molecular orbital analysis using group theory.[16,67,68] Similar studies were extended for experimental structures such as B_4Cl_4, B_8Cl_8, $B_{10}H_{10}^{2-}$, and $B_5H_5^{2-}$. In all these studies, the proposal of one *exo* 2c−2e bond for all boron atoms suggested earlier was tacitly assumed,[69,70] since *exo* B−H bond lengths are fairly constant and do not depend on the environment of the boron atoms involved or on the electron deficiency in the molecule.

This partitioning of molecular orbitals of the valence shell into "*endo*" and "*exo*" was found to be a reasonable approximation by Hoffmann and Lipscomb within the framework of LCAO−MO (LCAO = linear combination of atomic orbitals) theory for several high-symmetry structures of the type *closo*-B_nH_n.[69a] As Hückel's nearest neighbor approximation leads to inconsistencies, emphasis is given to all interactions in the polyhedron. Further, by employing different factorizations of the secular equations such as in-surface, apex-equatorial, and ring-polar separations, they concluded that the general predictions are not overly affected by the use of different overlap schemes. The *endo*−*exo* separation of the molecular orbitals was later substantiated experimentally by photoelectron spectroscopy.[71]

The experimental isolation of several polyhedral boranes finally enabled the boron chemist to have an effective and global view of polyhedral bonding.[19,20] The major breakthrough came from Williams' perception that the experimentally isolated *arachno*- and *nido*-boranes can be viewed as being derived from the respective *closo* structures rather than as fragments of the icosahedral $B_{12}H_{12}$ skeleton.[17] These and other observations enabled the derivation of Wade's rule by treating all the boron atoms of the polyhedron as sp-hybridized.[21] In this model, one sp hybrid is radiating away from the center of the sphere, forming the *exo* 2c−2e bond. Another sp hybrid points toward the center of the cage. The two remaining unhybridized AOs are tangential to the sphere. Hence, each atom contributes three AOs for skeletal bonding. The radial AOs combine in phase to generate a strong core BMO (bonding molecular orbtial). The tangential orbitals, upon linear combination, produce the remaining n surface BMOs, though they sometimes have contributions from the radial AOs of appropriate symmetry. The resulting $n + 1$ skeletal electron pair rule is a successful generalization, despite the existence of exceptions such as B_4Cl_4 and B_8Cl_8. Several attempts were made in constructing a general model to justify this rule and explore the reasons for the disobedient skeletons.

The initial attempts to justify Wade's rule were made using graph theory considering the hydrogen-depleted deltahedral graph by King and Rouvray.[1,72−74] They showed that a *closo*-borane, B_nH_n, when treated as a complete graph (K_n) leads to an unique positive eigen value that is are correlated with the most strongly bonding core molecular orbital proposed by Wade. But the deltahedral graph (D_n) seldom shows $n + 1$ positive eigenvalues as in the case of annulenes, owing to the inadequacy of the nearest neighbor approximation. The stabilization of n surface bonding molecular orbitals was attributed to the presence of multiple Hamiltonian circuits in the deltahedral graph that will result in n surface orbitals by pairwise interactions. This is substantiated by the results arrived earlier from aromatic hydrocarbons, where a single Hamiltonian circuit stabilizes the π molecular orbitals. The sp^2 hybridization for the boron atoms of the open face and sp hybridization for the remaining atoms were employed in treating open structures. Among the three sp^2-hybridized orbitals, one is involved in the *exo* 2c−2e bond and two are involved in surface bonding. The unhybridized p_z-orbitals of each atom in the open face together form one more strongly bonding molecular orbital. The exception of B_4Cl_4 is attributed to the presence of sufficient orbitals to make localized bonding, though no particular reason was suggested for B_8Cl_8 and other disobedient skeletons.

Alternatively, Stone employed a free electron model in which the skeletal atoms are treated as a spherical shell of unit radius.[75−77] From this, skeletal orbitals are generated as the angular parts of the solutions of the model Schrödinger equation for a particle in a sphere. Unlike the earlier free electron models[70,78,79] for polyhedral bonding, the values of the general spherical harmonics at the cluster atom positions are used as the coefficients in the LCAO expansion of the basis set of atomic orbitals in the generation of molecular orbitals. In this approach, the nodeless radial atomic orbitals arise as scalar surface harmonics and the tangential atomic orbitals are handled effectively by vector surface harmonics. The molecular orbitals formed from the radial atomic orbitals (σ-type) can be ordered energywise by the perception of the number of angular nodes. The most strongly bonding molecular orbital with no angular nodes is correlated with Wade's core molecular orbital. The bonding molecular orbitals arising from the tangential atomic orbitals fall under two categories, i.e., π and π^*, on the basis of the symmetry properties with respect to the inversion operation. The former one (π-type) correlates with Wade's surface orbitals[21] while the latter set is antibonding, thus confirming King's graph theoretical result.[1] However, except for the strongly bonding core orbital in the σ-type, mixing between π-type and other antibonding σ-type orbitals is symmetry allowed, but π^* will not interact with either the σ-type or the π-type owing to symmetry incompatibility. The π- and π^*-types of orbitals are mutually conjugate in the sense that one can be effectively converted into the other if each concerned atomic orbital is rotated by 90° about a radial axis through the atom.

The same model can be used to explain Wade's $n + 2$ and $n + 3$ rules for the electronic requirements of the *nido* and *arachno* structures, respectively.[77] This model is more influential than the rest as it also successfully rationalizes the exceptions so that they are unambiguously classified as accidental[24a] and intrinsic[24b] exceptions. The intrinsic exceptions arise when the total number of surface orbitals contains an odd (one for a three-dimensional sphere) number of self-conjugate species. In these cases, the odd number (one) of surface orbitals is forced to be self-conjugate by symmetry and may lie in the frontier region. The energy of this MO determines whether one more or one less than the number of electron pairs dictated by Wade's rule is required for stability. For the same reasons, the *nido* and *arachno* patterns require the same number of electron pairs as their *closo* counterparts. Fowler made a detailed analysis of these surface orbitals for *closo*-boranes B_nH_n ($n < 25$), and proved that the exceptions occur only in cases of (i) T_d or T symmetry with an odd number of sets of four equivalent atoms or (ii) C_m or C_{mv} ($m > 2$) symmetric clusters with an odd number of cage atoms on the C_m axis.[24b]

B. Three-Dimensional Aromaticity of Boranes

As mentioned earlier, the concept of "three-dimensional aromaticity" for polyhedral boranes was first proposed by Aihara[2a] on the basis of his graph theoretical studies. He tacitly assumed electronic requirements of *closo*-B_nH_n boranes ($3 < n < 13$) as found experimentally. Unlike Lipscomb,[65] he assumed the presence of a localized BBB bonding orbital in every triangular face.[80,81] The adjacent triangles that share an edge are assumed to interact with each other. Solving this Hückel determinant gives the energy in terms of α and β, which is compared with an acyclic reference as in the case of polycyclic hydrocarbons, where the stabilization energy due to aromaticity is expressed in the usual terms (β units).[82] These calculations predicted higher aromatic stabilization for $B_6H_6^{2-}$ and $B_{12}H_{12}^{2-}$, in complete agreement with the experimental observations. A new index termed the "valence structure index" is also defined, whose logarithmic value is correlated with aromaticity, analogous to the Kekulé valence structure count in polycyclic benzenoid hydrocarbons. The nucleus-independent chemical shift (NICS) is another recent approach to measure aromaticity on the basis of a magnetic criterion. NICS is defined as the negative of the absolute magnetic sheildings computed at the geometrical centers of the cage.[83a] A negative NICS value indicates aromaticity, and a positive value implies antiaromatic character. The application of NICS in explaining the three-dimensional aromaticity of polyhedral boranes has been well demonstrated using various systems such as five-membered aromatic and antiaromatic heterocycles, *closo*-borane dianions and their corresponding monocarba- and dicarbaboranes, etc. by Schleyer and co-workers.[30,83]

The conceptual link between the aromaticity of benzenoid hydrocarbons and polyhedral boranes realized long before[84,85] was represented elegantly by the six-interstitial-electron rule by Jemmis and Schleyer.[40] They employed the ring-cap fragmentation

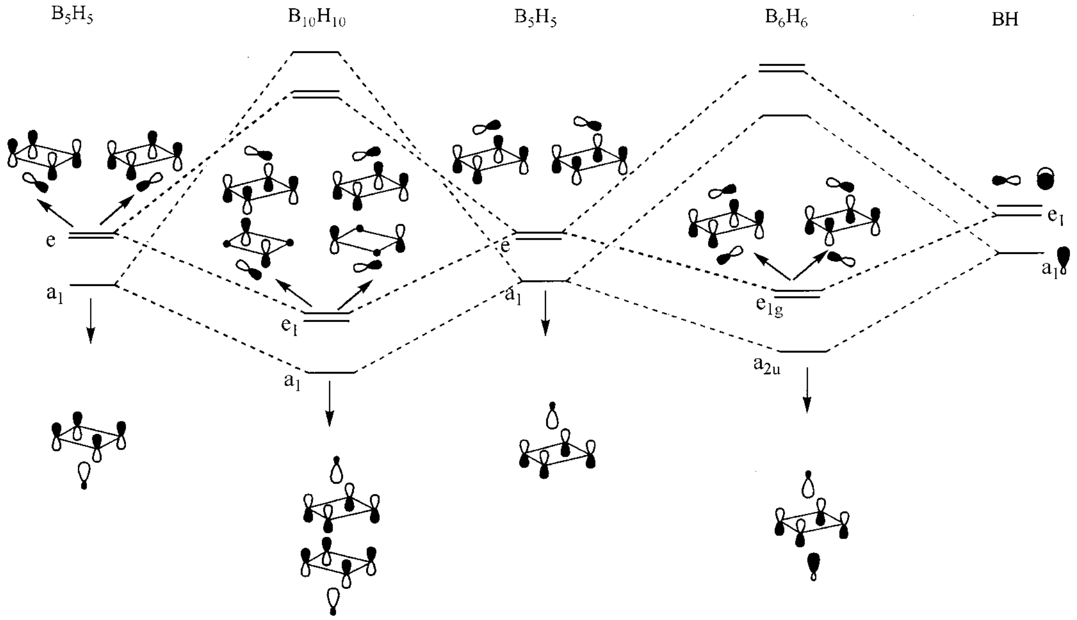


Figure 1. Schematic diagram indicating the interaction of two *nido*-B_5H_5 (C_{4v}) fragments to generate a *closo*-$B_{10}H_{10}$ (left). The same fragment interacts with a BH group to give the molecular orbitals of *closo*-$B_6H_6^{2-}$ on the right-hand side.

similar to the one used earlier.[69] They assumed all the ring boron atoms as sp^2-hybridized and caps as sp-hybridized. One of the sp^2 hybrids is directed out of the ring, forming an *exo* B−H bond. The other two sp^2 hybrids form the σ-framework for the ring. All three available electrons are exhausted in this process, and the unhybridized p_z-orbital lying perpendicular to the plane of the ring is left without electrons. These orbitals interact with the cap atoms on both sides to form the *closo* skeleton. One of the *sp* hybrids of the boron cap is used in the formation of the B−H bond. Hence, another sp hybrid and the two unhybridized p-orbitals are available for skeletal bonding. This capping B−H group has one electron pair left for skeletal bonding.

Figure 1 shows the interaction diagram between bonding molecular orbitals of the *nido*-B_5H_5 square pyramid with a capping B−H group and with itself. The B_5H_5 fragment has one low-lying highly bonding orbital and two degenerate molecular orbitals in the bonding region. Interaction of this fragment with another B−H cap results in *closo*-B_6H_6, which requires two more electrons to fill its doubly degenerate bonding molecular orbital. Interaction of two B_5H_5 units to form a *closo*-$B_{10}H_{10}$ skeleton also results in a similar MO pattern in the bonding region. It can be seen from the figure that all the borane fragments have three bonding molecular orbitals requiring six electrons, referred to as interstitial electrons. The MOs of all the interacting fragments shown in Figure 1 are bonding, whereas the resulting structure contains both the bonding and antibonding MOs arising from the interactions of the fragment MOs. It should also be noted that these MOs are not essentially those lying in frontier levels. This six-electron requirement is independent of the number of rings and caps present in the borane skeleton. A similar pattern can be observed even if the number of atoms in the ring is changed, but only four- and five-membered rings have effective matching with the capping group. This approach effectively explains the origin of aromaticity in polyhedral boranes, if they can be conveniently split into rings and caps as in the case of stable high-symmetry structures $B_5H_5^{2-}$, $B_6H_6^{2-}$, $B_7H_7^{2-}$, $B_{10}H_{10}^{2-}$, $B_{12}H_{12}^{2-}$, etc. and their open counterparts. It also explains the relative stabilities of boranes and carboranes with respect to the compatibility of orbitals between the ring and cap.[40]

C. Macropolyhedral Boranes

In the present section, we will be concerned with a theoretical model for the macropolyhedral boranes based on the perceptive MO theoretic interpretation given by Wade.[21] The main intention is to describe these interactions involved in an intelligible way, thereby avoiding certain pitfalls in the blind application of the counting rules. Nevertheless, this model provides the impetus for intriguing research on some miscellaneous interactions that may possibly arise in due course. The current emphasis is to acquire the general logic behind the use of electron counting in macropolyhedral boranes. With this understanding, it is easy to identify a small number of structural patterns whose perception is critical for assessing the electronic requirements.

The outcome of this analysis not only identifies the distinct modes of interaction between monoaromatic units but also provides an estimate of the extent to which these different interactions can be unambiguously classified under different headings. Overall, the model supports the hypothesis drawn as electron-counting rules for macropolyhedral boranes and provides the framework to initiate further studies in the isolobally related clusters such as transition-metal carbonyls.

As we have noted earlier, macropolyhedral boranes that are formed by the interaction of two or more monomeric units can be broadly classified into two categories. The first category involves the *exo* interactions, where the individual units are connected together by localized bonds. The second category involves the sharing of one or more atoms between the individual units, giving rise to condensed polyhedral boranes. This classification is rather artificial, and there are several molecules that cannot be unambiguously classified into any of these classes. Among the condensed polyhedral boranes, the single-vertex-sharing systems are treated separately, as their electronic requirements are different from those of the rest of the condensed systems. To illustrate the various possible modes of interaction, we will describe the study of two generalized *closo* polyhedral boranes by bringing them together from a noninteracting distance to form condensed systems, varying the distance periodically. *Exo* polyhedral interactions arise as the first case, followed by condensed systems, all of which are described in the following sections.[6,86]

1. Exo Polyhedral Interactions

Let us assume that two *closo* polyhedral boranes, $B_xH_x^{2-}$ and $B_yH_y^{2-}$, are brought close from infinity, with one of their *exo* B−H bonds lying in the line of interaction. When they are a safe distance apart, the overall electronic requirement of these two systems will be four electrons, as each unit requires one pair of electrons. With the decrease in distance, initially the two B−H bonds lying in the line of interaction will lead to a four-electron destabilizing interaction as shown in Figure 2A. A bridging interaction between the two boron atoms and the *exo*-hydrogen atoms as shown in pattern B appears similar to that of diborane (B_2H_6). But, unlike diborane, only one sp hybrid orbital is available with each boron, so that only a two-electron bond is possible. The second pair of electrons goes to a less stable level, resulting in an unstable system. But this antibonding orbital can be stabilized by transition metals having diffused orbitals. A similar effect is produced even with main group elements, but with bridging hydrogens substituted by groups such as $-CH_3$ or CO with unoccupied π^*- or pseudo-π^*-orbitals, which lowers the unstable level.

The removal of one of the bridging hydrogens from stable structure B leads to structure C. The orbitals available to form the 3c−2e bond are the two sp-hybridized orbitals of boron and the s-orbital of hydrogen. They interact together to form a stable BMO and two antibonding MOs. Three electrons are available, one with each atom involved in the three-centered interaction. As only two electrons are required for this 3c−2e bond, one electron has to be expelled from the system, resulting in charge reduction (−3). This pattern is a fairly stable mode of interaction provided the nonbonding interactions between adjacent B−H groups are minimal.

Further reduction of the inter-borane distance will render the 2c−2e overlap more favorable over the angular 3c−2e overlap. As a result, the bridging hydrogen atom has to be removed as a proton, thereby enabling the conversion of the 3c−2e bond to a 2c−2e bond. This interaction also results in a stable pattern D except for the high charges (−4). If the borane units concerned in this interaction are reasonably larger to spread the higher charge uniformly, or if heteroatoms such as carbon are substituted in place of boron, such systems can be stabilized. This pattern also requires a geometric arrangement that minimizes the nonbonding interactions between the adjacent B−H groups. Dendrimers where each subunit is condensed through a 2c−2e bond are a natural extension of this type of system.[87]

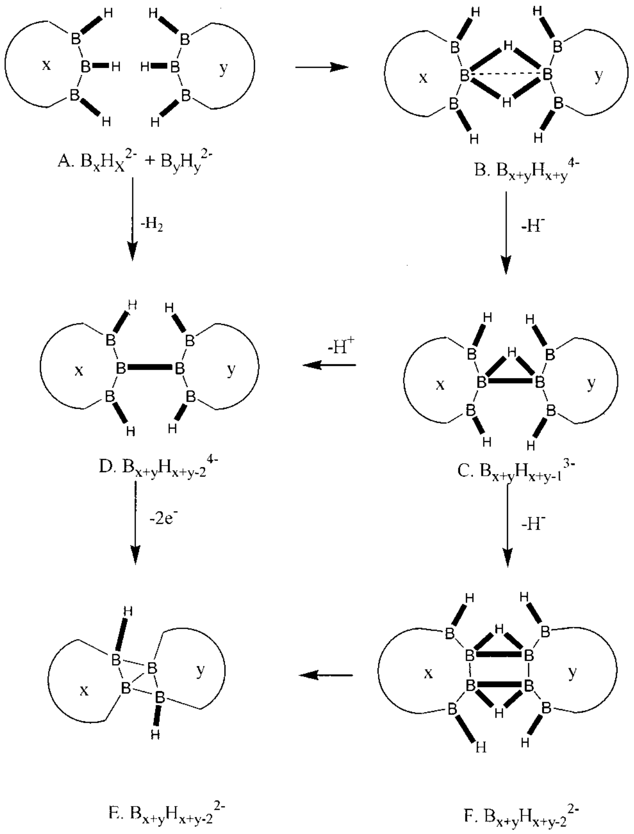


Figure 2. *Exo* polyhedral interactions arising from the approach of two polyhedral boranes. (B) represents the structure where the two units are joined by doubly bridging hydrogens. (C) has single-hydrogen bridging, which unites the two clusters. (D) involves a direct B−B 2c−2e bond. In (E) the interaction is through a multicenter B−B bonding. (F) has multiple B−H−B bonding. Examples for each of these bonding types are known experimentally.

An alternative way is to bend the structural pattern C so that more than one interaction center results. Two or more adjacent centers form a 3c−2e or 2c−2e bond as in pattern F. Every 3c−2e linkage will reduce the total charge by one, whereas the 2c−2e bonds keep the charge requirements constant. Such multiple linkages are quite possible even with pure borane clusters. Occasionally, atoms other than hydrogen may also bridge the two aromatic units by forming 3c−2e bonds on both sides. It is fairly easy to recognize and evaluate the electron requirement in these cases as they seldom form 3c−2e bonds.

When one of the boron atoms in pattern D is brought closer so that two adjacent boron atoms of the other borane unit are within bonding distance, as represented in structure E, the nature of interaction changes dramatically. It essentially implies that the boron atom caps the B−B bond of the other unit. Here, the two *exo*-hydrogens on the boron atoms that are connected by the concerned edge are still retained. Capping interactions do not alter the electronic requirement, as they will not add any BMOs to those already present in the polyhedra. The extra electron available at the boron atom then can be used to fill the BMOs of the polyhedra. These types of interactions occur pairwise, if the cluster geometry is favorable, where one boron atom from each borane unit caps an edge of the other boron as depicted in structure E. These systems exhibit a true macropolyhedral skeleton, as localized bonds do not separate these interacting borane units anymore. This pattern depicts the intermediate skeletal nature between connected and condensed polyhedral boranes, as they neither share any vertexes nor are separated by localized bonds (structure **14** in the illustrative examples, section VI). Capping interactions should be discriminated from 3c–2e interactions, where all the edges of the 3c–2e bond are absent in the individual polyhedral units and formed during the interaction process. The interactions discussed so far are all *exo* polyhedral and seldom affect the nature of the skeletal bonding of both the polyhedra. All these patterns were observed experimentally, in varying numbers. The careful identification of the nature of these interactions is necessary before the electron-counting rules are employed. In the following section, we will be concerned with the interactions where the interacting borane units share one or more vertexes, a situation that is entirely different from what we have discussed so far.

2. Condensed Polyhedral Interactions

Here, we are concerned with the macropolyhedral boranes sharing one or more vertexes for two or more polyhedra. Hence, condensation involves the reduction in the number of one or more boron atoms compared to the number present in the individual polyhedral fragments. As in the previous section, we will systematically increase the number of vertexes that are shared, considering all the possibilities of condensation.

When two polyhedral fragments are allowed to share one vertex as in Figure 3B, the electronic requirements of the system are affected significantly by the interaction between the vertexes adjacent to the shared atom lying on either side. When the distance between these vertexes is reasonably large, the number of BMOs remains the same. Here, the central atom is assumed to be sp-hybridized. The two sp-hybridized orbitals of the central boron point toward the center of each cluster that is shared. This hybrid interacts with the inwardly pointing sp hybrids of the other boron atoms in the monomer to form a single strongly bonding molecular orbital, as in the case of monopolyhedral boranes. The two unhybridized orbitals are involved in the surface BMOs. The number of surface BMOs required is not going to change as both the monomers B_xH_x and B_yH_y require their own set of x and y surface orbitals, respectively. As the total number of vertexes is one less than the total number of surface BMOs due to vertex sharing, each vertex sharing requires one more electron pair. To keep the nonbonding interactions to a minimum, the shared atom should be reasonably large or the size of the rings capped by the shared atom should be small. This can be practically realized when a larger heteroatom is present in the shared position. To achieve the single-vertex sharing with boron, the size of the ring which it is capping should be no more than three. Even with a ring size of four, the nonbonding interactions are significant enough to destabilize some of the BMOs as reported in the case of vertex-sharing octahedral aluminum clusters.[88]

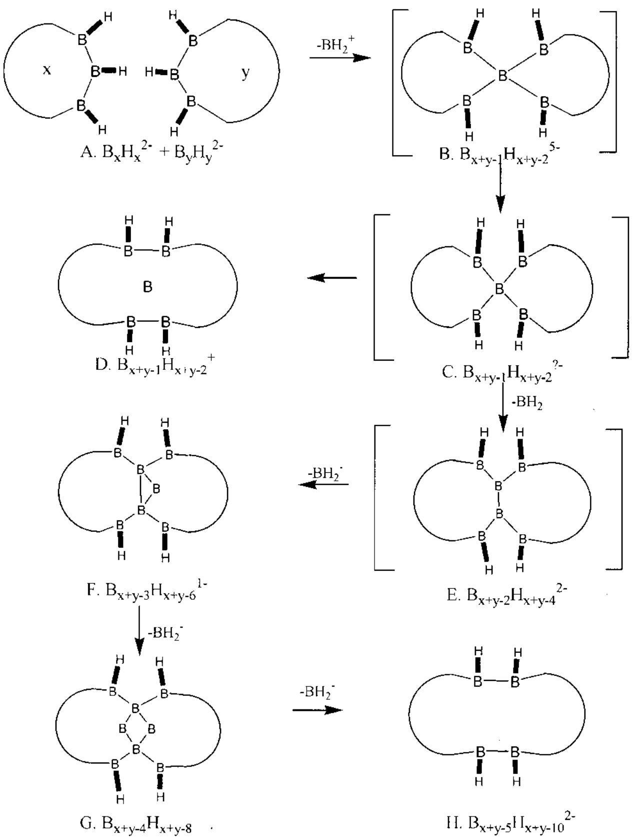


Figure 3. Range of condensations possible between two polyhedral boranes. (B) contains a single-atom bridging condensation known only when the shared atom is relatively large. (C) has an electron count different from that of (B) due to the nonbonded interactions arising between atoms adjacent to the bridging atom. This is known with metal clusters in solids. (D) represents endohedral boranes obtained by decreasing the nonbonded distance such that they are bonding. (E) shows the edge-shared system, known only with *nido* arrangements. (F) involves face-shared condensed structures, experimentally characterized in its *nido* form. (G) is a condensed structure with four-atom sharing. (H) represents the highest fusion (five-atom sharing) possible in polyhedral boranes, leading to a tubular structure, not known experimentally so far.

To rationalize the varying electronic requirements of single-vertex sharing, we prefer the ring-cap methodology adopted by Jemmis,[40] in the six-interstitial-electron-counting rule for aromaticity. This methodology simplifies the study by reducing the number of BMOs to be considered. The sp^2 and sp hybridizations adopted for rings and caps are rather subjective[52] and shown to be equally efficient with other factorizations in the study of polyhedral boranes.[69] The correlation diagram of the MOs that are affected is depicted in Figure 4 as a function of the distance between the rings. Here, the frontier orbitals of two square pyramidal B_5H_5 fragments interact with the valence orbitals of the central atom.

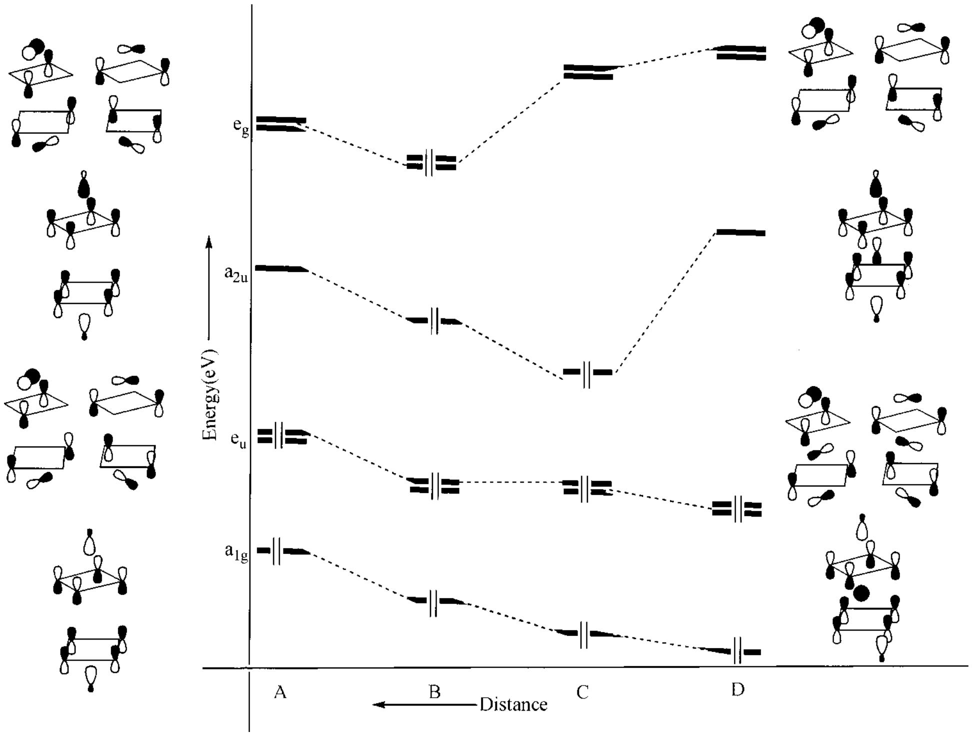


Figure 4. Schematic MO energy levels of two square pyramidal B_5H_5 units in D_{4d} symmetry (A). (B) represents the stabilization of these MOs after their interaction with a main group central atom larger than boron. The two B_5H_5 units come closer when the central atom is boron. This variation of energy levels is indicated in (C). Further reduction of the distance between the B_5H_5 units leads to the endohedral cluster (D).

Structure A has an energy separation between the e_u and e_g sets. This explains the requirement of four negative charges. When the interaction of the rings results in structure B, the e_g set becomes the LUMO, and this explains the *mno* rule. When the rings are kept within interacting distance as in structure C, the e_g orbitals are destabilized and raised to the antibonding region.[52] Further reduction results in the doped system, where one of the radial orbitals, a_{2u}, is also destabilized, resulting in a stuffed pattern, $B@B_{12}H_{12}$, as depicted in Figure 3D.[62]

The molecular orbital energy spectrum for transition-metal sandwiched boranes is shown in Figure 5. It has been correlated with the molecular orbital pattern of the main group complex. The change of the borane ligand from B_5H_5 (C_{4v}) to B_6H_6 (C_{5v}) does not alter the bonding molecular orbitals in the case of the main group borane complex. The study of molecular orbitals for transition-metal borane clusters has been done on the B_6H_6 ligand rather than B_5H_5 because the structures known are those in which the transition metal caps a five-membered ring[3b] whereas capping with four-membered rings is rare. The *mno* rule can be well understood from the BMO pattern of $(B_6H_6)_2M$, where M = Al or Si. An extension of the rule to transition-metal complexes usually results in additional terms to account for the d-orbitals. But, here, it can be seen from the figure that the BMOs which have a major contribution from the polyhedral skeleton remain the same whether M is a main group or a transition metal, hence the constancy in the rule. There are no major changes in the BMO pattern of the two correlated systems except in the e_g and e_u sets. The e_g set of the first system does not have a proper match from the orbitals of the main group element, though in the bonding region it will be slightly higher in energy, above the e_u set. The d_{xz}- and d_{yz}-orbitals of transition metals are of proper symmetry to interact with this particular orbital and hence stabilize the e_g set, lowering its energy below that of the e_u set. The LUMO of the transition-metal sandwich complex has an important significance in slipped structures. On the basis of the direction of slipping, one of the orbitals from the degenerate LUMO is affected mostly. If the molecule slips in the *y* direction, the MO involving the d_{yz}-orbital is stabilized. The MO with a metal d_{xz}-contribution will be lowered in energy if the distortion takes place in the *x* direction. The slipped distortion decreases the antibonding interaction and brings in slight bonding character in the MO. This explains why the molecules tend to slip when they have more electrons than required by the rule.[89,90,91] A simple example such as ferrocene is easily accommodated by the *mno* rule. The number of electron pairs available for skeletal bonding is 16 (15 from the two Cp groups and one from iron), while the *mno* rule also predicts 16 electron pairs.

When one more atom is shared between the monomeric units, the core BMOs that are formed by the strongly bonding interaction of the inward-pointing sp hybrid orbitals remain unchanged. The two surface BMOs are shared between both the units since they share more than one atom. Edge sharing allows the existence of Hamiltonian circuits that span the entire macropolyhedral framework, which enables the stabilization of exactly the same number of surface bonding orbitals as the number of vertexes in the system. A similar effect is observed in the three- and four-vertex-sharing macropolyhedral sys-

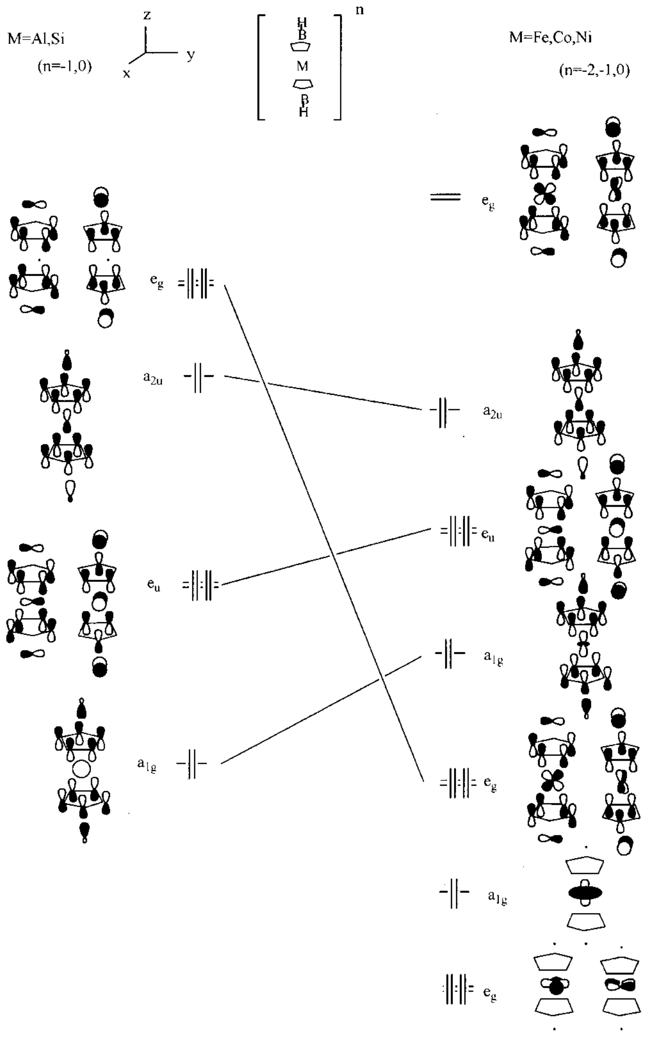


Figure 5. Correlation of a sandwich complex with a central main group atom and its corresponding transition-metal analogue. The higher lying e_g set explains the observed slipping in transition-metal sandwich complexes when the electron count exceeds that obtained from the *mno* rule.

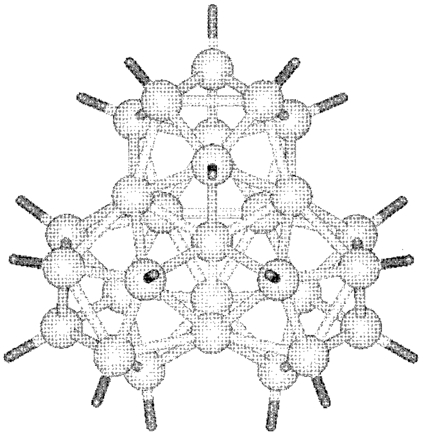


Figure 6. B_{28} unit seen in β-rhombohedral boron. The residual exohedral valencies are saturated to give the structure of $B_{28}H_{21}^+$.

tems. However, the sp hybrids of the boron atoms in these systems, unlike those of single-vertex-sharing systems, will not be ideally oriented toward each polyhedron. This requires a rehybridization of the shared boron to have more p-character to relieve strain and essentially reduces the s-orbital contribution. The core BMOs of these systems are stabilized by rehybridization owing to the increased overlap. In some very condensed systems such as $B_{28}H_{21}^+$ (Figure 6), which is found in β-rhombohedral boron,[92] the p-character of the hybrid orbitals of the central atom sharing the three polyhedra is close to sp^2 hybridization, since three radial orbitals are required.

As in the case of monopolyhedral boranes, the three-dimensional aromaticity exhibited by these macropolyhedral boranes is conceptually related to the two-dimensional aromaticity of polycyclic aromatic hydrocarbons.[41] Here, the electronic requirements dictated by the $n + m$ rule smoothly converge to those of the $4n + 2$ Hückel rule, as the macropolyhedral borane is finally reduced to naphthalene. For example, naphthalene, by successive transformation of a ring atom to the cap, transforms to an edge-sharing pattern of octahedra. In each step, the excess electrons can be removed from the system by replacing carbon by boron.

IV. Bonding Patterns

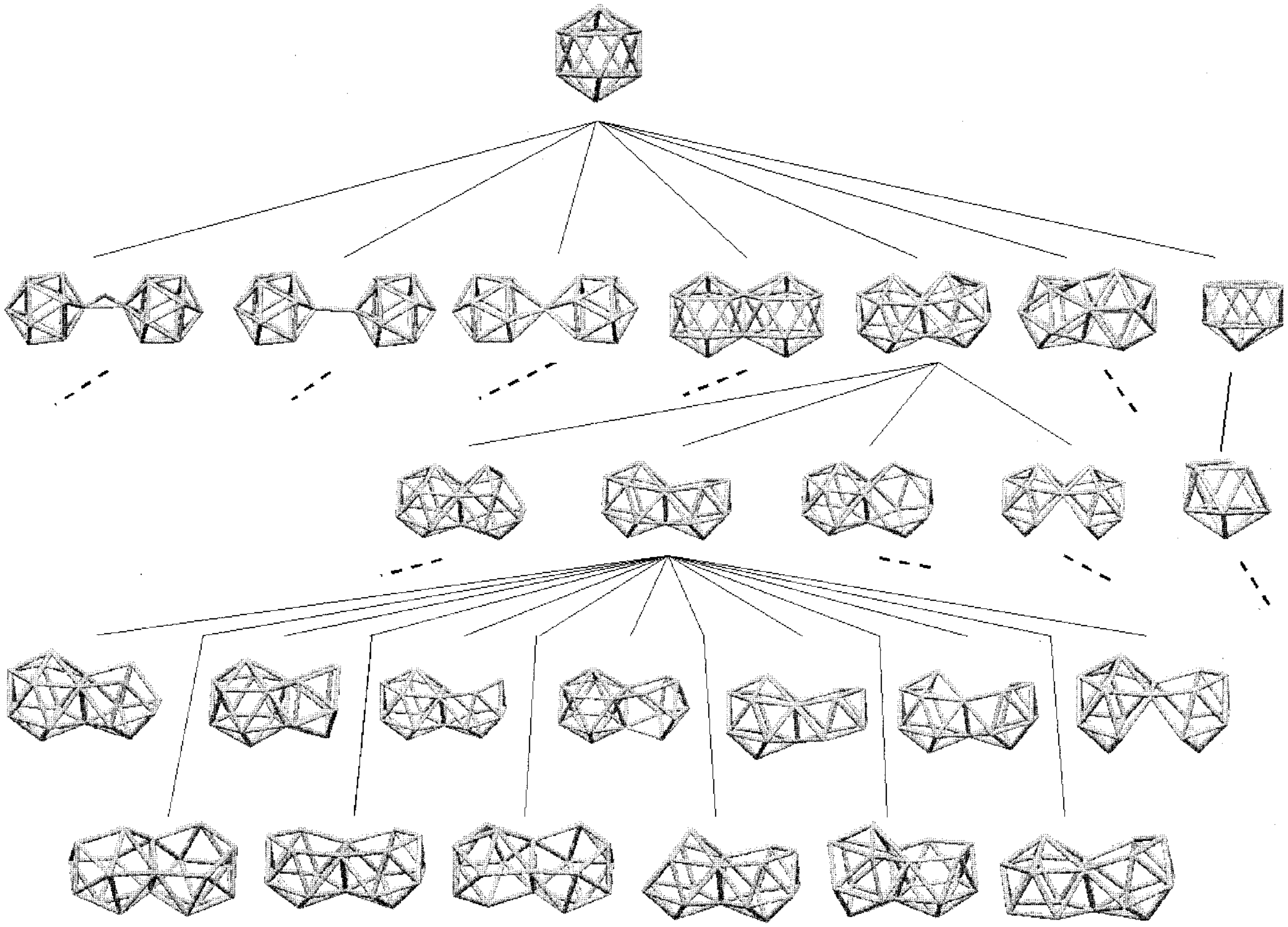
The variety of bonding patterns exhibited by main group elements is a result of their tendency to bond with their own type, thus attaining the octet rule. It is a historical fact that the variety of structures possible is enormous for a carbon atom. The property, which enables the carbon atom to form long-chain compounds, is termed catenation. While carbon exhibits catenation to a larger extent, other atoms of the periodic table are found to have a lesser tendency toward such a behavior. One of the many reasons for this extremely important property of carbon is that its valency is exactly half of the octet. Thus, the carbon atom has a one-to-one relation between the valency and the electron requirement. This enables the atom to form perfect 2c−2e bonds with others of its type and propagate in different directions by means of its sp^3, sp^2, or sp hybrid orbitals. The catenation property of carbon results in many planar mono- or polycyclic conjugated hydrocarbons where the bonds are of perfect 2c−2e type with a planar delocalization of the π-electrons. Elements on the left side of carbon in the periodic table require more neighbors to satisfy the octet rule. Boron with three electrons requires five more to attain the octet, which is not possible by forming perfect 2c−2e bonds with another boron. So boron alleviates this deficiency by forming multicenter bonds, where some of the electrons are delocalized to give a stable electronic configuration. It is similar to the planar delocalization of hydrocarbons. However, whereas the delocalized structure is just one of the resonance forms which contributes to the actual structure of an aromatic hydrocarbon, the three-dimensional delocalization in polyhedral boranes is unique. The elements on the right side of carbon in the periodic table also have an adverse effect. Even though the electronic requirement is less, the lone pairs generated during bond formation pose a problem in the easy packing of the molecules in three-dimensional space. If the catenation of carbon arises only because of its equality between valency and electronic requirement, all the remaining elements in group 14 should have a similar effect. But, as we go down group 14, electrons in the s-orbitals remain inert as the difference in the diffuseness of the orbitals decreases. Only the p-electrons are involved in bonding, thereby resulting in lone pairs, creating the same effect as discussed earlier.

The ability of carbon to form a large number of compounds owing to its special catenation property has been challenged by the striking growth of polyhedral borane compounds. Contrary to the expectations, the polyhedral bonding exhibited by boron leads to a variety of structural patterns. A monocyclic hydrocarbon exists as a charged or neutral species, satisfying its electron count according to Hückel's rule.[13] There is no possible way to alleviate the charge in such compounds. A comparison between benzene and $B_{12}H_{12}^{2-}$, which are the most stable forms of the two classes of compounds under discussion, gives a clear picture of the number of compounds originating from them. An icosahedron gives a greater variety of structures by various modifications, whereas all these possibilities are narrowed in the case of benzene. The Rudolph diagram is a simplified version, which correlates the different forms such as *closo*, *nido*, and *arachno* of a polyhedral borane.[22,93] A *closo* polyhedral borane will usually be dianionic to achieve the stable electron count. The *nido* form obtained by the removal of one vertex has to compensate for the loss of electrons by enhancing its charge, since the number of bonding molecular orbitals remains unaltered. Repeating the process successively gives the *arachno* framework, which would be highly charged by following the previous argument. But these systems instead of remaining charged, since it is a cause for instability, will tend to acquire the required electrons by incorporating bridging hydrogens. These hydrogens donate their shared electron pairs to the cluster, thereby decreasing the charge of the system or even making it neutral. This can also be achieved by electron donor substituents such as NH_3, OMe_2, etc., which form dative bonds with the cluster, providing electrons for skeletal bonding. Very few examples are known where the charge requirement is satisfied by *endo*-hydrogens which donate their shared electron pair to the skeletal bonding.[94a,b] These *endo*-hydrogens are different from the bridging hydrogens in that they will be bonded to only one boron atom but will be occupying the same inner spherical surface, with their orbitals directed toward the cluster. This necessitates the bonding electrons to be distributed within the cluster. The hydrogens can be differentiated as *endo* or *exo* by following Lipscomb's concept of polyhedral bonding.[69] According to this approach, a polyhedron consists of two concentric spheres. The atoms lying on the inner sphere participate in cluster bonding, whereas those on the outer sphere are *exo* polyhedral substituents, which do not influence the cluster bonding. The bridging hydrogens, *endo*-hydrogens, and boron atoms lie on the inner sphere. The determination of the hydrogen type can be done by an extended Hückel calculation on the particular system.[94c] Deleting the hydrogen in question will enhance the charge requirement if it is an *endo* type. The depletion of a terminal hydrogen will reduce the charge as the concerned bare boron will donate all its electrons for cluster bonding. Electron donor substituents on boron help in alleviating the charge by forming a dative bond, which enables the boron atom to donate all its electrons to the cluster. The bridging hydrogens can occupy different bonding sites of the open structures, which leads to positional isomers. All of these provide possibilities for the exponential growth of borane complexes, while in hydrocarbons these possibilities are always limited.

The condensation of two or more clusters provides yet another alternative to achieve different structural patterns. When two borane clusters undergo condensation, the fusions are of different types as mentioned earlier, which include linkage between two clusters by a usual 2c−2e or 3c−2e bond and fusion through a single vertex and one or more edges. The maximum number of shared edges known so far in the literature is four.[55−57] All the possible fusion modes are shown in Scheme 2, taking two icosahedral units. If a macropolyhedral borane is considered as a large single sphere, it is seen that the condensed systems have a negative radius of curvature at the shared position. This will be a maximum for a single-vertex condensation and a minimum for a four-atom-shared fusion. The next higher fusion possible is a five-vertex fusion. The diffuseness of boron orbitals allows maximum effective overlap with a five-membered ring. When a five-membered ring is at the shared position, it requires an equivalent ring of the same size or a BH group to cap. If the capping fragment is again a five-membered ring, it will become a stacked system of five-membered rings with all of the boron atoms having terminal hydrogens. This arrangement essentially makes the system cylindrical with a uniform radius of curvature. In other words, a five-edge fusion destroys the identities of the individual polyhedra involved in the fusion and they will emerge into a single polyhedron. Both Wade's $n + 1$ rule and the more general *mno* rule can be applied to such systems. A macropolyhedral borane with five edges in common is a nanotube equivalent of boron.[95] Higher fusions are not possible owing to the poor ring-cap compatibility of boron.[40]

The charge requirement of a condensed polyhedral borane depends on the mode of fusion. The charge on a macropolyhedral boron hydride is reduced as the number of fused atoms increases. This is because each such boron atom gives an additional electron to the cluster. For systems with the number of shared boron atoms ranging from two to four, the charge requirement varies from −2 to 0, respectively. A single-vertex-condensed system has an additional MO and hence is highly charged, provided the nonbonding interactions between the caps are neglected. These sandwich complexes are known with heteroatoms, mostly carbon. This is beneficial in reducing the cap−cap interactions and also in alleviating the charge of the system. The charge requirement of higher fusions suggests such systems to be stable in their *closo* form. However, an edge-shared *closo* form,

Scheme 2. Enormous Variety of Bonding Exhibited by Simple Polyhedral Boranes and Polycondensed Analogues Limited to Two Cages Shown with the Icosahedral Skeleton[a]



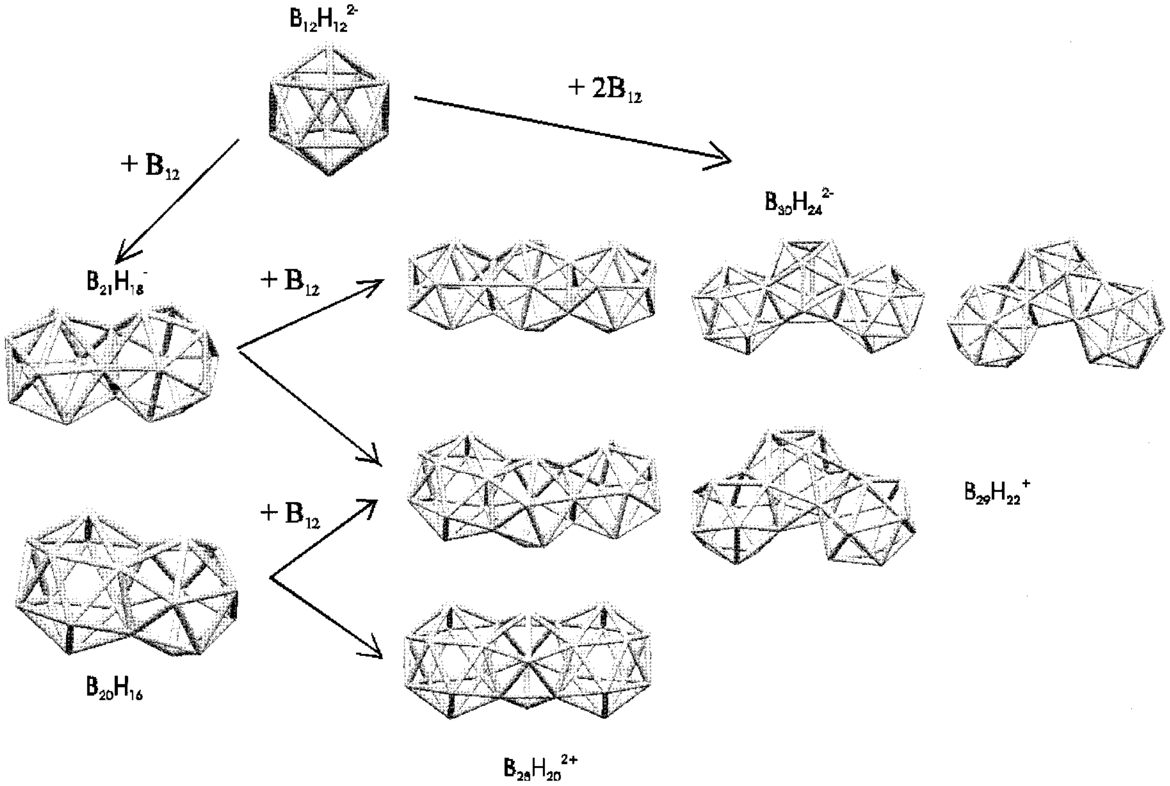
[a] Each row from the top represents *closo*, *nido*, *arachno*, and bis-*nido* structures, respectively. A correlation is given among these different patterns of macropolyhedral borane systems. At each level, one structure is expanded. Others also branch off in a similar fashion, as shown by dotted lines. Similar diagrams can be constructed using other polyhedra.

though predicted to be stable theoretically,[96a] is not isolated due to the possible nonbonding interactions. The triangular fusion is studied theoretically but is not yet realized as a *closo* form. But the open structural patterns of these systems are well established.

In the case of polycondensed polyhedral boranes, deleting even a single vertex has many options. Highly symmetric monoclusters such as $B_{12}H_{12}$ and B_6H_6 have all vertexes identical, whereas others have lower symmetry and the number of vertex types increases. However, during condensation, the symmetry is reduced for most of them and the number of different types of vertexes increases. So the number of *nido* structures possible from a condensed deltahedron is enormous. The different types of vertexes also include the shared atom. Scheme 2 gives the different *nido* patterns emerging from a face-shared $B_{21}H_{18}^-$ system. When we move from a *nido* to an *arachno* form, the possibilities are still greater. The *arachno* and bis-*nido* forms obtained from a single *nido* structure have been expanded in Scheme 2. We have tried to keep the scheme as simple as possible by expanding only a single set of structures at a time. The role of bridging hydrogens to reduce the overall charge of the system remains valid, giving rise to different positional isomers. It appears more in edge-shared *nido* or *arachno* structures where the *closo* form is not realizable owing to the interacting distance between nonbonded boron atoms of the two clusters.[96b,97] The impact of all these factors on the growth of the range of the polyhedral borane skeleton is always progressive.

Scheme 2 shows a representative diagram of the bonding patterns of condensed polyhedral boranes. Here, a comparison is made between monoclusters and fused clusters. The branch at the extreme right-hand side starting from the icosahedron indicates the *closo*, *nido*, and *arachno* path for monopolyhedral boranes discussed in the Rudolph diagram. The highly symmetrical icosahedron is taken as a model for simplicity. When for a single cluster only one *nido* type is possible, fusion creates 4 times the number of isomers. Only one branch of the tree diagram is expanded at a given time. The number of *arachno* and bis-*nido* structures emerging from a single *nido* structure among them has a further exponential growth. Expansion of the different types shown in the scheme indicates the enormity of the clusters just by a single fusion. A similar diagram can be drawn with other clusters taking similar or different subunits.

Scheme 3. Various Possibilites of Polycondensation Taking an Icosahedral Fragment as a Model[a]



[a] One cage is added at each step, and the number of isomers is seen to increase with extended condensation. This is represented in the scheme, limiting the condensation to three units. Single-atom bridging and edge sharing are not realistic with *closo* icosahedral arrangements.

A fused cluster connected further with one more cage provides yet another approach to branch off the scheme. Scheme 3 illustrates this for the triangular and four-vertex fusion modes. Here, there is one more possibility based on the different fusion modes at the two conjunctions. Structural isomers are also possible for the same type of fusion. Scheme 3 shows the three structural isomers when three polyhedra are fused through two B−B−B triangles. The next level of the scheme illustrates this for a combined three- and four-atom fusion. Expansion of each of these as before makes the number of possible isomers approach infinity. The known condensed hydrocarbons are of the linked type, spiro compounds, which essentially include carbon at a shared vertex, and the edge-shared annulene systems. However, these complexes remain as they are without any modifications of their skeletal framework. The fusion of polyhedral boranes attenuates the charge of the system except in *exo* polyhedral interactions and sandwich complexes, where the charge is found to enhance similar to what is found in fused hydrocarbons.

If the condensation is allowed to propagate in three dimensions, it may not always lead to stable entities. However, substitution by heteroatoms and variation of the condensation modes can lead to stable products with reasonable charges. Hydrocarbons on the other hand can extend to form polymers without any difficulty. Heteroboranes and their different positional isomers provide a path for structural diversity.

A generalization of the above discussion is that a balance is always possible in macropolyhedral borane systems to maintain the charge of the system. The factors which help in reducing the charge of the system are fusion through one or more edges, addition of bridging hydrogens or *endo*-hydrogens, and addition of substituents which form a dative bond to the cluster. The adverse effect is produced by joining two polyhedra through a 2c−2e bond or by single-vertex condensation, and by removing one or more vertexes. By keeping an intricate balance between all these factors, borane-based polymers can be realized.

There is current interest in oligomers of boranes, and research is going on in understanding their intermolecular interactions to generate supramolecular assemblies. Carboranes can act as building blocks of polymers because of the moderately acidic CH vertexes.[98] The CH vertex can be easily deprotonated and can be subsequently functionalized using electrophilic reagents. Although this method has been used in the synthesis of anion inclusion complexes, it can be modified and extended to boron-based polymers. The building blocks can be “active” or “passive” in nature. Stronger ligands as substituents on boranes or carboranes can become an active site, displacing weaker ligands from suitable borane species. Weaker ligands also help in polymerization by replacing themselves by stronger ligands of other borane units.[99] When polymerization can propagate through these means, the above generalization gives possible ways of tuning the charge of the system and stabilizing the polymer with appropriate charges.

V. Preliminaries in Applying the mno Rule

The application of the electron-counting rule requires some prior understanding of the molecule in terms of its bonding, modes of fusion, and topology. There are many terms in borane chemistry which have to be applied with caution while their electronic requirements are dealt with. The interaction patterns of two polyhedra to give a single cage have to be recognized while the skeletal electron pairs are enumerated, even though such knowledge is not essential for the rule (except for single-vertex condensations). The terms *nido* and *arachno* appear to overlap when the missing vertexes are adjacent. When heteroatoms are present, we should have an idea of the number of electrons contributed by such fragments. All these factors, which have to be considered while the electron pairs are evaluated, are discussed here.

A. Identification of the Fusion Type

In a macropolyhedral borane, the multiple cluster species may be linked by a σ-bond or fused with many possibilities. The fusion can occur by sharing a single atom, sharing an edge, sharing a triangular face, or sharing four atoms. The knowledge of the exact number of shared atoms is an important factor during the enumeration of the skeletal electron pairs contributed by constituent elements. Thus, the rule seems simple, but the knowledge of the different fusion types and their influence on the cluster bonding is essential to arrive at the charge of any system.

The first simple case of linkage between two polyhedral boranes occurs through a hydrogen bridge. This bridging hydrogen does not reduce the charge of the system since it forms its own 3c−2e bond independent of the skeletal electrons and is not supposed to be involved in cluster bonding. When the bridging hydrogen is lost as a proton, the resulting compound will have the two clusters linked by a usual 2c−2e bond between two boron atoms. This bonding electron pair is also separated from the skeletal bonding electrons.

The next type of linkage is through a 3c−2e bond. A 3c−2e bond formed between two polyhedra can be of two types. The simple case is where the two electrons come from a cluster, and the second type is one where the electrons are already involved in an inter-boron linkage. Examples for each type are **118** and **78**, respectively, of section VI. In the former case the electrons in the 3c−2e bonds affect the cluster bonding effectively. The latter type is the so-called *megalo*-boranes, where there is a central tetrahedral borane unit. One of the edges of this tetrahedral part is capped by either a boron atom or a metal, which is a part of another cluster. This central 3c−2e bond appears to be independent of cluster bonding. Examples for these types of linkages are very limited, which makes the generalizations rather difficult. Examples are known with two 3c−2e connectivities as well. In these systems a polyhedral bond of each unit is capped by a boron atom of the other, resulting in a multicenter linkage. The electrons in these multicenter bonds influence the cluster bonding. The proximity of atoms of two different clusters usually results in bonding interactions, forming intercluster linkages. This has to be differentiated from the usual modes of interaction. Structure **99** is one example where single-vertex condensation dominates and the B−B intercluster bond is a result of the proximity effect.

For single-vertex-shared condensed systems, each cage retains its electronic requirement and the parameter *o* for the number of single-vertex condensations has to be added to the $n + m$ rule.[6] The rule is well applicable for all systems where the central atom is larger than boron. Boron-shared compounds are impracticable owing to the possible nonbonding interactions between the caps of the two cages.[52−54] The only system in which a single boron bridges two polyhedra is found in the unit cell of β-rhombohedral boron.[54,92,100] It obeys the *mno* rule.

The presence of more than one common single vertex in a compound also presents difficulties in understanding the fusion. When two atoms join two polyhedra, they usually will be within bonding distance and can thus be regarded as an edge fusion. In such cases the term *o* remains zero. Even though such a *closo*-borane structure does not exist owing to the reasons mentioned earlier for single-vertex-shared complexes of boron, their respective open forms obey the rule with $o = 0$. There are also some very interesting examples where the two common atoms do not form a bond and cannot be defined as an edge-shared condensation. The number of such structures is very limited, and we could find only one in a Cambridge Structural Database (CSD) search. Structure **84** in Chart 6 of the illustrative examples represents this type of fusion.[101] They appear as analogues to annulenes, where two separated atoms bridge the cages. Such modes of fusion are accounted by the *mno* rule as two single-vertex condensations, and hence *o* has a value of two. The next higher fusion is a triangular mode of condensation, in which *o* has no significance. An analogous single-vertex condensation where $o = 3$ is unknown in the literature. When four atoms occupy the shared site, the two possibilities of fusion are again observed. In normal cases the four atoms will be bonded to the adjacent atoms, but not diagonally. Such cases are well-known and do not require any application of the term *o*. An identical fusion is observed but has to be differentiated from the usual ones. Structure **117** is an example of this type of fusion.[102] Here, it appears equivalent to **84**, where two nonbonded atoms connect the subunits. But the sulfur atoms are so placed that one of their lone pairs, which otherwise remains *exo*, now protrudes into the other subcluster. This essentially implies that sulfur contributes all its valence electrons and is at a point of fusion. In this way four atoms join the two clusters. Here, two bonds are missing compared to the usual four-vertex condensations. They obey the rule with *o* assigned a value of four.

B. Nido vs Arachno Conflicts

The terms *closo*, *nido*, *arachno*, *hypho*, etc. are used to describe the different cluster patterns exhibited by boron hydrides. Each of the types is obtained from the preceding ones by removing two electrons in the form of a vertex. This is the debor approach of nomenclature in which the cluster patterns are related to one or more missing vertexes with respect to the corresponding *closo* form. The seco approach treats a *nido* form as obtained from a *closo* by the removal of an edge, keeping the number of vertexes constant. Whatever approach is used to view the molecule, when a *closo* form with n vertexes is oxidized, the number of BMOs remains intact as $n + 1$ and thus the charge required by each of them varies as a factor of -2. The same is true when one face of a polyhedron is capped. This is explained by the capping principle of Mingos.[26,27] Since all of the orbital combinations of the capping fragment interact with the parent to form antibonding orbitals, the number of bonding MOs or electrons remains the same for both the capped and uncapped compounds.

The removal of two adjacent vertexes has an adverse effect on the MO pattern. The number of BMOs seems to decrease by one with the loss of each vertex. This has been studied by Burdett et al. while exploring the electronic structure of a triangular-face-shared $B_{21}H_{18}$ polyhedron.[48] The compound was split into two B_9H_9 deltahedra which appear to exhibit a *hypho* pattern of a B_{12} icosahedron and a middle B_3 triangle. The number of skeletal orbitals of the *hypho* structures instead of being 13, as is expected by Wade's rule, is only 10. Among the remaining three orbitals, a doubly degenerate orbital lies below the nondegenerate one, and all the others are high in energy. When the two *hypho* deltahedra interact, 22 skeletal orbitals are created. The two additional orbitals are the bonding combination of the high-lying degenerate level. This system is made to interact with the three boron atoms in a triangle, which generates 23 cluster orbitals. In the *hypho* structure the vacancies are adjacent to each other, which generates high-lying orbitals. Thus, Wade's rule, which assigns an equal number of skeletal electrons to *closo*, *nido*, and *arachno* deltahedra of a given size, does not work here. The contradiction arises only from an *arachno* skeleton. Generalizing this observation, the absence of two adjacent vertexes from an n-vertex *closo* deltahedron results in $n - 1$ BMOs. The resulting structure can then be assigned a *nido* form of $n - 2$ vertexes derived from a *closo* form with $n - 1$ vertexes $((n - 2) + 1)$ rather than from an *arachno* form of an n-vertex *closo* structure. Subsequent removal of one more vertex leads to $n - 2$ BMOs. These observations complicate the idea of the above terminology. Such terms seem to be arbitrary in macropolyhedral borane chemistry. The deduction of a structural framework by its topology alone seems impossible. This dilemma is overcome by relying on electron-counting rules. A comparison of the number of BMOs predicted by the rule and the number of electron pairs contributed by the fragments to the cluster successfully predicts the cluster pattern.

C. Heteroboranes

Heteroboranes where a boron atom is substituted in its polyhedral cluster by an atom from the main group or transition elements are known. Heteroboranes, in general, exhibit a much greater variety of structural behavior than do the binary parent boron hydrides themselves. In fused systems, the heteroatom occupies either a terminal or a shared site. In fusions other than single-vertex condensation, locating a main group element as a shared atom is difficult. However, the probability of a transition metal at a shared site is very high. This is due to the diffuseness of the d-orbitals of transition metals, which can result in effective overlap with the cluster orbitals. In heteroboranes with main group elements, the major heteroatoms are carbon, oxygen, sulfur, and nitrogen, which cannot replace a shared boron due to the low diffuseness of the valence orbitals. Beryllium, silicon, germanium, etc. can be effective substituents for boron. However, even though they are known in single-vertex condensation, no complexes have been isolated with these atoms at higher points of fusion. Boranes containing transition metals are treated separately in the next section, and an account has been given as to how many electrons the metal vertex contributes to cluster bonding.

The most commonly used main group element is carbon, which leads to the broad area of carboranes. A $-$CR group usually contributes three electrons for polyhedral bonding. In oxa- and thiaboranes, both sulfur and oxygen have a tendency to retain one of their lone pairs, providing four electrons for the cluster. In ambiguous cases it is better to have a theoretical understanding of the molecule from an electronic structure calculation. Nitrogen, if present as a terminal atom, will be a four-electron donor. If a main group element is at a shared position, it donates all its valence electrons for cluster bonding.

D. Transition-Metal Boranes

A polyhedral metallaborane can be viewed as a metal complex of a boron ligand.[12] The variation of the metal, its ligands, and the heteroatoms in the cage permits a plethora of stable structures. Owing to the close proximity of the subclusters, intercluster interactions are possible, which may vary from a weak agostic involvement to a strong conventional bond.[3]

A metallaborane is related to its parent binary boron hydride by isolobal analogy. In monocage metallaborane clusters, the number of skeletal electrons, E, contributed by a metal vertex is determined by using the equation $E = V + X - 12$, where V is the number of valence shell metal electrons and X is the number of electrons contributed by *exo* polyhedral ligands.[21b] This equation derived by Wade is a direct consequence of isolobal analogy.[29] In such cases, a d^{10} ML fragment and a d^8 ML_3 fragment are two-electron donors and are isolobal to BH and therefore take part in cluster bonding in a similar manner. Perturbation by the replacement of a BH by a transition-metal analogue in a binary boron hydride is found to be quantitative rather than qualitative. There may be some impact on the properties associated with cluster bonding, but the qualitative aspects of the bonding network remain the same.[103a]

The removal of a proton does not alter the donor property of a molecular fragment. The fragments involved are isoelectronic. This implies the fact that variable isolobal behavior is possible for transition-metal fragments. Thus, a d^{10} ML_2 fragment can be treated either as a two-orbital−two-electron donor or a three-orbital−four-electron contributor to cluster bonding; i.e., it can be isolobally related to either a CH_2 fragment or a CH^- fragment. The difference in behavior of the transition-metal fragments is not very easy to identify. Often this is achieved by an MO calculation at the extended Hückel level. However, in macropolyhedral systems all metals with at least one ligand appear to behave as BH groups or boron atoms depending on whether they are at an unshared site or at a joining point as far as their electron contribution to cluster formation is considered. Thus, the metal fragment is substituted by its boron analogue by applying isolobal analogy followed by isoelectronic replacement. For electron-counting purposes it is essential to replace a shared metal by a boron atom and a terminal one by a BH fragment. This maintains the basic assumption that only three orbitals are involved in cluster bonding when it occupies an unshared site on the cluster. If the metal occupies the junction, like a shared boron atom it contributes four orbitals.

Complexes with metal−metal bonds are found to deviate from the *mno* rule with an excess of two electrons. These two electrons can be attributed to the metal−metal bond, which is not a part of the cluster bonding. However, such systems are very rare, which makes a detailed study difficult. They have been classified as ambiguous types in the section of illustrative examples. Woolley has attempted to explore the analogy between borane and a transition-metal cluster.[103b] The method involves the examination of MOs of an octahedral metal cluster by interacting six $M(CO)_3$ ligands, bringing them from a nonbonding distance to the equilibrium overlap. A d^8 ML_3 fragment is similar to BH electronically on the assumptions that the three valence orbitals of both the fragments are nonbonding or nearly so and the sets of three skeletal orbitals interact with other fragments in a similar fashion. At large separations of ML_3 fragments, the d-orbital interactions can be neglected. Hence, at these weak interactions, the skeletal hybrids are identical to BH and hence both are electronically equivalent. The same is found to be true in metallaboranes where two metals are adjacent to each other. If the two metals are at pretty long distance and still bonding, the concept of isolobal analogy can be applied. However, an equilibrium separation between the metals breaks down the application of isolobal analogy.

Unsaturated metallaboranes have been isolated and characterized with early transition metals such as Cr, Mo, etc. Either such systems have a multiple M−M bond or the unsaturation is delocalized throughout the cluster bonding network.[103a] They exhibit the enhanced reactivity expected for an unsaturated species. Such species are not very common in macropolyhedral boranes, since 90% of the macropolyhedral boranes known are with late transition metals.

When the fusion involves a single atom, there is difficulty in applying the concept of isolobal analogy. Such sandwich complexes are approximated to octahedral complexes so that the electrons in the e_g set of the transition metal become a part of the skeletal bonding. This is usually the case except in complexes similar to the high-spin species ferrocenyl cation and cobaltocene. In these systems the complex will be paramagnetic and can be differentiated from the usual examples. Slipped sandwich complexes are also known in sandwich complexes of polyhedral boranes. They have an excess electron pair and do not follow the *mno* count. This excess electron pair essentially fills an antibonding orbital. This MO is effectively stabilized by slipping.

Macropolyhedral boranes with late transition metals such as copper, zinc, and mercury have also been isolated, usually as single-vertex-condensed species with the metal at the shared site. They have s-electrons in addition to those in the e_g set which can be recognized as cluster electrons. However, the electronic contributions from these metals are not well understood. In some cases they contribute electrons from both the e_g set and s-orbital (structure **83**). However, examples exist in which the donation is restricted entirely to be from s-orbitals, where they tend to be similar to main group elements, providing only the s-electrons to the cluster bonding. This happens mostly when the metal has a lower coordination (**100**, **135**). They have similarity with the structural pattern exhibited by aluminium in aluminaboranes (structures **55** and **56**) and are different from slipping. They have a *closo* count and show some *isonido* characteristics. It is clear that further theoretical studies are required to understand the bonding in metallaboranes completely.

VI. Illustrative Examples

Any comprehensive review of the development of macropolyhedral borane chemistry must surely begin with the two seminal papers published simultaneously on the condensed *closo* macropolyhedral borane $B_{20}H_{16}$[55,56] from the research groups of the pioneers of boron chemistry, Lipscomb and Muetterties. But, for the sake of clarity, this section is classified differently into four subsections. In the first section we present several ideal examples of “bare” borane clusters in which all the atoms in the polyhedral skeleton are boron alone. The change in the electron count caused by introducing different main block elements is illustrated in the next section. The following section deals with the impact of embedding transition metals in the skeleton. The last section deals with the complex examples where several different “heteroatoms” are present in the same skeleton. The variety of structural patterns exhibited by these systems are depicted by distinct figures as much as possible, and only those most ubiquitous patterns which occur in several closely related molecules are left out. Almost all of the structures discussed here have been obtained from the CSD,[104] though some are theoretical novelties. Hence, any ambiguities in refining the positions of hydrogens in the reported structures are reflected here. Thus, some of the structures shown in the Charts 1−10 may represent only the skeletal framework. In such cases the hydrogens, both terminal and bridging types on the skeletal atoms, will be missing. All of the theoretical structures presented here are characterized as minima by higher-level MO calculations. Throughout this section, the following conventions are used. Boron atoms are represented as light spheres and *exo*-hydrogen atoms as radiating bonds. Small spheres are used for bridging hydrogen atoms to discriminate them from the *exo*-hydrogen atoms. However, if the experimental structure available in the CSD lacks hydrogen atoms, it is presented as it is, though electron counting may prove the presence of these, either as *exo*-hydrogen atoms or as bridging ones. The Cp and Cp* groups are not discriminated as the presence of a methyl group does not alter the electron count of the macropolyhedral system. Heteroatoms are darkened and labeled with their respective symbols. Substituents that are connected to the skeletal atoms are represented as dark spheres, and all of them are labeled as L irrespective of their nature since the focus here is mainly on the polyhedral skeleton. Other substituents are labeled with R, since many of them are organic moieties, although this generalization is not strictly valid for all structures.

A. Pure Borane Clusters

Macropolyhedral boranes composed of only boron atoms in the polyhedral skeleton have been known for a long time. Owing to the increase in the charge requirements, individual polyhedra connected by localized bonds are not found to be common. However, condensed systems and exohedral interactions involving polyhedral linkages are found frequently due to their propensity to reduce the charge requirements. Among the condensed polyhedral boranes, the entire set of molecules except $B_{20}H_{16}$ has one or more open faces to avoid steric crowding around the shared atoms. Among these molecules, edge-sharing patterns with more than one open face are found to be dominant. Although the structures of many of these molecules are well characterized, some of their structures are still not determined unambiguously due to the difficulty involved in the perception of bridging hydrogen atoms.

$B_{12}H_{12}^{2-}$ (I_h) (**1**). Although it is not a macropolyhedral borane, $B_{12}H_{12}^{2-}$ is included in the list due to the ubiquitous presence of its icosahedral pattern in many macropolyhedral borane systems. Its stability as a dianion was predicted by theoretical calculations[64,67,68] long before its experimental isolation, and it is the most stable of all the polyhedral skeletons exhibited by boranes. Using the present electron-counting scheme, $n = 12$ and $m = 1$ leads to 13 electron pairs for the polyhedral skeleton, which reduces to Wade's $n + 1$ rule for *closo*-boranes.

$B_{24}H_{22}^{4-}$ (D_{5d}) (**2**). This is an idealized example of two icosahedral B_{12} units connected together by a 2c−2e bond. As $n = 24$ and $m = 2$, the number of electron pairs required is 26, simply the sum of the individual electronic requirements. As each of the boron atoms contributes one electron pair to the polyhedral skeleton, two more electron pairs are required for aromaticity. This D_{5d} structure is centrosymmetric since the two inner pentagonal rings are in the staggered form and is calculated to be a minimum despite its −4 charge.[96a] Although $B_{24}H_{22}^{4-}$ is not experimentally characterized, several carborods[88] in which two carbon atoms are present in each individual fragment are well characterized.

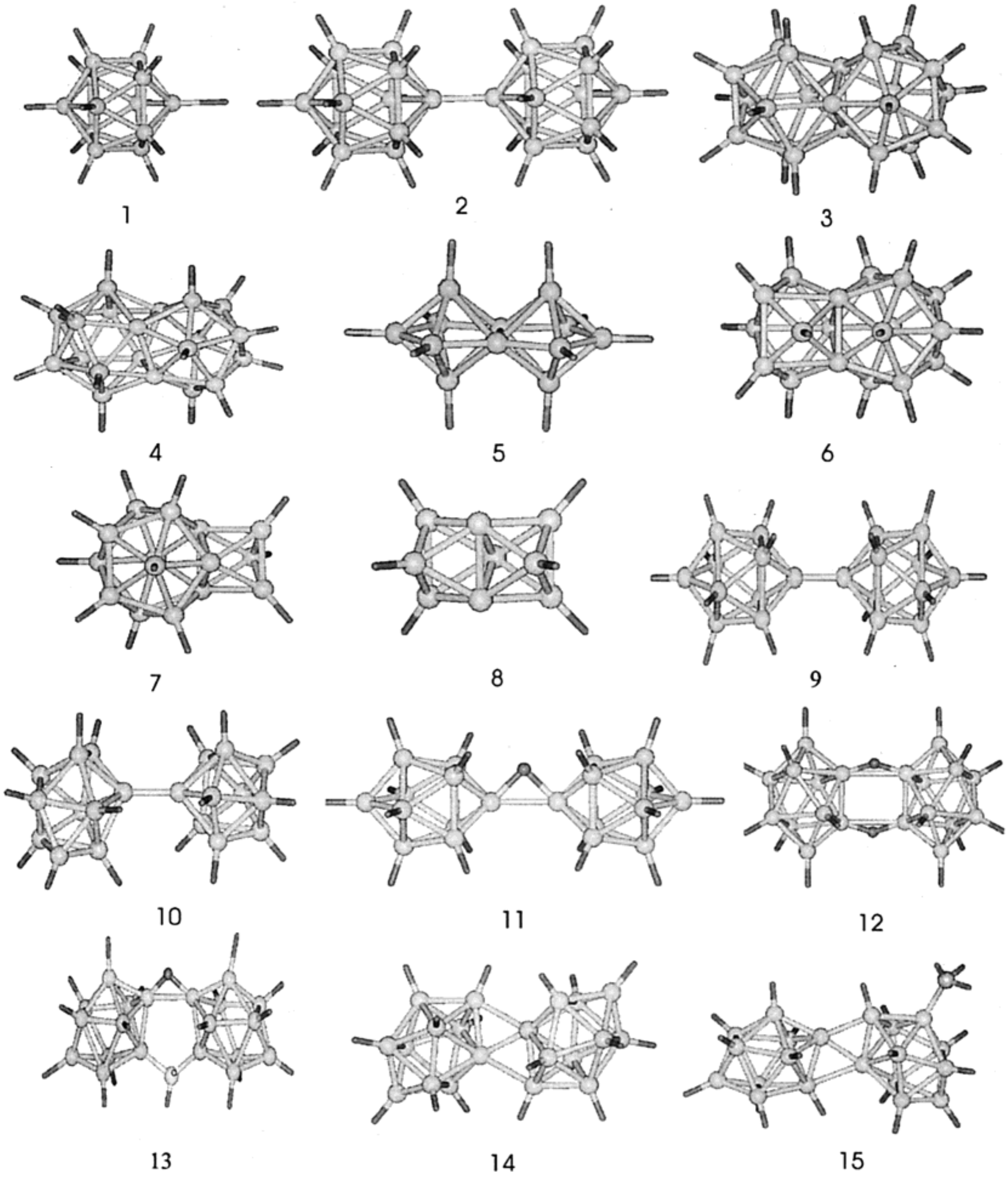
$B_{21}H_{18}^{-}$ (D_{3h}) (**3**). This molecule represents a typical example of a face-sharing icosahedral B_{12} fragment. Here, $n = 21$ and $m = 2$, and hence, 23 electron pairs are required for aromatic stability. There are 18 B−H fragments, each of which contributes one electron pair for skeletal bonding. The three shared boron atoms contribute nine electrons, since all three valence electrons in the shared boron are available for skeletal bonding owing to the absence of *exo* 2c−2e bonds. Hence, this molecule requires one more electron for aromatic stability. This centrosymmetric D_{3h} skeleton is characterized as a minimum by theoretical calculations with a single negative charge.[96a] Several theoretical studies unambiguously confirmed the single-electron requirement,[48,53] which was intuitively predicted by Lipscomb in the 1960s.[106,107] Also referred to as twinned icosahedra, this molecule has not been isolated experimentally. Nevertheless, this face-sharing skeleton is found in the β-tetragonal polymorph of boron[108] and is also exhibited by boron-rich solids such as the α- and γ-forms of AlB_{12}.[109]

$B_{20}H_{16}$ (D_{2d}) (**4**). This molecule is unique among all the known macropolyhedral boranes since it shares four boron atoms between two icosahedra[55a,56] and its structure and chemistry are well characterized.[110] This molecule retains the maximum symmetry D_{2d} that is the ideal symmetry for four-atom sharing despite the strain involved and is the convenient entry point for the preparation of several macropolyhedral boranes.[110] As $n = 20$ and $m = 2$, this structure requires 22 skeletal electron pairs, 16 of which are available from the B−H group. The four shared boron atoms each contribute three electrons so that the remaining six electron pairs are available within the skeleton and the molecule exists as a neutral species. Owing to the strain involved in sharing four atoms, this molecule rapidly undergoes rearrangement into a three-vertex-sharing skeleton like $B_{21}H_{18}^{2-}$ discussed above, in which one of the boron atoms adjacent to the shared boron is absent.

$B_{12}H_{10}^{2-}$ (D_{2h}) (**5**). This hypothetical example illustrates an edge-sharing macropolyhedral borane in which two pentagonal bipyramids share two boron atoms. Here, $n = 12$ and $m = 2$, and hence, 14 electron pairs are required. The 10 B−H groups contribute 10 electron pairs, and the 2 shared boron atoms together contribute 6 electrons. Hence, this molecular skeleton requires two more electrons. This one-electron-pair requirement is confirmed by EH calculations, and $B_{12}H_{10}^{2-}$ is found to be a minima on the potential energy surface at the B3LYP/6-31G* level of theory.[96a]

$B_{18}H_{15}^{-}$ (C_{3v}) (**6**). This example shows a face-sharing interaction between the icosahedron and the nine-vertex *closo*-borane. Here, $n = 18$ and $m = 2$,

Chart 1



and hence, 20 electron pairs are required. The 15 B−H groups each contribute 15 electron pairs, and the 3 shared boron atoms contribute 4.5 electron pairs. One more electron is needed, and hence, this molecule should exist as a stable monoanion. The one-electron requirement is confirmed by EH calculations, and $B_{18}H_{15}^-$ is calculated to be a minimum at the B3LYP/6-31G* level of theory.[96a] This molecule has not been experimentally isolated. However, several macropolyhedral boranes exhibiting the fusion with nine-vertex polyhedra are reported with some vertexes absent, which is compensated by bridging hydrogen atoms.

$B_{15}H_{12}^-$ (C_{3v}) (**7**). This hypothetical example illustrates a face-sharing macropolyhedral borane in which an icosahedron and octahedron share three boron atoms. Here, $n = 15$ and $m = 2$, and hence, 17 electron pairs are required. The 12 B−H groups contribute 12 electron pairs, and the 3 shared boron atoms together contribute 9 electrons. Hence, this molecule skeleton requires one more electron. This electron requirement is confirmed by EH calculations, and $B_{15}H_{12}^-$ is found to be a minimum on the potential energy surface at the B3LYP/6-31G* level of theory.[96a]

$B_9H_6^-$ (C_{3v}) (**8**). This is the smallest of all the macropolyhedral boranes that is found to be stable by theoretical calculations. It involves the sharing of a face between two octahedral clusters. Here, $n = 9$ and $m = 2$, and hence, 11 electron pairs are required. The 6 B−H groups each contribute 6 electron pairs, and the 3 shared boron atoms contribute 4.5 electron pairs. Like all the face-shared systems shown above, this molecule is stable with a single negative charge as predicted by the B3LYP/6-31G* level of theory.[96a] All the above-mentioned, face-sharing *closo* systems (except $B_{20}H_{16}$, which is well characterized by experiment) are very promising candidates for synthesis and are presented here to illustrate different possible modes of condensation. This will also help in under-

standing the slightly more complex open systems containing bridging hydrogen atoms.

*$B_{20}H_{18}^{4-}$ (D_{4h}) (**9**).* This is a well-characterized experimental structure[111,112] exhibiting a pattern very similar to that of the theoretically predicted $B_{24}H_{22}^{4-}$ discussed above. This macropolyhedral system has two B_{10} units connected through a 2c−2e single bond. Here, $n = 20$ and $m = 2$, and hence, this structure requires four electrons. As it has only 20 B−H groups, which contribute 20 electron pairs to the skeleton, it exists as a tetraanion to compensate for its 4-electron deficiency. The stable existence of this structure both in solution and in the solid state suggests the possibility of the stable existence of $B_{24}H_{22}^{4-}$ (**2**).

*$B_{20}H_{18}^{4-}$ (C_i) (**10**).* This is an isomer of the structure discussed[113] above in which the *exo* 2c−2e bond connects the apical atom to the equatorial atom of the other cluster. One more isomer where two equatorial boron atoms are connected is also known[114] and is the precursor of both apical−apical and apical−equatorial isomers. All these isomers exist as stable tetraanions and are characterized by ^{11}B NMR and single-crystal X-ray studies.[113] These isomers are obtained by the reduction of $B_{20}H_{18}^{2-}$. Its equivalent icosahedral counterpart remains to be explored.

*$B_{20}H_{19}^{3-}$ (C_{2v}) (**11**).* This is the protonated form of apical−apical $B_{20}H_{18}^{4-}$ ion where the additional proton forms a bridge between the two boron atoms connecting the cages. Though two or more tautomeric forms were indicated by ^{11}B NMR studies, only one has been isolated in the solid state.[115] The hydrogen bridge resembles the bridging in the $B_2H_7^+$, and the two boron atoms are still within bonding distance (1.936 Å). The number of electron pairs required is not altered by the formation of this 3c−2e bond, which requires its own electron pair separately. The nature of interaction between the two B_{10} units is similar to that of $B_{20}H_{18}^{4-}$ (**9**) except that they are linked through the 3c−2e bond. The additional electron available reduces the overall charge, and this species exists as a stable trianion.

*$B_{20}H_{18}^{2-}$ (C_{2h}) (**12**).* This molecular skeleton has a centrosymmetric structure with two bridging hydrogen atoms connecting the adjacent apical boron atoms of two B_{10} units.[116,117] However, the intercluster distance between the apical boron atoms is longer than that in $B_{20}H_{19}^{3-}$ (∼2.04 Å) as illustrated from the single-crystal X-ray studies. As in the case of $B_{20}H_{19}^{3-}$, each B_{10} unit requires 11 electron pairs. As one more electron pair is available for skeletal bonding from the two bridging hydrogen atoms, this molecule exists as a stable dianion. This system can be viewed as two individual B_{10} units separated by two 3c−2e bonds. This molecule is well characterized by single-crystal X-ray crystallography.[117]

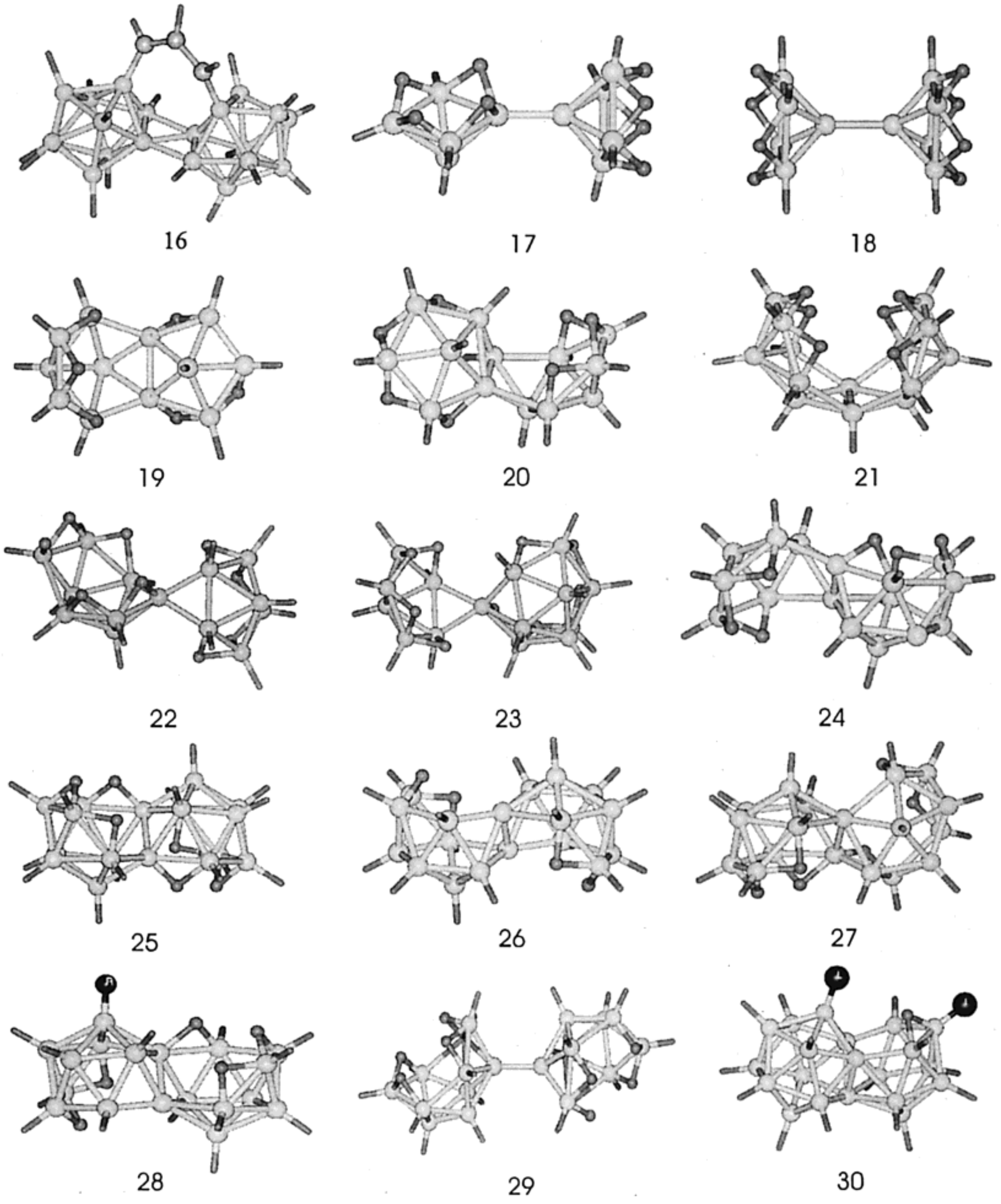
*[μ-$B_{20}H_{17}OH]^{2-}$ (C_{2v}) (**13**).* This molecular skeleton is similar to $B_{20}H_{18}^{2-}$ (**12**) described above except that one of the bridging hydrogen atoms is replaced by an OH group bridging between two equatorial boron atoms.[118] Though the bond between the apical boron atoms is not shown in the figure in the original publication,[118] their interatomic distance (1.907 Å) is less than that in $B_{20}H_{18}^{2-}$ (**12**) itself. No bonding interaction exists between the apical boron atoms that are connected by the oxygen bridge as they are well separated by *exo* 2c−2e B−O bonds. This type of pattern is observed in $[B_{20}H_{18}NO]^{3-}$ in which the nitrogen atom in the NO group bridges the two $B_{10}H_9$ units, providing an extra electron for the polyhedral skeleton. As one negative charge is reduced owing to the protonation of the bridging oxygen, this molecule exists as a stable dianion. The same skeleton is exhibited by another molecule, where the −OH group is replaced by the −OMe group. The important feature of these systems is the involvement of the oxygen lone pair in bonding, though it is not possible to designate a particular bond as dative. All these structures are well characterized by X-ray studies.

*$B_{20}H_{18}^{2-}$ (C_i) (**14**).* This isomer was isolated in the early 1960s and is actually the precursor for the photoisomer **12**.[119] Here, the interaction of the two individual B_{10} units results in a unified macropolyhedral skeleton as they are not separated by a conventional 2c−2e bond or 3c−2e bond and the edges connecting these two individual polyhedra become an integral part of the combined polyhedra. The number of electron pairs required is still 22, but this structure differs from other B_{20} skeletons discussed so far as it has 18 B−H groups each contributing an electron pair. Two boron atoms are without any *exo* 2c−2e bond and hence contribute three electron pairs. Hence, this molecule exists as a stable dianion. Because of the absence of bridging hydrogens, additional electrons are not required for connecting the two B_{10} units, as these edges are part of the macropolyhedral B_{20} skeleton.

*$B_{20}H_{17}(NH_3)^-$ (C_1) (**15**).* This is a known positional isomer[114] of **14** in which the two B_{10} units are fused in a cisoid fashion; i.e., the two B_{10} units are not symmetrically equivalent, unlike in the *trans* isomer **14**. The NH_3 group replaces one of the hydrogen atoms, forming a dative bond and thereby providing one more electron for the skeleton. Hence, it exists as a monoanion as characterized by ^{11}B NMR and electrospray ionization mass spectrometry (ESI-MS) and confirmed by single-crystal X-ray studies. The parent cisoid $B_{20}H_{18}^{2-}$ is also well studied and is relatively unstable owing to its dianionic nature. Its acetonitrile solution rapidly rearranges to the stable transoid $B_{20}H_{18}^{2-}$ (**14**) isomer even at room temperature.

*[μ-$CH_3C(NH_2)B_{20}H_{16}]^-$ (C_1) (**16**).* This molecule consists of two B_{10} units fused together in a transoid fashion as in **14**. In addition, these two B_{10} units are joined together by a bridging amidinium group, which provides an additional electron for the polyhedral skeleton. Hence, this molecule exists as a monoanion and is well characterized by ESI-MS, ^{11}B NMR, and single-crystal X-ray studies.[120] In both this structure and **14**, although briefed as having two 3c−2e connections between B_{10} units, the electron count shows that it is a polyhedral bond and is clearly distinct from the 3c−2e bond in the photoisomer of $B_{20}H_{18}^{2-}$ (**12**). The HOMO is concentrated more between the intercluster bonds and acts as a functional center for its reactivity. All these B_{20}-skeleton-based molecules

Chart 2



are considered as promising candidates for boron neutron capture therapy (BNCT).

$B_{10}H_{16}$ (**17**, **18**). This is the smallest macropolyhedral borane synthesized which has two *nido*-B_5H_8 units connected through a 2c−2e bond. Here, $n = 10$, $m = 2$, and $p = 2$ as there are two missing vertexes.[121−124] The total number of electron pairs required is 14 [$F(e) = n + m + p$]. There are eight B−H units each contributing one electron pair, and the B−B group contributes two electron pairs, one pair from each boron atom. The remaining four electron pairs are acquired by the system by having eight bridging hydrogen atoms each giving its one electron to skeletal bonding. Three isomers are possible (1:1′[B_5H_8]$_2$, 1:2[B_5H_8]$_2$, 2:2′[B_5H_8]$_2$) depending on the nature of the boron atoms involved in the interpolyhedral 2c−2e bond, and all of them were experimentally reported 40 years ago.[121] The structure of **17** was confirmed by single-crystal X-ray studies a little later.[124]

$B_{12}H_{16}$ (C_1) (**19**). This is the smallest macropolyhderal borane system exhibiting an edge-sharing pattern between two *nido* polyhedral fragments.[125] Here, $n = 12$, $m = 2$, and $p = 2$ as both are *nido* cages. Hence, the total number of electron pairs required is 16. There are twelve B−H units each contributing one electron pair, and the two shared boron atoms each provides three electrons owing to the absence of the *exo* B−H bond. The remaining three electron pairs are available from the six bridging hydrogen atoms each giving one electron. However, in the experimental report of the structure, it was computed to have 28 electrons as this macropolyhedral skeleton was compared with the monocage $C_4B_8H_{12}$ skeleton. The molecule exhibits centrosymmetry in solution due to the presence of two tautomeric forms by the migration of a bridging hydrogen atom between two symmetrically equivalent positions. However, single-crystal X-ray studies confirmed the C_1 symmetric structure as depicted in the figure (**19**).

*$B_{13}H_{19}$ (**20**).* This is another example of an edge-sharing polyhedron in which a *nido*-B_9 unit interacts with a *nido*-B_6 unit. Here, $n = 13$, $m = 2$, and $p = 2$, which requires 17 electron pairs for skeletal bonding. There are twelve B−H units each contributing one electron pair, and the shared boron atom without an *exo* B−H bond gives all of its three valence electrons. The remaining seven electrons are provided for the skeleton by seven bridging hydrogen atoms. This structure was reported experimentally, and the proposed structure was confirmed by single-crystal X-ray studies.[126] The experimental report suggests that a bridging hydrogen atom, owing to its shortened B−H distance, has predominant terminal character. The electron-counting analysis presented above clearly rules out such a possibility as there has to be a bridging hydrogen to fill the skeletal bonding orbitals and the shortening of the bond length can be attributed solely to the reduction of nonbonding interactions.

*$B_{14}H_{20}$ (C_{2v}) (**21**).* This is a classical example of a higher borane system that contains more than 12 vertexes, all of them falling within a single, pseudospherical surface. Experimental isolation of this molecule proved to be difficult and gave low yield. However, the structure was well established using X-ray diffraction studies.[127] Here, $n = 14$, $m = 1$, and $p = 2$, and the structure requires 17 electron pairs. There are 14 B−H groups each contributing one electron pair for the skeletal bonding. The remaining three electron pairs are obtained from six bridging hydrogen atoms, each contributing one electron for skeletal bonding. In the experimental report, the structure is described as a macropolyhedral borane exhibiting an edge-sharing interaction between two B_8 *nido* fragments in a cisoid fashion. However, this is not true since all the skeletal atoms lie in a single pseudospherical surface. The above electron-counting analysis also implies that this system is a simple polyhedral borane and not a condensed system. The hypothetical *trans* isomer will require one more electron pair as the value of *m* will be 2, in which case the two boron atoms at the shared position will be deprived of their *exo*-hydrogen atoms to compensate for the increased electronic requirement.[105]

*$B_{14}H_{22}$ (C_1) (**22**).* This molecule exhibits the relatively rare capping of one polyhedral skeleton to another, in which the capping atom is boron itself. This is different from the single-vertex-sharing interaction, where the central vertex belongs to both the polyhedra. The structure of the molecule is tentatively assigned by ^{11}B NMR chemical shifts,[128] and has an *arachno*-B_8 unit interacting with a *nido*-B_6 unit with one of the edges of the B_6 unit capped by a vertex of the B_8 unit. Here, $n = 14$, $m = 2$, and $p = 3$, and hence, this structure requires 19 electron pairs for skeletal bonding. The proposed structure was optimized at the B3LYP/6-31G* level of theory, and frequency calculations characterized the resulting geometry as a minimum on the potential energy surface.[105] The optimized structure has 13 B−H groups contributing 13 electron pairs for skeletal bonding. The central boron atom contributes all its three valence electrons due to the absence of the *exo* B−H bond. The eight bridging hydrogen atoms contribute four electron pairs for skeletal bonding. One of the boron atoms has two hydrogen atoms, one of which is *endo*; i.e., one hydrogen atom lies within the inner sphere of the macropolyhedra. Hence, this group contributes three electrons to the skeleton, making this molecule neutral. The structure has yet to be confirmed by X-ray crystallography.

*$B_{15}H_{23}$ (C_i) (**23**).* This molecule exhibits a similar capping pattern between an *arachno*-B_9 unit and a *nido*-B_6 unit with a vertex of the other unit capping one of the trigonal faces of the B_6 unit. As in the previous example (**22**), on the basis of the ^{11}B NMR chemical shifts, a tentative structure is assigned which has an *arachno*-B_9 unit interacting with a *nido*-B_7 unit with a vertex of the B_9 unit capping one of the edges of the B_6 unit.[128] Here, $n = 15$, $m = 2$, and $p = 3$, and hence, this structure requires 20 electron pairs for skeletal bonding. The proposed structure was optimized at the B3LYP/6-31G* level of theory, and frequency calculations characterized the resulting geometry as a minimum on the potential energy surface.[105] The optimized structure has 14 B−H groups that contribute 14 electron pairs for skeletal bonding. The central boron atom contributes all of its three valence electrons owing to the absence of the *exo* B−H bond. The nine bridging hydrogen atoms contribute nine electrons for skeletal bonding. Owing to the unavailability of suitable crystals, this structure has not yet been confirmed by X-ray crystallography.

*$B_{16}H_{20}$ (C_1) (**24**).* This molecule shows an edge-sharing pattern of two *nido*-B_{10} units. Here, $n = 16$, $m = 2$, and $p = 2$, and the molecule requires 20 electron pairs for skeletal bonding. There are 14 B−H groups each contributing an electron pair for skeletal bonding. Six electrons are contributed to the skeleton by the two boron atoms that are common to both the B_{10} units. The remaining three electron pairs are made available to the skeleton by the six bridging hydrogen atoms, which make the molecule neutral. The structure of the molecule was confirmed by X-ray studies in its first experimental report.[129]

*n-$B_{18}H_{22}$ (C_i) (**25**).* The reaction of $B_{20}H_{18}^-$ ion with acids produces this edge-sharing $B_{18}H_{22}$ isomer as the major product.[96b,97a,130] This structure can be described as the fusion of two decaborane ($B_{10}H_{14}$) clusters in such a manner that the edges open up in opposite directions. Here, $n = 18$, $m = 2$, and $p = 2$, and hence, the molecule requires 22 electron pairs for skeletal bonding. Also called *anti*-$B_{18}H_{22}$, this molecule is centrosymmetric and exhibits strong acidic properties comparable to those of mineral acids, resembling the $B_{10}H_{14}$ borane. There are 16 B−H groups, each contributing one electron pair for skeletal bonding. Three electron pairs are available from the boron atoms lying at the shared position. The remaining six electrons are available from the six bridging hydrogen atoms, which make the molecule neutral. This structure is confirmed by single-crystal X-ray diffraction studies.[97a]

*n-$B_{18}H_{20}^{2-}$ (C_i) (**26**).* This molecule is obtained by the removal of two protons from *n*-$B_{18}H_{22}$ (**25**) and exists as a stable dianion.[13b] The bridging hydrogen atoms in the shared position are lost during deprotonation. The loss in the total number of electrons owing to the absence of the bridging hydrogens is compensated by the dinegative charge, and hence, the number of skeletal electron pairs remains constant. The structure of this dianion has been characterized by two-dimensional [$^{11}B-^{11}B$] COSY, [$^{1}H-^{1}H$] COSY, and $^{1}H\{^{11}B(selective)\}$ NMR spectroscopy in addition to single-crystal X-ray diffraction studies.[13b]

iso-$B_{18}H_{22}$ (C_2) (**27**). Also referred to as *syn*-$B_{18}H_{22}$, this molecule is formed as a byproduct in the reaction that produces *n*-$B_{18}H_{22}$ from $B_{20}H_{18}^{2-}$ and is the first example of geometrical isomerism in polyhedral boranes. Contrary to *n*-$B_{18}H_{22}$, the structure consists of two $B_{10}H_{14}$ units fused in such a way that their open faces are in the same direction.[97b,131] The symmetry is reduced to C_2 owing to this cisoid fusion, and one of the bridging hydrogen atoms at the shared position is shifted to the other side to avoid steric interactions. The electronic requirements remain the same as those of structure **25**. The geometry is confirmed by single-crystal X-ray diffraction studies.[97b]

7-{(MeNH)C$_3$N$_2$HMe$_2$}B$_{18}$H$_{20}$ (**28**). This molecule has the same skeletal pattern exhibited by *n*-$B_{18}H_{22}$ since it is prepared by the reaction of MeNC with *n*-$B_{18}H_{22}$.[132] One of the *exo*-hydrogen atoms is replaced by a imidazole-based carbene group. Since this bond is dative, an extra electron is available for the skeletal bonding. Hence, one of the hydrogen atoms that forms the bridge between the shared boron is removed, as in the absence of reorganization of the skeleton, the electronic requirements should be conserved. This is the first macropolyhedral borane reported to exhibit carbene coordination. The structure of the compound is well established by single-crystal X-ray diffraction analysis along with NMR spectroscopy and mass spectrometry.

$B_{20}H_{26}$ (**29**). There are a set of isomers consisting of two $B_{10}H_{14}$ units connected by a 2c−2e bond. Of the 11 possible geometrical isomers, 7 isomers have been structurally characterized by NMR spectroscopy.[133−138] Four among these are confirmed by single-structure X-ray studies. Here, $n = 20$, $m = 2$, and $p = 2$, and hence, the molecule requires 24 electron pairs. Each boron atom contributes one electron pair for skeletal bonding, and the remaining four electron pairs arise from the eight bridging hydrogen atoms. In all four isomers, the shorter intercluster B−B bond length (∼1.66−1.70 Å) indicates the 2c−2e nature of this linkage.

$B_{20}H_{16}L_2$ (C_1) (**30**). This structural pattern is observed in a series of compounds in which L forms a dative bond to the boron atom. These are formed when $B_{20}H_{16}$ (**4**) reacts with ligands such as $(CH_3)_2S$ and CH_3CN without the loss of hydrogen. Both of these isomers were characterized by single-crystal X-ray studies.[139] Here, $n = 20$, $m = 2$, and $p = 1$. This structure requires 23 electron pairs for skeletal bonding. The 15 B−H groups provide 15 electron pairs. The 3 boron atoms together contribute 4.5 electron pairs. The two B−L groups owing to their dative linkage together contribute three electron pairs. The remaining single electron is available to the skeleton from the bridging hydrogen atom. This is the only experimentally isolated macropolyhedral borane with a face-sharing skeleton.

$B_{20}H_{18}^{2-}$ (C_1) (**31**). This hypothetical example illustrates a face-sharing macropolyhedral borane that can be obtained by removing dative bonded ligands L from $B_{20}H_{16}L_2$ (**30**) discussed above. This skeleton needs two more electrons to compensate for the two electrons from each B−L group. This two-electron requirement is confirmed by EH calculations, and $B_{20}H_{18}^{2-}$ is found to be a minimum on the potential energy surface at the B3LYP/6-31G* level of theory.[96a] The same structural pattern is predicted to exist in the $B_{20}H_{17}(OH)^{2-}$ structure, which is formed by the reaction of $B_{20}H_{16}$ (**4**) with water by using the principle of conservation of electronic requirements, though the position of substitution of the OH group is not known.[55a,56] The unknown structures of other similar compounds such as $[B_{20}H_{17}(OC_2H_5)]^{2-}$ have been deduced in a similar way.

$B_{22}H_{22}^{2-}$ (**32**). This is the largest condensed macropolyhedral borane isolated so far, and it has a *nido*-decaborane unit fused to a *closo*-dodecaborane cluster. Here, $n = 22$, $m = 2$, and $p = 1$, and hence, this molecule requires 25 electron pairs for skeletal bonding. The 20 B−H groups provide 20 electron pairs, and the 2 shared boron atoms together provide 3 electron pairs. Two more electrons are available to the skeleton by the two bridging hydrogen atoms. Still, this structure requires two more electrons and hence exists as a stable dianion. This structure has been characterized by single-crystal X-ray studies and spectral analysis.[140]

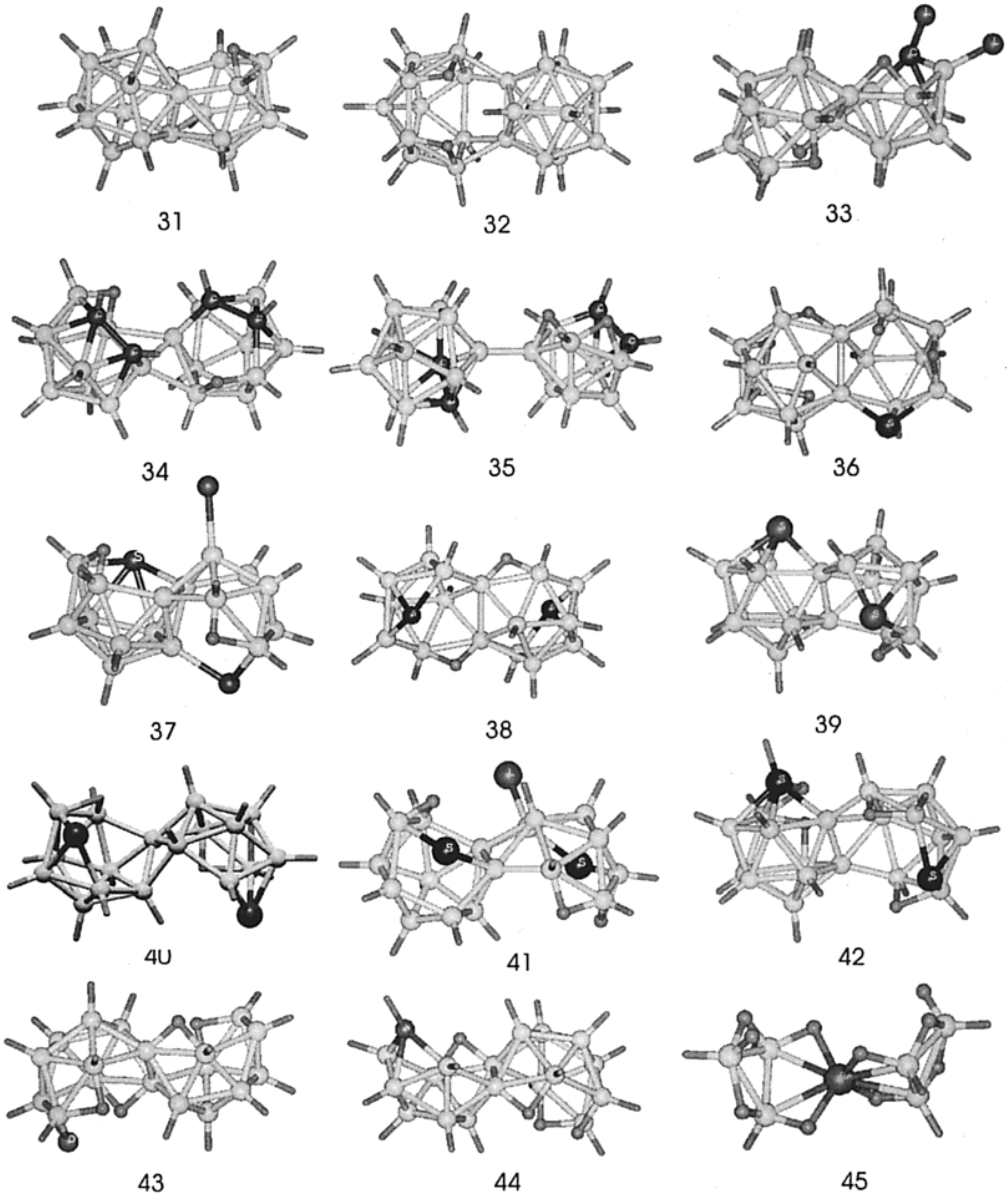
B. Boranes with Main Block Elements

Numerous macropolyhedral boranes are known with one or more heteroatoms in the skeleton. While the structures of the macropolyhedral carboranes are found to dominate *closo* skeletons connected through localized bonds, bigger atoms such as aluminum, gallium, silicon, etc. are found to exhibit a single-vertex-sharing pattern owing to the diffuse nature of their valence orbitals. However, all thiaboranes, azaboranes, oxaboranes, etc. known so far exhibit condensed polyhedral patterns in which the shared vertexes are occupied exclusively by boron atoms.

$[(MeCNH_2)CB_{17}H_{18}(CN)]$ (**33**). Though numerous monocage carboranes are known, this is the first condensed polyhedral carborane characterized definitely.[141] Here, $n = 18$, $m = 2$, and $p = 2$, and hence, this skeleton requires 22 electron pairs for skeletal bonding. The 14 B−H groups and one B−CN group contribute 15 electron pairs. The two shared boron atoms together contribute three electron pairs. Owing to the dative nature of the *exo*-carbon bond, the carbon atom contributes all its four valence electrons to the skeleton. The remaining two electron pairs are available to the cluster as four bridging hydrogen atoms. Its structure has two *nido*-B_{10} units sharing an edge similar to the *n*-$B_{18}H_{22}$ pattern (**25**) except that in the 9-position boron is replaced by the amine-substituted carbon. This structure is well established by NMR, mass spectrometric studies, and single-crystal X-ray crystallography.[141]

neo-$C_4B_{18}H_{22}$ (**34**). This molecule consists of two *nido*-C_2B_9 units involved in *exo* polyhedral interac-

Chart 3



tions in a pattern similar to the interaction of *closo*-B_{10} units in the $B_{20}H_{18}^{2-}$ (**14**) structure. Here, $n = 22$, $m = 2$, and $p = 2$ so that the structure requires only 26 electron pairs for skeletal bonding. The 16 B−H groups contribute 16 electron pairs. The two central boron atoms without the *exo*-hydrogen atoms contribute all of their three valence electrons. The four C−H groups together contribute six electron pairs. The remaining electron pair originates from the two bridging hydrogen atoms. Contrary to the earlier claims,[142] the interaction of these two C_2B_9 units does not involve 3c−2e bonds as the edges involved in the interaction are part of a single continuous macropolyhedral bonding pattern, which keeps the number of skeletal bonding molecular orbitals unaltered. This structure is well established by NMR, mass studies, and single-crystal X-ray data.[142]

*iso-$C_4B_{18}H_{22}$ (***35***).* This molecule is an isomer of **34** formed along with **34** in the preparative reaction and is the first known neutral species with a structure consisting of a *closo* unit (C_2B_{10}) clearly joined by a 2c−2e bond to a *nido* unit (C_2B_8). Though the values of m and n are the same as those of **34**, the number of open faces p is one, and hence, the total number of electron pairs required for this isomer is 25, one less than that of its isomer **34**. The two extra electrons available due to the reduction in the number of skeletal bonding molecular orbitals are now involved in the 2c−2e bond separating the two subunits. This structure is also well established by NMR, mass spectral studies, and single-crystal X-ray data.[143]

*$SB_{17}H_{20}^{-}$ (***36***).* This molecule exhibits the unique macropolyhedral skeleton with a single sulfur atom in its skeleton.[144] This consists of a *nido*-SB_{10} unit sharing a B−B edge with a *nido*-B_{10} unit. Here, $n = 18$, $m = 2$, and $p = 3$, and hence, this pattern requires 23 electron pairs for skeletal bonding. The 15 B−H groups contribute 15 electron pairs, and the sulfur atom provides 2 additional electron pairs for skeletal bonding. The two shared boron atoms at the

cluster junction provide three electron pairs. Four more electrons are available to the cluster from the bridging hydrogen atoms. Still, it needs one more electron pair to fill all its skeletal bonding molecular orbitals. The *endo*-hydrogen atom on one of the boron atoms lies within the inner sphere of the polyhedral skeleton, thereby providing one additional electron. Hence, this molecule exists as a stable monoanion. Prepared from the *n*-$B_{18}H_{22}$ (**25**) precursor, the structure of the molecule is well established by ^{11}B and ^{1}H NMR studies and single-crystal X-ray crystallography.[144]

*$S_2B_{16}H_{14}(PPh_3)$ (**37**).* This molecule exhibits the rare face-sharing pattern between a *nido*-SB_8 unit and an *arachno*-SB_{10} unit. Here, $n = 18$, $m = 2$, and $p = 3$, and this structure requires 24 electron pairs for skeletal bonding. The 13 B−H groups contribute 13 electron pairs. The three boron atoms in the shared position and the boron having the dative (PPh_3) linkage each contribute all of their three valence electrons. Each sulfur atom contributes two electron pairs as in the case of monocage thiaboranes. The remaining electron pair is made available to the skeleton by two bridging hydrogen atoms. This structure is well established by NMR, mass studies, and single-crystal X-ray data.[145]

*$S_2B_{16}H_{16}$ (**38**).* This molecule exhibits an edge-sharing pattern between two *nido*-SB_8 units similar to the *anti* fusion in *n*-$B_{18}H_{22}$ (**25**) and is synthesized by the novel fusion of two molecules of *arachno*-4-SB_8H_{12} by thermolysis.[146] Here, $n = 18$, $m = 2$, and $p = 2$, and hence, this pattern requires 22 electron pairs for skeletal bonding. The 14 B−H groups contribute 14 electron pairs, and the pair of shared boron atoms together contribute 3 electron pairs. The two sulfur atoms each contribute two electron pairs to the skeleton. The remaining one electron pair is made available to the system through the two bridging hydrogen atoms. The structure of the molecule is well characterized by mass and NMR spectral data.[146]

*$S_2B_{17}H_{16}^-$ (**39**).* This molecule exhibits an edge-sharing pattern of a *nido*-SB_{10} unit and a *nido*-SB_9 unit.[147] The *nido*-SB_9 unit appears to be an *arachno* skeleton as it implies the absence of two vertexes, but since they are removed from adjacent positions, they still retain the *nido* electron count as discussed earlier. Here, $n = 19$, $m = 2$, and $p = 2$, and the skeleton requires 23 electron pairs for skeletal bonding. The 15 B−H groups contribute 15 electron pairs. The two shared boron atoms together contribute three electron pairs. The two sulfur atoms each contribute two electron pairs. Still, one more electron pair is required to fill the skeletal molecular orbitals. As only one bridging hydrogen atom is available, this molecule exists as a monoanion. This structure is well established by NMR, mass spectral studies, and single-crystal X-ray data.[147]

*$S_2B_{17}H_{18}^-$ (**40**).* This is the first structurally characterized condensed heteropolyhedral borane, prepared from the action of elemental sulfur on *n*-$B_{18}H_{20}^{2-}$ (**26**).[100] This pattern consists of two *nido*-SB_{10} units sharing a central boron atom. Since the adjacent vertexes on both sides of the shared atom have finite bonding interaction and the shared atom is not a heteroatom, the tangential bonding molecular orbitals of these clusters are shared. It is as though one of the atoms is removed from the shared position. The more open pattern exhibited by this structure enabled its description as *arachno* for both the units, but since they are removed from the adjacent position, in terms of electron counting, they should be treated only as *nido* clusters, as exemplified by Burdett in his molecular orbital studies.[48] Here, $n = 19$, $m = 2$, and $p = 2$, and hence, 23 electron pairs are required for skeletal bonding. The 16 B−H groups contribute 16 electron pairs. The two sulfur atoms together contribute four electron pairs, and the shared boron atom contributes all its three valence electrons. Two bridging hydrogen atoms together contribute one elecron pair. Still, one more electron is required for skeletal bonding, and hence, this structure exists as a stable monoanion.

*$S_2B_{17}H_{17}$ (SMe_2) (**41**).* This molecule exhibits the first true example of *arachno*−*nido* fusion.[148] The skeletal pattern consists of a *nido*-SB_{10} unit and the more open *arachno*-SB_9 unit sharing an edge prepared by the thermolysis of SB_8H_{10} (SMe_2). Here, $n = 19$, $m = 2$, and $p = 3$, and hence, the structure requires 24 electron pairs for skeletal bonding. The 14 B−H groups contribute 14 electron pairs. The two shared boron atoms, as usual, provide three electron pairs. The two sulfur atoms account for four more electron pairs. The three bridging hydrogen atoms each contribute one electron to the skeleton. The remaining three electrons are contributed by the unique boron atom, which has the dative SMe_2 linkage. Another interesting feature of this skeleton is the existence of a seven-coordinate boron atom, which caps a six-membered ring for which the orbital overlap tends to be poor owing to ring-cap mismatch.[40] The structure of the molecule is well characterized by NMR and X-ray studies.[148]

*$S_2B_{18}H_{19}^-$ (**42**).* This molecule consists of a *nido*-$B_{10}S$ cluster sharing an edge with a more open *arachno*-$B_{10}S$ hitherto unknown in the monopolyhedral heteroboranes. This is prepared from iso-$B_{18}H_{22}$ and elemental sulfur.[149] Here, $n = 20$, $m = 2$, and $p = 3$, and hence, the structure requires 25 electron pairs for skeletal bonding. The 16 B−H groups contribute 16 electron pairs, and the 2 shared boron atoms together contribute 3 electron pairs. The pair of sulfur atoms together contribute four electron pairs. One more electron pair is needed for the skeletal bonding. Since the molecule has only one bridging hydrogen atom, it exists as a stable monoanion. As in the previous example, one of the boron atoms in the *arachno*-SB_{10} unit exhibits seven-coordination as it caps a six-membered ring. The intriguing feature of the molecule is that it is reported to disassemble and reassemble reversibly upon protonation followed by deprotonation through a DSD[150] mechanism. The structure of the molecule is well characterized by ^{1}H and ^{11}B NMR and X-ray studies.[149]

*$OB_{18}H_{21}^-$ (**43**).* This is the only macropolyhedral hetero-borane reported to have an oxygen atom as part of the contiguous polyhedral skeleton.[151] How-

ever, the oxygen atom is only two-coordinate. The skeleton consists of a *nido*-OB_{10} unit interacting with a *nido*-B_{10} unit by sharing a common edge. Here, $n = 19$, $m = 2$, and $p = 2$, and hence, this pattern requires 23 electron pairs for stability. The 16 B−H groups contribute 16 electron pairs, and the 2 shared boron atoms provide 3 electron pairs for skeletal bonding. The oxygen atom provides two electron pairs for the skeleton. The five bridging hydrogen atoms add five more electrons to the skeletal electron count. Hence, this molecule exists as a stable anion. Prepared using the *n*-$B_{18}H_{21}^-$ precursor discussed above, the structure of the molecule is well characterized by ^1H and ^{11}B NMR and X-ray studies.[151]

$NB_{17}H_{20}$ (**44**). This is the only macropolyhedral hetero-borane reported to have a nitrogen atom as part of the contiguous polyhedral skeleton, and like the oxaborane, the coordination of the nitrogen is limited to its valency.[152] The skeleton consists of a *nido*-NB_9 unit interacting with a *nido*-B_{10} unit by sharing a common edge. Here, $n = 18$, $m = 2$, and $p = 2$, and hence, this pattern requires 22 electron pairs for stability. The 15 B−H groups contribute 15 electron pairs, and the 2 shared boron atoms provide 3 electron pairs for skeletal bonding. In addition, the nitrogen atom provides two electron pairs to the skeleton. The remaining required two electron pairs come from the four bridging hydrogen atoms. Prepared using the *n*-$B_{18}H_{22}$ precursor (**25**), the structure of the molecule is well characterized by ^1H and ^{11}B NMR and X-ray studies. This skeleton differs from the oxaborane skeleton discussed above (**43**) since nitrogen substitutes on one of the boron atoms in the B_{18} skeleton.

$Be(B_3H_8)_2$ (C_2) (**45**). This is the smallest macropolyhedral borane that can be isolated, and any skeleton smaller than this cannot possibly be considered as a macropolyhedral system. The structure of $Be(B_3H_8)_2$ consists of two *arachno*-B_3H_8 units bridged together by a beryllium at the center. Here, $n = 7$, $m = 2$, $o = 1$ (the number of single hetero-vertex-sharing junctions), and $p = 2$, and hence, this structure requires 12 electron pairs for skeletal bonding. Here, the BeB_3H_8 fragment should be treated as a *nido* system derived from the *closo* pattern of $B_5H_5^{2-}$. The four B−H groups contribute four electron pairs for skeletal bonding. The eight bridging hydrogen atoms contribute four electron pairs. Beryllium contributes both of its valence electrons to the skeleton. The remaining three electron pairs are made available to the skeleton by the presence of an *endo*-hydrogen atom in the pair of BH_2 groups, which lie in the inner spheres of the polyhedra. The bonding between beryllium and boron is ∼1.97 Å, which indicates the polyhedral nature of the beryllium atom, though it is not shown in the figures published earlier. This molecule exhibits fluxional behavior in normal conditions, though single-crystal X-ray data and NMR studies well characterized the presence of C_2 symmetry of the molecule.[22,93,94]

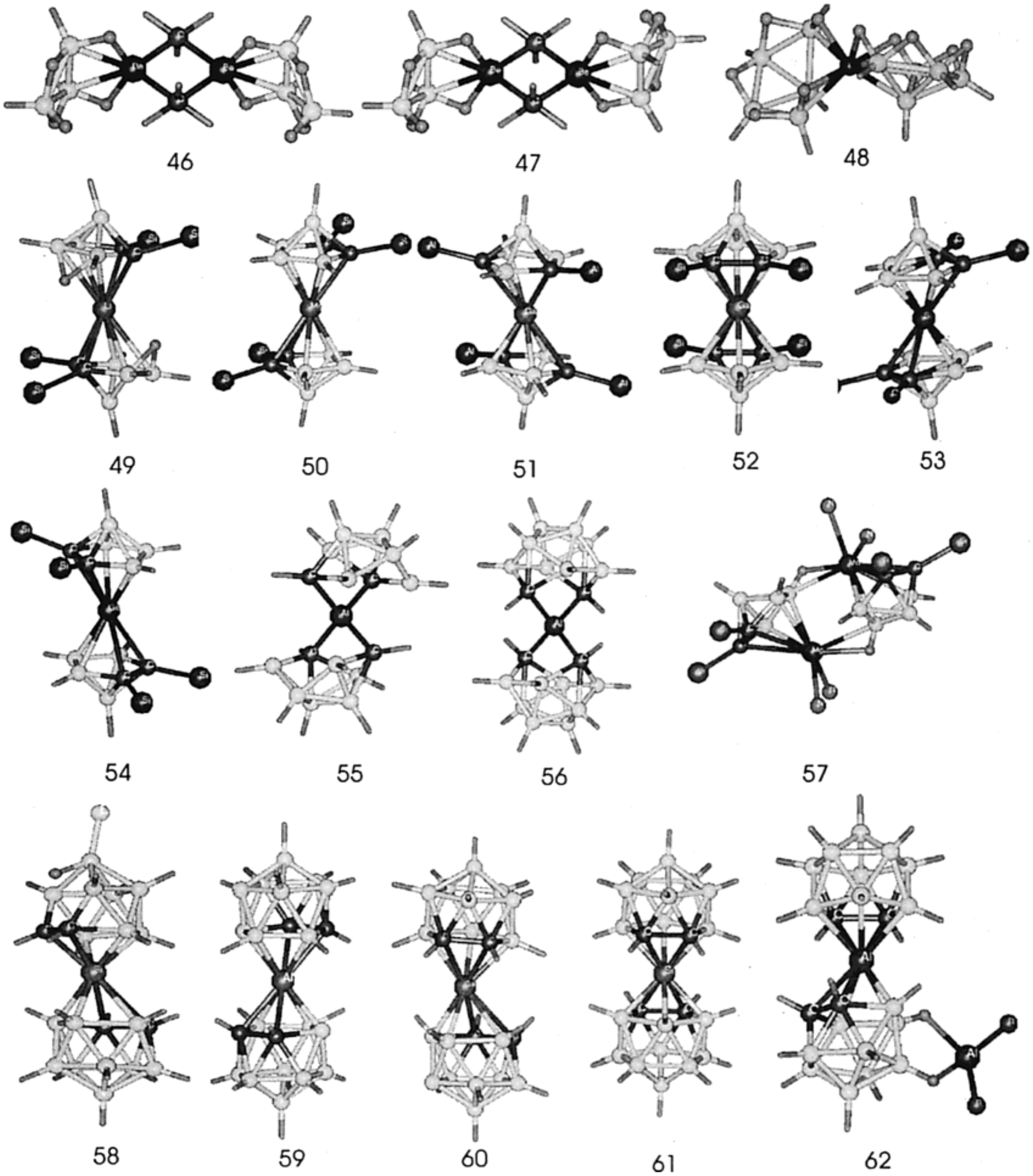
$(Be(B_3H_8)CH_3)_2$ (**46**, **47**). The reaction of $Be(B_3H_8)_2$ (**45**) with $Zn(CH_3)_2$ produces $(Be(B_3H_8)CH_3)_2$, in which the interaction between the two $BeB_3H_8(CH_3)$ units is through the methyl bridge, similar to the hydrogen-bridged interaction observed in the photoisomer of $B_{20}H_{18}^{2-}$ (**12**). Here, $n = 8$, $m = 2$, and $p = 2$, and hence, this structure requires 12 electron pairs for skeletal bonding. The four B−H groups contribute four electron pairs for skeletal bonding. The eight bridging hydrogen atoms contribute four electron pairs. Each beryllium atom contributes one electron for the skeletal bonding since the other electron is required for the 3c−2e bridge to the methyl group. The remaining three electron pairs are made available to the skeleton by the presence of an *endo*-hydrogen atom in the pair of BH_2 groups, as in the case of $Be(B_3H_8)_2$. Two possible isomeric forms are reported, the molecule exhibiting fluxional character converting rapidly from one isomer to the other.[94] The structure is predicted on the basis of NMR studies. X-ray data are not yet available.[94]

$Be(B_5H_{10})_2$ (C_2) (**48**). This molecule consists of two *nido*-BeB_5 units sharing the beryllium vertex.[153] Here, $n = 11$, $m = 2$, $o = 1$, and $p = 2$, and hence, this molecule requires 16 electron pairs for skeletal bonding. The 10 B−H groups contribute 10 electron pairs. Beryllium contributes one electron pair for the skeleton. The remaining 5 electron pairs are available to the skeleton by the 10 bridging hydrogen atoms. All these beryllium vertex-sharing clusters (**45**−**48**) earlier assumed the role of beryllium as from 3c−2e bridges. This resulted in erroneous conclusions and contradictions. However, beryllium is an integral part of the macropolyhedral system. Allocating a definite number of electrons to the hydrogen bridges as 3c−2e or 2c−2e instead of a polyhedral bond leads to the inevitable orbital deficiency for beryllium. The solid-state structure of this molecule is well characterized by X-ray diffraction.[153]

$[Li((SiMe_3)_2C_2B_4H_5)_2]^-$ (**49**). This is the only macropolyhedral carborane system in which a lithium atom is sandwiched between two borane units. Here, $n = 13$, $m = 2$, and $o = 1$, and hence, this structure requires 16 electron pairs for skeletal bonding. This ion is also unique in having bridging hydrogen atoms in a *closo*-borane pattern. The B−H groups contribute eight electron pairs for skeletal bonding. The four C−$SiMe_3$ groups contribute six electron pairs. Two electrons are available as bridging hydrogen atoms. The lithium contributes its only electron. Since one more electron is required, this species exists as a stable monoanion. The molecular structure is well characterized by IR spectroscopy, ^1H, ^{11}B, ^{13}C, and ^7Li NMR spectroscopy, and X-ray crystallographic studies.[154]

$[Mg((SiMe_3)_2C_2B_4H_4)_2]^{2-}$ (**50**). This structure exhibits a sandwich pattern with magnesium similar to the pattern discussed above except that the bridging hydrogen atoms of the *closo* skeleton are absent. Here, $n = 13$, $m = 2$, and $o = 1$, and hence, this structure requires 16 electron pairs for skeletal bonding. The eight B−H groups contribute eight electron pairs for skeletal bonding. The four C−$SiMe_3$ groups contribute six electron pairs. The magnesium atom contributes its one electron pair, and still, the pattern requires one more electron pair. Hence, this species exists as a stable dianion. This molecule is also well characterized by IR spectroscopy, ^1H, ^{11}B,

Chart 4



and ^{13}C NMR spectroscopy, and X-ray crystallographic studies.[155]

[Ga((SiMe$_3$)$_2$C$_2$B$_4$H$_4$)$_2$]$^-$ (**51**, **52**). In these isomers, the gallium atom is sandwiched between two *nido*-C_2B_4 units.[156] Here, $n = 13$, $m = 2$, and $o = 1$, and hence, this molecule requires 16 electron pairs for skeletal bonding. The eight B−H groups contribute eight electron pairs. The four $C-SiMe_3$ groups contribute six electron pairs for polyhedral bonding. Gallium contributes all its three valence electrons for the skeleton. Since the structure needs one more electron, this molecule exists as a stable monoanion. The solid-state structure of this molecule is well characterized by X-ray studies. Both of the isomers were prepared from the respective $[(SiMe_3)_2C_2B_4H_4]^{2-}$ isomers by direct reaction with $GaCl_3$. The structures of both of these isomers are well characterized by IR spectra and ^{1}H, ^{11}B, and ^{13}C NMR spectra in addition to single-crystal X-ray crystallography.

Si((SiMe$_3$)$_2$C$_2$B$_4$H$_4$)$_2$ (C$_i$) (**53**). This structure exhibits another similar sandwich pattern but with silicon as the central atom.[157,158] Here, $n = 13$, $m = 2$, and $o = 1$, and hence, this structure requires 16 electron pairs for skeletal bonding. The eight B−H groups contribute eight electron pairs for skeletal bonding. The four $C-SiMe_3$ groups contribute six electron pairs. The silicon atom contributes two electron pairs, thus perfectly balancing the electronic requirement. This molecule is well characterized by IR spectroscopy, ^{1}H, ^{11}B, and ^{13}C NMR spectroscopy, and X-ray crystallographic studies.[157]

Ge((SiMe$_3$)$_2$C$_2$B$_4$H$_4$)$_2$ (C$_i$) (**54**). This structure exhibits a sandwich pattern with the germanium, the next element of the group 14 series.[159,160] The electronic requirements and the contributions of the individual groups to the polyhedra are similar, though the Ge−C bond distance is very large (2.38 Å) when compared to the normal Ge−C distances (∼2.08−2.04 Å). Here, also $n = 13$, $m = 2$, and $o = 1$, and hence, this structure requires 16 electron pairs for skeletal bonding. The eight B−H groups contribute eight electron pairs for skeletal bonding. The four

$C-SiMe_3$ groups contribute six electron pairs. The silicon atom contributes all its valence electrons. This molecule is also well characterized by IR spectroscopy, ^1H, ^{11}B, and ^{13}C NMR spectroscopy, and X-ray crystallographic studies.[159]

$[Al(C_2B_6H_8)_2]^-$ (**55**). This molecule consists of two *nido*-C_2B_6 units interacting through a common aluminum atom.[161] In the solid state, it exists in two enantiomeric forms but exhibits fluxional behavior at room temperature, as one enantiomer gets converted into the other rapidly. The aluminum is shared between two C_2B_6 units. However, the aluminum has a definite bonding interaction only with the carbon atoms of the polyhedral skeleton. The Al−B distance is more than 2.2 Å, and hence, the molecule appears to have open faces. As mentioned earlier, this type of single-vertex-sharing interaction seldom has open faces surrounding the central vertex. This has to be treated as two *closo* skeletons sharing a single vertex. Though it may appear like slipping commonly encountered in sandwich borane complexes ubiquitously known in transition-metal-containing boranes, this slipping is due to the preference of aluminum for tetrahedral coordination owing to the involvement of the less aromatic eight-vertex *closo* skeleton. Here, $n = 17$, $m = 2$, and $o = 1$, and hence, this pattern requires 20 cluster electron pairs for stability. The 12 B−H groups contribute 12 electron pairs for the skeletal bonding. The four C−H groups each contribute three electrons. As aluminum has only three electrons in the valence shell, this molecule exists as a stable monoanion. The structure of this molecule is well characterized by ^1H, ^{11}B, and ^{13}C NMR spectra and single-crystal X-ray crystallography.[161]

$[Al(C_2B_8H_{10})]_2]^-$ (S_4) (**56**). This molecule exhibits a single-vertex-sharing pattern with aluminium, very similar to the one discussed above but with two *nido*-C_2B_8 units.[162] Owing to the symmetric distribution of carbon atoms in the open face of the C_2B_8 units, the preference of aluminum for tetrahedral coordination toward carbon does not require any slipping from the central position. Owing to this tetrahedral preference, the two C_2B_6 units are aligned orthogonal to each other, leading to a highly symmetric pattern. Here, $n = 21$, $m = 2$, and $o = 1$, and hence, this structure requires 24 electron pairs for skeletal bonding. The 16 B−H groups contribute 16 electron pairs to the skeleton. The four C−H units contribute six electron pairs. As aluminum contributes its three valence electrons, the structure exists as a stable monoanion. The molecule is also well characterized by ^1H, ^{11}B, and ^{13}C NMR spectra and single-crystal X-ray crystallography.[162]

$[Mg((SiMe_3)_2C_2B_4H_4)]_2^{2-}$ (C_i) (**57**). This molecule consists of two *closo*-MgC_2B_4 units interacting through two 3c−2e bonds along the cap.[155] This is a unique macropolyhedral borane in which a main block element is interacting through a 3c−2e hydrogen bridge. Here, $n = 14$ and $m = 2$, and hence, this skeleton requires 16 electron pairs for skeletal bonding. The eight B−H groups contribute eight electron pairs for skeletal bonding. The four $C-SiMe_3$ groups contribute six electron pairs. The two magnesium atoms contribute one electron pair each since the *exo* bonds of TMEDA are dative in nature. The two electrons required for the 3c−2e bond connection are available from the boron and hydrogen atoms, each contributing one electron. The molecular structure is well characterized by IR spectroscopy, ^1H, ^{11}B, ^{13}C, and ^7Li NMR spectroscopy, and X-ray crystallographic studies.[155]

$[(C_2B_9H_{11})Si((Me_3P_2BH)C_2B_8H_{10})]^{2-}$ (**58**). This structure exhibits a single-vertex-sharing pattern with silicon, sandwiched between C_2B_9 and C_2B_8 units.[162] The unique feature of this pattern is the presence of one open face of which silicon is not a part. Here, also $n = 22$, $m = 2$, $o = 1$, and $p = 1$, and hence, this structure requires 26 electron pairs for skeletal bonding. The 16 B−H groups contribute 16 electron pairs for skeletal bonding. The four C−H groups contribute six electron pairs. Two more electron pairs are required for the skeletal bonding molecular orbitals. The $B(PMe_3)_2$ group contributes three electrons as the *exo* bond is dative in nature. The remaining electron is available to the skeleton as an *endo*-hydrogen atom that lies within the inner sphere of the macropolyhedral skeleton. The silicon atom contributes all of its valence electrons. This molecule is also well characterized by IR spectroscopy, mass spectrometry, ^1H, ^{11}B, and ^{13}C NMR spectroscopy, and X-ray crystallographic studies.[162]

$[Al(C_2B_9H_{11})_2]^-$ (**59**). This structure exhibits a single-vertex-sharing sandwich pattern in which aluminium is sandwiched between two C_2B_9 units.[163,165] Unlike the single-vertex-sharing patterns (**55** and **56**) discussed earlier, in this molecule the aluminum makes polyhedral interactions with all of the atoms in the five-membered ring. Here, $n = 23$, $m = 2$, and $o = 1$, and hence, this structure requires 26 electron pairs for skeletal bonding. The 18 B−H groups contribute 18 electron pairs for skeletal bonding. The four C−H groups contribute six electron pairs. Aluminum contributes all of its three electrons, but still, the structure requires one more electron. Hence, this species exists as a stable monoanion. This molecule is also well characterized by IR spectroscopy, ^1H and ^{11}B NMR spectroscopy, and X-ray crystallographic studies.[163]

$[Ga(C_2B_9H_{11})_2]^-$ (**60**). This molecule consists of two C_2B_9 units interacting through the central gallium atom.[164] Unlike the previous structure, this structure exhibits slip distortion, with the gallium atom slipping away from the carbon atoms. The electronic requirements remain the same; i.e., $n = 23$, $m = 2$, and $o = 1$, and hence, this structure requires 26 electron pairs for skeletal bonding. The 18 B−H groups contribute 18 electron pairs, and the 4 C−H groups contribute 6 electron pairs for the skeletal bonding. Gallium contributes all of its three electrons, but still, the structure requires one more electron. Hence, this species exists as a stable monoanion. This molecule has the unique feature of the two C_2B_9 units in the eclipsed configuration and is well characterized by IR spectroscopy, ^1H and ^{11}B NMR spectroscopy, and X-ray crystallographic studies.[165]

$Si(C_2B_9H_{11})_2$ (D_{5d}) (**61**). This molecule is isostructural and isoelectronic with all the other C_2B_9 sand-

wich complexes, and it requires the same 26 electron pairs for skeletal bonding.[166] The structure exhibits a center of symmetry, and the silicon atom lies equidistant between the centers of the two C_2B_3 rings. The 18 B−H groups contribute 18 electron pairs, and the 4 C−H groups contribute 6 electron pairs for the skeletal bonding. Silicon contributes all of its four valence electrons, and hence, the molecule exists as a neutral species. This molecule is also well characterized by IR spectroscopy, ^1H and ^{11}B NMR spectroscopy, and X-ray crystallographic studies.[166]

Al(exo-[μ-H]$_2$AlEt$_2$C$_2$B$_9$H$_9$)(C$_2$B$_9$H$_{11}$) (**62**). This molecule exhibits a sandwich pattern very similar to the aluminum sandwich discussed above but exists as a neutral species owing to the availability of one more electron from the exohedral 3c−2e bonding. Consequently, the electronic requirements also remain the same; i.e., $n = 23$, $m = 2$, and $o = 1$, and this structure requires 26 electron pairs for skeletal bonding. The 16 B−H groups contribute 16 electron pairs, and the 4 C−H groups contribute 6 electron pairs for the skeletal bonding. The central aluminum atom contributes all of its three electrons, but still, the pattern requires one more electron. However, two of the adjacent boron atoms in one of the C_2B_9 groups form two 3c−2e hydrogen bridges with another aluminum atom. In addition, the second aluminum is bonded to two ethyl groups that require two electrons from aluminum, thereby leaving one electron for the 3c−2e bonds. Since five electrons are available for the two 3c−2e bonds (one from each atom), the extra electron is made available to the cluster for skeletal bonding. The structure of this molecule is well characterized by ^1H and ^{11}B NMR spectroscopy and X-ray crystallographic studies.[167]

C. Boranes with Transition Metals

Macropolyhedral boranes containing transition metals occupy a major part in borane chemistry. The charge requirements in many macropolyhedral boranes are nullified by the introduction of analogous transition-metal fragments, which contribute more electrons with their diffused orbitals. Among the transition metals, platinum appears to have an innate tendency to occupy any site regardless of the position or the mode of fusion. Most of the known structures are with platinum possessing one or more ligands. As far as other metals are considered, they are usually found in vertex-condensed structures and in systems with *exo* polyhedral contacts. Only limited examples are known in which a metal other than platinum is involved in other condensed structures.

[(PMe$_2$Ph)$_2$PtB$_{18}$H$_{20}$] (**63**−**65**). For all three structures discussed in this section, there were ambiguities in refining the positions of hydrogens, and hence, they have not been reported. Thus, the chart shows only the skeletal atoms. However, we have attempted to assign the hydrogen atom locations in the various structures on the basis of the electron-counting rule.

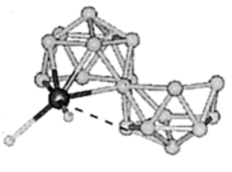
There are three isomeric forms with the same molecular formula. **63** and **64** are the platinaborane derivatives of *syn*- and *anti*-$B_{18}H_{22}$, respectively. The descriptors *syn* and *anti* have the same implications of iso and normal, respectively, which were used earlier. The distances between platinum and boron atom in **63** and **64** shown by dotted lines are 3.04 and 2.96 Å, respectively. In **65**, this particular bond length is 2.12 Å, indicating a strong bonding between the two atoms. In all of these structures $m = 2$ and $n = 19$. For structures **63** and **64** $p = 2$, which suggests 23 electron pairs ($n = 19$, $m = 2$, $p = 2$) for stability. This is accounted for by the electronic contribution from 16 BH groups (16 electron pairs), two shared boron atoms (3), four bridging hydrogens (2), and a ML_2 fragment (2) taken as a BH^{2-} analogue. Thus, the structure corresponds to a *nido*−*nido* type with two boron atoms in common.[168]

The observation of the geometry does not give a clear picture of the polyhedral pattern exhibited by structure **65**. However, a comparison between the number of electron pairs predicted by the electron-counting rule and those actually contributed by the various fragments helps to describe the structure as an edge-shared system with two *nido* subclusters. The platinum bonded to the boron atom of the second subcluster can be considered as an *exo* bond, with the boron atom contributing only one electron pair for skeletal bonding. The terminal hydrogen of the boron in question is converted to a bridging hydrogen to compensate for the skeletal electron from platinum, which goes to the *exo* 2c−2e bond. Thus, in structure **65** there are a total of five bridging hydrogens.[168]

[(PMe$_2$Ph)$_4$Pt$_2$B$_{18}$H$_{16}$] (**66**). The diplatinum compound is a derivative of *anti*-$B_{18}H_{22}$. The hydrogen atom positions for this structure also are not reported, and hence, the structure is shown in the chart as obtained from the CSD. Each of the platinums contributes four electrons to the cluster bonding. One of the platinum atoms is η^4-bonded, whereas the other platinum also has four closest neighbor boron atoms with two other boron atoms more distant away but still in the bonding region. Hence, it can be considered as an η^6 borane−metal bonding mode. An electron pair count of 23 from 15 BH groups, 3 boron atoms, and a bridging hydrogen and by the substitution of $Pt(PMe_2Ph)_2$ by its isolobal BH^{2-} corresponds to $n + m + 1$, where $n = 20$ and $m = 2$. The electron count combined with the geometrical observations suggests a *closo*−*nido* structure with a confacial conjunction.[168]

[(PMe$_2$Ph)$_3$HReB$_{20}$H$_{15}$Ph(PHMe$_2$)] (**67**). This structure is one of the examples where the combination of the $n + m$ rule and Mingos' capping principle[23,26,27] finds its application. The metal is actually *exo* to the borane cluster capping one of the triangular faces.[110] If the molecule is considered without the cap, the skeleton contains 20 vertexes and 2 cages. The *nido* structure increases the electron pair count to 23 for stability. The number of electron pairs contributed by the constituent elements works out to be 22 (17 BH groups, 3 shared boron atoms, 1 dative bond). So the cluster requires two more electrons for stability. The capping of a d^6-ML_4 fragment (a BH analogue) results in donation of its electrons to the cluster, thus compensating for the shortage in electrons. The electronic requirement of 23 electron pairs matches with $n + m + p - q$ ($21 + 2 + 1 - 1 = 23$) when the cap is counted as one of the vertexes. The increase

Chart 5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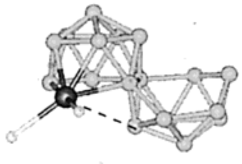
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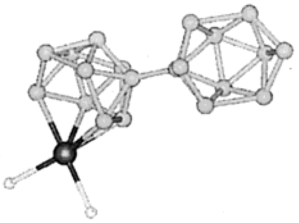
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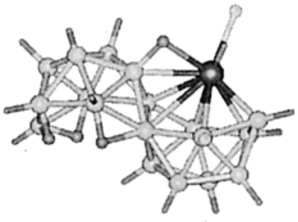
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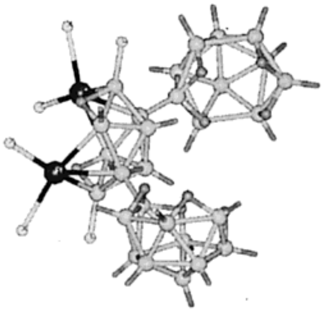
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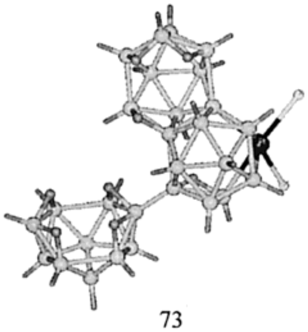
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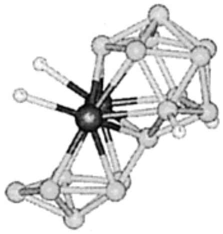
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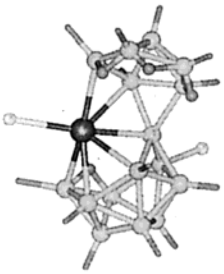
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in the number of vertexes as a cap does not alter the number of bonding molecular orbitals.

[(PMe$_2$Ph)$_2$PtB$_{20}$H$_{24}$] (**68**). This compound has a d^{10}-ML$_2$ fragment, which is a BH^{2-} mimic. Six bridging hydrogen atoms are present on the basis of the ^{1}H$-^{11}$B NMR spectroscopic studies.[169] But the exact positions of these hydrogens were not refined, and hence the structure presented lacks these hydrogen atoms. The electron pair count provided by 20 BH groups, 6 bridging hydrogen atoms, and the Pt(PMe$_2$-Ph)$_2$ fragment totals 25. The electron pair count is in tune with $n + m + 2$ ($n = 21$, $m = 2$, $p = 2$). From the topology, it is inferred without doubt that the compound consists of a *nido*-B$_{10}$Pt 11-vertex system and a *nido*-B$_{10}$ unit linked by an intercluster B$-$B bond.

[CO(PMe$_3$)$_2$IrB$_{16}$H$_{14}$Ir(CO)(PMe$_3$)$_2$] (**69**). The electronic requirement according to the rule is 21 electron pairs ($n = 18$, $m = 2$, $p = 1$) for a *closo*$-$*nido* framework. The bond between the iridium atom of the *nido* subcluster and a boron atom of the *closo* subcluster being longer (2.24 Å vs 2.07 Å for the usual Ir$-$B σ bonds) prompted the authors to explain the compound as a *closo*$-$*nido* edge-sharing system with a suprafacial two-center$-$two-electron bond linking the two subclusters.[170] If the molecule exhibits this type of bonding as is observed in structure **65**, its skeletal electron count is two electrons short. The total of 20 electron pairs comes from the 14 BH groups (including the boron bonded *exo* to iridium), 2 shared boron atoms, a bridging hydrogen, and 2 d^9-ML$_3$ fragments, a 3-electron donor. The metal, which is bonded to the boron atom of the second cluster, utilizes one of its electrons, which leaves it with only two cluster electrons. The shortage of one electron pair can be solved only if the bonded electrons considered to be *exo* (Ir$-$B) are also involved in cluster bonding. Both the topology and the electron-counting rule support the fact that the two clusters are intimately fused as *closo*$-$*nido* sharing a trian-

gular face. The *exo* bond in **65** should be differentiated from the present case by the topology of the respective compounds.

[(CO)(PMe$_3$)$_2$IrB$_{17}$H$_{20}$] (**70**). This cluster is analogous to the hypothetical *syn*-$B_{18}H_{21}^-$ anion, where one of the BH groups is replaced by an ML_3 fragment.[171] Iridium with three neutral ligands is a three-electron donor. According to the *mno* rule, the structure with $m = 2$, $n = 18$, and $p = 2$ requires (18 + 2 + 2) 22 electron pairs. Fifteen electron pairs are obtained from 15 BH groups, 2 shared boron atoms provide 3 electron pairs, 5 bridging hydrogens contribute 2.5 electron pairs, and iridium contributes its 1.5 electron pairs to provide the total requirement of 22 electron pairs for stability. Hence, the cluster is neutral.

[(PPh$_3$)HIrB$_{18}$H$_{18}$] (**71**). This complex, even though it appears as an edge-shared *closo*–*nido* system, is actually a triangular fusion with one vacancy on each subcluster. The metal to boron distances on the subcluster which appears as a 10-vertex *closo* part are not uniform, and the longest distances of 2.596 and 2.487 Å suggest a *nido* framework.[172] This is also suggested by the electron-counting rule, according to which 23 skeletal electron pairs ($m = 2$, $n = 19$, $p = 2$) are needed. There are 15 BH groups (15 electron pairs), 3 boron atoms (4.5), 4 bridging hydrogens (2), a d^8-ML$_2$ fragment (1), and a dative bond (0.5), which account for the 23 cluster electron pairs.

[(PMe$_2$Ph)$_2$(PMe$_2$C$_6$H$_4$)$_2$Pt$_2$B$_{28}$H$_{32}$] (**72**). This complex consists of a central *arachno*-B_8Pt_2 unit joined to two *nido*-$B_{10}H_{14}$ clusters by a direct 2c–2e bond.[172] The molecule requires 37 electron pairs for stability ($n = 30$, $m = 3$, $p = 4$). This has been ascribed to 28 BH groups (the boron atoms which are linked to other subclusters are also counted), 10 bridging hydrogens, and 2 d^{10}-ML$_2$ fragments (each one is a 4-electron donor), thereby establishing the neutrality of the structure.

[(PMe$_2$Ph)$_2$PtB$_{18}$H$_{19}$(B$_{10}$H$_{13}$)] (**73**). One of the *nido*-B_{10} units of the above complex is fused through an edge with the central cluster PtB_{10}. The third *nido* cluster remains σ-linked to the PtB_{10} unit.[172] The central cluster has one more vertex than the previous one. This results in the reduction of the total number of vertexes and open faces by one. The net electronic requirement is reduced by 2, and hence, only 35 electron pairs ($m = 3$, $n = 29$, $p = 3$) are needed. The required electron pairs are obtained from 26 BH groups, 2 shared boron atoms, 8 bridging hydrogens, and a d^{10}-ML$_2$ fragment (26 + 3 + 4 + 2).

[(PMe$_2$Ph)$_2$Pt$_2$B$_{16}$H$_{15}$(C$_6$H$_4$Me)(PMe$_2$Ph)] (**74**). The Pt(PMe$_2$Ph) unit is replaced as a B^- fragment at a fused position. The 2 B^--mimicking units of the metal, 15 BH groups in addition to the dative bond, 2 bridging hydrogen atoms, and a shared boron atom provide 22 electron pairs for cluster bonding. This is consistent with two open faces ($n = 18$, $m = 2$, $p = 2$), which explains the bonding as *closo*–*arachno* fusion with a BPt_2 face in common. The positions of the hydrogen atoms are in agreement with multiple resonance NMR spectroscopy.[173] But the exact locations of the hydrogen atoms were not assigned, and hence, the structure shown lacks them. However, a comparison between this structure and structure **77** Chart 5 clearly indicates that the open structures are equivalent by geometry considerations, but the former is reported as a *nido* structure and the latter as an *arachno* structure. However, the rule clearly suggests an *arachno* framework rather than a *nido* one. The discrepancy that arises when two adjacent metals share a macropolyhedron is not found here owing to the almost nonbonding interactions between the two (2.9 Å). Still, the molecule obeys the *mno* rule as a condensed structure sharing a triangle.

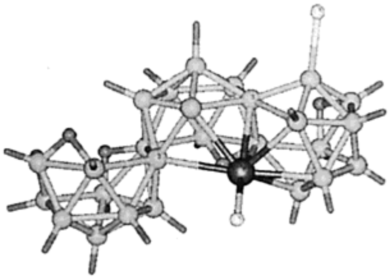
[(PMe$_2$Ph)PtB$_{16}$H$_{18}$(PMe$_2$Ph)] (**75**). The M–L fragment is at a shared position and can be treated as a B^- rather than a BH fragment. Summing the electron pairs contributed by the M–L unit, 15 BH groups, 1 shared boron atom, a dative B–P bond, and 4 bridging hydrogen atoms gives a total of 21. This is in accordance with a structure having two missing vertexes ($n = 17$, $m = 2$, $p = 2$) and therefore predicts a *nido*–*nido* cluster framework condensed through a Pt–B edge, which is in support of the observation.[174]

[(PMe$_2$Ph)PtB$_{26}$H$_{26}$(PMe$_2$Ph)] (**76**). This complex is one of the very few examples known where there is an intimate fusion of more than two larger single clusters. The aggregation is through an edge and a face of boron atoms.[175] The Pt–L fragment at a shared position is effectively substituted by B^-. In addition, there are 5 bridging hydrogen atoms, 22 BH groups, one dative bond, and 4 shared boron atoms. All these sum to an electron pair count of 33, which are contributed to the cluster network. The *mno* rule gives the same value with $n = 27$, $m = 3$, and $p = 3$. This suggests a *nido*–*nido* cluster with two common boron atoms, which in turn is joined to a *nido* 11-vertex PtB_{10} unit having a PtB_2 face shared between the two clusters.

[(PMe$_2$Ph)$_4$Pt$_3$B$_{14}$H$_{16}$] (**77**). Even though the positions of the hydrogen atoms are missing, the formula suggests three hydrogen atoms to be of the bridging type.[176] This is based on the fact that the shared boron does not possess any terminal hydrogen atoms. The structure shown is obtained from the CSD and lacks the hydrogen atom positions. Two Pt(PMe$_2$Ph) fragments occupy a shared position that can be replaced by B^- units. The Pt(PMe$_2$Ph)$_2$ unit is related isolobally to a BH^{2-} fragment. The cluster has in addition 13 BH groups and a shared boron atom. The electron pair count is calculated to be 22. This is in full support of a *nido*–*arachno* arrangement with the Pt_2B triangular face keeping the two clusters fused. Thus, the compound follows the *mno* rule. The shared metals at adjacent positions (Pt–Pt = 3.376 Å) do not produce any adverse impact on the molecule similar to structure **74**.

[(PMe$_3$)$_2$IrB$_{26}$H$_{24}$Ir(CO)(PMe$_3$)$_2$], [(PPh$_3$)$_3$(PPh$_2$)$_2$-Pd$_4$B$_{20}$H$_{16}$] (**78**, **79**). Structure **78** can be treated as a 19-vertex macropolyhedral borane (A), which has an inter-boron linkage that is also entailed in multicenter bonding to the third subcluster, IrB_8 (B).[177] The compound with a tetrahedral arrangement of boron atoms represents a *megalo*-borane, which is gaining interest due to its similarity to the arrangements in β-rhombohedral boron. A strong intercluster

Chart 6



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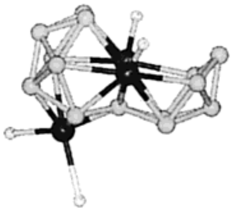

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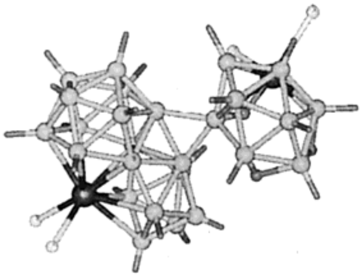

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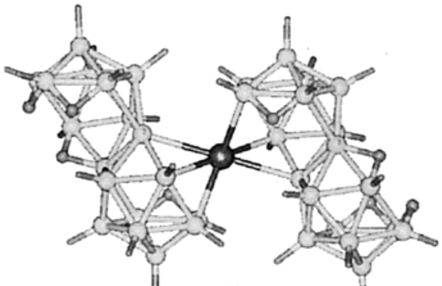

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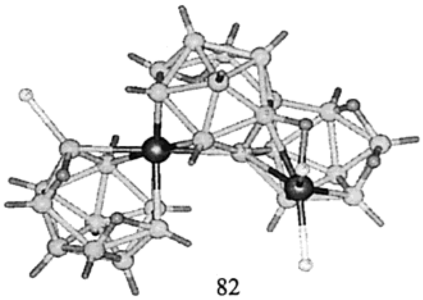

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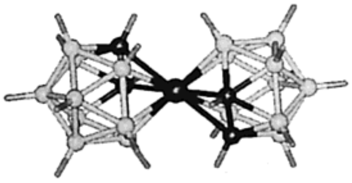

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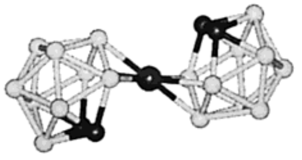

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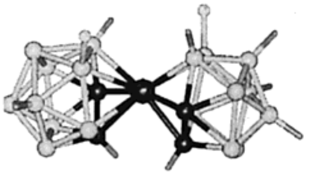

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bond between the two boron atoms defining a perfect tetrahedron results in an additional cage and hence an enhancement in the electronic requirement. These interactions should be dealt with with caution while the rule is applied. A weak intercluster interaction may not generate an additional cage even though it looks like a tetrahedron. Usually such “pseudo”-*megalo*-borane clusters result when an attempt is made to protonate the two intercluster bonded borons, which are a part of the tetrahedron.

The present molecule is synthesized from *arachno*-[(CO)(PMe$_3$)$_2$HIrB$_8$H$_{12}$] and B$_{10}$H$_{14}$ and can undergo further cluster incorporation owing to the availability of an open structure on the subcluster IrB$_8$. Evaluation of the electronic requirement from the different fragments results in 34 electron pairs. They are contributed from 21 BH groups, 5 shared boron atoms, 3 bridging hydrogens, a d^9-ML$_2$ fragment isolobal to B^{2-} (being at the shared position), and a d^9-ML$_3$ unit analogous to BH$^-$. From this one electron pair goes to the multicenter bonding and does not participate in cluster bonding. The remaining 33 electron pairs correspond to $n + m + p$, where $n = 28$, $m = 4$, and $p = 1$. Thus, the electron-counting rule interprets the open part as a *nido* framework.

The compound [(PPh$_3$)$_3$(PPh$_2$)$_2$Pd$_4$B$_{20}$H$_{16}$] structure (**79**) is also a member of the *megalo*-boranes.[92b] However, here the capping atom is a metal. In both these cases the intercluster linkage is made possible by the presence of a metal atom at the shared position. The molecule has 16 BH groups, 4 shared boron atoms, a d^{10}-ML fragment at a shared position equivalent to B$^-$, 2 d^{10}-ML fragments isolobal to BH, a central palladium atom, 2 bridging hydrogens, and 2 bridging PPh$_2$ ligands available for cluster bonding. Counting the electron pairs from these various fragments gives 31 cluster electron pairs. The structure has four subunits including the tetrahedron and the metal cluster ($m = 4$). The metal cluster part appears as an *arachno* unit. The total number of vertexes is 24. So applying the rule, the molecule requires (24 + 4 + 2) 30 electron pairs for its stability. An additional electron pair coming in from the fragments can be attributed to the 3c−2e bond as before. However, the bonding in these types of systems is not clear and requires an elaborate study of its own. We are exploring such systems in our attempt to establish some well-defined explanations for the cluster bonding observed in these compounds.

*$[Pt(B_{18}H_{20})_2]^{2-}$ (**80**).* In this complex, more than two clusters are joined by a common linkage with platinum at the common site. Even though the appearance of the structure gives a misconception of four open faces, the complex is actually a slipped one with only two open faces.[178] Owing to slipping, the metal fails to bond with some boron atoms, preventing it from being a perfect *closo* structure. Here, $m = 4$, $n = 37$, $o = 1$, and $p = 2$, and the *mno* rule predicts 44 electron pairs for stability. There are 32 BH groups, each contributing one electron pair, 4 boron atoms providing 6 electron pairs, 8 bridging hydrogens giving 4 electron pairs to the cluster, and platinum donating 2 electron pairs available in the e_g set. All these sum to 44 electron pairs. The compound in addition has a −2 charge, which when added to the cluster electrons amounts to 45 electron pairs. The one extra electron pair goes into an antibonding orbital (Figure 5). The molecule in its attempt to stabilize this unstable level gets distorted, thereby stabilizing the concerned orbital.

*$[Ni(B_{10}H_{12})_2]^{2-}$ (**81**).* This is a complex of Ni^{2+} sandwiched between two $(B_{10}H_{12})^{2-}$ units which are derived from the *closo*-$B_{11}H_{11}^{2-}$ species. So replacement of the removed vertex by a metal results in a *closo* form. The number of electron pairs from the various fragments is 25 (20 BH groups, 4 bridging hydrogens, a nickel atom, and −2 charge). According to the *mno* rule $m = 2$, $n = 21$, and $o = 1$, and the *closo* structure requires 24 electron pairs. The additional electron pair essentially results in a distortion in the structure even though to a lesser extent.[179a] Similar structural patterns are exhibited by metals such as Co, Pd, Pt, Zn, etc.[180] The ring size at the open face is then one of the factors which govern the slipping. In terms of the 18-electron rule, it is said that the structural changes are induced at a lower oxidation state of the metal. Such a metal demands fewer electrons from the ligand, hence the decrease in hapticity.[179b] So we feel that a combined effect is operative here.

*$[(PMe_2Ph)_2\ PtB_{16}H_{17}PtB_{10}H_{11}(PMe_2Ph)]$ (**82**).* This complex has two open faces, both of them on the same subcluster that has been supported by the long Pt−B distance of 2.602 Å.[181] In this case also, the complex is a distorted one with the electron-rich metal ion d^8-Pt^{2+}. The description of the compound as an edge fusion between the middle subcluster and the terminal one rather than a face fusion is disproved by the *mno* rule. The 23 BH groups, a dative bond, 3 shared boron atoms, 6 bridging hydrogens, a d^{10}-ML_2 fragment equivalent to BH^{2-}, and a platinum atom make 35 electron pairs available for cluster bonding. The rule suggests 34 electron pairs ($m = 3$, $n = 28$, $o = 1$, $p = 2$) for the stability of the compound. The excess electron pair slips the complex at the single-vertex-condensed site. The two open faces then lie on the same subunit.

*$[(B_{11}H_{11})_2Cu]^{3-}$(**83**).* This complex is isoelectronic with the dicarbollide compounds of transition metals, **85**. This is a very rare example where two B_{11} units sandwich a metal.[182] The metal has five electrons to donate to the cluster. The 22 BH groups contribute one electron pair each. The cluster has 24.5 skeletal electrons. With $m = 2$, $n = 23$, and $o = 1$, the rule suggests a requirement of 26 electron pairs. The complex is trianionic and obeys the *mno* rule.

*$[(OEt_2)Cd(B_{10}H_{12})]_2$ (**84**).* This compound lacks the hydrogen atom positons as observed with the structure deposited in the CSD. $(OEt_2)Cd(B_{10}H_{12})$ exists in a dimeric form. This example serves as one of the extreme cases where two vertexes share two clusters and the two sharing atoms are not at all in the bonding region.[101] The *mno* rule can be applied here; $n = 22$, $m = 2$, $o = 2$, and two open faces lead to an electron pair requirement of 28. The 20 BH groups (20 electron pairs), 2 d^{10}-CdL_2 units (isolobal to B^{3-}) contributing 6 electron pairs, and 4 bridging hydrogens (2 electron pairs) make a total of 28 electron pairs. Thus, the structure obeys the *mno* rule.

D. Mixed Borane Clusters

When both transition metals and main block elements are present as heteroatoms, the common site is occupied by either a transition metal or boron itself, except for a single structure where sulfur is forced to share all its electrons with the cluster. This can be just an extension of what is seen in boranes with main group elements, as there are no mixed clusters known with aluminum or germanium or any such atoms which have diffused orbitals. Indeed, one structure is known with silicon, but the fragment occupies a terminal position. If one excludes carbon as one of the omnipresent heteroatoms in boranes, sulfur forms the next main block heteroatom, which is usually mixed up with metallaboranes. They are found without any *exo* substituents.

*$[C_4H_{22}B_{18}M]^n$ (**85**). Symmetrical Sandwich Complexes.* The dicarbollide−metal chemistry, a vast field with a large number of complexes known, has been covered here. Two dicarbollide ligands with the metal sandwiched between them leads to five general patterns (structures **85**−**89**), each of which is represented by a single structure owing to their structural similarity. The enumeration of electron pairs of each complex is illustrated in Table 1.

The symmetrical sandwich complexes contain metals with seven or fewer d-electrons in their formal valence state. A variety of such complexes have been structurally characterized. All of them have a similar structure as shown. They are of the general formula $[C_4H_{22}B_{18}M]^n$ known with M = Fe, Co, Cr, and Ni and n ranging from −2 to 0 depending on the nature of the metals. All the complexes of this type obey the *mno* rule. As an example, consider the complex $[C_4H_{22}B_{18}Co]^-$, for which the *mno* rule predicts an electron pair count of 26 for stability ($n = 23$, $m = 2$, $o = 1$). The four CH groups contribute six electron pairs, and the BH groups contribute one electron pair

Table 1. Enumeration of Electron Pairs for the Various Single-Vertex Condensation Systems[a]

structure	m	n	o	p	N	BH	CH	B	α	γ	N′	x	ref
Type 1													
$[(C_2B_9H_{11})_2Co]$	2	23	1	0	26	18	6	0	1.5	0	25.5	−1	184
$[(C_2Me_2B_9H_9)_2Ni]$	2	23	1	0	26	18	6	0	2.0	0	26	0	185
$[C_6H_{26}B_{18}O_2Ni]$	2	23	1	0	26	18	6	0	2.0	0	26	0	186
$[(C_2IB_9H_{10})_2Co]$	2	23	1	0	26	18	6	0	1.5	0	25.5	−1	187
$[C_4B_{18}H_{21}ICo]$	2	23	1	0	26	18	6	0	1.5	0	25.5	−1	188
$[(C_2B_9H_8Br_3)_2Co]$	2	23	1	0	26	18	6	0	1.5	0	25.5	−1	189
$[(C_2B_9H_{10}Ph)_2Co]$	2	23	1	0	26	18	6	0	1.5	0	25.5	−1	190
$[(C_2B_9H_{11})_2Fe]$	2	23	1	0	26	18	6	0	1.0	0	25	−2	191
$[(C_2Me_2B_9H_9)_2Cr]$	2	23	1	0	26	18	6	0	1.5	0	25.5	−1	192
$[(C_2B_9H_{11})_2Ni]$	2	23	1	0	26	18	6	0	2.0	0	26	0	193
$[(C_2B_9H_{11})_2Co]$	2	23	1	0	26	18	6	0	1.0	0	25	−2	194
$[C_{12}H_{38}B_{18}O_4Co]$	2	23	1	0	26	18	6	0	1.5	0	25.5	−1	194
$[(C_2Et_2B_9H_9)_2Co]$	2	23	1	0	26	18	6	0	1.5	0	25.5	−1	195
$[(C_2B_9H_{11})_2Ni]$	2	23	1	0	26	18	6	0	1.5	0	25.5	−1	196
$[C_{12}H_{26}B_{18}S_2Fe]$	2	23	1	0	26	18	6	0	1.5	0	25.5	−1	197
[(C2B9H11)2Cr]	2	23	1	0	26	18	6	0	1.5	0	25.5	−1	196b, 197c
$[(C_2B_9H_{10}Cl)_2Co]$	2	23	1	0	26	18	6	0	1.5	0	25.5	−1	198
$[(C_2B_9H_{11})_2Fe]$	2	23	1	0	26	18	6	0	1.5	0	25.5	−1	196b, 199
$[(C_2B_9H_{10}Cl)_2Fe]$	2	23	1	0	26	18	6	0	1.5	0	25.5	−1	200
$[C_{22}H_{34}B_{18}Rh_2]$	2	23	1	0	26	18	6	0	2	0	26	0	201
$[C_{10}H_{26}B_{18}Co]$	2	23	1	0	26	18	6	0	1.5	0	25.5	−1	202
Type 2													
$[(C_2B_9H_{11})_2Au]$	2	23	1	0	26	18	6	0	2.5	0	26.5	−1	203
$[(C_2B_9H_{11})_2Ni]$	2	23	1	0	26	18	6	0	2.0	0	26	−2	204
$[(C_2B_9H_{11})_2Cu]$	2	23	1	0	26	18	6	0	2.5	0	26.5	−1	205
$[(C_2B_9H_{11})_2Cu]$	2	23	1	0	26	18	6	0	2.0	0	26	−2	206
$[(C_7H_{23}B_{18}CuN_2]$	2	23	1	0	26	18	6	0	2.5	0.5^{γ}	27	0	207
Type 3													
$[C_8H_{32}B_{18}S_2Fe]$	2	23	1	0	26	18	6	0	1.0	1.0^{γ}	26	0	208, 209
$[C_{16}H_{50}B_{18}N_2Fe]$	2	23	1	0	26	18	6	0	1.0	1.0^{γ}	26	0	210
$[C_7H_{30}B_{18}CoP]$	2	23	1	0	26	18	6	0	1.5	0.5^{γ}	26	0	211
$[C_8H_{32}B_{18}S_2Fe]$	2	23	1	0	26	18	6	0	1.5	1.0^{γ}	26	0	212
$[C_8H_{25}B_{18}O_2Co]$	2	23	1	0	26	18	6	0	1.5	0.5^{γ}	26	0	213
Type 4													
$[C_5H_{23}B_{18}FeO]$	2	23	1	0	26	18	6	0	1.5	0.5^{γ}	26	0	214
$[C_5H_{21}B_{18}CoS_2]$	2	23	1	0	26	18	6	0	1.5	0.5^{γ}	26	0	215
$[C_7H_{25}B_{18}Co_2S]$	2	23	1	0	26	18	6	0	1.5	0.5^{γ}	26	0	216
$[C_7H_{26}B_{18}CoNO_2]$	2	23	1	0	26	18	6	0	1.5	0.5^{γ}	26	0	217
$[C_{20}H_{37}B_{18}CoS_2]$	2	23	1	0	26	18	6	0	1.5	1.5^{γ}	26	0	218
$[C_6H_{26}B_{18}CoP]$	2	23	1	0	26	18	6	0	1.5	0.5^{γ}	26	0	211
$[C_7H_{23}B_{18}CoS]$	2	23	1	0	26	18	6	0	1.5	0.5^{γ}	26	0	219
$[C_8H_{22}B_{18}CoN_2O_2]$	2	23	1	0	26	18	6	0	1.5	0.5^{γ}	26	0	220
$[C_7H_{23}B_{18}CoN_2]$	2	23	1	0	26	18	6	0	1.5	0.5^{γ}	26	0	207
$[C_7H_{23}B_{18}N_2Ni]$	2	23	1	0	26	18	6	0	1.5	0.5^{γ}	26	0	207
$[C_7H_{23}B_{18}N_2Fe]$	2	23	1	0	26	18	6	0	1.5	0.5^{γ}	26	0	207
Type 5													
$[C_4H_{20}B_{18}CoO]$	2	23	1	0	26	18	6	0	1.5	0.5^{γ}	26	0	221
$[C_4H_{20}B_{18}CoS]$	2	23	1	0	26	18	6	0	1.5	0.5^{γ}	26	0	222
$[C_{10}H_{24}B_{18}Co]$	2	23	1	0	26	18	6	0	1.5	0	25.5	−1	223
$[C_7H_{26}B_{18}Co]$	2	23	1	0	26	18	6	0	1.5	0	25.5	−1	224
$[C_8H_{28}B_{18}Co]$	2	23	1	0	26	18	6	0	1.5	0	25.5	−1	224
$[C_8H_{28}B_{18}Fe]$	2	23	1	0	26	18	6	0	1.5	0	25.5	−1	224
$[C_8H_{28}B_{18}Ni]$	2	23	1	0	26	18	6	0	1.5	0	25.5	−1	224
$[C_4H_{16}B_{18}CoO_4S]$	2	23	1	0	26	18	6	0	1.5	0	25.5	−1	225
$[C_6H_{23}B_{18}CoS]$	2	23	1	0	26	18	6	0	1.5	0	25.5	−1	226
$[C_{14}H_{28}B_{18}Co]$	2	23	1	0	26	18	6	0	1.5	0	25.5	−1	227

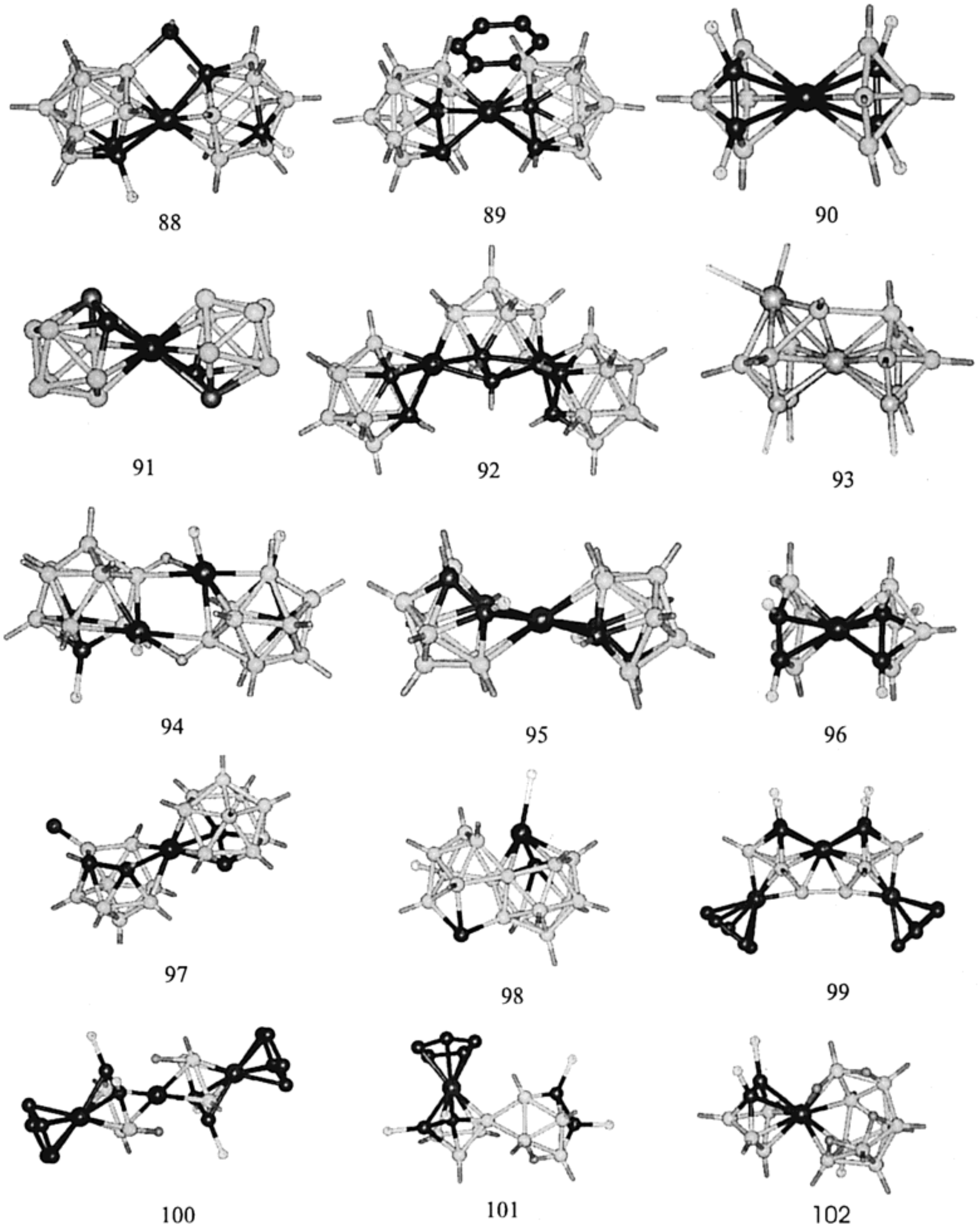
[a] α stands for the metal atom and γ for the dative bonds, the electron pair counts according to the rule and enumerated from the fragments are given by N and N', respectively, and x is the charge of the system.

each. Co donates 1.5 electron pairs, which makes a total of 25.5 electron pairs. This accounts for a charge of −1 for the complex.

Examples are known where some of the hydrogen atoms are replaced by substituents such as −Me, −Ph, −Br, −I, etc. However, this does not affect the electron count unless the bond is dative in nature.

$[C_4H_{22}B_{18}M]^n$ (**86**)*. Slipped Sandwich Complexes.* This distorted structure has a skeleton as shown. The structure chosen lacks the hydrogen atoms. It contains electron-rich metal ions with a d^8- or d^9-electronic configuration. The electron-rich nature of the metal atom and heterocyclic nature of the ligand are found to be the factors which influence the distortion from a symmetrical π sandwich complex to a slipped one. Upon distortion the metal−boron bonds shrink and the metal−carbon distances increase accordingly with a concomitant shortening in

Chart 7



88 89 90 91 92 93 94 95 96 97 98 99 100 101 102

the carborane C−C bond. These types of complexes are known with Ni^{2+}, Cu^{2+}, Cu^{3+}, and Au^{2+}. All of these slipped complexes have an excess electron pair than required by the *mno* rule.

*$[(N(C_2H_5)_3C_2B_9H_{10})_2Fe]$ (***87***)*. This exemplifies how a dative bond influences the skeletal electron count. Thus, the dianion complex of $Fe(C_2B_8H_{11})_2$ becomes neutral owing to the presence of two dative bonds that jointly contribute one electron pair to the cluster. Here, also the positions of the hydrogen atoms are not refined, and hence, the structure lacks them.

*$[(SEt)Co((Ph)(SEt)C_2B_9H_8)(PhC_2B_9H_9)]$ (***88***)*. Complexes are known where the two dicarbollide ligands are bridged by certain moieties such as OR, SR, NR_2, PR_2, etc. which together with the metal form a zwitterionic complex. One such structure is shown. Excluding the SR moiety, which bridges the two dicarbollide ligands, the complex should be anionic. The SEt fragment forms a dative bond with one of the atoms of the cluster, thus making the whole complex neutral.

*$[C_7H_{26}B_{18}Co]^-$ (***89***)*. The linkage can also be through $(CH_2)_n$ or a phenyl group. One such compound is illustrated here. This type of linkage does not affect the cluster electronic requirement, and the cobalt complex remains anionic.

*$[M(C_2R_2B_4H_4)_2]^n$ (***90***)*. In contrast to the icosahedral systems, the number of structures reported in simple transition-metal complexes of the form $[M(C_2R_2B_4H_4)_2]^n$ is quite limited: examples are known with Ni^{2+}, Ni^{4+}, Cr^{3+}, Cr^{4+}, Co^{3+}, Mn^{3+}, etc.[3b] As expected, the Ni^{2+} complex is a slipped sandwich type.[89]

*$[Co(B_7C_2H_9)_2]^-$ (***91***)*. The CSD structure lacks the hydrogen atoms as there were problems in refining the positions, and hence, the compound shown here reflects the same. Complexes with less than 12 vertexes and with a metal ion in common have also

been isolated. An example of this type with two nine-vertex $B_7C_2H_9$ clusters and a Co^{3+} metal ion sandwiched between them is shown. The *mno* count clearly indicates a *closo* form with 22 electron pairs ($n = 19$, $m = 2$, $o = 1$). The electron pairs contributed by 4 CH groups, 14 BH groups, and a Co^{3+} ion sum up to 21.5. The complex hence should be negatively charged and is found to be so.[228]

$[(C_2B_9H_{11})Co(C_2B_8H_{10})Co(C_2B_9H_{11})]^{2-}$ (**92**). This is an example of a complex in which more than two polyhedra are fused by a common vertex.[229] The compound has a bent structure. Here, $m = 3$, $n = 34$, and $o = 2$. The electron pair count of 39 (26 BH groups, 6 CH groups, 2 cobalt atoms) is in accord with the *mno* rule of a *closo* structure with a −2 charge. A system with four polyhedra has also been synthesized with the three-cage system fused with one more cluster through a cobalt ion.[230] The complex is trianionic and satisfies the electron pair requirement of the *mno* rule. The structure has yet to be established by X-ray crystallography.

$[CoFe(Me_4C_4B_8H_8)(PEt_3)_2]$ (**93**). This compound is a member of the so-called wedged complexes[23b] in which the wedged atom occupies a crevice between two carborane ligands. Here, $n = 14$, $m = 2$, $o = 1$, and $q = 1$. One BH group acts as a cap between the two polyhedra and contributes only one electron pair to the skeleton. Without this capping the complex would have been an electron-deficient complex. $Co(PEt_3)_2$ is isolobally related to CH_2^+ that in turn is related to BH^-, a four-electron donor by isoelectronic replacement. The complex as a whole obeys the *closo* electron count of *mno* and thus is in accord with predictions. Other examples are also known in which the cap or terminal BH is replaced by its isolobal fragments.[231]

$[Ni_2(CO)_2(Me_2C_2B_9H_9)_2]$ (**94**). This complex obeys the electron-counting rule with a typical 3c−2e fusion.[232] Though the Ni−Ni distance (2.744 Å) corresponds to a direct metal−metal interaction, it is within the range of applicability of the isolobal analogy.[103b] The two 3c−2e bonds which allow the fusion do not affect the cluster bonding. The electron pairs from 18 BH groups, 4 CR groups, and 2 d^{10}-ML fragments treated as a BH analogue are enumerated as 26. The *mno* rule ($m = 2$, $n = 24$) also predicts the same electron pair count for the stability of a *closo* pattern.

$[(C_3B_7H_9Me)_2M]$ (**95**). This type of compound is known with M = Ni, Pd, and Pt and is isoelectronic with $[(B_{11}H_{11})_2M]^{2-}$ (structure **82**), which has four bridging hydrogens. Here, the electronic requirement is met with six carbon atoms (three on each subcluster) instead of the four bridging hydrogens so that the complex is neutral. These complexes are *closo* with a slipped pattern since the total electron pairs of 25 (14 BH groups, 6 CH groups, and a Ni atom) exceeds the *mno* rule ($m = 2$, $n = 21$, $o = 1$).[233,234]

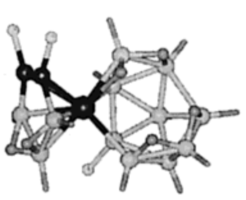
$[CpCoCp][Me_2C_2B_4H_3CoMe_2C_2B_3H_5]$ (**96**). This complex has a sandwich structure with Co^{3+} at the common vertex. One of the substituents on boron is a $[CpCoCp]^+$ group, which is abbreviated as L in the figure. Without this group the complex should possess a negative charge. A *closo* structure is uninegative by the *mno* rule. The requirement of an additional electron pair arising from the vacant site is satisfied by incorporating two bridging hydrogens at the open site, and the complex still remains anionic.[235] Thus, with $m = 2$, $n = 12$, $o = 1$, and $p = 1$ an electron pair count of 16 is obtained. By enumerating the electron pairs from the different groups (7 BH groups, 4 CR groups, 2 bridging hydrogens, a cobalt ion, and a uninegative charge), it is found to be in accord with the rule.

$[(B_9C_2H_{11})Co(B_8C_2H_{10})(C_5H_5N)]^-$ (**97**). Sandwich complexes of two dicarbollide ligands with a common metal ion have been studied in detail, and a plethora of them have been experimentally characterized. Open structures obtained from such complexes, although limited in number, are also well established. This complex is also among such complexes, which obey the *mno* rule. Here, the additional requirement due to the *nido* structure is met by a bridging hydrogen and a dative bond.[236] The dative bond with a boron atom is from a nitrogen of a pyridine ring. Since such substituents are very rare, the pyridine has been abbreviated as Py in the structure. The number of electron pairs from the 4 CH groups, 17 BH groups, a Co ion, one bridging hydrogen, and a dative bond contributing to the skeletal framework amounts to 25.5. The number of electron pairs from the *mno* rule for a *closo*−*nido* form is 26 ($n = 22$, $m = 2$, $o = 1$, $p = 1$). This requires a negative charge.

$[(PPh_3)NiS_2B_{16}H_{12}PPh_3]$ (**98**). An NBO analysis of the cluster shows that both sulfur atoms have one lone pair each, thus contributing the remaining two electron pairs for skeletal bonding. Further replacement of $Ni(PPh_3)$ by isolobal BH and allowing for the $BPPh_3$ dative bond give an electron pair count of 23, the rest from 13 BH groups and 3 shared boron atoms. This is equivalent to $n + m + 2$ ($n = 19$, $m = 2$, $p = 2$), which explains the bonding as a *closo*−*arachno* fusion with the three boron atoms in common.[237]

$Cp_2^*Co_3Me_4C_4B_8H_7$ (**99**). This example serves as one of the types where the adjacency of boron atoms of two subclusters causes an intercluster linkage. The mode of interaction is essentially a single-vertex condensation.[237] The complex has a B−B linkage between the two subclusters. All of the boron atoms except those two have terminal hydrogen atoms.[238] The structure has an ambiguity in the position of one extra hydrogen atom. The possibilities of a B−H−B bridge or a wedge atom bonding the metal were ruled out by spectroscopic studies. Considering the two Cp's also as a part of the skeleton, the values of m, n, o, and p are 4, 25, 3, and 2, respectively, which gives an electron pair count of 34. The evaluation of the number of electron pairs from 14 CH groups, 6 BH groups, 2 bare boron atoms, and 3 cobalt atoms is 34.5. One electron is extra, which has to be removed. This is possible only if the extra hydrogen is a terminal one. This supports the observation of seven terminal BH resonances from ^1H NMR spectra. The *mno* rule provides an additional proof for the fact that this extra hydrogen tautomerizes between the terminal positions of the two linked boron atoms.

Chart 8



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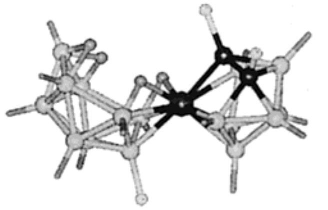

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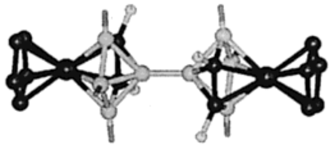

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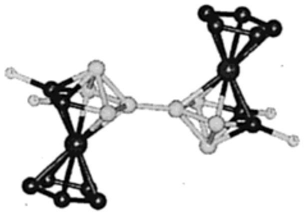

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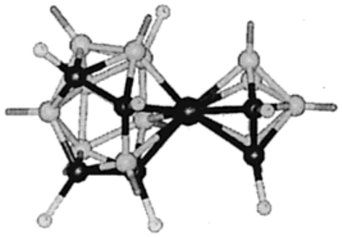

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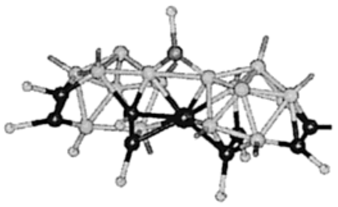

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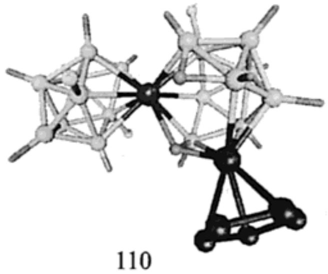

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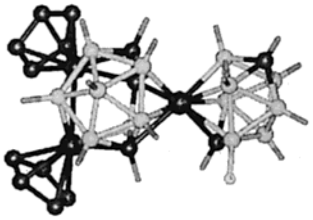

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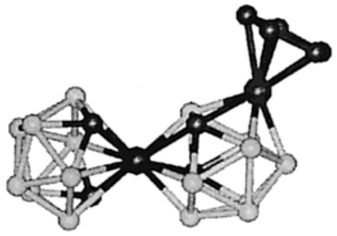

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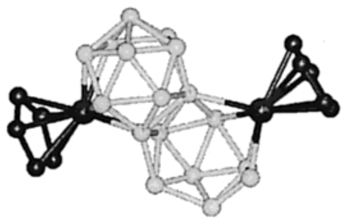

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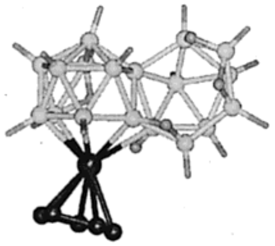

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[$Cp^*CoMe_2C_2B_3H_4$]$_2$Hg (**100**). The presence of the late transition metal mercury makes the complex one among the rare examples known. The two $Me_2C_2H_4B_3$-$CoCp^*$ groups are sandwiched by a Hg^{2+} metal ion. The Hg atom is at a low coordination site, donating only the two valence s-electrons to the cluster.[239] The complex requires two more electrons to exhibit a *closo* structure according to the *mno* rule. This is accomplished by the presence of two bridging hydrogen atoms at the available open faces where the metal to boron coordination is absent. Here, $n = 23$, $m = 4$, $o = 3$, and $p = 2$ considering the Cp ligands too as a part of the skeleton. Thus, the *mno* electron pair count is 32. This can be easily verified from the electron pair count contributed by 14 CH groups, 6 BH groups, 2 bridging hydrogens, 2 cobalts, and one mercury ion. The electron-counting rule treats the molecule as a *closo* structure at the mercury position, even though vacant sites appear to be present. This is similar to the pattern observed for aluminum sandwiched borane clusters. It indicates that the copper and zinc groups of the periodic table have more resemblance to main group elements in terms of polyhedral bonding.

[$CpCoMe_2C_2B_4H_3$][$Me_2C_2B_4H_5$] (**101**). Here, one of the edges of the six-vertex C_2B_4 unit is capped by a boron atom of the other cluster. Even though the two cages are joined by such a B−B−B 3c−2e bond, it is continuous with the macropolyhedron and does not form an isolated bond. This complex is the first structurally characterized example with this type of linkage.[240] The electrons in the 3c−2e bond affect the cluster bonding differently from structure **78**. The rule suggests an electron pair count of 24 ($m = 3$, $n = 18$, $o = 1$, $p = 2$) for stability. The skeletal electron pairs from various sources which include 7 BH groups, one boron atom, 9 CH groups, one bridging hydrogen, and a cobalt atom are enumerated to 24, and hence, the neutral complex obeys the electron-counting rule.

[($Et_2C_2B_4H_4$)Co($B_9H_{12}O(CH_2)_4$)] (**102**). The *nido* part of the compound is similar to $B_{10}H_{14}$ except for the

replacement of a B−H group by a cobalt atom. This in turn forms a *closo* polyhedron with the C_2B_4 fragment.[241] The rule predicts 20 electron pairs for the complex to be stable ($m = 2$, $n = 16$, $o = 1$, $p = 1$). The 13 BH groups, a dative bond, 2 CH groups, 4 bridging hydrogens, and a cobalt ion all donate their usual electrons to the cluster, thus making the neutral complex in perfect agreement with the rule.

*[($Me_2C_2B_3H_5$)Co($B_9H_{12}O(CH_2)_4$)] (***103***).* The skeleton is identical to the previous structure except that one of the BH vertexes from the *closo* form is absent.[241] Removal of the single vertex keeps the BMOs intact, and hence the structure still requires 20 electron pairs. The extra electrons have been obtained in the form of two bridging hydrogens on the new open face.

*[($Et_2C_2B_7H_7$)Co($B_9H_{12}O(CH_2)_4$)] (***104***).* This complex differs from those in the above two examples with respect to the position of the metal ion in the $B_{10}H_{14}$ unit. The other unit becomes a 10-vertex *closo* form. The structure is a single-vertex-condensed *closo*−*nido* framework.[241] Here, $m = 2$, $n = 19$, $o = 1$, and $p = 1$ according to the rule, and hence, the structure requires 23 skeletal electron pairs. This arises from the different groups BH (16), a dative bond (0.5), CH (3), 4-hydrogen bridge (2), and a cobalt ion (1.5).

*[($C_2B_5H_6$)($Cp_2Co_2C_2B_5H_6$)] (***105***).* This complex has a linked skeleton of two carboranes, among which one has two metals as vertexes.[242] The generalized electron-counting rule when applied to this structure suggests an electron pair count of 34 ($m = 4$, $n = 26$, $o = 2$, $p = 2$). This is achieved by the contribution of various fragments (10 BH groups, 14 CH groups, and 2 cobalt atoms) which make up the cluster.

*[Cp*Co($Et_2C_2B_4H_3$)]$_2$ (***106***,* ***107***).* This complex exists in two dimeric forms, **106** and **107**. **107** lacks the hydrogen atoms as they were not reported. Structure **106** has an apical linkage between the boron atoms of two units, and structure **107** has an equatorial linkage. These types of complexes readily undergo linking and stacking reactions and are of interest as routes to metal-containing chain polymers.[243] The number of electron pairs contributed by the fragments toward skeletal bonding amounts to 32. The electron pairs are provided by 8 BH groups that include 2 boron atoms with a 2c−2e bond between them and behave as isolated bonds not involved in cluster bonding, 14 CH groups, and 2 cobalt atoms. According to the rule, $m = 4$, $n = 24$, $o = 2$, and $p = 2$, and the structure should have 32 electron pairs. The complex is neutral as is consistent with the electron-counting scheme.

*[($Et_2C_2B_4H_4$)Co($Et_4C_4B_8H_7OC_4H_8$)] (***108***).* A *nido* 13-vertex cluster is fused through a cobalt ion to a *closo* 7-vertex cluster.[244] According to the *mno* rule, $m = 2$, $n = 19$, $o = 1$, and $p = 1$, and the structure requires 23 electron pairs for skeletal bonding. There are 12 BH groups, a dative bond, 6 CH groups, and a cobalt ion that provide the required electron pairs and thus enable the complex to obey the *mno* rule.

*[($Et_4C_4B_8H_7$)$_2$($COMe_2$)$_2$Co] (***109***).* This complex has two *nido* clusters joined through a cobalt ion. In addition, the two carborane ligands are bridged through a O=CMe_2 group. All boron atoms except the two which are bridged have either terminal hydrogens or $COMe_2$ as a substituent. The bridged B−B distance of 2.259 Å avoids any possibility of a multicenter bonding among B−O−B.[245] Thus, the compound has 16 BH groups, 8 CH groups, which provide 12 electron pairs, and a cobalt ion contributing 1.5 electron pairs. Summing up all these electron pairs gives 29.5 and urges for one more electron as the skeletal electron pair count by the rule is 30 electron pairs for a *closo* system ($m = 2$, $n = 25$, $o = 1$, $p = 2$). This additional electron is made available by the hydrogen atom, most probably a bridging one, which was not located in the X-ray study.

*[Cp*RhB_9(SMe_2)H_{10}RhB_9H_7(SMe_2)$_2$] (***110***).* This compound consists of a *closo*-B_9Rh unit conjoined through the rhodium atom to an open RhB_9 unit.[246] Considering the Cp ligand as part of the cluster, the total electronic requirement is 32 electron pairs ($n = 25$, $m = 3$, $o = 2$, $p = 2$). However, the number of electron pairs obtained by the skeletal fragments is only 31 (18 BH groups, 5 CH units, 2 bridging hydrogens, 3 dative bonds, and 2 rhodium atoms). The open part is found to have some *isonido* characteristic. There is theoretical interest in *isocloso* species, which have been manifested in 10- and 11-vertex systems.[247] A $B_{11}H_{11}^{2-}$ model species is fluxional, implying alternative open structures of very similar energy.[172] The transformation from a normal species to an *isocloso* one converts a spherical deltahedron to a polar deltahedron so that when it is distorted a π-orbital and a π^*-orbital become approximately nonbonding. According to the MO pattern, it requires one electron pair less.[248] When this concept is extended to macropolyhedral systems, the present complex belongs to such iso species, where it has a *closo* count but topologically it is a *nido* species. We are carrying out more systematic studies on these types of complexes.

*[($C_3B_7H_{10}$($CoCp$)$_2$)Co($C_2B_7H_8$(CH_2CH_2CN))] (***111***).* This complex contains three cobalt atoms, three CH groups, and seven BH groups in the primary cluster with one of the cobalts sharing a ten-vertex cage containing two carbon atoms and seven boron atoms.[249] The electron pair count for stability is 41 ($m = 4$, $n = 32$, $o = 3$, $p = 2$) when the Cp ligands are also considered. This has been attained from 14 BH groups, 15 CH groups, and 3 cobalt atoms, making the complex neutral.

*[($C_2B_8H_{10}$)Co($C_2B_8H_{10}$CoCp)]$^-$ (***112***).* The hydrogen atoms are not present in the structure shown here, as their positions were not assigned by X-ray studies. The shared cobalt atom is coordinated in an η^6-fashion to one of the subclusters. The complex has one open face at the Cp ligand. The rule suggests 33 skeletal electron pairs for stability ($m = 3$, $n = 27$, $o = 2$, $p = 1$). The electronic requirement is satisfied by 16 BH groups, 9 CH groups, and 2 cobalt atoms, which sum to 32.5 so that this species is a uninegative anion.[250]

[Cp$_2$Rh$_2$$B_{17}H_{19}$] (***113***).* During the synthesis of the complex [Cp_2*$Rh_2B_{17}H_{19}$] an isomerization from *n*-$B_{18}H_{22}$ to iso-$B_{18}H_{22}$ was observed by Fontaine et al.[251] They proposed that the process involved the insertion of a metal vertex into one edge of a *n*-B_{18} framework followed by elimination of a BH unit on

Chart 9

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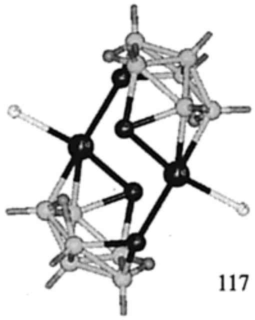

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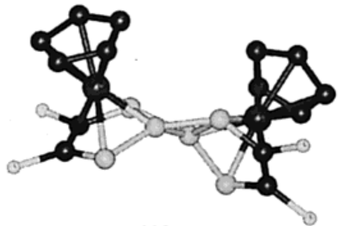

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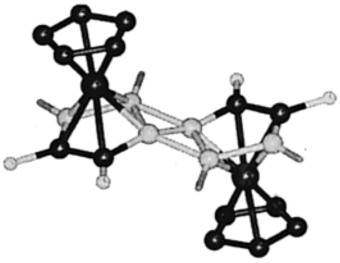

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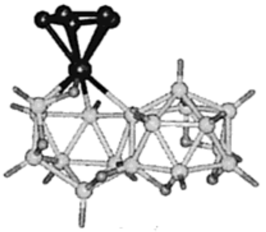

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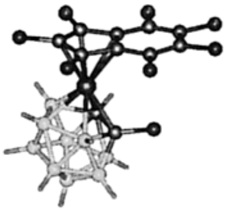

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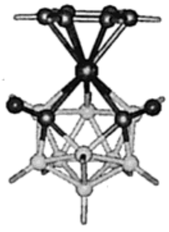

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the opposite side of the same cage. In addition, the insertion process converts an edge-fused structure into a face-fused structure. When the structure is subjected to the *mno* rule, the Cp ligand is also considered a part of the cluster. It requires 39 electron pairs for stability according to the *mno* rule taking into account 4 *nido* structures ($m = 4$, $n = 29$, $o = 2$, $p = 4$). The complex has 5 bridging hydrogen atoms, 14 BH groups, 3 boron atoms, 10 CH groups, and 2 rhodium atoms, which enable it to attain the *mno* count and thus be neutral. Though the structure does not show the hydrogen atoms as the CSD structure was devoid of hydrogens, their positions were assigned on the basis of the electron-counting rule.

*[Cp*IrB$_{18}$H$_{20}$] (***114***).* The metal is treated as part of the three subclusters including the Cp ligand. There are five bridging hydrogen atoms, one of them between iridium and the shared boron atom. Three boron atoms are at shared positions. The *mno* rule suggests an electronic requirement of 31 electron pairs ($n = 24$, $m = 3$, $o = 1$, $p = 3$) for the stability of the compound. They are obtained from 15 BH groups, 3 boron atoms, 5 bridging hydrogens, 5 CH groups, and an iridium atom. Thus, the borane part is said to be a *nido*−*nido* macropolyhedral skeleton fused with a triangular face in common.[252]

*[Cp*IrB$_{18}$H$_{19}$S]$^-$ (***115***).* An additional vertex in the form of a sulfur atom increases the number of vertexes and hence the electronic requirement by one compared to the earlier compound. As mentioned before sulfur is a four-electron donor. The two bridging hydrogen atoms and two shared boron atoms contribute a total of 3.5 electron pairs. The electron pairs provided by 5 CH groups and 16 BH fragments were also considered, which gave a total of 31.5. Geometrical considerations predict a *nido*−*nido* cluster fused through an edge. Thirty-two electron pairs are required ($n = 25$, $m = 3$, $o = 1$, $p = 3$) according to the rule. The compound should have a −1 charge, which is consistent with experiment.[252]

[$Cp^*_2Rh_2S_2B_{15}H_{14}(OH)$] (**116**). This compound consists of two bridging hydrogen atoms and two shared B atoms. The two rhodium atoms are common to a Cp ligand and the macropolyhedral borane. With this structure the number of electron pairs contributed to the skeletal bonding is 39. The number of vertexes is 29 (n), the number of clusters (m) involved in condensation is 4, and the number of vertex-shared atoms (o) is 2. An electron pair count of 39 is equivalent to a skeleton with 4 open faces. The predicted structure is thus a *nido*-$Cp^*RhSB_9H_8(OH)$ 11-vertex cluster fused by an edge with a *nido* 10-vertex cluster, $Cp^*RhSB_8H_7$.[253]

[$Pd(PPh_3)S_2B_6H_8]_2$ (**117**). This is the first metallathiaborane[102] containing sulfur atoms that bond simultaneously as a cluster atom and as a two-electron donor to the metal atom in other cluster cages.[254] The structure can be considered as two *nido* units bridged by two metal fragments and two sulfur atoms. One shared atom does not bond to the other of its type. $S_3Pd_2B_6H_8$ forms one *nido* unit in which the lone pairs of two of the sulfur atoms are at the shared position. The structure is in accord with the *mno* rule, where the number of single-vertex condensations (o) is four. The sulfur atoms at the nonshared position behave as a BH^{2-} fragment, and the shared sulfur atoms donate all of their valence electrons. Pd-(PPh_3) was treated as a BH by isolobal arguments. In addition, four bridging hydrogen atoms contribute to the skeletal bonding. The electron pair count of 26 is also derived from $n + m + o + 2$ ($n = 18$, $m = 2$, $o = 4$, $p = 2$), which corresponds to two open faces.

[$Cp^*Co(Et_2C_2B_3H_4)]_2$ (**118**). This complex involves an intercluster 3c−2e linkage.[243] This complex is similar to structure **101** in which the multicenter bonding influences the skeletal framework. It has 32 skeletal electron pairs enumerated from the fragments (5 BH groups, one boron atom, 14 CH groups, 2 cobalt atoms, and 3 hydrogen bridges), which is in accordance with the *mno* rule ($m = 4$, $n = 22$, $o = 2$, $p = 4$), and therefore, the complex is neutral.

[$Cp^*Co(Et_2C_2B_3H_3)]_2$ (**119**, **120**). Structures **119** and **120** are the two isomeric forms. The first one is a bent complex owing to the steric interactions between the Cp ligands. When the Cp ligands are made *trans* to each other in **120**, the complex becomes planar. In both cases $m = 4$, $n = 22$, $o = 2$, and $p = 4$ leading to a requirement of 32 skeletal electron pairs. The 4 BH groups (4 electron pairs), 2 boron atoms (3 electron pairs), 14 CH groups (21 electron pairs), 2 cobalt ions (3 electron pairs), and 2 hydrogen bridges (one electron pair) make a total of 32 electron pairs, thus making the complex neutral.[255]

[$CpCoB_{17}H_{21}$] (**121**). This complex is a product of the reaction of metal vapor with cyclopentadiene and n-$B_{18}H_{22}$.[256] However, the structure is derived from an iso-$B_{18}H_{22}$ framework as in the case during the synthesis of $Cp_2^*Rh_2B_{17}H_{19}$ (**113**).[251] Here, the edge fusion is maintained in the reaction. According to the electron-counting rule $m = 3$, $n = 23$, $o = 1$, and $p = 3$, leading to 30 skeletal electron pairs. The 15 BH groups, 2 shared boron atoms, 6 bridging hydrogens, a cobalt atom, and 5 CH groups contribute to the stable electron count. Thus, the complex is an edge-shared system with three open faces including the Cp ligand as part of the cluster.

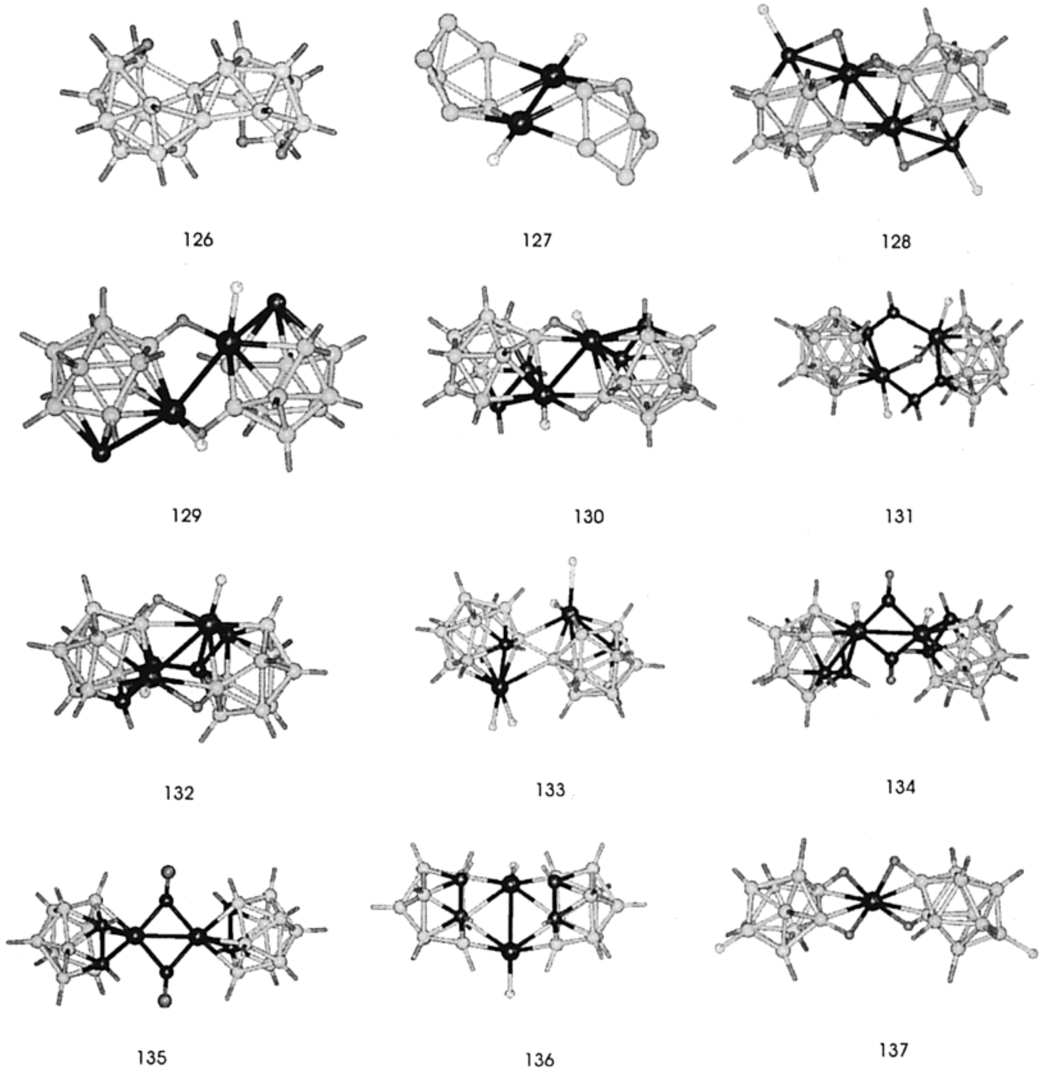
[$Cp^*RhC_5Et_5BMeCoB_4H_4$] (**122**). The mismatch between a bridged atom and the ring size is seen in simple multidecker sandwiches in which a single five-membered ring bridges two metals. They are known with a range of electronic requirements including the ones dictated by the *mno* rule. When the shared metal is of smaller size, there are the usual nonbonding interactions mentioned earlier. If the metal atom is of bigger size, there is a tendency toward metal−metal bond formation. Both of these factors introduce additional interactions than what is considered in the formulation of the *mno* rule. Molecules with the *mno* electron count as in the example [$C_{23}H_{42}B_6CoRh$][257] (structure **122**) and with less and more electrons are known. The requirement of 24 electron pairs is met with the components of the polyhedral cluster.

[$Cp^*_3Ir_3B_{18}H_{15}(OH)$] (**123**). This compound is essentially a triangular fused system. The synthesis of this structure is part of the interest in exploring the new area of *megalo*-boranes. The tetrahedral core formation is not complete here, even though there is a slight interaction between the metal and boron atoms (2.6433 Å).[258] This is true whenever attempts are made to create a tetrahedron by means of a metal atom. Structure **71** is one such case. As pointed out earlier, the electron count of these systems is very much dependent upon these intercluster interactions, which complete a tetrahedron. The reasons for these differences are under detailed investigation by our group. Thus, the additional tetrahedral core does not alter the electronic requirement, and the compound has only two primary subclusters. Considering the Cp ligands, there are a total of five subunits. The number of vertexes is 36, and $p = 3$. Hence, the number of electron pairs required by the molecule is 44. The complex has 15 BH groups, 3 boron atoms, 15 CH units, and 3 iridium atoms, providing 46.5 electron pairs. An additional electronic requirement is met with a hydrogen, claimed to be bridging the two iridium atoms, though not located in the X-ray structure.

[$(C_9Me_7)RhPhC_2B_9H_{10}$] (**124**). This is a representative example of a compound where there is only one polyhedral borane system and the remaining one or more subunits are a hydrocarbon part. In this particular example a C_2B_9 unit is condensed to a hydrocarbon part through a rhodium atom. The hydrocarbon is in turn an edge-shared system.[259] Here, without any partitioning, we can consider the whole molecule as a delocalized skeleton. Thus, $n = 21$, $m = 3$, $o = 1$, and $p = 3$, and hence, the molecule requires 28 electron pairs. There are 9 BH groups, 9 CR groups (R=H, Ph), 2 shared carbons, which donate all their electrons, and a rhodium atom contributing 3 electrons, making the electron count 28 electron pairs.

In this category, one more type of structure, which is noteworthy, is one where the hydrocarbon part includes pyridine or pyrimidine units, resulting in a donor−acceptor kind of compound.[260] Here, the borane unit is capped by atoms such as tin, lead,

Chart 10



germanium, etc., which accept the electron pair from nitrogen atoms of the pyrimidine unit. In pericondensed benzenoid systems with more than three rings, Hüuckel's $4n + 2$ rule breaks down. A similar effect is observed here when the hydrocarbon part has more than three rings. Such examples disobey the *mno* rule as well, whereas others satisfy the electron count. As they are essentially monopolyhedral as far as the borane unit is concerned, they are not discussed in detail.

[(C_6H_6)Ru$C_2Ph_2B_9H_9$] (**125**). This structure is a token example of so-called pseudo-*closo* compounds.[261] The bulky substituents on the carbon atoms impart a steric hindrance on the polyhedron and cleave the C−C bond in the C_2B_9 unit. This essentially brings the boron atom neighboring the two carbons closer to the metal to alleviate the electron deficiency. The structure has $n = 18$, $m = 2$, $o = 1$, and $p = 1$ and requires 22 electron pairs. The 9 BH groups, 8 CR groups, and a Ru atom contribute a total of 22 electron pairs, thus satisfying the *mno* electron count.[261a]

E. Ambiguous Structures

The structures discussed in this section include those whose number of skeletal electron pairs does not match the electronic requirement predicted by the *mno* rule. Owing to the variable nature of transition metals, there is always a chance for metallaboranes to disobey the rule. Only one pure borane cluster is classified as disobedient, but is found to be unstable by theoretical studies. The rest of the section involves metallaboranes. Even though there is an alternative way to perceive the molecule, there are many ambiguities which need to be resolved. The direct metal−metal interactions and the occupancy of the metal at a shared site of *exo* polyhedral connections are found to be the major factors which cause the molecule to deviate from the rule.

$B_{19}H_{20}^-$ (**126**). As per the *mno* rule, this structure requires ($n = 19$, $m = 2$, $p = 2$) $19 + 2 + 2 = 23$ electron pairs, taking into account the two *nido* fragments. However, $B_{19}H_{20}$ is reported[262] to be a monoanion having $17 + 3 + 2\ (3H + e^-) = 22$ electron pairs. The number of hydrogens was assumed to be 20, and their initial positions were generated from the skeletal geometry for the X-ray structure analysis. During the refinement of diffraction data, the number of hydrogens was unaltered as there were no bonding considerations to do so. This was despite the compelling experimental observation from the

MALDI mass spectra of the ions, which showed two additional mass units consistently.

We have calculated the energy levels at the extended Hückel and B3LYP/6-31G* levels[263] and found all indications for the reported $B_{19}H_{20}$ to be a stable species only as a trianion.[264] Frequency calculations at the same level characterized the structure $B_{19}H_{20}^{3-}$ as a minimum on the potential energy surface. But the same structure with -1 charge failed to converge. The formulation presented for $B_{19}H_{20}^{-}$ requires two additional electrons, and hence, most likely the structure has two additional bridging hydrogens as observed mass spectrometrically.

[Pt(B₆H₉)₂(PMe₂Ph)₂] (**127**). The conclusions from NMR spectroscopy, regarding the position of the hydrogen atoms,[265] indicate that each subcluster has three bridging hydrogen atoms in addition to the terminal hydrogen atoms. The M−L fragment being at a shared position is equated to a B^- unit, i.e., a four-electron donor. The number of electron pairs contributed to the skeletal bonding is calculated to be 19. This corresponds to $n + m + 3$ ($n = 14$, $m = 2$, $p = 3$), i.e., a structure with three open faces. But the topology clearly shows a *nido*−*nido* arrangement and requires only 18 electron pairs for stability ($14 + 2 + 2 = 18$). So there is one extra electron pair than what is predicted by the electron-counting rule, and that is actually taken care of by the metal−metal bond at the shared position. The overall structure can be related to the hypothetical isomer of neutral $B_{14}H_{20}$ with C_2 symmetry.

[HFe(MeSiB₁₀H₁₀)]₂²⁻ (**128**). This compound can be perceived in two ways. One method is to take the complex as two subclusters that are linked by more than one 3c−2e bond. Such a model requires ($n = 24$, $m = 2$) 26 electron pairs. There are 20 BH groups, 2 SiMe fragments, 2 Fe atoms (which contribute one electron pair each), and 2 cluster hydrogens, which bridge Fe and Si of each cluster. The other bridging hydrogens are considered to be a part of an external 3c−2e bond, which does not affect the cluster bonding. Enumeration of the electron pairs considering the negative charges leads to 27. As we have described earlier, the presence of metal−metal bonds seems to localize one bond pair so that subtracting one gives 26 skeletal electron pairs.

An alternate explanation is by considering the molecule as consisting of four polyhedra. The two FeB_2 triangles form a trigonal antiprism and can be treated as a new polyhedron.[266] The M−M bond splits it into two tetrahedra. The electronic requirement becomes 30 electron pairs ($m = 4$, $n = 24$, $p = 2$). The 16 BH groups (16), 4 boron atoms (6), 2 SiMe groups (3), 2 Fe atoms (2), and 6 bridging hydrogens (3) contribute 30 electron pairs for cluster bonding. The two negative charges make a total of 31 electron pairs. When one electron pair is assigned to the M−M bond, the molecule is left with 30 electron pairs, which is actually the amount required for skeletal bonding by the *mno* rule.

[(PPh₃)RhTeB₁₀H₁₀]₂ (**129**). This complex has two *closo* units joined through two bridging hydrogens.[267] The number of electron pairs expected from the constituent fragments is 26 ($m = 2$, $n = 24$). The 20 BH groups, 2 tellurium atoms, which are essentially 4-electron donors, and 2 d^9-ML fragments together contribute only 25 electron pairs. Most of the macropolyhedral metallaboranes with only a few exceptions, which have either a σ-link or a multicenter bonding, are found short of one electron pair.

[(CO)Co(C₂B₉H₁₁)]₂ (**130**). This complex is similar to the previous example by its structure. Here, the two tellurium atoms and two boron atoms have been replaced by four carbon atoms,[268] thus making it isoelectronic with the above structure. The complex requires 26 electron pairs ($m = 2$, $n = 24$). The 18 BH groups contribute one electron pair each, and the 4 CH groups contribute 3 electron pairs each. The d^9-ML fragment behaves as a BH^+ unit. All these sum to 25 electron pairs. Hence, this too is found short of one electron pair of what is required by the electron-counting rule.

[(PPh₃)Rh(NH₂)CB₁₀H₁₀]₂⁻ (**131**). This compound consists of two polyhedra bridged through two NH_2 moieties and a hydrogen atom.[269] The rule indicates 26 skeletal electron pairs ($m = 2$, $n = 24$). However, the number of electron pairs contributed from 20 BH groups (20), 2 CH groups (3) (the terminal hydrogen is replaced by a NH_2 moiety, which forms a dative bond with the carbon atom), 2 dative bonds (1), 2 d^9-ML fragments (1), and a negative charge sum to 25.5 electron pairs. However, the hydrogen bridge between two rhodium atoms takes an electron from one of the rhodium atoms to form the 3c−2e bond. This leaves the metal with only one skeletal electron. So only 25 cluster electron pairs are left, which is in disagreement with the predictions.

[(PEt₃)RhC₂B₉H₁₀]₂ (**132**). When two clusters are brought together with one triangular face from each facing each other, the *exo* polyhedral interactions which result are exemplified by this system. Such interactions are more in this case as the occupying atoms also involve transition metals. The two clusters are joined by two types of bonds, namely, two 3c−2e bonds and two 2c−2e bonds.[270] A carbon atom of one cluster is bonded to the same of the other by a 2c−2e bond, and there is also a metal−metal bond. There are 3c−2e bonds formed among B−H−Rh. The electrons involved in these bonds seem to be localized without participating in the cluster bonding. Excluding these electrons and calculating the number of electron pairs from different fragments gives a value of 25 (18 BH groups, 4 CH groups, and 2 d^9-ML fragments). A d^9-ML fragment is treated as a BH^+ fragment. The electron pair count for a *closo* form ($m = 2$, $n = 24$) is 26 electron pairs according to the *mno* rule. So there is a shortage of one electron pair for the complex.

[Pt₂(CB₁₀H₁₀)₂] (**133**). Condensed metallaboranes fused by *exo* polyhedral interactions are not well understood when the metal occupies the interacting site. In parent boron hydrides the influence of σ-links to cluster bonding is well characterized. In such complexes it is clear that the electrons in the multicenter bonding are involved in skeletal bonding. However, in metallaboranes it appears as though they are separate entities.[271]

According to the electron-counting rule the molecule needs 26 electron pairs for stability. If the multicenter bonding is considered as participating in the cluster bonding, the electron pair comes to 28. However, if the two electron pairs in the two 3c−2e bonds are isolated, the electron pair count matches what is required. Here, the d^{10}-ML_2 fragment is treated as BH^{2-} by the isolobal analogy followed by isoelectronic replacement rather than as BH.

The similarity of the d^{10}-ML_2 to BH is based on the direct isolobal analogy or Wade's rule. If it has to be treated as a BH fragment, the multicenter bonding involves only two electrons. However, such types of bonding are not well established.

*$[B_9C_2H_{11}Fe(CO)]_2^{2-}$ (**134**).* This complex is more similar to the organometallic complex $[Cp_2Fe_2(CO)_4]$.[272] Here, the cyclopentadienyl ligand has been replaced by the dicarbollide ligand. This structure establishes the equivalence between a cyclopentadiene ligand and a dicarbollide ligand. Both are six-electron donors. This along with the terminal and bridging carbonyls and the metal−metal bond enables the metal to attain the 18-electron rule.[273]

*$[B_9C_2H_{10}(PPh_3)Ni(CO)]_2$ (**135**).* This complex[274] is analogous to the previous example (**130**). Nickel−cyclopentadienyl complexes are known where there are no terminal carbonyls.[275]

*$[(C_2B_9H_{11})ZnNMe_3]_2$ (**136**).* The topology suggests the complex to be a single cluster with three vertexes being depleted.[276] With this consideration, the electron-counting rule suggests an electronic requirement of 28 skeletal electron pairs ($m = 1$, $n = 24$, $p = 3$). The number of electron pairs enumerated from the various fragments amounts to 26 by treating the Zn−L fragment as a BH analogue and excluding four B−H−Zn interactions. The electron pairs are not sufficient according to the rule. If the hydrogen bridges are taken into account, the electron pair requirement is exceeded by two. By following the argument that the removal of two or more vertexes from adjacent sites has an adverse effect than what Wade's rule has established, the electron pair count falls to 26 ($m = 1$, $n = 24$, $p = 1$). The first enumerated electron count works with this, but the second does not. Obviously there are ambiguities. As suggested by Wade, a detailed electronic structure study is warranted.

*$[(B_{10}H_9N_2)_2Cu]^-$ (**137**).* This complex has to be differentiated from the usual single-vertex condensation. Here, the copper atom just caps one of the edges on each borane ligand.[277] With this concept of bonding, the molecule requires ($n = 21$, $m = 2$, $q = 1$, $n + m - q$) 22 electron pairs for cluster bonding. There are 20 BH groups, 2 dative bonds, and a copper atom providing one electron, and the complex is uninegative to attain the stable electron pair count.

Even though this concept explains the bonding exhibited by this particular molecule, there cannot be any well-defined explanations as long as the area of late-transition-metal boron chemistry, especially those involving the copper and zinc groups, remains unexplored.

VII. Summary

In this review, a retrospective look at the evolution of electron-counting rules is made in pursuit of understanding the nature of bonding in macropolyhedral boranes. The pioneering work of many scientists, especially Lipscomb, Wade, and Mingos, in polyhedral boranes helped us in our analysis. Each of these electron-counting rules adopts a particular perspective in its attempt to account for the electronic requirements, its central concern being the recognition that the concerned domain will have a majority of molecules obeying the rules, which will provide the chemist with a handy tool for explorative research. Exceptions do occur to varying degrees. However, if the electron-counting rule is deduced from or substantiated by a mathematical model, it is possible to account for these exceptions. This enhances the understanding of the root motifs and paves the way for further research.

Though polyhedral boranes have been known for a long time, a definitive characterization of their bonding is hindered by the complexity of their bonding patterns. In addition, the isolation of individual molecules was the result of arduous work of many groups and has not followed any logical order. This delayed the birth of a generalized view. In the case of aromatic hydrocarbons, the symmetric and most stable benzene was well characterized both experimentally and theoretically by Hückel's molecular orbital model, resulting in the $4n + 2$ rule followed by the annulenes and polycyclic systems. But, in polyhedral boranes, the less symmetric structures such as B_4H_{10}, B_5H_9, B_5H_{11}, $B_{10}H_{14}$, etc., were isolated almost 50 years before the experimental characterization of the more symmetric and highly stable *closo*-boranes such as $B_{12}H_{12}^{2-}$ and $B_{10}H_{10}^{2-}$. Wade's rule was constructed on the basis of empirical findings only after the characterization of these structures. It took another decade to have a definite spherical tensor harmonics model to unambiguously justify the empirical Wade's rules. The spherical tensor harmonics model also successfully characterized the intrinsic exceptions, distinguishing them from coincidental exceptions that arise exclusively from *exo* substituents. Though major questions have been solved effectively in monopolyhedral systems, significant observations were made even in the past decade as evidenced from the results of Burdett et al., which removes the ambiguities in discriminating between *nido* and *arachno* isomers while Wade's $n + 1$ rule is applied. Owing to these complications in the monopolyhedral systems, the macropolyhedral boranes, although known from the 1960s, were not given serious attention until recently. As Mingos had successfully deduced the electronic requirements of condensed transition-metal clusters through the polyhedral skeletal electron pair theory, it is tempting to extend the rule for macropolyhedral boranes. Unfortunately, the parallelism between transition-metal clusters and polyhedral boranes ends with monopolyhedral systems. Macropolyhedral boranes exhibit a wide variety of interaction patterns between individual clusters. Attempts have been made to extend Mingos' approach for a class of macropolyhedral boranes having one, two, and three shared vertexes. However, the analysis shows that it is necessary to use different numbers for different shared systems to justify the empirical findings. For example, the expression for one-, two-, and three-vertex-sharing clusters requires the subtraction of the values 4, 12, and 18, respectively, with no explicit reason for these numbers. Teo's topological approach also suffers from the same drawback of lacking generality in the sense that the different types of interactions require distinct expressions. We have found that extending the peripheral part of the model used for Wade's rule and at the same time maintaining several of its main ideas, a generalized electron-counting scheme can be developed. The *mno* rule, which gives a general expression with a few easily perceivable variables (i.e., $F(e) = m + n + o$, where n = the number of vertexes, m = the number of individual cages, and o = the number of vertex-sharing fusions), is rather intuitive in modeling all the different kinds of interactions observed in the domain of macropolyhedral boranes. This rule reduces to Wade's rule along with all its ramifications in the case of monopolyhedral systems and Hückel's $4n + 2$ rule in the case of polycyclic aromatic hydrocarbons. This facilitates a global view between these two heavily dovetailing classes of delocalized systems. It is also possible to account for all of the ramifications of monopolyhedral systems without any additional principles since the presence of capping and stuffed vertexes as well as the absence of skeletal vertexes in a *closo* macropolyhedral skeleton, like its mono counterpart, seldom alters the electronic requirements. The clear MO theoretical origins for these variables are given using the classical molecular description employed for monopolyhedral systems, for all possible modes of interactions which explain the working principle of the *mno* rule. In both the *exo* polyhedral interactions and the single-vertex-sharing interactions, the numbers of bonding molecular orbitals required for stability are the sums of the number of MOs of individual cages. However, if more than one vertex is shared, each cage requires a separate radial bonding molecular orbital. But the number of surface bonding molecular orbitals formed from the tangential atomic orbitals is equal to the number of vertexes in these polyhedral systems.

Like all other electron-counting rules, the *mno* rule has two phases. The estimation of m, n, o, and other parameters so that the total number of skeletal electron pairs required can be evaluated forms the first step. The next part is to sort out the nature of interactions between the individual clusters. Interactions that involve the sharing of two or more atoms do not involve the variable o and are straightforward. If the interaction involves the sharing of a single vertex, then care has to be taken in determining whether it really involves the sharing of an atom or a capping interaction. The easiest guiding principle in deciding about o is to rely on the size of the atom. If the size of the shared atom is big enough to avoid antibonding interactions between the vertexes on either side of the shared vertex, then o has to be introduced. If the central atom is a main block element, sometimes owing to its propensity to satisfy the octet rule, it forms fewer bonds than expected for a *closo* skeleton, forming pseudo open faces. Care should be taken not to confuse these pseudo open faces as they show electronic requirements of a *closo* skeleton. However, transition-metal sandwiched macropolyhedral systems, owing to their prevalent tendency to exhibit multiple oxidation states, sometimes accommodate more electrons than is necessary for polyhedral bonding. These extra electrons occupy the molecular orbitals that are antibonding between the central atom and its neighbors, which results in "slipping". This reduces the magnitude of these destabilizing interactions. If the central atom is boron itself, it is very likely a capping interaction in which a boron atom of one of the cages caps an edge or face of the other cage. However, in such cases o should not be used. This is well exemplified by molecules such as $B_{14}H_{22}$ and $B_{15}H_{23}$. In the case of *exo* polyhedral interactions, where the vertexes of each cluster are not shared, it is necessary to sort out the presence of localized 2c−2e or 3c−2e bonds. We employ a rather contrived distinction between polyhedral bonding and localized bonds that aids in the counting process. The innate difficulty of perceiving the localized bonds is unavoidable since it arises from the inherent nature of MO theory itself, on which the *mno* rule is framed. Finally, in this phase, care should be taken in estimating the number of missing vertexes in the open faces. Some faces may appear to lack more than one vertex, but electronically they correspond to *nido* systems owing to the proximity effect where only one vertex is supposed to be absent.

The second and relatively easy phase of the application of the rule is the actual estimation of the number of electrons contributed by the individual fragments to the polyhedral bonding. In the case of macropolyhedral systems involving only main block elements, it is fairly straightforward. All of the electrons in the element except one *exo* polyhedral bond or a lone pair contribute to the skeletal bonding. The presence of *exo* dative bonds forces the element to contribute all its electrons for skeletal bonding. In the transition-metal-containing macropolyhedral systems, the number of electrons donated by the transition-metal fragment should be evaluated by replacing it with the isolobal main block element. If two or more transition metals are present in adjacent positions, one more electron pair is found to be necessary exclusively for metal−metal bonding. This additional requirement of electrons is found to vary with respect to the bond length, and at longer distances these exceptions disappear.

Icosahedral B_{12} units are known to be fundamental building blocks for elemental boron and many boron-rich solids, but $B_{12}H_{12}^{2-}$ eluded synthesis for a long time despite its higher stability. Similarly, many macropolyhedral skeletons such as face-sharing icosahedra (twinned icosahedra) are found to be present in the polymorphs of elemental boron, though the corresponding borane so far has not been characterized experimentally. We hope that the present review will provide the framework to design logical experiments to arrive systematically at the innumerable varieties of macropolyhedral systems, and to characterize unambiguously their structure and bonding.

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