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A Unifying Electron-Counting Rule for Macropolyhedral Boranes, Metallaboranes, and Metallocenes

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Abstract: A generally applicable electron-counting rule—the *mno* rule—that integrates macropolyhedral boranes, metallaboranes, and metallocenes and any combination thereof is presented. According to this rule, $m + n + o$ number of electron pairs are necessary for a macropolyhedral system to be stable. Here, m is the number of polyhedra, n is the number of vertices, and o is the number of single-vertex-sharing condensations. For *nido* and *arachno* arrangements, one and two additional pairs of electrons are required. Wade's $n + 1$ rule is a special case of the *mno* rule, where $m = 1$ and $o = 0$. $B_{20}H_{16}$, for example has $m = 2$ and $n = 20$, leading to 22 electron pairs. Ferrocene, with two *nido* polyhedral fragments, has $m = 2$, $n = 11$, and $o = 1$, making the total $2 + 11 + 1 + 2 = 16$. The generality of the *mno* rule is demonstrated by applying it to a variety of known macropolyhedral boranes and heteroboranes. We also enumerate the various pathways for condensation by taking icosahedral B_{12} as the model. The origin of the *mno* rule is explored by using fragment molecular orbitals. This clearly shows that the number of skeletal bonding molecular orbitals of two polyhedral fragments remains unaltered during exohedral interactions. This is true even when a single vertex is shared, provided the common vertex is large enough to avoid nonbonding interactions of adjacent vertices on either side. But the presence of more than one common vertex results in the sharing of surface orbitals thereby, reducing the electronic requirements.

Introduction

Polyhedral boranes have provided excitement in all branches of chemistry.[1] Aesthetically pleasing structures, pathbreaking bonding characteristics, unusual physiochemical properties, promising materials for the future, boron neutron capture therapy,[1e] membrane-specific spherical structures,[1f] templates for catalysis[1g]—the range of areas spanned by boranes is indeed vast.[1] In recent years there have also been attempts to merge another thriving area, viz., organometallics, with boranes through the intermediacy of metallaboranes and metallocenes.[2] A generally applicable electron-counting rule should help in this process. We provide here such a generalization that brings polyhedral boranes, polycondensed polyhedral boranes, and metallocenes under the same umbrella. In the following paper[2e] in this issue, we show that this generalization helps to determine the missing links between macropolyhedral boranes and β-rhombohedral boron. The variety of bonding patterns exhibited by polyhedral boranes was explored by Lipscomb (styx),[1a] Williams,[3a] Wade,[3b−d] and many others in the second half of the past century. A major breakthrough came from William's perception that the experimentally isolated *arachno* and *nido* boranes can be viewed as being derived from the nearest *closo* structures by removal of a vertex rather than as fragments of the icosahedral $B_{12}H_{12}$ skeleton.[4] This enabled the derivation of Wade's $n + 1$ electron pair rule for a polyhedron exhibiting a *closo* pattern, where n is the number of vertices.[3] According to the Williams−Wade formalism, the number of skeletal electron pairs required for the stability of a *nido* or an *arachno* skeleton is $n + 1 + p$, where p is the number of missing vertices. Thus, $B_{12}H_{12}$ (**1**, Figure 1) requires a charge of −2 to obey Wade's rule. Application of the rule generated a paradigm for the electron requirements of clusters (PERC approach), reported by Rudolph.[5] Rudolph's often reproduced chart gave a mnemonic way to correlate the different cluster patterns by both the debor approach and the seco approach and has been textbook material for years.[6] According to the debor approach, a *nido* cluster will have one BH group (one vertex) less with respect to its nearest *closo* form. The seco approach treats a *nido* unit as derived from its *closo* analogue by the removal of a bond pair. An *arachno* cluster can be differentiated from its *nido* in a similar fashion. Wade's rule was extended to include electron-deficient clusters with capped vertices, where each cap normally donates an electron pair. The electronic requirement then depends on the number of capping vertices as well.[7] The number

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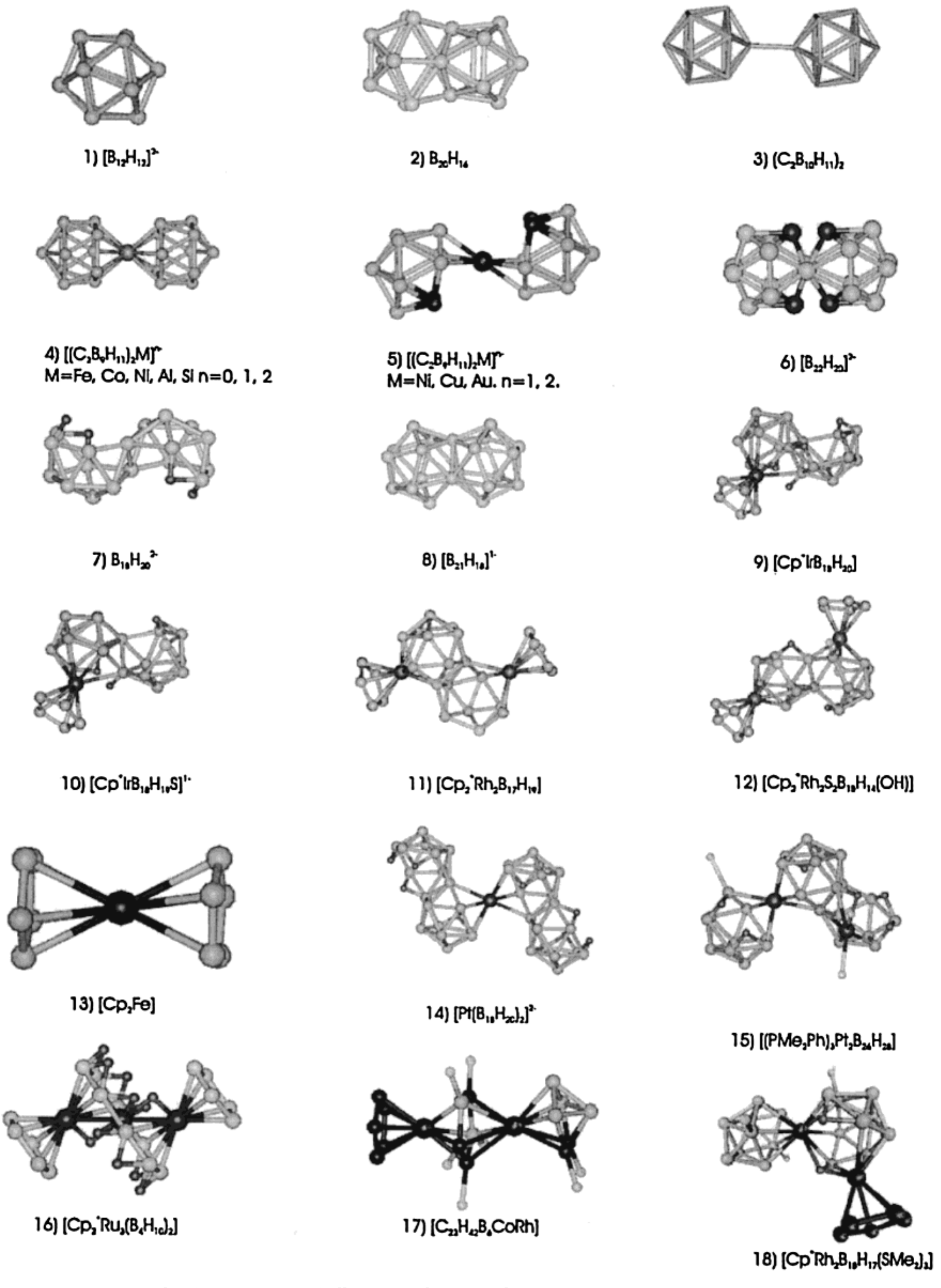

1) $[B_{12}H_{12}]^{2-}$
2) $B_{20}H_{16}$
3) $(C_2B_{10}H_{11})_2$
4) $[(C_2B_9H_{11})_2M]^{n-}$
M=Fe, Co, Ni, Al, Si n=0, 1, 2
5) $[(C_2B_9H_{11})_2M]^{n-}$
M=Ni, Cu, Au. n=1, 2.
6) $[B_{22}H_{22}]^{2-}$
7) $B_{18}H_{20}^{2-}$
8) $[B_{21}H_{18}]^{1-}$
9) $[Cp^*IrB_{18}H_{20}]$
10) $[Cp^*IrB_{18}H_{19}S]^{1-}$
11) $[Cp_2^*Rh_2B_{17}H_{19}]$
12) $[Cp_2^*Rh_2S_2B_{18}H_{14}(OH)]$
13) $[Cp_2Fe]$
14) $[Pt(B_{18}H_{20})_2]^{2-}$
15) $[(PMe_2Ph)_3Pt_2B_{24}H_{28}]$
16) $[Cp_2^*Ru_3(B_4H_{10})_2]$
17) $[C_{23}H_{42}B_6CoRh]$
18) $[Cp^*Rh_2B_{18}H_{17}(SMe_2)_2]$

Figure 1. Representative examples (structures **1**−**18**) illustrating the *mno* rule.

of electron pairs required for the stability of the monopolyhedral borane system is therefore given by $n + 1 + p - q$, where q is the number of capping vertices.

In this treatment of polyhedral bonding, all the boron atoms were treated as sp hybrids. One sp hybrid radiates away from the center of the sphere, forming the exo two-center, two-electron (2c-2e) bond with the hydrogen atom or other substituents. Another sp hybrid points toward the center of the cage. The two remaining unhybridized atomic ortitals are tangential to the sphere. Hence, each atom contributes three orbitals for skeletal bonding. The radial orbitals combine in phase to generate a strong core bonding molecular orbital (BMO). The tangential orbitals upon linear combination produce the remaining n surface BMOs. The $n + 1$ electron pairs of a *closo* polyhedron occupy all BMOs, so that a favorable structure results. The $n + 1$ rule was justified using graph theory as reported by King and Rouvray.[8] Stone[9] derived it using the

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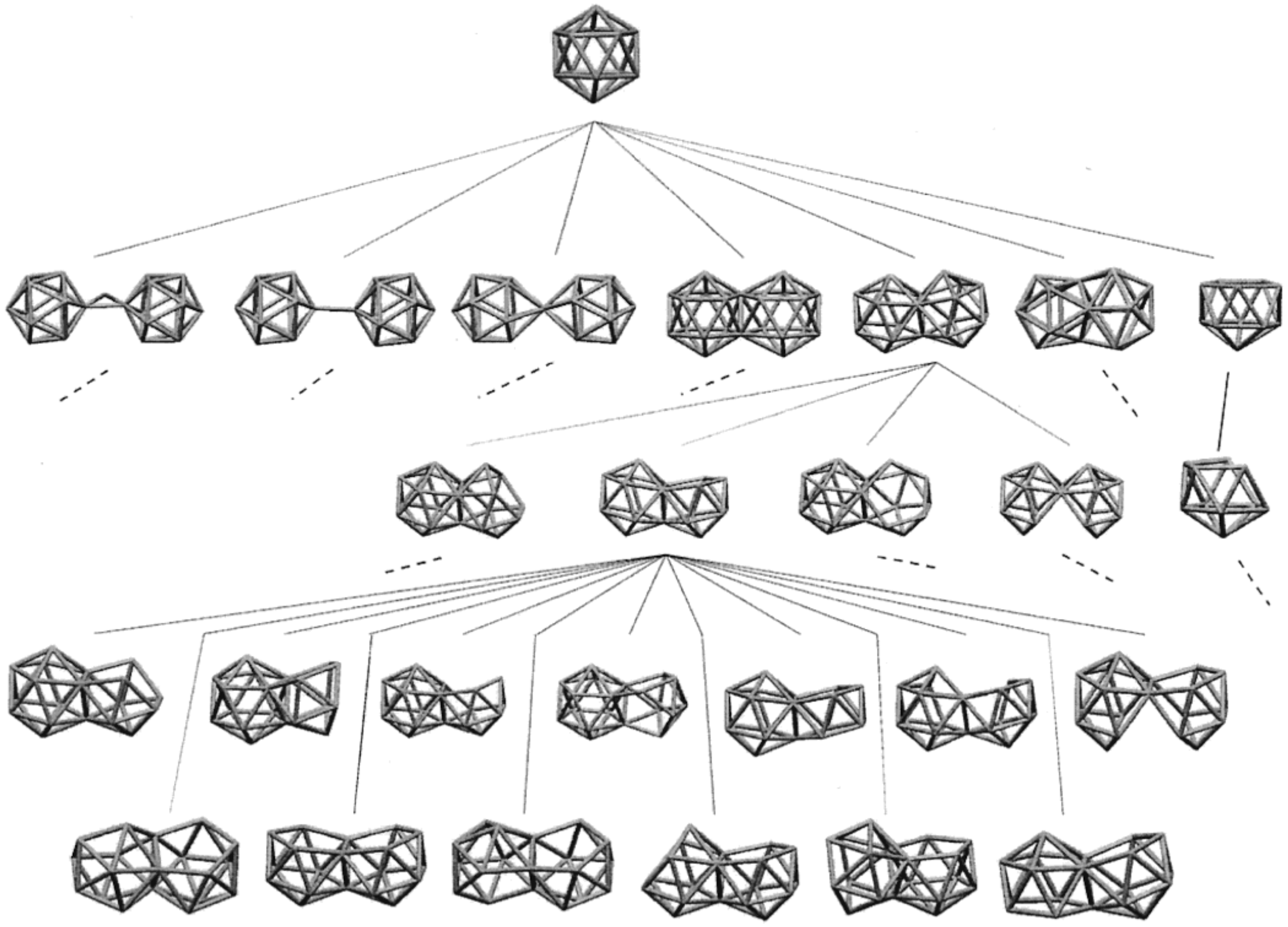

Figure 2. Comparison of the variety of polyhedral bonding exhibited by simple polyhedral boranes and polycondensed analogues. A correlation between *closo*, *nido*, and *arachno* patterns of macropolyhedral borane systems is shown. The last set includes both the *arachno* and *bisnido* structures. At 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.

tensor surface harmonic theory. The chemistry of boranes flourished along with this easily applicable electron-counting rule.[1,6,10]

Early on, there were examples of borane structures with condensed polyhedra. The first macropolyhedral borane, $B_{20}H_{16}$ (**2**, Figure 1), was isolated as a neutral species in the 1960s.[11] It involves the sharing of four atoms between two icosahedra. This gave a clear indication that polycondensation of polyhedral boranes would reduce the electron requirement. Until then, only polyhedral boranes with negative charges were known, and the neutrality of $B_{20}H_{16}$ was a mystery. Condensed structures, where the delocalized electronic structure of the individual polyhedra is not disturbed, can be understood by the Wade's $n + 1$ electron pair rule. For example, structure **3** (Figure 1) may be visualized as a combination of two polyhedra where the electronic structure of the individual icosahedral units is retained. However, there are many other ways in which the condensation can take place (Figure 2). The absence of an electron-counting rule, which can be applied to all these condensed structures, is immediately felt.

We published a preliminary communication[12] on the nature of the interaction between individual aromatic units of polyhedral boranes in all the possible modes. This has resulted in a generalized electron-counting scheme[12] that is applicable to the whole range of main group elements. The rule gives the requirement of electron pairs as $n + m$ for a *closo* macropolyhedral borane cluster, where m is the number of individual polyhedra involved in the condensation and n is the total number of vertices. For example, the $n + m$ electron pair count for $B_{20}H_{16}$ (**2**) is $20 + 2 = 22$. The number of available electron pairs is also 22 (16 electron pairs from 16 BH groups and six from four boron atoms). *Nido* and *arachno* arrangements call for additional electron pairs.

Our attempts to modify the $n + m$ rule to include the single-vertex condensations as well have paved the way for a new rule, which we christen the *mno* rule and is presented here. It unifies polycondensed polyhedral boranes, metallaboranes, metallocenes, and any of their combinations. With the new parameter o standing for the number of single-vertex bridging, the rule states that $m + n + o$ skeletal electron pairs are required for condensed polyhedral boranes involving *closo* arrangements to be stable. A generalized electron-counting rule, which also takes into account the open structures and capping vertices,[7] is given by $N = m + n + o + p - q$, where N is number of the skeletal electron pairs, m, n, and p have the same meanings as

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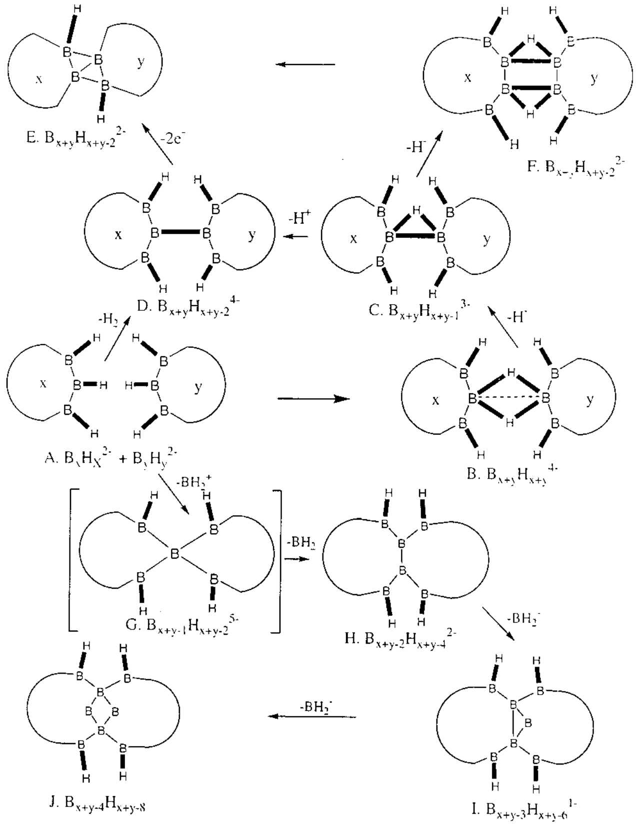

Figure 3. Different modes of interaction (A−J) between two polyhedra, ranging from exo-polyhedral to condesed ones. All patterns except G are known experimentally. Structural pattern G is observed in the unit cell of β-rhombohedral boron and also when the central boron atom is replaced by heavier elements.

above, and q is the number of capping vertices. The electron-counting rule presented here is applied to a wide variety of boranes, heteroboranes, and metallaboranes. A justification similar to that of the $n + 1$ rule is also presented.

Condensation of polyhedra provides infinite variety. Figure 2 demonstrates this using two polyhedra with different modes of condensation, as described in Figure 3. For simplicity, the correlation has been drawn considering only an icosahedral fragment, though it will be applicable to other polyhedral clusters in all possible combinations. Expansion of a macropolyhedral *closo* form to different *nido* patterns has been done only on a single cluster. The possibility of open structures starting with an icosahedron alone grows exponentially, and hence only one structure is expanded at a given level of this tree diagram. Similarly, the *arachno* and *bisnido* structures emerging from a single *nido* pattern have been shown. 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 variety available in polycondensation is immediately obvious.

The success of any electron-counting rule is in its applicability to a range of experimentally known systems and projections for the unknown. We demonstrate here the generality of the *mno* rule by applying it to a large set of structures. Despite the success, it is good to remember that electron-counting rules are just that—electron-counting rules. Just as $B_nH_n^{2-}$ ($n = 5-12$) exhibits varying stability, the detailed thermodynamic and kinetic stability of the favorable condensed structures depend on many factors and need to be studied individually. However, the evaluation of the number of cluster electrons from the constituent elements and its comparison with that predicted from the electron-counting rules help in arriving at the charge of an unknown molecule, thus providing a tool for rationalizing data and exploring new avenues.

Application of the Rule

We begin the application of the *mno* rule with the icosahedron (**1**, Figure 1). Here, the number of polyhedron $m = 1$, the number of vertices $n = 12$, and the number of single-vertex-sharing $o = 0$, ($m + n + o = 13$), so that the $n + 1$ electron pair rule of Wade for single polyhedra is obtained. Each vertex with one terminal atom contributes all electrons for cluster bonding except one, which is involved in the exo covalent bond. Thus, in the icosahedral $C_2B_{10}H_{12}$, the BH groups donate one electron pair each, and CH contributes three electrons to the polyhedral bonding, satisfying the *mno* rule ($m = 1$, $n = 12$, $o = 0$). The simplest possible condensation is obtained by connecting two icosahedral fragments through a single bond as in structure **3**, represented by $(C_2B_{10}H_{11})_2$. The electron count is twice that of the single polyhedral system ($m + n + o = 2 + 24 + 0$). The structure has 26 skeletal electron pairs. Table 1 provides a breakdown of electron pairs needed to satisfy the *mno* rule for structures discussed here and also for an additional selection of compounds that span a spectrum of structural types.

Let us consider the condensation of two icosahedra through a single vertex to give **4** (Figure 1). The *mno* rule gives $2 + 23 + 1 = 26$ electron pairs. For the aluminacarborane, $[(C_2B_9H_{11})Al(C_2B_9H_{11})]$,[13] with the overall structure **4**, the *mno* electron count predicts a charge of −1, since the electron pairs contributed from the various fragments amount only to 25.5 (BH groups, 18; CH groups, 6; Al, 1.5). The anionic structure is well characterized.[13] Compounds in which Al is replaced by Fe, Co, Ni, and Si are also known with appropriate charges.[14] The transition metal sandwich complexes can be approximated to octahedral complexes so that the valence d orbitals of the transition metal are split into the t_{2g} and e_g sets. The contribution of a transition metal in sandwich complexes toward skeletal bonding originates from this e_g set. This is usually found to be true, except in cases such as the high-spin species, ferrocenyl cation and cobaltocene. The magnetic property is an indicator of the electronic structure of such complexes. A search of the Cambridge Crystallographic Database[15] gave over 80 structures with this skeleton, most of which follow the electron count. Examples are known with the same skeleton as **4** having dative bonds, which affect the charge requirements.[16] When an external bond is dative in nature, all the valence electrons on the vertex atom participate in the polyhedral bonding. Compounds are also isolated with bridging groups between two dicarbollide ligands.[17]

Structure **5** has the skeleton of a slipped sandwich complex. The distorted skeleton is known with transition metals such as Ni, Cu, and Au.[18] All of them have one or more additional electron pairs than expected from the *mno* rule. Consider the slipped complex of nickel. Treating the structure as *closo*, it

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Table 1. Number of Skeletal Electron Pairs Required According to the *mno* Rule for the Polyhedra and Comparison with That Provided from the Constituent Elements[a]

structure	m	n	o	p	q	N	BH	B	CH	α/β	a/b	N'	x	ref
1	1	12	0	0	0	13	12	0	0	0	0	12	−1	
2	2	24	0	0	0	26	20	0	6	0	0	26	0	10
3	2	23	1	0	0	26	18	0	6	Fe-1	0	25	−2	13, 14
										Co, Al − 1.5		25.5	−1	
										Ni, Si − 2.0		26	0	
4*	2	23	1	0	0	26	18	0	6	Ni − 2.0	0	26	−2	18
										Cu, Au − 2.5		26.5	−1	
5	2	22	0	0	0	24	20	3	0	0	0	23	−2	
6	2	18	0	2	0	22	16	3	0	0	2^{a}	21	−2	20
7	2	21	0	0	0	23	18	4.5	0	0	0	22.5	−1	21
8	2	20	0	0	0	22	16	6	0	0	0	22	0	11
9	3	24	1	3	0	31	15	4.5	7.5	1.5^{α}	2.5^{a}	31	0	22
10	3	25	1	3	0	32	16	3	7.5	$1.5^{\alpha},2^{\beta}$	1.5^{a}	31.5	−1	22
11	4	29	2	4	0	39	14	4.5	15	3^{α}	2.5^{a}	39	0	23
12	4	32	2	4	0	42	16	3	15	3^{α}, 4^{β}	1^{a}	42	0	24
13	2	11	1	2	0	16	0	0	15	1^{α}	0	16	0	
14*	4	37	1	2	0	44	32	6	0	2^{α}	4^{a}	44	−2	25
15*	3	28	1	2	0	34	23	4.5	0	4^{α}	3^{a}, 0.5^{b}	35	0	26
16	4	21	3	4	0	32	8	0	15	3^{α}	6^{a}	32	0	27
17	3	18	2	1	0	24	6	0	15	3	0	24	0	32
18*	3	25	2	2	0	32	18	0	7.5	3^{α}	1^{a}, 1.5^{b}	31	0	38
$B_{20}H_{18}$	2	20	0	0	0	22	20	0	0	0	0	20	−4	41
$B_{20}H_{19}$	2	20	0	0	0	22	20	0	0	0	0.5^{a}	20.5	−3	40
$B_{20}H_{18}$	2	20	0	0	0	22	20	0	0	0	1^{a}	21	−2	43
$B_{20}H_{18}O$	2	20	0	0	0	22	20	0	0	0	0.5^{a}, 0.5^{b}	21	−2	47
$B_{20}H_{18}$	2	20	0	0	0	22	18	3	0	0	0	21	−2	44
$B_{20}H_{20}N$	2	20	0	0	0	22	18	3	0	0	0.5^{b}	21.5	−1	44
$B_{20}H_{21}C_2N$	2	20	0	0	0	22	18	3	0	0	0.5^{b}	21.5	−1	48
$B_{10}H_{16}$	2	10	0	2	0	14	10	0	0	0	4^{a}	14	0	49
$B_{12}H_{16}$	2	12	0	2	0	16	10	3	0	0	3^{a}	16	0	50
$B_{13}H_{19}$	2	13	0	2	0	17	12	1.5	0	0	3.5^{a}	17	0	51
$B_{14}H_{20}$	1	14	0	2	0	17	14	0	0	0	3^{a}	17	0	52
$B_{16}H_{20}$	2	16	0	2	0	20	14	3	0	0	3^{a}	20	0	53
$B_{18}H_{22}$	2	18	0	2	0	22	16	3	0	0	3^{a}	22	0	54
$B_{18}H_{31}C_6N$	2	18	0	2	0	22	16	3	0	0	2.5^{a}, 0.5^{b}	22	0	55
$B_{20}H_{26}$	2	20	0	2	0	24	20	0	0	0	4^{a}	24	0	56
$B_{20}H_{16}L_2$	2	20	0	1	0	23	17	4.5	0	0	0.5^{a}, 1^{b}	23	0	57
$B_{22}H_{22}$	2	22	0	1	0	25	20	3	0	0	1^{a}	24	−2	58
$B_{17}H_{23}C_4N_2$	2	18	0	2	0	22	15	3	1.5	0	2^{a}, 0.5^{b}	22	0	59
$C_4B_{18}H_{22}$	2	22	0	2	0	26	16	3	6	0	1^{a}	26	0	60
$C_4B_{18}H_{22}$	2	22	0	1	0	25	18	0	6	0	1^{a}	25	0	60
$SB_{17}H_{20}$	2	18	0	3	0	23	15	3	0	2^{β}	2.5^{a}	22.5	−1	61
$S_2B_{16}H_{29}C_{18}P$	2	18	0	3	0	23	13	4.5	0	4^{β}	1^{a}, 0.5^{b}	23	0	62
$S_2B_{16}H_{16}$	2	18	0	2	0	22	14	3	0	4^{β}	1^{a}	22	0	63
$S_2B_{17}H_{16}$	2	19	0	2	0	23	15	3	0	4^{β}	0.5^{a}	22.5	−1	64
$S_2B_{17}H_{18}$	2	19	0	2	0	23	16	1.5	0	4^{β}	1^{a}	22.5	−1	65
$S_3B_{17}H_{35}C_2$	2	19	0	3	0	24	15	3	0	4^{β}	1.5^{a}, 0.5^{b}	24	0	66
$S_2B_{18}H_{19}$	2	20	0	3	0	25	16	3	0	4^{β}	1.5^{a}	24.5	−1	67
$OB_{18}H_{21}$	2	19	0	2	0	23	16	3	0	1^{β}	2.5^{a}	22.5	−1	68
$NB_{17}H_{20}$	2	18	0	2	0	22	15	3	0	2^{β}	2^{a}	22	0	69
BeB_6H_{16}	2	7	1	2	0	12	6	0	0	1^{β}	5^{a}	12	0	39, 70
$Be_2B_6H_{22}C_2$	2	8	0	2	0	12	6	0	0	1^{β}	5^{a}	12	0	39
$BeB_{10}H_{20}$	2	11	1	2	0	16	10	0	0	1^{β}	5^{a}	16	0	71
$B_8H_{44}C_{16}Si_4Mg$	2	14	0	0	0	16	8	0	6	2^{β}	0	16	0	72
$B_{18}H_{42}C_{16}P_2Pt$	2	19	0	2	0	23	16	3	0	2^{α}	2^{a}	23	0	73
$B_{18}H_{42}C_{16}P_2Pt$	2	19	0	2	0	23	16	3	0	1.5^{α}	2.5^{a}	23	0	73
$B_{18}H_{60}C_{32}P_4Pt_2$	2	20	0	2	0	24	15	4.5	0	4^{α}	0.5^{a}	24	0	73
$B_{20}H_{61}C_{33}P_4Re$	2	21	0	1	1	23	17	4.5	0	1^{α}	0.5^{b}	23	0	74
$B_{20}H_{46}C_{16}P_2Pt$	2	21	0	2	0	25	20	0	0	2^{α}	3^{a}	25	0	75
$B_{16}H_{50}C_{14}O_2Ir_2$	2	18	0	1	0	21	13	4.5	0	3^{α}	0.5^{a}	21	0	76
$B_{17}H_{38}COP_2Ir$	2	18	0	2	0	22	15	3	0	1.5^{α}	2.5^{a}	22	0	77
$B_{18}H_{34}C_{18}PIr$	2	19	0	2	0	23	15	4.5	0	1^{α}	2^{a}, 0.5^{b}	23	0	78
$B_{28}H_{74}C_{32}P_4Pt_2$	3	30	0	4	0	37	28	0	0	4^{α}	5^{a}	37	0	78
$B_{28}H_{54}C_{16}P_2Pt$	3	29	0	3	0	35	26	3	0	2^{α}	4^{a}	35	0	78
$B_{16}H_{55}C_{31}P_3Pt_2$	2	18	0	2	0	22	15	1.5	0	4^{α}	1^{a}, 0.5^{b}	22	0	79
$B_{16}H_{40}C_{16}P_2Pt$	2	17	0	2	0	21	15	1.5	0	2^{α}	2^{a}, 0.5^{b}	21	0	80
$B_{26}H_{48}C_{16}P_2Pt$	3	27	0	3	0	33	22	6	0	2^{α}	2.5^{a}, 0.5^{b}	33	0	81
$B_{14}H_{60}C_{32}P_4Pt_3$	2	17	0	3	0	22	13	1.5	0	6^{α}	1.5^{a}	22	0	82
$B_{26}H_{60}C_{13}OP_4Ir_2$	3	28	0	2	0	33	21	6.5	0	3.5^{α}	2^{a}	33	0	83
$B_{20}H_{44}C_8O_2Cd_2$	2	22	2	2	0	28	20	0	0	6^{α}	2^{a}	28	0	84
$B_{14}H_{18}C_4Co$	2	19	1	0	0	22	14	0	6	1.5^{α}	0	21.5	−1	85
$B_{26}H_{32}C_6Co_2$	3	34	2	0	0	39	26	0	9	3^{α}	0	38	−2	86

Table 1 (Continued)

structure	m	n	o	p	q	N	BH	B	CH	α/β	a/b	N'	x	ref
$B_8H_{50}C_{20}P_2CoFe$	2	14	1	0	1	16	8	0	6	2^{α}	0	16	0	87
$B_{18}H_{30}C_{10}ONi_2$	2	24	0	0	0	26	18	0	6	2^{α}	0	26	0	88
* $B_{14}H_{18}C_6M$ (M = Ni, Pd, Pt)	2	21	1	0	0	24	14	0	9	2^{α}	0	25	0	89
$B_7H_{30}C_{18}Co_2$	2	12	1	1	0	16	7	0	6	1.5^{α}	1^{a}, 0.5^{b}	16	0	90
$B_{17}H_{26}C_9NCo$	2	22	1	1	0	26	17	0	6	1.5^{α}	0.5^{a}, 0.5^{b}	25.5	−1	91
$B_{16}H_{42}C_{36}S_2P_2Ni$	2	19	0	2	0	23	13	4.5	0	1^{α},4^{β}	0.5^{b}	23	0	92
$B_8H_{49}C_{28}Co_3$	4	25	3	2	0	34	7	1.5	21	4.5^{α}	0	34	0	93
$B_6H_{50}C_{28}Co_2Hg$	4	23	3	2	0	32	6	0	21	4^{α}	1^{a}	32	0	94
$B_8H_{25}C_{13}Co$	3	18	1	2	0	24	7	1.5	13.5	1.5^{α}	0.5^{a}	24	0	95
$B_{13}H_{34}C_{10}OCo$	2	16	1	1	0	20	13	0	3	1.5^{α}	2^{a}, 0.5^{b}	20	0	96
$B_{12}H_{31}C_8OCo$	2	15	1	2	0	20	12	0	3	1.5^{α}	3^{a}, 0.5^{b}	20	0	96
$B_{16}H_{34}C_{10}OCo$	2	19	1	1	0	23	16	0	3	1.5^{α}	2^{a}, 0.5^{b}	23	0	96
$B_{10}H_{22}C_{14}Co_2$	4	26	2	2	0	34	10	0	21	3^{α}	0	34	0	97
$B_8H_{56}C_{32}Co_2$	4	24	2	2	0	32	8	0	21	3^{α}	0	32	0	98
$B_{12}H_{49}C_{22}OCo$	2	19	1	1	0	23	12	0	9	1.5^{α}	0.5^{b}	23	0	99
$B_{16}H_{66}C_{30}O_2Co$	2	25	1	2	0	30	16	0	12	1.5^{α}	0	29.5	−1	100
$B_{14}H_{32}C_{18}NCo_3$	4	32	3	2	0	41	14	0	22.5	4.5^{α}	0	41	0	101
$B_{16}H_{25}C_9Co_2$	3	27	2	1	0	33	16	0	13.5	3^{α}	0	32.5	−1	102
$B_{12}H_{46}C_{36}S_4Pd_2$	2	18	4	2	0	26	12	0	0	2^{α},10^{β}	2^{a}	26	0	103
$B_6H_{58}C_{32}Co_2$	4	22	2	4	0	32	5	1.5	21	3^{α}	1.5^{a}	32	0	98
$B_6H_{56}C_{32}Co_2$	4	22	2	4	0	32	4	3	21	3^{α}	1^{a}	32	0	104
$B_{17}H_{26}C_5Co$	3	23	1	3	0	30	15	3	7.5	1.5^{α}	3^{a}	30	0	105

[a] m = number of polyhedra; n = number of vertices; o = number of single-vertex bridge; p = number of missing vertices; q = number of capping vertices; α = number of electrons from the metal; β = number of electrons from a main group element other than boron; a = number of electron pairs donated by bridging hydrogen atoms; and b = number of electrons from a dative bond. Last column gives the references to experimental structures wherever available. * implies electron count ambiguous for various reasons described in the text.

requires 26 electron pairs. Nickel donates its two electron pairs, which along with the 24 electron pairs originating from the two dicarbollide ligands lead to an electron pair count of 26. An additional charge of −2 makes the electron pair count exceed the *mno* count for *closo* structures. An alternative is obviously to have a *nido* arrangement. The detailed electronic structure study of the slipped structures and the occupancy of the metal−ligand antibonding orbitals that cause the distortion in these complexes have been well documented.[19]

Next we consider two atoms (edge) sharing structures. Two *closo* structures condensed by an edge lead to severe steric crowding. The atoms represented in dark colors in **6** (Figure 1) are too close to each other. We are not aware of any example of this kind. However, if one or more vertex is removed, as happens in the *nido* arrangements, edge sharing should be practical. For example $B_{18}H_{20}^{2-}$ (**7**) is well characterized and adheres to the *mno* rule.[20] The compound has 16 BH groups (16 electron pairs), two boron atoms (three electron pairs), and four bridging hydrogens (two electron pairs). The molecule achieves the *mno* electron count as a dianion. The steric interaction is reduced in a triangular face-sharing (three atoms sharing) polyhedron, $B_{21}H_{18}^{-}$ (**8**),[21] and the four-atom-sharing polyhedral borane, $B_{20}H_{16}$ (**2**),[11] which was discussed earlier. In **8**, $m = 2$, $n = 21$, and $o = 0$, and hence 23 electron pairs are required. This is accounted from the 18 BH groups, three boron atoms, and a negative charge.

The importance of the *mno* rule is obvious in its applicability to a variety of polyhedral boranes where condensation has taken place by any combination of one-, two-, three-, or four-atom sharing. Let us take the formidable-looking structure **9**, $[Cp^{*}IrB_{18}H_{20}]$.[22] With three *nido* arrangements, the *mno* rule leads to 31 electron pairs ($m = 3$, $n = 24$, $o = 1$, $p = 3$). The skeleton gets its electron pairs from 15 BH groups (15), 5 CH groups (7.5), 3 shared boron atoms (4.5), 5 bridging hydrogens (2.5), and Ir atom (1.5). The next structure we consider, $[Cp^{*}IrB_{18}H_{19}S]^{-}$ (**10**), has an additional vertex in the form of a sulfur atom so that the number of electron pairs required is 32. Sulfur is found to be a four-electron donor, with two electrons remaining as a lone pair orienting outward from the cluster. Three bridging hydrogens, 16 BH, 2 boron atoms, 5 CH groups, the metal, and four electrons from sulfur together contribute 31.5 electron pairs to the skeletal framework. Therefore, the *mno* rule requires an additional electron, as indeed is observed.[22] $[Cp_2^{*}Rh_2B_{17}H_{19}]$ (**11**) requires 39 electron pairs ($m = 4$, $n = 29$, $o = 2$, $p = 4$) for stability, taking into account the four *nido* structures. The complex has five bridging hydrogen atoms, which enable it to attain the *mno* electron count, and is found to be neutral.[23] $[Cp_2^{*}Rh_2S_2B_{15}H_{14}(OH)]$ (**12**) is in perfect agreement with the *mno* electron count for a cluster with four *nido* structures and 42 skeletal electron pairs for stability.[24] Metallocenes can be easily included if one considers them as having two open (*nido*) faces. Taking the simplest case, ferrocene (**13**), the molecule has 16 electron pairs (15 from the 10 CH groups and one electron pair from iron). The *mno* rule suggests the same count for a skeleton with two open faces ($m = 2$, $n = 11$, $o = 1$, $p = 2$).

The *mno* rule is necessary to account for the skeletal electron pairs of structures **14** and **15** because the metal platinum is sandwiched between two polyhedral boranes, of which either one or both are condensed to one more subcluster.[25,26] A

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transition metal with external ligands is related to its BH analogue with appropriate charges when it occupies an unshared site. Otherwise, it is replaced by a boron equivalent. This is done by applying the concept of isolobal analogy[27] followed by deprotonation.[27] Thus, the d^{10} ML_2 fragment at a nonshared position in **15** is isolobally equivalent to a CH_2 fragment and, in turn, to BH^{2-}. Hence, it is a three-orbital, four-electron donor. The number of electron pairs in **14** and **15** is 45 and 35, respectively. The *mno* rule suggests an electron pair count of 44 and 34, respectively, for a skeleton with two absent vertices. The extra electrons lead to a slipped geometry around the metal, as is found in the nickel complex, **5**.[18] The highly mixed up organometalloborane skeleton, **16**, finds its 32 electron pairs in $[Cp^*Ru(B_4H_{10})Ru(B_4H_{10})RuCp^*]$.[2c]

The nonbonding interactions expected in single-vertex-sharing polyhedra become prominent when the shared vertex is a boron atom. The smaller size of the central atom results in the shortening of the distance between the neighboring ring atoms, which are bridged by a single vertex. This raises the energy of some of the BMOs, where the antibonding interactions become significant. As a result, the number of BMOs will be fewer than $m + n + o$, and such systems deviate from the electron-counting rule. To achieve a boron atom sandwiched borane, the size of the ring has to be reduced. Even with a four-membered ring, the interactions are significant enough to cause deviations, as has been observed in octahedral aluminum clusters.[28,31] No isolated molecule is experimentally characterized with this framework, though this pattern is observed in the solid state for aluminum clusters of the type AeM_2Al_9 (Ae = Ba, M = Fe, Co, Ni; Ae = Sr, M = Co; Ae = Ca, M = Co) and $CaNiAl_9$.[28−30] With heavier elements in the ring, such a possibility has been suggested.[31] The only known structure with sandwich-type bonding to boron is found as part of the $B_{10}-B-B_{10}$ unit of the β-rhombohedral boron unit cell (see the following paper in this issue).[2e]

The mismatch between a bridged atom and the ring size is seen in simple multidecker sandwiches, where a single five-membered ring bridges two metals. They are exceptions to the *mno* rule, in the sense that complexes are known with a range of electronic requirements, including the ones dictated by the *mno* rule.[19] When the shared metal is of smaller size, there will be 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 are factors which bring in additional interactions than those considered in the formulation of the *mno* rule. Molecules with the *mno* electron count as in the example, $[C_{23}H_{42}B_6CoRh]$[32] structure **17**, and with fewer and more electrons are known. The requirement of 24 electron pairs in **17** is met with the building fragments of the polyhedral cluster. Details of the individual bonding requirements have been published separately.[19]

Compounds are known that have fewer electrons than the Wade's electron count and are called "hypercloso" or "isocloso" compounds.[33] They are well-debated structures and have been studied theoretically.[34] Similarly isonido[35] and isoarachno[36] structures also exist which are stable with $n + 1$ and $n + 2$ electron pair counts, respectively. The hypothetical *closo* 11-vertex $B_{11}H_{11}^{2-}$ species is found to be highly fluxional, suggesting other open structures for the complex.[35] Results of Mingo's calculations on two models of $B_{10}H_{10}^{2-}$, a spherical deltahedron and a polar deltahedron, gave a clear molecular orbital picture.[34,37] A deltahedron, which can be approximated as a sphere, has an equal number of bonding and antibonding π MOs, whereas once it is distorted a π and a π^* orbital become approximately nonbonding and are at the frontier range. Obviously, the nonbonding MO need not be filled, so that the molecule prefers one electron pair fewer than the Wade's $n + 1$ count. When this anomalous behavior is extended to condensed clusters, many of the apparently anomalous structures can be accounted for. Structure **18**, $[Cp^*RhB_9(SMe_2)H_{10}RhB_9H_7(SMe_2)_2]$, is a case in point. This compound consists of a *closo* B_9Rh unit conjoined through a rhodium atom to an open RhB_9 unit. Considering the Cp ligand as part of the cluster, the total electron requirement is 32 electron pairs ($n = 25$, $m = 3$, $o = 2$, $p = 2$). But the total number of electron pairs obtained by the skeletal fragments is only 31. Thus, the open part has some isonido characteristics.[38]

Considering the plethora of structures known, the selection of the structures given in Table 1 is arbitrary. Attempts were made to cover one example, each involving different modes of fusion, and then to present representative examples with any combination of the possible fusion modes. Emphasis is placed on bringing out structures that have ambiguities. We have applied the rule to all of the experimental structures obtained by searching the CSD;[15] only structures with differing structural patterns are listed in Table 1.

Justification for the *mno* Rule

To illustrate the various possible modes of interactions and the evolution of the rule, we bring two generalized *closo*-polyhedral boranes together from a noninteracting distance to condensed systems, varying the distance gradually. Exo-polyhedral interactions arise first, followed by condensed systems, all of which are described in the following sections.

Exo-Polyhedral Interactions. Let us assume that one B−H bond each of the two *closo*-polyhedral boranes $B_xH_x^{2-}$ and $B_yH_y^{2-}$ are brought along a line of interaction. With the decrease in distance, the nonbonding interactions dominate (Figure 3A), giving a doubly bridging structure (Figure 3B) as a possibility. The resulting structure is very similar to that of diborane (B_2H_6), but, unlike diborane, has only one sp hybrid orbital on each bridging boron. It is not sufficient to generate two stable levels. The charge requirements remain the same as for four electrons. The electrons that are earlier involved in the exo-B−H bonds are enough to stabilize the one 4c-2e bond. The second pair of electrons necessarily goes to a less stable level, resulting in an unstable system. But this shortcoming is alleviated when any

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one of these two boron atoms is replaced with transition metals, which have diffused orbitals to lower the unstable level. It is even possible with a main group element, where the bridging hydrogens are replaced by groups such as CO or $-CH_3$, with unoccupied π* or pseudo-π* orbitals to stabilize the antibonding level. An example which illustrates this type of interaction is $(Be(B_3H_8)CH_3)_2$.[39] This linkage can also be viewed as the equivalent of the doubly protonated C_2H_4, the neutral analogue being B_2H_6.

Another way to arrive at a stable structure from B (Figure 3) is to remove one of the hydrogen atoms, which leads to structure C (Figure 3). Here, the two sp-hybridized orbitals of boron and the s-orbital of hydrogen will interact to form a stable BMO and two antibonding MOs. Three electrons are available, one with each atom involved in the three-center interaction. As only two electrons are required for this 3c-2e bond, one electron has to be expelled from the system, which reduces the charge to -3. This pattern is a fairly stable mode of interaction, provided the nonbonding interactions between adjacent B$-$H groups are minimum. $(B_{10}H_9)_2H$ involves a protonated B$-$B linkage between two of its B_{10} units and exemplifies this type of linkage[40] ($B_{20}H_{19}^{3-}$, Table 1).

Removal of a proton from C leads to the most familiar form of condensation, resulting in a new 2c-2e B$-$B bond (Figure 3D). Here the electron count is the sum of the electron counts for two polyhedral systems. Thus, $B_{12}H_{11}-B_{12}H_{11}$ requires $m + n + o$ $(2 + 24 + 0 = 26)$ electron pairs, supporting the anticipated four negative charges. With several arms ready for condensation, dendrimers are a natural extension, as is found experimentally.[41] These systems have eliminated the unfavorable enhanced charge requirement by replacing borons with carbons.[41] Two B_{10} units are known to have this type of linkage, exhibiting *closo* or *nido* patterns.[42]

Alternatively, structural pattern C (Figure 3) can be bent to have more than one interacting center, by the linking of two or more adjacent centers with a 3c-2e or 2c-2e bond as in pattern F. In the case of 3c-2e linkages, every such bond 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 2c-2e bonds on both the sides. It is fairly easy to recognize and evaluate the electron requirement in these cases, as they seldom form 3c-2e bonds. Cases where two B_{10} units interact through this type of multiple linkage have been experimentally characterized.[43]

Conversely, if 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 E, the nature of interaction dramatically changes. This interaction gives rise to the capping of an edge by a boron atom, where the two exo-hydrogens of the boron atoms that are connected by the concerned edge are still retained. Since capping interactions will not add any BMOs beyond those that are already present in the polyhedra, the extra electron available on a boron atom 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 E. These systems exhibit true macropolyhedral skeleton, as localized bonds do not separate these interacting borane units any more. This pattern depicts the intermediate skeletal nature between connected and condensed polyhedral boranes, as they neither share any vertices nor are separated by localized bonds. Many examples are known with this type of bonding. One among them is $B_{20}H_{18}^{2-}$ (Table 1).[44] A capping interaction should be differentiated from 3c-2e interactions, where none of the edges of the 3c-2e bond are common with the individual polyhedral units formed during the interaction. 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 employing the electron-counting rules. In the following section, we will be concerned with the interactions where the interacting borane units share one or more vertices, a situation that is entirely different from what we have discussed so far.

Condensed Polyhedral Boranes. Though the structures discussed so far may be categorized as products of condensation, here we discuss those structures in which the process of condensation has reduced at least one vertex in comparison to the isolated polyhedra. As in the previous section, we will systematically increase the number of vertices that are shared, considering all the possibilities of condensation.

The first mode of condensation is through a single vertex (Figure 3G), leading to a sandwich. The bonding molecular orbital pattern and hence the electronic requirement are very much dependent on the distance between the two polyhedral fragments when they are allowed to share a single vertex. When the distance between the nonbonded vertices is reasonably large, the number of BMOs remains the same. This is achieved by replacing the central atom by atoms larger than boron. Since Figure 3 deals with different modes of interaction between two polyhedral boranes, the central atom was maintained as boron. The electron count here depends on the central atom. When we assigned the charge of -5 to system G (Figure 3), it was assumed that the nonbonding interactions were absent. With a smaller central atom, the nonbonding interactions involving B$-$H groups on neighboring polyhedra raise some of the BMOs. The details of these destabilizing interactions and the consequent reduction in the negative charge to -1 are discussed below.[28,30,31] In these sandwich systems, the central atom is assumed to be sp hybridized. The two sp-hybridized orbitals of the central atom are ideally directed toward the center of each cluster that is shared. One of the sp hybrids interacts with the inwardly pointing sp hybrids of the other boron atoms in one cage to form a single strongly bonding molecular orbital, as in the case of mono-polyhedral boranes. One more strongly bonding molecular orbital is formed by the interaction with the other cage atomic orbitals. So, the number of core orbitals formed by the overlap of the radial orbitals on each vertex equals the number of cages in the polycondensed system, *m*. The two tangential orbitals on the shared vertex are mutually perpendicular to each other, and they contribute to the surface BMOs. Each subcluster retains its electronic requirement. If the number

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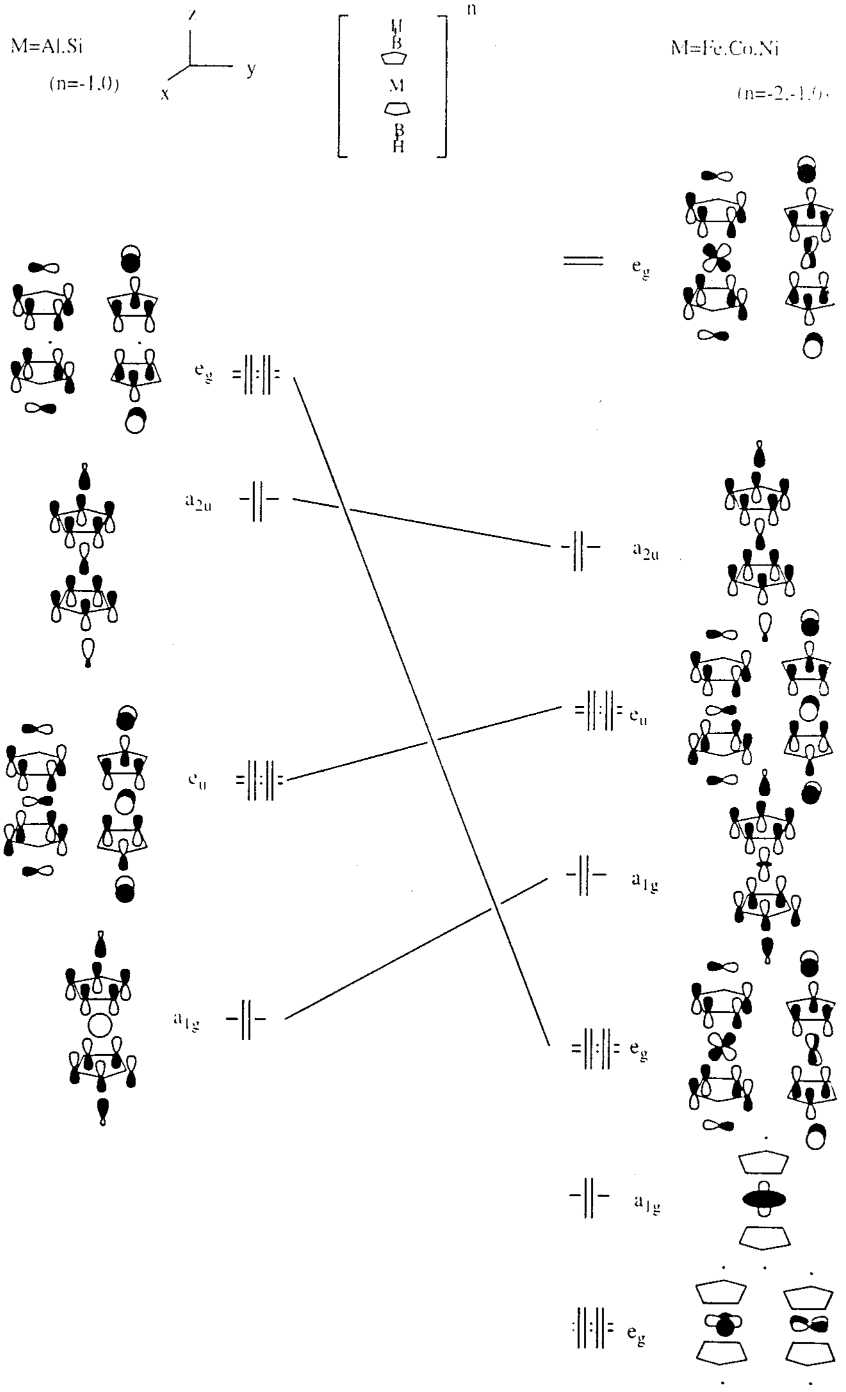

Figure 4. Molecular orbital diagram of sandwich complexes correlating main group sandwiches and corresponding transition metal systems.

of vertices on each subcluster of a two-polyhedra condensed complex, excluding the shared atom, are a and b, respectively, such that $a + b + 1 = n$, the total number of vertices, then the bonding surface molecular orbitals formed from the tangential orbitals on each subcluster will be $a + 1$ and $b + 1$, respectively. The total amounts to $n + 1$, which when generalized gives $n + o$, where o is the total number of single-vertex condensations. So the total bonding MOs is $m + n + o$, which is the basis of the rule, already applied to structure **4** in Figure 1.

The electronic requirements of single-vertex sharing can also be rationalized using a fragment molecular orbital approach, starting with a ring-cap division used by one of us in explaining the relative stability of *closo*-borane isomers.[45] This approach simplifies the problem by reducing the number of BMOs to be considered. The ring atoms are considered as sp^2 hybrids, interacting with an sp hybrid cap. The frontier MOs of the ring will be the π molecular orbitals formed by the linear combination of the unhybridized p orbitals similar to conjugated hydrocarbons. Figure 4 gives a correlation between the simplified MO pattern of both a main group sandwich complex and a transition metal complex.

The left-hand side of Figure 4 shows the molecular orbital pattern for a main group sandwich in which the central atom is larger than boron. It is correlated with the transition metal compound on the right-hand side. The *mno* rule can be well understood from the BMO pattern of $(B_6H_6)_2M$, where M = Al, Si, etc. An extension of any rule to transition metal

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complexes usually results in additional terms to account for the d-orbitals. But it can be seen from Figure 4 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, and 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 and is the highest among the occupied levels. It is this e_g set which is affected when a larger central atom is replaced by boron, leading to a charge of -1 instead of -5, as given in Figure 3G. This, in addition to other repulsive interactions, makes the existence of single-boron-bridged condensation unlikely. The d_{xz} and d_{yz} orbitals of transition metals are of proper symmetry to interact with these particular orbitals and hence stabilize the e_g set, bringing it below the e_u set (Figure 4, rhs). The LUMO of the second system is doubly degenerate. When the number of electrons exceeds the *mno* count, this antibonding MO has to be occupied. The resulting antibonding interactions can be reduced with slipping. The distortion provides some bonding character to the otherwise antibonding orbital. This explains the additional requirement of the slipped sandwiches, which results in more electrons than required according to the rule.[19]

One more atom at the shared position between two monomeric units leads to an edge-shared polyhedron (Figure 3H). As discussed earlier, the *closo* form is not practical for these systems. The core BMOs of this polycondensed polyhedron that are formed by the strongly bonding interaction of the inward-pointing sp hybrid orbitals remain unchanged. However, the two surface BMOs are shared between the two units, since they share more than one atom. Edge sharing allows the existence of Hamiltonian circuits[8] that span the entire macropolyhedral framework, which enables the stabilization of exactly the same number of surface bonding orbitals as the number of vertices in the system. A similar effect is observed in the three- and four-vertex-sharing macropolyhedral systems (Figure 3I,J). However, the sp hybrids of the boron atoms in these systems, unlike in the case of single-vertex-sharing systems, will not be ideally oriented toward each polyhedron. This necessitates 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 due to the increased overlap. In some very condensed systems, such as $B_{28}H_{21}^+$, which is found in β-rhombohedral boron, 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. Polycondensation by sharing five atoms leads to boron nanotubes. This arrangement makes the system cylindrical in shape, with a uniform radius of curvature. Such a system emerges as a single polyhedron, and the rule can be applied.[46] Higher fusions are not possible due to the poor ring-cap compatibility of boron.

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Conclusions

A unifying electron-counting rule—the *mno* rule—explains the bonding patterns exhibited by single and condensed polyhedral borane clusters. According to the *mno* rule, $m + n + o$ elecron pairs are necessary for a polycondensed polyhedral system. Here m is the number of polyhedral clusters, n is the number of vertices, and o is the number of single-vertex fusions. Wade's $n + 1$ rule is a special case of the *mno* rule, where $m = 1$ and $o = 0$. Similarly, the $m + n$ rule is a special case with $o = 0$. The rule can also be extended to metallocenes, which can be merged with the borane systems. The rules of condensation allow for infinite possibilities. A glimpse of the dimension of the problem is seen in Figure 2, which treats condensation of icosahedral fragments alone. There are endless mixing and matching possible. The *mno* rule will be a useful guide to achieve the different goals wherein efforts are made to unify the two fields. The justification provided here for the *mno* rule also accounts for some of the apparent exceptions to the rule.

To conclude, the *mno* rule, which takes into account the number and type (*closo*, *nido*, etc.) of polyhedra and the mode of their condensation, should lead to further thought about boranes and metallocenes.

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