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Reversal of Stability on Metalation of Pentagonal-Bipyramidal ($1\text{-}MB_6H_7{}^{2-}$, $1\text{-}M\text{-}2\text{-}CB_5H_7{}^{1-}$, and $1\text{-}M\text{-}2,4\text{-}C_2B_4H_7$) and Icosahedral ($1\text{-}MB_{11}H_{12}{}^{2-}$, $1\text{-}M\text{-}2\text{-}CB_{10}H_{12}{}^{1-}$, and $1\text{-}M\text{-}2,4\text{-}C_2B_9H_{12}$) Boranes (M = Al, Ga, In, and Tl): Energetics of Condensation and Relationship to Binuclear Metallocenes

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Abstract: The usual assumption of the extra stability of icosahedral boranes (**2**) over pentagonal-bipyramidal boranes (**1**) is reversed by substitution of a vertex by a group 13 metal. This preference is a result of the geometrical requirements for optimum overlap between the five-membered face of the ligand and the metal fragment. Isodesmic equations calculated at the B3LYP/LANL2DZ level indicate that the extra stability of $1\text{-}M\text{-}2,4\text{-}C_2B_4H_7$ varies from 14.44 kcal/mol (M = Al) to 15.30 kcal/mol (M = Tl). Similarly, $M(2,4\text{-}C_2B_4H_6)_2{}^{1-}$ is more stable than $M(2,4\text{-}C_2B_9H_{11})_2{}^{1-}$ by 9.26 kcal/mol (M = Al) and by 6.75 kcal/mol (M = Tl). The preference for $(MC_2B_4H_6)_2$ over $(MC_2B_9H_{11})_2$ at the same level is 30.54 kcal/mol (M = Al), 33.16 kcal/ mol (M = Ga) and 37.77 kcal/mol (M = In). The metal−metal bonding here is comparable to those in CpZn−ZnCp and $H_2M{-}MH_2$ (M= Al, Ga, and In).

Introduction

The pentagonal-bipyramid (**1**) and the icosahedron (**2**), Scheme 1, are the two related polyhedra that dominate the chemistry of polyhedral boranes. The icosahedral boranes are usually considered to be the most stable among the polyhedral boranes. The pentagonal-bipyramidal *closo*-borane $B_7H_7{}^{2-}$ (**1**), in contrast, is highly reactive.[1] However, this difference in reactivity appears to be altered with the substitution of one of the vertexes by a heavier group 13 metal. During the last three decades, several molecules isoelectronic with $B_nH_n{}^{2-}$ (n = 7, 12), containing one or two heteroatoms other than carbon in the cage, have been prepared.[1−6] These include metallacarboranes involving heavier elements of the boron group. Early examples of the group 13 *closo*-metallacarboranes, especially in the smaller cage, such as the galla- and indacarboranes [*closo*-$1\text{-}CH_3\text{-}1,2,3\text{-}MC_2B_4H_6$(M = Ga and In)] were synthesized by Grimes and co-workers.[3b] These complexes have varying distortions from the pentagonal-bipyramidal geometry, but the metal occupies the apical position above the open pentagonal face of the carboroane. The most common distortion of the metal in $1\text{-}M\text{-}2,4\text{-}C_2B_{n-3}H_n$ (n = 7, 12) is along the pseudomirror plane of the molecule, toward the unique boron atom. Several similar structures, **1a−n**, were characterized over the years with

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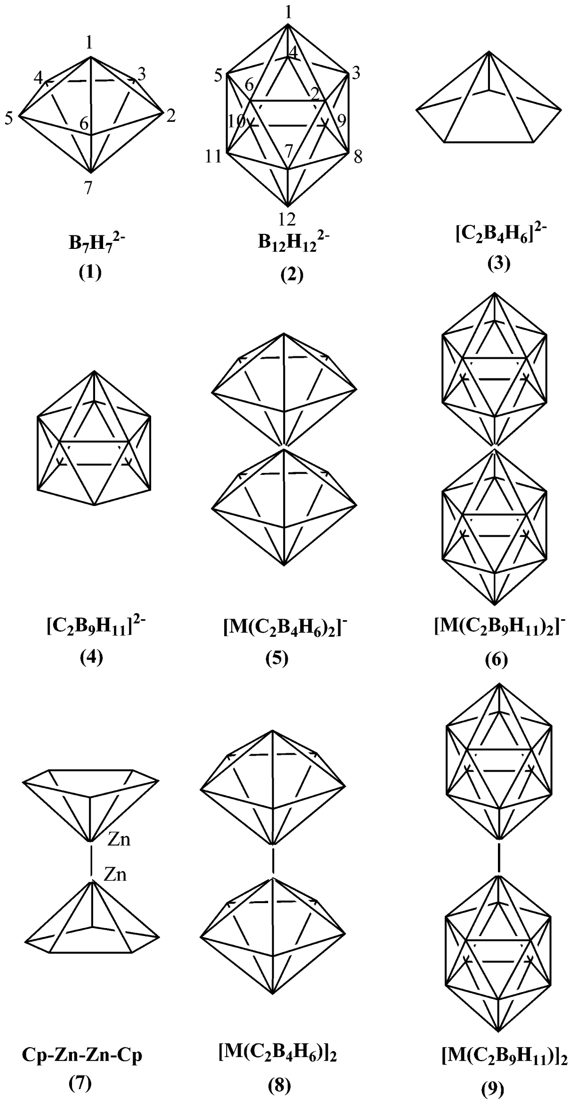
Table 1. Experimentally Characterized Structures of Pentagonal-Bipyramidal and Icosahedral Metallaboranes and Carboranes (from Cambridge Structural Database[3a]) with One of the Vertices Substituted by Heavier Group 13 Elements

molecular formula	ref
1. $M(R)\text{-}C_2B_4H_6$	
a. $Ga(CH_3)\text{-}2,3\text{-}C_2B_4H_6$	3b
b. $Ga(CMe_3)\text{-}2,3\text{-}(CSiMe_3)_2B_4H_4$	3c
c. $Ga(CMe_3)\text{-}2,4\text{-}(CSiMe_3)_2B_4H_4$	3d
d. $Ga(C_{10}N_2H_8)(tBu)\text{-}2,3\text{-}(CSiMe_3)_2B_4H_4.\ 2C_6H_6$	3d
e. $Ga(C_{10}N_2H_8)(tBu.\ \text{-}2,4\text{-}(CSiMe_3)_2B_4H_4.2C_6H_6$	3d
f. $Ga(C_8N_4H_6)(tBu)\text{-}2,4\text{-}(CSiMe_3)_2B_4H_4$	3d
g. $Ga(Cl)(CH_2NMe_2)_2\text{-}2,3\text{-}(CSiMe_3)_2B_4H_4.\ C_6H_6$	3e
h. $Ga(Cl)(CH_2NMe_2)_2\text{-}2,4\text{-}(CSiMe_3)_2B_4H_4.\ C_6H_6$	3e
i. $In(CH_3)\text{-}2,3\text{-}C_2B_4H_6$	3b
j. $In(CHMe_2)\text{-}2,3\text{-}(CSiMe_3)B_4H_4$	3f
k. $In(CHMe_2)\text{-}2,4\text{-}(CSiMe_3)B_4H_4$	3c
l. $In(C_{10}N_2H_8)(CHMe_2)\text{-}2,3\text{-}(CSiMe_3)_2B_4H_4$	3c
m. $In(C_{10}N_2H_8)(CHMe_2)\text{-}2,4\text{-}(CSiMe_3)_2B_4H_4$	3c
n. $In(C_8N_4H_6)\ (CHMe_2)\text{-}2,3\text{-}(CSiMe_3)_2B_4H_4$	3d
2. $M(R)\text{-}C_2B_9H_{11}$	
a. $Ga(C_2H_5)\text{-}2,3\text{-}C_2B_{10}H_{11}$	3g
b. $[Al\ (Me)\ B_{11}H_{11}]^{2-}.[AsPh_3]_2$	3h
c. $Al(Me)\text{-}2,3\text{-}C_2B_9H_{11}$	3g
d. $Al(C_2H_5)\text{-}2,3\text{-}C_2B_9H_{11}$	3i
e. $Al(Me)_2\text{-}2,3\text{-}C_2B_9H_{11}$	3i
f. $Al(Et)(PEt_3)_2\text{-}2,3\text{-}C_2B_9H_{11}$	3j
g. $Tl\text{-}2,3\text{-}C_2B_9H_{11}.PPh_3$	3k
5. $M(C_2B_4H_6)_2$	
a. $Ga[(2,3\text{-}CSiMe_3)_2B_4H_4]_2^{-}[Na(TMEDA)_2]^{+}$	3e
b. $Ga[(2,4\text{-}CSiMe_3)_2B_4H_4]_2^{-}[Na(TMEDA)_2]^{+}$	3e
6. $M(C_2B_9H_{11})_2$	
a. $Ga[2,3\text{-}C_2B_9H_{11}]_2^{1-}\ Tl^{+}$	3j,3l
b. $Al[2,3\text{-}C_2B_9H_{11}]_2^{1-}$	3j
8. $C_2B_4H_6\text{-}M\text{-}M\text{-}C_2B_4H_6$	
a. $[Ga\text{-}(2,4\text{-}(CSiMe_3)_2B_4H_6]_2$	11
$^{b}[1\text{-}C(Ph)B_6H_6]^{1-}[N(Et)_4]^{1+}$ [a]	3m
$^{c}[1\text{-}CB_5(I)_2H_4]^{1-}[P(Ph)_4]^{1+}$ [a]	3n

[a] The last two *b* and *c* structures are included for their references.

Scheme 1



one Al, Ga or In in place of boron and these are tabulated here (Table 1)).

In contrast there is less information available on the icosahedral structures with group 13 metals, although the first structure of a group 13 metallacarborane in the icosahedral system (**2**) [$1\text{-}R\text{-}1,2,3\text{-}AlC_2B_9H_{11}$ ($R{=}CH_3$, C_2H_5)] was reported by Hawthorne and co-workers in 1970.[4] Structures **2a**−**g** (Table 1) form the characterized members of this family. Metallaborane structures with a pentagonal-bipyramidal skeleton are more common than those with the icosahedral skeleton. While this may be the result of a greater synthetic effort toward the pentagonal-bipyramidal skeletons, is there in addition a thermodynamic preference? We have reasons to expect so and this is, in part, the motivation to undertake the present study.

The term dicarbollide was introduced by Hawthorne to describe the *nido*-$C_2B_9H_{11}^{2-}$ anion, indicating the bowl-like shape. The *nido*-$C_2B_4H_6^{2-}$ (**3**) and -$C_2B_9H_{11}^{2-}$ (**4**) carborane ligands have been compared to Cp^- so the metallocene like structures $C_2B_4H_6MC_2B_4H_6^{1-}$ (**5**) and $C_2B_9H_{11}MC_2B_9H_{11}^{1-}$ (**6**) are expected to be stable. Several derivatives of **5** and **6** are known and Table 1 provides well characterized examples which can be considered as condensed products from structure **1** and **2**, respectively. While the well-known Wade's $n + 1$ skeleton electron pair rule is applicable to **1** and **2**, it is outside of its realm for **5** and **6**.[7] The electron-counting rule that applies equally well for metallocenes, metallacarboranes and condensed polyhedral boranes has been introduced by us.[8] According to this rule, commonly known as *Jemmis* Rule, where *m* is the number of polyhedra, *n* is the number of vertexes, and *o* is the

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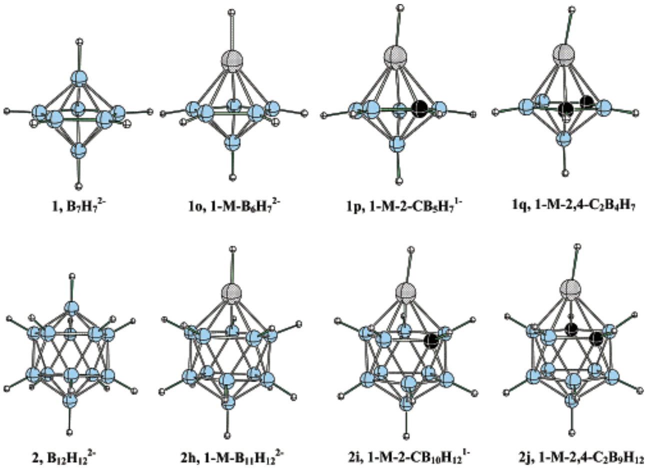

$1, B_7H_7^{2-}$ $1o, 1\text{-}M\text{-}B_6H_7^{2-}$ $1p, 1\text{-}M\text{-}2\text{-}CB_5H_7^{1-}$ $1q, 1\text{-}M\text{-}2,4\text{-}C_2B_4H_7$

$2, B_{12}H_{12}^{2-}$ $2h, 1\text{-}M\text{-}B_{11}H_{12}^{2-}$ $2i, 1\text{-}M\text{-}2\text{-}CB_{10}H_{12}^{1-}$ $2j, 1\text{-}M\text{-}2,4\text{-}C_2B_9H_{12}$

Figure 1. Structures of pentagonal-bipyramidal and icosahedral metallaboranes and metallacarboranes indicating the numbering scheme.

number of single-vertex-sharing condensation structures with $m+n+o$ skeletal electrons that are extra stable. Thus, for structure **5**, we have $m = 2$, $n = 13$, and $o = 1$ so that 16 electron pairs are required for skeleton bonding. The number of electron pairs in 5a (Table 1), for example, is 15.5 (8 from 8 BH groups, 6 from 4 CH groups, and 1.5 from the Ga) so that the complex has a negative charge. Similarly, the *Jemmis* Rule stipulates 26 electron pairs for **6**. A negative charge is required to meet the target as found experimentally. Here we would also like to see any inherent preference, if any, for this.

Another connection between metallaboranes and metallocenes is brought to attention by the recent synthesis of $Me_5C_5-Zn-Zn-C_5Me_5$ (**7**), which are commonly called binuclear metallocenes.[9] This is indeed a new development in metallocene chemistry of the main group, but main group metallacarboranes have a similar precedent. In general, compounds having bonds between two Ga atoms or other heavier group 13 elements are rare. There are a few classical inorganic compounds with Ga−Ga bond such as Ga_2Br_3, $[GaC(SiMe_3)_3]_4$ and Ga_2R_4 [$R = (Me_3Si)_2CH$, 2,4,6-$^iPr_3C_6H_2$, and 2,4,6-$(CF_3)_3C_6H_2$)] that have been known for some time.[10] In 1995, Hosmane and co-workers synthesized a novel class of compounds (**8**) where the Ga−Ga bond is stabilized by two 2,4-dicarba-nido-hexaborate(2-) carborane ligands.[11] This is an equivalent of CpZn−ZnCp (**7**). We compare the metal−ligand and metal−metal bonding in the binuclear metallocenes and binuclear metallacarboranes. There are no equivalent metal−metal bonded icosahedral structures. We search here for reasons, if any, that prevent the formation of such species.

The group 13 metallacarboranes serve as useful reagents for the introduction of carborane cage moieties.[12] The high reactivity of the aluminacarboranes, coupled with their excellent solubility in organic solvents, have led to their potential usefulness as transmetalation reagents. The insoluble thallacarboranes[13] are highly valued as synthetic reagents. The present study on the structure and bonding compliments the experimental study of carboranes in relation to nano carborarods and bundles.[14] Our focus is on the differential effect of a group 13 element as a cap on the icosahedral and pentagonal-bipyramidal cage systems.

Computational Details

All the polyhedral structures of molecular formula $HM\text{-}B_nH_{n-1}^{2-}$, $HM\text{-}2CB_{n-2}H_{n-1}^{1-}$ $HM\text{-}2,4\text{-}C_2B_{n-3}H_{n-1}$, $2,4\text{-}C_2B_{n-3}H_{n-1}\text{-}M\text{-}2,4\text{-}C_2B_{n-3}H_{n-1}$, and $2,4\text{-}C_2B_{n-3}H_{n-1}\text{-}M-M\text{-}2,4\text{-}C_2B_{n-3}H_{n-1}$ [where $n = 7$, 12 and M = B, Al, Ga, In, and Tl] are optimized at B3LYP method using LANL2DZ basis set.[15a] This uses well-known three parameters functional of Becke's, including Hatree-Fock exchange contribution with non local corrections for exchange potential, together with non local correction for the correlation energy suggested by Lee, Young, and Parr.[15b−c] In addition, we have used 6-31G* basis set for compounds having Aluminum and Gallium. All calculations were carried out using the Gaussian 03 program package.[16] Total energies and the Cartesian coordinates of the structures studied are given in the supplementary information. Energetic comparisons were made after Basis set superposition error wherever possible.

Results and Discussion

We begin the analysis by describing the structural features of metallaborane dianions, monoanionic metallacarboranes and neutral metallacarboranes based on pentagonal-bipyramidal (**1**) and icosahedral (**2**) skeletons. Among the monocarbaboranes, only structures with carbon at 2-postion are considered. The dicarbaborane structures considered have the carbon atoms in the 2,4-positions (Figure 1). The details of the structure and bonding of the icosahedral and pentagonal-bipyramidal structures are given in sections A and B. Isodesmic equations (1−4) are used to estimate the relative preferences for these two structures. A relationship is then brought out between the geometric parameters and the preference of the polyhedra for a particular metal using fragment molecular orbitals. This approach is extended to the condensed structures based on **5** and **6** in section C. The preference of specific polyhedra for the M−M bonded structures is discussed at the end.

(A) Bonding in the pentagonal-bipyramidal systems. The electron requirements of the polyhedral structure is well-defined by the Wade's Rules.[7] The variations in the structure of $B_7H_7^{2-}$ (D_{5h}) when a BH group is substituted by an AlH group are noteworthy. The ring hydrogens of the five-membered ring, which is in the B5 plane in $B_7H_7^{2-}$, bend away from Al−H in $AlB_6H_7^{2-}$ by 9.3° (Table 2). See the extended overlap approach (Scheme 2). The π MOs of the B_5H_5 ring span exhibit too large an area to have optimum overlap with the MOs of the two BH fragments (Scheme 2). The extend of bending of B_4H_4 ring or of a B-H bond depends on the metal and decreases to 8.5 in

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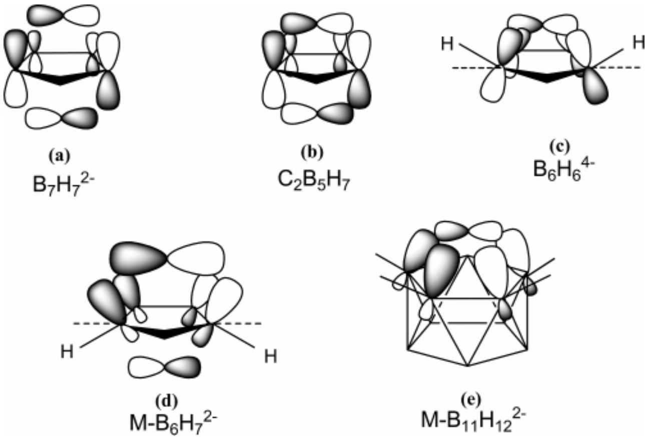
Table 2. Out-of-Plane Bending (180° − <X1BH, where X1 Is the Centroid of the Five-Membered Ring and the X1−M−H Bonds Bend Away from the Capping Atom Denoted by the Negative Sign) Values of the *exo*-Polyhedral Bonds in the Pentagonal-Bipyramidal Boranes and Carboranes (Figure 1) at B3LYP/LANL2DZ[a]

structures	angles in deg	M = BH	AlH	GaH	InH	TlH
1-M-$B_6H_6^{2-}$	X1−M−H	0.00	−0.02	−0.03	−0.05	−0.31
	X1−B_{1-6}−H	0.00	−9.34	−8.51	−10.45	−10.64
1-M-2-$CB_5H_6^{1-}$	X1−M−H	−8.32 (−9.80)[b]	−12.87	−15.43	−18.65	−32.58
	X1−C2−H	−0.01 (−1.83)	−10.74	−10.07	−12.51	−13.87
	X1−B3/6−H	−5.74 (−8.22)	−9.75	−9.32	−10.84	−12.00
	X1−B_4−5−H	−0.35 (−3.04)	−7.66	−7.00	−8.37	−8.70
1-M-2,4-$C_2B_4H_6$	X1−M−H	−6.66	−12.43	−15.41	−20.38	−43.78
	X1−C2/4−H	−1.09	−10.01	−9.32 (−8.56)[1h]	−11.22 (9.75)[1k]	−12.14
	X1−B3−H	−1.10	−5.92	−5.99 (−8. 43)	−7.27 (−11.85)	−8.12
	X1−B5/6−H	−5.61	−8.49	−7.01 (−8.79)	−8.67 (−8.99)	−6.62

[a] Geometrical parameters of the corresponding experimentally characterized structures are in parentheses, and the superscript on the parentheses corresponds to experimental structures listed in the Table 1.

Scheme 2



Ga. However, it increases to 10.5 and to 10.6 with In and Tl, respectively. The corresponding B−B bond lengths (Table 3) of the five membered rings are 1.68, 1.74, 1.74, 1.75, and 1.76 Å for BH, AlH, GaH, InH, and TlH, respectively, indicating an enlargement of the five-membered ring. Considerable ring expansions (Table 3) and bending of ring hydrogens (Table 2) were observed for their carborane analogues too. These out-of-plane bendings can be understood using a fragment MO caps with more diffuse orbitals representing the ideal situation. However, the $C_2B_3H_5$ ring is smaller by virtue of shorter B−C bonds. This helps to have better overlaps with the ring and cap orbitals, thus explaining the better stability of $C_2B_5H_7$ over $B_7H_7^{2-}$ (Scheme 2b). When one of the apical B−H groups in $B_7H_7^{2-}$ is substituted by the M−H group such as Al−H, an advantageous situation arises for both the B−H and the M−H groups (Figure 1). The B−H bonds of the B_5H_5 ring bend out of the B5 plane and rehybridize the orbitals so that the larger lobe is directed toward the group with more diffuse orbitals (Scheme 2d). The process of rehybridization increases the B−B bond lengths of the B_5 ring, bringing the apical B−H group closer to the centroid of the B_5 ring. This also helps to increase orbital span for the B_5 fragment toward the M−H cap. The out-of-plane bending of the ring B−H toward the unique B−H increases with increasing diffuse nature of the orbitals of the M−H groups; the largest bending is calculated for Tl−H. The advantage of the out-of-plane bending for the interaction between B−H cap and B_5H_5 ring is indicated by the decrease of the ringBH−capBH distance of 1.87, 1.84, 1.84, 1.83, and 1.81 Å for BH, AlH, GaH, InH, and TlH, respectively (Table 3).

The general considerations of structure and bonding do not change in the monoanionic carborane 1-M-2-$CB_5H_7^{1-}$ and the neutral 1-M-2,4-$C_2B_4H_7$ derivatives (Figure 1). Major differences come from the distortions arising from the lower symmetry of the five-membered ring resulting from the carbon atoms. The calculations refer to molecules where all exohedral substituents are replaced by hydrogens (Tables 2 and 3). The geometrical parameters of the corresponding experimental structures are also indicated in parentheses. Experimental structures are available for the neutral derivatives with Ga (1h in Table 1) and In (1k in Table 1) as the metals. The geometrical parameters of these experimentally characterized structures are compared with the model structures. The calculated ring B−B, B−C and C−C bond distances fall within ±0.06 Å of the experimental values (Table 3). The in-plane bending of the *exo*-polyhedral bonds vary somewhat more (Table 2) from the experimental values, probably because of the bulkier substituents present in the experimental structures. The slip-distortions of the −MR groups located above the C_2B_3 face of the carborane toward the boron side of the face has been noted earlier for Ga and In derivatives and a molecular orbital explanation provided.[3b,17] Here the ring-cap bonding is fine-tuned by the reorientation of orbitals by shifting the substituent of the metal toward the carbon side of the five-membered ring. Detaild MO studies to explain these structural distortions are available in the literature.[17]

(B) Bonding in the Icosahedral Boranes and Comparison to Pentagonal-bipyramids. Icosahedral [M(R)$C_2B_9H_{11}$)] species are isoelectronic with *closo*-1,*n*-$C_2B_{10}H_{12}$ (n = 2, 7, 12), *closo*-1-$CB_{11}H_{12}^{1-}$, and *closo*-$B_{12}H_{12}^{2-}$. The extra stability of the icosahedral *closo*-$B_{12}H_{12}^{2-}$ is attributed to its high symmetry and the consequent orientation of the exohedral bonds it provides. This orientation is very close to that required for ideal bonding in a pentagonal-pyramidal borane. For example, the exohedral B−H bonds of the five membered ring in $B_6H_6^{4-}$ or B_6H_{10} are bent toward the apical B−H group by about 25° (Scheme 2c). The pentagonal pyramid, which can be obtained by halving the icosahedron, provides an angle of 26.6° by the icosahedral symmetry. This coincidence of the requirement of a pentagonal-pyramidal borane and the symmetry dictated angle available for the icosahedron leads to the unusual stability for icosahedral $B_{12}H_{12}^{2-}$. The fragment orbitals of the $B_{11}H_{11}^{2-}$ are oriented toward the missing vertex. Substitution of two boron

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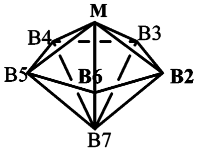
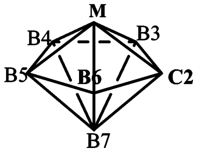
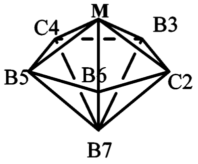
(17) (a) Canadell, E.; Eisenstein, O.; Rubio, J. *Organometallics* **1984**, *3*, 759. (b) Maguire, J. A.; Hosmane, N. S.; Saxena, A. K.; Zhang, H.; Gray, T. G. *Phosphorus, Sulfur, Silicon* **1994**, *87*, 1299.

Table 3. Important Interatomic Distances of Pentagonal-Bipyramidal Boranes and Carboranes (Figure 1) at the B3LYP/LANL2DZ Level of Theory (where X1 Is the Centroid of the Five Membered Ring)[a]

Structures	Distance (Å)	M=BH	AlH	GaH	InH	TlH
	Ring B-B	1.68	1.74	1.74	1.75	1.76
	M- $B_{2\text{-}6}$	1.87	2.22	2.22	2.39	2.51
	B7-$B_{2\text{-}6}$	1.87	1.84	1.84	1.83	1.81
	M-X1	1.20	1.66	1.66	1.87	2.02
	B7-X1	1.20	1.09	1.09	1.06	1.03
	C2-B3/6	1.57 (1.56)[b]	1.60	1.59	1.59	1.58
	B3/5-B4/6	1.67 (1.65)	1.72	1.72	1.73	1.72
	B4-B5	1.70 (1.66)	1.76	1.76	1.79	1.82
	M-C2	1.79 (1.74)	2.18	2.22	2.41	2.75
	M-B3/6	1.87 (1.82)	2.23	2.25	2.42	2.66
	M-B4/B5	1.83 (1.80)	2.18	2.17	2.33	2.41
	M-X1	1.21 (1.16)	1.68	1.69	1.90	2.14
	B7-X1	1.21 (1.16)	1.11	1.11	1.09	1.07
	C2/4-B3	1.56	1.58	1.58 (1.52)[1h]	1.58 (1.57)[1k]	1.57
	C2/4-B5/6	1.59	1.62	1.62 (1.56)	1.62 (1.60)	1.58
	B5-B6	1.68	1.72	1.73 (1.76)	1.74 (1.71)	1.85
	M-C2/4	1.76	2.16	2.18 (2.88)	2.38 (2.44)	2.75
	M-B3	1.90	2.28	2.31 (3.08)	2.50 (2.52)	2.92
	M-B5/B6	1.83	2.20	2.18 (2.25)	2.33 (2.32)	2.44
	M-X1	1.21	1.71	1.72 (2.27)	1.94 (1.99)	2.28
	B7-X1	1.208	1.132	1.132 (1.083)	1.119 (1.060)	1.123

[a] Geometrical parameters of the corresponding experimentally characterized structures are in parentheses, and the superscript on the parenthesis corresponds to experimental structures listed in the Table 1.

Table 4. In-Plane- Bending (180° − <X1BH, where X1 Is the Centroid of the Five-Membered Ring) Values of the *exo*-Polyhedral Bonds of the Icosahedral Boranes and Carboranes (Figure 1) at the B3LYP/LANL2DZ Level of Theory[a]

structures	angle in deg	M = AlH	GaH	InH	TlH
1-M-$B_{11}H_{11}^{2-}$	X1−M−H	0.00 (1.60)[2b]	0.00	0.00	0.00
	X1−B_{2-6}−H	20.81 (25.46)	20.87	19.31	18.89
	X2−B_{7-11}−H	27.70 (25.40)	27.71	27.94	27.96
1-M-2-$CB_{10}H_{11}^{1-}$	X1−M−H	12.85	15.05	19.36	33.28
	X1−C2−H	22.73	23.46	22.89	24.84
	X1−B3/6−H	24.69	24.39	22.91	23.32
	X1−B4/5−H	20.92	20.64	18.77	17.45
	X2−B_{7-8}−H	23.54	21.80	21.75	21.49
	X2−B_{9-11}−H	27.10	27.50	27.64	26.80
1-M-2,4-$C_2B_9H_{11}$	X1−M−H	11.54	14.34	21.16	45.81
	X1−C2/4−H	21.62	22.11	21.65	25.77
	X1−B3−H	28.46	28.18	27.91	31.63
	X1−B5/6−H	24.13	23.38	20.84	16.71
	X2−B_{7-10}−H	21.51	21.75	21.30	20.51
	X2−B11−H	26.82	27.05	27.22	27.23

[a] Geometrical parameters of the corresponding experimentally characterized structures are in parentheses, and the superscript on the parenthesis is the corresponding experimental structure listed in the Table 1.

atoms of $B_{12}H_{12}^{2-}$ by two carbon atoms does not change this considerably. However, metal atoms with highly diffuse orbitals affect the stability. These metals have more diffuse orbitals that require a larger orbital span of the B_5 ring. We have studied the variations in geometry in going from $B_{12}H_{12}^{2-}$ to M-$B_{11}H_{12}^{2-}$, 1-M-2-$CB_{11}H_{12}^{1-}$ and 1-M-2,4-$C_2B_9H_{12}$ (where M = Al, Ga, In, and Tl) (Tables 4 and 5). There is substantial ring expansion as the size of M increases. The overlap of fragment MOs requires rehybridization to regain better overlap (Scheme 2e vs d). This leads to the distortion of *exo*-polyhedral B−H bonds farther away from the metal so that there is better orbital match. By symmetry the angle that B−H makes with the B5 plane is calculated as 26.6° in $B_{12}H_{12}^{2-}$ (Figure 1). It changes to 29.9° (average of 28.8, 31.7, and 29.2) in 2,4-$C_2B_{10}H_{12}$. This is changed to 24.7 (average of 21.6, 28.5, and 24.1) in 1-Al-2,4-$C_2B_9H_{12}$. The average B−H in-plane bending of their carborane derivatives decreases (going away from the metal) when we go down the group 13 elements from Al to Tl (Tables 4 and 5). The symmetry of the top B_5H_5 plane is decreased from substituting one or two boron atoms by carbons. This is the main reason for not following the same trends for all in-plane bending of *exo*-polyhedral H-bonds in their carborane derivatives. These distortions, however, decrease the overall stability

Table 5. Important Interatomic Distances of Icosahedral Boranes and Carboranes (Figure 1) at the B3LYP/LANL2DZ Level of Theory (where X1 Is the Centroid of the Five-Membered Ring)[a]

structures	distances	M = BH	M = AlH	M = GaH	M = InH	M = TlH
1-MB$_{11}$H$_{11}$$^{2-}$	ring B−B	1.82	1.88 (1.84)[2b]	1.889	1.90	1.92
	M−B$_{2-6}$	1.82	2.18 (2.14)	2.18	2.34	2.47
	M−X1	0.95	1.48 (1.46)	1.47	1.69	1.85
	B12−X2	0.95	0.95 (0.93)	0.95	0.94	0.94
	X1−X2	1.54	1.52 (1.50)	1.52	1.51	1.51
1-M-2-CB$_{10}$H$_{11}$$^{1-}$	C2−B3/B6	1.74	1.75	1.75	1.73	1.69
	B3/5−B4/6	1.80	1.84	1.85	1.86	1.85
	B4−B5	1.82	1.89	1.91	1.94	2.04
	M−C2	1.74	2.17	2.20	2.42	2.74
	M−B3/6	1.81	2.18	2.19	2.37	2.60
	M−B4/5	1.80	2.16	2.15	2.30	2.40
	M−X1	0.96	1.53	1.53	1.77	2.03
	B12−X2	0.95	0.95	0.95	0.95	0.94
	X1−X2	1.53	1.51	1.51	1.51	1.51
1-M-2,4-C$_2$B$_9$H$_{11}$	C2/4−B3	1.72	1.70	1.71	1.69	1.65
	C2/4−B6/5	1.75	1.76	1.77	1.76	1.67
	B5−B6	1.80	1.82	1.84	1.85	1.98
	M−C2/C4	1.74	2.16	2.18	2.41	2.93
	M−B3	1.83	2.21	2.23	2.44	2.98
	M−B5/6	1.80	2.15	2.14	2.29	2.47
	M−X1	0.97	1.57	1.58	1.84	2.35
	B12−X2	0.96	0.95	0.95	0.95	0.95
	X1−X2	1.52	1.51	1.51	1.51	1.52

[a] Geometrical parameters of the corresponding experimentally characterized structures are in parentheses, and the superscript on the parenthesis corresponds to experimental structures listed in the Table 1.

Table 6. Reaction Energies (Δ*H*, kcal/mol) of These Reactions (eqs 1−4) Calculated at the B3LYP/LANL2DZ Level of Theory

equations	M = Al	Ga	In	Tl
1	27.20	27.04	34.78	41.40
2	22.52	22.78	30.54	40.78
3	24.95	24.50	35.03	49.05
4	14.44	15.87	18.01	15.3

of the system. Thus, the initial orientation of the fragment orbitals of B$_6$H$_6$ away from the vacant vertex and of B$_{11}$H$_{11}$ toward the vacant vertex predisposes the former for capping groups with more diffuse orbitals and the latter to caps with less diffuse orbitals (Scheme 2e). This should lead to a reversal of relative stabilities in relation to the parent systems for the metallaboranes. The calculated structural parameters agree with the experimental data for most of the structures, given in parentheses in Tables 3 and 4.

We have used isodesmic equations (equations 1−4) to estimate the relative stabilities of various group 13 metallaboranes and their carborane analogues based on pentagonal pyramid and icosahedron (Table 6):

$$\mathrm{B_{12}H_{12}}^{2-} + \mathrm{HM\text{-}B_6H_6}^{2-} \rightarrow \mathrm{HM\text{-}B_{11}H_{11}}^{2-} + \mathrm{B_7H_7}^{2-} \quad (1)$$

$$\mathrm{B_{12}H_{12}}^{2-} + \mathrm{HM\text{-}2\text{-}CB_5H_6}^{1-} \rightarrow \mathrm{HM\text{-}B_{11}H_{11}}^{2-} + \mathrm{2\text{-}CB_6H_7}^{1-} \quad (2)$$

$$\mathrm{B_{12}H_{12}}^{2-} + \mathrm{HM\text{-}2,4\text{-}C_2B_4H_6} \rightarrow \mathrm{HM\text{-}B_{11}H_{11}}^{2-} + \mathrm{2,4\text{-}C_2B_5H_7} \quad (3)$$

$$\mathrm{2,4\text{-}C_2B_{10}H_{12}} + \mathrm{HM\text{-}2,4\text{-}C_2B_4H_6} \rightarrow \mathrm{HM\text{-}2,4\text{-}C_2B_9H_{11}} + \mathrm{2,4\text{-}C_2B_5H_7} \quad (4)$$

The endothermicity of these reactions is a reflection of the extra stability of pentagonal-bipyramidal geometry when group 13 metals form a part of the skeleton and thus supports our analysis. The energies of reactions for Al and Ga derivatives are similar, in tune with their nearly equal atomic radii. The decrease in the endothermicity for the carborane is due to the decreased size of the C$_2$B$_3$ ring, making the difference between the effective orbital span of the two five-membered rings in **3** and **4** less than that in the parent boranes. The relatively larger number of metallaboranes based on the pentagonal bipyramid is not an accident after all.

(C) Condensation through Single-Atom Sharing: Sandwich Structures involving Pentagonal-Bipyramidal (5) and Icosahderal (6) Metallaboranes. There are only two well-characterized examples where two pentagonal-bipyramidal metallacarboranes (**5a**−**b**, Table 1) are condensed to form a sandwich structure, both from the Hosmane group. The Hawthorne group contributed the three condensed structures involving icosahedron with Al and Ga (**6a**−**c**, Table 1).[3j−k] The structures of the series [commo-1,1′-M(1,2,4-GaC$_2$B$_{n-3}$H$_{11}$)$_2$] (where n = 7, 12) at the B3LYP/LANL2DZ level indicate several interesting trends. The structural variations in formation of these sandwich structures are to be seen in relation to the corresponding changes noted in the metallocenes. The metallocenes involving cyclopentadienyl rings retain the planar or nearly-planner geometry of the C$_5$H$_5$ ring. The variation of the hydrogen atoms from the C$_5$ plane is small. The *nido*-C$_2$B$_4$H$_6$$^{2-}$ and C$_2$B$_9$H$_{11}$$^{2-}$ ligands, equivalent of the Cp$^-$, are very different from each other. In C$_2$B$_4$H$_6$$^{2-}$, the ring hydrogens are bent away from the incoming metal ion. In the large *nido*-C$_2$B$_9$H$_{11}$$^{2-}$ ion, the ring hydrogens are oriented toward the incoming metal ion (Table 7).

It is therefore reasonable to assume that pentagonal-pyramidal anions can be more easily brought together as the B−H and the C−H bonds of the five-membered ring are bent away from the central metal atom. We have used isodesmic eqs 5 and 6 to compare the relative stability. The anticipation based on the decreased steric interaction in 5 in comparison to 6 is confirmed by energies of eq 5. Formation of the sandwich complex involving two pentagonal pyramidals are more favored than those involving two icosahedral fragments by energies ranging from 6 to13 kcal/ mol. Despite the possible steric interaction, the B−H and C−H out-of-plane bending are not dramatically changed in forming the sandwich complex. Instead, the M-ligand distances are increased as much as 0.2−0.4 Å. It is interesting to note that a mixed complex involving one each of **3** and **4** as ligand is favored over a combination of **5** and **6**:

$$\mathrm{2,4\text{-}C_2B_4H_6\text{-}M\text{-}2,4\text{-}C_2B_4H_6} + 2\ \mathrm{2,4\text{-}C_2B_{10}H_{12}} \rightarrow \mathrm{2,4\text{-}C_2B_9H_{11}\text{-}M\text{-}2,4\text{-}C_2B_9H_{11}} + 2\ \mathrm{2,4\text{-}C_2B_5H_7} \quad (5)$$

where ΔH = 9.26 (Al), 10.53(Ga), 12.19 (In), and 6.75 (Tl) kcal/mol, calculated at B3LYP/LANL2DZ level of theory, and

$$2\ \mathrm{2,4\text{-}C_2B_9H_{11}\text{-}M\text{-}2,4\text{-}C_2B_4H_6} \rightarrow \mathrm{2,4\text{-}C_2B_9H_{11}\text{-}M\text{-}2,4\text{-}C_2B_9H_{11}} + \mathrm{2,4\text{-}C_2B_4H_6\text{-}M\text{-}2,4\text{-}C_2B_4H_6} \quad (6)$$

where ΔH = 4.75(Al), 4.61(Ga), 3.57(In), and 3.11(Tl) kcal/ mol, calculated at B3LYP/ LANL2DZ level of theory.

(D) Binuclear metallocenes. The recent synthesis of CpZn−ZnCp has brought much attention to the study of binuclear metallocenes.[10] The strength of the M−M bond in this and in many hypothetical binuclear metallocenes has been investi-

Table 7. Comparisons of Geometrical Parameters Are Made between Half-Sandwich and Single-Atom Sharing Condensed Systems (Scheme 1) and Calculated at the B3LYP/LANL2DZ Level of Theory[a]

geometrical parameters	H-M-$C_2B_4H_6$			M$[C_2B_4H_6]_2^{1-}$			$HMC_2B_9H_{11}$			M$[C_2B_9H_{11}]_2^{1-}$		
	Al	Ga	In	Al	Ga	In	Al	Ga	In	Al	Ga	In
X1−C2/4−H	10.01	9.32	11.220	9.75	9.9 (12.07)[5b]	11.48	21.62	22.11	21.65	22.80	26.70	24.80
X1−B3−H	5.92	5.99	7.275	6.56	7.71 (20.10)	8.40	28.46	28.18	27.91	27.46	29.23	29.30
X1−B5/6−H	8.49	7.01	8.673	9.18	9.30 (20.09)	9.48	24.13	23.38	20.84	23.16	26.00	23.76
M−X1	1.71	1.72	1.94	1.84	1.93 (1.92)	2.13	1.57	1.58	1.85	1.73	2.28	2.13

[a] The data of the corresponding experimentally characterized structures are in parentheses and the superscript on the parentheses corresponds experimental structure listed in the Table 1.

Table 8. Geometrical Parameters of the Binuclear Complexes Calculated at the B3LYP/ LANL2DZ Level of Theory[a]

geometrical parameters	$[MC_2B_4H_6]_2$			$[MC_2B_9H_{11}]_2$		
	Al	Ga	In	Al	Ga	In
X1−M−X2/M	12.41	14.70 (15.6)[8a]	20.85	9.19	15.75	22.70
X1−C2/4−H	9.68	9.99 (9.38)	10.97	21.52	22.10	21.70
X1−B3−H	5.93	6.00 (10.8)	7.40	27.70	27.90	26.90
X1−B5/6−H	8.20	8.26 (6.01)	8.41	23.15	23.25	20.88
M−X1/X2	1.72	1.73 (1.68)	1.95	1.58	1.59	1.85
X1−X2	5.90	5.80 (5.55)	6.45	5.64	5.51	6.22
M1−M2	2.52	2.45 (2.34)	2.75	2.52	2.44	2.75

[a] The data for corresponding experimentally characterized structures are in parentheses, and the superscript on the parentheses corresponds experimental structures listed in the Table 1.

gated.[18] The Cp^- and the *nido*-carboranes $C_2B_4H_6^{2-}$ (**3**) and $C_2B_9H_{11}^{2-}$ (**4**) are considered as comparable ligands. The synthesis of CpZn−ZnCp complex naturally leads to the question of similar binuclear complexes involving **3** and **4**. In fact, **5** and **6** must be considered as experimentally characterized forerunners of binuclear metallocenes. Hosmane et al. synthesized the first binuclear metallacarborane involving gallium, 8a (Table 1).[12] We have studied the structure and bonding of a series of binuclear metallaboranes involving pentagonal bipyramid and icosahedron with metals ranging from Al to Tl, but structures involving Tl atoms are not minima on the potential energy surfaces. The first indications of the strongly bonding nature of the M−M bond in these complexes come from comparisons to the bond lengths in $H_2M{-}MH_2$ (D_{2d}) (Table 8). The M−M bond distances in the binuclear metallacarboranes are shorter by about 0.1 Å, indicating the stabilizing influence of these $C_2B_4H_6^{2-}$ and $C_2B_9H_{11}^{2-}$ ligands on the M−M bond. However, the experimental Ga−Ga distance in **8a** is considerably shorter than that of the model at the B3LYP/LANL2DZ level. We have studied the same system using a larger all electron basis set, 6-311++G** at the same level. The Ga−Ga distance of 2.397 Å (Table 10) at this level is close to the experimental value of 2.340 Å. Similarly, we have studied Cp_2Zn_2 complex using the 6-311++G** basis set for comparison and found that Zn−Zn bond distance (2.339 Å) is close to the experimental value of 2.305 Å. However, this did not change the energetics as much. The calculated hydrogenation energies of $H_2M{-}MH_2$ (D_{2d}) are −0.83, 2.31, and 9.18 for Al, Ga, and In, respectively (eq 7, Table 9). The hydrogenation energy increases (eqs 7−10) as we go down the group 13 elements form Al to In. The M−M bond distances in these binuclear complexes are comparable to the distances calculated for the simple dimeric hydrides $H_2M{-}MH_2$. The bond energies are compared between the reactions 7−10 and it has been found that Al−Al bond in binuclear complex **8** is 7.41 kcal/mol stronger (Scheme 1) than in its dimeric hydride complex. It becomes 7.11 kcal/mol stronger in the case of Ga−Ga bond and 6.31 kcal/mol stronger for the In−In bond. These relative hydrogenation energies are the reflections of their extra bonding character in these binuclear complexes. We have calculated hydrogenation energy of Ga_2H_4 (D_{2d}) and $Ga_2(2,4\text{-}C_2B_4H_6)_2$ using 6-311++G** basis set of the same method (Table 8) and the values are −5.52 and −11.70 kcal/mol, respectively, which are comparable with the data calculated at B3LYP/LANL2DZ level of theory. The basis set superposition error (BSSE), associated with the M−M bond energy was calculated directly by the counterpoise method.[19] The values are −0.94 (Al), −0.89 (Ga), and −0.55 (In) kcal/mol for complex **8** and −1.41 (Al), −1.58 (Ga) and −1.34 (In) kcal/mole for complex **9**:

Table 9. Energies (Δ*H*, Kcal/Mol) of the Reactions (eqs 7−12) Calculated at B3LYP/LANL2DZ Level of Theory (Values are in Parentheses Calculated at B3LYP/6-311++G**)

equations	M=Al	Ga	In
7	-0.83	2.31 (5.52)	9.18
8	6.58	9.12 (11.70)	15.50
9	4.94	7.65	13.74
10	5.94	8.57	14.65
11	30.54	33.16	37.77
12	21.56 (M=Zn)		

$$H_2M\text{-}MH_2\ (D_{2d}) + H_2 \rightarrow 2MH_3 \qquad (7)$$

$$2,4\text{-}C_2B_4H_6\text{-}M\text{-}\ M\text{-}2,4\text{-}C_2B_4H_6 + H_2 \rightarrow 1\text{-}M\text{-}2,4\text{-}C_2B_4H_7 + 1\text{-}M\text{-}2,4\text{-}C_2B_4H_7 \qquad (8)$$

$$2,4\text{-}C_2B_9H_{11}\text{-}M\text{-}\ M\text{-}2,4\text{-}C_2B_9H_{11} + H_2 \rightarrow 1\text{-}M\text{-}2,4\text{-}C_2B_9H_{11} + 1\text{-}M\text{-}2,4\text{-}C_2B_9H_{11} \qquad (9)$$

$$2,4\text{-}C_2B_9H_{11}\text{-}M\text{-}\ M\text{-}2,4\text{-}C_2B_4H_6 + H_2 \rightarrow 1\text{-}M\text{-}2,4\text{-}C_2B_9H_{11} + 1\text{-}M\text{-}2,4\text{-}C_2B_4H_6 \qquad (10)$$

$$2,4\text{-}C_2B_4H_6\text{-}M\text{-}M\text{-}2,4\text{-}C_2B_4H_6 + 2C_2B_{10}H_{12} \rightarrow 2,4\text{-}C_2B_9H_{11}\text{-}M\text{-}M\text{-}2,4\text{-}C_2B_9H_{11} + 2C_2B_5H_7 \qquad (11)$$

$$CpZn\text{-}ZnCp + H_2 \rightarrow 2CpZnH \qquad (12)$$

The low exothermocities of these reactions, demonstrating that formation of binuclear metallocenes are more stable with respect to their half-sandwich complexes. Binuclear metallocenes with $C_2B_4H_6^{2-}$ ligands are more stable than the $C_2B_9H_{11}^{2-}$. So the structures with pentagonal bipyramids are more favorable than

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Table 10. M−M Bond Distances and Bond Orders for Group 13 Binuclear Complexes Calculated at the B3LYP/LANL2DZ Level of Theory (Values Are in Parentheses Calculated at B3LYP/6-311++G**)

compounds	M-M bond distance (Å)	EH Population	Mulliken Population	Wiberg Bond Index	Mayer-Mulliken bond order
H−C−C−H (**10**)	1.222	1.892	1.007	2.997	3.067
H−Zn−Zn−H (**11**)	2.591 (2.445)	0.619	0.354	0.482	0.887
Cp−Zn−Zn−Cp (**12**)	2.458 (2.339)	0.616	0.312	0.881	0.935
H−Be−Be−H (**13**)	2.086	0.919	0.455	0.705	1.053
Cp−Be−Be−Cp (**14**)	2.028	0.941	0.310	0.926	1.019
Al_2H_4 (D2h) (**15**)	2.641 (2.622)	0.868	0.336	0.901	0.856
Al_2H_4 (D2d) (**16**)	2.604	0.881	0.353	0.916	0.870
$Al_2H_6^{2-}$ (**17**)	2.756	0.102	0.394	1.027	1.052
$H_6C_2B_4$−Al−Al−$C_2B_4H_6$ (**18**)	2.520	0.865	-0.226	0.966	0.682
$H_{11}C_2B_9$−Al−Al−$C_2B_9H_{11}$ (**19**)	2.522	0.888	-0.672	0.937	0.470
Ga_2H_4 (D2h) (**20**)	2.586 (2.525)	0.769	0.307	0.879	0.791
Ga_2H_4 (D2d) (**21**)	2.543	0.810	0.328	0.900	0.809
$Ga_2H_6^{2-}$ (**22**)	2.695	0.112	0.376	1.026	0.980
$H_6C_2B_4$−Ga−Ga−$C_2B_4H_6$ (**23**)	2.445 (2.397)	0.738	-0.062	0.951	0.552
$H_{11}C_2B_9$−Ga−Ga−$C_2B_9H_{11}$ (**24**)	2.444	0.754	-0.185	0.926	0.464

the icosahedrons and it is seen in their corresponding half sandwich complexes too.

Partitioning of electrons in a molecule into contributions to specific bonds is always contentions. Despite this, we have also applied the natural bond orbital (NBO)[20] analysis and other methods to study the M−M bonding in these molecules. The Wiberg bond indexes[21] and Mayer−Mulliken[22] bond orders (Table 10) of M−M clearly demonstrate that there is a covalent single metal−metal bond in these complexes. The metal−metal σ-bonding is stronger in $H_6C_2B_4$-M−M-$C_2B_4H_6$ than in the corresponding $H_{11}C_2B_9$-M−M-$C_2B_9H_{11}$ by comparing their relative bond orders (Table 10). The Mulliken overlap populations[22] do not do as well; overlap population between Al−Al in $Al_2(C_2B_4H_6)_2$ and $Al_2(C_2B_9H_{11})_2$ are −0.2261 and −0.6716, respectively.

Conclusions

The trend that group 13 metals prefer pentagonal-bipyramidal skeleton, rather than an icosahedron, is well explained by the orientation of the π-orbitals of the ring in both cases. In $B_7H_7^{2-}$, the π MOs of the B_5H_5 ring will span too large an area to have optimum overlap with the MOs of the two BH fragments. A B_4H_4 ring or caps with more diffuse orbitals would have been better suited for such interaction. Thus, the B−H bonds of the B_5H_5 ring would bend out of the B5 plane, rehybridizing the orbitals so that the larger lobe is directed toward the group with more diffuse orbitals. The overlap of fragment MOs in $B_{11}H_{11}^{2-}$ requires rehybridization for better overlap with the metal atom. This leads to the distortion of *exo*-polyhedral B−H bonds farther away from the metal so that there is a better orbital match. The overlap between ring π-orbitals and the cap orbitals is improved by the out-of-plane bending of ring hydrogens. The five-membered ring of a pentagonal bipyramid makes better overlap with the diffuse orbital of metals more effectively than that of an icosahedron. Five-membered faces of the $C_2B_4H_6$ ring can be more easily brought together to form a sandwich because the B−H and the C−H bonds of the five-membered rings are bent away from the central metal atom. This explains the relative stability of the single-atom sharing complexes involving $C_2B_4H_6$ over their icosahedral analogues. The binuclear metallocenes with $C_2B_4H_6^{2-}$ ligands are more stable than those having $C_2B_9H_{11}^{2-}$ because of their strong metal−metal σ-bonding, as is indicated by NBO analysis.

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Supporting Information Available: Listing of total energies and Cartesian coordinates of all structures and complete ref of 16. These materials are available free of charge via the Internet at http:// pubs.acs.org.

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