

## Control of Stability through Overlap Matching: *closo*-Carborynes and *closo*-Silaborynes

Boggavarappu Kiran, Anakuthil Anoop, and Eluvathingal D. Jemmis\*

Contribution from the School of Chemistry, University of Hyderabad, Hyderabad, India 500046

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**Abstract:** The matching of ring and cap orbitals for overlap is used to arrive at the best carborynes among the many possibilities. Accordingly, 1,2-carboranes, 1,2-silaboranes ( $C_2B_nH_{n+2}$ , and  $Si_2B_nH_{n+2}$ ,  $n = 4, 5, 8$ , and 10), and their dehydrogenated derivatives were studied with use of the Density Functional Theory (B3LYP/6-311+G\*). The dehydrogenation of 2,3- $C_2B_5H_7$  (**6a**) to 2,3- $C_2B_5H_5$  (**13a**) is estimated to be even less endothermic than those of benzene and 1,2- $C_2B_{10}H_{12}$  (**1a**) to benzyne and 1,2- $C_2B_{10}H_{10}$  (**8a**) by more than 21 kcal/mol. This is due to the extra stabilization gained through better overlap of the  $C_2B_3H_3$  ring with the 2 BH caps. The relatively larger size of the Si atom leads to overlap requirements in silaboranes that are different from those in carboranes. The lower Si–Si single bond energy and the preference of Si for lower coordination result in unusual structures in dehydrogenosilaboranes. One of the Si atoms moves away from the surface in  $Si_2B_{10}H_{10}$  (**15**),  $Si_2B_8H_8$  (**16**, **17**, and **18**), and 1,2- $Si_2B_5H_5$  (**19**). One Si atom forms a bridge to a trigonal surface in 2,3- $Si_2B_5H_5$  (**20**) and 1,2- $Si_2B_4H_4$  (**21**). Estimates of three-dimensional aromaticity with NICS calculations show that the exohedral double bond does not influence three-dimensional aromaticity.

### Introduction

Icosahedral carboranes had taken the natural lead among polyhedral boranes as stable, neutral, aromatic, polyhedral compounds.<sup>1</sup> After years of explorative studies, carboranes have become important reagents in many different applications. Derivatives of carboranes, which can act as carriers of  $^{10}B$  selectively to tumor cells, have found application in the Boron Neutron Capture Therapy (BNCT) of cancer.<sup>2</sup> Camouflaged carboranes<sup>3</sup> where hydrogens are substituted by appropriate organic substituents are used as modules for the formation of specific molecular assemblies. Carborods with linearly connected 1,12- $C_2B_{10}H_{10}$  and macrocycles containing carborane cages in their peripheries find uses in nanotechnology and molecular recognition.<sup>4</sup> Mercuracarborands<sup>5</sup> resemble crown

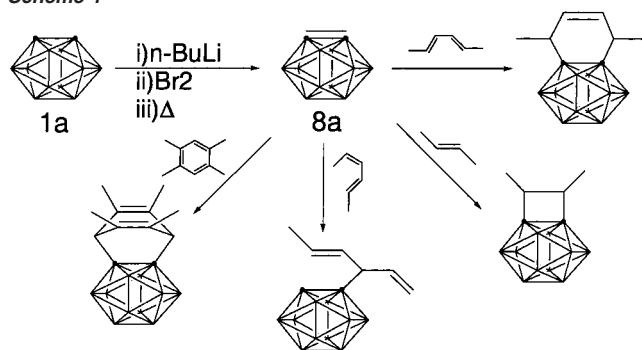
ethers with reverse coordination properties and are useful in anion complexation chemistry. Carboranes can be used as building blocks for dendrimers which can have as many as 12 primary branches.<sup>6</sup>

Getting a handle on carboranes for further manipulation is important in any such endeavor. The chemistry of benzene provides a hint. One of the dramatic aspects of benzene chemistry has been the generation of benzyne.<sup>7</sup> An equivalent “carboryne” would provide a handle to introduce substituents on the carborane skeletons. This has indeed been achieved experimentally with the icosahedral 1,2- $C_2B_{10}H_{12}$  (**1a**, Scheme 1).<sup>8</sup> The resulting carboryne,  $C_2B_{10}H_{10}$  (**8a**), undergoes cycloadditions and ene reactions with dienes, acetylenes, and other unsaturated species (Scheme 1).<sup>9</sup> Obviously, many applications with the derivatives of icosahedral carboranes remain to be discovered. Are there other carboranes of importance? In view

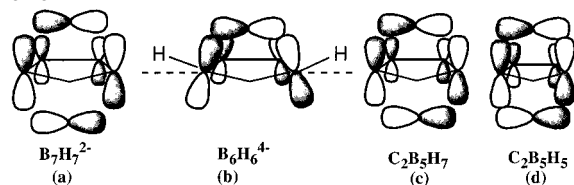
\* Address correspondence to this author. E-mail: jemmis@uohyd.ernet.in.

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Scheme 1



Scheme 2



of the many polyhedral carborynes available with adjacent C–C bonds (**2a–7a**),<sup>1,10</sup> there should be many such “benzynes equivalents”. How do these compare in stability to  $C_2B_{10}H_{10}$ ?

The replacement of two boron atoms of polyhedral boranes by carbon atoms and the dehydrogenation to carborynes must have dramatically different consequences depending on the polyhedra involved. The shorter C–C and B–C distances required in going from  $B_{12}H_{12}^{2-}$  to 1,2- $C_2B_{10}H_{12}$  did not bring in substantial instability, as the skeleton could accommodate the decreased size by decreasing the overall size of the cluster; the average B–B distances in  $B_{12}H_{12}^{2-}$  and 1,2- $C_2B_{10}H_{12}$  (**1a**) are 1.787 and 1.781 Å respectively.<sup>11</sup> Further shrinking of the C2 part of the skeleton (**8a**, Figure 2) increases the strain and leads to stretching of the B–B distances in the remaining parts of the molecule resulting in longer average B–B distances (1.796 Å). The icosahedral skeleton cannot be changed further. However, according to the compatibility of orbitals in overlap based on the ring-cap interaction,<sup>12</sup> such shortening of C–C bond lengths could be advantageous in other polyhedra. Let us consider, for example,  $B_7H_7^{2-}$  ( $D_{5h}$ ), which is highly reactive, even though synthesized experimentally.<sup>13</sup> The MOs that control the stability of  $B_7H_7^{2-}$  ( $D_{5h}$ ) can be constructed from the interaction of the  $\pi$ -MOs of the  $B_5H_5$  and the fragment MOs of the BH caps. One of the resulting MOs is given in Scheme 2a. The strength of this interaction depends on the extent of the overlap of the ring and cap orbitals. The reactivity of the  $B_7H_7^{2-}$  is an indication that the overlap in question is not optimum for  $B_7H_7^{2-}$ ;<sup>13</sup> both  $B_6H_6^{2-}$  and  $B_{12}H_{12}^{2-}$  are far more stable. The fragment orbitals of the BH group are not as diffuse as is required by the  $\pi$ -MOs of  $B_5H_5$ . It is possible to judge the extent of this compatibility of orbitals from pyramidal molecules by noticing the out-of-plane bending of the ring B–H bonds. For example, in the hypothetical  $B_6H_6^{4-}$  or the well-known  $B_6H_{10}$ ,

the ring-cap overlap is improved by the out-of-plane bending of the ring B–H bonds (Scheme 2b).<sup>12</sup>

When there are two caps such possibilities do not exist; the ring B–H bonds must remain in the plane of the ring by symmetry. One of the ways to solve the problem is to reduce the ring size. This can be done by introducing two carbon atoms in the ring. The shorter C–C and B–C distances reduce the ring size;  $C_2B_5H_7$  is a stable molecule (Scheme 2c).<sup>14</sup> We reason that further reduction in ring size should enhance the ring-cap overlap and consequent stabilization. Formation of the carboryne must help in this direction further (Scheme 2d). We study the energetics of formation of the various carborynes to examine this idea and to delineate the more favorable ones. The results do point out that there are many carborynes that are thermodynamically more favorable than  $C_2B_{10}H_{10}$ . A reverse of this trend must be anticipated with Si atoms which are larger than B and C atoms. The reversal of relative stability among the different isomers is seen in the case of silaboranes.<sup>15</sup> Since the ring containing Si is large, the dehydrogenation must be favored, which will reduce the ring size. This is probed by studies on disilaboranes and disilaborynes. The preference of Si for lower valency leads to several novel structures. We also studied the details of bonding in these unexpected structures.

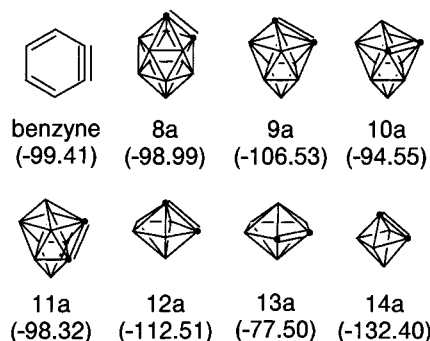
The carborynes are aromatic. The variation in aromaticity in going to the carborynes is probed by using Nuclear Independent Chemical Shift (NICS) values.<sup>16</sup> The relative stability and aromaticity of 1,2-carboranes and dehydrogenated derivatives and their Si analogues are presented here to get further insight into the nature of these polyhedral systems when the bonding is disturbed by dehydrogenation. Recent developments in the chemistry of polyhedral carborynes<sup>17</sup> and silaboranes<sup>18</sup> and lack of similar attempts in smaller polyhedral structures prompted us to present the details of our study.

## Methods

All the structures ( $C_2B_nH_{n+2}$  (**1a–7a**),  $C_2B_nH_n$  (**8a–14a**),  $Si_2B_nH_{n+2}$  (**1b–8b**), and  $Si_2B_nH_n$  (**15–21**)) were optimized at the B3LYP/6-31G\*<sup>19,20</sup> level of theory. The stationary points were characterized

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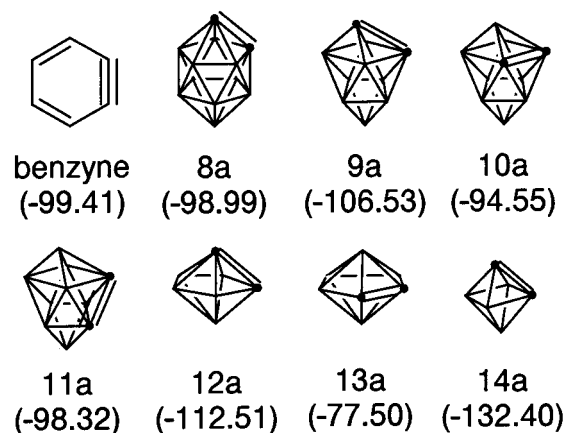


**Figure 1.** (a) Schematic drawings of *closo*-dicarbaboranes **1a–7a** ( $C_2B_nH_{n+2}$ ) and *closo*-disilaboranes **1b–7b** ( $Si_2B_nH_{n+2}$ ). The two black dots indicate the position of the CH or SiH groups. Relative energies of the isomers are given in parentheses (kcal/mol) wherever more than one isomer is considered.

through vibrational frequency analyses. NICS<sup>21</sup> values were computed at the GIAO-HF/6-31+G\* level by using geometries optimized at B3LYP/6-31G\*. The structures were further optimized at the B3LYP/6-311+G\* level and the resulting energies were used for comparison. The GAUSSIAN94 package<sup>22</sup> of programs was used for all calculations. Optimized geometries at B3LYP/6-311+G\* levels are given as Supporting Information.

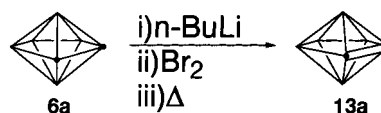
## Results and Discussion

**1,2-Dicarbaboranes and Dehydrogenocarboranes.** Many of the *closo*-dicarbaboranes ( $C_2B_nH_{n+2}$ ,  $n = 4, 5, 8, 10$ ) where carbon atoms occupy adjacent positions are known experimentally and several theoretical studies are also available.<sup>1,10</sup> The geometries of these polyhedral structures with carbon atoms in adjacent positions (**1a–7a**) and their dehydrogeno derivatives (**8a–14a**) are optimized and found to be minima. The only dehydrogeno derivative, synthesized as a transient species,  $C_2B_{10}H_{10}$  (**8a**),<sup>8</sup> shows interesting reactivity,<sup>9</sup> comparable to that of benzyne.<sup>7</sup> The C–C bond length of 1.625 Å in **1a** is reduced to 1.356 Å in **8a**. The Wiberg bond index (WBI) for C–C of 1.648 indicates double bonding, in contrast to the corresponding value in **1a** of 0.740. This C–C bond length is still considerably longer than that calculated for benzyne (1.245 Å). The skeletal requirement of the rigid icosahedral borane cage does not allow a further decrease in the C–C distance. Just as the rigid icosahedral skeleton demands a rather long C–C distance in **1a**, varying C–C distances are demanded by the peculiar structures in the nonicosahedral analogues. For example, isomers of the 10 vertex polyhedra have relatively long C–C distances (e.g., 1.668 Å in **3a** and 1.481 Å in **10a**). On the other hand, structures based on the pentagonal bipyramid have short distances (1.464 Å in **6a** and 1.305 Å in **13a**). Among the contributors to these structural variations is the ring-cap orbital overlap matching anticipated in the Introduction.<sup>12</sup> The four-membered  $C_2B_2$  rings in **3a** and **10a** have poor overlap with the more diffused orbitals of the BH cap. The ring-cap overlap can be enhanced by stretching the bonds involved in the four-



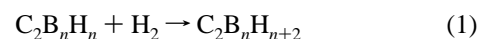
**Figure 2.** Dehydrogenocarboranes with their hydrogenation energies (in parentheses, kcal/mol) from eq 1. Corresponding silicon analogues **8b–14b** are not minima in the PES.

### Scheme 3



membered rings, explaining the C–C distances in **3a** and **10a** which are longer than those in **1a** and **8a**, respectively. On the other hand, the five-membered rings in **6a** and **13a** are too large in relation to the caps. The ring-cap overlap can be improved by decreasing the bond lengths of the five-membered rings; this is especially seen in the short C–C distance of 1.464 Å in **6a** and 1.305 Å in **13a**. Thus the C–C distance in  $C_2B_nH_{n+2}$  spans a large range of 1.464 Å in 2,3- $C_2B_5H_7$  (**6a**), 1.535 Å in 1,2- $C_2B_8H_{10}$  (**2a**), 1.543 Å in  $C_2B_4H_6$  (**7a**), 1.625 Å in  $C_2B_{10}H_{12}$  (**1a**), 1.642 Å in 1,2- $C_2B_5H_7$  (**5a**), and 1.668 Å in 2,3- $C_2B_8H_{10}$  (**3a**). This is indeed a large range for structures with similar polyhedral bonding. Dehydrogenation shifts this range to 1.304–1.481 Å. Obviously structures that naturally require a contraction of the cage are better candidates for the carboryne formation.

In contrast to the large number of experimental studies involving  $C_2B_{10}H_{10}$ ,<sup>8,9</sup> the dehydrogenation of lower vertex dicarbaboranes has not been attempted so far. We compare here the energetics of dehydrogenation of *closo*-dicarbaboranes,  $C_2B_nH_{n+2}$  ( $n = 4, 5, 8, \text{ and } 10$ ) (**1a–7a**) to carborynes (**8a–14a**, Figure 2):



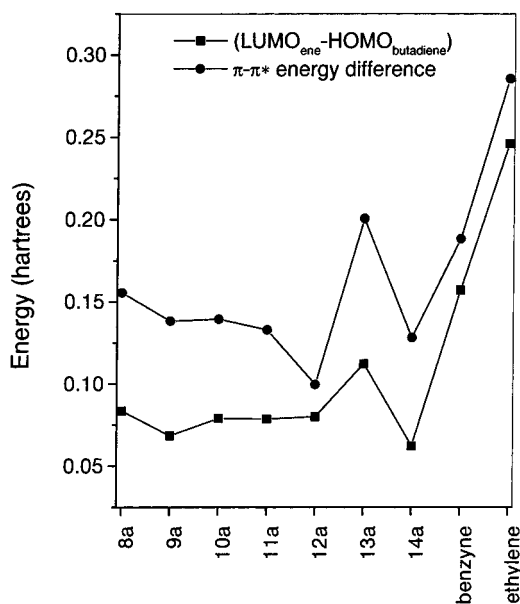
where  $n = 4, 5, 8, \text{ and } 10$ .

The formation of **8a** and benzyne is comparable energetically (–99.41 and –98.99 kcal/mol, Figure 2). Among the isomers of 10-vertex dehydrogenocarboranes, formation of 1,2- $C_2B_8H_8$  (**9a**) is more endothermic than benzyne whereas the formation of 2,3- $C_2B_8H_8$  (**10a**) is more favorable by 5 kcal/mol. Formation of  $C_2B_5H_5$  (**13a**) is even more favorable (Figure 2). Thus the anticipation based on the ring-cap matching described earlier is supported by these results. The parent and derivatives of  $C_2B_5H_7$  are known experimentally.<sup>14</sup> A possible approach to  $C_2B_5H_5$  is indicated in Scheme 3. Attempts to synthesize dehydrogenocarboranes, 2,3- $C_2B_5H_5$  (**13a**), should be rewarding. The first step in this reaction, viz., the formation of  $C_2B_5H_6Li$ , can be compared with that of the experimentally known

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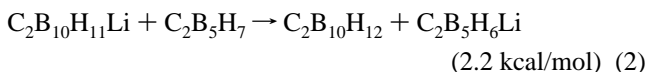
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**Figure 3.** The energy difference between HOMO of butadiene and LUMO of **8a–14a**, ethylene, and benzyne, shown as dark squares. The dark spheres indicate the  $\pi-\pi^*$  energy difference for the  $\pi$ -bond in **8a–14a**, benzyne, and ethylene. The  $\text{HOMO}_{\text{ene}}-\text{LUMO}_{\text{diene}}$  differences were consistently larger and hence not presented.

$\text{C}_2\text{B}_{10}\text{H}_{10}$  by the following equation.



The formation of  $\text{C}_2\text{B}_5\text{H}_6\text{Li}$  is only 2.2 kcal/mol less favorable than the formation of  $\text{C}_2\text{B}_{10}\text{H}_{11}\text{Li}$  and hence should be worth trying.

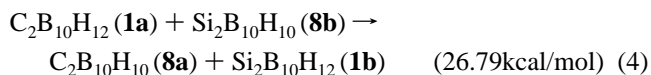
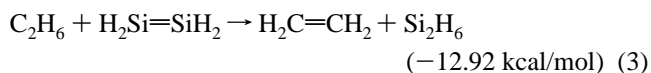
An estimate of the reactivity of dehydrogenocarboranes toward Diels–Alder reactions can be made by using the Frontier molecular orbital theory. The relative reactivity of a diene–dienophile system is reflected in the interaction between the appropriate Frontier molecular orbitals of the reactants. The smaller the difference in energy between the interacting orbitals, the higher is the reactivity. For the systems studied here, the relevant orbital pairs are the HOMO of butadiene and the LUMO of the ene ( $\text{C}_2\text{B}_n\text{H}_n$ ). The  $E(\text{HOMO}_{\text{diene}}-\text{LUMO}_{\text{ene}})$  for all the systems in our study is lower than that for ethylene and benzyne (Figure 3). It is also possible to have the reverse Frontier orbital control, viz.,  $E(\text{HOMO}_{\text{ene}}-\text{LUMO}_{\text{diene}})$ . However, these are much larger for each pair and hence not considered further. Since the Diels–Alder reactions of ethylene, benzyne, and **8a** with butadiene are known, other dehydrogenocarboranes are also expected to show similar reactivity. 2,3- $\text{C}_2\text{B}_5\text{H}_5$  (**13a**) is particularly interesting because of the short C–C distance of 1.301 Å and the large  $\pi-\pi^*$  energy difference which indicate a relatively strong bond. The  $E(\text{HOMO}_{\text{butadiene}}-\text{LUMO}_{\text{ene}})$  value indicates less reactivity for **13a** than for **8a** so it may be possible to isolate **13a**.

**closo-o-Disilaboranes and closo-o-Dehydrogenodisilaboranes.** The arguments based on the compatibility of overlap between rings and caps must depend on the heteroatom involved. While silaboranes are still a novelty, replacement of the carbon atoms in carboranes by silicon must bring dramatic changes in its structure bonding and reactivity.<sup>18</sup> Si with diffused orbitals fits better with larger rings. This effect is seen in the contrasting

relative stabilities of position isomers of silaboranes.<sup>15</sup> This reversal of trend must be seen in dehydrogenation as well. While the decrease in bond length required by dehydrogenation increases the strain in the dodecadicarboranes, decreasing bond length is favored in dehydrododecadisilaboranes.<sup>11</sup>

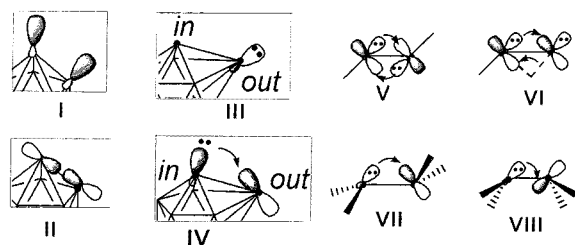
The icosahedral 1,2- $\text{Si}_2\text{B}_{10}\text{H}_{10}\text{Me}_2$  was synthesized in 1990.<sup>23</sup> The calculated structure of 1,2- $\text{Si}_2\text{B}_{10}\text{H}_{12}$  (**1b**) compares well with the salient features of the experimental structure. The topological features of  $\text{Si}_2\text{B}_n\text{H}_{n+2}$  are very similar to those of the corresponding  $\text{C}_2\text{B}_n\text{H}_{n+2}$  skeletons. However, the inherently longer Si–Si distance, in relation to the C–C distance, has dramatic energetic and structural consequences. For example, in 1,2- $\text{C}_2\text{B}_{10}\text{H}_{12}$  (**1a**) the standard C–C distance of 1.54 Å is lengthened to 1.625 Å to accommodate the rigid polyhedral skeleton with an average B–B distance of 1.781 Å. On the other hand, in  $\text{Si}_2\text{B}_{10}\text{H}_{12}$  (**1b**), the standard Si–Si distance of 2.34 Å of  $\text{Si}_2\text{H}_6$  is compressed to 2.316 Å to accommodate the shorter B–B distance of the polyhedral skeleton. In general, the replacement of carbon by silicon in *closo*-carboranes substantially changes the energetics. This is reflected in the relative energies of the various isomers (**2b–4b**, **5b–6b**, Figure 1). Since the valence orbitals of SiH are more diffused compared to those of CH, SiH prefers to cap large rings. Thus, SiH is better suited to cap five-membered rings, while CH is the better choice for four-membered rings. Among the three isomers of 10-vertex systems, the 1,2 isomer in which SiH caps a four-membered ring is higher in energy than the others. In the seven-vertex system, the 2,3-isomer has a  $\text{Si}_2\text{B}_3$  ring for which even the BH cap is not large enough. Therefore the 1,2-isomer in which one of the ring Si atoms is replaced by B is calculated to be lower in energy.

The dehydrogeno structure  $\text{Si}_2\text{B}_{10}\text{H}_{10}$  (**8b**) has a slightly shorter Si–Si distance than  $\text{Si}_2\text{B}_{10}\text{H}_{12}$  (**1b**). The icosahedral skeleton is highly strained to accommodate the long Si–Si distance in **1b**. Any decrease in the Si–Si distance is stabilizing for the icosahedron. The requirement of the relatively long distances for icosahedral structures is also satisfied in the contrasting energetics of the eqs 3 and 4.



The exothermicity of eq 3 is attributed, among other factors, to the strong C–C  $\pi$ -bonds. However, eq 4 is endothermic. A probable explanation of the reversal could be obtained from the structural details of the icosahedral skeletons. The B–B distance in  $\text{B}_{12}\text{H}_{12}^{2-}$  is 1.787 Å. To accommodate this skeletal distance, the C–C bond in **1a** is stretched to 1.625 Å. The strain goes up further in **8a** (Figure 2) because the C–C double bond is energetically more expensive to stretch. The calculated distance of 1.356 Å in **8a** is only marginally longer than that in ethylene (1.329 Å) and the structure **8a** is distorted considerably from an ideal skeleton. Disilaboranes bring a different trend. A reduction of strain is achieved in going from  $\text{Si}_2\text{B}_{10}\text{H}_{12}$  (**1b**) to

(23) (a) Seyferth, D.; Buchner, K.; Rees, W. S.; Davis, W. M., Jr. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 918. (b) Seyferth, D.; Buchner, K. D.; Rees, W. S., Jr.; Wesemann, L.; Davis, W. M.; Bukalov, S. S.; Leites, L. A.; Bock, H.; Solouki, B. *J. Am. Chem. Soc.* **1993**, *115*, 3586.



**Figure 4.**  $\text{Si}_2\text{B}_{10}\text{H}_{10}$  (**8b** is the transition state and **15** is the minima). Important orbitals are shown. Orbitals of *trans*- $\text{Si}_2\text{H}_2$  (**V**) and *monobridged*  $\text{Si}_2\text{H}_2$  (**VI**) and *trans*- (**VII**) and *cis*- $\text{Si}_2\text{H}_4$  (**VIII**).

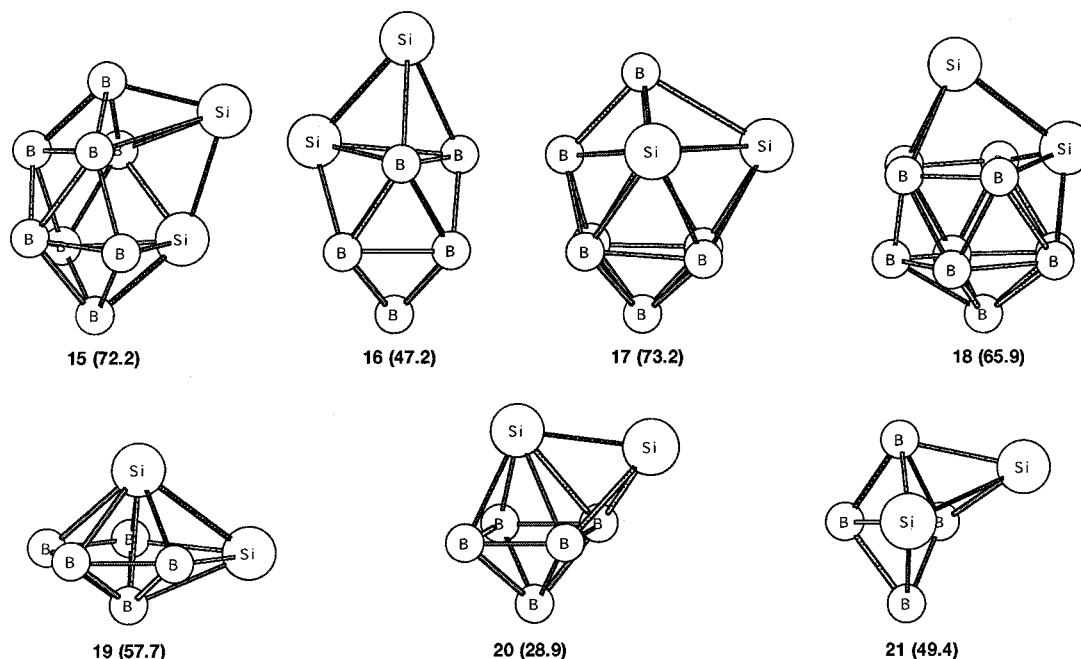
$\text{Si}_2\text{B}_{10}\text{H}_{10}$  (**8b**). The resulting Si–Si distance of 2.228 Å (**8b**), though much longer than desired, is considerably shorter than the value of 2.316 Å. In addition, the pyramidalization of Si is less demanding energetically. Thus, the combination of **1a** and **8b** is better compared to **8a** and **1b**. Despite this, **8b** is calculated to be a transition state. Following the imaginary frequency led to an unusual structure **15** with  $C_s$  symmetry.

The surface of **15** is not even. One Si atom has moved out of the icosahedral surface ( $\text{Si}_{\text{out}}$ , Figure 4) and the other has moved slightly in ( $\text{Si}_{\text{in}}$ ). The average Si–B bond distance of 2.121 Å in **8b** has gone to 2.360 Å for the  $\text{Si}_{\text{out}}$  and 2.043 Å for the  $\text{Si}_{\text{in}}$ . The Si–Si distances and WBI values in **1b** (2.316 Å, 0.57) and **8b** (2.325 Å, 0.67) are comparable. However, the Si–Si bond in **15** is very different from that in **1b**. A good approximation to bonding can be obtained by starting with the interaction of two  $\text{sp}^2$  hybrid Si groups. In a symmetrical arrangement as in **8b**, there is a  $\pi$  orbital and a  $\sigma$  orbital (**I** and **II**, Figure 4). In **15** one of the Si atoms goes up and the other goes down, resulting in two different MOs. The  $\sigma$  MO arises from the interaction of the p orbital on  $\text{Si}_{\text{out}}$  with the  $\text{sp}^n$  hybrid on  $\text{Si}_{\text{in}}$  (**IV**). A lone pair formed on  $\text{Si}_{\text{out}}$  is the HOMO (**III**). There are a few examples in the literature where the p orbital of one Si accepts electrons from the hybrid orbital of the adjacent Si. The *trans* and the *monobridged*  $\text{Si}_2\text{H}_2$  (**V** and **VI**, Figure 4)

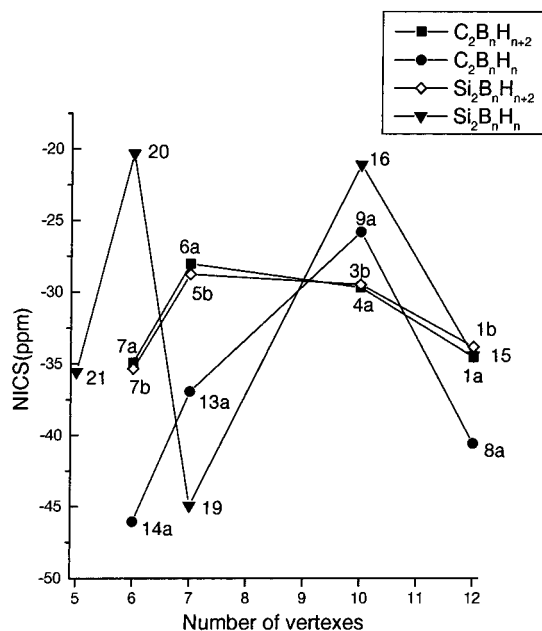
present the closest comparison.<sup>24</sup> Although the environment around Si is very different in  $\text{Si}_2\text{H}_2$  and **15**, the  $\text{Si}_2\text{H}_2$  structures present such an interaction. The  $\text{Si}_2$  unit in **15** can also be compared to that in  $\text{Si}_2\text{H}_4$ . The *trans* structure (**VII**) is calculated to be more favorable than the *cis* (**VIII**) structure; the latter is not even a stationary point. However, the constraints of the  $\text{B}_{10}$  template force a *cis* arrangement with the unusual bonding pattern (**III** and **IV**).

Similarly other  $\text{Si}_2\text{B}_n\text{H}_n$  (**9b**–**11b**, Figure 2) structures also distort to give **16**–**18** (Figure 5). The 1,2- $\text{Si}_2\text{B}_3\text{H}_5$  structure (**19**) has a pentagonal bipyramidal structure. The Si that is part of the five-membered ring has a lone pair of electrons. Structure **19** completes the  $n+1$  skeletal electron pair count by accepting the formal lone pair of electrons from the capping Si atom to the skeletal bonding. The 2,3- $\text{Si}_2\text{B}_3\text{H}_5$  (**13b**) distorts to a qualitatively different structure (**20**) and can be visualized as an octahedron with the silicon capping one of the faces. Similarly,  $\text{Si}_2\text{B}_4\text{H}_4$  (**21**) also distorts to a trigonal bipyramidal structure with silicon capping one face. These structures with reduced cage size (**20** and **21**) satisfy the  $(n+1)$  electron count by accepting two electrons from the bridging atom. In this respect, these structures are equivalent to BH bridging structures such as  $\text{B}_{13}\text{H}_{13}$  (a  $\text{B}_{12}\text{H}_{12}$  with one of the triangular faces bridged by a BH group) and smaller analogues described earlier.<sup>25</sup> The BH–Si isolobal analogy anticipates this equivalence.<sup>26</sup>

**Aromaticity of Carboranes and Silaboranes.** It is interesting to check the influence of the exohedral  $\pi$ -bond on three-dimensional skeletal delocalization. The aromatic character is estimated from the magnitudes of Nucleus Independent Chemical Shift (NICS).<sup>16</sup> Absolute chemical shieldings (with the sign reversed) calculated at the cage center of the molecule indicate the ring current: positive values indicate antiaromatic and negative values aromatic nature. NICS is an inherently unobservable property, but despite this deficiency it has come to be widely used as a measure of aromaticity. We have calculated



**Figure 5.** Structure of dehydrogenosilaboranes ( $\text{Si}_2\text{B}_n\text{H}_n$ ) optimized at B3LYP/6-31+G\*. The numbers in parentheses give the dehydrogenation energies in kcal/mol from the corresponding  $\text{Si}_2\text{B}_n\text{H}_{n+2}$ .



**Figure 6.** Plots of nuclear independent chemical shifts (NICS, ppm) of most stable positional isomers of  $C_2B_nH_{n+2}$ ,  $C_2B_nH_n$ ,  $Si_2B_nH_{n+2}$ , and  $Si_2B_nH_n$ .

NICS for structures 1–7 and 15–21 and the values are plotted in Figure 6. When there is more than one isomer with the same vertex size, the NICS value of the most stable one is used in the plot. NICS is plotted against the number of vertices in the skeleton. Thus the structures with one Si atom bridging a face will have one vertex fewer than the parent structure from which the bridged structure is derived. Thus  $Si_2B_5H_5$  (20) obtained from 13b is treated as a six-vertex system. Multiple bonds on carborane surfaces have very little effect on the three-dimensional aromatic nature of carboranes in general. The plot of NICS values (Figure 6) shows that the magnetic criterion of aromaticity is affected more by the symmetry of the cage. The delocalization is more for the most symmetrical cages. Six-vertex octahedral and twelve-vertex icosahedral compounds of carboranes are more aromatic than the others. The dehydrogenodisilaboranes bring in an additional complication. The 6-vertex  $Si_2B_4H_4$  has a pentagonal bipyramidal structure, 21, with an Si bridging a face, and is represented as a five-vertex structure in Figure 6. Similarly, the more favorable 2,3- $Si_2B_5H_5$

structure is based on the octahedron (20). Thus the NICS are strictly plotted according to the shapes in Figure 6. The aromaticity criterion follows the general trends of reactivity and stability.

## Conclusions

A major controlling factor in the stability of carboranes is the compatibility of ring and cap orbitals in the overlap. This is used to arrive at thermodynamically more stable carborynes among the many possibilities. Two isomers of dehydrogenocarboranes, 2,3- $C_2B_8H_8$  (10a) and 2,3- $C_2B_5H_5$  (13a), were found to be thermodynamically more favorable than benzyne. According to Frontier molecular orbital analysis, these could be ideal dienophiles in pericyclic reactions. The structural features of silaboranes are similar to those of the carboranes though with modifications resulting from the larger size of Si. Relative stabilities are reversed in going from carborynes to silaborynes. Attempts to avoid the Si–Si multiple bond result in unusual structures for silaborynes. One of the Si atoms moves away from the surface in  $Si_2B_{10}H_{10}$  (15),  $Si_2B_8H_8$  (16, 17, and 18), and 1,2- $Si_2B_5H_5$  (19). One Si atom forms a bridge to a trigonal surface in 2,3- $Si_2B_5H_5$  (20) and 1,2- $Si_2B_4H_4$  (21). Three-dimensional aromaticity estimated by using NICS calculations shows that the exohedral double bond does not influence aromaticity.

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**Supporting Information Available:** Total energies (hartrees) and relative energies (kcal/mol) at B3LYP/6-311+G\*, bond length and Wiberg bond index at B3LYP/6-31G\* and NICS at the GIAO-HF/6-31+G\*\*/B3LYP/6-31G\* level and the geometries of structures (1a–14a, 1b–8b, 15–21,  $C_2B_{10}H_{11}Li$ , and  $C_2B_5H_6Li$ ) in Cartesian coordinates (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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