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The Rearrangement of Dicarboranyl Methyl Cation: A Possible Synthetic Strategy Toward Cationic *closo*-Tricarbaboranes

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A quantitative study on cationic *closo*-tricarbaboranes proved their stability and a possible use for them as weakly coordinating ions due to the dispersal of positive charge throughout the cage. The current study explores computationally a synthetic strategy toward their realization in parallel with the benzyl cation–tropylium ion rearrangement. This study shows that cage expansion along with the incorporation of a carbon atom into the cage starting from the dicarboranyl methyl cation is in the realm of the possible. The rearrangements are found to have favorable energy barriers with one transition state. The geometry of the dicarboranyl methyl cations (benzyl cation analogues) with bent CH_2 groups favors the rearrangement into the tropylium analogues. Thus, the comparison of well-known benzyl ion–tropylium ion rearrangement with similar reactions among polyhedral boranes unravels the feasibility of cationic tricarboranes.

The literature on carbon substituted *closo*-polyhedral boranes is restricted to mono and dicarbaboranes;[1] tricarbaboranes and higher carbaboranes are not known in the *closo*-family. We recently pointed out the stability of the isomers of *closo*-$C_3B_nH_{n+3}^+$, which are potentially weakly coordinating cations with the charge dispersed throughout the cage.[2a] Though many synthetic approaches toward the neutral *nido* or *arachno* multi-carba systems are known,[3] *closo*-cationic tricarboranes remain elusive. Here we propose a synthetic strategy to cationic *closo*-carboranes based on the well-known benzyl cation−tropylium ion rearrangement.[4] Computational studies on carboranyl cations (*closo*-$C_2B_nH_{n+1}$-CH_2^+) indicate that a cage expansion reaction similar to the expansion of the six-membered ring to seven-membered ring must lead to *closo*-$C_3B_nH_{n+3}^+$. Specific synthetic targets toward this end are suggested.

In comparison to the benzyl cation−tropylium ion rearrangement, which is calculated to be exothermic by 10.2 kcal mol^{-1} at B3LYP/6-31G*, the cluster expansion reactions are generally more exothermic (Scheme 1).[5] The octahedral 1-CH_2-2,3-$C_2B_4H_5^+$ (**1**) is less stable than 2,4,5-$C_3B_4H_7^+$ (**2**) by 54.0 kcal mol^{-1}. The 11-vertex *closo*-dicarboranyl methyl cation, 1-CH_2-7,9-$C_2B_9H_{10}^+$ (**3**), is also less stable than the cationic *closo*-icosahedral tri-carba species, 2,8,10-$C_3B_9H_{12}^+$ (**4**), by 41.3 kcal mol^{-1}. However, eq III (Scheme 1) which generates a 13-vertex *closo*-tricarborane (**6**) is endothermic; 2,9,11-$C_3B_{10}H_{13}^+$ (**6**) is higher in energy than 12-vertex 1-CH_2-8,10-$C_2B_{10}H_{11}^+$ (**5**) by 10.5 kcal mol^{-1}, possibly from the inherent extra stability of the icosahedral skeleton.[6] There are several isomers possible for each tricarbaborane family; **2** is the most stable isomer among the pentagonal bipyramidal tricarba species, and **4** is the second-most stable one among the icosahedral family.[2b]

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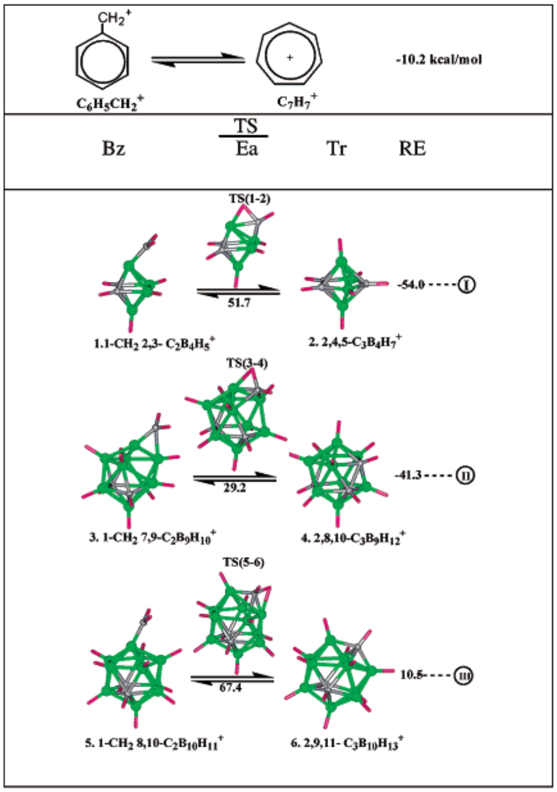
Scheme 1. The Benzyl−Tropylium Ion Equivalent Equilibria Computed for the Tricarbaboranes[a]



[a] The optimized geometry of the reactants (Bz), transition states (TS), and the products (Tr); the energy barrier, Ea (kcal mol^{-1}); and the relative energies, RE (kcal mol^{-1}) at B3LYP/6-31G* are given. TS is characterized with one imaginary vibrational frequency.

In light of favorable exothermicities, the transition states for the conversion of **1** to **2**, **3** to **4**, and **5** to **6** are computed. These are represented by **TS(1−2)**, **TS(3−4)**, and **TS(5−6)** (Scheme 1). The energy barrier for the conversions from **1** to **2** is calculated to be 51.7 kcal mol^{-1}. The conversion of 11-vertex **3** to icosahedral species **4** is computed to have a barrier of 29.2 kcal mol^{-1}. The highest energy barrier of 67.4 kcal mol^{-1} is computed for **5** to **6**. Thus, the transformation from a less stable 11-vertex to the most stable icosahedral form is more feasible than from either icosahedral or octahedral carbaborane to the corresponding 13-vertex and 7-vertex carbaboranes. These are to be compared to the barrier of 62.1 kcal mol^{-1} calculated on the path of benzyl cation−tropylium ion conversion.[7] Thus, the energy barriers for the cationic boranes appear to be accessible. All the rearrangements are one-step processes; the transition states are characterized with one imaginary vibrational frequency. The reaction path for the formation of these tropylium ion equivalent structures is traced out by IRC calculations.[8]

The primary cations **1**, **3**, and **5** have the CH_2^+ tilted away from the pseudo-C_n axis and toward one of the boron vertices (B_β). This tilting is observed in all the cases except for **1** where the bending is toward an edge forced by the symmetry.

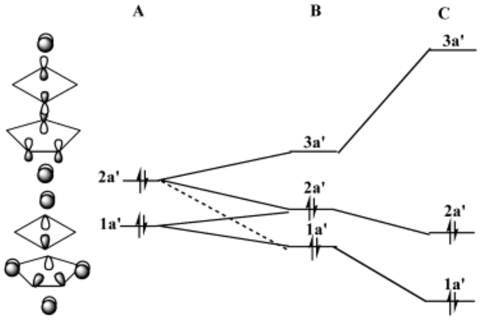


Figure 1. The cage orbitals of $C_2B_9CH_2^+$ which interact with the vacant p-orbital of the CH_2 group (A) and the resulting molecular orbitals of $C_2B_9CH_2^+$ with linear CH_2 (B). The tilting of CH_2 group enhances the interaction leading to the stabilization of bonding molecular orbitals, 1a′ and 2a′, and the destabilization of the LUMO, 3a′ (C).

Table 1. The Tilting Angle (θ, deg), the Distance between the Methyl Carbon and the Boron (B_α) to Which It Is Connected (l_1), as Well as the Boron (B_β) toward Which It Is Bent (l_2), and the Corresponding Wiberg Bond Indices (WBIs)[5]

		C−B_α (Å)		C−B_β (Å)	
compd	θ	l_1	WBI	l_2	WBI
$C_2B_4H_5CH_2^+$(**1**)	45.4	1.457	1.308	2.496	0.185
$C_2B_9H_{10}CH_2^+$(**3**)	45.1	1.463	1.232	1.895	0.472
$C_2B_{10}H_{11}CH_2^+$(**5**)	30.4	1.499	1.141	2.328	0.198

In **3**, the CH_2 group tilts to one of the vertex by 45.1°. But in the known dicarboranyl methane ($C_2B_9H_{10}CH_3$), there is no tilting for the CH_3 group, and the methyl carbon is colinear to the capping atoms.[9] It is the interaction of the vacant p-orbital on the CH_2 group with bonding skeletal orbitals 1a′ and 2a′ of the cage (**A**, Figure 1) that leads to the tilting. This delocalization is reflected in the natural charge on the CH_2 group (0.082). The molecular orbitals, 1a′ and 2a′, are stabilized while 3a′ which is the LUMO gets destabilized in this process (**C**, Figure 1). If this is indeed correct, CH_2 substituent with two electrons in the p-orbital should not tilt, as is confirmed from the optimized geometries of $C_2B_nH_{n+1}CH_2^{1-}$. These are minima on their respective potential energy surface as well.

The B_α−C bond length in **3** is 1.482 Å (WBI = 1.148; B_α is the boron to which the CH_2 carbon is bonded).[10] There is a C−B_α−B_β three-center bond which shows enhanced delocalization due to the stabilizing interaction. This is further supported by the formation of a weak bond (WBI = 0.627) between the carbon and the cage boron (B_β) toward which it is tilted. The tilting angle is less for **5** (30.4°, Table 1) where the reaction is calculated to be endothermic (Scheme 1).

The reaction path for the formation of the icosahedral cations starting from other CH_2^+ substituted isomers of the experimentally known 11-vertex dicarbaborane is also computed.[9b] Two cases are studied here where the reactant is with the CH_2 group attached on the boron vertex (**13**) and on the carbon vertex (**15**). Their energy barriers can be compared with II in Scheme 1. The rearrangement from

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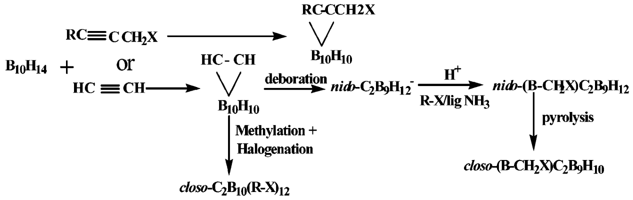
13 is slightly less favorable than from **3** with an energy barrier of 34.2 kcal mol^{-1}, and that from **15** is highly unfavorable with a barrier of 70.1 kcal mol^{-1}. This shows the lower preference of C-substituted dicarboranyl methyl cation as the reactant. A similar strategy toward the formation of monocarbaboranes is studied and is found to be equally favorable (details are given in the Supporting Information).

All the transition state structures have one of the $-CH_2$ hydrogens bridging the carbon$-$boron bond. One of the ring B$-$B bonds is elongated to 2.780 Å in **TS(3$-$4)** and 1.980 Å in **TS(1$-$2)** whereas the $B_\alpha-B_\beta$ bond is lengthened in **TS(5$-$6)** (2.292 Å) to accommodate the $-CH_2$ carbon.

There are many known reactions to emulate. The reactant with an icosahedral framework could be achieved by many ways such as the reaction between $B_{10}H_{12}$(ligand)$_2$ and C_2-RR′X, halogenation of the methyl derivatized *closo*-icosahedral borane, and insertion of the properly substituted vertex on to a *nido* face.[1c,d] This reactant can be either directly employed for the formation of 13-vertex cluster or made to undergo base promoted degradation to obtain the nido product.[11] The pyrolysis of the *nido*-B-derivatized $C_2B_9H_{13}$ leads to the closo-11-vertex dicarboranyl methyl system.[12]



Thus, the prospect of synthesizing other similar carboranyl compounds, either by extending an analogous pathway as that of icosahedral systems or by starting with a B-derivatized *nido*-system, is sure to bring excitement in the area of carbon rich carboranes.[13]

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Supporting Information Available: Total energies, optimized coordinates of all the structures, geometries of $C_2B_nH_{n+1}CH_2{}^{1-}$, details of computed reaction path for monocarbaboranes and with reactants from experimentally known 11-vertex dicarbaboranes. This material is available free of charge via the Internet at http://pubs.acs.org.

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