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Cage Opening of *closo*-$C_2B_6H_8$ with Hydride Ion and with Trimethylamine: Preparation of a New Carborane Anion and of a Trimethylamine Adduct of $C_2B_6H_8$

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The reaction of *closo*-$C_2B_6H_8$ with lithium hydride in tetrahydrofuran produces a $[C_2B_6H_9]^-$ ion. Trimethylamine reacts with *closo*-$C_2B_6H_8$ to give a weakly bound adduct and eventually forms a more strongly bound $(CH_3)_3N{\cdot}C_2B_6H_8$ adduct. The NMR (^{11}B and ^1H) spectra of both the $[C_2B_6H_9]^-$ ion and the more strongly bound adduct, $(CH_3)_3N{\cdot}C_2B_6H_8$, are consistent with C_1 structural symmetry for both compounds and with the assignment of a single bridging hydrogen in each. It is proposed that the cage carbon and boron atoms in both products, the $[C_2B_6H_9]^-$ ion and the $(CH_3)_3N{\cdot}C_2B_6H_8$ adduct, are arranged in a fashion in which they could be considered as a fragment of an icosahedron and in which the carbons are in 1,3-positions relative to one another around a six-atom open face. The bridging hydrogen in each compound is located between two adjacent low-coordination borons along the open face.

Introduction

The structure of *closo*-1,7-$C_2B_6H_8$, first isolated as the C,C'-dimethyl derivative,[1,2] was proposed to be that of a specific dodecahedron, the bisdisphenoid, and this was supported by microwave studies[3] on the parent compound[4] and by X-ray studies[5] on the C,C'-dimethyl derivative.[1,6] Although this type of molecule has been prepared in several other studies,[7,8] it has not been the subject of a significant amount of chemistry other than in connection with transition metal incorporation studies[9-12] as well as a few other studies.[13,14]

Ab initio MO studies[15-17] support the suspicion that the 1,7-$C_2B_6H_8$ isomer is the most stable of the various possible, but not yet isolated, carbon position isomers with a closo (bisdisphenoid) framework.[2] Variable-temperature ^{11}B NMR experiments on $C_2B_6H_8$ and its C,C'-dimethyl derivative carried out as low as -140 °C show only two sets of resonances, in a ratio of 4:2, and give no indication of the requisite three pairs of boron atoms expected for the proposed static structure.[18]

In previous studies[19-21] with the smaller *closo*-carboranes, the (near)-octahedral 1,6-$C_2B_4H_6$ and pentagonal bipyramidal 2,4-$C_2B_5H_7$, it was found that both hydride ion and trimethylamine react slowly with the former but not at all with the latter carborane. In the case of *closo*-1,6-$C_2B_4H_6$ the products are a result of cage opening to a (nido) pentagonal pyramidal framework,[19-21] and thus the results were consistent with cage electron counting theory.[1,2,22,23] It is to be noted that the 2,3-isomer of *closo*-$C_2B_5H_7$ has been found to react with a hydride ion source to give a compound exhibiting a nido structure[24,25] predictable from cage structural rules.[1,2,22,23]

We wished to explore the effect of nucleophilic reagents such as hydride ion and trimethylamine on 1,7-$C_2B_6H_8$ in order to assess the reactivity of each reagent on this carborane and to identify the nature of any products.

Experimental Section

Materials. The parent *closo*-1,7-$C_2B_6H_8$ was a gift from R. E. Williams. It was purified by repeated cold-column fractionation[26] under vacuum; *closo*-1,7-$C_2B_6H_8$ emerged from the column in the temperature range of -65 to -75 °C. A ^{11}B NMR spectrum of the purified $C_2B_6H_8$ exhibited the expected two doublets: $\delta = -8.45$, $J(BH_t) = 178$ Hz (area 2); $\delta = +7.77$, $J(BH_t) = 169$ Hz (area 4). Lithium hydride (Aldrich) was used without further purification, and trimethylamine (Union Carbide) was used after removing trace amounts of moisture by application of cold-trap fractionation techniques. Both tetrahydrofuran-d_8 and benzene-d_6 were obtained from Aldrich.

Reaction of LiH with $C_2B_6H_8$. Tetrahydrofuran-d_8 (ca. 4 mmol) and $C_2B_6H_8$ (0.22 mmol) were added to LiH (5.7 mmol), and the mixture was allowed to stand, with occasional shaking, for 4 days at room temperature. A ^{11}B NMR spectrum of the mixture indicated that some of the $C_2B_6H_8$ had reacted to form the $[C_2B_6H_9]^-$ ion. After approximately

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Table I. ^{11}B and ^1H NMR Data for the $[1,3\text{-}C_2B_6H_9]^-$ Ion ^{11}B NMR Data

δ	coupling, Hz (rel area, assgnt)
−27.02	$J(BH_t) = 115$, $J_{BB} = 47$ (area 1, B(4))
−25.34	$J(BH_t) = 136$ (area 1, B(7))
−24.57	$J(BH_t) = 147$ (area 1, B(8))
+3.38	$J(BH_t) = 165$ (area 1, broad doublet which, upon proton decoupling, gave rise to a broad peak with evidence of (with resolution enhancement) a mutliplet structure attributed to BB coupling, B(5))
+10.57	$J(BH_t) = 150$, $J(BH_\mu) = 46$ (area 1, B(6))
+18.87	$J(BH_t) = 144$ (area 1, B(2))

^1H NMR Data

δ	assgnt (area)	δ	assgnt (area)
−5.67	H(μ) (area 1)	+3.48	$H_tB(5)$ (area 1)
+0.69	$H_tB(7,8)$ (area 2)	+3.54	$H_tC(3)$ (area 1)
+0.74	$H_tB(4)$ (area 1)	+3.81	$H_tB(6)$ (area 1)
+2.19	$H_tC(1)$ (area 1)	+3.93	$H_tB(2)$ (area 1)

10 days at room temperature, with occasional shaking of the sample, nearly all of the $C_2B_6H_8$ had reacted to form $[C_2B_6H_9]^-$. Small amounts of impurities ($C_4B_2H_6$ and $B\text{-}CH_3\text{-}2,4\text{-}C_2B_5H_6$ isomers) in the original $C_2B_6H_8$ remained unreacted. The quantity of noncondensables in the mixture was measured to be less than 0.05 mmol. All of the volatiles were removed by high-vacuum techniques, and a fresh sample of tetrahydrofuran-d_8 (ca. 1 mmol) was added to the nonvolatile portion. All of the nonvolatile portion, except for unreacted LiH, dissolved in the tetrahydrofuran-d_8. The liquid portion of the sample was then transferred to a fresh NMR tube for analysis.

Reaction of $C_2B_6H_8$ with $(CH_3)_3N$. Trimethylamine (1.5 mmol) was added to $C_2B_6H_8$ (0.5 mmol) at −190 °C, and the sealed sample mixture was warmed to room temperature. A significant quantity of white solid was then observed, but when an attempt was immediately made to vacuum evaporate the volatile materials from the solid portion, the solid phase also partially disappeared. A ^{11}B NMR spectrum of the solids that remained, dissolved in tetrahydrofuran-d_8 (ca. 1–2 mmol), showed that both $C_2B_6H_8$ and $(CH_3)_3N$ were present in the undissociated form only. When a $(CH_3)_3N/C_2B_6H_8$ mixture was allowed to stand at room temperature for 1–3 days, a slightly viscous oily liquid, primarily the adduct $(CH_3)_3N{\cdot}C_2B_6H_8$, formed. NMR spectra ($^{11}B$ and ^1H) were taken of this oily liquid after dissolving the sample in tetrahydrofuran-d_8. The spectra showed that some $C_2B_6H_8$ (ca. 35%) was still present along with the adduct $(CH_3)_3N{\cdot}C_2B_6H_8$. The volatile fraction, largely tetrahydrofuran, $(CH_3)_3N$, and trace quantities of impurities that were present in the original $C_2B_6H_8$ (e.g. $3\text{-}CH_3\text{-}2,4\text{-}C_2B_5H_6$ and $1\text{-}CH_3\text{-}2,4\text{-}C_2B_5H_6$ isomers), was vacuum distilled from the $(CH_3)_3N{\cdot}C_2B_6H_8$ adduct into a −190 °C trap. In the process it was noticed that the $(CH_3)_3N{\cdot}C_2B_6H_8$ adduct, at room temperature, was very slowly disappearing from the "nonvolatile" solid phase into a −30 °C trap which was sandwiched between the −190 °C trap and the container housing the nonvolatile adduct. Before much of the solid phase had volatilized, the fractionation was stopped and a fresh sample of tetrahydrofuran-d_8 (ca. 1 mmol) was added to dissolve the nonvolatile portion of the adduct. A boron-11 NMR spectrum of the sample showed that the "free" $C_2B_6H_8$ had diminished in quantity but still represented about ca. 5% of the adduct quantity. After the sample was allowed to stand for 3 days at room temperature the quantity of free $C_2B_6H_8$ increased to ca. 35–40% of the $(CH_3)_3N{\cdot}C_2B_6H_8$ adduct present. A boron-11 NMR spectrum of the sample in the −30 °C trap showed the presence of both the $(CH_3)_3N{\cdot}C_2B_6H_8$ adduct and free $C_2B_6H_8$.

When a sample of the $(CH_3)_3N{\cdot}C_2B_6H_8$ adduct was dissolved in benzene-d_6, the room temperature equilibrium quantities of adduct vs free $C_2B_6H_8$ were assessed, by boron-11 NMR spectra, at ca. 1:6, respectively. Proton NMR analyses of the above samples, both in benzene solvent and tetrahydrofuran-d_8 solvent, gave bound-trimethylamine: unbound-trimethylamine ratios that were in agreement with the above boron-11 NMR results.

Nuclear Magnetic Resonance. Boron-11 and ^1H spectra were recorded on a Bruker AM-400 instrument. The ^{11}B and ^1H NMR data, and assignments, for the $[C_2B_6H_9]^-$ ion and the $C_2B_6H_8{\cdot}N(CH_3)_3$ adduct are given in Tables I and II, respectively. The ^{11}B spectra were recorded, both coupled and ^1H decoupled, for each of the two compounds; the ^1H spectra were recorded both coupled and ^{11}B decoupled. Variable-temperature NMR studies of the tetrahydrofuran solutions of the $[C_2B_6H_9]^-$ ion, and of the adduct $C_2B_6H_8{\cdot}N(CH_3)_3$, down to −30 °C do not show significant changes in patterns for either. Below −30 °C all of the resonances in each sample broaden in a similar fashion, suggesting the domination of viscosity effects on the spectrum rather than implying any structural changes. ^{11}B–^{11}B 2-D NMR results were obtained using the homonuclear shift-correlated COSY 2D and COSYX.AUR (homonuclear shift-correlated 2D for X-nuclei with proton decoupling) applications. The 2D NMR spectra showed, for the $[C_2B_6H_9]^-$ ion, strong ^{11}B–^{11}B cross peaks between the resonances at $\delta = -27.02$ (B(4)) and +3.38 (B(5)) and between resonances at $\delta = -24.57$ (B(8)) and +10.57 (B(6)). Other weaker cross peaks are found between $\delta = -24.57$ (B(8)) and +3.38 B((5)) and between $\delta = -25.34$ (B(7)) and −24.57 (B(8)), and very weak cross peaks are found between $\delta = -25.34$ (B(7)) and +18.87 (B(2)). The 2D NMR spectra showed, for the $C_2B_6H_8{\cdot}N(CH_3)_3$ adduct, a strong ^{11}B–^{11}B cross peak between resonances at $\delta = -5.00$ (B(4)) and −2.83 (B(5)), a moderately strong cross peak between $\delta = -25.07$ (B(7,8)) and +13.01 (B(6)), weaker cross peaks between $\delta = -25.07$ (B(7,8)) and −5.00 (B(4)) and between $\delta = -25.07$ (B(7,8)) and −2.83 (B(5)), and very weak cross peaks between the resonances at $\delta = -25.07$ (B(7,8)) and +19.78 (B(2)).

Table II. ^{11}B and ^1H NMR Data for the $C_2B_6H_8{\cdot}N(CH_3)_3$ Adduct ^{11}B NMR Data

δ	coupling, Hz (rel area, assgnt)
−25.07	$J(BH_t) = 157$ (slightly unsym doublet in undecoupled spectrum) (area 2, B(7,8))
−5.00	broad (peak width at half-height remains the same, ca. 160 Hz, upon proton decoupling) (area 1, $(CH_3)_3N$-B(4))
−2.83	broad (peak width at half-height diminishes from ca. 300 Hz to ca. 180 Hz upon proton decoupling) (area 1, B(5))
+13.01	$J(BH_t) = 160$, $J(BH_\mu) = 40$ (area 1, B(6))
+19.78	$J(BH_t) = 152$ (area 1, B(2))

^1H NMR Data

δ	area (assgnt)	δ	area (assgnt)
−5.29	H(μ) (area 1)	+3.45	$H_tB(5)$ (area 1)
+1.03	$H_tB(8)$ (area 1)	+3.74	$H_tC(3)$ (area 1)
+1.28	$H_tB(7)$ (area 1)	+3.91	$H_tB(6)$ (area 1)
+2.82	$(CH_3)_3N$ and $H_tC(1)$ (area 10)	+4.00	$H_tB(2)$ (area 1)

Calculational Methods for the Geometry Optimizations and Respective Energies. All geometry optimization calculations were carried out at both the 3-21G and 6-31G* levels using the Gaussian-90 codes;[27] single point energy calculations were carried out at both the MP2/6-31G*//3-21G level. The trimethylamine adduct of $C_2B_6H_8$ was calculationally analyzed as the NH_3 adduct. The calculated energies (in au) of the compounds are as follows: $[C_2B_6H_9]^-$ ion, −227.78516 at the 3-21G//3-21G level, −229.89058 at the MP2/6-31G*//3-21G level, −229.08139 at the 6-31G*//6-31G* level; $C_2B_6H_8{\cdot}NH_3$ adduct, −283.08863 at the 3-21G//3-21G level, −285.64636 at the MP2/6-31G*//3-21G level, −284.67849 at the 6-31G*//6-31G* level. Vibrational frequencies were determined at both the 3-21G and the 6-31G* levels for both molecules; no imaginary frequencies were encountered. It is to be noted that stationary points in the geometry optimizations are assessed as true minima when no imaginary frequencies are found; stationary points are saddle points (transition state) when an imaginary frequency is found. The Gaussian calculations were carried out on, variously, Multiflow-Trace and Elxsi minisupercomputers. The structure depicted for the $[C_2B_6H_9]^-$ ion (Figure 1) was constructed directly from the optimized coordinates using the Molecular Editor application on a Mac-IIci computer.

Results and Discussion

The known *closo*-$C_2B_6H_8$ reacts with lithium hydride, in tetrahydrofuran, to form a $[C_2B_6H_9]^-$ ion. Unlike the starting *closo*-carborane, the ^{11}B NMR spectrum of the $[C_2B_6H_9]^-$ solution indicates that each of the six boron atoms of the ion product are unique (Table I) implying C_1 symmetry. Proton coupled, and decoupled, ^{11}B NMR spectra of the product ion further indicate that each of the six borons contains one terminal hydrogen and that two (adjacent) borons are bonded to a single bridging

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[27] Gaussian-90: Frisch, M. J.; Head-Gordon, M.; Trucks, G. W.; Foresman, J. B.; Schlegel, H. B.; Raghavachari, K.; Robb, M.; Binkley, J. S.; Gonzalez, C.; Defrees, D. J.; Fox, D. J.; Whiteside, R. A.; Seeger, R.; Melius, C. F.; Baker, J.; Martin, R. L.; Kahn, L. R.; Stewart, J. J. P.; Topiol, S.; Pople, J. A. Gaussian, Inc., Pittsburgh, PA.

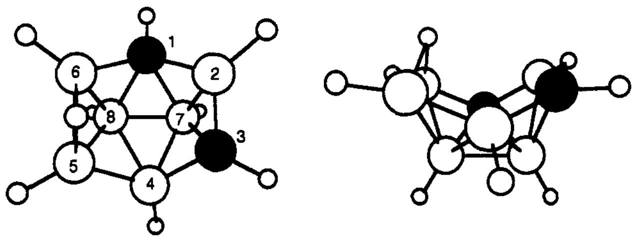

Figure 1. Proposed structure of the $[1,3\text{-}C_2B_6H_9]^-$ ion shown from two perspectives. The depicted structure is constructed directly from the optimized 6-31G* coordinates. The carbons are represented by closed black circles, the boron atoms are represented by the large open circles, and hydrogen are represented by the smaller open circles. The $C_2B_6H_8{\cdot}N(CH_3)_3$ adduct is proposed to have essentially the same carborane geometry as the $[C_2B_6H_9]^-$ ion with the hydride on B(4) replaced with a trimethylamine group.

hydrogen. The proton NMR spectrum of the $[C_2B_6H_9]^-$ ion, in tetrahydrofuran-d_8, confirms that there is a single bridging hydrogen at high field, $\delta = -5.67$; a boron-11 decoupled proton NMR spectrum also confirms that there are six H_t–B groups and two different H–C hydrogens. Of the six H_t–B hydrogens, two at high field (but at lower field than the high-field bridging hydrogen) are overlapped. A 2-D ^{11}B–^{11}B NMR spectrum is consistent with the assignment of the boron resonances (Table I) to the structure depicted in Figure 1. Ab initio calculations on all carbon-position isomers of the $[C_2B_6H_9]^-$ ion structure shown in Figure 1 indicate that the isomer shown in Figure 1 is the most stable, at the MP2/6-31G*//3-21G level.[28] The shortest B–B bond distance of the isomer shown in Figure 1, as a result of the MO calculations, is found to be that for B(4)–B(5); coincidentally, the strongest 2D ^{11}B–^{11}B NMR cross peak is observed between these two assigned boron resonances in the ^{11}B NMR spectrum. Another strong cross peak is observed for B(6)–B(8), and this bond distance is found to be shorter than the comparison distance B(5)–B(8). The bridging hydrogen attached to B(6) exhibits visible coupling to this B(6) atom and also shows a calculated distance that is shorter than that of H_μ–B(5).

One might expect that the structure of the $[C_2B_6H_9]^-$ ion would follow the general structural cluster boron rules,[1,2,22,23] i.e., a nido framework related to nine-vertex closo system minus a high-coordination vertex. Intuitively, one could begin with the known *closo*-1,7-$C_2B_7H_9$,[4,29] subtract a high-coordination vertex located between the two low-coordinate cage carbon atoms of the tricapped trigonal prism framework, and thus end up with a "partially-open" C_2B_6 structure in which both carbons reside along an open face. Then, adding a bridging hydrogen across the only B–B bond of the consequent five-membered open face should give a satisfactory structure. This leads to a $[C_2B_6H_9]^-$ structure, however, that has higher symmetry, and higher energy (at the MP2/6-31G*//3-21G level), than that found for our obtained $LiH/C_2B_6H_8$ product (Figure 1). A fairly extensive ab initio investigation[28] of numerous (over 20) plausible structures of a $[C_2B_6H_9]^-$ ion leads to the conclusion that the one shown in Figure 1 is the most stable (at the MP2/6-31G*//3-21G level) of those subjected to calculational methods. And it is pleasing to note that this structure has the C_1 symmetry demanded by the NMR data. This framework (Figure 1) is similar to one suggested for $C_2B_6H_{10}$,[30] except that our $[C_2B_6H_9]^-$ ion has the cage-carbon atoms located in 1,3-positions around the six-atom open face whereas the previously reported $C_2B_6H_{10}$ has carbons located in 1,4-positions relative to one another. The essential difference between the cage structure shown in Figure 1 (related to an icosahedral structural fragment) and a "classical" nido arrangement of cage atoms is that a bond between boron atoms 2 and 6 is either absent or present, respectively.

Trimethylamine reacts with *closo*-$C_2B_6H_8$ to give a very weakly bound adduct which in turn slowly converts to a more strongly bound monoamine adduct. The NMR (^{11}B and ^1H) spectra (Table II) of the more strongly bound adduct, $(CH_3)_3N{\cdot}C_2B_6H_8$, point in the direction of C_1 structural symmetry. The NMR spectra also suggest to us that this adduct is related to the above $[C_2B_6H_9]^-$ ion and that one of the terminal hydrogens (as a hydride) of the latter ion is replaced with a trimethylamine group. We strongly suspect that this is B(4) of the structure shown in Figure 1. A bridging hydrogen is found at $\delta = -5.29$ ppm in the proton NMR spectrum, and the fine structure, and/or broadness, of the proton-coupled boron resonances at $\delta = +13.01$ and -2.83 ppm indicate that those borons are most probably attached to the one bridging hydrogen. A boron resonance at $\delta = +19.78$ ppm does not show strong coupling to any of the other boron atoms in the molecule, and its downfield chemical shift is reminiscent of open-face borons that neighbor cage carbon(s).[31] The high-field doublet resonance at $\delta = -25.07$ is not entirely symmetrical, and various preparations of the adduct all exhibit ^{11}B NMR spectra which show that the left member of this doublet is about 5–10% taller than the right member of the doublet. This is most probably due to the accidental overlap of two doublet resonances that have slightly different coupling constants and in which the chemical shifts are such that the low-field members of each doublet reinforce each other to a greater degree than the high-field members of the two doublets. The boron-11 decoupled proton NMR spectrum of the compound indicates that the protons attached to each of these two borons (assigned to the 7- and 8-positions) are seen at slightly different chemical shifts, differing by about 0.25 ppm. A 2-D ^{11}B NMR spectrum is consistent with the structural assignment, and furthermore the strongest ^{11}B–^{11}B cross peaks are noted between resonances B(4)–B(5) that are assigned to directly-bonded boron atoms having the shortest cage B–B distance, as assessed by a full (Gaussian) 6-31G* geometry optimization.

The more strongly bound $(CH_3)_3N{\cdot}C_2B_6H_8$ adduct appears in various solvents to be in a slow equilibrium with the dissociated trimethylamine and $C_2B_6H_8$. After the adduct stands at room temperature in tetrahydrofuran for several days, the free $C_2B_6H_8$ builds up to a quantity of about 40% of that of the $(CH_3)_3N{\cdot}C_2B_6H_8$ adduct so that the equilibrium ratio of $(CH_3)_3N{\cdot}C_2B_6H_8/C_2B_6H_8$ is close to 2.5. When the adduct is dissolved in solvents less polar than tetrahydrofuran, such as benzene, the equilibrium shifts more toward the dissociated substances with the $C_2B_6H_8$ now present to the extent of ca. 6 times that of the quantity of the $(CH_3)_3N{\cdot}C_2B_6H_8$ adduct. This results in a $(CH_3)_3N{\cdot}C_2B_6H_8/C_2B_6H_8$ ratio close to 0.17 in benzene. These results are consistent with the expectation that the $(CH_3)_3N^+$–$C_2B_6H_8^-$ zwitterion might be better solvated and stabilized in the more polar tetrahydrofuran solvent and less well solvated and thus less stable in the less polar benzene solvent.

The nature of the weakly bound $C_2B_6H_8$ adduct with $(CH_3)_3N$ (vide supra) cannot be ascertained because all attempts to isolate the compound or take a solution NMR spectrum of the ***initial*** solid that formed from the mixture of $(CH_3)_3N$ and $C_2B_6H_8$ (see Experimental Section) resulted in immediate dissociation; it may be that the initial weakly bound adduct represents an attempt on

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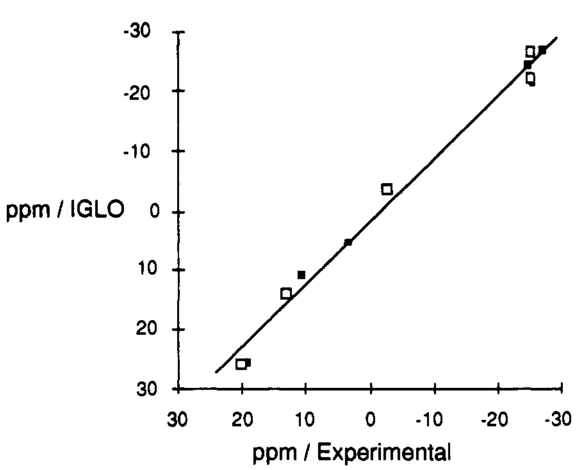

Figure 2. Plot of IGLO [dz//6-31G*][34] vs experimental ^{11}B NMR chemical shifts for the data of both the $[1,3\text{-}C_2B_6H_9]^-$ ion and $C_2B_6H_8 \cdot N(R)_3$ (R = H for IGLO calculations, R = CH_3 for experimental data), with the exception of B(4)–N(R)$_3$ (see Discussion): Black squares = $[1,3\text{-}C_2B_6H_9]^-$; open squares = $C_2B_6H_8 \cdot N(R)_3$. A linear correlation value of r = 0.99 is found.

the part of the molecule to assume a classical nido geometry but that this is unstable relative to the dissociated reactants and unstable relative to the more strongly bound adduct mentioned above. A parallel could be drawn between these observations and what was previously observed in the reaction of trimethylamine with *closo*-1,6-$C_2B_4H_6$.[19–21] The latter closo compound reacts with the amine to form 5-Me_3N-*nido*-2,4-$C_2B_4H_6$, and when this product is allowed to stand for some time, it rearranges to the 3-Me_3N-*nido*-2,4-$C_2B_4H_6$ isomer. Apparently, the kinetically favored isomer is not the more stable of the two.

IGLO chemical shift calculations[32] using both the 3-21G optimized and 6-31G* optimized geometries[33] for both the $[C_2B_6H_9]^-$ ion[34] and the adduct $(CH_3)_3N \cdot C_2B_6H_8$[34] are consistent with the boron and proton NMR shift assignments. It has been previously assessed that geometry optimization calculations at higher levels, e.g. MP2/6-31G*, are probably required to obtain quantitative agreement between IGLO chemical shift calculations and experimental data;[32] however, IGLO calculations[34] carried out on the 6-31G* fully-optimized geometries, and even on the 3-21G fully-optimized geometries, show the expected chemical shift trends and good correlations to the experimental NMR data in our two compounds (see Figure 2 for the ^{11}B chemical shift comparisons). The only exception, the ca. 14 ppm chemical shift difference between IGLO and experimental results for B(4) of the adduct, can be justified by considering the following: (a) The geometry optimization calculations were necessarily carried out on the NH_3, rather than the experimentally obtained NMe_3, adduct of the carborane because of computational resource limitations. (b) The observed ^{11}B chemical shifts for the monoboron adduct analogues H_3BNH_3 and H_3BNMe_3[35] indicate that substitution of ammonia for trimethylamine in this adduct shifts the boron chemical shift of this monoboron complex upfield by approximately 15 ppm. (c) This difference value of 15 ppm is then applied as a correction factor on the IGLO-predicted B(4) chemical shift; i.e., the IGLO-calculated value ($\delta = -19$)[34] for B(4) of the NH_3-carborane adduct (when adjusted downfield by 15 ppm) brings the chemical shift value ($\delta = -4$ ppm) very close to that observed experimentally ($\delta = -5.0$ ppm; Table II) for B(4)–NMe_3 of $(CH_3)_3N \cdot C_2B_6H_8$. Borons 7 and 8 of both compounds, the $[C_2B_6H_9]^-$ ion and the $R_3N \cdot C_2B_6H_8$ (R = CH_3, experimental; R = H, calculational) adduct, are found (from IGLO calculations) to be at significantly higher field than borons 2, 5, and 6. This agrees well with the assignments assessed by simple inspection of the experimental NMR data as well as the expectation that these two boron positions, 7 and 8, could be considered the apex positions of pentagonal pyramids (the basal atoms of the pyramid with B(7) at the apex are cage atoms 1, 2, 3, 4, and 8; the basal atoms of the pyramid with B(8) at the apex are cage atoms 1, 7, 4, 5, and 6). Thus, the resonances for these atoms, B(7,8), are anticipated to occur at higher field than strictly equatorial, open-face, boron positions (in particular those equatorial boron atoms with low coordination, positions 2, 5, and 6). The proton NMR assignments (Tables I and II) were assisted by IGLO computational results and decoupling experiments.

Both the 3-21G and 6-31G* optimized geometries[33] of the $[1,3\text{-}C_2B_6H_9]^-$ ion (Figure 1) and of the 4-$(CH_3)_3N$-1,3-$C_2B_6H_8$ adduct (the latter examined by MO calculations as 4-H_3N-1,3-$C_2B_6H_8$) are true minima on their respective potential energy surfaces as determined by vibrational calculations on both; e.g. no negative frequencies are found in either calculation. It should be mentioned that an extensive effort was made to find a 3-21G optimized structure for a $[C_2B_6H_9]^-$ ion[36] that would be more stable than that shown in Figure 1 but to no avail. After numerous attempts no "true" nido structure with a single bridging hydrogen could be found that is vibrationally stable, and several symmetry-imposed "nido" structures, when allowed to fully optimize, settled to the vibrationally stable geometry that is shown in Figure 1. Several isomeric structures of the H_3N-1,3-$C_2B_6H_8$ adduct have also been examined by MO calculations at the 3-21G level,[28] but none are found to be more stable than the 4-R_3N-1,3-$C_2B_6H_8$ isomer in which the cage arrangement of atoms is structurally related to that shown in Figure 1.

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(33) Some of the bond distances for the $[1,3\text{-}C_2B_6H_9]^-$ ion, as calculated from a Gaussian-90 6-31G* optimization, are (in Å): C(1)–B(2) = 1.603, B(2)–C(3) = 1.485, C(3)–B(4) = 1.615, B(4)–B(5) = 1.717, B(6)–C(1) = 1.611, C(1)–B(7) = 1.755, B(2)–B(7) = 1.828, C(3)–B(7) = 1.652, B(4)–B(7) = 1.856, B(4)–B(8) = 1.891, B(5)–B(8) = 1.782, B(6)–B(8) = 1.744, C(1)–B(8) = 1.719, B(7)–B(8) = 1.735, B(5)–H_μ = 1.335, B(6)–H_μ = 1.329. Distances for the adduct $C_2B_6H_8 \cdot NH_3$ (4-H_3N-1,3-$C_2B_6H_8$) (Å) are as follows: C(1)–B(2) = 1.607, B(2)–C(3) = 1.492, C(3)–B(4) = 1.580, B(4)–B(5) = 1.690, B(6)–C(1) = 1.619, C(1)–B(7) = 1.722, B(2)–B(7) = 1.829, C(3)–B(7) = 1.652, B(4)–B(7) = 1.835, B(4)–B(8) = 1.856, B(5)–B(8) = 1.792, B(6)–B(8) = 1.735, C(1)–B(8) = 1.698, B(7)–B(8) = 1.755, B(5)–H_μ = 1.315, B(6)–H_μ = 1.348.

(34) The IGLO calculated (at the dz level) ^{11}B NMR chemical shift values using the 6-31G* optimized geometrie(s) are as follows: for the $[1,3\text{-}C_2B_6H_9]^-$ ion, $\delta = -27.0$ for B(4), -24.4 for B(8), -21.5 for B(7), $+11.1$ for B(6), $+5.3$ for B(5), $+25.6$ for B(2); for the adduct 4-H_3N-1,3-$C_2B_6H_8$, $\delta = -26.7$ for B(8), -22.2 for B(7), -19.5 for B(4), -3.7 for B(5), $+13.9$ for B(6), $+25.9$ for B(2).

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