Articles

Interaction of Trimethylamine and *closo*-1,6-$C_2B_7H_9$. Evidence for an "Open" Cage $C_2B_7H_9$/Amine Adduct

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Strong evidence for the low-temperature formation of an axially positioned NR_3 (R = H, CH_3) adduct of an "open" cage $C_2B_7H_9$ structure is obtained via comparison of the experimentally obtained ^{13}C and ^{11}B NMR data (R = CH_3) with that obtained from ab initio/IGLO/NMR and ab initio/GIAO/NMR approaches (R = H, CH_3). The amine is positioned at a boron surrounded by the two carborane carbon atoms along a chair arrangement of a six-atom $CBCB_3$ open face belonging to a cluster that can be formally derived by removing a triangular set of three adjacent vertices from a 12-vertex icosahedral unit. Rapid equilibration of the adduct $NR_3{\cdot}C_2B_7H_9$ with dissociated NR_3 and *closo*-$C_2B_7H_9$ is proposed to explain the NMR chemical shift observations.

Introduction

Adduct formation between Lewis bases and boranes has been the subject of numerous studies over many decades; of course, the strong adduct between trimethylamine and BH_3 (the source of BH_3 often obtained via B_2H_6) has been extensively studied.[1] The adducts obtained from reaction of trimethylamine and polyboranes such as pentaborane(9) have also received considerable attention.[1] For parent polyborane cage compounds known as carboranes, it has been noted that trimethylamine reacts very readily with the smallest *closo* cage system (1,5-$C_2B_3H_5$) to form an adduct, the structure of which has proven very elusive.[2−4] The next larger carborane (*closo*-1,6-$C_2B_4H_6$) cage reacts slowly, but quantitatively, with Me_3N to form 5-Me_3N-*nido*-2,4-$C_2B_4H_6$ which, in turn, slowly but quantitatively rearranges to the 3-Me_3N-*nido*-2,4-$C_2B_4H_6$ isomer.[3,5,6] The parent *closo*-2,4-$C_2B_5H_7$ does not appear to react with Me_3N,[3] whereas this same tertiary amine will react under ambient conditions with halogenated derivatives of this same five-boron carborane to yield 1:1 adducts which, in turn, can be converted to [*B*-Me_3N-*closo*-2,4-$C_2B_5H_6$]$^+$ ions by way of halide extraction.[7,8] The next higher *closo*-carborane, 1,7-$C_2B_6H_8$, initially forms a very weak adduct with Me_3N but gives rise to substantial quantities of a somewhat stronger adduct upon allowing a mixture to stand at ambient temperature for 1 or 2 days.[9] In the two solvents tetrahydrofuran and benzene, this latter adduct is in slow equilibrium with the dissociated materials 1,7-$C_2B_6H_8$ and Me_3N, with adduct formation favored to a degree of about 2.5:1 in THF (at ambient temperatures) and the dissociated materials favored to the extent of about 6:1 in benzene.[9] Neither the *closo*-carborane 1,10-$C_2B_8H_{10}$ nor the three *closo*-$C_2B_{10}H_{12}$ isomers (1,2-, 1,7-, and 1,12-) appear to react with trimethylamine under reasonable thermal conditions.[1,4] The *closo*-2,3-$C_2B_9H_{11}$ carborane reacts with trimethylamine[10] to afford what is believed to be 3-Me_3N-*nido*-7,9-$C_2B_9H_{11}$.

No information is available, to our knowledge, on the interaction of the *closo*-carborane 1,6-$C_2B_7H_9$[11] with trimethylamine. Another Lewis base, the F^- ion, is known to react with 1,6-$C_2B_7H_9$ to yield a carborane anion that is the result of partial cage degradation of the starting material.[12] In the present study, we provide experimental data and calculational information which strongly indicates that a measurable degree of adduct formation takes place between 1,6-$C_2B_7H_9$ and $(CH_3)_3N$ and also points to a very reasonable structure for this adduct. This study was initiated when we[13] carried out ab initio geometry optimizations at the STO-3G, 3-21G, and 6-31G* levels of theory on both symmetry-constrained and -unconstrained 1,6-

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(1) For the many primary sources, consult the references in the pertinent volumes of the Boron Compound series of the *Gmelin Handbook of Inorganic and Organometallic Chemistry*. In particular pp 249−288 of the *Gmelin Handbook of Inorganic Chemistry*; Springer-Verlag: Berlin, FRG, 1974, Borverbindungen 2, pp 1−288. Also, see *Gmelin Handbook of Inorganic Chemistry*; Springer-Verlag: Berlin, FRG, 1975, Borverbindungen 6, pp 1−150; 1977, Borverbindungen 11, pp 1−207; 1977, Borverbindungen 12, pp 1−306; 1977, Borverbindungen 14, pp 149−233; 1977, Borverbindungen 15; 1977, Borverbindungen 18; 1978, Borverbindungen 20, pp 1−239; 1980, Boron Compounds, 1st Suppl., *Vol. 1*, pp 84−108; 1980, Boron Compounds, 1st Suppl., *Vol. 3*, pp 105−256; 1983, Boron Compounds, 2nd Suppl., Vol. 1, pp 84−204; 1982, Boron Compounds, 2nd Suppl., Vol. 2, pp 223−335; 1987, Boron Compounds, 3rd Suppl., Vol. 1, pp 90−240; 1988, Boron Compounds, 3rd Suppl., Vol. 4, pp 153−254; 1993, Boron Compounds, 4th Suppl., Vol. 4, pp 178−321.

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$C_2B_7H_9$ and found essentially the same results concerning the close energy competition between an "open" (*nido*?) vs "closed" (*closo*) structure, as has been more recently reported[14] in the literature. This motivated us to explore the possibility that $C_2B_7H_9$, most probably as the "open" cage form, might welcome an extra pair of electrons from a Lewis base such as trimethylamine.

Experimental Section and Data Presentation

Through the employment of a high-vacuum apparatus, a sample of 1,6-$C_2B_7H_9$ (ca. 0.16 mmol) was sublimed into a 5-mm NMR tube. The tube was subsequently sealed after adding trimethylamine (1.0 mmol). The tube contents were subjected to variable temperature NMR measurements (Table 1). At temperatures below −35 °C, the mixture formed two phases, a solid layer and liquid layer. Variable temperature NMR spectra were recorded both on a Bruker AM-400 instrument (for ^{11}B) and a Bruker AC-300 (for ^{13}C) instrument. The data and assignments are given in Table 1. The ^{11}B and ^{13}C spectra were recorded both coupled and ^1H decoupled. Below −35 °C all of the resonances in the carborane/trimethylamine sample broadened and the carborane peaks became significantly weaker which, along with the visual observations of precipitate formation, suggested a combination of partial carborane−amine adduct (see discussion section) precipitation and viscosity effects on the spectrum.

Table 1. ^{13}C and ^{11}B NMR Chemical Shifts (ppm) of $C_2B_7H_9$ in Trimethylamine[a]

type of atom	δ(rt)	δ(−35 °C)	δ(−35 °C) − δ(rt)
^{13}C	+71.9	+62.5	−9.4
^{11}B(area 1)	+31.5	+25.3	−6.2
^{11}B(area 2)	−7.1	−5.9	+1.2
^{11}B(area 4)	−12.1	−7.0	+5.1

[a] ^{13}C NMR shifts are relative to tetramethylsilane; ^{11}B NMR shifts are relative to $Et_2O\cdot BF_3$; negative values are to high field. To within 0.4 ppm, the δ(rt) chemical shift values of $C_2B_7H_9$ in trimethylamine are the same as those in either CCl_4, hexane, Freon-12 (CCl_2F_2), or in Freon-22 ($HCClF_2$).[11,12]

A mixture of 1,6-$C_2B_7H_9$ (ca. 0.6 mmol) and Freon-12 (CCl_2F_2) (4.8 mmol) was sealed into a 5-mm NMR tube, a mixture of 1,6-$C_2B_7H_9$ (ca. 0.21 mmol) and Freon-22 (HCF_2Cl) (5.4 mmol) was sealed into a second 5-mm NMR tube, and in still another tube was sealed a molar ratio of approximately 1:2:8 of 1,6-$C_2B_7H_9$/$(CH_3)_3N$/CCl_2F_2. All samples were subjected to variable temperature NMR experiments.

Calculational Methods for Geometry Optimizations and for IGLO/NMR Chemical Shift Determinations

Energy-optimized structures for all molecules were carried out using the ab initio Gaussian 92 and Gaussian 94 codes[15] at the HF/3-21G and HF/6-31G* levels of theory. Single-point energies were calculated at the MP2/6-31G*//6-31G* and (DFT)BLYP/6-31G*//6-31G* levels of theory. The total energies for those molecules which are a part of this study are given in Table 2. Depicted in Figure 1 are the pertinent carborane molecules that were optimized at the HF/6-31G* level. The energy-optimized structures were used to calculate the chemical shieldings (Tables 3−6), using the IGLO/NMR[16−18] and GIAO/NMR[19] methods. All IGLO calculations were performed with a double-ζ set (DZ) in the contractions (21) for H and (4111/21) for first row-elements.[20] Additionally, GIAO(6-31G*)/NMR[19] calculations were carried out on the HF/6-31G* geometry-optimized structures.

All calculated ^{11}B shielding values σ were referenced to B_2H_6 (the latter geometry optimized at 6-31G* for the purposes of the GIAO calculations) as a secondary reference point and then converted to the standard $F_3B\cdot OEt_2$ scale (Tables 3−6). This is assisted by the experimental knowledge that $\delta(F_3B\cdot OEt_2)$ is 16.6 ppm upfield from $\delta(B_2H_6)$.[21] Thus, for the IGLO calcula-

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Table 2. Energies (hartrees) for NR_3, $C_2B_7H_9$, and the Stable $NR_3/C_2B_7H_9$ Adduct

	level of theory			
compound	3-21G//3-21G	6-31G*//6-31G*	MP2/6-31G*//6-31G*	BLYP/6-31G*//6-31G*
NH_3	−55.87220	−56.18436	−56.35371	−56.51696
NMe_3	−172.31027	−173.26930	−173.82758	−174.36023
$C_2B_7H_9$ (*closo*) (I)	−252.78242	−253.78242	−254.68112	−255.46961
$C_2B_7H_9$ (open) (II)	−252.34242	−253.78468	−254.67758	−255.46935
$NH_3{\cdot}C_2B_7H_9$ (III)	−308.23831	−309.96418	−311.04111	−311.99025
$NMe_3{\cdot}C_2B_7H_9$ (III)	−424.66968	−427.03894	−428.51904	−429.82224

Table 3. ^{13}C and ^{11}B NMR Chemical Shift Changes, Experimental Vs Calculated (IGLO; DZ//6-31G*) of $C_2B_7H_9$ in NR_3 (R = CH_3 for exptl and R = H for calcd)

	IGLO calcd (DZ//6-31G*)[a]				exptl[a]
type of atom	δ(c)	δ(n)[b]	δ(n) − δ(c)	0.24[δ(n) − δ(c)][c]	δ(−35 °C) − δ(rt)
^{13}C	+64.6	+25.8	−38.8	−9.3	−9.4
^{11}B(area 1)	+32.8	+6.9	−25.9	−6.2	−6.2
^{11}B(area 2)	−4.0	−3.4	+0.6	+0.1	+1.2
^{11}B(area 4)	−10.1	+6.8	+16.9	+4.1	+5.1

[a] ^{13}C NMR chemical shifts are in ppm relative to tetramethylsilane; ^{11}B NMR shifts are in ppm relative to $Et_2O{\cdot}BF_3$; negative values are to high field. The DZ//6-31G* = IGLO calculations are performed at the double-ζ level on the 6-31G*-optimized geometry. δ(c) = chemical shifts of the *closo* structure; δ(n) = chemical shifts of the adduct, with the nitrogen of NH_3 in an axial position attached to one of the two borons with two adjacent cage carbon atoms. [b] The boron to which the nitrogen is bonded (III, Figure 1) was moved 15 ppm downfield from the calculated value as per discussion in the experimental section. Fast equilibration of two equivalent forms of the adduct demands the averaging here of the two boron chemical shifts associated with the two boron atoms containing two adjacent cage carbon atoms each. Also, the chemical shifts of the four borons containing one adjacent cage carbon atom each are also averaged here for the same reason. [c] A linear comparison between 0.24[δ(n) − δ(c)] and exptl [δ(−35 °C) − δ(rt)] results in a relationship ΔIGLO = 0.91Δexptl − 0.71 with the linear correlation coefficient r^2= 0.999.

tions, $\delta(^{11}B \text{ of compd}) = \sigma(^{11}B \text{ of } B_2H_6) - \sigma(^{11}B \text{ of compd}) + 16.6$ ppm. The shielding for B_2H_6 [$\sigma(^{11}B$ of $B_2H_6)$] is 115.5 ppm at the double-ζ//6-31G* level, which then implies that the shielding (σ) for $F_3B{\cdot}OEt_2$ is 132.1 ppm. For the (6-31G*) GIAO calculations, the shielding for the 6-31G*-optimized B_2H_6 [$\sigma(^{11}B$ of $B_2H_6)$] is 106.8 ppm, which then implies that the shielding for $F_3B{\cdot}OEt_2$ is 123.4 ppm. The ^{13}C NMR chemical shifts δ are referenced to TMS. For the GIAO calculations, the shielding for the 6-31G*-optimized TMS [$\sigma(^{13}C$ of TMS)] is 201.7 ppm at the 6-31G* level of theory. Thus, $\delta(^{13}C) = 201.7 - \sigma(^{13}C)$.

Computational resources limited our initial calculations to the NH_3 rather than the NMe_3 adduct of the carborane; in this regard, the observed ^{11}B chemical shifts for the monoboron adduct analogues $H_3B{\cdot}NH_3$ and $H_3B{\cdot}NMe_3$[22] indicate that substitution of the ammonia for trimethylamine in this adduct shifts (experimentally) the boron chemical shift of this monoboron complex upfield by approximately 15 ppm. Therefore, in Tables 3 and 5 we made a 15 ppm "correction" to the IGLO and GIAO values of the ammonia complex of the carborane in this study in order to convert the chemical shift of the NH_3-attached boron to one expected of a trimethylamine adduct.

All calculations were carried out, variously, on Multiflow Trace minisupercomputers, SUN 4/280, and SUN SPARC station model 10 computers. Gaussian 94 calculations were carried out on the Cray C90 available at the San Diego Supercomputer Facility.

Results and Discussion

At ambient temperature the ^{11}B and ^{13}C NMR spectra of a homogeneous liquid mixture of 1,6-$C_2B_7H_9$ (a 1:2:4 area ratio of three 1:1 $^{11}B{-}^1H$ doublets in the ^{11}B region and one 1:1 $^{13}C{-}^1H$ doublet in the ^{13}C region) and trimethylamine (molar ratio of 6:1 for trimethylamine:1,6-$C_2B_7H_9$) are essentially identical to those of 1,6-$C_2B_7H_9$ when dissolved in freons such as CCl_2F_2 and $HCClF_2$. When the freon/$C_2B_7H_9$ mixtures were cooled to −35 °C and even further to ca. −100 °C, no significant changes in the ^{13}C and ^{11}B NMR patterns or in their chemical shifts were observed. However, upon cooling the $Me_3N/C_2B_7H_9$ mixture, some dramatic chemical shift changes are observed in both the ^{11}B and ^{13}C NMR spectra. Also, a small degree of peak broadening is observed in the temperature region just below −35 °C where solids begin to form. The carborane ^{13}C resonance shifts a little over 9 ppm upfield upon lowering the temperature from ambient to −35 °C; although the position of the area-2 ^{11}B resonance remains not far from its original

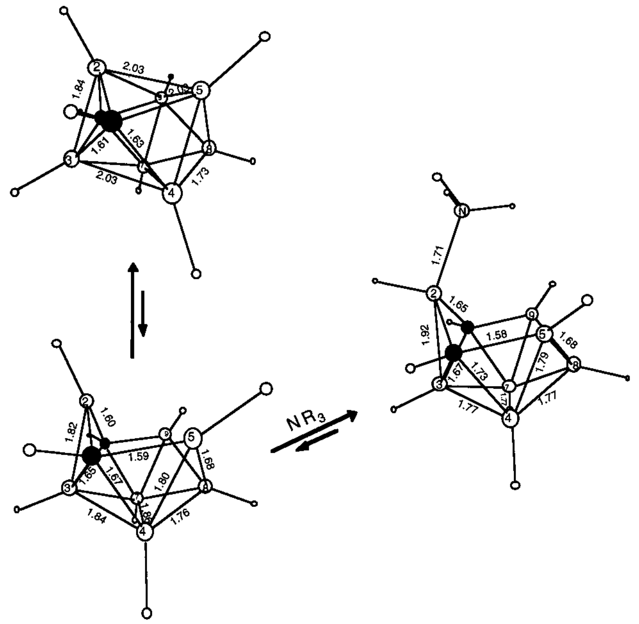

Figure 1. Depiction of 6-31G*-optimized structures for the *closo* structure of $C_2B_7H_9$ (I, upper left), the open structure of $C_2B_7H_9$ (II, lower left), and the calculationally most stable NR_3 (R = H) *B*-bonded adduct of $C_2B_7H_9$ (III, middle right).

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Table 4. ^{13}C and ^{11}B NMR Chemical Shift Changes, Experimental Vs Calculated (IGLO; DZ//6-31G*) of $C_2B_7H_9$ in NR_3 (R = CH_3 for exptl and for calcd)

	IGLO calcd (DZ//6-31G*)[a]				exptl[a]
type of atom	δ(c)	δ(n)[b]	δ(n) − δ(c)	0.26[δ(n) − δ(c)][c]	δ(−35 °C) − δ(rt)
^{13}C	+64.6	+29.4	−35.2	−9.2	−9.4
^{11}B(area 1)	+32.8	+6.5	−26.3	−6.8	−6.2
^{11}B(area 2)	−4.0	−4.2	−0.2	−0.05	+1.2
^{11}B(area 4)	−10.1	+7.9	+18.0	+4.7	+5.1

[a] ^{13}C NMR chemical shifts are in ppm relative to tetramethylsilane; ^{11}B NMR shifts are in ppm relative to $Et_2O{\cdot}BF_3$; negative values are to high field. The DZ//6-31G* = IGLO calculations are performed at the double-ζ level on the 6-31G*-optimized geometry. δ(c) = chemical shifts of the *closo* structure; δ(n) = chemical shifts of the adduct, with the nitrogen of NR_3 in an axial position attached to one of the two borons with two adjacent cage carbon atoms. [b] Fast equilibration of two equivalent forms of the adduct demands the averaging here of the two boron chemical shifts associated with the two boron atoms containing two adjacent cage carbon atoms each. Also, the chemical shifts of the four borons containing one adjacent cage carbon atom each are also averaged here for the same reason. [c] A linear comparison between 0.26[δ(n) − δ(c)] and exptl [δ(−35 °C) − δ(rt)] results in a relationship ΔIGLO = 0.95Δexptl − 0.62 with the linear correlation coefficient r^2 = 0.994.

Table 5. ^{13}C and ^{11}B NMR Chemical Shift Changes, Experimental Vs Calculated (GIAO; 6-31G*//6-31G*) of $C_2B_7H_9$ in NR_3 (R = CH_3 for exptl and R = H for calcd)

	GIAO calc (6-31G*//6-31G*)[a]				exptl[a]
type ofatom	δ(c)	δ(n)[b]	δ(n) − δ(c)	0.26[δ(n) − δ(c)][c]	δ(−35 °C) − δ(rt)
^{13}C	+61.7	+25.5	−36.2	−9.4	−9.4
^{11}B(area 1)	+32.5	+10.6	−21.9	−5.7	−6.2
^{11}B(area 2)	−7.3	−0.1	+7.2	+1.9	+1.2
^{11}B(area 4)	−10.9	+7.3	+18.2	+4.7	+5.1

[a] ^{13}C NMR chemical shifts are in ppm relative to tetramethylsilane; ^{11}B NMR shifts are in ppm relative to $Et_2O{\cdot}BF_3$; negative values are to high field. The GIAO 6-31G*//6-31G* = GIAO calculations are performed at the 6-31G* level on the 6-31G*-optimized geometry. δ(c) = chemical shifts of the *closo* structure; δ(n) = chemical shifts of the adduct, with the nitrogen of NH_3 in an axial position attached to one of the two borons with two adjacent cage carbon atoms. [b] The boron to which the nitrogen is bonded (III, Figure 1) was moved 15 ppm downfield from the calculated value as per discussion in the experimental section. Fast equilibration of two equivalent forms of the adduct demands the averaging here of the two boron chemical shifts associated with the two boron atoms containing two adjacent cage carbon atoms each. Also, the chemical shifts of the four borons containing one adjacent cage carbon atom each are also averaged here for the same reason. [c] A linear comparison between 0.26[δ(n) − δ(c)] and exptl [δ(−35 °C) − δ(rt)] results in a relationship ΔGIAO = 1.000Δexptl + 0.049 with the linear correlation coefficient r^2 = 0.995.

Table 6. ^{13}C and ^{11}B NMR Chemical Shift Changes, Experimental Vs Calculated (GIAO; 6-31G*//6-31G*) of $C_2B_7H_9$ in NR_3 (R = CH_3 for exptl and for calcd)

	GIAO calc (6-31G*//6-31G*)[a]				exptl[a]
type of atom	δ(c)	δ(n)[b]	δ(n) − δ(c)	0.26[δ(n) − δ(c)][c]	δ(−35 °C) − δ(rt)
^{13}C	+61.7	+28.8	−32.9	−8.6	−9.4
^{11}B(area 1)	+32.5	+10.3	−22.2	−5.8	−6.2
^{11}B(area 2)	−7.3	−0.4	+6.9	+1.8	+1.2
^{11}B(area 4)	−10.9	+9.1	+20.0	+5.2	+5.1

[a] ^{13}C NMR chemical shifts are in ppm relative to tetramethylsilane; ^{11}B NMR shifts are in ppm relative to $Et_2O{\cdot}BF_3$; negative values are to high field. 6-31G*//6-31G* = GIAO calculation performed at the 6-31G* level on the 6-31G*-optimized geometry. δ(c) = chemical shifts of the *closo* structure; δ(n) = chemical shifts of the adduct, with the nitrogen of NR_3 in an axial position attached to one of the two borons with two adjacent cage carbon atoms. [b] Fast equilibration of two equivalent forms of the adduct demands the averaging here of the two boron chemical shifts associated with the two boron atoms containing two adjacent cage carbon atoms each. Also, the chemical shifts of the four borons containing one adjacent cage carbon atom each are also averaged here for the same reason. [c] A linear comparison between 0.26[δ(n) − δ(c)] and exptl [δ(−35 °C) − δ(rt)] results in a relationship ΔGIAO = 0.978Δexptl + 0.295 with the linear correlation coefficient r^2= 0.995.

position, the area-4 ^{11}B peak shifts nearly 5 ppm to lower field, and the area-1 ^{11}B NMR resonance shifts a little over 6 ppm upfield (Table 1). These chemical shift changes are reversible, and are suggestive of a significant interaction between the trimethylamine and the $C_2B_7H_9$ carborane at the lower temperatures.

We embarked on an ab initio calculational effort in order to determine if an amine adduct of the “open” $C_2B_7H_9$ structure could account for the experimental observations. The initial calculational study of such a species necessarily involved NH_3 as the Lewis base rather than NMe_3 owing to obvious computational resource limitations. After reasonable B−N-bonded $NH_3{\cdot}C_2B_7H_9$ structures were subjected to geometry optimizations at both the 3-21G and 6-31G* levels of theory, it was determined that the isomer (III, Figure 1) with the nitrogen of NH_3 axially attached to the open-faced boron between the two carbon atoms is the most stable among structurally related isomers that differ in the position of the NH_3 attachment to any of the boron atoms along the open portion of the cage. IGLO/NMR calculations at the double-ζ level on all of the $NH_3{\cdot}C_2B_7H_9$ adducts were then carried out, and only the most stable one of these adducts (III, Figure 1) appears to give ^{11}B and ^{13}C chemical shift results that can satisfactorily account for the experimental NMR observations. At the lowest temperature (−35 °C) at which the adduct remained essentially in solution, very favorable comparisons between the experimental NMR data and the calculational IGLO/NMR information are noted upon assuming that about 25 ± 1% of the (calculationally) most stable $NR_3{\cdot}C_2B_7H_9$ adduct (III) is present in rapid equilibrium with the dissociated compounds NR_3 (R = H, Me for the calculational portion of the study and R = Me for the experimental portion of the study) and *closo*-$C_2B_7H_9$[23] (see Tables 3 and 4). Similarly, the results of GIAO/NMR calculations on the *closo*-$C_2B_7H_9$ species averaged with those on the most stable $NR_3{\cdot}C_2B_7H_9$ adduct give the best results when about 25 ± 1% of the adduct is considered in rapid equilibrium with the dissociated *closo*-carborane at −35 °C (see Tables 5 and 6). A comparison of the experimental results with either the ab initio/

IGLO or the ab initio/GIAO calculational results (Tables 3−6) gave correlation coefficients r^2, between 0.99 and 1.00.

When the sum of the electronic energies for NH_3 and *closo*-$C_2B_7H_9$ are compared with the most stable $NH_3{\cdot}C_2B_7H_9$ adduct (Table 2), it is noticed that at the 3-21G level of theory the difference in energies favors the dissociated materials, whereas at the 6-31G* level the calculated energy difference is nearly the same (within a couple of kcal/mol). At the correlated levels, the energies begin to favor the adduct. A similar comparison using the open structure of $C_2B_7H_9$ does not significantly change this. It is therefore concluded, from theoretical considerations alone, that adduct formation is possible but not necessarily favored over dissociation. This is in good agreement with the experimental findings since ca. 25% of the carborane is found as the adduct at −35 °C. Frequency calculations carried out at the 6-31G* level of theory yield an entropy change of −43 cal/mol·K for the reaction $NH_3 + closo\text{-}C_2B_7H_9 \rightarrow H_3NC_2B_7H_9$ (III). For the temperature change from ambient to −35 °C, this entropy change is equivalent to about 2.6 kcal/mol in favor of the adduct. This is in the range expected (ca. +2 kcal/mol in favor of the adduct) for a phenomenon in which a 75:25 ratio of the dissociated-carborane/adduct at the lower temperature (−35 °C) proceeds to mostly dissociated materials (>98%) when the temperature is raised to ambient.

Of the two freon/$C_2B_7H_9$ samples, the one with freon-12 initially seemed to us to be the more promising in producing a solvent-soluble $NMe_3{\cdot}C_2B_7H_9$ adduct at low temperatures; but even then, after adding NMe_3 to the $C_2B_7H_9$/freon-12 mixture, the adduct precipitates out of solution at ca. −50 °C, and at slightly above that temperature only small ^{11}B and ^{13}C chemical shift changes, favoring less than 5% of the $NMe_3{\cdot}C_2B_7H_9$ adduct, are evident (ca. 2−3% from the ^{11}B NMR shift data and about 1−2% from the ^{13}C shift data, each with an estimated 1% error). It is concluded that the effect of the freon solvent permits the temperature to be lowered to ca. −50 °C before a significant amount of adduct precipitates but that the NMR observations on the dissolved materials are strongly dependent on a "dilution effect". The dilution of the reagents by the freon expectedly results in a shift of the equilibrium quantities of the reaction $R_3N + C_2B_7H_9 \rightleftharpoons R_3N{\cdot}C_2B_7H_9$ toward the left, which obviously means that less association is taking place as compared to when trimethylamine is used solely as the solvent.

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(23) A question can be raised about the percentage of *closo* vs open cage $C_2B_7H_9$ in a neat $C_2B_7H_9$ sample. NMR calculations support the presence of mostly, if not nearly exclusively, the *closo* structure. Clearly, if the open cage structure were to be present only, there most probably would be a fast equilibration between two mirror image structures. Otherwise, the experimentally observed 4:2:1 ratio for the boron areas would not be properly accounted for. When we averaged the appropriate IGLO/ab initio ^{11}B chemical shifts for the open cage structure, two (those with areas 2 and 4) of the three sets of values are not in good agreement with, but not far from, the experimentally observed values; the third type of boron is the unique area-1 boron with no attached carbons. The calculated (DZ//6-31G*) shift for this boron of the open cage structure is +16.6 ppm, which is about 15 ppm different from the observed value. On the other hand, the calculated value for this boron of the *closo* structure is within 1 ppm of the observed chemical shift (see Tables 1 and 3). It is thus concluded that the open cage structure plays a rather insignificant part in contributing to the NMR chemical shifts of the parent $C_2B_7H_9$. We have reached a similar conclusion from the results of GIAO calculations at the 6-31G*//6-31G* level of theory on both the *closo* and open cage structures of $C_2B_7H_9$.