0.251 V in the case of bpy and to ≳0.75 V for dmbp. The same ligands reduce the Ag^+/Ag^{2+} potential from 1.9 to 1.45 V (bpy)[11] and to ≳1.7 V (dmbp, dmp). The major reason for the increase of the Cu^+/Cu^{2+} potential is the tetrahedral distortion of the CuL_2^{2+} ions, especially for the hindered ligands.[4] The unhindered ligands tend to form octahedral *cis*-$CuL_2(H_2O)_2^{2+}$ species in aqueous solution, which lowers the potential. On the other hand, the reduction in the Ag^+/Ag^{2+} potential appears to be due to the extensive delocalization of charge via σ- and π-bonding interactions. Here again, the tetrahedral distortions in the case of dmbp and dmp complexes tend to raise the potential.

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Microwave Spectra and Molecular Structures of 3*H*-3-Azacyclotriboroxane and 3-Oxacyclotriborazane

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The species 3*H*-3-azacyclotriboroxane ($B_3H_4NO_2$) and 3-oxacyclotriborazane ($B_3H_5N_2O$) have been identified by microwave spectroscopy to be among the products of the reaction of diborane with nitrogen monoxide. The rotational constants obtained for the normal species are A = 5663.80 (15), B = 5616.39 (11), and C = 2820.405 (15) MHz for $B_3H_4NO_2$, and A = 5472.32 (10), B = 5427.24 (9), and C = 2725.013 (8) MHz for $B_3H_5N_2O$, with 3 standard deviations in parentheses. Analysis of the spectra for the normal, deuterated, ^{15}N, and ^{10}B species leads to the structural parameters of the skeletal rings. The reaction mechanism for the formation of these molecules is discussed.

Introduction

In the past several years many stable and unstable borane derivatives have been investigated by microwave spectroscopy in our laboratory, and the existence of new molecules has been established spectroscopically.[2–6] As an extension of the above study, we tried to detect a borane containing the NO group or NO groups by the reaction of diborane (B_2H_6) with nitrogen monoxide (NO).

The existence of BH_3NO has been suggested by Hoffmann and Engelhardt on the basis of mass spectrometry.[7] They examined mixtures of BH_3CO and NO by the use of mass spectrometry and demonstrated the possibility that BH_3NO might exist as an intermediate during the formation of N_2O and boric acid from BH_3CO and NO. In the previous studies of the reaction products of diborane with water,[2] ammonia,[5] etc. by microwave spectroscopy, the borane derivatives tended to be detected rather than the addition complexes of borane. Therefore, we expected to detect BH_2NO by the reaction of B_2H_6 with NO. However, a strong spectrum of BH_2NH_2 was observed and no spectrum due to BH_2NO was found. It was not easy to understand the reaction mechanism of how the BH_2NH_2 was produced by the reaction of B_2H_6 with NO. Therefore, we investigated the products of this reaction carefully, and found new spectra in addition to those due to BH_2NH_2,[5] $B_2H_5NH_2$,[8] and N_2O.[9] Although the origins of the new spectra were difficult to deduce by consideration of the only possible reactions, they were identified to be 3*H*-3-aza-cyclotriboroxane ($B_3H_4NO_2$) and 3-oxacyclotriborane ($B_3H_5N_2O$) from the rotational constants and other information for the various isotopic species obtained by microwave spectroscopy. Similar molecules, boroxin[10] and borazine[11], are well-known, whereas there is no report of $B_3H_4NO_2$ and $B_3H_5N_2O$. The results of this study are reported herein.

Experimental Section

A high-temperature reaction system using a flow-through method was adopted for the production and detection of the new molecules.[2] A mixture of B_2H_6 and NO was passed through a quartz tube heated by a nichrome wire coil and pumped continuously through a 3-m X-band brass wave-guide cell of a conventional 100-kHz Stark modulated spectrometer at a typical pressure of 20 mTorr. The quartz tube had an inner diameter of 4 mm, a thickness of 1.5 mm, and a length of 300 mm.

Optimum conditions for the production of new molecules were obtained when the temperature of the quartz tube was 450 °C and the mixing ratio of B_2H_6 and NO was about 1:2. This temperature was also optimal for the production of BH_2NH_2 and $B_2H_5NH_2$, while a higher temperature was advantageous for the production of N_2O. The spectra of the ^{10}B species were observed in their natural abundances. The spectra of the D and ^{15}N species were obtained by using B_2D_6 and ^{15}NO, respectively. All measurements were carried out with the cell cooled to about −20 °C. The spectral intensity of $B_3H_5N_2O$ was always weaker than that of $B_3H_4NO_2$; the intensity ratio was about 1:2.

When the reaction products were closed in the cell by stopping the flow-through system, the spectra of both molecules decreased gradually and disappeared in several minutes. However, it is not certain that they are essentially unstable transient molecules because the deposition of the reaction products might affect the stability of the molecules.

Results

Analysis of the Spectra. Survey scans of the 30–50-GHz region showed spectra due to BH_2NH_2, $B_2H_5NH_2$, and N_2O. In addition, condensed bunches of spectra consisting of a characteristic Q-branch series from a nearly symmetric rotor were observed at 31.0, 36.7, 42.3, and 48.0 GHz. An example of an observed Q-branch series is shown in Figure 1. The Q-branch series lines showed a slight intensity alternation due to spin weights, suggesting the existence of C_2 symmetry. No a-type R-branch series with a characteristic nearly prolate symmetric top pattern was observed in spite of a careful search. These facts suggest that the molecule in question is a planar oblate nearly symmetric top. Therefore, R-branch transitions were searched for and found by using the values of $A-C$ and κ derived from the analysis of the Q-branch transitions and the assumption that $A \approx B \approx 2C$.

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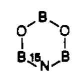
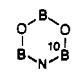
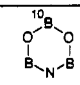
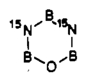
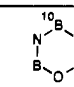
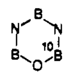
Table I. Rotational Constants, Inertia Defects, and Transition Types of Five Isotopic Species for 3*H*-3-Azacyclotriboroxane[a]

	normal species				all D species
A/MHz	5663.80 (15)	5616.39 (6)	5761.38 (11)	5786.17 (28)	5024.34 (13)
B/MHz	5616.39 (11)	5544.06 (3)	5648.13 (6)	5615.82 (19)	4830.37 (6)
C/MHz	2820.405 (15)	2790.400 (15)	2852.515 (27)	2850.278 (30)	2463.343 (26)
τ_{aaaa}/MHz	−0.0082 (30)	−0.0041 (10)	−0.0082 (21)	−0.0092 (50)	−0.0039 (15)
τ_{bbbb}/MHz	−0.0082 (25)	−0.0035 (8)	−0.0040 (18)	−0.0038 (38)	−0.0028 (10)
τ_{aabb}/MHz	0.0018 (36)	0.0096 (27)	0.0051 (61)	0.0002 (71)	0.0052 (42)
τ_{abab}/MHz	−0.0029 (27)	−0.0072 (9)	−0.0056 (21)	−0.0051 (29)	−0.0044 (14)
Δ/u Å^2	−0.0259 (23)	−0.0262 (10)	−0.0261 (18)	−0.0259 (41)	−0.0517 (24)
transition type	b	a	a, b	b	a

[a] Error limits represent 3 standard deviations.

Table II. Rotational Constants, Inertia Defects, and Transition Types of Four Isotopic Species for 3-Oxacyclotriborazane[a]

	normal species			
A/MHz	5472.32 (10)	5372.44 (8)	5555.55 (6)	5583.70 (12)
B/MHz	5427.24 (9)	5303.00 (7)	5471.65 (5)	5436.04 (11)
C/MHz	2725.013 (8)	2668.896 (7)	2756.813 (6)	2754.610 (6)
τ_{aaaa}/MHz	−0.0079 (7)	−0.0087 (5)	−0.0083 (5)	−0.0092 (19)
τ_{bbbb}/MHz	−0.0059 (6)	−0.0051 (5)	−0.0065 (3)	−0.0062 (13)
τ_{aabb}/MHz	0.0018	0.0018[b]	0.0018[b]	0.0018[b]
τ_{abab}/MHz	−0.0029	−0.0029[b]	−0.0029[b]	−0.0029[b]
Δ/u Å^2	−0.0016 (16)	−0.0105 (13)	−0.0115 (10)	−0.0112 (19)
transition type	a	b	b	a (b)

[a] Error limits represent 3 standard deviations. [b] Constrained to the value of the normal species.

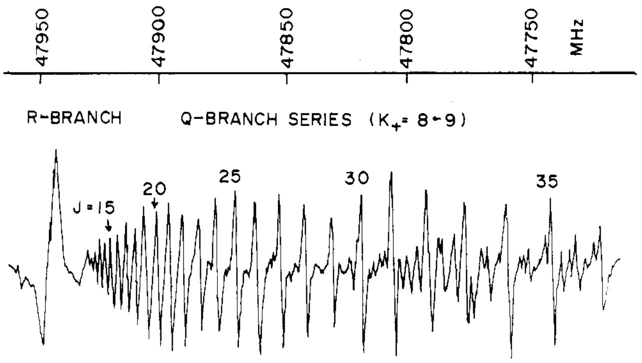


Figure 1. Example of a Q-branch series observed for 3*H*-3-azacyclotriboroxane.

The rotational constants thus determined without knowledge of the carrier of the spectrum only indicated that the molecule was likely to have a five- or six-membered ring structure with boron, oxygen, and/or nitrogen atoms. In order to identify the molecule, isotopically substituted species were measured. The spectra of all deuterated and ^{15}N species were observed by using B_2D_6 and ^{15}NO for the reaction. The spectra of ^{10}B species were measured in their naturally occurring abundance; 20% for ^{10}B and 80% for ^{11}B. Two different spectra were observed for ^{10}B-substituted species, one being twice as strong as the other. This fact indicates that the molecule has three boron atoms, with two of them located at symmetric positions. Only one spectrum was measured for the ^{15}N-substituted species. From these results and the structural analysis, which will be described later, the molecule was identified to be $B_3H_4NO_2$. The rotational constants, centrifugal distortion constants, inertia defects, and transition types for the various isotopic species of $B_3H_4NO_2$ are listed in Table I. It should be noted that the transitions are b type for the normal and 6-^{10}B species, a type for the ^{15}N and tetradeuterated species, and both a and b types for the 2-^{10}B species. Such changes in the direction of principal axes due to isotopic substitution are explained satisfactorily by use of the molecular structure obtained in the present analysis. Isotopic substitution of the boron atom at the 2-position causes 47.4° rotation of the principal axes and, therefore, the 2-^{10}B species showed nearly equal intensities of a- and b-type transitions.

In the course of the above measurements, other spectra, which showed similar aspects but whose carrier seemed to be a different molecule, were found. They also showed the characteristic Q-branch series of a nearly symmetric rotor with fairly weak spectral intensity, but the intensity alternation was not obvious. By a procedure similar to that used above, the molecule was identified to be $B_3H_5N_2O$. A change in transition type upon isotopic substitution was also found for this molecule. Structural analysis indicated that the rotation of the principal axes by substitution of the boron atom at the 2-position is 22°. Therefore, b-type transitions of the 2-^{10}B species were too weak to be observed.

The rotational and centrifugal distortion constants of $B_3H_5N_2O$ determined by least-squares fitting are listed in Table II. Since a large correlation exists among the τ's for isotopically substituted $B_3H_5N_2O$, τ_{aabb} and τ_{abab} were constrained to the values of the normal species in the least squares fitting.

No hyperfine structure due to boron and nitrogen nuclei was observed for both molecules. This may be because both boron and nitrogen generally have small nuclear quadrupole coupling constants, and many hyperfine components due to four or five nuclear quadrupole couplings should exist in a small frequency region. If we neglect the effect of the hyperfine splittings due to the boron and nitrogen nuclei, the statistical spin weights for normal $B_3H_4NO_2$ and $B_3H_5N_2O$ should be

K_{-1}, K_{+1} ↔ K_{-1}, K_{+1}	wt	
even, even ↔ odd, odd	36	for $B_3H_4NO_2$
odd, even ↔ even, odd	28	
even, odd ↔ even, even	47	for $B_3H_5N_2O$
odd, even ↔ odd, odd	49	

These values are consistent with the observation that the Q-branch series of $B_3H_4NO_2$ showed a slight intensity alternation, while

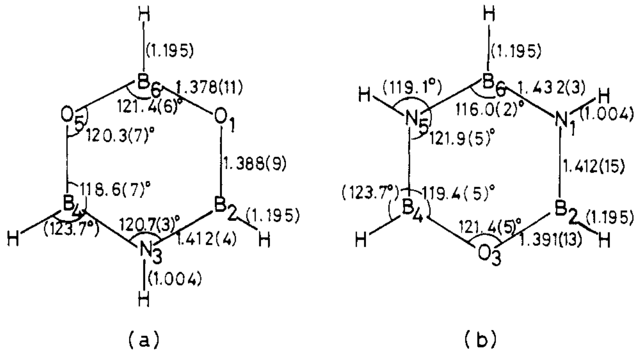


Figure 2. r_0 structural parameters for (a) 3*H*-3-azacyclotriboroxane and (b) 3-oxacyclotriborazane. Error limits represent 3 standard deviations. Figures in parentheses are constrained values. See text.

Table III. r_s Coordinates of 3*H*-3-Azacyclotriboroxane and 3-Oxacyclotriborazane, and Comparison of r_0 and r_s Parameters (in Å and deg)[a]

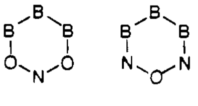
atom	*a* coord	*b* coord	param	r_s	r_0
		3*H*-3-Azacyclotriboroxane			
B_6	0.0	1.3679	$r(B_2-N_3)$	1.412 (3)	1.412 (4)
B_2/B_4	±1.2277	−0.7019	$\angle B_2N_3B_4$	120.9 (4)	120.7 (3)
N_3	0.0	−1.3986	$r(N_3\cdots B_6)$	2.767 (4)	2.761 (11)
H_2/H_4	±2.2953		$r(H_2\cdots H_4)$	4.591 (2)	4.590
		3-Oxacyclotriborazane			
B_6	1.4603	0.0	$r(B_6-N_1)$	1.435 (3)	1.432 (3)
N_1/N_5	0.6985	±1.2160	$r(B_2-N_1)$	1.412 (3)	1.412 (15)
B_2/B_4	−0.7132	±1.2113	$\angle B_2N_1B_6$	121.8 (8)	121.9 (5)
			$\angle N_1B_6N_5$	115.9 (8)	116.0 (2)

[a] For numbering of atoms, see Figure 2.

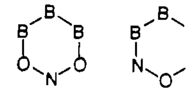
such an alternation was scarcely noticed for the series of $B_3H_5N_2O$.

Molecular Structure. In order to confirm the identification of the molecules newly found in the present investigation, the analysis of the molecular structures was carried out. Small negative values for the inertia defects ($\Delta = I_c - I_a - I_b$) have been obtained for all the isotopic species of $B_3H_4NO_2$ and $B_3H_5N_2O$. These values suggest that the molecules are nearly planar or that they are exactly planar, with out-of-plane vibrations lower in frequency than the in-plane vibrations. As to the planarity of borazine, the results of electron diffraction[11] are not unambiguous either, while the ab initio calculation[12] shows a complete planar structure. Even if $B_3H_4NO_2$ and $B_3H_5N_2O$ are not exactly planar, the deviation from the planar ring structure of the skeletal rings would be very small, considering the smallness of the inertia defects. Therefore, the structures were analyzed with the assumption of planarity. Each structure of the skeletal ring has been determined by a least-squares fit of all the rotational constants. Since the isotopic species measured are not enough to determine all the structural parameters, the B–H and N–H lengths are assumed to be 1.195 and 1.004 Å, respectively, which are the same as those of BH_2NH_2.[13] For the assumed B–H length, the ∠HBN angle in $B_3H_4NO_2$ was derived as 123.7° from the ΔI between $B_3H_4NO_2$ and $B_3D_4NO_2$, and this value was fixed in the least-squares analysis. The same value was assumed for the corresponding ∠HBN in the analysis of $B_3H_5N_2O$. The molecular structures thus determined are shown in Figure 2. The partial r_s structural parameters have also been determined by using Kraitchman's equations. They are listed in Table III, and compared with the r_0 parameters. The agreement between r_0 and r_s is excellent.

However, from the rough estimate of the rotational constants and the molecular symmetry deduced from the spectral feature, the molecules with the ring skeletons



can also be candidates for the carriers of the spectra. However, they were rejected by the results of the structural analysis. The convergence of the least-squares fitting was poor with very large residuals that are more than a hundred times as large as those in the former analysis. Furthermore, if some parameters are fixed to the r_s values derived by the Kraitchman equations, the residuals in the fitting become much larger, and rather different values are obtained. These facts clearly show that the assumed molecular models with the



skeletons are definitely wrong.

Discussion

The explanation for the formation of $B_3H_4NO_2$ and $B_3H_5N_2O$ by the reaction of B_2H_6 with NO is not straightforward. It was expected that the similar molecules boroxin and borazine were also produced in the same reaction. Therefore, the mass spectrum of the reaction products was also investigated in the present study. The mass spectrometry of a heated mixture of B_2H_6 and NO showed clear peaks at $m/q = 84$–81 and weak peaks below 80. This result is consistent with the above assumption. Boroxin and borazine are trimers of HBO and HBNH, respectively. The two new ring compounds found in the present study are considered as complexes of HBO and HBNH monomers combined in a manner similar to that observed for boroxin and borazine. Therefore, these two monomers seem to be involved with the formation of the above four ring compounds. In the present study an attempt was made to observe the microwave spectrum of HBO. The spectral line was searched for in the region where the $J = 1 \leftarrow 0$ transition was expected from the assumed molecular structure. This attempt was not successful, but later, Y.K. identified both HBO[14] and HBNH[15] produced by the discharge through a mixture of B_2H_6 and NO using infrared diode laser and microwave spectroscopy. These intermediates have very short lifetimes, and they were detected only in the glow discharge. These experimental results suggest that the same intermediates also exist in the thermal reaction of diborane with NO. However, it is still ambiguous whether the HBNH monomer is the main source of the ring compounds, because the reaction in which BH_2NH_2 first forms the intermediate ring compounds which then lose hydrogen also seems possible.

It is clear that boroxin and borazine are thermodynamically favored over diborane and NO in consideration of the heat of formation of these compounds. The values of ΔH_f^0 for boroxin and borazine are both large and negative, −1218 (42) and −510 (13) kJ/mol, respectively, while those for diborane and NO are positive, 31.4 and 90.4 kJ/mol, respectively.[16] Since the heat of formation for $B_3H_4NO_2$ and $B_3H_5N_2O$ should be similar to boroxin or borazine, the formation of the newly identified molecules seems to be also thermodynamically favored.

On the other hand, the mechanism by which HBO and BH_2NH_2 or HBNH are produced from diborane and NO is quite ambiguous. It would be necessary to find the initial products of the reaction in order to clarify the complete reaction process. However, it is interesting to note that $B_2H_5NH_2$ was found along with BH_2NH_2, but $BH(NH_2)_2$[17] was not detected in the present study. This was true in spite of the fact that the reaction of diborane with NH_3 gave BH_2NH_2 and $BH(NH_2)_2$ but did not

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give $B_2H_5NH_2$. These facts show that BH_2NH_2 is not formed through NH_3 in the present reaction.

The comparison of B–O and B–N lengths obtained for $B_3H_4NO_2$ and $B_3H_5N_2O$ with those for similar compounds shows that the change in B–O and B–N bond lengths has different trends. Both the B–O lengths found in the two molecules are around 1.385 Å, and this value is almost the same as that of boroxin.[10] On the other hand, the two B–N lengths in $B_3H_5N_2O$ are fairly different: 1.412 and 1.432 Å. The smaller one is the same as the B–N length in $B_3H_4NO_2$, 1.412 Å, and the larger one is close to that in borazine, 1.4355 (40) Å.[11] The shortening of the B–O bond adjacent to the O atom may be ascribed to the conjugation between B–N and B–O bonds. It is interesting to compare the B–N lengths with those in BH_2NH_2, 1.391 Å,[13] and in $BH(NH_2)_2$, 1.418 (1) Å.[17] Since borane is an electron-deficient molecule and amine has a lone pair, the B–N bonds in above molecules have large double-bond character, and the amount of double-bond character seems to decrease in the order BH_2NH_2, $BH(NH_2)_2$, $B_3H_4NO_2$, $B_3H_5N_2O$, and borazine.

Registry No. B_2H_6, 19287-45-7; NO, 10102-43-9; BH_2NH_2, 14720-35-5; $B_2H_5NH_2$, 39046-41-8; N_2O, 10024-97-2; B_2D_6, 20396-66-1; ^{15}NO, 15917-77-8; $B_3H_5N_2O$, 118496-08-5; $B_3H_4NO_2$, 118496-03-0; $B_3H_4NO_2$-*3*-^{15}N, 118496-04-1; $B_3H_4NO_2$-*2*-^{10}B, 118496-05-2; $B_3H_4NO_2$-*6*-^{10}B, 118496-06-3; $B_3D_4NO_2$, 118496-07-4; $B_3H_5N_2O$-*1,5*-$^{15}N_2$, 118496-09-6; $B_3H_5N_2O$-*6*-^{10}B, 118496-10-9; $B_3H_5N_2O$-*2*-^{10}B, 118496-11-0.

Supplementary Material Available: Tables of observed transition frequencies for nine isotopic species (9 pages). Ordering information is given on any current masthead page.

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Thermal Rearrangement Studies on Ethyl and Chloro Diethyl Derivatives of *closo*-2,4-$C_2B_5H_7$: Elimination of a 1,2-Substituent-Shift Mechanistic Hypothesis and Further Support of the DSD Cage Rearrangement Mechanism

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The thermal (295–340 °C) rearrangement pattern for 3-Cl-5,6-$(C_2H_5)_2$-*closo*-2,4-$C_2B_5H_4$ supports a DSD cage mechanism but, more importantly, rules out a 1,2-substituent-shift mechanism. The rate constants for the 295 °C rearrangement of 5-C_2H_5-*closo*-2,4-$C_2B_5H_6$ and 5,6-$(C_2H_5)_2$-*closo*-2,4-$C_2B_5H_5$ are determined, and equilibrium percentages of the three *B*-C_2H_5-2,4-$C_2B_5H_6$ isomers and the five *B,B'*-$(C_2H_5)_2$-2,4-$C_2B_5H_5$ isomers are obtained.

Introduction

Kinetic studies on the rearrangements of mono- and dimethyl derivatives,[1-3] mono- and dichloro derivatives,[3-5] mono- and dibromo derivatives,[6] and mono- and diiodo derivatives[6] of 2,4-$C_2B_5H_7$ have been reported. Among three plausible rearrangement mechanisms (Figure 1 illustrates the various mechanistic models) for the above substituted *closo*-2,4-$C_2B_5H_7$ compounds—diamond–square–diamond (DSD),[7-9] triangle face rotation (TFR),[8,10] and surface-substituent migration (SSM, also known as 1,2-substituent-shift mechanism)[10]—it appears that the TFR mechanism can be ruled out.[2,3,5,6] It should be mentioned that previous considerations of the DSD and TFR mechanisms (above references) have argued the common constraint: cage carbon atoms are returned to low-coordination nonadjacent positions of the *closo*-dicarbaheptaborane polyhedron after each cage-movement cycle.

In the present study, a rearrangement of 3-Cl-5,6-$(C_2H_5)_2$-2,4-$C_2B_5H_4$ has been conducted in an attempt to differentiate between the DSD and 1,2-substituent-shift mechanisms. In addition, kinetic studies have been carried out on mono- and diethyl derivatives of the same cage carborane. Relative stabilities within each isomer set are evaluated and correlated.

Experimental Section

Materials and Handling of Chemicals. The parent carborane *closo*-2,4-$C_2B_5H_7$, obtained from R. E. Williams, was used without further purification, and 3-Cl-2,4-$C_2B_5H_6$ was prepared according to a literature procedure.[11] Aluminum trichloride (Aldrich Chemical Company Inc.) was sublimed directly into the reaction vessel prior to use. Chloroethane (Matheson) was used without further purification. All materials were handled by using conventional high-vacuum techniques or in a nitrogen drybox. Purification of volatile compounds was accomplished either by cold-column separation[12] or by trap-to-trap fractionation in a standard high-vacuum apparatus.[13]

Nuclear Magnetic Resonance. Boron-11 (160.44 MHz) NMR data, Table I, were gathered by using a Bruker WM-500 FT spectrometer at the California Institute of Technology, Pasadena, CA, and a Bruker AM-400 FT spectrometer at CSULA. All ^{11}B chemical shift data are based on $\delta(BF_3{\cdot}Et_2O) = 0.00$ ppm, with 2,4-$C_2B_5H_7$ used as a secondary standard, with $\delta(1,7) = -21.73$ ppm, $\delta(3) = +7.02$ ppm, and $\delta(5,6) = +3.83$ ppm. Negative chemical shift values are upfield of the $BF_3{\cdot}OEt_2$ resonance. Approximate chemical shift and coupling constant errors for all dicarbaheptaboranes are as follows: ±0.02 ppm and ±3 Hz, for the 1, 3, and 7 cage positions of the carborane; ±0.06 ppm, ±10 Hz, for the 5 and 6 cage positions. Proton (60 MHz) NMR spectra were obtained

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