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Synthesis and Properties of $(C_5H_5Co)B_9H_9C{\cdot}N(CH_3)_3$ and Related Derivatives

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Reaction of $B_9H_{11}C{\cdot}N(CH_3)_3$ with NaH and subsequent treatment with NaC_5H_5 and $CoCl_2$ formed $(C_5H_5Co)B_9H_9C{\cdot}N(CH_3)_3$. This closo 11-atom molecule is fluxional at +70 °C and static at −40 °C on the ^{11}B NMR time scale. Thermal degradation of the cobalt complex formed $B_9H_9C{\cdot}N(CH_3)_3$. Reaction of $B_9H_{11}C{\cdot}N(CH_3)_3$ with sodium polyselenide formed *nido*-$SeB_9H_9C{\cdot}N(CH_3)_3$ in moderate yield.

Introduction

Since its first report in 1966, monocarbon carborane chemistry has developed slowly relative to that of two-carbon carboranes. Nevertheless many *closo*-$CB_nH_{n+1}^-$, *nido*-$CB_nH_{n+3}^-$, and *arachno*-$CB_nH_{n+5}^-$ ions or their protonated forms or their metallocarborane derivatives are known.[1,2] Several neutral derivatives with an amine bonded at carbon such as $B_{10}H_{12}C{\cdot}N(CH_3)_3$ have also been reported.[2-4] The compound $B_9H_{11}C{\cdot}N(CH_3)_3$ should have an interesting derivative chemistry. One or two more cage units of various types (both nonmetal and metal) might be inserted into the B_9C structure to form new types of heteroatom boranes. Our synthetic efforts in this area have been hindered by our inability to obtain a useful yield of $B_9H_{11}C{\cdot}N(CH_3)_3$ with previously reported procedures.[5] In this paper we report a modified synthesis of this starting material as well as our initial chemical studies in this area.

Experimental Section

Instrumentation and Methods. Boron (^{11}B) NMR spectra were obtained at 70.6 MHz with a Varian HR-220 spectrometer and were externally referenced to $BF_3{\cdot}O(C_2H_5)_2$. Integrations were computer calculated within manually selected limits of integration.[6] Proton (^1H) NMR spectra were obtained on a Varian HR-220 spectrometer (220 MHz) and on a Varian T-60-A spectrometer (60 MHz) and referenced to tetramethylsilane (Me_4Si). Negative chemical shifts indicate higher shielding values for both ^{11}B and ^1H spectra.

Elemental analyses were performed by Schwarzkopf Microanalytical Laboratories, Woodside, N.Y. Infrared spectra were obtained on a Perkin-Elmer 283 spectrometer using KBr disks. Low-resolution mass spectra were obtained on an Atlas CH-7 instrument. High-resolution mass spectra were obtained on an AEI MS-902 spectrometer.[7] Melting points were obtained in evacuated, sealed capillaries and are uncorrected.

Preparation of $B_9H_{11}C{\cdot}N(CH_3)_3$ from $Cs_2B_{10}H_{13}CN$. $Na_2B_{10}H_{13}CN$ was prepared by reaction of $B_{10}H_{14}$ and NaCN in aqueous solution, according to the literature method.[5] An excess of a suitable cesium salt was added to the reaction mixture to precipitate $Cs_2B_{10}H_{13}CN$, and the resulting white solid was filtered and dried under vacuum for several hours at 50 °C.

The reaction of $Cs_2B_{10}H_{13}CN$ with concentrated HCl was carried out in a *well-ventilated* fume hood, and appropriate safety measures (especially gloves and eye protection) were used at all times. The experimental procedure is a modified version of the reported procedure.[5]

Concentrated HCl (100 mL) was placed in a 1-L wide-neck, round-bottom flask equipped with magnetic stirring. A large wide-stem funnel was positioned in the neck of the flask. With the hood door closed as far as possible, $Cs_2B_{10}H_{13}CN$ (30 g) was added in one portion to the stirring HCl. An extremely vigorous, exothermic reaction ensued. If the cesium salt is added to the HCl slowly, the yield of $B_9H_{11}CNH_3$ is substantially reduced. The reaction was allowed to proceed until most of the solid had dissolved; then dioxane (40 mL) was added to the mixture. The white solid which formed, a mixture of $[B_9H_{11}C{\cdot}NH_3]{\cdot}C_4H_8O_2$ and $[B_{10}H_{12}C{\cdot}NH_3]{\cdot}C_4H_8O_2$, was filtered and washed with small amounts of cold distilled water. The dioxanates were then dissolved in aqueous NaOH (10%, 100 mL) and treated with $(CH_3)_2SO_4$ to precipitate a mixture of $B_9H_{11}C{\cdot}N(CH_3)_3$ and $B_{10}H_{12}C{\cdot}N(CH_3)_3$. This mixture was filtered and dried under vacuum at 50 °C to give 8 g of a mixture which was 40% $B_9H_{11}C{\cdot}N(CH_3)_3$ and 60% $B_{10}H_{12}C{\cdot}N(CH_3)_3$.

Table I. Elemental Analyses

	anal., %					
	C		H		B	
compd	calcd	found	calcd	found	calcd	found
I	35.85	35.34	7.69	7.79		
II					54.89	54.95
III	18.70	17.36	7.07	7.03	37.94	37.41

Prior to chromatography, the following procedure was used to concentrate the $B_9H_{11}C{\cdot}N(CH_3)_3$ in the sample. The mixture was dissolved in acetone and adsorbed onto TLC silica gel (30 g) by evaporation of the solvent. This silica gel was placed in a chromatography column and extracted with 80-mL portions of $CHCl_3$. Each fraction was checked via thin-layer chromatography using $CHCl_3$ as eluant. The TLC strips were sprayed with ethanolic $AgNO_3$ and allowed to develop completely (at least 10 min—$B_9H_{11}C{\cdot}N(CH_3)_3$ develops more slowly than $B_{10}H_{11}C{\cdot}N(CH_3)_3$). The fractions containing $B_9H_{11}C{\cdot}N(CH_3)_3$ as the major component were combined and evaporated to dryness to give 3 g of a mixture containing approximately 90% $B_9H_{11}C{\cdot}N(CH_3)_3$.

Final purification of the $B_9H_{11}C{\cdot}N(CH_3)_3$ was carried out by adsorption of a portion of the preconcentrated mixture of $B_9H_{11}{\cdot}C{\cdot}N(CH_3)_3$ and $B_{10}H_{12}C{\cdot}N(CH_3)_3$ (0.4 g) onto TLC grade silica gel (1 g). The mixture was applied to a column of regular silica gel (60 g, 100–200 mesh) packed in $CHCl_3$. The column remained translucent during elution of $B_9H_{11}C{\cdot}N(CH_3)_3$ with $CHCl_3$ and became transparent in the section containing $B_{10}H_{12}C{\cdot}N(CH_3)_3$ which eluted more slowly. The solvent was removed under vacuum, giving white needle crystals of $B_9H_{11}C{\cdot}N(CH_3)_3$ (0.25 g). The ^{11}B NMR spectrum of the product was identical with that reported earlier.[5]

$(C_5H_5)CoB_9H_9C{\cdot}N(CH_3)_3$ (I). In a Schlenk reaction vessel equipped with a coarse sintered-glass filter and magnetic stirrer, $B_9H_{11}C{\cdot}N(CH_3)_3$ (0.500 g, 2.79 mmol) was allowed to react with excess NaH in 35 mL of dry tetrahydrofuran (THF), freshly distilled from sodium benzophenone ketyl. In a separate but similar vessel, freshly cracked, dry cyclopentadiene (0.40 mL, 4.8 mmol) was allowed to react with excess NaH in 35 mL of dry THF. After 1 h, each of the solutions was filtered and then combined in a flask to which was subsequently added anhydrous $CoCl_2$ (0.40 g, 3.1 mmol). This mixture was stirred overnight under a nitrogen atmosphere. Solvent was removed under vacuum, and the resulting solid was extracted with several 20-mL portions of hexane to remove residual THF and some cobaltocene. The remaining brown solid was then extracted with small portions of CH_2Cl_2 until the extracts were pale yellow; the combined CH_2Cl_2 extracts were then reduced in volume. The mixture was chromatographed on a column of silica gel (100–200 mesh, 60 g) in CH_2Cl_2. Following elution of yellow cobaltocene, a dark red-brown band of I was collected and evaporated to dryness. The product was crystallized from CH_2Cl_2/hexane to give 0.160 g (20% yield) of $(C_5H_5)CoB_9H_9C{\cdot}N(CH_3)_3$.

Elemental analyses, infrared data, and ^1H NMR data are given in Tables I–III. This compound does not melt cleanly but decomposes with melting below 200 °C to give $B_9H_9C{\cdot}N(CH_3)_3$ as the major product. The low-resolution mass spectrum obtained at 341 °C shows a very small envelope at *m/e* 301 corresponding to the $^{12}C_9{}^1H_{23}{}^{11}B_9{}^{14}N^{59}Co^+$ ion. A high-intensity envelope of peaks which cut off at *m/e* 177 for $B_9H_9C{\cdot}N(CH_3)_3$ was also observed.

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Table II. Infrared Spectra[a]

compd	wavenumber, cm^{-1}
I	3097 vw, 3012 vw, 2952 vw, 2562 m, 2472 br s, 1480 m, 1459 m, 1407 m, 1351 vw
II	3100 vw, 3035 vw, 2960 vw, 2560 and 2520 br s, 1472 m, 1460 m, 1408 m
III	3018 vw, 2953 w, 2913 vw, 2543 br vs, 1481 m, 1458 sh, 1451 m, 1404 m

[a] Obtained as KBr disks.

Table III. ^1H NMR Spectra

	chem shift,[a] ppm	
compd	$N(CH_3)_3$[b]	other
I	+3.20	+4.90 (sharp s, C_5H_5)
II	+4.00	
III	+3.25	

[a] Solvent = acetone-d_6. [b] Sharp singlets.

$B_9H_9C{\cdot}N(CH_3)_3$ (II). A solution of $(C_5H_5)CoB_9H_9C{\cdot}N(CH_3)_3$ (0.075 g, 2.49 mmol) in CH_3CN was boiled in air for approximately 1 h. A dark gray insoluble decomposition product was removed by filtration, and the filtrate was evaporated to dryness. The dark brown solid obtained was extracted with CH_2Cl_2 (100 mL), and hexane (20 mL) was added. The volume of the solution was reduced until a pale orange precipitate formed. This precipitate was crystallized from CH_2Cl_2/hexanes to yield $B_9H_9C{\cdot}N(CH_3)_3$ (0.030 g, 67%).

Elemental analyses, infrared data, and ^1H NMR data are given in Tables I–III. This compound does not melt below 350 °C but appears to darken at 280 °C. The mass spectrum gives an envelope at *m/e* 177 corresponding to the parent ion of $B_9H_9C{\cdot}N(CH_3)_3$ and a base peak at *m/e* 58 corresponding to the trimethylamine fragment.

$SeB_9H_9C{\cdot}N(CH_3)_3$ (III). A solution of sodium polyselenide, Na_2Se_n, was prepared by heating Se metal (3.8 g, 50 mmol), NaOH (2 g, 50 mmol), and absolute ethanol (30 mL) at reflux for 20 min.

Pure $B_9H_{11}C{\cdot}N(CH_3)_3$ (0.200 g, 1.11 mmol) was placed in a separate 15-mL, two-neck flask equipped with a magnetic stirrer. An aliquot of the prepared polyselenide solution (4.0 mL) was added via syringe, and the mixture was allowed to stir at room temperature overnight. The solvent was removed under vacuum, and the resulting solid was extracted with CH_2Cl_2 (2 × 25 mL). A short (15 cm × 15 mm) low-pressure (60 psi maximum) liquid-chromatography column was prepared. The CH_2Cl_2 extract was reduced in volume and injected onto the column. Fractions were collected, bands were located by TLC (silica gel/CH_2Cl_2), and the first band eluted was isolated by evaporation of the solvent. This yielded off-white crystals of III (80 mg, 28%).

Elemental analyses, infrared data, and ^1H NMR data are given in Tables I–III. Compound III melts with decomposition at 290–292 °C. The high-resolution mass spectrum gives a peak at *m/e* 258.14743 corresponding to $^{10}B^{11}B_8{}^1H_{18}{}^{80}Se^{12}C_4{}^{14}N$ (calculated *m/e* 258.14784). The base peak in the low-resolution mass spectrum is at *m/e* 58 corresponding to the trimethylamine fragment.

Results and Discussion

The main reported[5] synthesis of $B_9H_{11}C{\cdot}N(CH_3)_3$ employed the set of reactions

$$B_{10}H_{14} + NaCN + S(CH_3)_2 \xrightarrow{\text{5 days}} Na[B_{10}H_{12}CN{\cdot}S(CH_3)_2]$$

$$Cs[B_{10}H_{12}CN{\cdot}S(CH_3)_2] \xrightarrow[\text{2. NaOH} \quad \text{3. }(CH_3)_2SO_4]{\text{1. H}^+\text{ ion exchange}} B_{10}H_{11}(OH)C{\cdot}N(CH_3)_3$$

$$B_{10}H_{11}(OH)C{\cdot}N(CH_3)_3 \xrightarrow{\text{NaOH/THF}} B_9H_{11}C{\cdot}N(CH_3)_3$$

This procedure requires 1 week to complete. The reported overall yield based on decarborane(14) was 17%,[5] but in our hands the yield never exceeded 10%. An alternate synthesis of $B_9H_{11}C{\cdot}N(CH_3)_3$, involving degradation and protonation of $Cs_2B_{10}H_{13}CN$, has been reported.[5] The overall reaction sequence is

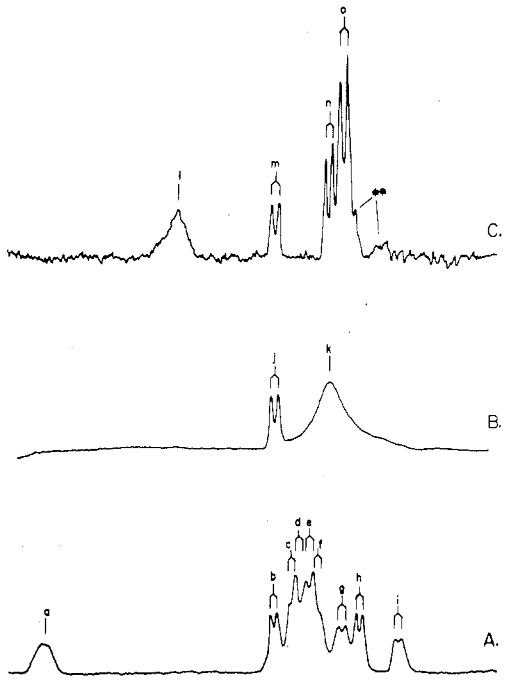

Figure 1. Variable-temperature, 70.6-MHz ^{11}B NMR spectra of $(C_5H_5)CoB_9H_9C{\cdot}N(CH_3)_3$. A. Spectrum at −40 °C in CH_2Cl_2. Chemical shifts for resonances a–i are as follows [ppm (*J*, Hz)]: +70.93, +3.86 (127); −1.71, −3.75, −6.83, −8.80, −16.20 (146); −21.18 (127); −32.94 (137). B. Spectrum at +16 °C in CH_2Cl_3. Chemical shifts for resonances j and k are as follows [ppm (*J*, Hz)]: +4.52 (127); ~−12. C. Spectrum at +70 °C in $C_2H_4Cl_2$. Chemical shifts for resonances l–o are as follows [ppm (*J*, Hz)]: +33.4, +5.11 (127); −10.56 (142); −14.96 (156). Chemical shifts for overlapping peaks were taken from a line-narrowed spectrum processed from the same data; coupling values are taken from normal spectrum where appropriate. Double asterisk peaks in the spectrum at +70 °C belong to $B_9H_9C{\cdot}N(CH_3)_3$, the major thermal decomposition product of $(C_5H_5)CoB_9H_9C{\cdot}N(CH_3)_3$ (see text).

$$B_{10}H_{14} + NaCN \xrightarrow{H_2O} Na_2B_{10}H_{13}CN$$

$$Cs_2B_{10}H_{13}CN \xrightarrow{HCl/H_2O} B_{10}H_{12}C{\cdot}NH_3 + B_9H_{11}C{\cdot}NH_3 \xrightarrow[\text{2. }(CH_3)_2SO_4]{\text{1. NaOH}} B_{10}H_{12}C{\cdot}N(CH_3)_3 + B_9H_{11}C{\cdot}N(CH_3)_3$$

We have developed this procedure into a relatively fast reproducible route to $B_9H_{11}C{\cdot}N(CH_3)_3$ in 22% overall yield based on decarborane(14).

Deprotonation of $B_9H_{11}C{\cdot}N(CH_3)_3$ with excess sodium hydride in THF and addition of NaC_5H_5 and then $CoCl_2$ to the reaction mixture formed red-brown crystalline $(C_5H_5)CoB_9H_9C{\cdot}N(CH_3)_3$ (I) in low yield. The room-temperature ^{11}B NMR spectrum of this complex was very unusual due to the lack of resolution of a majority of the resonances observed (see Figure 1B). This molecule has the valence-electron count corresponding to a closo octadecahedral geometry. Previous ^{11}B NMR studies of closo 11-atom polyhedra revealed that some (e.g., $B_9C_2H_{11}$,[8] 1-(C_5H_5)Co-2,3-$C_2B_9H_{10}$,[8,9] 1-(C_5H_5)Co-2,4-$C_2B_8H_{10}$,[8,10] and $C_5H_5CoB_9H_9CH^-$[11]) molecules are apparently static at room temperature while other molecules (e.g., $B_{10}H_{10}CH^-$,[12] $B_{11}H_{11}{}^{2-}$,[13] and $B_{11}H_9Se_3{}^{2-}$[14]) are apparently undergoing a rapid polyhedral rearrangement process relative to the NMR time scale. We considered it possible, therefore, that I might be undergoing polyhedral

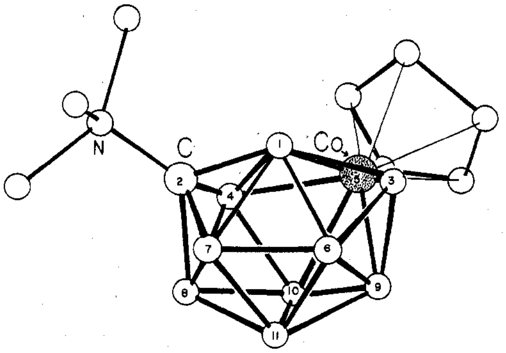

Figure 2. Gross geometry of $(C_5H_5)CoB_9H_9C{\cdot}N(CH_3)_3$ as determined by single-crystal X-ray diffraction (terminal hydrogen atoms have been omitted for clarity).

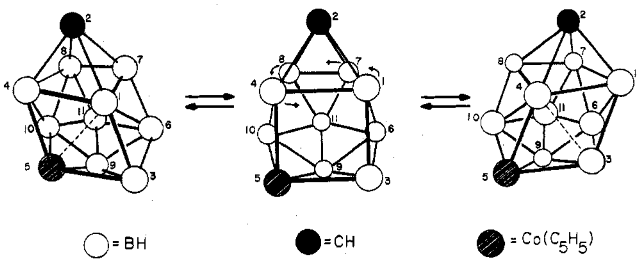

Figure 3. Sequence of "dsd" type rearrangements resulting in rotation of belts in an 11-member polyhedron.

rearrangement at a slower rate at room temperature than had been previously observed. A variable-temperature ^{11}B NMR spectral study of I between −40 and +70 °C (see Figure 1) confirmed our suspicion. At −40 °C the ^{11}B NMR spectrum of I contains nine overlapping resonances, suggesting an asymmetric static structure. At intermediate temperatures (−15 to +30 °C) the spectrum consists of a sharp doublet of area 1 at approximately 4 ppm and a very broad poorly defined multiplet. At +70 °C the spectrum sharpens to four resonances of area 2:1:2:4 reading upfield. It should be noted that the temperature limits of this particular study were imposed at low temperature by the instrumental design and at high temperature by the thermal stability of the complex. The high-temperature spectrum contains impurity peaks (marked with an asterisk) which are due to $B_9H_9C{\cdot}N(CH_3)_3$ (vide infra). These temperature limitations, therefore, preclude acquisition of cleaner spectra of the "static" and "fluxional" molecule. Nonetheless, this study represents the first complete demonstration that some eleven-atom closo cage compounds do undergo a polyhedral rearrangement process which is fast relative to the ^{11}B NMR time scale.

A single-crystal X-ray diffraction study of I has also been completed, and the structure is illustrated in Figure 2.[15] Note that the solid-state structure is very asymmetric as suggested by the −40 °C ^{11}B NMR spectrum. The isoelectronically related complex $C_5H_5CoB_9H_9CH^-$ has been prepared,[11] and in this case the authors propose that the C_5H_5Co unit is in the 1-position and the CH unit is in the 2-position (see Figure 2 for the numbering sequence). This assignment is based on their ^{11}B NMR results and the known structural preferences of other metallocarboranes. We suggest that the steric bulk of the C_5H_5 and $N(CH_3)_3$ units in I will preclude close approach of the cobalt and carbon atoms to one another in this molecule.

The 2:1:2:4 pattern in the spectrum at high temperature can be accommodated by a mechanism directly analogous to that described previously for the rearrangement of $B_{10}H_{10}CH^-$.[12] We suggest that the mechanism involves breaking the bond between positions 1 and 5 (or 1 and 6), followed by passage through an intermediate in which a single "square face" has been generated (see Figure 3). As the halves of the molecule continue their motion, a new bond is formed between positions 3 and 4 (or 3 and 7). This mechanism would equilibrate those boron atoms in positions 1, 4, 7, and 8 corresponding to the doublet of area 4 at −14.96 ppm (resonance "o") in the high-temperature spectrum. The belt of atoms defined by positions 3, 5, 6, 10, and 11 would through several cycles of this rearrangement mechanism effectively rotate, and two resonances would be expected, corresponding to the pair of boron atoms ortho to the cobalt and the pair meta to the cobalt. These are assigned to the broad resonance at +33.4 ppm and the doublet at −10.56 ppm, respectively. (This assignment will be further explained in the correlation of the high-temperature spectrum to the low-temperature spectrum.) The doublet at +5.11 ppm is assigned to the boron atom at position 9, which plays no role in this mechanistic scheme.

The correlation between the high- and low-temperature spectrum can be perceived in the following way. First, the doublet at +5.11 ppm in the high-temperature spectrum simply experiences a slight temperature shift to +3.86 ppm at low temperature. The broad resonance at +33.4 ppm in spectrum C must therefore be the product of the coalescence of the low-field resonance at +71.16 ppm and the resonance at −6.83 ppm ("a" and "e", respectively), when the temperature shift is taken into account. On the basis of empirical observations in other systems,[16,17] the low-field resonance at +71.16 ppm can probably be assigned to a low-coordinate boron atom located next to the cobalt. The boron atom at position 3 is such an atom, supporting the spectral assignment made above for the high-temperature spectrum.

The best fit for the coalescence of the remaining six peaks in the low-temperature spectrum to give resonances of areas 2 and 4 at the shifts observed in the high-temperature spectrum necessitates the following combination: (c, h) and (d, f, g, i). The resonances observed at −1.71 and −21.18 ppm in the low-temperature spectrum are, therefore, assigned to the pair of boron atoms at positions 6 and 11, which are meta to the cobalt atom. The four boron atoms in the ring that are ortho to the carbon atom are assigned resonances at −3.75, −8.80, −16.17, and −32.97 ppm. It is not possible to assign these resonances to particular boron atoms on the basis of the evidence available at this time.

The cobalt complex I degrades at reflux in acetonitrile to form *closo*-$B_9H_9C{\cdot}N(CH_3)_3$ (II) in good yield. The ^{11}B NMR spectrum of this compound (CH_3CN solvent) contains three doublets of relative areas at 1:4:4 at 31.8 (142), −17.3 (156), and −26.0 ppm (142 Hz). This spectrum is quite similar to that observed previously for the isoelectronic $B_9H_9CH^-$ ion.[12] Surprisingly, the isolation of II has not been reported to date. On the basis of the ^{11}B NMR, the structure of II is that of a symmetrically bicapped-square antiprism with the $CN(CH_3)_3$ unit in an apex position.

Recently we have prepared several new nido eleven-atom heteroatom borane molecules including $B_9H_9Se_2$,[18] $B_8H_8As_2S$,[19] and $B_8C_2H_{10}Se$.[20] Use of a valence-electron-counting system such as that outlined by Wade[21] allows one to predict that $SeB_9H_9C{\cdot}N(CH_3)_3$ (III) would be a nido molecule similar to those described above. Accordingly, we have found that treatment of $B_9H_{11}C{\cdot}N(CH_3)_3$ with sodium polyselenide in refluxing ethanol formed III in low yield.

The ^{11}B NMR spectrum of this molecule (see Figure 4) contained a complex set of overlapping resonances of area 8 at low field and a well-resolved doublet of area 1 at −40.9 ppm. Of particular interest is the presence of the doublet in the area 8 multiplet at −17.0 ppm, which is unusually sharp. This resonance can be attributed to a boron atom located between two heteroatoms in the open face of the cage, which would be expected to encounter less B–B spin coupling. This re-

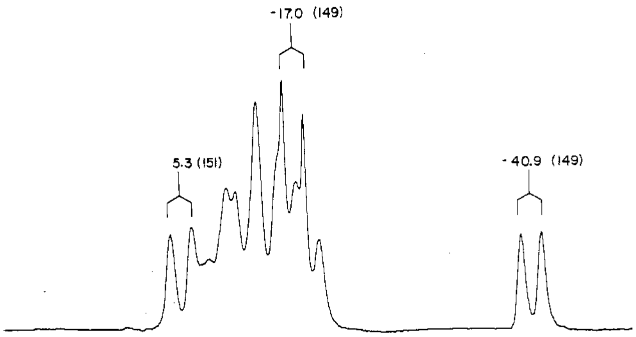

Figure 4. 70.6-MHz ^{11}B NMR spectrum of $SeB_9H_9C{\cdot}N(CH_3)_3$ (solvent = CH_3CN).

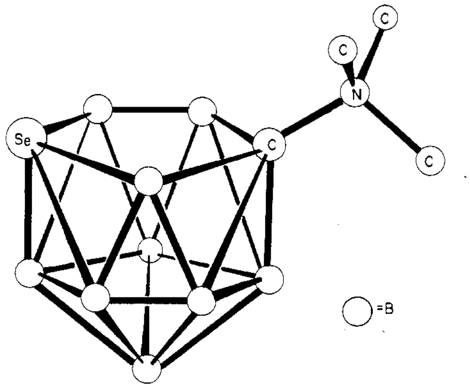

Figure 5. Proposed structure of $SeB_9H_9C{\cdot}N(CH_3)_3$ (all hydrogen atoms have been omitted for clarity).

duction in coupling would lead to a doublet with narrower line width. In addition, all of the known nido 11-member heteroboranes[22] exhibit a high-field doublet similar to the doublet observed at −40.9 ppm for $SeB_9H_9C{\cdot}N(CH_3)_3$. This doublet can be attributed to the "apical" boron atom located at the bottom of the cage. On the basis of the NMR data, we propose the structure given in Figure 5 for $SeB_9H_9C{\cdot}N(CH_3)_3$.

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Registry No. I, 71230-54-1; II, 71230-53-0; III, 71230-51-8; $B_9H_{11}C{\cdot}N(CH_3)_3$, 31117-20-1; $Cs_2B_{10}H_{13}CN$, 71250-00-5.

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Linked and Mercury-Bridged *nido*-Carboranes. High-Yield Synthesis of μ,μ'-$[(CH_3)_2C_2B_4H_5]_2Hg$, Conversion to 5,5′-$[(CH_3)_2C_2B_4H_5]_2$, Cleavage, and Oxidative Addition of Benzene. Synthesis of μ,μ'-$(B_5H_8)_2Hg$

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The *nido*-carborane anion $[2,3\text{-}(CH_3)_2C_2B_4H_5]^-$ reacts readily with anhydrous $HgCl_2$ in THF at room temperature, producing the bis(carboranyl)mercury(II) complex μ,μ'-$[(CH_3)_2C_2B_4H_5]_2Hg$ in which the metal is bound to two carborane ligands via B–Hg–B three-center, two-electron bridge bonds. On heating at 180 °C in benzene, this compound quantitatively expels free mercury and forms the B–B-linked *nido*-carborane 5,5′-$[(CH_3)_2C_2B_4H_5]_2$ as a single pure isomer. Air oxidation of the linked carborane in benzene solution results in cleavage of the carborane–carborane B–B bond and oxidative addition of benzene to give 4-C_6H_5-2,3-$(CH_3)_2C_2B_4H_5$, an apparently air-stable derivative of *nido*-2,3-$C_2B_4H_8$. Similar treatment of the linked carborane in C_6D_6 gives the corresponding hexadeuterated carborane product. The reaction of $B_5H_8^-$ ion with $HgCl_2$ in THF produces μ,μ'-$(B_5H_8)_2Hg$, a stable solid in which mercury is evidently bridge bonded to two pentaborane ligands.

Introduction

The small *nido*-carborane 2,3-$C_2B_4H_8$ and its substituted derivatives are exceedingly versatile ligands which readily form η^1, η^2, and η^5 complexes with metal and metalloid groups. Insertion of units such as $(CO)_3Fe$ or $(\eta^5\text{-}C_5H_5)Co^{2+}$ into the open face of the pyramidal species $R_2C_2B_4H_6$ (R = H, CH_3) or their anions ($R_2C_2B_4H_5^-$) yields *closo*-metallocarboranes in which the metal is η^5 bonded to the carborane and completes a seven-vertex MC_2B_4 polyhedral cage system. A rather extensive chemistry has been developed in this area[1] including the oxidative fusion of face-bonded C_2B_4 ligands coordinated to the same metal ion to give tetracarbon C_4B_8 cages. In

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