indicated a 2:1 mixture of the 2- and 1-isomers. The heating was continued at 175 °C for 70 h followed by 5 h at 180 °C, after which the ^{1}H and ^{11}B NMR spectra showed the isomerization to be essentially complete. Again, the presence of undissolved solid residues and of ferrocene (identified from its mass spectrum) indicated that some decomposition had occurred during the isomerization. The rearranged isomer [1-(η^5-C$_5$H$_5$)FeB$_5$H$_{10}$], a dark violet air-sensitive solid, was characterized from its ^{11}B and ^{1}H NMR and mass spectra.

Registry No. 2-(η^5-C$_5$H$_5$)FeB$_5$H$_{10}$, 71661-61-5; 1-(η^5-C$_5$H$_5$)-FeB$_5$H$_{10}$, 65188-99-0; 2-(η^5-C$_5$H$_5$)FeB$_{10}$H$_{15}$, 71661-62-6; (η^5-C$_5$H$_5$)$_2$Fe, 102-54-5; pentaborane(9), 19624-22-7.

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Improved Synthetic Routes to Small Carboranes. Bench-Scale Preparation of *nido*-2,3-C₂B₄H₈ Derivatives from B₅H₉ and from B₃H₈⁻ Salts

NARAYAN S. HOSMANE and RUSSELL N. GRIMES*

A method has been developed for producing the *C,C'*-dimethyl and *C*-phenyl derivatives of 2,3-C$_2$B$_4$H$_8$ in gram quantities and in yields of >50% without the use of heat, solvent, or large-volume gas bulb reactions. This approach involves formation of a B$_5$H$_9$·2L adduct (L = triethylamine or dimethyl sulfide) which reacts with 2-butyne or phenylacetylene in situ, at or below room temperature, to give the corresponding RR'C$_2$B$_4$H$_6$ carborane. The carborane product is easily isolated in high purity by vacuum fractionation. The most satisfactory results are obtained with triethylamine, with B$_5$H$_9$ maintained in excess, and with simultaneous incremental addition of the amine and alkyne to the borane. The use of dimethyl sulfide in place of triethylamine gives slightly higher carborane yields but results in a much slower reaction. The triethylamine method has been combined with a previously reported synthesis of B$_5$H$_9$ from B$_3$H$_8^-$ salts, to generate C$_2$B$_4$H$_8$ derivatives from B$_3$H$_8^-$ in a "one-pot" synthesis, thereby eliminating the isolation or handling of B$_5$H$_9$ and other volatile boranes. Since B$_3$H$_8^-$ salts are readily prepared from NaBH$_4$, this method offers a safe and relatively inexpensive route to lower carboranes.

Studies of the smaller carboranes and their metal-containing derivatives have been hampered by the absence of efficient, convenient, and safe preparative routes to the lower carborane starting materials. The commonly used preparative methods for these compounds utilize reactions of alkynes with volatile boranes, usually at elevated temperatures in the gas phase;[1,2] in most cases the products are obtained as complex mixtures of carboranes and organoboranes, which require gas chromatographic separation, together with solid waste materials. Since these reactions are conducted in the gas phase, consid-

erations of safety and practicality normally restrict such preparations to a scale of a few millimoles or less. Obviously, bench-scale methods that operate under mild conditions and generate easily separable carborane products would be desirable. Especially useful would be a means of producing carboranes directly from the inexpensive bulk chemical sodium borohydride (NaBH$_4$) or from salts of B$_3$H$_8^-$, which are easily prepared from that compound.[3]

A small carborane of particular importance in synthetic work is *nido*-2,3-C$_2$B$_4$H$_8$ [dicarbahexaborane(8)]. This com-
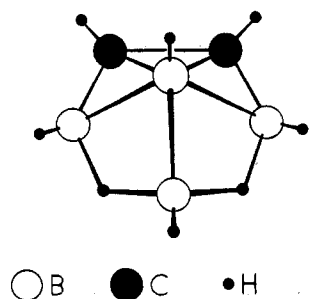
$\bigcirc$ B $\bullet$ C $\bullet$ H

Figure 1. Structure of 2,3-$C_2B_4H_8$.

pound (Figure 1) and its C-substituted derivatives can not only function as versatile ligands (η^1, η^2, and η^5 coordinate) in transition metal complexes but also serve as precursors to *closo*-carboranes, to tetracarbon carboranes, and to tetracarbon metallocarboranes.[1,2,4] The best available route to $C_2B_4H_8$ and its derivatives has been the method of Onak, Drake, and Dunks,[5a] in which alkyne–B_5H_9 mixtures are pyrolyzed in the gas phase. This procedure affords $R_2C_2B_4H_6$ species in varying yields (8–54% depending upon the alkyne employed) but owing to limitations imposed by the gas-phase conditions, the *absolute* quantity of product obtained is small; typically 1–3 mmol is produced in a 1-L reaction bulb. Moreover, the carborane products must be separated, usually via gas chromatography, from the complex mixtures obtained.

An alternative approach employs the alkyne–B_5H_9 reaction in the presence of weak Lewis bases, in a manner analogous to the synthesis[1,2] of 1,2-$C_2B_{10}H_{12}$ (*o*-carborane) from $B_{10}H_{14}$. Thus, C-substituted derivatives of $C_2B_4H_8$ have been obtained from reactions of B_5H_9, alkynes, and 2,6-dimethylpyridine,[5,6] but we have found this procedure experimentally inconvenient[7] and gas chromatographic separation of products is required, again limiting the scale of the synthesis. Accordingly, we have been exploring other reaction conditions including (1) the utilization of strong bases in the presence of B_5H_9 and alkynes and (2) the "one-pot" synthesis of carboranes from $B_3H_8^-$ salts. We report here two routes to C-substituted $C_2B_4H_8$ derivatives which afford multigram quantities of carboranes safely and cleanly with minimal problems of separation, the second of which *avoids altogether the isolation or handling of volatile boranes*.

Results and Discussion

Synthesis of C-Substituted $C_2B_4H_8$ Derivatives from B_5H_9, Alkynes, and Lewis Bases. The object of this work was to develop an efficient bench-scale route to *nido*-$R_2C_2B_4H_6$ carboranes by utilizing the net reaction

$$B_5H_9 + RC\equiv CR' + L \rightarrow RR'C_2B_4H_6 + L\cdot BH_3$$
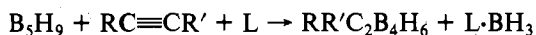
where R is CH_3 or C_6H_5, R' is CH_3 or H, and L is $(C_2H_5)_3N$, $(CH_3)_2S$, or other suitable base. The process presumably involves a $B_5H_9\cdot 2L$ adduct intermediate,[9] but these compounds were not isolated in this investigation. A variety of reaction conditions were examined, but all experiments were conducted without solvent (to facilitate the separation of products) and with temperatures no higher than 25 °C. The volatile products were easily isolated by vacuum-line fractionation, and usually consisted primarily of the desired carborane, the L·BH_3 adduct, and unreacted B_5H_9 and alkyne. In reactions involving triethylamine, it was found important to maintain an excess of alkyne and B_5H_9 over amine so that the B_5H_9–base adduct, once formed, can react immediately with alkyne; otherwise, the yield of carborane is reduced by reaction with base to generate polymer. All reactions examined generated solid polymer, and in some cases hydroboration of the alkyne occurred to a slight extent to give 2-(*sec*-C_4H_9)B_5H_8. Carborane yields were improved by addition of the amine and alkyne in

increments over a period of time (see Experimental Section).

In the following sections we present the conditions under which optimum production of each carborane was achieved; additional experiments are described in the Experimental Section.
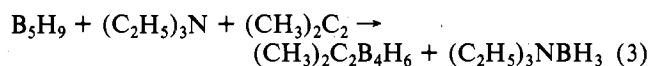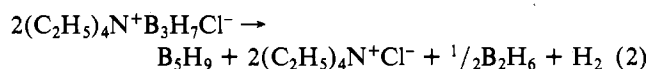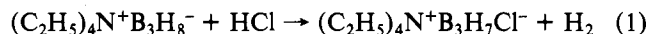
2,3-$(CH_3)_2C_2B_4H_6$. The most satisfactory preparation of the dimethyl carborane involved the reaction of 50 mmol of B_5H_9 with 2-butyne and triethylamine at 0 °C, with slow addition of the latter two reagents over a period of several days; this afforded 2.12 g of the carborane (20.4 mmol, 52% based on amine employed) with consumption of 45 mmol of B_5H_9. Larger quantities of carborane (but lower percentage yields) were obtained by more rapid addition of the amine and alkyne; when all reagents were added simultaneously, 14.0 mmol (28%) of 2,3-$(CH_3)_2C_2B_4H_6$ was isolated in a single run.

When dimethyl sulfide was employed in place of triethylamine, the *yield* of carborane rose to 61%, but the reaction was extremely slow and generated only 3.7 mmol of carborane in 8 days at room temperature; two-thirds of the original pentaborane was recovered under these conditions.

2-C_6H_5-$C_2B_4H_7$. Slow incremental addition of triethylamine to a mixture of phenylacetylene and pentaborane produced 14.1 mmol (47% based on amine) of the phenylcarborane, while 31 mmol of B_5H_9 was consumed. The optimum conditions appear to be very similar to those found for the production of the dimethyl carborane, described above. It is notable that this compound is *not* formed in appreciable yield in the gas-phase reaction of B_5H_9 with $C_6H_5C_2H$.

2-CH_3-$C_2B_4H_7$ and $C_2B_4H_8$. Attempts to prepare the *C*-monomethyl derivative and the parent carborane by the foregoing procedure were complicated by the rapid polymerization of propyne–B_5H_9 and acetylene–B_5H_9 mixtures in the presence of Lewis base. Yields of the monomethyl carborane were low under all conditions examined, amounting at best to 8% (1.2 mmol) with triethylamine and 14% (1.8 mmol) with dimethyl sulfide. Acetylene–B_5H_9 reactions conducted in the presence of either base gave no detectable $C_2B_4H_8$ (or other carborane) at all. Since the parent and monomethyl compounds are of lesser interest than are the *C,C'*-dimethyl and *C*-phenyl carboranes as precursors to metallocarboranes (owing to their lower stability), we did not further pursue their preparation by this method. For these compounds, the previously described[5a] gas-phase alkyne–pentaborane reaction continues to be the best available route.

Synthesis of 2,3-$(CH_3)_2C_2B_4H_6$ from $(C_2H_5)_4N^+B_3H_8^-$. Although several polyborane anions of the $B_nH_n^{2-}$ series ($n = 6–12$) can be prepared directly from salts of BH_4^-,[10] there are no reported syntheses of carboranes from BH_4^- or other small borane anions. In considering possible strategies for obtaining lower carboranes from BH_4^- salts, we noted that there are now efficient procedures for the conversion[3] of BH_4^- to $B_3H_8^-$ and $B_3H_8^-$ to B_5H_9.[11] It appeared feasible, therefore, to generate B_5H_9 in situ from $B_3H_8^-$ ion and then to combine the B_5H_9 with alkyne in situ in the presence of Lewis bases (vide supra) to produce $C_2B_4H_8$ derivatives. Accordingly, processes 1–3 have been utilized to generate carborane.

$$(C_2H_5)_4N^+B_3H_8^- + HCl \rightarrow (C_2H_5)_4N^+B_3H_7Cl^- + H_2 \quad (1)$$

$$2(C_2H_5)_4N^+B_3H_7Cl^- \rightarrow$$
$$B_5H_9 + 2(C_2H_5)_4N^+Cl^- + {}^1/_2B_2H_6 + H_2 \quad (2)$$

$$B_5H_9 + (C_2H_5)_3N + (CH_3)_2C_2 \rightarrow$$
$$(CH_3)_2C_2B_4H_6 + (C_2H_5)_3NBH_3 \quad (3)$$

Steps 1 and 2 are adapted from procedures reported previously,[11] while eq 3 is described above; all three reactions are conducted in the same vessel. The procedure was carried out several times on a progressively larger scale. In the largest synthesis, 25 g of $(C_2H_5)_4N^+B_3H_8^-$ was employed to produce

1.41 g (13.6 mmol) of pure $2,3\text{-}(CH_3)_2C_2B_4H_6$, which corresponds to 20% of the theoretical yield based on triethylamine employed, or about 19% on the basis of $(C_2H_5)_4N^+B_3H_8^-$ utilized.

Experimental Section

Materials. Pentaborane(9) was taken from laboratory stock and was checked for purity (IR spectrum and vapor pressure) before each use. 2-Butyne (Chemicals Procurement Laboratories, Inc., College Point, N.Y.) was passed through traps at −23 and −78 °C before use. Phenylacetylene (Aldrich) was passed through a 0 °C trap prior to use, and propyne and acetylene (Matheson) were used as received. Triethylamine (Matheson Coleman and Bell) was dried over molecular sieve, distilled onto barium oxide, redistilled, and finally passed through a −23 °C trap in vacuo. Sodium borohydride (98%) was obtained from Metal Hydrides, Inc., and used as received.

Procedures. Except when otherwise indicated, all operations were conducted in vacuo.

$2,3\text{-}(CH_3)_2C_2B_4H_6$ **from** B_5H_9, $C_2(CH_3)_2$, **and** $(C_2H_5)_3N$. Carborane yields in this synthesis are highly dependent on reaction conditions, particularly the ratio of reactants, order of addition, rate of addition, and temperature control. The formation of carboranes is favored by (1) maintenance of an excess of B_5H_9 over amine (to minimize attack of amine on the carborane product) and (2) addition of amine and alkyne simultaneously, so as to promote immediate reaction of the B_5H_9–amine adduct with alkyne and thereby reduce hydroboration. The hydroboration of 2-butyne to give 2-*sec*-butylpentaborane(9)[12] under these conditions occurs to only a very slight extent (<1%). The highest yield of carborane was obtained as follows. Pentaborane (50.0 mmol) was condensed into a 500 mL greaseless Pyrex reactor containing a magnetic stirring bar. Freshly distilled triethylamine (5.0 mmol) and 2-butyne (15.0 mmol) were added at −196 °C and the flask was warmed to 0 °C and stirred at that temperature for 24 h. After cooling of the mixture to −196 °C, accumulated noncondensable gas (0.08 mmol) was pumped out. Additional portions of $(C_2H_5)_3N$ (5.0 mmol each) and $C_2(CH_3)_2$ (15.0 mmol each) were added to the reactor at 24-h intervals, and the above procedure was repeated each time, until a total of 40.0 mmol of $(C_2H_5)_3N$ and 120.0 mmol of $C_2(CH_3)_2$ had been added over an 8-day period. Following this the volatiles were fractionated through traps at −30, −64, −95, and −196 °C, and the brownish red nonvolatile polymer was discarded. The trap at −30 °C contained mainly $(C_2H_5)_3NBH_3$ and a trace of 2-*sec*-C_4H_9-B_5H_8, identified from their ¹H NMR, IR, and mass spectra.[12] The −64 °C trap contained pure $2,3\text{-}(CH_3)_2C_2B_4H_6$ (2.12 g, 20.4 mmol, 52% yield based on $(C_2H_5)_3N$ employed), identified from its IR and mass spectra.[6,12b,13] The −95 and −196 °C traps contained, respectively, unreacted pentaborane (5.20 mmol) and 2-butyne (12.5 mmol).

In a somewhat different procedure, a mixture of 2-butyne (150.0 mmol) and pentaborane (60.0 mmol) was placed in vacuo into a 500 mL reactor and 10-mmol increments of triethylamine were introduced at −196 °C at 2-h intervals, with stirring of the mixture at 0 °C after each addition. Noncondensable gas was discarded each time. After a total of 50 mmol of triethylamine had been added, the mixture was stirred at 0 °C for 6 h and finally at room temperature for 2 days. Fractionation of the volatiles gave 2-*sec*-C_4H_9-B_5H_8 (1.20 mmol) and $(C_2H_5)_3NBH_3$ (2.40 g, 20.0 mmol), which condensed in a −30 °C trap but were separated by fractionation at −23 °C, which allowed only the C_4H_9-B_5H_8 to pass, $2,3\text{-}(CH_3)_2C_2B_4H_6$ (1.75 g, 16.8 mmol, 34% yield based on $(C_2H_5)_3N$ consumed), and unreacted B_5H_9 (7.30 mmol) and 2-butyne (15.0 mmol). In comparison to the first synthesis described above, this procedure gave a lower yield of carborane, but in less time (~3 days vs. 8 days). Hydroboration of the alkyne to produce C_4H_9-B_5H_8 occurred to a significant extent in the second experiment.

In still another procedure, all of the reactants (60.0 mmol of B_5H_9, 150.0 mmol of $C_2(CH_3)_2$, and 50.0 mmol of $(C_2H_5)_3N$) were condensed together and stirred for 6 h at 0 °C followed by 2 days at room temperature. This gave 1.46 g (14.0 mmol) of $2,3\text{-}(CH_3)_2C_2B_4H_6$ (28% yield based on amine consumed), with recovery of 4.0 mmol of B_5H_9 and 12.0 mmol of $C_2(CH_3)_2$. Finally, when a large *excess* of triethylamine was employed, the separation of carborane product from unreacted amine was difficult and the yield of carborane fell to below 20%, evidently due to reaction of the amine with carborane. We note also that a mixture of B_5H_9, $C_2(CH_3)_2$, and $(C_2H_5)_3N$ did not react noticeably at −23 °C.

$2,3\text{-}(CH_3)_2C_2B_4H_6$ **from** B_5H_9, $C_2(CH_3)_2$, **and** $(CH_3)_2S$. A mixture of 20.0 mmol of B_5H_9, 63.0 mmol of $C_2(CH_3)_2$, and 40.0 mmol of $(CH_3)_2S$ was stirred for 8 days at room temperature in a 500 mL greaseless flask. The mixture became yellow after 4 h and remained that color for the remainder of the 8-day period. No hydrogen was evolved. Fractionation of the volatiles through −23, −64, −78, −95, and −196 °C traps gave $(CH_3)_2S\cdot BH_3$ (identified from its IR and mass spectra) (collected at −23 °C), $(CH_3)_2S$ (16.6 mmol, condensed at −95 °C), $C_2(CH_3)_2$ (20.0 mmol, condensed at −196 °C), B_5H_9 (13.90 mmol, condensed at −78 °C), and $2,3\text{-}(CH_3)_2C_2B_4H_6$ (0.38 g, 3.70 mmol, 61% yield based on B_5H_9 consumed, condensed at −64 °C). The yellow polymer was not investigated. This method gave the highest carborane yield but the rate of reaction was inconveniently slow.

$2\text{-}C_6H_5\text{-}C_2B_4H_7$ **from** B_5H_9, $C_6H_5C_2H$, **and** $(C_2H_5)_3N$. Triethylamine (30.0 mmol total) was added in 5.0-mmol portions to a mixture of phenylacetylene (7.20 g, 60.0 mmol) and pentaborane (35.1 mmol) at −196 °C, with stirring for 2 h at 0 °C and for 2 h at room temperature after each addition. On completion of the triethylamine addition, the mixture was stirred at room temperature for 2 days, after which the volatiles were fractionated through traps at 0, −23, and −196 °C. The reddish brown polymer was discarded. The contents of the 0 °C trap were redistilled through 0 °C traps several times in order to remove the last traces of triethylamine–borane, $(C_2H_5)_3N\cdot BH_3$; the final 0 °C fraction contained pure $2\text{-}C_6H_5\text{-}2,3\text{-}C_2B_4H_7$ (2.15 g, 14.14 mmol, 47% yield based on amine consumed), identified from its, IR, ¹H NMR, and mass spectra.[5a] The −23 °C trap contained unreacted $C_6H_5C_2H$ (0.90 g, 8.82 mmol) and $(C_2H_5)_3N\cdot BH_3$ (not measured), which were separated by rapid passage through a 0 °C trap which retained the latter compound. Unreacted B_5H_9 (3.92 mmol) was collected in the −196 °C trap.

$2\text{-}CH_3\text{-}C_2B_4H_7$ **from** B_5H_9, CH_3C_2H, **and** $(C_2H_5)_3N$. Triethylamine (15.0 mmol total) was added in 3.0-mmol increments at −196 °C to a mixture of propyne (60.0 mmol) and pentaborane (20.0 mmol). After each addition, the reaction mixture was stirred for 4 h at 0 °C and for 2 h at room temperature. Following completion of the amine addition, the reaction mixture was stirred at room temperature for 2 days. The red-brown polymer was discarded and the volatiles were fractionated through traps at −30, −64, −95, and −196 °C. The −30 °C condensate was $(C_2H_5)_3N\cdot BH_3$, not measured. $2\text{-}CH_3\text{-}2,3\text{-}C_2B_4H_7$ (0.11 g, 1.2 mmol, 8% yield based on $(C_2H_5)_3N$ consumed) collected at −64 °C, unreacted B_5H_9 (4.50 mmol) was retained at −95 °C and unreacted propyne (20.4 mmol) collected in the −196 °C trap.

$2\text{-}CH_3\text{-}C_2B_4H_7$ **from** B_5H_9, CH_3C_2H, **and** $(CH_3)_2S$. A mixture of pentaborane (20.0 mmol), dimethyl sulfide (39.0 mmol), and propyne (60.0 mmol) was stirred for 7 days at room temperature. Fractionation as described in the foregoing experiments gave $2\text{-}CH_3\text{-}2,3\text{-}C_2B_4H_7$ (0.16 g, 1.80 mmol, 14% yield based on pentaborane consumed), with recovery of B_5H_9 (7.0 mmol), $(CH_3)_3S$ (10.0 mmol), and propyne (10.5 mmol).

Attempted Preparation of $2,3\text{-}C_2B_4H_8$. A mixture of pentaborane (20.0 mmol), acetylene (60.0 mmol), and triethylamine (20.0 mmol), was stirred at 0 °C for 6 h and at room temperature for 2 days. At the end of this period, 50 mmol of acetylene and an unmeasured quantity of $(C_2H_5)_3N\cdot BH_3$ were recovered but no $C_2B_4H_8$, $(C_2H_5)_3N$, or B_5H_9 were found.

A mixture of pentaborane (20 mmol), acetylene (60 mmol), and dimethyl sulfide (20 mmol) was stirred for 7 days at room temperature yielding only unreacted acetylene (48 mmol), dimethyl sulfide (13 mmol), and pentaborane (15 mmol); no carborane was obtained. Even after the above mixture was stirred at 100 °C for 14 days, no $C_2B_4H_8$ could be detected.

$2,3\text{-}(CH_3)_2C_2B_4H_6$ **from** $(C_2H_5)_4N^+B_3H_8^-$. Tetraethylammonium octahydrotriborate, $(C_2H_5)_4N^+B_3H_8^-$ (25.01 g, 146.3 mmol, prepared by the method of Nainan and Ryschkewitsch[3]), was placed in a 1-L greasless Pyrex flask and evacuated overnight. A 100-mL sample of dry CH_2Cl_2 followed by 20 mmol of anhydrous HCl was condensed into the reactor at −196 °C, and the mixture was stirred at room temperature. Evolution of H_2 began just below room temperature and continued for 30 min, after which the mixture was again frozen in liquid nitrogen and the H_2 (20.0 mmol) was pumped out. Additional 20-mmol portions of HCl were added, with the same procedure followed each time, until a total of 150 mmol had been added. The total of H_2 evolved was 152 mmol. The volatiles were distilled out of the flask, leaving behind a pale yellow residue which was heated in vacuo to 90–100 °C in an oil bath, during which the evolution of H_2 was continuously monitored via a manometer of the vacuum line. A total

of 78 mmol of H_2 was accumulated, and this was pumped out through a series of traps at −196 °C. The condensable material in the −196 °C traps was recondensed in the reactor, and 2-butyne (180 mmol) and triethylamine (67 mmol) were added in 15-mmol and 5-mmol increments, respectively, over a 6-day period with intervals of ∼12 h between successive additions, during which the mixture was stirred at 0 °C. After all reagents had been introduced, the mixture was maintained at 0 °C for 1 day, after which the volatiles were fractionated as in the B_5H_9–$(C_2H_5)_3N$–$C_2(CH_3)_2$ reaction described above, to give 1.41 g (13.6 mmol, 20.3% yield based on amine employed) of 2,3-$(CH_3)_2$-2,3-$C_2B_4H_6$. This material had exceptionally high purity as shown by gas phase IR analysis and was easily separated from all other materials by fractionation through traps at −30 °C (which retained $(C_2H_5)_3N$·BH_3 and a trace of 3,4-dimethyl-2-hexene, C_8H_{16}), −63 °C (which retained the carborane), and −196 °C (in which unreacted 2-butyne was collected).

As in several of the carborane syntheses described above, the time required for this procedure can be reduced significantly, at the cost of some reduction in yield. Thus, addition of the amine and alkyne in a single step (rather than incremental) followed by stirring for 3 days at room temperature gave a 16.2% yield of the carborane.

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Registry No. 2,3-$(CH_3)_2C_2B_4H_6$, 20741-68-8; 2-C_6H_5-2,3-$C_2B_4H_7$, 12080-12-5; 2-CH_3-2,3-$C_2B_4H_7$, 34228-46-1; 2-sec-C_4H_9-B_5H_8, 71672-52-1; $(C_2H_5)_3N$·BH_3, 1722-26-5; $(CH_3)_2S$·BH_3, 13292-87-0; B_5H_9, 19624-22-7; $(C_2H_5)_4N^+B_3H_8^-$, 12555-74-7; $C_2(CH_3)_2$, 503-17-3; C_6H_5-C_2H, 536-74-3; CH_3C_2H, 74-99-7; $(C_2H_5)_3N$, 121-44-8; $(CH_3)_2S$, 75-18-3.

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B-Halogenation of Ammonia–Borane: A Nuclear Magnetic Resonance Study

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Ammonia–borane and BX_3 (X = F, Cl, Br) were combined at low temperature in molar ratios from 3:1 to 1:2 with ether solvents. After warming and stirring of the mixtures at 25 °C for 18 h, NMR samples were taken of each reaction mixture. The [11]B spectra of products from the H_3N·BH_3–BCl_3 reactions gave evidence for the new compounds H_3N·BH_2Cl and H_3N·$BHCl_2$ along with H_3N·BCl_3, $(C_2H_5)_2O$·BH_2Cl, and $(C_2H_5)O$·$BHCl_2$. In the case of the BBr_3 reactions, products identified from their spectra include H_3N·BH_2Br, $(C_2H_5)_2O$·BH_2Br, and $(C_2H_5)_2O$·$BHBr_2$ along with ether cleavage products. A hydrogen–halogen exchange mechanism appeared to account satisfactorily for the products of the BCl_3 and BBr_3 reactions. The only major products from the H_3N·BH_3–BF_3 reactions were H_3N·BF_3 and $(\mu$-$H_2N)B_2H_5$. An acid displacement followed by a hydrogen elimination mechanism is proposed for the BF_3 reaction.

Introduction

Although the compound has been known for some 20 years,[1,2] the chemistry of ammonia–borane is relatively undeveloped. Most of the known B-substituted derivatives of ammonia–borane are not prepared from the parent compound but rather by direct combination of ammonia with an appropriate borane. Probably the best characterized example is H_3N·BHF_2, prepared from ammonia and difluoroborane.[3] On the basis of very early reports,[4,5] it is believed[6] that ammonia–B-chloroboranes are unstable with respect to ammonolysis of the boron–halogen bond. There is one report of H_3N·BH_2Cl as a decomposition product of $H_2B(NH_3)_2^+Cl^-$, but the adduct was not fully characterized.[7] In general, little is known about ammonia–B-haloboranes, their properties, or their stabilities.

The present investigation was undertaken to determine whether evidence could be obtained on the existence of B-halogenated ammonia–borane compounds. We wish to present such evidence obtained from a ^{11}B NMR investigation of the reaction of H_3N·BH_3 with BF_3, BCl_3, and BBr_3.

Experimental Section

Ammonia–borane was prepared by methods described elsewhere.[8] Anhydrous BF_3 (Matheson) was used as obtained. Trichloroborane was purified by the method of Brown and Holmes[9] and stored in a glass vessel with a Teflon stopcock and O-ring joint. Tribromoborane was purified by distilling it from copper wool and storing in a glass vessel fitted with a Teflon stopcock and an O-ring joint, all covered with aluminum foil. Trifluoroborane ethyl etherate (Eastman) was used as obtained. Solvents, ethyl ether, tetrahydrofuran, and glyme (1,2-dimethoxyethane), were stirred, first with CaH_2 and then with $LiAlH_4$, and vapor transferred to glass storage vessels fitted with Teflon stopcocks and O-ring joints. Sodium tetrahydroborate was obtained with Callery Chemical Co. and used without purification.

Reactions were carried out by using a standard vacuum system[10] and NMR sample tubes were filled within a nitrogen-filled glovebox.[10] ^{11}B NMR spectra were obtained in the FT mode by using a Varian XL-100-15 spectrometer at 32.1 MHz with a Nicholet 1080 data system and a Nicholet MONA, wide band probe which could accommodate 12- or 18-mm sample tubes. Samples were held in 12-mm tubes fitted with a 5-mm coaxial tube containing $CDCl_3$ for locking purposes. Chemical shifts (δ) are given downfield from external $(C_2H_5)_2O$·BF_3.

In a typical reaction, 3 mmol of H_3N·BH_3 was placed in a 50-mL flask which was then attached to the vacuum line via a Teflon valve and a 9-mm O-ring joint. After evacuation, 30 mL of dry $(C_2H_5)_2O$ and the desired quantity of trihaloborane were condensed into the flask at −196 °C. The Teflon valve was then closed and the reaction mixture was stirred as it warmed to room temperature and was stirred for 18 h thereafter. The reaction vessel was then briefly opened to a vacuum line trap at −196 °C containing THF in order to flash away