viewed the structures and bonding in these and related carboranes containing group 13 and 14 heteroatoms.[41]

The X-ray results for *nido*-3,4-$Et_2C_2B_5H_6^-$, which confirm that the cage carbons remain adjacent, in conjunction with the mild reaction conditions leading to the formation of the anion support a cage-opening process involving no major rearrangement of the *closo*-2,3-$Et_2C_2B_5H_5$ skeletal framework. Such a process resulting in the formation of the five-membered open face requires that hydride add exclusively at one of the apical (B1,7) positions and be accompanied by the opening of a triangular C-B-C face. These conclusions are also consistent with calculations[3a-d] of the ground-state charges in *closo*-2,3-$C_2B_5H_7$ which indicate that the apical borons are the only positively charged borons in the molecule and would, therefore, be the sites of nucleophilic attack.

A similar cage opening can be effected with a strong nucleophile such as Me_3P. Thus, as shown in eq 12, reaction of *closo*-2,3-$Et_2C_2B_5H_5$ with Me_3P results in cage opening and production of

excess Me_3P + *closo*-2,3-$Et_2C_2B_5H_5$ → *nido*-6-Me_3P-3,4-$Et_2C_2B_5H_5$ (12)
IX

the *neutral* seven-vertex species *nido*-6-Me_3P-3,4-$Et_2C_2B_5H_5$ (IX). The 64.2-MHz ^{11}B NMR spectrum (Figure 3d) of IX is similar to that of VIII, consisting of four doublets in a 1:1:2:1 area ratio. Upon ^1H decoupling (Figure 3c), the resonance at 0.0 ppm shows ^{31}P coupling (J_{BP} = 43 Hz), consistent with previous measurements of ^{31}P-^{11}B coupling in phosphine-borane adducts.[42] The ^{11}B-^{11}B two-dimensional NMR spectrum of IX exhibits all cross-peaks expected for the proposed seven-vertex nido geometry shown in Figure 5. The ^1H NMR spectrum in excess Me_3P shows, in addition to the equivalent cage ethyl resonances, a doublet at 0.79 ppm (J_{PH} = 2.9 Hz) for free Me_3P and an additional doublet at 0.46 ppm (J_{PH} = 11.2 Hz) for cage-bound Me_3P. As indicated in the Experimental Section, attempts to isolate IX as a discreet species resulted in loss of the Me_3P ligand and reversion to I, suggesting that a base-mediated closo-nido equilibrium exists. Additionally, I could not be completely converted to IX even in the presence of a large excess of Me_3P. Several other nucleophilic reagents were examined for their ability to effect cage-opening of the *closo*-2,3-$Et_2C_2B_5H_5$ framework. Amine bases such as Me_3N or C_5H_5N caused extensive cage degradation as evidenced by the appearance of an amine-borane resonance in the ^{11}B NMR spectrum of product mixtures.

In summary, we have reported new, viable synthetic routes to the *closo*-2,3-$R_2C_2B_5H_5$ cage system based on cluster expansion reactions of *nido*-2,3-$Et_2C_2B_4H_6$ utilizing Lewis base-borane adducts. These routes have allowed the production of *closo*-2,3-$Et_2C_2B_5H_5$ in sufficient quantities to begin an examination of its chemistry. In view of the unusual susceptibility of this closo system to attack by polar reagents, a wide range of further cage-opening and cage-expansion chemistry should be possible. We are currently exploring these possibilities as well as examining the extension of cluster growth reactions employing Lewis acid-base adducts to a variety of borane, carborane, and heteroatom systems.

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Synthesis and Characterization of Amine-Alkylcyanoboranes

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Synthetic methods for the conversion of alkyltrihydroborates to amine-alkylcyanoboranes have been developed. The most efficient of these is cyanation of the alkyltrihydroborates with mercuric cyanide to give the corresponding alkylcyanodihydroborates. These stable salts, when treated with 1 equiv of HCl in diethyl ether, followed by addition of an amine, produce the amine-alkylcyanoboranes (amine = Me_3N, py, TMED, quinuclidine; alkyl = methyl, benzyl, *sec*-butyl, isobutyl) in moderate yield. The new amine-alkylcyanoboranes are thermally, oxidatively, and hydrolytically stable and can be purified by using standard chromatographic methods.

Introduction

Amine-cyanoboranes (**1**, Figure 1) are useful precursors to boron-centered amino acid analogues (**2**). Many of these analogues have been prepared in the last decade.[1] Uppal and Kelly reported the first amine-cyanoboranes in 1970 with the synthesis of the trimethylamine, *p*-methylpyridine, morpholine, and TMED adducts of "BH_2CN".[2] They treated $NaBH_3CN$ with acidified THF to produce "THF·BH_2CN" and then added the desired amine to displace solvent. In 1978, Spielvogel combined their syntheses with the Schaefer and Anderson method for making amine-boranes[3] to produce the cyanoboranes **1** (amine = Me_3N, Me_2NH, $MeNH_2$, NH_3) in a single, high-yield step (eq 1).[4] Another

$$\text{amine·HCl} + NaBH_3CN \rightarrow \mathbf{1} + NaCl + H_2 \quad (1)$$

$$Me_3N{\cdot}BH_2I + NaCN \rightarrow Me_3N{\cdot}BH_2CN + NaI \quad (2)$$

$$Na[BH_3CN] \xrightarrow{I_2} [BH_2CH]_n \xrightarrow{\text{amine}} \text{amine·}BH_2CN + NaI \quad (3)$$

method was published in 1974 by Bratt, in which cyanide was introduced by the displacement of iodide (eq 2).[5] Martin et al.

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$A{\cdot}BH_2{-}CN$ (1) $A{\cdot}BH_2{-}C(O)Y$ (2)

$A{\cdot}BH(R){-}C(O)Y$ (3) $A{\cdot}BH(R){-}CN$ (4)

Figure 1. Compounds discussed: A = alkyl- and arylamines, pyridine, NH_3; Y = –OH, –OR, –NHR.

used Cl_2, Br_2, or I_2, in a third approach, to oxidize the cyanohydroborate followed by trapping of the intermediate oligomer, $[BH_2CN]_n$, with amines (eq 3).[6] Of the derivatives of **2** reported to date, the α-boron atom is substituted only by hydrogen, making them analogues of glycine ($H_2N{-}CH_2{-}COOH$). The preparation of analogues (**3**) of other amino acids, e.g. those with nonpolar side chains, requires a mono-B-alkylated amine–cyanoborane (**4**). There is presently only a single report of an alkylated derivative, $Me_2NH{\cdot}B(^iPr)_2CN$.[11] In this report, we describe the preparation of these previously unknown monoalkylated compounds (**4**).

Experimental Section

General Data. Unless otherwise noted, all reactions were performed under an atmosphere of N_2 by using methods described by Brown[7] and Shriver.[8] Where noted, reaction solvents were dried prior to use by distillation under N_2 from sodium and benzophenone (benzene, toluene, THF, pentane, cyclohexane) or $P_2O_5(CH_2Cl_2)$.[9] Diethyl ether was used as purchased from Mallinckrodt and stored under dry N_2. Chromatographic separations were conducted by using HPLC grade solvents. Alumina (Woehlm basic or neutral, Activity I or Fisher Brockman Activity I, 80-200 mesh) and silica gel (Fisher 100–200 mesh) were used for standard gravity chromatography. Flash chromatography was performed according to the method of Still[10] by using 230-400 mesh silica gel (Aldrich 60 Å or Merck grade 60).

Methyllithium, *sec*-butyllithium, and *n*-butyllithium were purchased as solutions from Aldrich and were standardized according to a published method.[11] Lithium aluminum hydride was purchased from Aldrich as a 1.0 M solution in diethyl ether and used as received. Hydrogen chloride solutions were prepared by using dry ether and gaseous HCl generated by means of a Brown hydrogenator.[12] Quinuclidine was purchased from Aldrich and sublimed under a static vacuum (ca. 20 Torr) with gentle heating and stored under N_2. Amine hydrochlorides were recrystallized (chloroform/ethyl acetate) and dried in a vacuum desiccator containing $CaSO_4$.

Proton NMR spectra were recorded in deuterated solvents on Bruker AM-500 (500.1 MHz) or Nicolet NT-360 (361.1 MHz) spectrometers locked to the solvent deuterium signal. Chemical shifts were established by internal reference to the residual protons in each solvent and are reported in δ, parts per million (ppm) downfield from tetramethylsilane: acetone-d_6, δ 2.08; acetonitrile-d_3, δ 1.93; chloroform-d, δ 7.24; dichloromethane-d_2, δ 5.32. Coupling constants (J) for ^1H spectra refer to H–H coupling unless otherwise noted. When not indicated, B–*H* resonances were not detected due to their low intensity, broad shape, and multiplicity ($I_{^{11}B} = {}^3/_2$). Boron-11 NMR spectra were recorded at 115.8 MHz on the Nicolet spectrometer in the solvents indicated. Chemical shifts are reported relative to $Et_2O{\cdot}BF_3$ used as an external standard. Downfield shift values are positive. Coupling constants indicate $^1H{-}^{11}B$ interactions unless otherwise noted. Carbon-13 NMR spectra were obtained in deuterated solvents by using Bruker (125.76 MHz), Nicolet (90.8 MHz) or Varian XL-300 (75.4 MHz) spectrometers. Chemical shifts are reported in ppm downfield of Me_4Si as established by comparison to the solvent chemical shifts: acetone-d_6, 206.0, 29.8; acetonitrile-d_3, 118.2, 1.3; chloroform-d, 77.0; dichloromethane-d_2, 53.8.

Infrared spectra were recorded in cm^{-1} on a Perkin-Elmer 283 spectrophotometer as neat oils or mineral oil mulls on sodium chloride plates or as KBr pellets. Intensities are reported in accordance with the literature.[13] Melting points were obtained by using a Meltemp device in sealed, evacuated capillaries and are uncorrected. Mass spectra were determined on a Kratos MS-80 instrument by using the technique indicated. Elemental analyses were performed by Galbraith Microanalytical Labs, Knoxville, TN.

Isobutyllithium. This reagent was synthesized by the method of Gilman et al.[14] for the preparation of isopropyllithium with minor variations. Instead of Li shot, lithium powder (1% Na, Aldrich) suspension in mineral oil was used.[15] The mineral oil was rinsed off with dry pentane or hexane, and the powder was dried under dynamic vacuum and weighed by difference. The ^{i}BuLi solution was filtered, standardized, and stored under N_2 in a freezer.

Alkyldiisopropoxyboranes. Methyldiisopropoxyborane (**9a**),[16] *sec*-butyldiisopropoxyborane (**9b**),[17] and isobutyldiisopropoxyborane (**9c**) were prepared in 60%, 80%, and 75% yields, respectively, from triisopropoxyborane and the appropriate alkyllithium reagent. ^{11}B NMR: **9a** (neat), δ 30.8; **9b** ($CDCl_3$), δ 30.7; **9c** (THF), δ 30.3.

Lithium Trihydromethylborate (5a). A modified method of Brown et al.[18] was used as follows: Ester **9a** (1.4 g, 9.7 mmol) was dissolved in 10 mL of dry pentane in a 40 mL centrifuge tube. One equivalent of lithium aluminum hydride (9.7 mL × 1.0 M) was added with stirring at 0 °C. A white precipitate of diisopropoxyalane formed immediately. After addition was complete, stirring was continued for 30 min. The tube was centrifuged and the supernatant liquid was removed by cannula. The residual alane was washed with fresh, dry pentane (2 × 20 mL). Evaporation of the combined solvent phases gave 1.4 g (theoretical 0.35 g) of a tacky, moisture-sensitive white solid, which was used without further purification.[19] The crude material could be purified as described in the following procedure for **5b**. ^1H NMR ($CDCl_3$, 361.1 MHz): δ 3.809 (second-order m, J = 6.5 Hz, $O[-CH_2-]_2$), 1.847 (second-order m, J = 3.3 Hz, $[-CH_2-]_2$), 0.073 (br 1:1:1:1 q of q, $^3J_{HH}$ = 5.06 Hz, $^1J_{^{11}B-^1H}$ = 73 Hz, $-BH_3$), -0.345 (br, m, $B-CH_3$).

Lithium *sec*-Butyltrihydroborate (5b). Lithium Aluminum Hydride Method. In a 1000-mL, three-neck, round-bottom flask, **9b** (35.1 g, 188.6 mmol) and dry pentane (400 mL) were combined. After the stirred solution was cooled to 0 °C, lithium aluminum hydride in ether (189 mL × 1 M) was added by cannula, drop-by-drop, to produce a milky mixture. After addition was complete (approximately 1 h), stirring was continued at 0 °C for 30 min. The mixture was briefly allowed to settle, and the cloudy supernatant liquid was decanted via a coarse-sintered-glass filter tube containing Celite filter aid. The residue was washed with fresh, dry ether (2 × 20 mL) and similarly filtered. The combined ethereal phases were reduced by rotary evaporator[20] to obtain a white, tacky semisolid. In most cases, this solid was used without further purification.

It was possible to isolate the crystalline produce in the following manner. The tacky semisolid was taken up in minimal THF and the solution was filtered via a coarse-sintered-glass frit, which was being warmed by the vapors of THF under reflux. The solvent was removed by rotary evaporator using a hot water bath to promote evaporation.[20] When only a thick paste remained, dry cyclohexane (5 mL) was added, the mixture was stirred (15 min), and the solvents were again evaporated until a cloudy, viscous mixture formed. The cyclohexane addition/evaporation cycle was repeated (6×) until distinct crystals of $Li(THF)_2{}^sBuBH_3$ began to form. The flask was allowed to cool to room temperature, and dry pentane (40 mL) was added. The flask was cooled to 0 °C and left to stand. The solvent was decanted from the white crystals of **5b**, which were then washed with fresh, dry pentane (3 × 10 mL) and dried under vacuum.

Me_2S Alkylation Method. A solution of ^{s}BuLi in cyclohexane (250 mL × 1.34 M) and dry pentane (50 mL) was cooled to −35 °C (solution temperature) by using an acetonitrile/dry ice bath (~−41 °C). Neat dimethyl sulfide–borane (33.5 mL × 10 M) was added very slowly, drop

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(19) Complete removal of the ethereal solvent was not possible. Additionally, a small amount of alane is soluble, as reported by Brown and co-workers.[18]
(20) The rotary evaporator was equipped with an inlet for dry N_2. After removal of solvent, the evacuated apparatus was filled with the inert atmosphere. All connections/disconnections were made under a brisk flow of N_2.

by drop, to the cold solution with rapid stirring. The rate of addition was carefully monitored so that the temperature of the thickening, milky reaction mixture remained at or below −30 °C. After addition was complete (1.5 h), the mixture was stirred as the temperature was allowed to rise to −20 °C with the cooling bath in place. The solvents were removed by vacuum transfer to a N_2(l) trap. During evaporation, the cooling bath was allowed to warm to room temperature. After 4 h, a slightly yellow, solid cake remained. ^{11}B NMR indicated it to be 98% **5b** (by integration), and the material was used without further purification.

Lithium Isobutyltrihydroborate (5c). This compound was prepared from ^{t}BuLi (93 mL × 1.5 M, 140 mmol) and $Me_2S{\cdot}BH_3$ (14 mL × 10 M) by using the Me_2S protocol described for **5b**. Again, temperature control is of utmost importance in order to control the very exothermic reaction. Relatively pure **5c** could be extracted from the crude solid with pentane. ^{11}B NMR indicated a mixture of BH_4^- and **5c** (84%): IR (NaCl): ν_{max} 2938 s, 2855 s, 2795 m, 2230 s, 1460 m cm^{-1}.

Lithium Benzyltrihydroborate–Tetramethylenediamine (5d). A typical large-scale preparation was performed as follows. TMED (tetramethylethylenediamine) (~63 mL, 47.7 g, 410.5 mmol) was dissolved in dry toluene (170 mL) in a flask equipped with a reflux condenser and an external bubbler. *n*-Butyllithium (171 mL × 2.4 M, 410.4 mmol) was added to the stirring amine solution via a cannula. The exothermic reaction solution was stirred at ambient temperature for 30 min. A deep red color developed. A solids-addition flask charged with $Me_3N{\cdot}BH_3$ (30.0 g, 411 mmol) was affixed to the reaction flask. The amine–borane was added to the reaction flask in one portion. The mixture was heated to reflux for 2 h, during which time the color deepened to brown. The mixture was allowed to cool under a brisk purge of N_2 for 15 min. The flask was well stoppered and placed in the freezer (−15 °C) overnight. The dark brown liquor was decanted via cannula, and the residual orange precipitate was washed with ice-cold, dry pentane (3 × 40 mL). The material was dried under vacuum to give 59.5 g of a yellow solid: ^{11}B NMR ($CHCl_3$): δ −2.8 (br t, $Me_3N{\cdot}BH_2$Bzl (**7a**), 20%), −27.5 (q, J = 76 Hz, **5d**, 70%), −40.7 (quintet, J = 81 Hz, (Li·TMED)BH_4, 10%). Pure **5d** was obtained by Soxhlet extraction using pentane to give 27.2 g (119 mmol, 29%) of a colorless, crystalline solid: ^{1}H NMR ($CDCl_3$, 361.1 MHz): δ 7.08 (s, Ph*H*), 7.07 (s, Ph*H*), 6.87 (quintet, J = 4.24 Hz, Ph*H*), 2.28 (s, N–CH_2–), 2.16 (s, N-CH_3), 1.82 (br m, B–CH_2–), 0.22 (1:1:1:1 q of t, J_{BH} = 76.5 Hz, J_{HH} = 5.2 Hz, –BH_3). Portions of the septet arising from the ^{10}B isomer ($I = {}^3/_2$) were also detected underlying the quartet at 0.22 ppm ($J_{^{10}BH}$ ~ 25 Hz).[21]

Lithium Alkyl-*B*-cyanodihydroborates. The cyanohydroborates were prepared by using the method of Emri and Györi for the cyanation of $NaBH_4$.[22] In general, these compounds were not isolated as pure materials. They were typically used in subsequent reactions as materials prepared in situ or as crude materials isolated by filtration and rotary evaporation of reaction solvents.

Lithium Cyanodihydromethylborate (6a). Unpurified **5a** (9.7 mmol) was dissolved in dry THF (5 mL) in a 50-mL, round-bottom flask equipped with a magnetic stir bar and a reflux condenser. A solution of mercury(II) cyanide (1.2 g, 4.9 mmol) in dry THF (15 mL) was added by cannula. The resulting dark gray mixture was heated to reflux until a clear, colorless solution was formed and elemental Hg precipitated (~2 h). The solution was decanted into a sintered-glass filter under N_2 and evaporated to yield approximately 1.0 g (theoretical 0.30 g)[23] of **6a** as a translucent, tacky solid.

Lithium Cyano-*sec*-butyldihydroborate (6b). Unpurified trihydroborate **5b** (11.7 mmol) in dry THF (25 mL) was treated with a solution of $Hg(CN)_2$ (1.47 g, 5.82 mmol) in dry THF (25 mL) as previously described. The solution warmed noticeably with evolution of gas. The reaction was stirred for 2 h at ambient temperature after addition was complete. A translucent, gelatinous solid was obtained (2.6 g, theoretical 0.60 g):[23] IR (NaCl): ν_{max} 2940 s, 2850 m, 2290 s, 2170 m, 1455 m cm^{-1}.

In a typical large-scale procedure, the crude borohydride (328 mmol) was dissolved in dry THF (150 mL). Mercuric cyanide (42 g, 167 mmol) was placed in a dry, solids-addition flask affixed to the reaction vessel. The mercury reagent was carefully added a few grams at a time. The vigorous, exothermic reaction was allowed to subside before further addition proceeded. After addition was completed, the warm mixture was allowed to cool to room temperature and stirred for 12 h. The resulting colorless solution was found to contain 96% **6b** by ^{11}B NMR analysis. The solution was decanted from the Hg residue and used without further manipulation.

Lithium Isobutylcyanodihydroborate (6c). Partially purified **5c** (140 mmol) in dry THF (330 mL) was treated with $Hg(CN)_2$ (21.4 g, 84.7 mmol) dissolved in dry THF (70 mL) as described for **6a**. A transparent, gelatinous solid was obtained containing mostly **6c**. IR (NaCl): ν_{max} 2942 s, 2860 s, 2800 m, 2270 s, 2183 m–s, 2102 w–m, 1462 s cm^{-1}.

Lithium Benzylcyanodihydroborate–Tetramethylenediamine (6d). Lithium benzyltrihydroborate (**5d**) (8.85 g, 38.8 mmol) in dry THF (15 mL) and $Hg(CN)_2$ (4.90 g, 19.4 mmol) in dry THF (40 mL) were combined as previously described. After the reaction was heated to reflux for 3.5 h, a thick paste was isolated.[23] IR (NaCl, mull): ν_{max} 3040 w, 2980 s, 2920 s, 2320 s, 2200 m, 1620 w, 1465 m, 1270 vs, 1100 vs, 1030 vs, 810 vs, 710 m cm^{-1}.

Quinuclidine–Benzylborane (7b). The benzylborohydride **5d** (0.66 g, 2.9 mmol) in dry ether (40 mL) was treated with $HCl{\cdot}Et_2O$ (1.35 mL × 2.15 M in ether, 2.9 mmol) at room temperature in a dropwise fashion. Gas evolution was monitored and vented through an external bubbler. After addition was complete, stirring was continued until gas evolution ceased (ca. 30 min). Freshly sublimed quinuclidine (1.0 g, 9.0 mmol) dissolved in ether was added to the reaction mixture, which then was heated to reflux for 60 h. The reaction solution was suction filtered in air and then evaporated. The solid residue was recrystallized from acetone/water to give 0.53 g (85%) of colorless, solid **7b**. ^{11}B NMR ($CDCl_3$): δ −3.55 (br t, J = 85 Hz). ^{1}H NMR ($CDCl_3$, 361.1 MHz): δ 7.146 and 7.133 (s, Ph*H*), 6.975 (m, J = 7.00 Hz, Ph*H*), 2.950 (second-order t, J = 7.98 Hz, N[CH_2–]$_3$), 1.971 (sep, J = 3.30 Hz, [–CH_2)$_3$C*H*), 1.848 (br t, J = 5.6 Hz, B–CH_2–), 1.702 (second-order m, [–CH_2]$_3$CH).

Quinuclidine–Benzyliodoborane (8b). Iodine (0.35 g, 1.4 mmol) in dry benzene (4.0 mL) was added to a benzene (6.0 mL) solution of **7b** (0.6 g, 2.8 mmol), drop by drop, over a period of 11 min. The dark yellow-to-brown solution was allowed to stir overnight and then was heated to 85 °C for 15 min. The color faded only slightly. The solution was filtered under N_2 and then evaporated under vacuum until well-defined crystals were noted. An equal volume of dry pentane was then added to the benzene solution, and a yellow-brown solid began to precipitate. The solid was isolated by decanting the solvent and was crystallized from toluene/pentane to give 2.1 g of a slightly yellow solid, which was comprised of 66 mol % of the iodoborane contaminated with boronic acid. ^{11}B NMR (toluene): δ 31.4 (s), −2.8 (br m). The material was used without further purification.

General Procedure for Preparation of Amine–Alkylcyanoboranes (4). $HCl{\cdot}Et_2O$ Protocol. In a typical experiment, the alkylcyanodihydroborates (**6**) were cooled to 0 °C in THF solution in a vessel equipped with an external bubbler to safely vent H_2. $HCl{\cdot}Et_2O$ (1.0–1.1 equiv) was added, drop by drop, via a cannula to the stirring borate solution. After addition was complete, the milky mixture was allowed to warm to room temperature and stirring was continued for 3–18 h until hydrogen evolution ceased. The mixture was filtered and the solvent was evaporated to give a tacky, amorphous white solid.

Amine Hydrochloride Protocol. To a THF solution of the cyanoborate was added the amine hydrochloride (1.5 equiv) under a brisk dinitrogen purge. The resulting mixture was heated to reflux for the time indicated. The mixture was filtered and evaporated to give the tacky crude solid.

Extractive Workup. The crude solid was stirred in $CHCl_3$ or diethyl ether and the resulting mixture was filtered, washed with water (3×) and brine (1×). The organic layer was dried ($MgSO_4$) and evaporated to give the amine–cyanoborane as an impure oil. The oil was purified as indicated below.

Trimethylamine–Methylcyanoborane (4a). Unpurified **6a** (30.0 mmol) and $Me_3N{\cdot}HCl$ (4.3 g, 45.0 mmol) were combined in dry THF (55 mL) according to the general procedure. After 24 h at reflux, the crude residue was extracted with ether (3 × 30 mL). The extracts were suction filtered through Celite. The solvent was evaporated to give approximately 4 g of an oily white solid. The solid was thoroughly washed with $CHCl_3$ and the combined, filtered washings were evaporated to give an oil (~2 g). Purification on basic alumina (300 g, Woehlm, $CHCl_3$) gave 1.6 g (14.3 mmol, 53%) of a solid (R_f 0.17, silica gel TLC, $CHCl_3$), mp 56–57 °C (recrystallized, $CHCl_3$/heptane). ^{1}H NMR ($CDCl_3$, 361.1 MHz): δ 2.956 (s, 9 H), 1.936 (1:1:1:1 quartet, J_{BH} = 103 Hz, 1 H), −0.114 (br s, 3 H). IR (neat): ν_{max} 2370 s, 2190 m, 2140 w, 1485 vs, 1470 vs, 1405 m, 1310 vs, 1250 s, 1130 vs, 1100 s, 1075 vs, 985 vs, 860 s, 835 s cm^{-1}. ^{13}C NMR ($CDCl_3$, 75.4 MHz): δ 134.5 (v br, –*C*N), 50.622 (N–*C*H_3), 0.083 (br, B–*C*H_3). HRMS (EI, 30 eV): *m/e* 110.1128 (M^+ – H, *m/e* calcd for $C_5H_{12}{}^{11}BN_2$ 110.1130).

Pyridine–Methylcyanoborane (4b). Dihydrocyanoborate **6a** (11.0 mmol) was combined with pyridine hydrochloride (1.40 g, 12.1 mmol) in dry THF (10 mL). Gas evolved immediately. After being stirred overnight at room temperature, the reaction mixture was dissolved in

(21) For one-bond coupling to boron it had been found that, generally, $J_{^{11}B-H} = 3J_{^{10}B-H}$. Kidd, R. G. In *NMR of Newly Accessible Nuclei*; Laszlo, P., Ed.; Academic Press: New York, 1983; Vol. 2, p 68.
(22) Emri, J.; Györi, B. *J. Chem. Soc., Chem. Commun.* **1983**, 1303.
(23) Complete removal of THF from the lithium salt was not possible, even when heat was applied under high vacuum.

water and the aqueous phase was washed with $CHCl_3$ (3 × 10 mL). The combined organic extracts were dried ($MgSO_4$) and evaporated. The resulting oil solidified when cooled with ice water. The solid was recrystallized from ether/hexane to give **4b** as a solid (0.9 g, 6.8 mmol, 62%), mp 36–40 °C. ^1H NMR (acetone-d_6, 361.1 MHz): δ 8.802 (d, J = 5.42 Hz, py α-H), 8.414 (tt, J = 2.89, 7.04 Hz, py γ-H), 7.978 (second-order t, J = 7.04 Hz, py β-H), 2.95 (br 1:1:1:1 q, $J_{^{11}BH}$ = ~100 Hz, -BH-), 0.124 (d, J = 6.14 Hz, B-CH_3). ^{13}C NMR (acetone-d_6, 125.8 MHz): δ 145.786 (py α-C), 141.382 (py γ-C), 135.6 (v br, -C≡N), 126.242 (py β-C), 4.935 (br, B-CH_3). IR (NaCl): ν_{max} 3105 w, 3060 w, 2390 s, 2185 m, 1620 s, 1300 s, 1100 br s, 770 m, 690 m cm^{-1}. MS (EI, 20 eV): m/e 132 (M^+, 1), 131 (8), 117 (29), 116 (9), 105 (5), 90 (4), 79 (100).

Pyridine–*sec*-Butylcyanoborane (4e). The crude cyanodihydroborate **6b** (21.5 g, 215 mmol) was stirred in dry ether (100 mL). The cloudy mixture was filtered under dry N_2 to give a colorless solution, which was added (1 h) to an ethereal suspension (100 mL) of dry py·HCl (31 g, 268 mmol). Hydrogen evolution occurred readily, and precaution was taken to vent it safely. The reaction mixture was stirred at room temperature for 18 h. The ether solution was filtered, the residue was washed with fresh ether, and the combined solvent portions were evaporated to give a yellow oil. Chloroform (50 mL) was added, and the resulting solution was washed with water (3 × 20 mL) and brine (3 × 20 mL). After drying ($CaCl_2$), the organic solvent was removed by rotary evaporator to recover the yellow oil. Purification on neutral alumina (Woehlm, 150:1 w/w, 32 mm diameter column, $CHCl_3$) gave the product as a slightly yellow oil (R_f 0.13, silica gel TLC, $CHCl_3$), bp > 200 °C dec. ^1H NMR (CD_2Cl_2, 361.1 MHz): δ 8.570 (d, J = 5.26 Hz, py α-H), 8.173 (dt, J = 1.6, 7.7 Hz, py γ-H), 7.742 (t, J = 7.0 Hz, py β-H), 1.310 and 1.176 and 0.943 (br multiplets, J = 5.4, 6.4, and 7.6 Hz, respectively, diastereotopic B-CHCH_2-), 0.85–0.45 (complex second-order pattern, B-CH[CH_3]CH$_2$CH_3). ^{13}C NMR (CD_2Cl_2, 75.4 MHz): δ 146.25, 141.98, and 126.56 (py C), 134.5 (br, -CN), 27.70 and 27.27 (diastereotopic B-CH(CH$_3$)CH_2-), 27.3 (br, B-CH-), 16.64 and 16.56 (diastereomeric B-CH-CH_3), 13.08 (B-CHCH$_2$CH_3). IR (neat, NaCl): ν_{max} 3100 w, 3060 w, 2950 s, 2860 s, 2390 m, 2190 w, 1620 m-s, 1490 m, 1460 vs, 1120 s, 1095 s, 770 s, 690 s cm^{-1}. HRMS (+CI, NH_3): m/e 172.1305 (M^+ - H, m/e calcd for $C_{10}H_{14}{}^{10}BN_2$ 172.1286).

Tetramethylenediamine–Bis(*sec*-butylcyanoborane) (4f). Unpurified **6b** (40 mmol) in dry THF (5 mL) was treated with HCl·OEt$_2$ (14.5 mL × 2.8 M, 40.2 mmol) according to the general procedure. TMED (20 mmol, 20.2 mL) was added, and stirring was continued for 2 h. Solvent was evaporated. The solid residue was dissolved in hot CH_2Cl_2, and the resulting solution was filtered in air. After the solution cooled to room temperature, pentane was added and the solution was cooled to 0 °C. The white, crystalline product was collected by suction filtration in air; mp 129.5–131 °C. ^1H NMR ($CDCl_3$, 361.1 MHz): δ 3.40 (m, N-CH_2, 4 H), 2.76 (s, N-CH_3, 3 H), 2.75 (s, N-CH_3, 3 H), 2.71 (s, N-CH_3, 3 H), 2.69 (s, N-CH_3, 3 H), 1.34 (m, J = 6.98 Hz, B-CH), 1.22 (m, J = 7.09 Hz, B-CH), 1.02 (d, J = 7.02 Hz, B-CH-CH_3), 0.91 (m, B-CH-CH$_2$-CH_3). ^{13}C NMR ($CDCl_3$, 75.4 MHz): δ 132.3 (v br, -CN), 57.503 and 57.222 (~2:3, N-CH_2-), 50.719 and 48.437 (~2:3, N-CH_3), 30.696 and 29.161 (~3:2, -CH-CH_2CH$_3$), 21.6 (br, B-CH), 20.040 and 19.584 (~2:3, -CH-CH_3), 13.452 and 13.090 (~2:3, -CH$_2$CH_3). Anal. Calcd for $C_{16}H_{36}B_2N_4$: C, 62.80; H, 11.85. Found: C, 62.21; H, 11.95.

Quinuclidine–*sec*-Butylcyanoborane (4g). The filtered reaction solution (THF) from the preparation of **6b** (325 mmol) was treated with HCl·OEt$_2$ (80 mL × 4.1 M, 328 mmol) according to the general procedure. After 2 h, quinuclidine (39.5 g, 355 mmol) was added, and the mixture was stirred at room temperature for 12 h. Following the extractive workup, a cloudy, pungent oil was obtained. The oil was filtered through a coarse-frit funnel (60 mL) containing silica gel (Merck 60, 230–400 mesh) with ethyl acetate; the solvent was evaporated and the oil was purified by flash chromatography (silica gel 50 g, 32 × 135 mm, hexane/ethyl acetate 1:1, 500 mL) in ~2-g portions to give a clear oil (R_f 0.84, silica gel TLC, EtOAc), which solidifed when cooled (-15 °C). Total yield of solid **4g** was 18.4 g (27.5% based on starting Me_2S·BH_3); mp 48–50 °C. ^{11}B NMR ($CDCl_3$, {^1H}): δ -5.94 and -6.24 (1:1 ratio of diastereomers). ^1H NMR ($CDCl_3$, 500.1 MHz): δ 3.047 (m, N-[CH_2-]$_3$), 2.010 (sep, J = 3.24 Hz, [-CH$_2$]$_3$CH), 1.744 (second-order quint, J = 4.68 Hz, [-CH_2]$_3$CH), 1.509 (dqd, J = 3.60, 7.04, 14.22 Hz) and 1.250 (m, J = 6.84 Hz) and 1.163 (complex m) and 1.096 (m, J = 7.04 Hz) (diastereotopic B-CH(CH$_3$)CH_2-), 0.906 and 0.811 (d, J = 7.04, 7.07 Hz, respectively, diastereomeric B-CH-CH_3), 0.858 and 0.811 (t, J = 7.34, 7.34, respectively, diastereomeric B-CH-CH$_2$CH_3), 0.422 (br m, J = 6.8 Hz, B-CH-). ^{13}C NMR ($CDCl_3$, 125.76 MHz): δ 133.8 (br, CN), 50.974 and 50.947 (N[CH_2-]$_3$), 30.327 and 28.648 (B-CH-CH_2-), 24.254 ([-CH_2]$_3$CH), 19.889 and 19.856 ([-CH$_2$]$_3$CH), 19.629 and 19.059 (B-CH-CH_3), 13.276 and 12.975 (B-CH-CH$_2$CH_3), 20.855 (br, B-CH-). IR (KBr): 2950 vs, 2880 s, 2400 s, 2180 m, 1460 s, 1110 s, 1050 s, 980 m, 855 s, 840 m sh, 820 m, 610 m br cm^{-1}. HRMS (+CI, NH_3): m/e 204.1904/205.1875 (M^+ - H, m/e calcd for $C_{12}H_{22}{}^{10}BN_2/C_{12}H_{22}{}^{11}BN_2$ 204.1912/205.1876). Anal. Calcd for $C_{12}H_{23}BN_2$ C, 69.92; H, 11.25; N, 13.59. Found: C, 70.26; H, 11.84; N, 13.71.

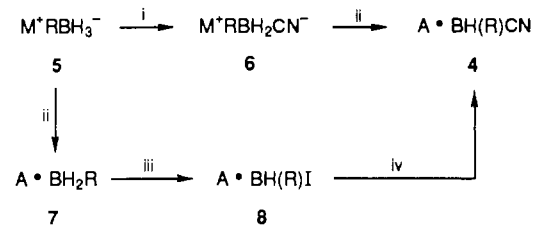
Pyridine–Isobutylcyanoborane (4h). Unpurified **6c** (ca. 47 mmol) was dissolved in dry THF (50 mL) under nitrogen, with a reflux condenser in place. Pyridine hydrochloride (10.0 g, 86.5 mmol) was added, and the mixture was heated to 50 °C. When hydrogen evolution had ceased (1.5 h), the resulting solution was evaporated and treated in the manner described for **4e**. The resulting oil (10.0 g) was purified by column chromatography (silica gel, 500 g, 65 mm diameter) using THF/hexane (1:1) and THF eluents. Pure **4h** was obtained as a colorless oil (2.6 g, R_f 0.63 [silica gel TLC, THF], 32%) with a pleasant odor faintly reminiscent of pyridine; bp > 150 °C dec. ^1H NMR ($CDCl_3$ 361.1 MHz): δ 8.575 (dd, J = 1.0, 6.06 Hz, py α-H), 8.078 (td, J = 1.04, 6.65 Hz, py γ-H), 7.649 (t, J = 6.73 Hz, py β-H), 2.9 (v br, B-H), 1.409 (septet, J = 6.60 Hz, -CH-[CH$_3$]$_2$), 0.820 and 0.784 (d's, J = 6.71, 6.71 Hz, diastereotopic -CH-[CH_3]$_2$), 0.599 and 0.476 (complex second-order m, diastereotopic B-CH_2-CH-). ^{13}C NMR ($CDCl_3$/acetone-d_6, 75.4 MHz): δ 145.56 (py α-C), 141.14 (py γ-C), 125.91 (py β-C), 134.9 (br, -C≡N), 32.79 (br, B-CH_2-CH), 26.02 (-CH-[CH$_3$]$_2$), 24.51 (-CH-[CH_3]$_2$). IR (neat, NaCl): ν_{max} 3118 w, 3102 w, 3078 w, 3055 w, 2940 s, 2856 s, 2796 m, 2395 s, 2182 w, 1616 ms, 1455 s, 1097 s, 763 ms, 684 s cm^{-1}. HRMS (+CI, NH_3): m/e 148.1385 (M^+ - CN + H, m/e calcd for $C_9H_{16}{}^{10}BN$ 148.1412).

Quinuclidine–Isobutylcyanoborane (4i). Unpurified **6c** (ca. 140 mmol) was reacted with HCl·OEt$_2$ (69 mL × 2.15 M, 147.0 mmol) at room temperature according to the general procedure. After gas evolution had ceased, freshly sublimed quinuclidine (17.0 g, 153.0 mmol) was dissolved in dry THF (40 mL) and added to the thick reaction mixture with vigorous stirring. The mixture was heated to reflux for 1 h. Following the extractive workup, the resulting orange-brown oil (37.98 g) was gravity filtered through silica gel (500 g, 65 × 450 mm) with hexane/ethyl acetate (1:1) and ethyl acetate to give solid **4i** (12.35 g, R_f 0.63 [silica gel TLC, $CHCl_3$], 43%). Successive recrystallization from acetone/water and CH_2Cl_2/hexane gave analytically pure material, mp 87–88 °C. ^1H NMR ($CDCl_3$, 361.1 MHz): δ 2.987 (second-order t, N[-CH_2]$_3$), 1.987 (septet, J = 3.15 Hz [-CH$_2$]$_3$CH), 1.714 (second-order quintet, [-CH_2]$_3$CH), 1.552 (second-order m, -CH-[CH$_3$]$_2$), 0.855 and 0.755 (d, J = 6.56, 6.54 Hz, diastereotopic -CH-[CH_3]$_2$), 0.313 and 0.125 (second-order diastereotopic septets, B-CH_2-CH-). ^{13}C NMR ($CDCl_3$, 90.8 MHz): δ 134.98 (br, -C≡N), 50.601 (N[CH_2-]$_3$), 26.611 and 24.011 (diastereotopic -CH-[CH_3]$_2$), 26.845 (-CH-[CH$_3$]$_2$), 24.253 ([-CH_2]$_3$CH), 19.949 ([-CH$_2$]$_3$CH), 26.4 (br, B-CH_2-CH-). IR (KBr): ν_{max} 2996 m, 2961 s, 2940 s, 2877 s, 2859 m, 2811 m, 2387 s, 2360 ms, 2227 vw, 2186 w-m, 1462 s, 1359 m, 1250 ms, 1177 s, 1041 s, 849 s, 606 w-m cm^{-1}. HRMS (CI$^+$, NH_3): m/e 180.1946 (M^+ - CN, m/e calcd for $C_{11}H_{23}{}^{11}BN$, 180.1923). Anal. Calcd for $C_{12}H_{23}BN_2C$: 69.92; H, 11.25. Found: C, 69.97; H, 11.36.

Trimethylamine–Benzylcyanoborane (4j). Unpurified **6c** (38.8 mmol) and Me_3N·HCl (6.0 g, 62.8 mmol) were combined in THF (40 mL) as described above. After 13.5 h at reflux, the solvent was evaporated and the residual tacky solid was purified by fractional sublimation. A white, crystalline compound identified as Me_3N·BH_2Bzl was obtained as the first fraction (0.05 Torr, 80 °C), mp 64–65 °C. ^{11}B NMR (acetone-d_6): δ -0.86 (t, J = 98 Hz). Sublimation was continued (100 °C, 0.05 Torr) for 36 h to obtain the desired cyanoborane (500 mg, 6.7%), mp 129.0–130.5 °C. ^{11}B NMR (acetone-d_6): δ -7.29 (d, J = 104 Hz). ^1H NMR (acetone-d_6, 361.1 MHz): δ 7.20 (m, Ph-H), 2.75 (s, N-CH_3), 1.91 (br d, J = 7.58 Hz, B-CH_2). ^{13}C NMR (acetone-d_6, 75.4 MHz): δ 145.39, 129.56, 128.47, and 124.37 (Ph-H), 133 (v br, -CN), 51.19 (N-CH_3), 26.2 (br, B-CH_2-).

Quinuclidine–Benzylcyanoborane (4l). HCl·OEt$_2$ Protocol. The filtered reaction solution (THF) from the preparation of **6d** was treated with HCl·OEt$_2$ (3.5 mL × 2.95 N) as previously described. After ca. 4 h, quinuclidine (2.3 g, 20.7 mmol) in dry CH_2Cl_2 (3 mL) was added and the mixture was heated to 40 °C for 12 h. The reaction solvent was evaporated, and CH_2Cl_2 (reagent) was added. The solids were filtered, and the solvent was removed to give an oil, which was purified by column chromatography on silica gel (R_f 0.2, EtOAC) to give **4l** (531 mg, 2.2 mmol, 5%), mp 128.0–130.0 °C. ^1H NMR (CD_2Cl_2, 361.1 MHz): δ 7.3–7.1 (m, PhH), 7.053 (tt, J = 2.05, 6.67 Hz, PhH), 3.109 (second-order t, J = 7.92 Hz, N-[CH_2-]$_3$), 2.058 (sep, J = 3.23 Hz, -[CH$_2$]$_3$CH), 1.980 (AB q, J = 3.7 Hz, $\Delta\nu$ = 11.49 Hz, B-CH_2-), 1.804 (second-order m, [-CH_2]$_3$CH). ^{13}C NMR (CD_2Cl_2, 75.4 MHz): δ 144.29 (Ph), 134 (br, CN), 128.70 (Ph), 127.995 (Ph), 123.84 (Ph), 50.992 (N-CH_2), 25 (br, B-CH_2-), 24.37 ([-CH_2]$_3$CH), 20.01 ([-CH$_2$]$_3$CH). IR (KBr): ν_{max} 3070 m, 3020 s, 2995 m-s, 2940 vs, 2900 s,

Scheme I[a]



5–6a, R = Me; M = Li
b, R = ^{s}Bu; M = Li
c, R = ^{i}Bu; M = Li
d, R = Bzl; M = Li·TMED

7–8a, A = Me_3N; R = Bzl
b, A = quin; R = Bzl
c, A = anil; R = Bzl
d, A = py; R = Bzl

4a, A = Me_3N; R = Me
b, A = py; R = Me
c, A = TMED; R = Me
d, A = Me_3N; R = ^{s}Bu
e, A = py; R = ^{s}Bu
f, A = TMED; R = ^{s}Bu
g, A = quin; R = ^{s}Bu
h, A = py; R = ^{i}Bu
i, A = quin; R = ^{i}Bu
j, A = Me_3N; R = Bzl
k, A = py; R = Bzl
l, A = quin; R = Bzl

[a] Key: (i) $Hg(CN)_2$, THF; (ii) A·HCl, THF or HCl·OEt_2, THF then A or I_2, THF, A; (iii) I_2, benzene; (iv) NaCN, THF.

2880 s-vs, 2390 vs, 2180 m, 1600 s, 1490 s, 1460 vs, 1450 s, 1280 vs, 1205 vs, 1100 vs, 1085 vs, 1045 vs, 980 d s, 900 s, 760 vs, 700 vs, 610 m, 525 m, 470 m cm^{-1}. HRMS (EI, 25 eV): *m/e* 240.1798 (M^+, *m/e* calcd for $C_{15}H_{21}{}^{11}BN_2$ 240.1798).

Iodide Displacement Protocol. The crude iodoborane **8b** was dissolved in THF and NaCN (powdered, oven dried) was added with stirring at room temperature. After 48 h, the mixture was allowed to settle and the solution was decanted and evaporated. The residual paste was extracted with several portions of chloroform. The combined organic extracts were filtered and evaporated to give an oil, which solidified overnight at room temperature. The crude solid was washed with water (2 mL) and dissolved in fresh chloroform. The resulting solution was dried over magnesium sulfate and concentrated. Crystallization was initiated by addition of heptane to the solution. A colorless solid was thus obtained (97.0 mg, 0.41 mmol) and analyzed as pure cyanoborane (15% overall yield from benzylborane).

Results and Discussion

Synthesis of Amine–Alkylcyanoboranes. Scheme I summarizes the synthetic routes we have investigated for preparing the alkylated cyanoboranes **4**. In general, the methods described above were adapted to these preparations using alkyltrihydroborates **5** as the precursors to the cyanoborohydrides **6**, or, alternately, the iodoboranes **8**. In addition, two other routes to the alkylcyanoborohydrides **6** were investigated. One was by the displacement of aniline from **7c** by cyanide as reported by Spielvogel for the preparation of $NaBH_2(CN)_2$ from $PhNH_2{\cdot}BH_2CN$.[24] Since the aniline–borane is derived from the corresponding benzylborohydride (**5c**), this method is somewhat circuitous in light of the possibility for the direct conversion of **5** to **6**. The second method involves direct alkylation of a neutral, two-electron donor (D) complex of "BH_2CN" (e.g., eq 4). The complexes are available

$$Me_2S{\cdot}BH_2CN + RLi \rightarrow Li[R{-}BH_2CN] \quad (4)$$

from sodium cyanoborohydride and acid in the donor's presence. Precedence for this approach is found in the work of Nöth et al. for the preparation of Li [RBH_3] (**6**) from D·BH_3 and alkyllithium reagents (vide infra).[25]

Preparation of Alkyltrihydroborates. The *n*-butyltrihydroborate anion was first reported by Kim et al. as a reducing agent for conjugated carbonyl systems.[26] It was prepared by treating dimethyl sulfide–borane with ^{n}BuLi, but the material was neither isolated nor characterized. Other examples of alkyltrihydroborates were prepared by Brown and co-workers by reacting tri-

Table I. ^{11}B NMR Data for Lithium Alkylhydroborate and Alkylcyanohydroborate Salts[34]

	δ, ppm (J_{BH}, Hz)[a]			
R	$[R{-}BH_3]^-$ (**5**)	$[R_2{-}BH_2]^-$	$[R{-}BH_2CN]^-$ (**6**)	$[R{-}BH(CN)_2]^-$ (**13**)
H	−40.7 (81)	−40.7 (81)	−43.8 (90)	−36.6 (78)
Me	−30.3 (73)	−21.8 (64)	−35.1 (84)	−33.9 (88)
^{s}Bu	−25.6 (75)	−9.6 (68)	−29.3 (81)	−29.3 (89)
^{i}Bu	−30.4 (74)	−19.1 (67)	−33.6 (86)	−33.0 (90)
Bzl[b]	−27.5 (76)	−12.9 (72)	−30.7 (br)	

[a] Measured in THF. All signals show the expected first-order BH coupling. [b] Counterion = $[Li{\cdot}TMED]^+$.

ethylenediamine–alkylboranes with lithium aluminum hydride.[18,27] The examples were limited to bulky alkyl groups derived from hydroboration.[28] Nöth looked in detail at the preparation of alkyltrihydroborates by addition of alkyllithium reagents to donor complexes of BH_3 (Me_3N, THF, and Me_2S).[25] The reaction was accompanied by significant amounts of product disproportionation, and yields were modest. Finally, Brown reduced boronic acids and their esters using alkali-metal hydrides to give the trihydroborates **5** in good yield (eq 5).[18,27]

$$\underset{\mathbf{9}}{R{-}B(OR^1)_2} + LiAlH_4 \rightarrow \underset{\mathbf{5}}{Li[R{-}BH_3]} + HAl(OR^1)_2 \quad (5)$$

The Brown protocol was used initially. The alkyldiisopropoxyboranes[16,17] Me–$B(O^iPr)_2$ (**9a**), ^{s}Bu–$B(O^iPr)_2$ (**9b**), and ^{i}Bu–$B(O^iPr)_2$ (**9c**) were reduced with $LiAlH_4$ (eq 6). The procedure

$$R{-}B(O^iPr)_2 + LiAlH_4 \rightarrow Li[R{-}BH_3] + H{-}Al(O^iPr)_2 \quad (6)$$

was very efficient on a small scale, but proved to be problematic when the scale was increased. Conversion of the boronic esters to alkyltrihydroborates was virtually quantitative. A compromise was necessary, however, since the optimum esters (isopropyl)[16,17] for alkylation introduced an alkoxy group that made separation of the alane byproduct[18] difficult. In the literature procedure, these byproducts were removed by centrifugation, but on a larger scale, this operation was impractical. The alternative of filtration was excruciatingly slow and required an inert atmosphere since the alanes are highly reactive (air/water sensitive). Another significant concern was the subsequent neutralization and disposal of the alane residues.

In response to the difficulties associated with the esters (**9**), they were converted into the corresponding boronic acid by stirring in water (eq 7).[29] The added complication of removing excess

$$R{-}B(O^iPr)_2 + 2H_2O \rightarrow R{-}B(OH)_2 + 2^iPrOH \quad (7)$$

water and 2-propanol from the boronic acids negated any advantage this route offered. The suggested use of excess $LiAlH_4$ in the presence of indicators to monitor the disappearance of the Al reagent[18] was also unsuccessful.[30]

The limitations of the boronate approach led us to examine the D·BH_3 route of Nöth.[25] The reactions of BuLi and $Me_2S{\cdot}BH_3$ showed promise under carefully controlled conditions. Nöth reported that disproportionation occurs to convert the desired alkyltrihydroborate into a mixture of di- and trisubstituted species and BH_4^- (eq 8–10). This process was minimized by the use of

$$D{\cdot}BH_3 + RLi \rightarrow Li[R{-}BH_3] \quad (8)$$

$$Li[R{-}BH_3] + D{\cdot}BH_3 \rightarrow D{\cdot}BH_2R + LiBH_4 \quad (9)$$

$$D{\cdot}BH_2R + RLi \rightarrow Li[R_2{-}BH_2] \text{ etc.} \quad (10)$$

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(30) Brown et al. [Brown, H. C.; Bakshi, R. K.; Singaram, B. *J. Am. Chem. Soc.* **1988**, *110*, 1529] alluded to similar difficulties when preparing very pure, chiral alkyltrihydroborates. Their problems were circumvented by using 1,3-propanediol esters of the boronic acids. They report that the alane derived from these esters is easily separated. This approach has not been attempted in our laboratory.

$Me_2S{\cdot}BH_3$ under carefully controlled, low-temperature conditions. Thus, to a stirred solution of ^{s}BuLi in cyclohexane/pentane at −35 °C was slowly added $Me_2S{\cdot}BH_3$ (neat or as a 2.0 N solution in toluene) at a rate that prevented the temperature from rising above −30 °C. After addition was complete, the temperature was allowed to rise only to −20 °C and then the solvents were evaporated under high vacuum into a liquid-nitrogen-cooled trap. The temperature was permitted to slowly rise (over 4 h) to room temperature once most of the solvent was removed. The thick residual paste was shown to be 98% Li[^{s}BuBH$_3$] (**5b**) by ^{11}B NMR (Table I). The byproducts included approximately 2% BH_4^- and a barely detectable trace of [^{s}Bu$_2$BH$_2$]$^-$. Pure **5b** could be isolated as its bis-THF complex, but generally, the crude material was used without further purification.

The preparation of [Li·TMED][BzlBH$_3$] (**5d**) was also reported by Nöth. In our hands, the BzlLi·TMED addition to $Me_3N{\cdot}BH_3$ was not straightforward. When the reaction scale was conducted at 60 mmol or less, reasonable yields of pure material were obtained although a dark brown impurity formed. Whenever the scale was larger, the reaction mixture darkened to almost black. The desired product was contaminated, often in excess, with $Me_3N{\cdot}BH_2Bzl$ (**7a**). Varying reaction temperatures, solvents, concentrations, and careful optimization of benzyllithium formation[31] failed to change the course of the reaction. Desired product (**5d**) of 70% or higher purity could be purified by Soxhlet extraction with pentane under N_2 in a slow, time-consuming process. Mixtures containing mostly **7a** were difficult to purify and degraded during the attempted purification procedure.

Cyanation of the Monoalkyltrihydroborates. Emri and Györi reported that mercury(II) cyanide converted $NaBH_4$ and $Me_2S{\cdot}BH_3$ to $NaBH_3CN$ and $Me_2S{\cdot}BH_2CN$, respectively.[22] In accordance with their method, trihydroborates **5a–c** were treated with $Hg(CN)_2$ in THF. Vigorous gas evolution and formation of a dark gray mixture occurred immediately in a very exothermic process. Addition must be controlled to prevent frothing, and provisions for reflux are needed for larger scale reactions. In most cases, to complete the reaction, one need only stir until the mixture becomes clear and elemental mercury forms (4–6 h). If desired, the reaction may be accelerated by heating to a gentle reflux for 1–2 h. However, heating promotes decomposition when other impurities are present, and if excess mercury cyanide is present, heating encourages dicyanation to form Li[R–BH(CN)$_2$] (**13**). The cyanoborohydrides **6a–c** are stable to water and air. No decomposition was noted, for example, of Li[^{s}BuBH$_2$CN] (**6b**) in water solution for up to 3 weeks. In general, compounds **6** were not isolated as pure substances. Typical impurities detected by ^{11}B NMR were usually minor and consisted of [BH_3CN]$^-$ salts, boronic acids, and the dicyanated derivatives **13**. Crude yields were consistently in apparent excess of 100%, and the salts were even partially soluble in hydrocarbon solvents. These results suggest strong association of THF solvent to the lithium cation. Attempts to isolate tetraalkylammonium salts of the cyanoalkyldihydroborates were not successful. However, over a 4-month period at room temperature, **6b** and Me_4NCl in acetonitrile/water were found to react to an extent of ~50%. The boron chemical shift of the new compound, δ −5.2 (br), is consistent with the formation of an amine–cyanoborane (**4**) (vide infra). This result is rationalized in eq 11.

$$Li[^sBuBH_2CN] + Me_4NCl \rightarrow Me_3N{\cdot}BH(^sBu)CN + CH_4 + LiCl \quad (11)$$

If the THF solvent is replaced by diethyl ether, the cyanation reaction does not proceed. It was determined that a minimum of 25% THF in ether was required for the conversion to occur. However, reaction time was lengthened to ca. 18 h at 35 °C. The failure to react may be due simply to the low solubility of $Hg(CN)_2$ in diethyl ether.

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Table II. Spectroscopic Data for the Amine–Alkylcyanoboranes (**4**)

compd	IR, cm^{-1} ν(BH)	IR, cm^{-1} ν(CN)	NMR shift, ppm (J, Hz)[a] δ(B)	NMR shift, ppm (J, Hz)[a] δ(*C*N)
$Me_3N{\cdot}BH(Me)CN$ (**4a**)	2370	2190	−8.9 (102)	134
pyr·BH(Me)CN (**4b**)	2390	2185	−9.7 (102)[b]	
TMED·2BH(Me)CN (**4c**)	2410	2185	−9.2 (96)	
$Me_3N{\cdot}BH(^sBu)CN$ (**4d**)			−6.5 (96)[c]	
py·BH(^{s}Bu)CN (**4e**)	2390	2190	−6.9 (95)	134[d]
TMED·2BH(^{s}Bu)CN (**4f**)			−6.5 (br)	132
quin·BH(^{s}Bu)CN (**4g**)	2400	2180	−5.90–6.2	134
py·BH(^{i}Bu)CN (**4h**)	2420	2200	−9.3 (100)	135
quin·BH(^{i}Bu)CN (**4i**)	2400	2190	−9.1 (98)	135
$Me_3N{\cdot}BH(Bzl)CN$ (**4j**)	2410	2190	−7.4 (115)	132
py·BH(Bzl)CN (**4k**)	2390	2190	−8.7 (100)	135
quin·BH(Bzl)CN (**4l**)	2390	2180	−8.6 (100)[d]	134

[a] Measured in $CDCl_3$. [b] Measured in acetone-d_6. [c] Measured in THF. [d] Measured in CD_2Cl_2.

Table III. Reactions of Li[R–BH_2–CN] with Amine Hydrochlorides[a]

R	amine	% convn	time, h
Me (**6a**)	Me_3N	90	40
^{s}Bu (**6b**)	Me_3N	50	114
	quin	<5	65
	pyr	90	12[b]
Bzl (**6d**)	Me_3N	40	100
	quin	<5	86

[a] All reactions were run in THF at reflux unless otherwise noted and analyzed by ^{11}B NMR. [b] Room temperature.

Synthesis of the Amine–Alkylcyanoboranes. Several approaches to the preparation of the amine–alkylcyanoboranes **4** were investigated. Acid attack on [R-BH_2-CN]$^-$ salts (**6**) to produce "BH(R)CN", which is then trapped by amine, proved to be a general route. This method required the refinement of several protocols in order to insure success under a variety of conditions. The syntheses, though conceptually straightforward, required careful attention to detail. Finally, direct displacement of iodide from quin·BH(I)Bzl (**8b**) by CN^- proved to be useful for the formation of **4l**. Table II lists the spectroscopic data for the final products.

Amine Hydrochloride Protocol. Initially, **6a** was treated with 1.5 equiv of trimethylamine hydrochloride in THF. Heating to reflux for approximately 3.5 h converted a few percent of the starting material to $Me_3N{\cdot}BH(Me)CN$ (**4a**) with only about 10% degradation products. Prolonged heating (40 h) was required for higher conversions (~90%). Higher temperatures, obtained by heating to reflux in glyme, resulted in a trace of **4a** after 18 h with extensive decomposition. The crude cyanoborane is usually an oil or an oily solid. During early work, the oil was purified by Kügelrohr distillation. However, the temperatures required to volatilize the product resulted in decomposition of the complex. As a result, yields were painfully low. Subsequently, column chromatography was found to be effective in purifying the air- and water-stable borane. The crude oil was eluted from a column of basic alumina with chloroform to obtain solid **4a**. During these reactions, it was observed that the Li[$MeBH(CN)_2$] byproduct from the cyanation was unaffected by the reaction conditions. In many cases, this impurity was undetected prior to reaction with the amine hydrochloride because its boron chemical shift is similar to that of the monocyano derivative **6a** (see Table I).

The prolonged reaction of Li[^{s}BuBH$_2$CN] (**6b**) with $Me_3N{\cdot}HCl$ at reflux in THF (114 h) produced only a 50% conversion of starting material to **4b** (Table III). The same reaction with Li[BzlBH$_2$CN] (**6c**) produced an average of 40% conversion to **4f**. When quinuclidine hydrochloride was used, <5% conversion of both **6b** and **6c** was detected. In the latter case, attempts to use cyanoalkyldihydroborate contaminated with $Me_3N{\cdot}BH_2Bzl$ (**7a**) (vide supra), resulted in formation of quin·BH_2Bzl (**7b**) and

inhibited the yield of the desired cyanoborane.

Two factors are important in explaining these results. First, the acidity of the amine hydrochloride affects the reactivity with respect to the B–H bond. Thus, trimethylamine (pK_a = 9.80) reacts more readily than does quinuclidine (pK_a = 10.95). Higher temperatures and longer reaction times are needed to promote the reaction, but these conditions are hostile to the N·B coordinate bond. Second, the cyano moiety renders the hydride relatively unreactive as exemplified by the comparative stability of $[BH_3CN]^-$ under low pH conditions that destroy BH_4^-.[32] This stability is desirable in the final products, but necessitates a more reactive amine hydrochloride. Therefore, pyridine hydrochloride, which has been reported to react very rapidly with $NaBH_3CN$,[4] was used in our study.

Treatment of **6b** with pyridine hydrochloride in THF at room temperature resulted in the immediate evolution of gas. The exothermic reaction generated sufficient heat that the solvent gently refluxed in a large-scale reaction. The mixture was allowed to stir at ambient temperature for 12 h. After an extractive workup, the cyanoborane **4e** was obtained in about 80–85% purity. It could be further purified by flash chromatography on silica gel to give the pure oil.

HCl·Et$_2$O Protocol. In order to alleviate the difficulty associated with low acidity of tertiary amine hydrochlorides, the general approach of Uppal and Kelly[2] was adapted to the preparation of the amine–alkylcyanoboranes. The two-step sequence shown in eq 12 was used.

$$\underset{\mathbf{6}}{Li[R\text{–}BH_2\text{–}CN]} + HCl\cdot Et_2O \rightarrow THF\cdot BH(R)CN + A \rightarrow \underset{\mathbf{4}}{A\cdot BH(R)CN} \quad (12)$$

6b, R = ^{s}Bu
c, R = ^{i}Bu
d, R = Bzl

4c, A = TMED; R = Me
f, A = TMED; R = ^{s}Bu
g, A = quin; R = ^{s}Bu
i, A = quin; R = ^{i}Bu
l, A = quin; R = Bzl

A solution of **6b** in THF was cooled to 0 °C. The hydrochloride etherate in ether was carefully added (slight excess). Gas evolution occurred readily and continued slowly as the temperature was allowed to rise to room temperature. Boron NMR analysis indicated formation of two products in about a 1:1 ratio. The resonances, δ −11.6 (d, J = 91 Hz) and −16.9 (br d), were assigned as THF·BH(^{s}Bu)CN and $[BH(^sBu)CN]_n$, respectively. The amine (TMED) was added at room temperature while stirring. After 2 h, boron NMR analysis indicated complete formation of the adduct **4f**. When this protocol was repeated for **6d** with quinuclidine, the conversion of cyanoborane **4l** improved to 20% from ~2% seen in the amine–hydrochloride protocol. The *sec*-butyl derivative **6b** was treated with acid at room temperature, followed by addition of quinuclidine. Stirring at room temperature overnight gave an 85% conversion of the starting material to **4g**. The cyanoborane was purified by column chromatography to afford an isolated yield of 28%, based on starting $Me_2S\cdot BH_3$.

Iodide Displacement Protocol. The still modest yields of quin·BH(Bzl)CN (**4l**) prompted the investigation of iodide displacement. quin·BH_2Bzl (**7b**) can be prepared from the benzyltrihydroborate **5c** by using the HCl·Et$_2$O protocol. It is obtained in about 80% yield after recrystallization (acetone/water). When **7b** was treated with I_2 in benzene,[33] a slightly colored solution was obtained that decolorized upon brief heating at reflux. The clear solution was filtered under N_2 and placed into a freezer (−15 °C) overnight. The liquor was decanted. The solid was washed with pentane and recrystallized from toluene/hexane to give a yellow solid, which analyzed (^{11}B NMR) as a mixture of 66% quin·BH(Bzl)I (**8b**) and 33% benzylboronic acid. The solid was stirred in THF with finely powdered, dry NaCN at room temperature for 48 h. Boron NMR indicated the absence of starting material and the presence of the cyanoborane. The crude material was obtained by solvent evaporation, and after recrystallization from $CHCl_3$/hexane, solid quin·BH(Bzl)CN (**4l**) was obtained in 20% yield from **7b**. We are presently investigating methods for the conversion of these amine–alkylcyanoboranes to the corresponding amides, esters, and carboxylic acids. A detailed report of these new derivatives, the first boron analogues of alanine, phenylalanine, leucine, and isoleucine will be published in the near future.

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Registry No. **4a**, 124287-25-8; **4b**, 124287-26-9; **4c**, 124287-39-4; **4d**, 124287-40-7; **4e**, 124287-27-0; **4f**, 124287-28-1; **4g**, 124287-29-2; **4h**, 124287-30-5; **4i**, 124287-31-6; **4j**, 124287-32-7; **4k**, 124287-41-8; **4l**, 124287-33-8; **5a**, 52950-75-1; **5b**, 84280-33-1; **5c**, 124287-19-0; **5d**, 84280-46-6; **6a**, 124287-20-3; **6b**, 124287-21-4; **6c**, 124287-22-5; **6d**, 124316-38-7; **7a**, 124287-34-9; **7b**, 124287-23-6; **7c**, 124287-35-0; **7d**, 100115-90-0; **8a**, 124287-36-1; **8b**, 124287-24-7; **8c**, 124287-37-2; **8d**, 124287-38-3; **9a**, 86595-27-9; **9b**, 86595-33-7; **9c**, 124287-18-9; quin, 100-76-5; $Me_2S\cdot BH_3$, 13292-87-0; $Me_3N\cdot BH_3$, 75-22-9; $Hg(CN)_2$, 592-04-1.

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(33) (a) Ryschkewitsch, G. E.; Wiggins, J. W. *Inorg. Chem.* **1970**, *12*, 116. (b) Nöth, H.; Beyer, H. *Chem. Ber.* **1960**, *93*, 2251.

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