Synthesis of Amine-dicyanohydroboranes, [Amine-bis(ethylnitrilium)hydroboron(2+)] Tetrafluoroborates, and Their Derivatives as Precursors of Amine-dicarboxyboranes

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Numerous amine-dicyanohydroboranes [A·BH(CN)$_2$, **1**, A = quinuclidine (Q, **c**), trimethylamine (Me_3N, **d**), 4-picoline (Pic, **e**), 4-(dimethylamino)pyridine (DMAP, **f**), *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA, **j**), 1,4-diazabicyclo[2.2.2]octane (DABCO, **k**)] have been prepared by base exchange reactions from 4-cyanopyridine-dicyanohydroborane (4-CN-py·BH(CN)$_2$, **1a**). In analogous experiments with secondary amines [piperidine (**g**), diethylamine (**h**), and morpholine (**i**)] **1a** underwent aminodecyanation also, probably via S_NAr mechanism, which demonstrates the strong electron-withdrawing effect of the >N·BHX$_2$ moiety toward the substituents on the nitrogen. Amine-dicyanohydroboranes have been transformed into [amine-bis(*C*-hydroxy-*N*-ethylimidate)hydroboron(2+)] (**3**), [amine-*N*-ethylcarbamoyl(*C*-hydroxy-*N*-ethylimido)hydroboron(1+)] (**4**), [amine-bis(*C*-methoxy-*N*-ethylimidate)hydroboron(2+)] (**5**), [amine-bis(amidinium)hydroboron(2+)] (**6**), and [amine-bis(triethylamidinium)-hydroboron(2+)] (**7**) cations, precursors of amine-dicarboxyboranes and their derivatives. These transformations were carried out in two steps. First, the otherwise nonreactive cyano groups were activated by ethylation employing Et_3OBF_4, yielding [amine-bis(ethylnitrilium)hydroboron(2+)] tetrafluoroborates (**2**), then **3**−**7** were obtained by nucleophilic addition to **2**. The pK_a values corresponding to the protonation of the *N*-ethylamide group were found to be extremely high (3.1−3.3), which demonstrates the strong electron-donating effect of >N·BHX$_2$ moiety toward the substituents on the boron.

Introduction

Amine carboxyboranes have been known for two decades,[1] and, as they were considered isoelectronic to protonated α-amino acids,[2,3] the biological activities of these compounds and their ester, amide, and peptide derivatives and transition metal complexes have been extensively studied. These investigations revealed anticancer,[4−6] antiosteoporotic,[7] antiinflammatory,[5,8,9] and hypolipidemic[5,9,10] properties, and these molecules have also been mentioned as possible boron carriers to tumor cells[11] for boron neutron capture therapy.[12] Initiated by these biological properties numerous derivatives of amine carboxyboranes have been prepared, nevertheless, attempts aimed at the synthesis of derivatives substituted on the boron resulted in only a limited number of new molecules.[13−15]

Recently we pointed out that using the B−N↔C−C rather than B↔C$^+$ isoelectronic analogy, and consequently regarding amine carboxyboranes as boron analogues of aliphatic carboxylic acids rather than α-amino acids, should be more appropriate, on the basis of experimental data.[16] Potentiometric studies revealed that amine carboxyboranes, only moderately depending on the nature of the amine, are very weak acids (p$K_a \geq 8$), and in protonated form they are generally very poorly soluble in water. To approach the acidities of the carboxylic groups in amine carboxyboranes and in aliphatic carboxylic acids, several new types of compounds have been prepared in our laboratory with electron withdrawing substituents on the boron (A·BH(X)COOH, X = Br,[16,17] amines,[16,18,19] COOH,[20] CN[21]). In addition, the existence of a number of these new derivatives renders the extension of the investigation of these valuable biological activities to structure−activity relationship studies possible.

Here we report the synthesis of a number of amine dicyanohydroboranes (isoelectronic analogues of substituted malononitriles), [amine-bis(*N*-ethylnitrilium)hydroborate(2+)] tetrafluoroborates and their nucleophilic addition derivatives formed with water, methanol, ammonia, and diethylamine, as precursors of amine dicarboxyboranes and their derivatives. The study of

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the hydrolysis of the complexes and their transformation into amine dicarboxyboranes (isoelectronic analogues of substituted malonic acids) and derivatives will be published later.

Experimental Section

Methods and Materials. All reactions, except those involving water or noted otherwise, were performed under an oxygen- and water-free N_2 atmosphere using the general Schlenk techniques in flamed or oven-dried glassware with absolutized solvents freshly distilled prior to use.

Acetonitrile was distilled from P_2O_5 after drying with CaH_2. Dichloromethane was distilled from CaH_2 and then refluxed with $NaBH_4$/diglyme and fractionally distilled. Ether was distilled from Na-benzophenone. Methanol was distilled from $Mg(OCH_3)_2$. Methyl sulfide was dried with sodium and then fractionally distilled. Pentane was fractionally distilled.

Ammonia was dried in a KOH-filled column before condensing. 4-Cyanopyridine and quinuclidine were recrystallized from ether. Diethylamine, 4-picoline, pyridine, and TMEDA were distilled from KOH. Morpholine was distilled from KOH, then from Na. Piperidine was distilled from CaH_2.

Bromine (Ferak), DABCO (Aldrich), DMAP (Janssen), $NaPF_6$ (Aldrich), and trimethylamine (Fluka) were used as received.

Cyanodihydroborane oligomer in methyl sulfide solution,[22] Et_3OBF_4[23] and LiCN·*n*THF[24] were prepared by known procedures.

$Li[BH_2(CN)_2]$, 4-CN-py·$BH(CN)_2$ (**1a**), py·$BH(CN)_2$ (**1b**), and pip·$BH(CN)_2$ (**1g**) are already known,[25] but their preparations have been considerably improved, and these newer syntheses are also included.

NMR spectra were recorded on a Bruker AM 360 instrument in 5 mm o.d. tubes at room temperature. ^{1}H (360.1 MHz) spectra were referred to internal DSS in D_2O and internal TMS in $CDCl_3$, acetone-d_6, and DMSO-d_6. ^{1}H NMR spectra of **2b**−**d** were recorded in CH_2Cl_2 without lock and were referred to the solvent signal (5.32 ppm). Protons adjacent to boron generally gave distinguishable but broad signals, and their chemical shifts are omitted. ^{13}C (90.5 MHz) spectra were referred to solvent signals ($CDCl_3$, 77.0 ppm; acetone-d_6, 29.9 ppm; DMSO-d_6, 39.5 ppm) and DSS in D_2O as external reference. Ambiguities in assigning ^{1}H and ^{13}C signals were cleared with homonuclear decoupling and chemical shift correlation (^{1}H−^{1}H and ^{13}C−^{1}H) experiments. ^{11}B (115.5 MHz) spectra were referred to $Et_2O{\cdot}BF_3$ in a capillary inserted into the tube. In cases when multiplicities could only be revealed by mathematical resolution enhancement, multiplets are marked "broad" and coupling constants are not given.

IR spectra were recorded on a Perkin-Elmer Paragon PC 1000 FT-IR spectrometer.

Potentiometric titrations were carried out at 25 ± 0.1 °C using a Radiometer PH M 52 pH-meter referenced to a saturated calomel electrode. Approximate acidity constants were estimated from the half-neutralization pH.

The boron content of the samples was determined with acid−base titration in the presence of mannitol, after fusion with NaOH and KOH. Analyses of BF_4 and PF_6 salts were performed in the presence of large excess of $CaCl_2$. LiCN·*n*THF was analyzed by the Liebig−Dénigès protocol.[26]

Safety Note! Dihydrocyanoborane oligomer was always handled in methyl sulfide solution, because explosions were experienced with neat $(BH_2CN)_n$.[27]

Syntheses. $Li[BH_2(CN)_2]$. Methyl sulfide solution of cyanodihydroborane oligomer (125.0 mL, 2.553 M; 319.1 mmol) was added to a stirred suspension of LiCN·0.03THF (11.60 g, 330.0 mmol) in methyl sulfide (125 mL), and the mixture was refluxed for 5 h. The insoluble parts were filtered off and extracted three times with the filtrate. The solvent was removed from the filtrate in vacuo. The semisolid residue was triturated with pentane (60 mL) which was then discarded, and the residue was kept under vacuum for 1 h. Upon treatment with pentane (80 mL) the residue completely solidified. It was collected on a filter, washed with pentane (2 × 80 mL), and dried in a N_2 stream. This product was used for the synthesis of **1a** and **1b** without further purification. Yield: 22.82 g (100%). ^{1}H NMR (D_2O, δ): 1.08 (q, $^1J_{HB}$ = 96 Hz). ^{11}B NMR (D_2O, δ): −42.14 (t, $^1J_{BH}$ = 96 Hz). ^{13}C NMR (D_2O, δ): 139.7 (q, $^1J_{CB}$ = 59 Hz).

The raw product can be purified through its dioxane adduct.[25] Note: The more THF the starting LiCN contains, the more tedious the removal of methyl sulfide becomes in the preparation.

4-CN-py·$BH(CN)_2$ (1a). 4-CN-pyridine (44.34 g; 425.9 mmol) was added to a solution of bromine (34.1 g; 213 mmol) in acetonitrile (125 mL) at 0 °C. A solution of $Li[BH_2(CN)_2]$ (15.280 g; 212.8 mmol) in acetonitrile (125 mL) was then added to the orange-colored solution at 0 °C, which gave rise to a precipitate in 5 min. The stirred suspension was then allowed to warm to room temperature for 1 h. The mixture was evaporated in vacuo to a viscous slurry, and water (30 mL) and, after trituration, $Na_2S_2O_3$ solution (10 mL, 0.2 M) were added. The mixture was then evaporated in vacuo to a resin, which was treated with water (35 mL), the mixture was filtered at 0 °C, and the product was washed with 0 °C water (3 × 25 mL) and dried in a N_2 stream. Yield: 31.55 g (88%). Anal. Found (calcd) for $C_8H_5BN_4$: B, 6.36 (6.44). ^{1}H NMR (acetone-d_6, δ): 9.19 (m, 2H, 2(6)-CH), 8.59 (m, 2H, 3(5)-CH). ^{11}B NMR (acetone-d_6, δ): −18.0 (d, J = 107 Hz). ^{13}C{^{1}H} NMR (acetone-d_6, δ): 153.94 (2(6)-CH), 136.23 (3(5)-CH), 132.94 (4-CH), 120.11 (py-CN). IR (KBr, cm^{-1}): ν(B−H), 2451; ν(C≡N), 2252 (CCN), 2218 (BCN).

py·$BH(CN)_2$ (1b). The procedure described for **1a** (above) was followed using pyridine (7.592 g; 95.98 mmol) instead of 4-cyanopyridine, bromine (7.375 g; 46.15 mmol) in acetonitrile (25 mL), and $Li[BH_2(CN)_2]$ (3.185 g; 44.36 mmol) in acetonitrile (30 mL); 8 mL of water was used for the first and 20 mL for the second treatment, and 4 × 5 mL was used for the washing. Yield: 5.470 g (86%). Anal. Found (calcd) for $C_7H_6BN_3$: B, 7.51 (7.56). ^{1}H NMR ($CDCl_3$, δ): 8.74 (d, 2H, 2(6)-CH), 8.37 (tt, 1H, 4-CH), 7.93 (dt, 2H, 3(5)-CH). ^{11}B NMR ($CDCl_3$, δ): −18.9 (d, J = 110 Hz). ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 146.66 (2(6)-CH), 143.78 (4-CH), 127.47 (3(5)-CH). IR (KBr, cm^{-1}): ν(B−H), 2482; ν(C≡N), 2216.

Q·$BH(CN)_2$ (1c). Quinuclidine (3.54 g; 31.8 mmol) was added to a stirred suspension of **1a** (5.19 g; 30.9 mmol) in acetonitrile (20 mL) at room temperature. The mixture, which turned into a clear brown solution, was evaporated to dryness in vacuo after 30 min, and the residue was suspended in ether (20 mL). The product was collected on a filter, washed with ether (3 × 7 mL), and dried in a N_2 stream. Yield: 5.206 g (96%). Anal. Found (calcd) for $C_9H_{14}BN_3$: B, 6.10 (6.18). ^{1}H NMR ($CDCl_3$, δ): 3.24 (m, 6H, N−CH_2), 2.19 (sept, 1H, CH), 1.91 (m, 6H, CCH_2). ^{11}B NMR ($CDCl_3$, δ): −18.5 (d, J = 110 Hz). ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 51.68 (NCH_2), 23.81 (CCH_2), 19.28 (CH). IR (KBr, cm^{-1}): ν(B−H), 2433; ν(C≡N), 2214.

Me_3N·$BH(CN)_2$ (1d). Trimethylamine gas (∼5 g, ∼85 mmol) was bubbled through a stirred suspension of **1a** (10.07 g, 60.00 mmol) in acetonitrile (40 mL) over 45 min at room temperature. During this period a Me_3N atmosphere of ∼1000 mmHg was maintained over the solution. The solvent was then evaporated in vacuo, and the residue was suspended in ether (35 mL). The product was collected on a filter, washed with ether (4 × 7 mL) and dried in a N_2 stream. Yield: 6.840 g (93%). Anal. Found (calcd) for $C_5H_{10}BN_3$: B, 8.90 (8.79). ^{1}H NMR ($CDCl_3$, δ): 2.87 (s, NMe). ^{11}B NMR ($CDCl_3$, δ): −17.2 (d, J = 110 Hz). ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 51.55 (NMe). IR (KBr, cm^{-1}): ν(B−H), 2455; ν(C≡N), 2217.

4-pic·$BH(CN)_2$ (1e). 4-Picoline (0.589 g; 0.615 mL; 6.32 mmol) was added to a solution of **1a** (0.980 g; 5.83 mmol) in acetonitrile (5 mL) at room temperature. After 1 h the solvent was evaporated in vacuo. The residual syrup was redissolved in CH_2Cl_2, and the solvent was evaporated. After we repeated the redissolution−evaporation with CH_2Cl_2, the solid residue was suspended in ether, the suspension was filtered, and the product was washed with ether (2 × 5 mL) and dried in a N_2 stream. Yield: 0.865 g (95%). Anal. Found (calcd) for $C_8H_8BN_3$: B, 6.93 (6.89). ^{1}H NMR ($CDCl_3$, δ): 8.55 (d, 2H, 2(6)-CH), 7.65 (d, 2H, 3(5)-CH), 2.65 (s, 3H, CH_3). ^{11}B NMR ($CDCl_3$, δ):

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−19.1 (d, J = 108 Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 157.39 (4-C), 145.96 (2(6)-CH), 127.98 (3(5)-CH), 21.93 (CH_3). IR (KBr, cm^{-1}): ν(B−H), 2460, 2450; ν(C≡N), 2216.

DMAP·BH(CN)$_2$ (1f). DMAP (0.754 g; 6.17 mmol) was added to a solution of **1a** (0.992 g; 5.91 mmol) in acetonitrile (5 mL) at room temperature. After 0.5 h the mixture was evaporated in vacuo and the residue was suspended in ether (5 mL). The product was collected on a filter, washed with ether (3 × 5 mL), and dried in a N_2 stream. Yield: 1.085 g (99%). Anal. Found (calcd) for $C_9H_{11}BN_4$: B, 5.83 (5.81). ^1H NMR ($CDCl_3$, δ): 7.99 (d, 2H, 2(6)-CH), 6.72 (d, 2H, 3(5)-CH), 3.22 (s, 6H, NCH_3). ^{11}B NMR ($CDCl_3$, δ): −20.3 (d, J = 103 Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 156.02 (4-CH), 144.91 (2(6)-CH), 107.46 (3(5)-CH), 39.82 (NCH_3). IR (KBr, cm^{-1}): ν(B−H), 2431; ν(C≡N), 2212, 2208.

Piperidine·BH(CN)$_2$ (1g). Piperidine (1.98 g; 23.3 mmol) was added to a solution of **1d** (0.966 g; 7.86 mmol) in acetonitrile (2 mL). The vessel was topped with a reflux condenser and placed into a 65 °C bath for 4 h. The atmosphere was purged with N_2 every 20 min. The mixture was then evaporated in vacuo, the residue was treated with ether (6 mL). The white crystals were collected on a filter, washed with ether (2 × 4 mL), and dried in a N_2 stream. Yield: 0.986 g (84%). Anal. Found (calcd) for $C_7H_{12}BN_3$: B, 7.24 (7.25). ^1H NMR ($CDCl_3$, δ): 5.39 (s, 1H, NH), 3.42 (m, 2H, eq NC*H*H), 2.74 (m, 2H, ax NCH*H*), 1.89 (m, 2H, eq NCH_2CHHCH_2), 1.6−1.8 (m, 3H, ax NCH_2CHHCH_2 and eq NCH_2CH_2CHH), 1.43 (m, 1H, ax NCH_2CH_2CHH). ^{11}B NMR ($CDCl_3$, δ): −21.6 (d, J = 103 Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 50.99 (NCH_2), 24.13 (NCH_2CH_2), 22.09 ($NCH_2CH_2CH_2$). IR (KBr, cm^{-1}): ν(N−H), 3112; ν(B−H), 2444; ν(C≡N), 2221.

Et$_2$NH·BH(CN)$_2$ (1h). Procedure described for **1g** (above) was applied for diethylamine (1.84 g; 25.1 mmol) and **1d** (1.032 g; 8.39 mmol) in acetonitrile (2 mL) for 5 h. A 6-mL amount of ether was used for the workup, and 2 × 4 mL was used for the washing. Yield: 1.020 g (89%). Anal. Found (calcd) for $C_6H_{12}BN_3$: B, 8.02 (7.89). ^1H NMR ($CDCl_3$, δ): 5.48 (br s, 1H, NH), 3.06 (m, 4H, NCH_2), 1.33 (t, 6H, CH_3). ^{11}B NMR ($CDCl_3$, δ): −22.8 (d, J = 105 Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 46.35 (NCH_2), 10.76 (CH_3). IR (KBr, cm^{-1}): ν(N−H), 3110; ν(B−H), 2455; ν(C≡N), 2225.

Morpholine·BH(CN)$_2$ (1i). Morpholine (2.25 g; 25.8 mmol) was added to a solution of **1a** (3.475 g; 20.69 mmol) in acetonitrile (20 mL). After 30 min the non-transparent dark violet mixture was evaporated in vacuo, the residue was treated with ether (40 mL), and the insoluble parts were filtered off and extracted six times with the filtrate. The solid on the filter was washed with dichloromethane (3 × 6 mL) and dried in a N_2 stream. Yield: 2.704 g (87%). Anal. Found (calcd) for $C_6H_{10}BN_3O$: B, 7.10 (7.16). ^1H NMR (acetone-d_6, δ): 6.6 (br s, 1H, NH), 4.06 (m, 2H, eq OC*H*H), 3.81 (m, 2H, eq NC*H*H), 3.32 (m, 2H, ax NCH*H*), 2.98 (m, 2H, ax OCH*H*). ^{11}B NMR (acetone-d_6, δ): −20.9 (d, J = 108 Hz). $^{13}C\{^1H\}$ NMR (acetone-d_6, δ): 65.54 (OCH_2), 50.36 (NCH_2). IR (KBr, cm^{-1}): ν(N−H), 3119; ν(B−H), 2479; ν(C≡N), 2216.

TMEDA·2BH(CN)$_2$ (1j). TMEDA (0.464 g; 450 mmol) was added to a solution of **1a** (1.508 g; 9.04 mmol) in acetonitrile (5 mL), which was stirred for 20 h at room temperature to allow a white precipitate to fall out. The mixture was then concentrated to half its volume and filtered, and the product was washed with ether (2 × 5 mL) and dried in a N_2 stream. Yield: 0.876 g (80%). Anal. Found (calcd) for $C_{10}H_{18}B_2N_6$: B, 8.74 (8.86). ^1H NMR (DMSO-d_6, δ): 3.43 (s, 4H, NCH_2), 2.84 (s, 12H, NCH_3). ^{11}B NMR (DMSO-d_6, δ): −18.0 (br d). $^{13}C\{^1H\}$ NMR (DMSO-d_6, δ): 54.22 (NCH_2), 48.75 (NCH_3). IR (KBr, cm^{-1}): ν(B−H), 2464; ν(C≡N), 2217.

DABCO·2BH(CN)$_2$ (1k). DABCO (0.747 g; 6.66 mmol) was added to a stirred suspension of **1a** (2.150 g; 12.80 mmol) in acetonitrile (7 mL). After 20 h stirring at room temperature, the mixture was filtered and the product was washed with ether (3 × 5 mL) and dried in a N_2 stream. Yield: 1.297 g (85%). Anal. Found (calcd) for $C_{10}H_{14}B_2N_6$: B, 8.99 (9.01). ^1H NMR (DMSO-d_6, δ): 3.46 (s, 12H, NCH_2). ^{11}B NMR (DMSO-d_6, δ): −18.0 (br). $^{13}C\{^1H\}$ NMR (DMSO-d_6, δ): 48.37 (NCH_2). IR (KBr, cm^{-1}): ν(B−H), 2453; ν(C≡N), 2222.

4-(*N*-Piperidino)pyridine·BH(CN)$_2$ (1l). Piperidine (0.591 g, 6.95 mmol) was added to a solution of **1a** (1.130 g, 6.73 mmol) in acetonitrile (7 mL) at room temperature. The deep violet solution was evaporated to dryness after 0.5 h. The solid residue was suspended in ether, the suspension was filtered and extracted with ether (10 × 25 mL) then dried in a N_2 stream. The product was a violet solid which slowly turned into brown. Yield: 0.993 g (65%). Anal. Found (calcd) for $C_{12}H_{15}BN_4$: B, 4.84 (4.78). ^1H NMR ($CDCl_3$, δ): 7.99 (d, 2H, 2(6)-CH), 6.77 (d, 2H, 3(5)-CH), 3.58 (m, 4H, 2′(6′)-CH_2), 1.68−1.84 (m, 6H, 3′(5′)- and 4′-CH_2). ^{11}B NMR ($CDCl_3$, δ): −20.3 (d, J = 105 Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 155.21 (4-C), 145.61 (2(6)-CH), 107.81 (3(5)-CH), 47.64 (2′(6′)-CH_2), 25.27 (3′(5′)-CH_2), 23.84 (4′-CH_2). IR (KBr, cm^{-1}): ν(B−H), 2464; ν(C≡N), 2212, 2208.

[py·BH(CNEt)$_2$](BF$_4$)$_2$ (2b). A solution of **1b** (3.920 g; 27.42 mmol) in dichloromethane (26 mL) was added to a stirred solution of Et_3OBF_4 (13.270 g; 69.85 mmol) in dichloromethane (5 mL), and the mixture was refluxed for 25 h and stirred at room temperature overnight. The lower layer of the biphasic system formed in the reaction slowly transformed into a white solid, which was collected on a filter, washed with dichloromethane (3 × 15 mL) and then with ether (2 × 20 mL), and dried in a N_2 stream. Yield: 9.265 g (90%). Anal. Found (calcd) for $C_{11}H_{16}B_3F_8N_3$: B, 8.83 (8.66). ^1H NMR (CH_2Cl_2, δ): 8.71 (br, 2H, 2(6)-CH), 8.44 (br, 1H, 4-CH), 7.90 (br, 2H, 3(5)-CH), 3.95 (br, 4H, Et-CH_2), 1.39 (br, 6H, Et-CH_3).

[Q·BH(CNEt)$_2$](BF$_4$)$_2$ (2c). A solution of **1c** (2.295 g; 13.11 mmol) in dichloromethane (7 mL) was added to a stirred solution of Et_3OBF_4 (6.238 g; 32.84 mmol) in dichloromethane (2 mL) and the mixture was refluxed for 12 h and vigorously stirred at room-temperature overnight. The precipitate was collected on a filter, washed with dichloromethane (2 × 6 mL) and then with ether (4 × 6 mL) and dried in a N_2 stream. Yield: 4.680 g (88%). Anal. Found (calcd) for $C_{13}H_{24}B_3F_8N_3$: B, 8.12 (7.97). ^1H NMR (CH_2Cl_2, δ): 4.08 (q, 4H, Et-CH_2), 3.29 (br, 6H, NCH_2), 1.99 (br, 1H, CH), 1.81 (br, 6H, CCH_2), 1.44 (t, 6H, Et-CH_3).

[Me$_3$N·BH(CNEt)$_2$](BF$_4$)$_2$ (2d). A solution of **1d** (3.504 g; 28.50 mmol) in dichloromethane (10 mL) was added to a stirred solution of Et_3OBF_4 (13.597 g; 71.57 mmol) in dichloromethane (5 mL), and the mixture was refluxed for 30 h and vigorously stirred at room-temperature overnight. The volatile components of the mixture were evaporated in vacuo, and the residual viscous oil was triturated with ether. Repeated evaporation in vacuo resulted in the formation of a semisolid. It was transferred to a filter and washed with a small amount of acetonitrile (2 mL). Yield: 4.459 g (44%). Anal. Found (calcd) for $C_9H_{20}B_3F_8N_3$: B, 9.30 (9.14). ^1H NMR (CH_2Cl_2, δ): 4.21 (br, 4H, Et-CH_2), 3.05 (br, 9H, NCH_3), 1.57 (br, 6H, Et-CH_3).

{py·BH[C(OH)═NHEt]$_2$}(BF$_4$)$_2$ (3b). Water (65 mg, 3.6 mmol) was added to a suspension of **2b** (0.336 g, 0.897 mmol) in ether (3 mL). After 10 min of vigorous stirring, the ether was discarded and the residual syrup was solidified by keeping under vacuum. It was then suspended in ether (10 mL), the suspension was stirred, the insoluble parts were collected on a filter, washed with ether (2 × 2 mL) and dried in a N_2 stream. Yield: 0.333 g (90%). Anal. Found (calcd) for $C_{11}H_{20}B_3F_8N_3O_2$: B, 8.02 (7.90). ^1H NMR (acetone-d_6, δ): 11.0 (br, OH) 8.81 (m, 2H, 2(6)-CH), 8.55 (tt, 1H, 4-CH), 8.07 (m, 2H, 3(5)-CH), 6.30 (br, NH), 3.36 (m, 4H, Et-CH_2), 1.08 (t, 6H, Et-CH_3).

{Q·BH[C(OH)═NHEt]$_2$}(BF$_4$)$_2$ (3c). The procedure described for **3b** was carried out using water (63 mg, 3.50 mmol) and a suspension of **2c** (0.355 g, 0.873 mmol) in ether (3 mL). Yield: 0.360 g (95%). Anal. Found (calcd) for $C_{13}H_{28}B_3F_8N_3O_2$: B, 7.41 (7.32). ^1H NMR (acetone-d_6, δ): 3.40 (m, 4H, Et-CH_2), 3.19 (m, 6H, Q-NCH_2), 1.99 (sept, 1H, CH), 1.84 (m, 6H, Q-CCH_2), 1.16 (t, 6H, Et-CH_3).

{Me$_3$N·BH[C(OH)═NHEt]$_2$}(BF$_4$)$_2$ (3d). The procedure described for **3b** was carried out using water (87 mg, 4.83 mmol) and a suspension of **2d** (0.427 g, 1.20 mmol) in ether (3 mL). To solidify the product, the ether was removed in vacuo, and the residue was partially redissolved in CH_2Cl_2 (3 mL) and then evaporated to dryness. The solid product was collected on a filter using ether, washed with ether (2 × 2 mL), and dried in a N_2 stream. Yield: 0.433 g (92%). Anal. Found (calcd) for $C_9H_{24}B_3F_8N_3O_2$: B, 8.38 (8.30). ^1H NMR (acetone-d_6, δ): 9.5 (br, OH), 6.2 (br, NH), 4.36 (m, 4H, Et-CH_2), 3.26 (s, 9H, NCH_3), 1.12 (t, 6H, Et-CH_3).

{py·BH[C(OH)═NHEt][C(O)NHEt]}(PF$_6$) (4b). 2b (0.320 g; 0.854 mmol) was dissolved in water (1.6 mL) and $NaPF_6$ solution (4.70 mL, 0.40 M) was added. The precipitate was redissolved by heating to

gentle boiling and dilution with water (2 mL). The clear solution was allowed to cool to room temperature for 3 h while the product crystallized as colorless needles. The mixture was then cooled to 0 °C, the crystals were collected on a filter, washed with 0 °C water (3 × 1 mL), and dried with air suction. Yield: 0.215 g (66%). Anal. Found (calcd) for $C_{11}H_{19}BF_6N_3O_2P$): B, 2.87 (2.84). ^{1}H NMR (acetone-d_6, δ): 8.86 (d, 2H, 2(6)-CH), 8.57 (tt, 1H, 4-CH), 8.46 (br s, OH and NH), 8.10 (dd, 3(5)-CH), 3.36 (m, 4H, Et-CH_2), 1.07 (t, 6H, Et-CH_3). ^{11}B NMR (acetone-d_6, δ): −11.3 (d, J = 101 Hz). ^{13}C{^{1}H} NMR (acetone-d_6, δ): 149.95 (2(6)-CH), 145.53 (4-CH), 129.19 (3(5)-CH), 35.48, 35.35 (Et-CH_2), 14.18 (Et-CH_3). IR (KBr, cm^{-1}): ν(N−H), 3414, 3245; ν(B−H), 2415; ν(C═N), 1559.

{Q·BH[C(OH)═NHEt][C(O)NHEt]}(PF$_6$) (4c). The procedure described for **4b** was followed using **2c** (0.278 g; 0.683 mmol) in water (0.9 mL) and $NaPF_6$ solution (3.75 mL, 0.40 M). Yield: 0.180 g (64%). Anal. Found (calcd) for $C_{13}H_{27}BF_6N_3O_2P$): B, 2.66 (2.62). ^{1}H NMR (acetone-d_6, δ): 3.43 (m, 4H, Et-CH_2), 3.23 (m, 6H, Q-NCH_2), 1.87 (m, 6H, Q-CCH_2), 1.18 (t, 6H, Et-CH_3) (the CH-septet coincides with the solvent signal). ^{11}B NMR (acetone-d_6, δ): −10.6 (d, J = 105 Hz). ^{13}C{^{1}H} NMR (acetone-d_6, δ): 53.11 (Q-NCH_2), 35.67 (Et-CH_2), 24.78 (Q-CCH_2), 20.14 (Q-CH), 14.02 (Et-CH_3). IR (KBr, cm^{-1}): ν(N−H), 3411; ν(B−H), 2441; ν(C═N), 1558.

{Me$_3$N·BH[C(OH)═NHEt][C(O)NHEt]}(PF$_6$) (4d). Procedure described for **4b** was followed using **2d** (0.360 g; 1.015 mmol) in water (1.8 mL) and $NaPF_6$ solution (5.50 mL, 0.40 M) and heating to 70 °C. Yield: 0.255 g (70%). Anal. Found (calcd) for $C_9H_{23}BF_6N_3O_2P$: B, 3.03 (2.99). ^{1}H NMR (acetone-d_6, δ): 9.80 and 9.11 (2 br s, OH and NH), 3.50 (m, 4H, Et-CH_2), 2.87 (s, 9H, NCH_3), 1.22 (t, 6H, Et-CH_3). ^{11}B NMR (acetone-d_6, δ): −9.9 (d, J = 105 Hz). ^{13}C{^{1}H} NMR (acetone-d_6, δ): 52.92 (NCH_3), 35.94, 35.80 (Et-CH_2), 14.05 (Et-CH_3). IR (KBr, cm^{-1}): ν(N−H), 3413, 3242; ν(B−H), 2467, 2434; ν(C═N), 1646, 1560.

{pic·BH[C(OH)═NHEt][C(O)NHEt]}(PF$_6$) (4e). 1e (0.560 mg, 3.567 mmol) was added to a solution of Et_3OBF_4 (1.825 g, 9.606 mmol) in CH_2Cl_2 (1.6 mL), the mixture was refluxed for 18 h and then the volatile components were removed in vacuo, yielding a viscous oil. The oil was then dissolved in water (8 mL), and $NaPF_6$ solution was added (29 mL, 0.4 M). The mixture was warmed to 60 °C and cooled to r.t. three times, and then it was placed in an ice−water bath for 0.5 h. The white crystalline product was filtered, washed with 0 °C water (3 × 2 mL), and dried by air suction. Yield: 0.970 mg (69%). Anal. Found (calcd) for $C_{12}H_{21}BF_6N_3O_2P$: B, 2.77 (2.74). ^{1}H NMR (acetone-d_6, δ): 8.65 (d, 2H, 2(6)-CH), 8.40 (br, OH+NH), 7.90 (d, 2H, 3(5)-CH), 3.36 (m, 4H, Et-CH_2), 2.65 (s, 3H, pic-CH_3), 1.07 (t, 6H, Et-CH_3). ^{11}B NMR (acetone-d_6, δ): −10.3 (d, J = 96 Hz). ^{13}C{^{1}H} NMR (acetone-d_6, δ): 158.88 (4-C), 149.04 (2(6)-CH), 129.54 (3(5)-CH), 35.44 (Et-CH_2), 21.74 (pic-CH_3), 14.20 (Et-CH_3).

{py·BH[C(OMe)═NHEt]$_2$}(BF$_4$)$_2$ (5b). 2b (1.020 g; 2.723 mmol) was dissolved in methanol (3 mL). After complete dissolution (∼3 min) the volatile components were evaporated in vacuo. The residue was suspended in ether (5 mL), the suspension was filtered, and the white crystals were washed with ether (3 × 5 mL) and dried in a N_2 stream. Yield: 1.104 g (92%). Anal. Found (calcd) for $C_{13}H_{24}B_3F_8N_3O_2$: B, 7.26 (7.39). ^{1}H NMR (acetone-d_6, δ): 9.85 (br s, 2H, NH), 8.96 (d, 2H, 2(6)-CH), 8.69 (tt, 1H, 4-CH), 8.21 (dd, 2H, 3(5)-CH), 4.32 (s, 6H, OMe), 3.65 (m, 4H, Et-CH_2), 1.24 (t, 6H, Et-CH_3). ^{13}C{^{1}H} NMR (acetone-d_6, δ): 149.71 (2(6)-CH), 147.03 (4-CH), 130.37 (3(5)-CH), 62.01 (OMe), 39.70 (Et-CH_2), 12.87 (Et-CH_3). IR (KBr, cm^{-1}): ν(N−H), 3422; ν(B−H), 2474; ν(C═N), 1628.

{Q·BH[C(OMe)═NHEt]$_2$}(BF$_4$)$_2$ (5c). Procedure described for **5b** was carried out using **2c** (0.525 g; 1.291 mmol). Yield: 0.580 g (95%). Anal. Found (calcd) for $C_{15}H_{32}B_3F_8N_3O_2$: B, 6.80 (6.89). ^{1}H NMR (acetone-d_6, δ): 9.85 (br, NH), 4.51 (s, 6H, OCH_3), 3.81 (m, 4H, Et-CH_2), 3.46 (m, 6H, Q-NCH_2), 1.94 (m, 6H, Q-CCH_2), 1.31 (t, 3H, Et-CH_3), (the Q-CH septet coincides with the solvent signal). ^{11}B NMR (acetone-d_6, δ): −0.3 (s, BF_4) −10.6 (br d, cation). ^{13}C{^{1}H} NMR (acetone-d_6, δ): 63.09 (OCH_3), 53.22 (Q-NCH_2), 41.03 (Et-CH_2), 24.59 (Q-CCH_2), 19.98 (Q-CH), 13.63 (Et-CH_3). IR (KBr, cm^{-1}): ν(N−H), 3422; ν(B−H), 2476; ν(C═N), 1617.

{Me$_3$N·BH[C(OMe)═NHEt]$_2$}(BF$_4$)$_2$ (5d). Procedure described for **5b** was carried out using **2d** (0.482 g; 1.36 mmol). Yield: 0.533 g (94%). Anal. Found (calcd) for $C_{11}H_{28}B_3F_8N_3O_2$: B, 7.73 (7.74). ^{1}H NMR (acetone-d_6, δ): 9.94 (br, NH), 4.57 (s, 6H, OCH_3), 3.86 (m, 4H, Et-CH_2), 3.07 (s, 9H, NCH_3), 1.33 (t, 6H, Et-CH_3). ^{13}C{^{1}H} NMR (acetone-d_6, δ): 63.36 (OCH_3), 53.11 (NCH_3), 41.20 (Et-CH_2), 13.70 (Et-CH_3). IR (KBr, cm^{-1}): ν(N−H), 3422; ν(B−H), 2471; ν(C═N), 1618.

{pic·BH[C(OMe)═NHEt]$_2$}(BF$_4$)$_2$ (5e). 1e (0.506 g; 3.22 mmol) was added to a solution of Et_3OBF_4 (1.835 g; 9.66 mmol) in dichloromethane (2.5 mL), the mixture was refluxed for 32 h, and then the volatile components were removed in vacuo. Methanol (10 mL) was added to the residue, and after complete dissolution the solvent was evaporated in vacuo. The residue, solidified by treatment with ether (10 mL), was collected on a filter, washed with ether (2 × 10 mL) and dried in N_2 stream. Yield: 1.268 g (88%). Anal. Found (calcd) for $C_{14}H_{26}B_3F_8N_3O_2$: B, 7.12 (7.16). ^{1}H NMR (acetone-d_6, δ): 9.77 (br s, 2H, NH), 8.74 (d, 2H, 2(6)-CH), 7.99 (d, 2H, 3(5)-CH), 4.30 (s, 6H, OMe), 3.64 (m, 4H, Et-CH_2), 2.69 (s, 3H, 4-CH_3), 1.24 (t, 6H, Et-CH_3). ^{11}B NMR (acetone-d_6, δ): −0.3 (s, BF_4), −10.3 (br d, cation). ^{13}C{^{1}H} NMR (acetone-d_6, δ): 160.93 (4-C), 148.58 (2(6)-CH), 130.76 (3(5)-CH), 61.93 (OMe), 39.63 (Et-CH_2), 22.03 (4-CH_3), 12.86 (Et-CH_3). IR (KBr, cm^{-1}): ν(N−H), 3336; ν(B−H), 2476; ν(C═N), 1697.

{py·BH[C(NH$_2$)═NHEt]$_2$}(BF$_4$)$_2$ (6b). 2b (2.280 g; 6.085 mmol) was dissolved in liquid ammonia (∼3 mL) in a −78 °C bath, and the stirred solution was refluxed for 0.5 h. The solvent was then allowed to evaporate moderately. The solid residue was kept under vacuum for 15 min and then suspended in ether (20 mL). The suspension was filtered, and the product was washed with ether and dried in a N_2 stream. To solidify the evaporation residue, much longer time under vacuum and more thorough treatment with ether was required than in cases of raw **6c** or **6d**. Yield: 2.387 g (96%). Anal. Found (calcd) for $C_{11}H_{22}B_3F_8N_5$: B, 7.79 (7.93). ^{1}H NMR (acetone-d_6, δ): 8.90 (d, 2H, 2(6)-CH), 8.57 (tt, 1H, 4-CH), 8.10 (m, 2H, 3(5)-CH), 3.43 (dq, 4H, Et-CH_2), 3.25 (br, NH), 1.25 (t, 6H, Et-CH_3). ^{11}B NMR (acetone-d_6, δ): −0.26 (s, BF_4), −5.8 (br d, cation). ^{13}C{^{1}H} NMR (acetone-d_6, δ): 149.09 (2(6)-CH), 145.80 (4-CH), 129.22 (3(5)-CH), 37.96 (NCH_2), 12.81 (Et-CH_3). IR (KBr, cm^{-1}): ν(N−H) 3344, 3245, 3163; ν(B−H), 2445; ν(C═N), 1670, 1600.

{Q·BH[C(NH$_2$)═NHEt]$_2$}(BF$_4$)$_2$ (6c). The procedure described for **6b** was carried out using **2c** (2.285 g; 5.619 mmol). Yield: 2.365 g (96%). Anal. Found (calcd) for $C_{13}H_{30}B_3F_8N_5$: B, 7.27 (7.36). ^{1}H NMR (acetone-d_6, δ): 8.52, 8.16, 8.12 (3 br s, NH), 3.44 (dq, 4H, Et-CH_2), 3.40 (m, 6H, Q-NCH_2), 1.94 (m, 6H, Q-CCH_2), 1.28 (t, 6H, Et-CH_3) (the Q-CH septet coincides with the solvent signal). ^{11}B NMR (acetone-d_6, δ): −0.24 (s, BF_4), −4.3 (br d, cation). ^{13}C{^{1}H} NMR (acetone-d_6, δ): 53.03 (Q-NCH_2), 38.20, 38.07 (Et-CH_2), 24.64 (Q-CCH_2), 20.09 (CH), 12.78 (Et-CH_3). IR (KBr, cm^{-1}): ν(N−H) 3444, 3369, 3288, 3172; ν(B−H), 2463; ν(C═N), 1683, 1595.

{Me$_3$N·BH[C(NH$_2$)═NHEt]$_2$}(BF$_4$)$_2$ (6d). The procedure described for **6b** was carried out using **2d** (1.920 g; 5.413 mmol). Yield: 1.985 g (94%). Anal. Found (calcd) for $C_9H_{26}B_3F_8N_5$: B, 8.42 (8.34). ^{1}H NMR (acetone-d_6, δ): 8.38 (br, EtNH), 8.06 (br, NH_2), 3.50 (m, 4H, Et-CH_2), 3.02 (s, 9H, NCH_3), 1.31 (t, 6H, Et-CH_3). ^{13}C{^{1}H} NMR (acetone-d_6, δ): 52.95 (NCH_3), 38.29, 38.12 (Et-CH_2), 12.75 (Et-CH_3). IR (KBr, cm^{-1}): ν(N−H) 3432, 3296, 3168; ν(B−H), 2457; ν(C═N), 1683, 1599.

{py·BH[C(NEt$_2$)═NHEt]$_2$}(PF$_6$)$_2$ (7b). Diethylamine (3 mL) and acetonitrile (2 mL) were added to **2b** (0.505 g; 1.348 mmol), and the volatile components were removed in vacuo after 3.5 h stirring at r.t. Water (3 mL) and $NaPF_6$ solution (7 mL 0.4 M) were added, and the mixture was vigorously agitated for 2 h. The solid precipitate was collected on a filter, washed with water, and dried in a N_2 stream. Yield: 0.465 g (54%). Anal. Found (calcd) for $C_{19}H_{38}BF_{12}N_5P_2$: B, 1.73 (1.70). ^{1}H NMR (acetone-d_6, δ): 9.14 (br, NH), 8.70 (m, 1H, 4-CH), 8.20 (m, 2H, 2(6)-CH), 7.56 (m, 2H, 3(5)-CH), 3.76 (q, 4H, HNEt-CH_2), 3.48−3.31 (m, 8H, NEt-CH_2), 1.35 (t, 6H, HNEt-CH_3), 1.19 (m, 12H, NEt-CH_3). ^{11}B NMR (acetone-d_6, δ): −9.0 (br d). ^{13}C-{^{1}H} NMR (acetone-d_6, δ): 146.6, 146.5 (4-C and 2(6)-CH), 129.99 (3(5)-CH), 48.87, 43.72, 41.96 (Et-CH_2), 15.11, 13.21, 11.39 (Et-CH_3).

{Q·BH[C(NEt$_2$)═NHEt]$_2$}(PF$_6$)$_2$ (7c). Diethylamine (3 mL) was added to **2c** (0.540 g; 1.328 mmol), and when the starting white solid

completely transformed into a dense orange oil (immiscible with diethylamine) (~0.5 h), the volatile components were removed in vacuo. The residue was dissolved in water (6 mL), and $NaPF_6$ solution (4.8 mL 0.40 M) was added and a pale orange amorphous semisolid precipitated. The mixture was allowed to stand at 5 °C overnight while the product solidified. It was collected on a filter, washed with water (4 × 3 mL), and dried by air suction. Yield: 0.580 g (65%). Anal. Found (calcd) for $C_{21}H_{46}BF_{12}N_5P_2$: B, 1.63 (1.61). ^{1}H NMR (acetone-d_6, δ): 10.56 (br, NH), 4.20 (q, 4H, HNEt-CH_2), 4.13−3.91 (m, 8H, Et-CH_2), 3.51 (m, 6H, Q-NCH_2), 2.15 (sept, 1H, Q-CH), 2.00 (m, 6H, Q-CCH_2), 1.6−1.4 (m, 18H, Et-CH_3). ^{11}B NMR (acetone-d_6, δ): −3.5 (d, J = 110). ^{13}C{^{1}H} NMR (acetone-d_6, δ): 54.08 (Q-NCH_2), 53.28, 46.67, 43.19 (Et-CH_2), 14.37, 14.05, 13.35 (Et-CH_3). IR (KBr, cm^{-1}): ν(N−H)3417, 3299; ν(B−H), 2507; ν(C═N), 1631, 1579.

Results and Discussion

Amine-dicyanohydroboranes. The first representatives of amine dicyanohydroboranes (A·$BH(CN)_2$) were prepared in our laboratory[25] by oxidation of $Li[BH_2(CN)_2]$ using amine perbromides in the presence of the corresponding amines (eq 1).

$$Li[BH_2(CN)_2] + A{\cdot}Br_2 + A \xrightarrow[A = 4\text{-CN-py (\mathbf{a}), py (\mathbf{b})}]{} \underset{\mathbf{1}}{A{\cdot}BH(CN)_2} + LiBr + A{\cdot}HBr \quad (1)$$

Investigation of this reaction, originally established for pyridine and 4-CN-pyridine, was continued in order to obtain complexes of dicyanohydroborane with a broad variety of amines (further pyridine bases as well as secondary and tertiary alkylamines and diamines). Unlike 4-CN-pyridine and pyridine, many of these amines do not form isolable perbromides, therefore, reactions were carried out by adding the acetonitrile solution of $Li[BH_2(CN)_2]$ to a mixture of two equimolar amines and one equimolar bromine in acetonitrile. We found that these reactions lead to the formation of amine dicyanohydroboranes **1c**−**k** as the most abundant products. ^{11}B (and sometimes ^{1}H) NMR monitoring of the reactions showed that the reactions, particularly those involving picoline and piperidine, were considerably slower than the formation of **1a**,**b**, and side reactions took place. In the reaction involving piperidine 54% of $Li[BH_2(CN)_2]$ was consumed after 8 h at 50 °C, whereas the reaction involving 4-cyanopyridine was complete in 30 min at 0 °C. On the basis of similar results starting from isolated amine perbromides (when it was feasible) and the reactivity order, showing the most nucleophilic amines to be the most sluggish ones, amine perbromides are assumed to be the reactive species. It should be noted, that in the presence of DABCO, only the dinuclear complex DABCO·$2BH(CN)_2$ could be observed and isolated in a quite low yield. Attempts aimed at the isolation of amine dicyanohydroboranes **1c**−**k** from the reaction mixtures were inefficient on preparative scale. However, most of them could be obtained in multigram quantities with fairly good overall yields via 4-CN-py·$BH(CN)_2$ (**1a**) in base exchange reactions (eq 2, a), taking the advantage of low basicity of 4-CN-py toward $BH(CN)_2$ and the fact that the isolated yield of **1a** could be improved to 88% by modification of the original procedure.

$$A{\cdot}BH(CN)_2 + A' \longrightarrow A'{\cdot}BH(CN)_2 \quad (2)$$

a) A = 4-CN-py (**a**); A' = Q (**c**), Me_3N (**d**), 4-pic (**e**), DMAP (**f**), morpholine (**i**) TMEDA/2 (**j**), DABCO/2 (**k**)

b) A = Me_3N (**d**); A' = pip (**g**), Et_2NH (**h**)

On the other hand, in analogous experiments involving secondary amines (i.e. piperidine, diethylamine and morpholine) aminodecyanation also took place on the aromatic ring (eq 3),

$$RRNH + \underset{\mathbf{1a}}{NC\text{-}C_5H_4N{\cdot}BH(CN)_2} \xrightarrow[RRNH = \text{piperidine (\mathbf{g}), } Et_2NH \text{ (\mathbf{h}), morpholine (\mathbf{i})}]{} \begin{cases} \xrightarrow{-HCN} \underset{\mathbf{1l}}{RRN\text{-}C_5H_4N{\cdot}BH(CN)_2} \text{ (if RRNH=piperidine)} \\ \longrightarrow \underset{\mathbf{1g\text{-}i}}{RRHN{\cdot}BH(CN)_2} \end{cases} \quad (3)$$

accompanied by the presence of an intensive blue color throughout the whole course of the reaction turning into rusty brown upon evaporation. Landquist observed a resembling reaction, showing similar color changes, between 4-cyano-1-methylpyridinium iodide and methylamine or hydrazine in water.[28] The indisputable verification of the mechanism of this nucleophilic aromatic substitution reaction would be far beyond the scope of this work. However, based on our observations, two of the four theoretical pathways[29] can be excluded: the S_N1 mechanism is hard to believe because the cyano group was stable in reactions with other amines, and the benzyne mechanism is unlikely because 3-aminopyridine borane complexes (product of the *cine*-substitution) were not detectable by ^{1}H NMR in the reaction mixtures. Of the remaining two options, the radical mechanism (S_NR1) seems less probable, as this mechanism, in the cases of dicyanopyridines,[30] required photochemical induction and no substitution took place via thermal activation. Furthermore, these reactions usually resulted in hydrodecyanation predominantly over aminodecyanation, due to the efficient hydrogen donor character of the amine radicals, and we could not observe pyridine dicyanoborane in the reaction mixtures. On the other hand, the S_NAr mechanism is favored to operate when (a) the leaving group is one with strong $-I$ effect or (b) there is a strong elecron-withdrawing group (here >$NBH(CN)_2$) situated ortho or para to the leaving group. Furthermore, S_NAr reactions are catalyzed by strong bases.[29] Based on these considerations and resembling reactions in the literature,[28,31] we assume that the mechanism of this aminodecyanation is, at least predominantly, S_NAr, though our direct observations were not eligible to decide whether the colored species is radical or the corresponding Meisenheimer complex.

The proportions of aminodecyanation and base exchange reactions varied markedly from amine to amine, i.e., 4-(piperidine-1-yl)pyridine dicyanohydroborane (**1l**) was isolated in 65% yield, 4-*N*,*N*-diethylaminopyridine dicyanohydroborane was present in ca. 30 mol % besides 70 mol % $Et_2NH{\cdot}BH(CN)_2$, whereas formation of 4-(morpholine-1-yl)pyridine complex did not reach 10 mol %. The same experiments carried out in THF showed considerable suppression of aminodecyanation, probably due to the much lower polarity of the solvent, whereas the color changes were observed in THF as well. After all, piperidine and diethylamine complexes of dicyanohydroborane (**1g**,**h**) were synthesized from $Me_3N{\cdot}BH(CN)_2$ in base exchange reactions (eq 2, b).

The infrared spectra of amine dicyanohydroboranes give characteristic bands in the 2431−2482 cm^{-1} (ν(BH)) and in

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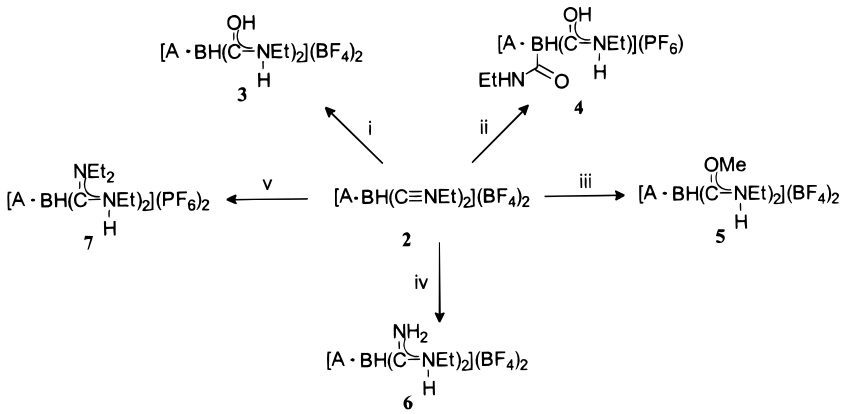
Scheme 1 [a]



[a] Reagents and conditions: (i) H_2O/Et_2O, r.t., <5 min; (ii) H_2O, $NaPF_6$, r.t.; (iii) MeOH, r.t., <5 min; (iv) Liq. NH_3, −33 °C, 5 min; (v) Et_2NH, r.t., 5−10 min, Then H_2O, $NaPF_6$.

the 2212−2225 cm^{-1} (ν(C≡N)) region in accordance with the known compounds.[25] These wavenumbers are considerably larger (ca. 45 cm^{-1} for ν(BH) and ca. 20 cm^{-1} for ν(CN)) than those in amine cyanodihydroboranes. Complexes of secondary amines give strong sharp bands also in the 3110−3119 cm^{-1} (ν(NH)) region. ^1H and ^{13}C NMR spectra represent the nuclei of the complexing amines only, as protons and carbons adjacent to boron atoms give very broad signals due to the quadrupole moment of boron. These spectra show considerable downfield shift of the signals relative to those in the free bases, due to the complexation. The effect is more expressed for the nuclei close to nitrogen. Nevertheless, ^1H NMR spectra of complexes of cyclic amines were not straightforward, their elucidation necessitated $^{13}C-^1H$ and $^1H-^1H$ correlation experiments. It can be concluded, that both in pip·$BH(CN)_2$ and morpholine·$BH(CN)_2$ the ring possesses a quite rigid chair conformation in solution with borane moiety in equatorial position, and this conformation is stable on the NMR time scale at room temperature. No other isomer could be observed in quantifiable amount. ^{11}B NMR spectra of amine dicyanohydroboranes show well-resolved doublets except those recorded in DMSO-d_6. Chemical shifts fall generally between −18 and −19 ppm for the complexes of tertiary amines (except complexes of Me_3N possessing the least, and 4-aminopyridines with the most shielded boron), and between −21 and −23 ppm for the complexes of secondary amines. Coupling constants ($^1J_{BH}$) are in a narrow region (103−110 Hz) and the more shielded borons generally show smaller J values.

Ethylation of Amine-dicyanohydroboranes. A number of [amine-bis(ethylnitrilium)hydroboron(2+)] tetrafluoroborates (**2**) could be synthesized from amine dicyanohydroboranes **1b**−**e** by Et_3OBF_4 (eq 4), and most of them (**2b**−**d**) could be isolated,

$$\underset{\mathbf{1}}{A{\cdot}BH(CN)_2} + 2\ Et_3OBF_4 \xrightarrow[A = py\ (\mathbf{b}),\ Q\ (\mathbf{c}),\ Me_3N\ (\mathbf{d}),\ pic\ (\mathbf{e})]{CH_2Cl_2,\ reflux,\ 12\text{-}32\ h} \underset{\mathbf{2}}{[A{\cdot}BH(CNEt)_2](BF_4)_2} + 2\ Et_2O \qquad (4)$$

since they precipitated from the reaction mixtures. ^1H NMR monitoring of the reaction mixtures, showing significant amounts of **1** and/or **2** besides the intermediate [amine-cyano(ethylnitrilium)hydroboron(1+)] cations during the whole reaction period (even when only one molar eqivalent of Et_3OBF_4 was employed), led to the conclusion that the rates of the consecutive steps are surprisingly close to each other, and the isolation of the intermediates does not seem feasible. The ethylation reaction of cyano groups in amine dicyanohydroboranes is considerably slower than that in the corresponding amine cyanodihydroboranes,[16] probably due to the strong electron-withdrawing effect of the cyano or ethylnitrilium group. Being a second-order reaction, the ethylation can be substantially accelerated by increasing the amount of Et_3OBF_4. Though unreacted Et_3OBF_4 does not give rise to contaminants during the preparation of their derivatives (**3**−**7**) described below, to make the isolation of **2** easier, it is advantageous to apply Et_3OBF_4 in low excess, as larger amounts prevent the precipitation of **2**.

Analogous reactions were attempted with further amine dicyanohydroboranes (**1f**−**i**) also. ^1H and ^{11}B NMR monitoring showed that at the end of these reactions boron was detectable in the form of BF_4^- ions and Lewis base complexes of BF_3 only, accompanied by intensive browning of the reaction mixtures. During the course of the reactions of **1f** and **1g** the expected ethylated products **2f**,**g** could be observed by ^1H NMR as intermediates in low concentrations. As a comparison, the ethylation of amine cyanodihydroboranes DMAP·BH_2CN, pip·BH_2CN, $Et_2NH{\cdot}BH_2CN$, and $MeNH(CH_2)_2NHMe{\cdot}(BH_2CN)_2$ was attempted under similar conditions. The reactions yielded the expected ethylnitrilium salts in rather fast reactions and without the appearance of considerable amounts of sideproducts. Thus, it can be concluded that ethylation failed in cases when the boron was simultaneously substituted with two cyano groups and an amine which was a strong Lewis base toward BHX_2.

Ethylation of diamine-bis(dicyanohydroboranes) (**1j**,**k**) could not be carried out in homogeneous phase due to their poor solubility in every inert solvents we tested (chlorohydrocarbons, benzene, toluene), consequently the monitoring of the reactions were not feasible, and our attempts to isolate any ethylated product or solvolytic derivative remained unsuccessful.

Nucleophilic Addition Reactions. Water, methanol, ammonia and diethylamine readily add to [amine-bis(ethylnitrilium)hydroboron(2+)] tetrafluoroborates (**2**) to yield the corresponding bis(*C*-hydroxy-*N*-ethylimidate) (**3**), bis(*C*-methoxy-*N*-ethylimidate) (**5**), bis(ethylamidine) (**6**), and bis(triethylamidine) (**7**) derivatives, respectively (Scheme 1), even in the presence of Et_3OBF_4.

[Amine-bis(*C*-hydroxy-*N*-ethylimidate)hydroboron(2+)] (**3**) salts cannot be prepared from water, due to the strong acidity of the dication. Thus, upon dissolution of **2** in water and then adding $NaPF_6$ results in the precipitation of [amine-*N*-ethylcarbamoyl(*C*-hydroxy-*N*-ethylimido)hydroboron(1+)] hexafluorophosphates (**4**) (Scheme 1, i and ii).

[Amine-bis(*C*-hydroxy-*N*-ethylimidate)hydroboron(2+)] tetrafluoroborates (**3**) were prepared after addition of water (2 molar equiv per ethylnitrilium group) to a vigorously stirred ethereal suspension of **2** (Scheme 1, i). Potentiometric titration proved these substances to be dibasic acids with $pK_{a1} < 1$ and $pK_{a2} = 3.1-3.3$ depending on the amine. In other words, the amide group in amine bis(*N*-ethylcarbamoyl)boranes is an extremely strong base, as the highest known corresponding pK_a values (those of the protonated acetamide and *N*-*n*-butylacetamide) are around −0.3.[32] The ease of the protonation of the amide group in such compounds is probably due to the strong electron releasing effect of the >N−B group toward the substituents on the boron.

Dissolving **2** in methanol yielded **5** in minutes (Scheme 1, iii). Unlike aliphatic and aromatic alkylnitrilium salts, **2** did not give ortho ester in methanol even after days.

Both types of [amine-bis(amidinium)hydroboron(2+)] salts (**6** and **7**) formed readily by dissolving **2** in liquid ammonia or diethylamine, respectively (Scheme 1, iv and v). The [amine-bis(triethylamidinium)hydroboron(2+)] cations were isolated as hexafluorophosphate salts, since our attempts to crystallize the tetrafluoroborate salts (the primary products of the reactions) remained unsuccessful.

Only a limited number of compounds has been prepared so far with imidate or amidinium groups on the boron. Morse et al. have shown that such derivatives are stable intermediates in the transformation of [amine-ethylnitriliumdihydroboron(1+)] tetrafluoroborates into amine-carboxyboranes.[33] Sutton et al. have put considerable effort into the synthesis of amine-alkyl(carboxy)boranes via e.g. [amine-alkyl(*C*-alkoxy-*N*-ethylnitrilium)hydroboron(1+)] cations,[15] but their attempts remained unsuccessful, similarly to those of Spielvogel et al.,[34] due to the presence of electron-donating alkyl group on the boron, which caused an increase in the hydridic character of the hydrogen attached to boron. Such compounds decomposed in acidic media instead of hydrolyzing into the corresponding carboxyborane complexes. Here we report the synthesis of various imidato and amidino complexes bearing hydrolytically more stable hydrogens on the boron. The detailed study of the acidic and alkaline hydrolytic behavior of **3**−**7** and their transformation into amine dicarboxyboranes and their derivatives is underway; for preliminary results, see ref 20.

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