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Synthesis and examination of amine-cyanocarboxyboranes, the boron analogues of α-cyanocarboxylic acids: X-ray structural study of the first lactam containing a boron atom in the lactam ring

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Abstract

The first representatives of chiral boron atom-containing amine-cyanomethoxycarbonyl boranes (A·BH(CN)COOMe) have been synthesized either from the corresponding amine-bromocyanomethoxycarbonylborane complexes with $[Bu_4N]CN$ or from $Me_3N·BH(CN)COOMe$ and an amine in a base-exchange reaction. Acid hydrolyses of methyl esters generated the free acids (A·BH(CN)COOH), which are isoelectronic to the α-cyano carboxylic acids. Their pK_a values and hydrolysis half-lives in acidic medium (that is rate of proton reduction) have been determined. Similarly to the alpha cyano carboxylic acids, the cyano group attached to the boron (in alpha position to the COOH group) increased the acid strength of carboxy boranes with 2.0–2.5 orders of magnitude. Independently from the type of the amine, pK_a values of the amine-cyanocarboxyboranes (6.34–5.82) decrease consistently with the increase of pK_b values of the amines. Hydrolytic decomposition rate of the alkylamine complexes increases with increasing pK_b values of the amines while the opposite was found for pyridine base complexes. When considering both types of the amines, hydrolysis half-lives of the complexes range over several orders of magnitude from 0.005 to 400 h. Based on these observations protonation of the amine nitrogen atom appears to be the rate determining step in the hydrolysis process. With loss of methanol, 2-NH_2-py·BH(CN)COOMe transformed into a five membered lactam derivative. X-ray diffraction revealed that the pyridine ring is coplanar with the five membered lactam ring. In the crystal two molecules are connected in a head to tail arrangement by strong intermolecular H-bonds between N(2)–H and the carbonyl oxygen (O1) with a donor and acceptor distance of 2.867(3) Å. Three new cyanomethoxycarbonylborates having the composition of $K[BH_n(CN)_{3-n}COOMe]$ ($n = 1, 2$) and $K[B(OH)(CN)_2$-COOMe] have also been synthesized and their properties examined.

Keywords: Amine-carboxyboranes; Borates; Complexes; Reduction; Acidity; Lactam

1. Introduction

Amine-carboxyboranes (A·BH_2COOH), on the basis of the C^+–B and CC–BN isoelectronic relationship, are considered as the boron analogues of protonated α-aminoacids [1] and carboxylic acids [2], respectively. Initiated by the similarities to α-aminoacids, amine-carboxyboranes and their precursor amine-cyanoboranes were tested in biological systems and significant antitumor [3] and antiinflammantory [4] activities were found.

Inspired by the initial results, several carboxylic acid derivatives (A·BH_2COX) of amine-carboxyboranes were synthesized including ester [5,6], amide [5,7], peptide [8] and hydroxamic acid [9] derivatives. Extensive

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biological and pharmacological studies revealed remarkable hypolipidemic [10,11], anticancer [8,10,12], antiosteoporotic [13] and antiinflammatory [10,11] activities. In addition, their mode of action has also been studied [12,14]. Recently these molecules [15] as well as carboranyl salts containing BH_2X (X = CN, COOH, COOMe) groups [16] have also been suggested as possible boron carriers to tumor cells for boron neutron capture therapy, although molecules with only one boron atom appear to be less suited for BNCT purposes.

However, only a limited number of amine-carboxyboranes containing an additional substituent on the boron atom [A·BH(Y)COX] have been synthesized so far [17]. Lately several new derivatives of amine-cyanoboranes and amine-carboxyboranes containing substituents on the boron atom have been prepared in our laboratory, such as amine-bromocyanoboranes (A·BH(Br)CN), amine-dibromocyanoboranes (A·BBr_2CN), salts of boronium ions having the composition of [AA′B(H)CN]$^+$ [18,19], amine-bromocarboxyboranes (A·BH(Br)COOH) and their ester derivatives (A·BH(Br)COOX, X = Me, Et, *i*-Pr) [2,6,20], amine-dibromocarboxyborane methyesters (A·BBr_2COOMe) [20], salts of diaminhydrocarboxyboronium cations [AA′B(H)COX]$^+$ (X = OH, OMe) [19], cyclic diazaborolidinium and diazaborinanium ions [[C_nN_2B](Y)COX] (n = 2–4; Y = H, Br; X = OH, OMe) [2], as well as amine-dicarboxyboranes and their ester and amide derivatives A·$BH(COX)_2$ (X = OH, OMe, NHEt) [21]. Our efforts were driven by the desire to find new or improved biological activities and to understand structure–activity relationships. After a short preliminary communication [22], we now report the synthesis and properties of a series of amine-cyanocarboxyboranes that contain a chiral boron atom and carry the two biologically active moieties A·B(H)CN and A·B(H)COOX in the same molecule.

2. Results and discussion

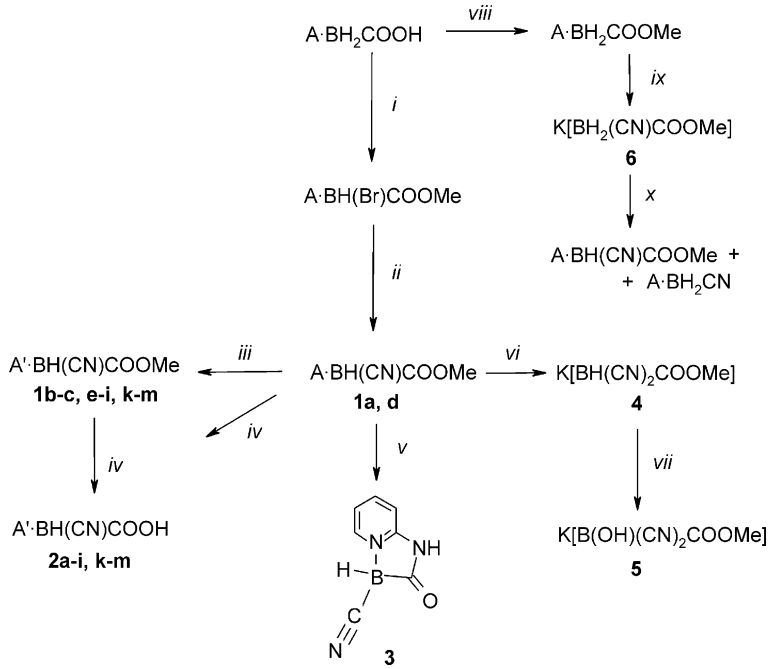
2.1. Synthesis of amine-cyano(methoxycarbonyl)boranes

A considerable number of reactions have been attempted for the synthesis of amine-cyanocarboxyboranes in our laboratory. One group of reactions was based on earlier examples for the formation of B–CN bond. These experiments included a variety of reactions between A·BH_2COOR or A·BH(Br)COOR (R = H, Me) and either $Hg(CN)_2$ [23], Me_3SiCN [24], or AgCN [25]. Considering the ability of trityl cation to abstract hydride from boron [26], the reaction between A·BH_2COOMe and Ph_3CCN [27] was also tested. Based on the analogy between amine-carboxyboranes and the aliphatic carboxylic acids, we examined the reaction between A·BH(Br)COOMe and acetone cyanohydrine, a reagent that has been used for the synthesis of α-cyanocarboxylic acids [28]. Encouraged by the successfull use of NBS for brominations [2,20], the conversion of A·BH_2COOMe into the cyano derivative with *N*-cyanosuccinimide was attempted. Unfortunately, all of the above mentioned reactions failed and led to, instead of the recovery of the starting materials, the rupture of the B–N bond and/or the formation of inseparable multicomponent reaction mixtures.

Finally, by using [Bu_4N]CN as a cyanide source, the trimethylamine and quinuclidine complex of BH(CN)COOMe have been successfully prepared from the corresponding BH(Br)COOMe complexes in acetonitrile solution (Scheme 1). Progress of the reaction was monitored by taking and analyzing consecutive samples with ^{1}H, ^{11}B, quantitative ^{13}C NMRs and IR spectroscopy. The NMR data indicated that, beside the main product **1d**, the isomer Me_3N·BH(NC)COOMe and a small amount of [Bu_4N][$BH(CN)_2$COOMe] have also been formed, the latter one due to the replacement of the amine by the cyanide ion. In spite of optimization of the reaction conditions and performing several separation steps the isolated product (**1d**) was still contaminated with 2–3% of the starting material, 3–4% of Me_3N·BH(NC)COOMe and 1–3% of [Bu_4N][$BH(CN)_2$COOMe]. The reaction that led to the formation of **1a** proceeded similarly but more slowly and the amine–cyanide exchange was significantly slower. **1a** could be conveniently purified by adding water to the evaporation residue of the reaction mixture as its water solubility is much lower than that of the side products. It was also observed that no substitution reaction took place in $CDCl_3$ as the NMR samples remained unchanged for more than two weeks. Thus the successful synthesis of the two amine-cyanocarboxyboranes was likely due to the presence of the polar aprotic solvent acetonitrile.

Preliminary experiments showed that Q·BBr$(COOMe)_2$, which was prepared from Q·$BH(COOMe)_2$ [21] with NBS, also reacted with [Bu_4N]CN in acetonitrile. The reaction was significantly slower than that of Q·BH(Br)COOMe, probably because of the considerably larger steric hindrance on the boron. After 50% conversion it gave two products in ca. 1:1 molar ratio. These products were identified as Q·$BCN(COOMe)_2$ and [Bu_4N][$B(CN)_2(COOMe)_2$] by ^{1}H and ^{11}B NMR and IR spectroscopy.

Molecule **1d** proved to be an excellent starting material for the preparation of several A·BH(CN)COOMe complexes in base exchange reactions. These reactions were performed in refluxing acetonitrile except for **1c**, where Et_2NH acted both as reactant and solvent. **1c** was isolated as a colourless oil while the other compounds were white crystalline solids. Unlike **1d**, the majority of the complexes prepared by this reaction were practically pure. The isocyano isomer probably undergoes isomerization during the 2–14 h reflux time, while the majority of the other two impurities are removed



Scheme 1. Schematic representation of the synthesis of compounds **1a**–**6**. *Reagents and conditions*. (i) *N*-bromosuccinimide, methanol, room temperature, 30 min; (ii) 1.5 mol equiv. $[Bu_4N]CN$, acetonitrile, reflux, 1 h (**1a**), 1.4 mol equiv. $[Bu_4N]CN$, acetonitrile, room temperature, 30 h (**1d**); (iii) from **1d**, 2–3 mol equiv. of A, acetonitrile (or Et_2NH for **1c**), reflux, 2–14 h; (iv) 0.45 mol equiv. HCl in 0.05–0.2 M HCl in water or water–acetone mixture, 55–100 °C, 0.50–2.5 h; (v) 3 mol equiv. 2-aminopyridine, acetonitrile, reflux 22 h, water, reflux, 1 h; (vi) from **1d**, 2 mol equiv. of $[Bu_4N]CN$, acetonitrile, reflux, 2.5 h, ion exchange; (vii) 1 mol equiv. bromine, 2.8 mol equiv. KHCO3, water, 0 °C – room temperature; (viii) methanol, room temperature, 3 mol% HBr, 10 min; (ix) 3 mol equiv. LiCN, acetonitrile, reflux, 200 h, ion exchange; (x) 1 mol equiv. 4-CN-py·Br_2 + 1 mol equiv. 4-CN-py, THF, 0 °C, 2 h. [A or A′ = quinuclidine, Q (**a**); piperidine, pip (**b**); Et_2NH (**c**); Me_3N (**d**); 4-dimethylaminopyridine, DMAP (**e**); 4-aminopyridine, 4-NH_2-py (**f**); morpholine, Morf (**g**); *N*-methylmorpholine, *N*-Me-Morf (**h**); 1-methylimidazole, Mimid (**i**); 2-aminopyridine, 2-NH_2-py (**j**); 3-aminopyridine, 3-NH_2-py (**k**); picoline, pic (**l**); pyridine, py (**m**)].

in the purification steps. Due to the presence of an asymmetric centre in the molecule geminal CH_2 protons in **1a**–**c**, **g**, **h**, **2a**, 2,6 and 3,5 carbons in **1b**, **g**, **h**, **2b**, **g**, and methylene and methyl carbons in **1c**, **2c** are in diastereotopic relationship. Thus, the observed splitting of these signals indicates that the configuration of the chirogenic boron atom is stable on the NMR time scale in these compounds.

2.2. Lactam formation with 2-NH_2-py (*3*)

The base exchange reaction between **1d** and 2-NH_2-py is very slow in acetonitrile. While the reaction with threefold excess of 3-NH_2-py or with twofold excess of 4-NH_2-py at reflux temperature takes place quantitatively in 6 h, it reaches only 75–78% conversion in 10 h and 92–94% conversion in 19 h with 2-NH_2-py. Simultaneously with the base exchange reaction metanol splits slowly off from **1j** and molecule **3** is formed (Scheme 1). The conversion to **3** is still not complete in 40 h in acetonitrile. In water, however, at reflux temperature the reaction is complete in 1 h. It is interesting to note that **3** is isoelectronic with the 3-substituted indolin-2-ones, a novel class of tyrosine kinase inhibitors [29].

In acidic medium **3** is fairly stable, its decomposition half-life at 100 °C in 0.5 M D_2SO_4 is 2.9 h as determined from time dependent changes observed in the ^1H and ^{11}B NMR spectra of the hydrolysis mixture. Simultaneously with the protonated amine and boric acid neither **2j** nor other intermediary products can be observed by NMR. For the hydrolysis half-life of **2j** an approximately 16 min value is expected as calculated from the pK_b value (7.07) of 2-NH_2-py (see later). If the hydrolysis proceeded through the splitting of the lactam ring, the amount of **2j** should be at the highest level (approximately 7% or more) in the hydrolysis mixture in the 0.8–1.4 h range, and it would be well visible by ^{11}B NMR. As this was not observed, it is concluded that the dominant hydrolysis pathway is probably the breaking of the B–N bond rather than splitting of the C–N bond.

In NaOD/D_2O solution the lactam ring is partially cleaved and an equilibrium exists between **3** and the 2-NH_2-py·$BH(CN)COO^-$ ion (**2j**N–H^+). For example, in a 0.046 M solution of lactam **3** (**3**:NaOD = 1:4) at 100 °C the equilibrium is reached in 50–60 min and the equilibrium mixture contains 52–55% of **2j**–H^+. At room temperature it requires 16–18 weeks to reach the

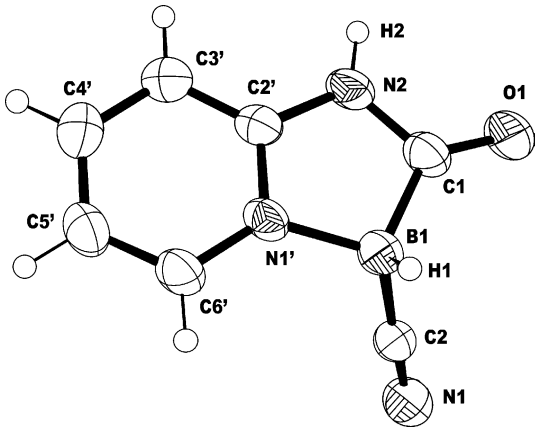


Fig. 1. ORTEP view of **3** at 50% probability level with numbering scheme. Selected bond length (Å), angle and torsion angle (°) data include B1–N1′ 1.564(3), B1–C2 1.569(4), B1–C1 1.616(4), B1–H1 1.08(4), N1–C2 1.142(4), C1–O1 1.222(3), N1′–C2′ 1.349(4), C2′–N2 1.372(4), N2–C1 1.384(4); N1′–B1–C1 98.3(2), N1′–B1–C2 112.5(2), C2′–N1′–B1 110.7(2), C6′–N1′–B1 129.0(2); N1–C2–B1–C1 79.4, N1–C2–B1–N1′ −169.6, N1–C2–B1–H1 −46.9.

equilibrium and the relative concentration of **2j**–H^+ in the equilibrium mixture is 87–89%.

The structure of **3** as well as selected bond length and angle data are shown on Fig. 1.

The pyridine ring is coplanar with the five membered ring (root mean square (rms) deviation from the plane is 0.0240 Å, distance of the B1 boron and C1 carbon atoms from the plane is 0.0497 (0.0022) and 0.0446 (0.0021) Å, respectively). In the crystal two molecules are connected in a head to tail arrangement by strong intermolecular H-bonds between N(2)–H and the carbonyl oxygen (O1) with a donor and acceptor distance of 2.867(3) Å. According to the generally accepted graph set analysis [30] of hydrogen bond patterns developed by Etter et al. the pattern is $R_2^2(8)$. The hydrogen bond pattern is described as $G_d^a(n)$ where G stands for a designator letter (C for chains, R for rings, S for intramolecular pattern and D for other finite pattern), d is the number of H-donors while a is the number of acceptor atoms and n the total number of atoms in the pattern for example in the ring.

The latest edition of Cambridge Crystallographic Database [31] (November, 2002 release) contains no boron compound comparable to **3**. However, the structure of 3-methylindolin-2-one, which contains the isoelectronic ring system on the basis of the BN ↔ CC rule, is known [32], and the two structures show similar bond length and angle values.

2.3. Preparation, acidity and hydrolysis of 2

Hydrolysis of all esters **1** takes place in 0.1–0.2 M aqueous HCl or in aqueous HCl–acetone mixture at 60–100 °C. Simultaneously with ester hydrolysis, decomposition accompanied by H_2 formation occurs to various extents depending on the amines. The products **2** in the majority of cases were found to be considerably more stable, showing hardly any decomposition (gas evolution) under the hydrolysis conditions, so the end or the considerable decrease of the effervesence indicated completion of the ester hydrolysis. Although most products crystallized upon evaporation of the reaction mixtures at 0–5 °C, some of them formed oversaturated solutions in which initiation of the crystallization was rather difficult. All **2** except for **2i** were obtained in pure form as no impurities could be detected by NMR.

Since the preparation of their first representative, amine-carboxyboranes have been generally considered to be the boron analogues of the protonated α-amino acids [1], based on the isoelectronic relationship between CN^+ and BN groups. On the other hand, as we recently pointed out, experimental data suggests that it is more appropriate to consider the BN ↔ CC rather than B ↔ C^+ isoelectronic analogy as the guiding rule and to regard amine-carboxyboranes as boron analogs of aliphatic carboxylic acids [2]. Potentiometric studies revealed that amine-carboxyboranes are exceptionally weak acids (pK_a = 8.14–8.62, 12 compounds, A = NH_3, RNH_2, R_2NH) [33]. This fact suggests that the R_3N–B group has a marked electron-donating effect towards its substituents. In order to explore the electronic effects of the amines and the cyano group on the COO group we have determined the pK_a values of all **2** by pH potentiometry.

It is plausible to assume that the electron density of the hydrogen atom in the B–H bond (the hydride character) changes linearly with the electron density of the COO group. Initiated by the assumption that electron density of the hydrogen atom in the B–H bond shows correlation with the rate of acidic hydrolysis (reduction of protons) of amine-cyanocarboxyboranes (A·BH(CN)COOH), semiquantitative data were collected using ^1H and ^{11}B NMR spectroscopy to determine the half-lives of the hydrolysis reactions in 0.5 M D_2SO_4/D_2O solutions at 100 °C. ^1H NMR spectra indicated the conversion of amine ligands to ammonium ions while ^{11}B NMR spectra showed the decomposition of the complex (characterized by a doublett boron peak coupled with hydrogen) to boric acid (Table 1).

A comparison of the acidity of the A·BH_2COOHs, the carboxylic acids and their corresponding α-cyano derivatives revealed that cyano substitution on both the boron and the carbon atom results in the same 2–2.5 units drop in the pK_a values. Interestingly, the type of the amine has only a small impact on the pK_a values. One unit change in the pK_b value gives only 0.086 unit change in the pK_a value. A plot of pK_as versus the pK_bs of the amines shows a nearly linear correlation for all compounds except for **2i** (Fig. 2).

Table 1
pK_a values of amine-cyanocarboxyboranes (**2**) (25 °C, I = 1.0 M $NaClO_4$) and their hydrolysis half-lives in 0.5 M D_2SO_4/D_2O at 100 °C

Comp.	pK_b values of the amine	Hybridization state of donor N-atom	PK_a	Half-life/hour[a]
2a	2.85	sp^3	6.34 (0.001)[b]	>400
2b	2.88	sp^3	6.28 (0.002)	15
2c	2.89	sp^3	6.26 (0.002)	14
2d	4.02	sp^3	6.24 (0.002)	55
2e	4.45	sp^2	6.29 (0.003)	<0.005
2f	4.75	sp^2	6.23 (0.002)	<0.005
2g	5.26	sp^3	6.17 (0.002)	5
2h	6.23	sp^3	6.06 (0.002)	3.2
2i	6.86	sp^2	6.26 (0.002)	0.023
2k	7.84	sp^2	5.89 (0.002)	0.75
2l	7.89	sp^2	5.92 (0.002)	1.2
2m	8.59	sp^2	5.82 (0.004)	3.1

[a] Calculated from the integral ratios of the amine peaks of AH^+ and **2** in the ^1H NMR spectra and from the integral ratios of the boron peaks of $B(OH)_3$ and **2** in the ^{11}B NMR spectra.
[b] Standard deviations are in parentheses.

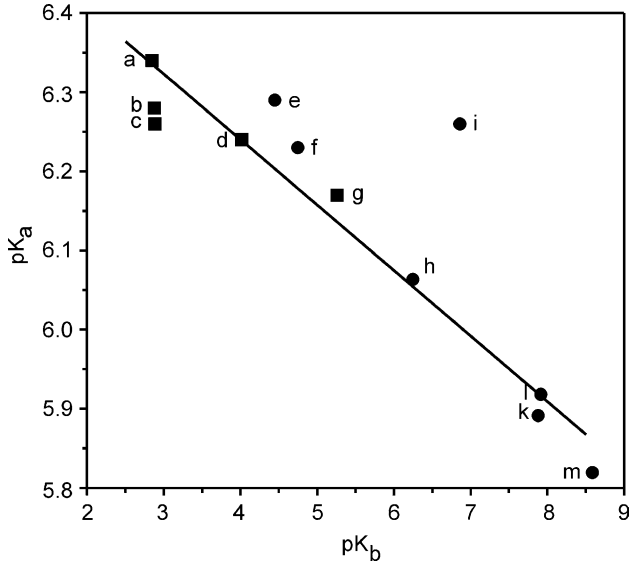


Fig. 2. Plot of pK_as of A·BH(CN)COOHs (**2**) versus pK_bs of amines (■ and ● indicate amines with sp^3 and sp^2 hybridization state, respectively.) $K_b = [BH^+][OH^-]/[B]$.

It clearly indicates that, in accordance with our expectations, weaker amines donate less electrons to the borane moiety and thus to the carboxylic group, and therefore they form stronger acids.

We have found it quite unexpected that soft pyridine bases with sp^2 nitrogen donor atoms did not result in an extra increase in the electron density on the soft cyanoborane moiety and did not result in an extra drop of acidity of molecules **2e**, **f** and **2i**–**m**.

In contrast to acid stengths, hydrolysis rates in 0.5 M D_2SO_4 showed exceptionally strong dependance on the quality of the amine part. Plots of logarithms of hydrolysis half-lives of complexes with either sp^2 (■) or sp^3 (●) nitrogen donor atoms versus pK_b values of the corresponding amines resulted in two straight lines with different slopes for all data points with one (**i**) or two exceptions (**b**, **c**) for sp^2 and sp^3 amines, respecively (Fig. 3).

The decomposition (proton reduction) rates of these complexes can not be explained with the hypothesis that the hydrolysis rates are basically determined by the hydride character of the B–H hydrogen. Since pyridine base complexes do not show higher than usual electron densities on the carboxylate groups, it is quite unlikely that high electron densities could appear on the B–H hydrogens. Consequently, several orders of magnitude faster hydrolysis rates of strong pyridine base complexes can only be explained by an initial attack of protons on the trigonal planar sp^2 pyridine nitrogen atoms which are sterically freely available in contrast to strong sp^3 donor nitrogens, which are sterically fairly crowded and may have a rigid structure. On the other hand,

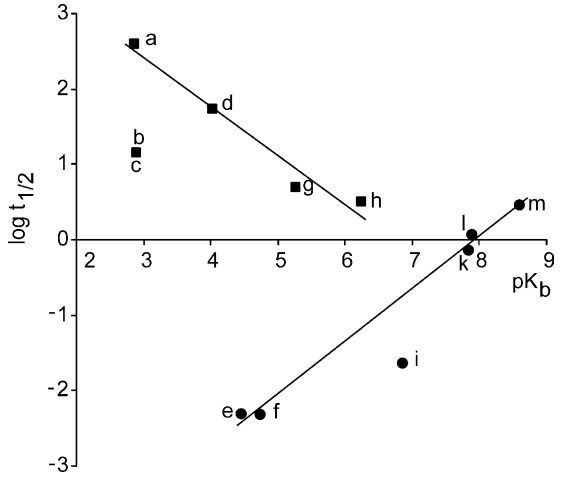


Fig. 3. Plots of logarithms of half-lives of amine-cyanocarboxyboranes versus pK_b values of the amines (■ and ● indicate amines with sp^3 and sp^2 hybridization state, respectively).

decrease in the basicity of the amine part results in a decrease in the virtual concentration of the transition state $[AH \cdot BH(CN)COOH]^+$ ions resulting in an increase in the hydrolytic stabilities of complexes.The decomposition of $[AH \cdot BH(CN)COOH]^+$ ions may occur by either the cleavage of the B–N bond or directly by the elimination of an H_2 molecule. Decomposition mechanism of alkylamine complexes could not have been explained so far mainly due to the very low number of amines belonging to the same group of bicyclic, tertiary or secondaryalkyl amines.

In a recent publication Funke and Mayr [34] found pyridine base complexes significantly stronger hydride donors than trialkylamine complexes in reduction of carbenium ions by amine-boranes following a polar mechanism. In the light of our results the reduction of carbenium ions more likely goes through a transition state in which nitrogen atom of the pyridine base complexes are involved rather than a direct attack by the B–H bond.

Simple aliphatic carboxylic acids have pK_a values around 3–5. Strongly electron withdrawing subtituents such as F, Cl or NO_2 increase the acidity (for example, the pK_a of nitroacetic acid is 1.68, trifluoroacetic acid 0.5) while electron donating groups have the opposite effect. The pK_a of amine-cyanocarboxyboranes (around 6) at least partially fills the gap that exists between the pK_a values of monocarboxylic acids and amine-carboxyboranes (pK_a = 8.1–8.6). We belive that the synthesis and investigation of amine-cyanocarboxyboranes may be the first step towards the systematic design, synthesis and characterization of monocarboxylic compounds whose pK_as would cover the entire 0.5–8.6 pK_a range.

2.4. Examinations of the synthesis of amine-isocyano(methoxycarbonyl)borane

To the best of our knowledge only the trimethylamine [35–37], pyridine and picoline [37] complexes of $BH_2(NC)$ have been prepared so far. The synthesis of the trimethylamine complex from trimethylamine-iodoborane has been achieved by several reagents including silver cyanide [35], or $[Bu_4N][Ag(CN)_2]$, which was prepared from AgCN and $[Bu_4N]Br$ in methylenechloride solution [36], or the cyanocomplexes $[Bu_4N][M(CN)_4]$ (M = Ni, Zn). The latter ones were used for the synthesis of pyridine and picoline complexes as well.

In our hands, in reactions with $A \cdot BH(Br)COOMe$, AgCN has failed to achieve B–Br to B–CN or B–NC substitution (see Section 2.1). Therefore, we decided to test $[Bu_4N][Ag(CN)_2]$ for this purpose. This reagent first was prepared in pure solid form in our laboratory (see Section 3.7.4). In the reaction mixture of $Me_3N \cdot BH(Br)COOMe$ and $[Bu_4N][Ag(CN)_2]$ only Me_3N $BH(CN)COOMe$ could be detected. When the reaction was run with the corresponding quinuclidine complex $Q \cdot BH(Br)COOMe$ in acetonitrile at reflux temperature, formation of an intermediate was detected. When monitoring the raction mixture by ^{11}B NMR the disappearence of the bromoborane doublet ($\delta = -6.1$ ppm) and simultaneous appearence of a very broad peak of the intermediate ($\delta = -9.45$ ppm, $\nu_{1/2} \approx 330$ Hz) were observed. Peak intensity of the intermediate then started to decrease and simultaneously $Q \cdot BH(CN)COOMe$ was formed. When more than 90% of the total boron content was observed under the peak of −9.45 ppm the reaction mixture was evaporated and the residue was treated in methylene chloride with H_2S and then Ag_2S was filtered off. Evaporation of the filtrate resulted in a white solid whose main component was $Q \cdot BH(NC)COOMe$ as indicated by its characteristic IR absorbance (2131 cm^{-1}) and its quantative ^{13}C NMR spectrum (sharp peak at 170.37 ppm and broad peak at 185.12 ppm). Unfortunately all of our efforts to isolate this compound in pure form failed. The intermediate was identified as $Q \cdot BH(NCAgCN)COOMe$ based on our previous observations and literature data published for $Me_3N \cdot BH_2(NCAgCN)$ [35].

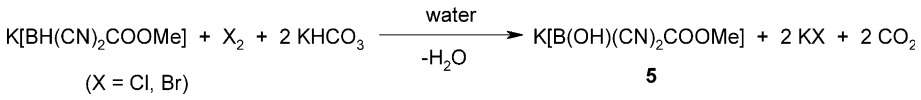
2.5. Cyano(methoxycarbonyl)borates

As we have already mentioned (Section 2.1) in the reaction of $Me_3N \cdot BH(Br)COOMe$ with $[Bu_4N]CN$ in acetonitrile at room temperature, in parallel to the bromide to cyanide exchange, the exchange of the amine by the cyanide also occurs leading to the formation of $[BH(CN)_2COOMe]^-$ ion. This type of exchange has already been published in the literature [38]. At reflux temperature in the presence of a large excess of $[Bu_4N]CN$ the reaction takes place quantitatively. After cation exchange the pure product $K[BH(CN)_2COOMe]$ (**4**) has been isolated in high yield.

Salt **4** failed to produce the desired $A \cdot B(CN)_2COOMe$ complexes when treated with bromine in the presence of an amine (Q, 4-CN-py, 4-Me_2N-py) in acetonitrile. In aqueous solution however, in the presence of $KHCO_3$ the following reaction takes place (Scheme 2) with both chlorine and bromine, that may be considered an unexpected reaction in the meaning that it yielded the hydroxyl group-containing compound **5**, which is a unique representative of stable anionic hydroxoborates:

Chemical composition of compound **5** has been confirmed by boron elemental analysis, ^1H NMR (presence of a OMe group), ^{11}B NMR (a singlet peak only), quantitative $^{13}C\{^1H\}$ NMR(OMe:CN:*C*OOMe = 1:2:1) and IR spectroscopy (characteristic absorption of non-associated OH). Compound **5** decomposes in water in one day.

Reaction of $Me_3N \cdot BH(Br)COOMe$ with LiCN in acetonitrile was examined at reflux temperature and the process was monitored by ^1H and ^{11}B NMR spectroscopy. The rate of Br–CN exchange reaction was approximately two orders of magnitude lower than with



Scheme 2.

$[Bu_4N]CN$, while the rate of amine to cyanide exchange decreased less significantly as compared to $[Bu_4N]CN$. Thus, after a 120 h of reaction time virtually the total boron content was transformed into $Li[BH(CN)_2COOMe]$. None of the monitoring samples taken over the course of the reaction indicated the presence of any $Me_3N\cdot BH(NC)COOMe$ in the reaction mixture. Recently a succesful Br–CN exchange reaction has been reported in the literature for the reaction of $Cy_3P\cdot BH(Br)COOMe$ (Cy = cyclohexyl) and LiCN without the replacement of the phosphine base with cyanide ions [39].

$Me_3N\cdot BH_2COOMe$ reacted reluctantly with LiCN in refluxing acetonitrile in an amine–CN^- ion exchange reaction. The product has been isolated, after a cation exchange procedure, in the form of its potassium salt (**6**). Molecule **6** was synthesized in order to develop a new reaction in which **6** and amine perbromides would react in the presence of amines to produce molecules **1** since **1d** could not be transformed with very weakly basic amines into their BH(CN)COOMe complexes. We have attempted to synthesize 4-CN-py·BH(CN)-COOMe in this way and found that, in addition to the oxidation of the B–H hydrogen, the oxidation of the carboxymethyl group had occured simultaneously and the reaction product was contaminated with approximately 40% of 4-CN-py·BH_2(CN). All of our efforts to separate the individual components of the reaction product have failed so far.

3. Experimental

3.1. General

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. Extractions of solids were carried out according to the standard Schlenk period extraction techniques [40]. All solid products were dried in a dry nitrogen stream to constant weight. Absolutized solvents were freshly distilled prior to use. Acetone was distilled from a 1.5 m Raschig packed column. Acetonitrile was distilled from P_2O_5 after drying with CaH_2. Dichloromethane was distilled from CaH_2, then refluxed with $NaBH_4$/diglyme and fractionally distilled. Chloroform was shaken with cc. H_2SO_4, dried over $CaCl_2$ and distilled from P_2O_5. Ether and THF were distilled from Na-benzophenone. Methanol was distilled from $Mg(OCH_3)_2$. Pentane was fractionally distilled. Water denotes twice distilled water. Methanolic HBr solution was prepared by dropwise addition of concentrated aqueous HBr solution to P_2O_5 under vigorous stirring and dissolving the liberated HBr gas, after drying with Granusic A (J. T. Baker), in methanol. Molecular sieves were activated by keeping under dynamic vacuum for 3 h at 220 °C, and stored under dry N_2. Quinuclidine was recrystallized from ether. 4-Aminopyridine was extracted with ether. Diethylamine, pyridine, 1-methylimidazole and picoline were distilled from KOH. Morpholine and *N*-methylmorpholine was distilled from KOH and then from Na. Piperidine was distilled from CaH_2. 3-Aminopyridine and 2-aminopyridine were recrystallized from ether and ether-pentane mixture, respectively. NBS was recrystallized from water and dried in a N_2 stream before use. Bromine (Ferak), $[Bu_4N]I$ (Fluka) and 4-DMAP (Janssen) were used as received. $Me_3N\cdot BH_2COOH$ [3], Q·BH_2COOH [41], $[Bu_4N]CN$ [42] and LiCN·*n*THF [43] were prepared by known procedures. 4-Cyanopyridine and 4-dimethylaminopyridine perbromides were prepared by the procedure published for pyridine perbromide [44]. Syntheses of $Me_3N\cdot BH(Br)COOMe$, Q·BH(Br)COOMe, LiCN·MeCN and $[Bu_4N][Ag(CN)_2]$ are given in Section 3.6.

NMR spectra were recorded on a Bruker AM 360 instrument in 5 mm o.d. tubes at room temperature. ^1H (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. Protons adjacent to boron generally gave distinguishable but broad signals in the ^1H NMR spectra 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 ^1H and ^{13}C signals were cleared with homonuclear decoupling and chemical shift correlation (^1H–^1H and ^{13}C–^1H) experiments. Carbons attached directly to boron could be observed in a few complexes only, because of the line-broadening due to the nuclear spin and quadrupolar effect of boron nuclei. ^{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. X-ray structure analysis of **3** was performed on a colourless block crystal ($0.45\times0.35\times0.3$ mm) prepared by slow evaporation of an acetonitrile solution. Molecular formula $C_7H_6BN_3O$,

$M = 158.96$, monoclinic, $a = 7.5697(10)$ Å, $b = 13.0452(10)$ Å, $c = 7.7453(10)$ Å, $\beta = 92.31(1)^{\circ}$, $V = 764.21(15)$ Å^3, $Z = 4$, space group: $P21/n$, $\rho_{calc} = 1.382$ g cm^{-3}. Data were collected at 293(1) K, Enraf Nonius MACH3 diffractometer, Mo Kα radiation $\lambda = 0.71073$ Å, ω–2θ motion, $\theta_{max} = 25.3^{\circ}$, 1387 measured, 1007 reflections were unique with $I > 2\sigma(I)$, decay: none. Absorption coefficient $\mu = 0.095$ mm^{-1}, empirical absorption correction was applied using the psi scan method. The structure was solved using the SIR-92 software [45] and refined on F^2 using SHELX-97 program [46], publication material was prepared with the WINGX-97 suite [47], $R(F) = 0.0476$ and $wR(F^2) = 0.2107$ for 1387 reflections, 115 parameters, goodness of fit $G = 0.836$. Residual electron density: 0.23/−0.24 e Å^{-3}. Hydrogen atoms were placed into geometric position except H1 (B–H) and H2 (N–H) atoms which were found at the difference electron density map and their coordinates were also refined.

The boron content of the samples was determined with acid–base titration in the presence of mannitol, after fusion with sodium hydroxide and potassium hydroxide. Lithium content of LiCN·MeCN has been determined by acid–base titration. pK_b values of amines were determined at 25 °C in 1.0 M ionic strength media except for amines **h** and **k** where 0.5 M ionic strength was applied. [48]. Protonation constants of the products were determined by pH-potentiometric technique in 1.0 M ionic strength media ($NaClO_4$) at 25 °C. For the measurements a RADIOMETER PHM85 pH-meter, a pHG211 glass working electrode and K401 calomel reference electrode filled with saturated LiCl was used. Standardized base solution (0.2 M) was added by a ABU 80 automatic burette. Titrated solutions contained the selected compounds at 0.002 M initial concentration. Disturbing effect of carbon dioxide content of the air was avoided by passing argon gas through the solution. pH difference originated from the diffusion potential appearing on the surface of the reference electrode has been taken into account by the method of Irving et al. [49]. Protonation constants were calculated by the computer program PSEQUAD [50].

3.2. Preparations of amine-cyano(methoxycarbonyl)boranes

3.2.1. General remarks

Compounds **1a** and **1d** were prepared from the corresponding BH(Br)COOMe complexes with [Bu_4N]CN, while other complexes were synthesized from **1d** by amine exchange processes. Liberated Me_3N was purged from the reaction atmosphere by a slow N_2 stream into a gas-washing bottle containing a solution of methylorange indicator and a known amount of standardized aqueous HCl solution (5% of the calculated stoichiometric amount) in order to monitor the progress of the reaction. When all acid had been consumed by Me_3N (as shown by the color change of the indicator) another 5% portion of standardized HCl solution was added.

3.2.2. Q·BH(CN)COOMe (*1a*)

To an acetonitrile (20 ml) solution of [Bu_4N]CN (3.74 g, 13.93 mmol) was added Q·BH(Br)COOMe (2.44 g, 9.31 mmol). The mixture was refluxed for 1 h then evaporated under reduced pressure to an oily residue that was taken up and triturated in ether (40 ml) until it solidified. The solid was filtered off, extracted with the filtrate ten times, then the filtrate was evaporated to dryness. The solid residue was stirred in water (10 ml) at 0 °C, then the insoluble product was filtered off, washed with icy water (3 × 5 ml). Yield: 1.37 g (71%). Anal. Found: C, 57.45 (calc: 57.73%) H, 8.18 (calc: 8.24%) N, 13.56 (calc: 13.46%) B, 5.13 (calc: 5.20%); ^{1}H NMR ($CDCl_3$, δ): 1.84 (m, 6H, CCH_2), 2.12 (h, 1H, CH), 3.33 (m, 6H, NCH_2), 3.59 (s, 3H, OCH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 19.58 (CH), 24.03 (C*C*H_2), 48.93 (OCH_3), 50.84 (NCH_2), 128.7 (br BCN). ^{11}B NMR ($CDCl_3$, δ): −14.6 (d, $J = 96$ Hz). IR (KBr, cm^{-1}): 2397 ν(B–H), 2204 ν(CN), 1688 ν(C=O).

3.2.3. pip·BH(CN)COOMe (*1b*)

1d (220 mg, 1.41 mmol) was dissolved in acetonitrile (2 ml), piperidine (360 mg, 4.23 mmol) was added and the solution was refluxed for 2 h. The reaction mixture was evaporated under reduced pressure. The residue was taken up and triturated with ether (2 ml) until it solidified. It was then filtered off, washed with ether (0.5 ml) then extracted with ether (5 ml). The extract was concentrated to 0.5 ml volume to which pentane (4 ml) was added. A crystalline solid formed that was filtered off after 30 min, washed with pentane (2 × 1 ml). Yield: 169 mg (66%). Anal. Found: C, 52.35 (calc: 52.79%) H, 8.27 (calc: 8.31%) N, 15.21 (calc: 15.39%) B, 5.91 (calc: 5.94%); ^{1}H NMR ($CDCl_3$, δ): 1.47 (m, 1H, 4-CH_2 ax), 1.71 (m, 2H, 3,5-CH_2 ax), 1.90 (m, 3H, 3,5-CH_2 eq + 4-CH_2 eq), 2.86 (m, 2H, 2,6-CH_2 ax), 3.32 (m, 2H, 2,6-CH_2 eq), 3.64 (s, 3H, OCH_3), 4.68 (br, NH). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 22.10 (4-CH_2), 24.27, 24.32 (3,5-CH_2), 49.42, 51.31 (2,6-CH_2), 129.2 (br, BCN), 188.5 (br, B*C*OOCH$_3$). ^{11}B NMR ($CDCl_3$, δ): −15.4 (d, $J = 96$ Hz). IR (KBr, cm^{-1}): 3154 ν(N–H), 2396 ν(B–H), 2212 ν(C≡N), 1654 ν(C=O).

3.2.4. Et_2NH·BH(CN)COOMe (*1c*)

To **1d** (217 mg, 1.39 mmol) was added diethylamine (3 ml) and the solution was refluxed for 4.5 h. The reaction mixture was evaporated under reduced pressure to a viscous oil to which ether was added (4 ml) and was allowed to stand for 5 h to produce a small amount of a solid that was filtered off. The filtrate was evaporated under reduced pressure to a colorless viscous oil which

was then kept under dynamic vacuum until constant weight was reached. Yield: 138 mg (64%). Anal. Found: B, 6.40 (calc: 6.36%); ^{1}H NMR ($CDCl_3$, δ): 1.31 (m, 6H, Et-CH_3), 2.96–3.18 (m, 4H, CH_2), 3.64 (s, 3H, OCH_3), 4.93 (br, 1H, NH). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 10.89, 11.38 (Et-CH_3), 46.51, 46.93 (Et-CH_2), 49.55 (OCH_3). ^{11}B NMR ($CDCl_3$, δ): −16.7 (d, $J = 96$ Hz). IR (net, cm^{-1}): 3164 ν(N–H), 2426 ν(B–H), 2209 ν(C≡N), 1682 ν(C=O).

3.2.5. $Me_3N\cdot BH(CN)COOMe$ (**1d**)

$Me_3N\cdot BH(Br)COOMe$ (1.36 g, 6.48 mmol) was added to the solution of $[Bu_4N]CN$ (2.42 g, 9.03 mmol) in acetonitrile (9 ml) and the mixture was stirred for 30 h at room temperature. The volatile components were then evaporated in vacuo, without warming the flask. The residue was suspended in ether (25 ml), the insoluble parts were filtered off and extracted six times with the filtrate. A small volume of an oily layer had been formed in the solution on standing. The upper solution phase was removed and the oily residue was vigorously stirred and washed with ten portions of fresh ether (15 ml each). The upper phase and the washing portions were combined and evaporated and the residue was triturated with pentane (10 ml) until solidification. The solid product was then filtered off, washed with pentane (2×4 ml). Yield: 0.85 g (84%). (As determined by ^{1}H and ^{11}B NMR, the product was still contaninated by 2, 4 and 3 mol% of $Me_3N\cdot BH(Br)COOMe$, $Me_3N\cdot BH(NC)$-COOMe and $[Bu_4N][BH(CN)_2COOMe]$, respectively.) Anal. Found: C, 45.85 (calc: 46.20%) H, 8.45 (calc: 8.40%) N, 17.78 (calc: 17.96%) B, 6.81 (calc: 6.93%); ^{1}H NMR ($CDCl_3$, δ): 2.90 (s, 9H, NCH_3), 3.61 (s, 3H, OCH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 48.77 (OCH_3), 51.90 (NCH_3), 128.9 (br q, BCN), 185.54 (br q, B*C*OOCH$_3$). ^{11}B NMR ($CDCl_3$, δ): −12.4 (d, $J = 105$ Hz). IR (KBr, cm^{-1}): 2409, 2432 ν(B–H), 2208 ν(C≡N), 1689 ν(C=O).

3.2.6. 4-DMAP$\cdot BH(CN)COOMe$ (**1e**)

1d (206 mg, 1.32 mmol) was dissolved in acetonitrile (5 ml) and 4-dimethylaminopyridine (325 mg, 2.66 mmol) was added. The solution was refluxed for 8 h then evaporated under reduced pressure to a gel-like material, which was then triturated in ether (6 ml) and, after solidification, filtered off. The solid was then extracted three times with the filtrate. The extraction was continued with a fresh portion of ether (20 ml) until a sticky solid remained on the filter disc. The etheral extract was evaporated to 5 ml final volume, the solid was then filtered off. Yield: 133 mg (46%). Anal. Found: B, 4.99 (calc: 4.94%); ^{1}H NMR ($CDCl_3$, δ): 3.18 (s, 6H, NCH_3), 3.61 (s, 3H, OCH_3), 6.64 (d, 2H, 3,5-CH), 8.03 (d, 2H, 2,6-CH). $^{13}C\{^1H\}$ NMR($CDCl_3$, δ): 39.71 (NCH_3), 49.26 (OCH_3), 106.83 (3,5-CH), 145.96 (2,6-CH), 155.86 (*ipso*-C). ^{11}B NMR ($CDCl_3$, δ): −14.3 (d, $J = 96$ Hz). IR (KBr, cm^{-1}): 2415 ν(B–H), 2204 ν(C≡N), 1693, 1641 ν(C=O).

3.2.7. 4-NH_2-py$\cdot BH(CN)COOMe$ (**1f**)

To **1d** (207 mg, 1.33 mmol) dissolved in acetonitrile (6 ml) was added 4-aminopyridine (254 mg, 2.70 mmol) and the solution was refluxed for 6 h. After evaporation of the reaction mixture to dryness the residue was suspended in ether (10 ml), filtered and the solid was extracted with the filtrate eight times. The solid was further extracted fifty times with a fresh portion of ether (20 ml). The solid that formed and settled from the ether during the extraction was filtered off. Yield: 114 mg (45%). Anal. Found: B, 5.65 (calc: 5.66%); ^{1}H NMR (DMSO-d_6, δ): 3.44 (s, 3H, OCH_3), 6.73 (d, 2H, 3,5-CH), 7.64 (br s, 2H, NH), 7.87 (d, 2H, 2,6-CH). $^{13}C\{^1H\}$ NMR (DMSO-d_6, δ): 48.32 (OCH_3), 108.18 (3,5-CH), 146.22 (2,6-CH), 157.07 (*ipso*-C). ^{11}B NMR (DMSO-d_6, δ): −14.0 (br). IR (KBr, cm^{-1}): 3439, 3357, 3251 ν(N–H), 2403 ν(B–H), 2211 ν(C≡N), 1689, 1650 ν(C=O).

3.2.8. Morf$\cdot BH(CN)COOMe$ (**1g**)

To an acetonitrile solution (2 ml) of **1d** (220 mg, 1.41 mmol) was added morpholine (370 mg, 4.25 mmol) and the solution was refluxed for 3 h, after which it was evaporated to a viscous oil. The residue was triturated in ether (5 ml) and the solid formed was filtered off, washed with ether (2×2 ml) and dried in a nitrogen stream. This was then extracted with chloroform until a gel-like substance remained on the filter disc. Evaporation of the extract gave a solid which was then suspended in ether (10 ml), filtered off, extracted six times with the filtrate. Yield: 142 mg (55%). Anal. Found: B, 5.92 (calc: 5.88%); ^{1}H NMR ($CDCl_3$, δ): 3.00–3.33 (m, 4H, NCH*H* ax + OCH*H* ax), 3.65 (s, 3H, OCH_3), 3.80 (m, 2H, NC*H*H eq), 4.01 (m, 2H, OC*H* H eq), 5.39 (br, 1H, NH). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 49.00, 50.04 (NCH_2), 49.73 (OCH_3), 65.16 (OCH_2). ^{11}B NMR ($CDCl_3$, δ): −15.5 (d, $J = 96$ Hz). IR (KBr, cm^{-1}): 3148 ν(N–H), 2417 ν(B–H), 2195 ν(C≡N), 1668 ν(C=O).

3.2.9. N-Me-Morf$\cdot BH(CN)COOMe$ (**1h**)

To an acetonitrile solution (2 ml) of **1d** (215 mg, 1.38 mmol) was added *N*-Me-morpholine (420 mg, 4.15 mmol), the solution was refluxed for 12 h and then it was evaporated to a viscous oil, which solidified on standing. Ether (5 ml) was added and the solid was filtered off, washed with ether (2×2 ml) and dried in a nitrogen stream. This was then washed down with chloroform (4 ml) leaving a gel-like material behind on the filter disc. Evaporation of the chloroform solution resulted in a solid which was suspensed in 1:1 ether-pentane mixture (5 ml), and filtered off. Yield: 173 mg (63%). Anal. Found: B, 5.44 (calc: 5.46%); ^{1}H NMR

($CDCl_3$, δ): 3.00 (s, 3H, NCH_3), 3.05, 3.17, 3.48, 3.73 (multiplets, 4×1 H, NCH_2), 3.62 (s, 3H, OCH_3), 3.81–4.03 (m, 4H, OCH_2). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 45.00 (NCH_3), 49.24 (OCH_3), 56.04, 57.69 (NCH_2), 60.51, 60.64 (OCH_2). ^{11}B NMR ($CDCl_3$, δ): −13.6 (d, $J = 105$ Hz). IR (KBr, cm^{-1}): 2422 ν(B–H), 2207 ν(C≡N), 1687 ν(C=O).

3.2.10. mimid·BH(CN)COOMe (**1i**)

1d (292 mg, 1.87 mmol) was dissolved in acetonitrile (4 ml) and 1-methylimidazole (456 mg, 5.55 mmol) added and the solution was refluxed for 5 h. The solution was then evaporated to an oil under reduced pressure and dried to a constant mass under vacuum. To the oily residue ether was added (4 ml), magnetically stirred for approximately 5 min then supernatant etheral solution was removed. To the oil a fresh portion of ether was added, stirred and removed. This procedure was repeated ten times until a solid material was obtained, which was finally dried to a constant mass under vacuum. Yield: 266 mg (79%). Anal. Found: C, 46.78 (calc: 46.97%) H, 5.50 (calc: 5.63%) N, 23.41 (calc: 23.48%) B, 5.91 (calc: 6.04%); ^1H NMR ($CDCl_3$, δ): 3.61 (s, 3H, OCH_3), 3.90 (s, 3H, NCH_3), 7.11 (s, 1H, 5-CH), 7.26 (s, 1H, 4-CH), 8.23 (s, 1H, 2-CH). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 35.48 (NCH_3), 49.23 (OCH_3), 121.80 (4-CH), 126.36 (5-CH), 137.46 (2-CH). ^{11}B NMR ($CDCl_3$, δ): −18.1 (d, $J = 105$ Hz). IR (KBr, cm^{-1}): 2398 ν(B–H), 2205 ν(C≡N), 1685 ν(C=O).

3.2.11. 3-NH_2-py·BH(CN)COOMe (**1k**)

To **1d** (210 mg, 1.35 mmol) dissolved in acetonitrile (2 ml) was added 3-aminopyridine (382 mg, 4.06 mmol) freshly recrystallized from ether. The solution was refluxed for 6 h, evaporated under reduced pressure and then kept under dynamic vacuum (0.1 mbar). To the residue ether (10 ml) was added and stirred for 30 min. Ether was distilled out and the resultant resin-like substance was kept under vacuum for 30 min. When the majority of the resin recrystallized water (1.5 ml) was added, stirred for 10 min and the solid was filtered off and washed with water (4×0.2 ml). Yield: 112 mg (44%). Anal. Found: B, 5.60 (calc: 5.66%); ^1H NMR ($CDCl_3$, δ): 3.62 (s, 3H, OCH_3), 4.49 (br 2H, NH_2), 7.36 (m, 1H, 4-CH), 7.42 (m, 1H, 5-CH), 7.94 (m, 1H, 6-CH), 8.04 (m, 1H, 2-CH).$^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 49.61 (OCH_3), 126.31, 126.40 (4,5-CH), 133.36 (2-CH), 136.61 (6-CH), 145.49 (*ipso*-C). ^{11}B NMR ($CDCl_3$, δ): −13.0 (d, $J = 86$ Hz). IR (KBr, cm^{-1}): 3418, 3346, 3244 ν(N–H), 2451, 2427 ν(B–H), 2210 ν(C≡N), 1680, 1655 ν(C=O).

3.2.12. pic·BH(CN)COOMe (**1l**)

A solution of **1d** (213 mg, 1.37 mmol) and picoline (3.82 mg, 4.10 mmol) in acetonitrile (2 ml) was refluxed for 2.5 h then evaporated under reduced pressure to an oil. Ether (10 ml) was added and the mixture was stirred for 10 min meanwhile the oil solidified. The solid was filtered off, washed with ether (1 ml) then extracted with fresh ether (5 ml) until a loose and slowly sedimenting solid remained on the filter disc. The ether extract was concentrated to a 3 ml volume and the fine needle crystals formed were filtered off and washed with ether (2×0.5 ml). Yield: 178 mg (69%). Anal. Found: C, 56.82 (calc: 56.89%) H, 5.77 (calc: 5.84%) N, 14.83 (calc: 14.74%) B, 5.67 (calc: 5.69%); ^1H NMR ($CDCl_3$, δ): 2.61 (s, 3H, CCH_3), 3.62 (s, 3H, OCH_3), 7.56 (d, 2H, 3,5-CH), 8.49 (d, 2H, 2,6-CH). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 21.26 (C*C* H_3), 48.98 (OCH_3), 126.89 (3,5-CH), 128.70 (br, BCN), 146.05 (2.6-CH), 155.92 (*ipso*-C), 186.6 (br, B*C*$OOCH_3$). ^{11}B NMR ($CDCl_3$, δ): −13.3 (d, $J = 96$ Hz). IR (KBr, cm^{-1}): 2434 ν(B–H), 2207 (C≡N), 1684 ν(C=O).

3.2.13. py·BH(CN)COOMe (**1m**)

A solution of **1d** (216 mg, 1.38 mmol) and pyridine (219 mg, 2.77 mmol) in acetonitrile (4 ml) was refluxed for 14 h then evaporated under reduced pressure to an oil, which was kept under dynamic vacuum to reach constant weight. Ether was added to the viscous oily residue and the mixture was stirred for 10 min. The ether was then distilled off and the residue was kept under dynamic vacuum until the oil solidified completely. The solid was suspended in pentane (8 ml), filtered off, and dried in a nitrogen stream. The dry solid was then extracted with ether (10 ml) until a yellowish powder remained on the filter disc. The extract was concentrated to a 4 ml volume and the crystals formed were filtered off and washed with ether (2×0.5 ml). Yield: 161 mg (66%). Anal. Found: B, 6.17 (calc: 6.14%); ^1H NMR ($CDCl_3$, δ): 3.64 (s, 3H, OCH_3), 7.80 (m, 2H, 3,5-CH), 8.25 (m, 1H, 4-CH), 8.69 (m, 2H, 2,6-CH). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 49.69 (OCH_3), 126.42 (3,5-CH), 142.53 (4-CH), 147.46 (2,6-CH), ^{11}B NMR ($CDCl_3$, δ): −12.9 (d, $J = 105$ Hz). IR (KBr, cm^{-1}): 2431 ν(B–H), 2209 (C≡N), 1677 ν(C=O).

3.3. Preparations of amine-cyanocarboxyboranes

3.3.1. Q·BH(CN)COOH (**2a**)

0.1 M hydrochloric acid (5.0 ml) and acetone (1.5 ml) were added to **1a** (199 mg, 0.96 mmol) and the mixture was heated for 3 h in a flask that was equipped with a reflux condenser and immersed in an oil bath at a temperature of 60–64 °C. The acetone was evaporated with a nitrogen stream meanwhile the temperature of the oil bath was gradually increased to 75 °C. Finally, the temperature of the oil bath was increased to 100 °C in 10 min, kept at this value for an additional 10 min and then the reaction mixture was removed from the bath, allowed to cool to room temperature and placed into an ice-water bath for 1 h. The resulting crystals were fitered

off and washed with ice water (4 × 0.4 ml). Yield: 137 mg (74%). Anal. Found: B, 5.55 (calc: 5.57%); ^{1}H NMR ($CDCl_3$, δ): 1.86 (m, 6H, CCH_2), 2.12 (h, 1H, CH), 3.35 (m, 6H, NCH_2), 10.49 (br, 1H, COOH). $^{13}C\{^1H\}$ NMR($CDCl_3$, δ): 19.66 (CH), 24.13 (C*C* H_2), 50.98 (NCH_2). ^{11}B NMR ($CDCl_3$, δ): −13.7 (d, J = 96 Hz). IR (KBr, cm^{-1}): 2406 ν(B–H), 2210 ν(CN), 1653 ν(C=O).

3.3.2. *pip·BH(CN)COOH* (**2b**)

To **1b** (101 mg, 0.55 mmol) was added 0.1 M hydrochloric acid (2.5 ml) and the solution was kept at 70 °C in a bath for 30 min followed by heating the reaction mixture to boiling for a short period. It was cooled and stored in a refrigirator overnight. The crystals formed were filtered off and washed with ice water (4 × 0.4 ml). Yield: 67 mg (73%). Anal. Found: B, 6.45 (calc: 6.43%); ^{1}H NMR (D_2O, δ): 1.43 (m, 1H, 4-CH_2 ax), 1.65 (m, 2H, 3,5-CH_2 ax), 1.81 (m, 3H, 3,5-CH_2 eq + 4-CH_2 eq), 2.75 (m, 2H, 2,6-CH_2 ax), 3.28 (m, 2H, 2,6-CH_2 eq). $^{13}C\{^1H\}$ NMR (D_2O, δ): 24.49 (4-CH_2), 26.67 (3,5-CH_2), 52.42, 53.61 (2,6-CH_2). ^{11}B NMR (D_2O, δ): −16.3 (d, J = 96 Hz). IR (KBr, cm^{-1}): 3207 ν(N–H), 2403 (B–H), 2215 ν(C≡N), 1695, 1639 (C=O).

3.3.3. *Et_2NH·BH(CN)COOH* (**2c**)

1c (119 mg, 0.70 mmol) was suspended in 0.1 M hydrochloric acid (3.0 ml), stirred at 60 °C in a water bath, and the temperature of the bath was gradually increased to 80 °C over 70 min. The solution was evaporated to a 1 ml volume under reduced pressure and allowed to stand. When crystal formation started the solution was stirred for a few minutes then placed in a ice water bath. After 2 h the crystals were filtered off and washed with ice water (3 × 0.2 ml). Yield: 44 mg (40%). Anal. Found: B, 6.92 (calc: 6.93%); ^{1}H NMR (D_2O, δ): 1.24 (t, 6H, Et-CH_3), 2.84–3.12 (m, 4H, CH_2).$^{13}C\{^1H\}$ NMR (D_2O, δ): 12.90, 13.10 (Et-CH_3), 48.79, 49.28 (Et-CH_2). ^{11}B NMR (D_2O, δ): −17.6 (d, J = 96 Hz). IR (KBr, cm^{-1}): 3118 ν(N—H), 2425 ν(B–H), 2217 ν(C≡N), 1661 ν(C=O).

3.3.4. *Me_3N·BH(CN)COOH* (**2d**)

1d (204 mg, 1.31 mmol) was dissolved in a mixture of water (2.6 ml) and 1 M hydrochloric acid (0.66 ml) and the solution was heated at 60 °C for 5 min in a water bath, then bath temperature was increased to 100 °C for 24 min. The solution was evaporated to dryness under reduced pressure, and the residue was co-evaporated with methylene chloride twice (2 ml each) to remove residual water. The solid was then redissolved in methylene chloride (5 ml) and filtered. The filtered-off solid was washed with methylene chloride (3 × 0.4 ml). The filtrate and washes were combined and evaporated to dryness. The residue was triturated in ether (12 ml), filtered off and extracted with the filtrate until a small amount of a waxy solid remained on the filter disc. The extract was concentrated to a 5 ml volume, the solid formed was filtered off and washed with ether (3 × 0.5 ml). Yield: 122 mg (66%). Anal. Found: B, 7.57 (calc: 7.62%); ^{1}H NMR ($CDCl_3$, δ): 2.89 (s, 9H, NCH_3), 9.87 (br, 1H COOH). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 48.77 (OCH_3), 51.48 (NCH_3). ^{11}B NMR ($CDCl_3$, δ): −12.6 (d, J = 105 Hz). IR (KBr, cm^{-1}): 2419 ν(B–H), 2210 ν(C≡N), 1662 ν(C=O).

3.3.5. *DMAP·BH(CN)COOH* (**2e**)

1e (170 mg, 0.78 mmol) was dissolved in a mixture of 0.1 M hydrochloric acid (4.0 ml) and acetone (4.0 ml). The flask was equipped with a reflux condenser, placed into a 50 °C bath for 30 min, then the temperature was increased to 60 °C for 80 min. Then nitrogen gas was bubbled through the solution with mild warming to remove the acetone, which resulted in the precipitation of a solid. Water (4 ml) was added and the solution was heated to boiling to redissolve the solid. This solution was then allowed to crystallize at room temperature for 2 h. The crystals formed were filtered off and washed with water (3 × 0.5 ml). Yield: 128 mg (80%). Anal. Found: B, 5.25 (calc: 5.27%); ^{1}H NMR (DMSO-d_6, δ): 3.13 (s, 6H, NCH_3), 6.89 (d, 2H, 3,5-CH), 7.94 (d, 2H, 2,6-CH), 10.98 (s, 1H, COOH). $^{13}C\{^1H\}$ NMR (DMSO-d_6, δ): 39.24 (NCH_3), 49.26 (OCH_3), 107.20 (3,5-CH), 145.47 (2,6-CH), 155.56 (*ipso*-C). ^{11}B NMR (DMSO-d_6, δ): −14.2 (br). IR (KBr, cm^{-1}): 2400 ν(B–H), 2204 ν(CN), 1653 ν(C=O).

3.3.6. *4-NH_2-py·BH(CN)COOH* (**2f**)

1f (80 mg, 0.42 mmol) was dissolved in 0.1 M hydrochloric acid (2.0 ml), the solution was kept at 65 °C for 18 min then cooled to room temperature. Crystal formation was initiated by scratching inner walls of the flask with a glass rod. After several hours the crystals were filtered off and washed with water (3 × 0.3 ml). Yield: 64 mg (86%). Anal. Found: B, 6.06 (calc: 6.11%); ^{1}H NMR (D_2O, δ): 6.77 (d, 2H, 3,5-CH), 7.89 (d, 2H, 2,6-CH).$^{13}C\{^1H\}$ NMR (D_2O, δ): 112.50 (3,5-CH), 149.19 (2,6-CH), 160.91 (*ipso*-C). ^{11}B NMR (D_2O, δ): −14.8 (d, J = 96 Hz). IR (KBr, cm^{-1}): 3459, 3355 ν(N–H), 2448 (B–H), 2203 ν(C≡N), 1643 ν(C=O).

3.3.7. *Morf·BH(CN)COOH* (**2g**)

To **1g** (124 mg, 0.67 mmol) was added 0.1 M hydrochloric acid (2.9 ml) and the mixture was kept at 65 °C until the starting material completely dissolved. The solution was gradually heated to 100 °C in 1 h and kept at this temperature for 15 min and then it was evaporated under reduced pressure to an oily solid. This was suspended in acetonitrile (2 ml), allowed to stand for 1 h and then the acetonitrile was distilled off. The solid residue was re-suspended in acetonitrile (3 ml), filtered

off, dried in a nitrogen stream and extracted ten times with ether (8 ml). Yield: 66 mg (58%). Anal. Found: B, 6.43 (calc: 6.36%); ^{1}H NMR (D_2O, δ): 3.08 (m, 2H, NCH*H* ax), 3.26 (m, 2H, OCH*H* ax), 3.78 (m, 2H, NC*H*H eq), 4.03 (m, 2H, OC*H*H eq). $^{13}C\{^1H\}$ NMR (D_2O, δ): 51.00, 51.97 (NCH_2), 67.58 (OCH_2). ^{11}B NMR (D_2O, δ): −16.3 (d, $J = 96$ Hz). IR (KBr, cm^{-1}): 3106 ν(N–H), 2425 ν(B–H), 2213 ν(C≡N), 1678 ν(C=O).

3.3.8. N-Me-Morf·BH(CN)COOH (2h)

Hydrochloric acid (0.1 M, 4.6 ml) was added to **1h** (136 mg, 0.69 mmol) and the solution was kept in a 100 °C bath for 38 min. The solution was then cooled to room temperature, evaporated to a 1 ml volume under reduced pressure and stored in a refrigerator overnight. The crystals formed were dispersed and the solution was placed in an ice water bath for several hours. The product was filtered off and washed with ice water (3×0.2 ml). Yield: 48 mg (38%). Anal. Found: B, 5.87 (calc: 5.88%); ^{1}H NMR (D_2O, δ): 2.98 (s, 3H, NCH_3), 3.11–3.24, 3.39–3.59 (multiplets, 2×2 H, NCH_2), 3.88–4.05 (m, 4H, OCH_2). $^{13}C\{^1H\}$ NMR(D_2O, δ): 46.82 (NCH_3), 58.85, 59.82 (NCH_2), 63.15, 63.23 (OCH_2). ^{11}B NMR (D_2O, δ): −13.4 (d, $J = 96$ Hz). IR (KBr, cm^{-1}): 2440 ν(B–H), 2210 ν(C≡N), 1658 ν(C=O).

3.3.9. Mimid·BH(CN)COOH (2i)

1i (142 mg, 0.79 mmol) was dissolved in 0.1 M hydrochloric acid (3.0 ml) and kept at 75 °C for 50 min. The solution was evaporated to a 1 ml volume and, after the crystallization started, placed in a refrigerator overnight. The slurry was then immersed in a ice-water bath for 1 h then the crystals were filtered off and washed with ice water (3×0.15 ml). Yield: 49 mg (38%). Anal. Found: B, 6.62 (calc: 6.55%); ^{1}H NMR (D_2O, δ): 3.84 (s, 3H, NCH_3), 7.24 (s, 1H, 5-CH), 7.32 (s, 1H, 4-CH), 8.31 (s, 1H, 2-CH). $^{13}C\{^1H\}$ NMR (D_2O, δ): 37.62 (NCH_3), 125.93 (4-CH), 127.89 (5-CH), 141.62 (2-CH). ^{11}B NMR (D_2O, δ): −18.8 (d, $J = 96$ Hz). IR (KBr, cm^{-1}): 2445 ν(B–H), 2209 ν(C≡N), 1668 ν(C=O).

3.3.10. 3-NH$_2$-py·BH(CN)COOH (2k)

1k (98 mg, 0.51 mmol) was dissolved in a mixture of 0.1 M hydrochloric acid (2.2 ml) and acetone (1.5 ml). The flask was equipped with a reflux condenser and heated in a bath at 70 °C for 20 min then the bath temperature was increased to 80 °C and kept at this temperature for 30 min. The acetone was removed by bubbling nitrogen gas through the solution at 50 °C. After several hours a crystalline product settled, which was filtered off and washed with water (3×0.2 ml). Yield: 79 mg (88%). Anal. Found: B, 6.11 (calc: 6.11%); ^{1}H NMR (D_2O, δ): 7.58 (m, 2H 4,5-CH), 7.93 (m, 1H, 6-CH), 8.00 (m, 1H, 2-CH).$^{13}C\{^1H\}$ NMR (D_2O, δ): 129.86 (4-CH), 130.99 (5-CH), 136.55 (2-CH), 139.46 (6-CH), 149.49 (*ipso*-C). ^{11}B NMR (D_2O, δ): −13.7 (d, $J = 96$ Hz). IR (KBr, cm^{-1}): 3433, 3347, 3228 ν(N–H), 2428 ν(B–H), 2216 ν(C≡N), 1646 ν(C=O).

3.3.11. Pic·BH(CN)COOH (2l)

1l (117 mg, 0.62 mmol) was dissolved in a mixture of 0.1 M hydrochloric acid (2.8 ml) and acetone (1.4 ml). The flask was equipped with a reflux condenser and heated in a bath at 75 °C for 2 h, then the acetone was evaporated by bubbling nitrogen gas through the solution. The solution was then heated at 80–85 °C for 30 min, cooled to room temperature. A few drops of the solution was evaporated to dryness and then the solution was seeded with the resulting solid. After storing the solution in a refrigerator overnight the crystals were removed from the walls of the flask and the slurry was placed in a ice-water bath for a few hours to complete the crystallization. The product was filtered off and washed with ice water (3×0.2 ml). Yield: 57 mg (52%). Anal. Found: B, 6.09 (calc: 6.14%); ^{1}H NMR (D_2O, δ): 2.58 (s, 3H, CCH_3), 7.70 (d, 2H, 3,5-CH), 8.45 (d, 2H, 2,6-CH). $^{13}C\{^1H\}$ NMR (D_2O, δ): 23.66 (CCH_3), 130.31 (3,5-CH), 149.21 (2.6-CH), 160.46 (*ipso*-C). ^{11}B NMR (D_2O, δ): −13.9 (d, $J = 89$ Hz). IR (KBr, cm^{-1}): 2429 ν(B–H), 2209 ν(C≡N), 1656 ν(C=O).

3.3.12. Py·BH(CN)COOH (2m)

To **1m** (116 mg, 0.66 mmol) was added 0.1 M hydrochloric acid (2.9 ml), the solution was kept at 75 °C for 2.5 h then evaporated to the half of its volume and cooled to room temperature. After the beginning of the crystallization the solution was placed in an ice-water bath for 2 h, then the crystals were filtered off and washed with ice water (4×0.15 ml). Yield: 69 mg (66%). Anal. Found: B, 6.64 (calc: 6.68%); ^{1}H NMR (D_2O, δ): 7.91 (m, 2H, 3,5-CH), 8.39 (m, 1H, 4-CH), 8.67 (m, 2H, 2,6-CH). $^{13}C\{^1H\}$ NMR (D_2O, δ): 129.86 (3,5-CH), 146.69 (4-CH), 150.24 (2.6-CH). ^{11}B NMR (D_2O, δ): −13.6 (d, $J = 96$ Hz). IR (KBr, cm^{-1}): 2432 ν(B–H), 2208 ν(CN), 1659 ν(C=O).

3.4. Preparation and/or NMR data of compounds with 2-NH$_2$-py

3.4.1. 2-NH$_2$-py·BH(CN)COOMe (1j)

^{1}H NMR ($CDCl_3$, δ): 3.63 (s, 3H, OCH_3), 5.93 (br 2H, NH_2), 6.83 (m, 2H, 3,5-CH), 7.70 (m, 1H, 4-CH), 8.09 (m, 1H, 6-CH). ^{11}B NMR ($CDCl_3$, δ): −16.08 (d, $J = 96$ Hz). ^{1}H NMR (D_2O, δ): 3.62 (s, 3H, OCH_3), 6.84 (m, 1H, 3-CH), 6.94 (m, 1H, 5-CH), 7.77 (m, 1H, 4-CH), 7.87 (m, 1H, 6-CH).^{11}B NMR (D_2O, δ): −17.2 (d, $J = 96$ Hz).

*3.4.2. 2-NH_2-py·BH(CN)COONa (Na salt of **2j**)*

^{1}H NMR (D_2O, δ): 6.82 (m, 1H, 3-CH), 6.91 (m, 1H, 5-CH), 7.73 (m, 1H, 4-CH), 7.87 (m, 1H, 6-CH). $^{13}C\{^1H\}$ NMR(D_2O, δ): 116.07, 116.48 (3,5-CH), 144.34, 145.95 (4,6-CH), 170.81 (*ipso*-C). ^{11}B NMR (D_2O, δ): −16.6 (d, J = 96 Hz).

*3.4.3. –HN-C_5H_4N–BH(CN)CO–, (lactam) (**3**)*

1d (206 mg, 1.32 mmol) and 2-NH_2-py (398 mg, 4.22 mmol) were dissolved in acetonitrile (2 ml) and the solution was refluxed for 22 h then the solvent was evaporated under reduced pressure. Ether (4 ml) was added to the oily residue, stirred for a few minutes then the ether was removed from the oil. This procedure was repeated three times to afford a semi-solid residue that was redissolved in water (10 ml) and refluxed for 1 h. The solution was cooled to and kept at 40 °C, treated with charcoal, stirred for 30 min and then filtered. The filtrate was evaporated to dryness under reduced pressure, then the residue was dispersed in methanol (3 ml) and evaporated to dryness again. The resulting solid was triturated in chloroform (3 ml), filtered off and washed with chloroform (3 × 0.4 ml). Yield: 82 mg (39%). Anal. Found: B, 6.84 (calc: 6.80%); ^{1}H NMR (DMSO-d_6, δ): 7.17 (m, 1H, 3-CH), 7.29 (m, 1H, 5-CH), 8.14 (m, 1H, 4-CH), 8.41 (m, 1H, 6-CH), 10.67 (br, 1H, NH).$^{13}C\{^1H\}$ NMR(DMSO- d_6, δ): 110.22 (3-CH), 117.86 (5-CH), 141.92 (4-CH), 144.87 (6-CH), 155.55 (*ipso*-C). ^{11}B NMR (DMSO-d_6, δ): −17.3 (br).^{1}H NMR (D_2O, δ): 7.27 (m, 1H, 3-CH), 7.36 (m, 1H, 5-CH), 8.14 (m, 1H, 4-CH), 8.32 (m, 1H, 6-CH).$^{13}C\{^1H\}$ NMR(D_2O, δ): 113.59 (3-CH), 121.87 (5-CH), 144.80 (4-CH), 147.87 (6-CH), 157.40 (*ipso*-C). ^{11}B NMR (D_2O, δ): −17.6 (d, J = 96Hz). ^{1}H NMR (0.183M NaOD, complex:NaOD = 1:4): 6.93 (m, 1H, 3-CH), 7.01 (m, 1H, 5-CH), 7.81 (m, 1H, 4-CH), 8.05 (m, 1H, 6-CH). $^{13}C\{^1H\}$ NMR(0.183M NaOD, complex:NaOD = 1:4): 116.92 (3-CH), 117.71 (5-CH), 143.43 (4-CH), 145.60 (6-CH), 158.89 (*ipso*-C). ^{11}B NMR (0.183 M NaOD, complex:NaOD = 1:4): −17.7 (d, J = 96 Hz). IR (KBr, cm^{-1}): 3080 ν(N–H), 2447 ν(B–H), 2210 ν(C≡N), 1695, 1637 ν(C=O).

3.5. A Q·BH(NC)COOMe, NMR data

^{1}H NMR ($CDCl_3$, δ): 1.87 (m, 6H, CCH_2), 2.15 (h, 1H, CH), 3.28 (m, 6H, NCH_2), 3.59 (s, 3H, OCH_3). $^{13}C\{^1H\}$ NMR(quantitative) ($CDCl_3$, δ): 19.32 (1C, CH), 23.42 (3C, CCH_2), 48.49 (1C, OCH_3), 49.02 (3C, NCH_2), 170.37 (1C, BNC), 185.12 (1C, B*C*OOCH$_3$). ^{11}B NMR ($CDCl_3$, δ): −9.8 (d, J = 96 Hz).

3.6. Preparations of cyano(methoxycarbonyl)borates

*3.6.1. K[BH(CN)$_2$COOMe] (**4**)*

[Bu_4N]CN (3.38 g, 12.58 mmol) was dissolved in acetonitrile (8.5 ml) and MeN·BH(Br)COOMe (1.29 g, 6.15 mmol) was added. The solution was refluxed for 2.5 h, then diluted to a 14 ml volume with acetonitrile and this solution was chromatographed with acetonitrile on a column containing 60 g of Silica gel 60 (particle size: 0.04–0.063 mm). 5 ml fractions were collected and all fractions were checked with TLC (HP-TLC Silica 60, eluent: 40% acetonitrile, 60% chloroform, spots were visualized by iodine vapour and then with the Dragendorff's reagent) and fractions containing the pure product (R_f = 0.55) were combined and evaporated under reduced pressure to yield a dense oil, which was dissolved in methanol (30 ml) and then water (60 ml) was added under stirring. The moderately opalescent solution was treated with charcoal, filtered and passed through a column containing potassium ion form of Dowex 50X8-200 cation exchange resin, which was washed with a mixture of water and methanol (2:1) prior to separation. Water–methanol mixture (2:1 volume ratio, 80 ml) was used for the elution of K[BH(CN)$_2$-COOMe] after loading of a solution of [Bu_4N][BH-(CN)$_2$COOMe] on the column. The eluted solution was evaporated under reduced pressure to a solid, which was further dried in vacuum to constant weight. The solid was then triturated in methylene chloride (5 ml), filtered off and washed with methylene chloride (5 × 1 ml). Yield: 720 mg (72%). Anal. Found: B, 6.62 (calc: 6.67%); ^{1}H NMR (D_2O, δ): 2.02 (q, 1H, BH, J = 94.3 Hz), 3.60 (s, 3H, OCH_3).$^{13}C\{^1H\}$ NMR(quantitative) (D_2O, δ): 52.85 (1C, OCH_3), 134.42 (2C, BCN, J_{BC} = 63.1 Hz), 193.63 (1C, B*C* $OOCH_3$, J_{BC} = 73.8 Hz). ^{11}B NMR (D_2O,): −32.7 (d, J = 96 Hz). IR (KBr, cm^{-1}): 2406 ν(B–H), 2216 ν(C≡N), 1700 ν(C=O).

*3.6.2. K[B(OH)(CN)$_2$COOMe] (**5**)*

4 (203 mg, 1.25 mmol) and $KHCO_3$ (350 mg, 3.50 mmol) were dissolved in water (5 ml) and the solution was cooled to 0 °C. Bromine (205 mg, 1.28 mmol) was placed in a Schlenk-type flask and flushed completely into the aqueous solution with nitrogen gas over a period of 1.5 h. When approximately 20% of the bromine remained in the flask the cooling of the reaction mixture was stopped. Half-an-hour after total consumption of the bromine a sample was taken and checked with ^{11}B NMR to determine the degree of conversion of **4** and then if it was necessary a calculated amount of bromine was added to complete the reaction. The pH of the reaction mixture was checked and set between pH 7 and 8 with $KHCO_3$, then the solution was evaporated to dryness under reduced pressure in a 40 °C water bath. The residue was kept under vacuum to reach a constant weight. The solid was suspended in acetonitrile (3 ml), filtered off, washed with acetonitrile (3 × 1.5 ml). The filtrate and washings were combined, decolorized with charcoal and evaporated to dryness. The residue was dissolved in methanol (4 ml), evaporated to dryness

after 20 min, suspended in ether (5 ml) and filtered off. Yield: 185 mg (83%). Anal. Found: B, 6.11 (calc: 6.07%); ^{1}H NMR (D_2O, δ): 3.64 (s, OCH_3).$^{13}C\{^{1}H\}$ NMR(quantitative) (D_2O, δ): 52.91 (1C, OCH_3), 134.08 (2C, BCN, $J_{BC} = 64.1$ Hz), 192.03 (1C, B*C*OOCH$_3$, $J_{BC} = 77.8$ Hz). ^{11}B NMR (D_2O,): −15.84 (s). ^{1}H NMR (CD_3CN, δ): 1.54 (s, 1H, BOH), 3.53 (s, 3H, OCH_3). $^{13}C\{^{1}H\}$ NMR(CD_3CN, δ): 49.95 (OCH_3). ^{11}B NMR (CD_3CN, δ) −15.1. IR (KBr, cm^{-1}): 3607 ν(O–H), 2208, 2201 ν(C≡N), 1671 ν(C=O).

3.6.3. K[BH$_2$(CN)COOMe] (6)

$Me_3N\cdot BH_2COOMe$ (1.47 g, 11.22 mmol) was dissolved in acetonitrile (18 ml) and LiCN·MeCN (2.47 g, 33.37 mmol) was added. The suspension was refluxed for 200 h then the solid was filtered off and washed with acetonitrile (3 × 3 ml). The filtrate and washings were combined and evaporated under reduced pressure to a viscous oil, which was kept in vacuum (0.01 mbar) until constant weight was reached. The residue was redissolved in water (15 ml), treated with charcoal, filtered, then loaded onto a column containing 80 ml of potassium ion form of Dowex 50X8-200 cation exchange resin. The product was eluted with water over a period of 2 h at an approximate rate of 1 drop per second. The presence of hydroborate ions in the downcoming solution was identified from one drop of the solute by adding silver nitrate solution followed by moderate warming which produced finely dispersed silver as a black precipitate. The precipitation of silver occurred at room temperature from more concentrated solutions. The eluted solution was evaporated to dryness, and the residue was triturated in chloroform (5 ml), filtered off, washed with chloroform (4 × 3 ml) and dried in a nitrogen stream. The crude product, which still contained a significant amount of potassium cyanide, was washed with acetonitrile (4 × 3 ml then 4 × 1 ml). The washings were combined and evaporated under reduced pressure to dryness. The solid residue was titurated in methylene chloride (5 ml) and filtered off. Yield: 973 mg (63%). Anal. Found: B, 7.93 (calc: 7.89%); ^{1}H NMR (D_2O, δ): 1.30 (q, 1H, BH, $J = 90.4$ Hz), 3.52 (s, 3H, OCH_3).$^{13}C\{^{1}H\}$ NMR(quantitative) (D_2O, δ): 52.09 (1C, OCH_3), 141.98 (1C, BCN, $J_{BC} = 57.2$ Hz), 201.68 (1C, B*C*OOCH$_3$, $J_{BC} = 69.1$ Hz). ^{11}B NMR (D_2O, δ): −33.5 (t, $J = 90$ Hz). IR (KBr, cm^{-1}): 2402, 2371 ν(B–H), 2193 ν(C≡N), 1653 ν(C=O).

3.7. Preparations of starting materials

3.7.1. Me$_3$N·BH(Br)COOMe

$Me_3N\cdot BH_2COOH$ (5.14 g, 43.95 mmol) was dissolved in distilled methanol (85 ml). NBS (7.89 g, 44.33 mmol) was added to the solution in 15 portions. The second portion was added 5 min after the first one (ca. 5%) and subsequent portions were added when the pale yellow colour of the mixture disappeared. The temperature was kept at 25 °C by employing a cooling bath. The volatile parts were then evaporated in vacuo, the residue was triturated with ether which was then evaporated. The solid residue was suspended in 0.01 M HBr solution (25 ml) at 0 °C, the product was filtered off, washed with 0.01 M HBr (2 × 10 ml), and then with water (2 × 5 ml). Yield 8.02 g (87%). Anal. Found: B, 5.19 (calc: 5.15%). ^{1}H, ^{11}B NMR and IR-spectra were identical with the previously published values [20].

3.7.2. Q·BH(Br)COOMe

The reaction between $Q\cdot BH_2COOH$ (3.18 g, 18.81 mmol) and NBS (3.36 g, 18.88 mmol) and the workup of the mixture was carried out analogously to that described for Me_3N complex under 3.7.1. Yield 4.31 g (87%). Anal. Found: B, 4.11 (calc: 4.13%). ^{1}H, ^{11}B NMR and IR-spectra were identical with the previously published values [20].

3.7.3. LiCN·MeCN

To crude LiCN·(0.05–0.1)THF (2.25 g) [43] was added acetonitrile (60 ml) in portions and the mixture was refluxed for 50 min. A microcrystalline solid formed which was filtered off and extracted with the filtrate five times. Yield: 4.19 g. (The product slowly lost MeCN at a rate of approximately 0.1 mol equivalent per hour when kept in the nitrogen stream after drying). Anal. Found: Li, 9.30 (calc: 9.38%). ^{1}H NMR (D_2O, δ): 2.07 (CH_3). $^{13}C\{^{1}H\}$ NMR(D_2O, δ): 122.07 (CH_3), 167.98 (CN).

3.7.4. [Bu$_4$N][Ag(CN)$_2$]

Acetonitrile solution of $[Bu_4N]I$ (3.52 g, 9.53 mmol in 12.5 ml) was added to finely ground AgCN (2.55 g, 19.06 mmol) suspended in acetonitrile (7.5 ml). After 30 min stirring at room temperature the insoluble AgI was filtered off and washed with acetonitrile (25 ml). The filtrate was evaporated to dryness, the solid residue was suspended in ether, filtered off and washed with ether (2 × 5 ml). Yield 3.70 g (97%). ^{13}C NMR (quantitative) ($CDCl_3$, δ): 13.39 (4C, CH_3), 19.36 (4C, CH_3CH_2), 23.67 (4C, NCH_2CH_2), 58.57 (4C, NCH_2), 143.78 (2C, CN).

4. Supplementary material

Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 202629 for compound **1**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033; e-mail: depos-

it@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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