Bromo derivatives of amine and phosphine complexes of cyanodihydroborane. Synthesis and reactivity

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Abstract

Bromocyanohydroborane complexes [L·BH(Br)CN], containing a chiral boron atom and dibromocyanoborane complexes (L·BBr_2CN) have been synthesized from amine- and phosphine-dihydrocyanoboranes [L·BH_2CN, where L = trimethylamine (Me_3N), tetramethylethylenediamine (TMEDA)/2, quinuclidine (Q), picoline (Pic), tributylphosphine (Bu_3P) and triphenylphosphine (Ph_3P)] and bromine. Trialkylamine-bromocyanohydroboranes show fairly high hydrolytic stability, while the analogous picoline complexes hydrolyze readily. The leaving group character of bromine in amine-bromocyanohydroboranes was tested in reactions with amines. TMEDA·$2BH_2CN$, on reaction with tetramethylethylenediamine, picoline or on heating, is transformed into a cationic complex [(TMEDA)B(H)CN^+]Br^- which contains a five-membered ring. This compound is also formed under mild conditions in the reaction of Pic·BH(Br)CN and TMEDA. A chiral cationic complex [Pic(Q)B(H)CN^+]Br^- was formed from Q·BH(Br)CN and picoline whereas reaction of Me_3N·BH(Br)CN with picoline resulted in the formation of pure [$Pic_2B(H)CN^+$]Br^- through substitution and transamination. Amine-dibromocyanoboranes, in contrast to amine-bromocyanohydroboranes, did not react with amines even under harsher reaction conditions. These experiments indicate that bromine can be considered as a good leaving atom in amine-bromocyanohydroboranes and these new molecules might be useful as starting materials for the synthesis of novel boron analogs of α-amino acids.

Key words: Boron complexes; Borane complexes; Amine complexes; Phosphine complexes

Introduction

Several amine-carboxyboranes and their derivatives have been synthesized in the last 15 years and were considered as boron analogues of protonated α-amino acids [1–11]. These new molecules showed significant biological activity in rodents, i.e. antihyperlipidemic [12, 13], anticancer [14] and antiinflammatory [15] activities, the results prompting further research in this area.

Amine-carboxyboranes are prepared from the corresponding cyano derivatives, which are the boron analogues of α-amino acid nitriles and they themselves are biologically active compounds [1, 2, 8–10]. In view of their biological importance, extended research was initiated to prepare new boron analogs of α-amino acids with potential biological activity.

Since bromine is usually a good leaving atom and the bromo derivatives can easily be transformed, our aim was to synthesize bromo derivatives of amine-cyanoboranes and amine-carboxyboranes. In this paper we present the syntheses of novel mono and dibromo derivatives of several amine- and phosphine-cyanoboranes. Although numerous derivatives of amine-cyanoboranes have been synthesized [16–19], $Me_3N·BBr_2CN$ is the only brominated derivative described to date [20].

In order to get information on the leaving group character of a bromine attached to a boron atom bearing a cyano group with a strong -I effect, we were interested in finding conditions under which amine-bromocyanohydroboranes can react with amines.

Experimental

General

With the exception of the reactions performed in aqueous medium, the experiments were carried out using Schlenk techniques in oxygen- and water-free nitrogen atmosphere. The solvents used were also free from water and oxygen. Amine-cyanoboranes were prepared according to the literature [18]. A methyl sulfide solution of cyanodihydroborane [18] has been prepared

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by a novel procedure from sodium cyanoborohydride and iodine.

$$2NaBH_3CN + I_2 + 2Me_2S \xrightarrow{Me_2S} 2Me_2S \cdot BH_2CN + 2NaI \quad (1)$$

The bromine content of the compounds was determined by the Volhard method after fusion with sodium hydroxide and potassium hydroxide. IR and NMR spectra were recorded on Perkin-Elmer 16PC FT-IR and Bruker WP 200 SY instruments, respectively. Internal TMS and boron trifluoride ethylether complex in a coaxial tube were used as references for the ^1H and ^{11}B NMR spectra, respectively. The IR and NMR data are summarized in Table 1.

Solution of BH_2CN in methyl sulfide

To a suspension of sodium cyanoborohydride (14.13 g; 224.9 mmol in 60 ml methyl sulfide), a solution of iodine (28.53 g; 112.4 mmol in 60 ml methyl sulfide) was added over 3 h under stirring at room temperature. The solution was then refluxed for 30 min. The remaining brownish color was removed by adding small portions of solid sodium cyanoborohydride. Sodium iodide was filtered off and the BH_2CN residue, encapsulated in the solid, was extracted into hot methyl sulfide, which, in turn, was distilled off from the filtrate. The extract and the residue of the filtrate were unified and the whole distillation–extraction cycle was repeated 6–8 times. The BH_2CN content of the final solution was 208.7 mmol, 93%.

Syntheses of the complexes

$Me_3N \cdot BH(Br)CN$ (1), $Q \cdot BH(Br)CN$ (2), $TMEDA \cdot 2BH(Br)CN$ (3)

To a suspension of amine cyanoborane complex (10 mmol) in water (10 ml) was added saturated bromine–water (5% excess) dropwise under vigorous stirring at 0 °C. The mixture was stirred for a further 30 min at room temperature and 50 °C for **2** and **3**, respectively. The product formed was filtered off, washed with water (3×20 ml for **2** and **3** and 3×6 ml iced water for **1**) and dried under nitrogen.

Complex **1**: yield 0.97 g, 54%. *Anal.* Found: B, 6.02; Br, 45.19. Calc. for $C_4H_{10}BBrN_2$: B, 6.11; Br, 45.15%.

Complex **2**: yield 1.88 g, 82%. *Anal.* Found: B, 4.60; Br, 35.12. Calc. for $C_8H_{14}BBrN_2$: B, 4.72; Br, 34.90%.

Complex **3**: yield 2.89 g, 82%. *Anal.* Found: B, 6.21; Br, 45.14. Calc. for $C_8H_{18}B_2Br_2N_4$: B, 6.15; Br, 45.44%.

$Pic \cdot BH(Br)CN$ (4), $Bu_3P \cdot BH(Br)CN$ (5), $Ph_3P \cdot BH(Br)CN$ (6)

To a methylene chloride (10 ml) solution of the corresponding amine-cyanoborane complex (5 mmol) was added bromine in methylene chloride (8.62 ml, 0.58 M) dropwise with stirring in 1 h. The reaction mixture was kept at room temperature for 1 h and 2 days for **4**, **5** and **6**, respectively, then evaporated to dryness under nitrogen. The evaporation residues of **4** and **6** were extracted into hot ether (20 ml). The crystals formed were filtered off, washed with ether (2×5 ml) and dried under nitrogen. Crude **5** was purified by silica chromatography (silica gel 60, 0.040–0.063 mm, eluted with methylene chloride). The fractions were checked by TLC and those which contained the product were combined and evaporated under reduced pressure.

Complex **4**: yield 0.67 g, 68%. *Anal.* Found: B, 5.05; Br, 37.56. Calc. for $C_7H_8BBr_2N_2$: B, 5.13; Br, 37.89%.

Complex **5**: yield 1.08 g, 67%. *Anal.* Found: B, 3.35; Br, 25.10. Calc. for $C_{13}H_{28}BBrNP$: B, 3.38; Br, 24.97%.

Complex **6**: yield 1.58 g, 83%. *Anal.* Found: B, 2.75; Br 21.13. Calc. for $C_{19}H_{16}BBrNP$: B, 2.84; Br, 21.03%.

$Me_3N \cdot BBr_2CN$ (7), $Q \cdot BBr_2CN$ (8), $TMEDA \cdot 2BBr_2CN$ (9), $Pic \cdot BBr_2CN$ (10)

The corresponding amine-cyanoborane complex or Q·BH(Br)CN (**2**) (5 mmol) which had been suspended in water (10 ml, for **7** or **8**) or dissolved in methylene chloride (3 ml, for **9** or **10**) and bromine (1 ml, 3 ml or 8 ml for **7** and **10**, **8** or **9**, respectively) was added dropwise under vigorous stirring at 0 °C for aqueous and −78 °C for methylene chloride solutions. The solution was left to warm to room temperature. For **7** and **8**: the mixture was kept at 70 °C as long as the excess bromine distilled out. An orange colored solid settled out on cooling, which was filtered off, washed with water (3×5 ml) and dried. For **9** and **10**: the solution was stirred at room temperature for 5 h then evaporated to dryness. The crude product was dissolved in acetone (5 ml) and refluxed until complete disappearance of the color. For **7**–**9**: the solution was concentrated to a volume of 2–3 ml and water (10 ml) was added. The precipitate was filtered off, washed with water (3×8–10 ml) and dried. **9** was recrystallized from acetonitrile. For **10**: the solution was evaporated to dryness and the crude product was extracted into hot ether (20 ml). The crystals were filtered off, washed with ether (2×10 ml) and dried under nitrogen.

Complex **7**: yield 0.76 g, 59%. *Anal.* Found: B, 4.12; Br, 62.12. Calc. for $C_4H_9BBr_2N_2$: B, 4.23; Br, 62.49%.

Complex **8**: yield 1.32 g, 86%. *Anal.* Found: B, 3.46; Br, 51.71. Calc. for $C_8H_{13}BBr_2N_2$: B, 3.51; Br, 51.92%.

Complex **9**: yield 1.40 g, 55%. *Anal.* Found: B, 4.20; Br, 62.56. Calc. for $C_8H_{16}B_2Br_4N_4$: B, 4.24; Br, 62.74%.

Complex **10**: yield 0.81 g, 56%. *Anal.* Found: B, 3.78; Br, 55.22. Calc. for $C_7H_7BBr_2N_2$: B, 3.73; Br, 55.15%.

$Bu_3P \cdot BBr_2CN$ (11)

$Bu_3P \cdot BH_2CN$ (1.20 g, 5.00 mmol) was dissolved in methylene chloride (6 ml) and a solution of bromine

TABLE 1. Spectroscopic data for new cyanobromoborane and cyanodibromoborane complexes and cyanoboron (+1) compounds

Compound	^{1}H NMR		^{11}B NMR			IR (KBr) (cm^{-1})	
	Solvent	σ(ppm)[a]	Solvent	σ(ppm)	J(B–H) (Hz)	ν(B–H)	ν(CN)
$Me_3N \cdot BH(Br)CN$ (1)	$CDCl_3$	2.86 (sg, 9H, N-CH_3)	$CDCl_3$	−15.82	133	2472	2208
Q·BH(Br)CN (2)	$CDCl_3$	1.89 (m, 6H, C-CH_2) 2.17 (h, 1H, C-CH) 3.29 (t, 6H, N-CH_2)	$CDCl_3$	−7.20	131	2472	2200
TMEDA·2BH(Br)CN (3)	CD_3CN	2.88 (d, 12H, N-CH_3) 3.45 (m, 4H, N-CH_2)	CD_3CN	−7.36	129	2520	2210
Pic·BH(Br)CN (4)	$CDCl_3$	2.61 (sg, 3H, C-CH_3) 7.60 (d, 2H, CH) 8.69 (d, 2H, CH)	$CDCl_3$	−18.02	133	2502	2210
$Bu_3P \cdot BH(Br)CN$ (5)	$CDCl_3$	0.96 (t, 3H, C-CH_3) 1.50 (m, 4H, C-CH_2) 1.88 (m, 2H, P-CH_2)	$CDCl_3$	−33.54	89	2440	2192
Ph_3P BH(Br)CN (6)	$CDCl_3$	7.60 (m, 15H, CH)	$CDCl_3$	−26.02	105	2438	2200
$Me_3N \cdot BBr_2CN$ (7)	$CDCl_3$	3.08 (sg, 9H, N-CH_3)	$CDCl_3$	−14.51			2216
$Q \cdot BBr_2CN$ (8)	$CDCl_3$	1.93 (m, 6H, C-CH_2) 2.23 (h, 1H, CH) 3.57 (t, 6H, N-CH_2)	CD_3CN	−5.19			2214
$TMEDA \cdot 2BBr_2CN$ (9)	DMSO	3.06 (sg, 12H, N-CH_3) 3.88 (sg, 4H, N-CH_2)	DMSO	−9 58			2214
$Pic \cdot BBr_2CN$ (10)	$CDCl_3$	2.70 (sg, 3H, C-CH_3) 7.71 (d, 2H, CH) 9.07 (d, 2H, CH)	$CDCl_3$	−11.55			2218
$Bu_3P \cdot BBr_2CN$ (11)	$CDCl_3$	0.96 (t, 3H, C-CH_3) 1.51 (m, 4H, C-CH_2) 1.89 (m, 2H, P-CH_2)	$CDCl_3$	−27.31	135[b]		2202
$Ph_3P \cdot BBr_2CN$ (12)	$CDCl_3$	7.63 (m, 15H, CH)	$CDCl_3$	−20.50	133[b]		2198
[(TMEDA)B(H)CN]Br (13)	D_2O	3.07 (d, 12H, N-CH_3) 3.74 (m, 4H, N-CH_2)	D_2O	1.89	125	2488	2224
[(TMEDA)B(H)CN][PF_6] (14)	$(CD_3)_2O$	3.22 (d, 12H, N-CH_3) 3.95 (m, 4H, N-CH_3)	CD_3CN	3.24	105	2504	2222
[Pic(Q)B(H)CN][PF_6] (15)	D_2O	1.85 (two t's, 6H, C-CH_2) 2.10 (h, 1H, CH) 2.66 (sg, 3H, CH_3) 3.19 (m, 6H, N-CH_2) 7.88 (d, 2H, CH) 8.66 (d, 2H, CH)	CD_3CN	−0.72	119	2466	2218
[Pic_2B(H)CN]Br (16)	D_2O	2.67 (sg, 6H, CH_3) 7.88 (d, 4H, CH) 8.75 (d, 4H, CH)	D_2O	−1.86		2494	2216
[Pic_2B(H)CN][PF_6] (17)	$(CD_3)_2O$	2.68 (sg, 6H, CH_3) 7.99 (d, 4H, CH) 8.94 (d, 4H, CH)	CD_3CN	−0.56	109	2504	2222

[a]Abbreviations: sg = singlet, d = doublet, t = triplet, h = heptet, m = multiplet. [b]J(B–P).

in methylene chloride (20.7 ml, 0.490 M) was added. The solution was kept at room temperature for two days and then evaporated under nitrogen. The residue was purified by silica gel chromatography (for more details see procedure for **5**). Yield 0.590 g, 81%. *Anal.* Found: B, 2.70; Br, 39.77. Calc. for $C_{13}H_{27}BBr_2NP$: B, 2.71; Br, 40.06%.

$Ph_3P \cdot BBr_2CN$ (12)

$Ph_3P \cdot BH_2CN$ (1.50 g, 5.0 mmol) was dissolved in methylene chloride (15 ml) and bromine (3.00 ml) was added. The solution was stirred for 20 min then evaporated to dryness under nitrogen. The residue was dispersed in water (15 ml) and filtered. The solid was washed with sodium hydrogensulfite solution (10 ml, 1%) and water (3×10 ml) and then dried. The crude product was extracted into hot ether (45 ml). A white solid, settled out from the extract, was filtered off, washed with cold ether (3×5 ml) and dried under nitrogen. Yield 1.60 g, 70%. *Anal.* Found: B, 2.31; Br, 34.91. Calc. for $C_{19}H_{15}BBr_2NP$: B, 2.36; Br, 34.82%.

[(TMEDA)B(H)CN]Br (13) and [Pic$_2$B(H)CN]Br (16)

3 (0.495 g, 1.41 mmol) was dissolved in picoline (4 ml) and the solution was refluxed for 15 min. The precipitate formed was filtered off, washed with ether (3×5 ml) and dried under nitrogen yielding a white solid (0.518 g). This solid was suspended/dissolved in acetonitrile (5 ml). The insoluble part was filtered off, washed with acetonitrile (2×2 ml) and dried under nitrogen yielding pure **13**. Yield 0.316 g, 96%.

The acetonitrile filtrate was evaporated to dryness under reduced pressure. The residue was suspended in ether (10 ml), filtered off, washed with ether (3×10 ml) and dried. This second product was a pale yellow solid that proved to be **16**. Yield 0.193 g, 45%.

[(TMEDA)B(H)CN]Br (13)

(a) **3** (0.453 g, 1.29 mmol) was suspended in diglyme (10 ml) and TMEDA (0.5 ml) was added. The mixture was refluxed for 5 min then it was cooled down. The product formed was filtered off, washed with diglyme (2 ml) and ether (2×5 ml) and dried under nitrogen. Yield 0.531 g, 88%. *Anal.* Found: B, 4.60; Br, 34.00. Calc. for $C_7H_{17}BBrN_3$: B, 4.62; Br. 34.16%.

(b) **3** (0.510 g, 1.45 mmol) was suspended in diglyme (10 ml) and the mixture was refluxed for 5 min. After cooling the solid was filtered off, washed with diglyme (2 ml) and ether (2×5 ml) and dried under nitrogen. Yield 0.280 g, 82%.

(c) **4** (0.311 g, 1.47 mmol) was dissolved in acetonitrile (5 ml) and TMEDA (0.27 ml, 1.79 mmol) was added. The mixture was stirred first at room temperature for 4 h then at 60 °C for 2 h. After cooling the product was filtered off, washed with acetonitrile (3×2 ml) and ether (3×2 ml) and dried under nitrogen. Yield 0.274 g, 79%.

[(TMEDA)B(H)CN][PF$_6$] (14)

13 (0.537 g, 2.30 mmol) was dissolved in water (5 ml) and a solution of KPF_6 (5 ml, 9%) was added. The precipitate formed was filtered off, washed with water (3×2 ml) and dried. The product is a white powder. Yield 0.589 g, 86%. *Anal.* Found: B, 3.63; C, 28.71; H, 5.53; N, 14.26. Calc. for $C_7H_{17}BF_6N_3P$: B, 3.62; C, 28.12; H, 5.73; N, 14.05%.

[Pic(Q)B(H)CN][PF$_6$] (15)

2 (1.21 g, 5.29 mmol) was dissolved in picoline (10 ml), refluxed for 1 h and then reduced to half of its volume by evaporation. The product formed was filtered off, washed with picoline (2×2 ml) and ether (2×5 ml). The solid (1.02 g) was dissolved in water (4 ml) and a solution of KPF_6 (6 ml, 10%) was added. The crystalline precipitate formed was filtered off, washed with water (2×5 ml) and dried. Yield 0.701 g, 34%. *Anal.* Found: B, 2.71; C, 43.79; H. 5.92; N, 10.87. Calc. for $C_{14}H_{21}BF_6N_3P$: B, 2.79; C, 43.44; H, 5.47; N, 10.85%.

[Pic$_2$B(H)CN]Br (16)

1 (0.358 g, 2.02 mmol) was dissolved in picoline (3 ml) and the solution was refluxed for 5 min. After cooling ether (5 ml) was added, the product was filtered off, washed with ether (5×10 ml) and dried under nitrogen yielding a pale yellow, very hygroscopic solid. Yield 0.54 g, 87%. *Anal.* Found: B, 3.53; Br, 26.36. Calc. for $C_{13}H_{15}BBrN_3$: B, 3.56; Br, 26.29%.

[Pic$_2$B(H)CN][PF$_6$] (17)

16 (0.459 g, 1.51 mmol) was dissolved in water (2 ml) and a solution of KPF_6 (3.25 ml, 10%) was added. The precipitate was filtered off, washed with water (3×2 ml) and dried. The product is a white crystalline material. Yield 0.50 g, 90%. *Anal.* Found: B, 2.92; C, 42.31; H, 4.42; N, 11.51. Calc. for $C_{13}H_{15}BF_6N_3P$: B, 2.93; C, 42.31; H, 4.10; N, 11.39%.

Results and discussion

Trialkylamine-cyanoboranes react readily with bromine–water at room temperature with formation of amine-bromocyanohydroboranes.

$$A\cdot BH_2CN + Br_2 \xrightarrow{H_2O} A\cdot BH(Br)CN + HBr \quad (2)$$

A = Me_3N, Q, TMEDA/2

Usually, the reaction is complete in 1 h.

TMEDA·2BH(Br)CN does not react with bromine in water even when in excess. Q·BH_2CN and Me_3N·BH_2CN form monobromo derivatives readily and dibromo derivatives fairly slowly, and the monobromo derivatives can be isolated without difficulties. These molecules contain chiral boron atoms. Since TMEDA·2BH(Br)CN has two chiral centers, the product is a mixture of diastereomers. The existence of the diastereomers is indicated by doubling of the N–CH_3 resonances in the ^{1}H NMR spectrum.

Trimethylamine-dihydrocyanoborane gives rise to the formation of $Me_3N\cdot BBr_2CN$ in bromine–water mixture.

$$Me_3N\cdot BH_2CN + 2Br_2 \xrightarrow{H_2O\text{–}Br_2} Me_3N\cdot BBr_2CN + 2HBr \quad (3)$$

Quinuclidine-bromocyanohydroborane gives quinuclidine-dibromocyanoborane under similar conditions.

$$Q\cdot BH(Br)CN + Br_2 \xrightarrow{H_2O\text{–}Br_2} Q\cdot BBr_2CN + HBr \quad (4)$$

TMEDA·2BH_2CN can be transformed into its dibromo derivative under much harder conditions, only in refluxing bromine.

$$TMEDA \cdot 2BH_2CN + 4Br_2 \xrightarrow{Br_2} TMEDA \cdot 2BBr_2CN + 4HBr \quad (5)$$

Picoline·BH_2CN reacts differently with bromine in water. The complex consumes 3 mol of bromine, and picoline hydrobromide, boric acid and BrCN can be identified in the reaction mixture.

$$Pic \cdot BH_2CN + 3Br_2 + 3H_2O \longrightarrow Pic \cdot HBr + BrCN + H_3BO_3 + 4HBr \quad (6)$$

However, depending on the molar ratios of the reactants, both monobromo and dibromo derivatives can be prepared in anhydrous methylene chloride. Bu_3P and Ph_3P react similarly in methylene chloride.

$$L \cdot BH_2CN + nBr_2 \xrightarrow{CH_2Cl_2} L \cdot BH_{2-n}(Br)_nCN + nHBr \quad (7)$$

L = Pic, Bu_3P, Ph_3P

The hydrolytic stabilities of the amine-bromocyanohydroboranes are fairly high. They do not hydrolyze in 1 molar hydrochloric acid at 60 °C, and hydrolyze slowly at reflux temperature. In contrast, hydrolysis of trialkylamine-dibromocyanoboranes does not occur even at reflux temperature in 1 molar acid or base. The hydrolytic stabilities of picoline-bromoboranes is much lower. The hydrolysis of Pic·BH(Br)CN and Pic·BBr_2CN is complete in 1 h at room temperature and at 60 °C, respectively.

In testing the reactions of the monobrominated derivatives with amines we found that TMEDA·2BH(Br)CN reacted with TMEDA in refluxing diglyme. The product is a cationic cyanoboron compound containing a five-membered ring and it is very soluble in water.

$$TMEDA \cdot 2BH(Br)CN + TMEDA \xrightarrow{diglyme} 2[(TMEDA)B(H)CN^+]Br^- \quad (8)$$

The structure of the cation is proved by ^1H NMR and MS. In the ^1H NMR spectrum, the N-methyl resonances are doubled and the molecular peak appears at 154 *m/e* in the mass spectrum. It is worth noting that the same product was formed when a diglyme suspension of TMEDA·2BH(Br)CN was refluxed.

$$TMEDA \cdot 2BH(Br)CN \xrightarrow[reflux]{diglyme} [(TMEDA)B(H)CN^+]Br^- \quad (9)$$

Monobromocyanoborane complexes of TMEDA, Q and Me_3N react differently with picoline at reflux. The type of reaction depends on the structure of the amine. When TMEDA·2BH(Br)CN was boiled in picoline, it was transformed into a crystalline product that proved to be a mixture of $[(TMEDA)B(H)CN^+]Br^-$ and $[Pic_2B(H)CN^+]Br^-$.

$$TMEDA \cdot 2BH(Br)CN + 2Pic \xrightarrow{Pic} [(TMEDA)B(H)CN^+]Br^- + [Pic_2B(H)CN^+]Br^- \quad (10)$$

The two components can easily be separated on the basis of their very different solubilities in acetonitrile.

The crude product formed in the reaction of quinuclidine-bromocyanoborane with picoline was a mixture of several products. However, the hexafluorophosphate salt of the asymmetric cation was the only component to be precipitated from aqueous solution.

$$Q \cdot BH(Br)CN + Pic \xrightarrow[(ii)\ KPF_6]{(i)\ Pic} [Pic(Q)B(H)CN^+][PF_6^-] \quad (11)$$

In the reaction of $Me_3N \cdot BH(Br)CN$ with picoline $[Pic_2B(H)CN^+]Br^-$ was formed. This shows that besides cation formation a transamination reaction has taken place as well.

$$Me_3N \cdot BH(Br)CN \xrightarrow[(ii)\ KPF_6]{(i)\ Pic} [Pic_2B(H)CN^+][PF_6^-] + Me_3N \quad (12)$$

In acetonitrile, Pic·BH(Br)CN reacts with TMEDA under mild conditions forming the cyclic cation.

$$Pic \cdot BH(Br)CN + TMEDA \xrightarrow{CH_3CN} [(TMEDA)B(H)CN^+]Br^- + Pic \quad (13)$$

The formation of the cation $[(TMEDA)B(H)CN^+]$ containing a five-membered ring occurs in all cases when BH(Br)CN and TMEDA moieties are present in the reaction mixture simultaneously (see reactions nos. (8)–(10), (13)); this can be explained by the chelate effect. The different behaviors of quinuclidine- and trimethylamine-bromocyanoboranes can be explained by the fact that the steric hindrance on the nitrogen atom in quinuclidine is less than in trimethylamine, thus quinuclidine is a stronger base towards the borane species.

These experimental results point out, that the leaving group character of the bromine in amine-monobromocyanoboranes is especially good, consequently, these compounds will very likely be suitable for the synthesis of new α-amino acid analogous compounds. Dibromocyanoborane complexes did not react with picoline under similar conditions, which indicates that in these derivatives the leaving group character of the bromine is much decreased.

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References

1 B.F. Spielvogel, L Wojnowich, M.K Das, A.T. McPhail and K.D Hargrave, *J Am. Chem Soc., 98* (1976) 5702.
2 B.F. Spielvogel, F. Harchelroad, Jr. and P. Wisian-Neilson, *J. Inorg Nucl. Chem, 41* (1979) 1223.
3 B. Kemp, S. Kalbag and R.A. Geanangel, *Inorg Chem, 23* (1984) 3063.
4 M.P. Kaushik, M.R.M D. Charandabi, M.L. Ettel, T. J Lofthouse and K.W Morse, *Inorg. Chem, 28* (1989) 897.
5 M. Mittakanti and K.W. Morse, *Inorg Chem., 29* (1990) 554.
6 M. Mittakanti and K.W. Morse, *Inorg Chem, 30* (1991) 2434.
7 M.K. Das and P. Mukherjee, *J. Chem Res S,* (1985) 66.
8 W J. Mills, C.H. Sutton, M W. Baize and L.J Todd, *Inorg Chem, 30* (1991) 1046.
9 B. Gyori, I. Lázár and J. Emri, *J Organomet Chem, 344* (1988) 29
10 B. Gyori, I. Lázár and J. Emri, *Magy Kém. Foly, 94* (1988) 100.
11 A. Sood, C K Sood, B.F. Spielvogel and I.H. Hall, *Eur J Med Chem, 25* (1990) 301.
12 I H. Hall, M.K Das, F. Harchelroad, Jr., P Wisian-Neilson, A.T. McPhail and B F. Spielvogel, *J Pharm Sci, 70* (1981) 339.
13 I.H. Hall, B.F. Spielvogel, A Sood, F.U. Ahmed and S. Jafri, *J Pharm Sci, 76* (1987) 359.
14 H. Hall, C.O. Starnes, B.F. Spielvogel, P. Wisian-Neilson, M.K Das and L. Wojnowich, *J Pharm. Sci., 68* (1979) 685.
15 I.H. Hall, C.O Starnes, A.T. McPhail, P. Wisian-Neilson, M K. Das, F. Harchelroad, Jr. and B.F. Spielvogel, *J. Pharm Sci., 69* (1980) 1025.
16 B. Gyori, J. Emri and L. Szilágyi, *J Organomet Chem, 152* (1978) 13.
17 B. Gyori and J. Emri, *J Organomet Chem, 238* (1982) 159.
18 B. Gyori, J. Emri and I. Fehér, *J Organomet Chem, 255* (1983) 17.
19 W.J. Mills, C.H. Sutton, E. Libby and L J. Todd, *Inorg Chem, 29* (1990) 302.
20 J.E. Repasky, C. Weidig and H.C. Kelly, *Synth React Inorg. Met.-Org Chem, 5* (1975) 337.