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PREPARATION AND STUDY OF HYDROLYTICALLY STABLE CYANOHYDRO(PYRROLYL-1)BORATES AND CHIRAL BORON CONTAINING AMINE-CYANO(PYRROLYL-1)BORANE COMPLEXES

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Summary

Lithium- and potassium cyanodihydropyrrolylborates * (made from monopyrrolylborane by reaction with the appropriate cyanide) as well as sodium- and potassium cyanohydrodipyrrolylborates (made from sodium hydrotripyrrolylborate with HCN and from pyridine-dipyrrolylborane with KCN, respectively) were prepared. The hydrolysis of the $BH(NC_4H_4)_2CN^-$ ion in acidic media is approximately 250 times faster than that of the BH_3CN^- ion. On the other hand the $BH_2(NC_4H_4)CN^-$ ion is easily protonated (pK_a = 1.84) at the α-position of the pyrrolyl ring, and is hydrolyzed very slowly even in strongly acidic media. Reaction of the $NaBH(NC_4H_4)_2CN$ with pyridine- and with 4-picoline hydrochlorides (AHCl) results in the formation of compounds $A \cdot BH(NC_4H_4)CN$ containing tetracoordinated chiral boron. Considerable amounts of $C_5H_5N \cdot BH(NC_4H_4)CN$ are also formed in a complex reaction which took place between $KBH_2(NC_4H_4)CN$ and pyridine hydrochloride. These base—borane complexes also undergo α-protonation on the pyrrolyl ring in strongly acidic medium. The boronium ions $ABH(NC_4H_5)CN^+$ formed in this way are stable even in concentrated mineral acids.

Introduction

Cyanotrihydroborate, the first and hitherto the only cyanohydroborate, was prepared in 1951 [1], but chemical properties [2,3] and the scope of its appli-

* In this paper "pyrrolyl" means pyrrolyl-1 throughout.

cation as a reducing agent [4,5] have been examined only in the last 8—10 years. These studies have established that the BH_3CN^- ion is stable in aqueous solution up to pH 2—3, readily undergoes H-D exchange, and is a versatile and selective reducing agent [6]. Another important property of the BH_3CN^- ion is its ability to form stable transition metal complexes in which either B—C—N—M or three-center B—H—M bonds are present [7,8]. We describe below the preparation and the study of some new cyanohydroborates.

Results and discussion

Unlike other aminoboranes, the pyrrolylboranes are fairly strong Lewis acids, so much so that they yield stable compounds (either borane complexes or borates) with numerous Lewis bases [9—11]. Thus, a rapid reaction takes place in THF between THF-monopyrrolylborane [11] and LiCN or KCN essentially according to the following scheme.

$$THF \cdot BH_2(NC_4H_4) + MCN \xrightarrow{THF} MBH_2(NC_4H_4)CN \quad (1)$$

(M = Li, K)

Both reactions yield products which consist of 80 ± 2% of $MBH_2(NC_4H_4)CN$, 10% of $MBH(NC_4H_4)_2CN$ and, probably 10% of MBH_3CN. Similarly, simultaneous formation of several borates takes place in the reactions between $THF \cdot BH_2(NC_4H_4)$ and alkali metal hydrides and pyrrolyls respectively, with the difference that, in these cases, the distribution of the various borates depends strongly on the alkali metal used [11]. Owing to their surprisingly high hydrolytic stability (vide infra), the lithium- and potassium cyanodihydropyrrolylborates can be separated easily from the other borates by hydrolytic decomposition of the latter, so that the former can be obtained pure as crystalline dioxane addition compounds.

The sodium- and potassium cyanohydrodipyrrolylborates were obtained by reactions 2 and 3, as follows:

$$NaBH(NC_4H_4)_3 + HCN \xrightarrow{Et_2O} NaBH(NC_4H_4)_2CN + HNC_4H_4 \quad (2)$$

$$C_5H_5N \cdot BH(NC_4H_4)_2 + KCN \xrightarrow{150^\circ C} KBH(NC_4H_4)_2CN + C_5H_5N \quad (3)$$

Reaction 2 goes to completion within a few hours at room temperature; there is no further cyanide exchange between HCN and the $NaBH(NC_4H_4)_2CN$ produced. The by-product $NaB(NC_4H_4)_3CN$ was also isolated in about 18% yield. These two borates can be easily separated from each other and from other by-products and were obtained pure. Reaction 3 was performed in the melt under a N_2 stream in order to remove the pyridine which was formed in the reaction. Only impure product could be isolated from this reaction, however.

The $BH(NC_4H_4)_2CN^-$ ion is hydrolyzed both in acidic and basic media. In acids the rate of hydrolysis depends essentially only on the H^+ concentration, and is about 250 times greater than that of BH_3CN^- ion. In basic media the hydrolysis proceeds with a half-life of about 1 h [12], and its velocity does not depend on the H^+ concentration. On the other hand, the hydrolysis of the

$BH_2(NC_4H_4)CN^-$ ion is very slow in both acidic and basic media: it decomposes very slowly even in fairly concentrated (several molar) mineral acids. The pH dependence of the UV spectrum of the $KBH_2(NC_4H_4)CN$ (Fig. 1) is very similar to that of the pyrrole itself [13], indicating a preferential protonation at the pyrrolyl ring of the $BH_2(NC_4H_4)CN^-$ ion in acidic media:

$$(C_4H_4N)BH_2CN^- + H^+ \rightleftharpoons (C_4H_5N)BH_2CN \quad (4)$$

The absorption maximum at 246 nm of the protonated form indicates that the protonation probably occurs in the α-position of the pyrrolyl ring [14]. This protonation proceeds more easily than that of the pyrrole itself. This can be clearly seen if we compare the value of the half protonation H_2SO_4 concentration for the pyrrole (5.34 M, $pK_a = -3.8$) [13] and for $BH_2(NC_4H_4)CN^-$ ion (1.46×10^{-2} M, $pK_a = 1.84$) determined by spectrophotometry. In strongly acidic media (pH < 1), in which the borate is practically completely protonated, the rate of hydrolysis is independent of the $[H^+]$ concentration and the hydrolysis is a first order process with a half life of about 3.5 h (t = 25°C, ionic strength = 1.0) [12]. In contrast to the protonated products obtained from pyrrole and from N- and C-substituted derivatives thereof, no polymerisation occurs with $(C_4H_5N)BH_2CN$ in the presence of oxygen. We were unable to detect the formation of a protonated product in the case of $BH(NC_4H_4)_2CN^-$ ion.

The ^1H NMR spectrum of $KBH_2(NC_4H_4)CN$ in 50% H_2SO_4 displays a resonance with two-proton intensity at δ 5.05 ppm, which clearly indicates [13] that the pyrrole ring undergoes α-protonation under these conditions.

Deuteration of the pyrrolyl ring according to eq. 4 occurs rapidly in slightly acidic medium but, in contrast to the result with the BH_3CN^- ion, no BH ⇌ BD exchange takes place even at higher D^+ concentrations. This is supported by the observation that no C-bonded deuterium could be detected by ^1H NMR in a sample of isopropanol which was prepared from acetone by reduction with a sample obtained from $KBH_2(NC_4H_4)CN$ after 50% of it had been decomposed

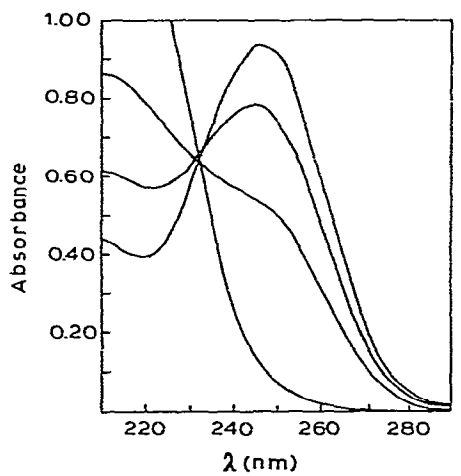

Fig. 1. UV spectrum of a 2×10^{-4} M solution of $KBH_2(NC_4H_4)CN \cdot 1.5\ C_4H_8O_2$, (1) water, (2) 0.0101 M HCl, (3) 0.0507 M HCl, (4) 2 M HCl in the order of increasing absorbance at 245 nm.

hydrolytically with DCl in D_2O. This reaction therefore represents a convenient route to pure $KBH_2(NC_4D_4)CN$.

We have explored the possibility of obtaining $BH(NC_4H_4)CN$ by treatment of $NaBH(NC_4H_4)_2CN$ with dry H_2SO_4 or HCl in THF. Instead of the expected borane, however, we obtained $B(NC_4H_4)_3$ and a polymeric product, which was not investigated further. This behaviour is probably due to the instability of the $BH(NC_4H_4)CN$ in THF solution. On the other hand, $NaBH(NC_4H_4)_2CN$ reacts smoothly with pyridine- and 4-picoline hydrochlorides to give chiral boron complexes as follows.

$$NaBH(NC_4H_4)_2CN + AHCl \xrightarrow{THF} A \cdot BH(NC_4H_4)CN + HNC_4H_4 + NaCl \qquad (5)$$

($A = C_5H_5N$, $4\text{-}CH_3\text{-}C_5H_4N$)

Fig. 2 shows the ^1H NMR spectra of the 4-picoline complex recorded in the absence and presence, respectively, of the chiral shift reagent, $Eu(hfc)_3$. The doubling of both the pyrrolyl α-proton (δ 7.65 and 7.72 ppm) and the picoline H-2 and H-6 (two overlapping broadened "doublets" centered around 9 ppm) resonances in Fig. 2B clearly indicates the presence of two enantiomers for the 4-picoline complex whose interconversion (if any) is slow in the NMR time scale. The pyridine and the 4-picoline complexes from reaction 5 thus represent two additions to the small list of known compounds containing tetracoordinated chiral boron [15,16,17].

Both complexes are hydrolytically very stable and are unchanged in concentrated H_2SO_4 or HCl. They are insoluble in water, and in acids their solubility increases with increasing concentration of the acid. Their ^1H NMR spectra recorded in mineral acids show the presence of the boronium ions, $ABH(NC_4H_5)CN^+$ in which the pyrrolyl group is protonated at the α-position.

It is noteworthy that $C_5H_5N \cdot BH(NC_4H_4)CN$ can also be obtained in ca. 35—40% yield through reaction of $KBH_2(NC_4H_4)CN$ with pyridine hydrochloride. The other 60% of the product mainly consists of polymeric compounds but, interestingly, no hydrogen evolution was observed. In view of the ease of protonation of the pyrrolyl group in $KBH_2(NC_4H_4)CN$ we propose the following scheme for the formation of $C_5H_5N \cdot BH(NC_4H_4)CN$:

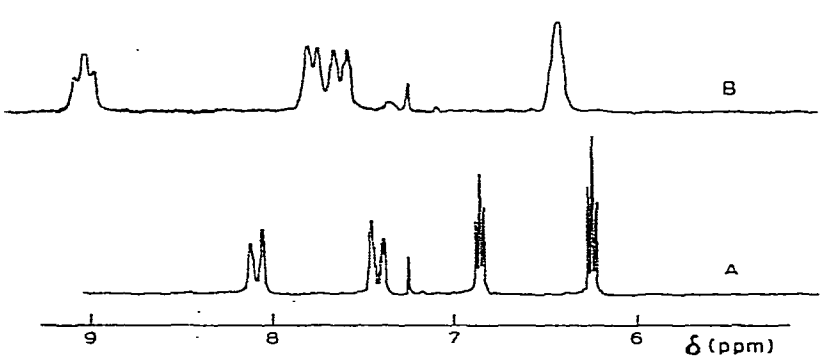

Fig. 2. Partial ^1H NMR spectra (100 MHz) of the 4-picoline complex of $BH(C_4H_4)CN$ in the absence (A) and in the presence (B) of the chiral shift reagent, $Eu(hfc)_3$.

$$KBH_2(NC_4H_4)CN + C_5H_5N \cdot HCl \xrightarrow{THF} BH_2(NC_4H_5)CN + C_5H_5N + KCl \quad (6)$$

$$BH_2(NC_4H_5)CN + KBH_2(NC_4H_4)CN + C_5H_5N \xrightarrow{THF} KBH_2(NC_4H_6)CN + C_5H_5N \cdot BH(NC_4H_4)CN \quad (7)$$

Protonation of the pyrrolyl ring according to eq. 6 leads to the formation of a diene which is easily reduced further by $KBH_2(NC_4H_4)CN$ (eq. 7). Through reactions with pyridine hydrochloride and further reductive steps the cyanodihydropyrrolinylborate could give the polymeric product mentioned above.

In order to explore the possibility of obtaining compounds containing tetracoordinated chiral boron, $KBH_2(NC_4H_4)CN$ was allowed to react with either methyl-(pyridyl-4)ketone or α-bromopropionic acid at a 1 : 1 molar ratio. Instead of the expected diastereoisomers, $KBH(NC_4H_4)CN(OR)$, however, only the borates, $KBHCN(OR)_2$, containing achiral boron, could be isolated. In the case of α-bromopropionic acid, further reaction, involving KBr elimination, was also observed.

Experimental

All experiments were conducted under dry nitrogen, and dry, oxygen-free solvents were used throughout. Diborane [18], $B(NC_4H_4)_3$ [11], $BH_2(NC_4H_4)$ in THF solution [11], $NaBH(NC_4H_4)_3$ in ether [9], $C_5H_5N \cdot BH(NC_4H_4)_2$ [11], and LiCN [19] were prepared by published procedures, LiCN · 0.5 THF was obtained from LiCN through recrystallization in THF. Perkin—Elmer, model 283 and Beckman Acta M V spectrophotometers were used for the IR and UV spectra, respectively. ^1H NMR spectra were obtained at 100 MHz with a Jeol model MH-100 spectrometer.

Preparation of $LiBH_2(NC_4H_4)CN \cdot 2\ C_4H_8O_2$

LiCN · 0.5 THF (2.26 g, 32.8 mmol) was suspended in THF (20 ml) and a 1.64 *M* solution of $BH_2(NC_4H_4)$ in THF (20.0 ml, 32.8 mmol) was added dropwise during 30—40 min. Evaporation at room temperature under reduced pressure afforded a thick oil which was dissolved in ether (70 ml). Upon addition of dioxane (6—7 ml) an oil separated, and this soon crystallized. The mixture was stirred further for a few hours, then filtered, and the solid was washed with ether and extracted with a mixture of ether (80 ml) and dioxane (6.5 ml). (This extraction is rather slow; it requires 6—8 h, but, when it was omitted no solid product could be obtained after the next purification step.) The residue was dissolved in water (25 ml), 0.5 *M* HCl (5.4 ml) was added in small portions and evaporated under reduced pressure. The residue was dissolved in dioxane (20 ml) at 40°C, the solution was filtered and evaporated to 6—7 ml, and ether (30 ml) was added. The crystalline precipitate was filtered and dried in a N_2-stream. Yield: 3.9 g (41%). IR(KBr): ν(B—H), 2298, 2367.3 cm^{-1}; ν(C≡N), 2198.8, 2207.2 cm^{-1}. (Found: B, 3.80; Li, 2.40. $C_{13}H_{22}BLiN_2O_4$ calcd.: B, 3.75; Li, 2.41%.)

Preparation of $KBH_2(NC_4H_4)CN \cdot 1.5\ C_4H_8O_2$

Purified KCN (6.16 g, 94.5 mmol) was suspended in THF (10 ml) cooled in

an ice bath, and a 1.535 *M* solution of monopyrrolylborane in THF (59.8 ml, 91.8 mmol) was added during 30 min. After stirring for 2 h the reaction mixture was evaporated under reduced pressure. The thick oil was dissolved in water (10 ml) and 0.1 *N* HCl solution (15 ml) was added. After standing for 30 min at room temperature the pH of the solution was adjusted to 9 with KOH, and solvent was evaporated off under reduced pressure (0.01 Torr). The residue was dissolved in dioxane (15—20 ml) at 40°C and the solution evaporated again. This was repeated with 40—50 ml of dioxane, and the residue dissolved in dioxane (50 ml). The solution was filtered, and the filtrate deposited fine needles during 1—2 hour's standing. These were filtered off and dried in a N_2-stream to constant weight. Yield: 15.7 g (62%). IR(KBr): ν(B—H), 2307.0, 2375.8 cm^{-1}; ν(C≡N), 2186.6, 2229.0 cm^{-1}. (Found: B, 4.04; K, 14.42. $C_{11}H_{18}BKN_2O_3$ calcd.: B, 3.91; K, 14.16%.)

Preparation of $KBH_2(NC_4D_4)CN \cdot C_4H_8O_2$

$KBH_2(NC_4H_4)CN \cdot 1.5\ C_4H_8O_2$ (4.02 g, 14.56 mmol) was dissolved in D_2O (15 ml) (99.5 atom % D) and 20% DCl in D_2O (0.1 ml) was added. The solution was evaporated under reduced pressure after 1 h, the residue dissolved in D_2O (7.5 ml), and 20% DCl solution (0.05 ml) was added. After standing for a few hours the solution was evaporated, and the residue was dissolved in dioxane (10—15 ml), and the solvent was then evaporated under reduced pressure. This procedure was repeated once more. The residue was dissolved in dioxane (10—15 ml) at 40—50°C and the solution filtered. The crystalline precipitate was dried in a N_2-stream. If the product becomes oily during drying, it is treated with dioxane (3—4 ml) and dried again. Yield: 2.60 g (76%). IR(KBr): ν(B—H), 2306, 2377.5 cm^{-1}; ν(C≡N), 2187.5, 2220.2 cm^{-1}. (Found: B, 4.43; K, 16.18; D : H (pyrrolyl ring), 1 : 0.012. $C_9H_{10}BD_4KN_2O_2$ calcd.: B, 4.58; K, 16.56%.)

Preparation of $NaBH(NC_4H_4)_2CN \cdot 3\ C_4H_8O_2$ *and* $NaB(NC_4H_4)_3CN \cdot 1.5\ C_4H_8O_2$

To a stirred solution of $NaBH(NC_4H_4)_3$ (21.74 g, 93.3 mmol) in ether (100 ml) at 0°C was added a 1.305 *M* solution of HCN in ether (72.8 ml, 95.0 mmol). The mixture was kept at room temperature for 15—20 h. The gelatinous precipitate was filtered off the filtrate was cooled to —40°C, and dioxane (11.0 ml) was added with vigorous stirring. An oil was first precipitated, but this gradually crystallized. The crystals were filtered off after stirring for 2 h at room temperature, then dissolved in dioxane (110—120 ml) at 80°C. The filtered solution was allowed to crystallize at room temperature for 2 h. The crystalline precipitate was filtered off, washed with dioxane (3 × 15 ml), and dried in a N_2-stream. Yield: 23.7 g (56%). IR(KBr): ν(B—H), 2402.2, 2413(sh), 2425(sh) cm^{-1}; ν(C≡N), 2206.7 cm^{-1}. (Found: B, 2.45; Na, 5.07. $C_{21}H_{33}BN_3NaO_6$ calcd.: B, 2.36; Na, 5.03%.)

The filtrate from $NaBH(NC_4H_4)_2CN \cdot 3\ C_4H_8O_2$ was evaporated to 40 ml under reduced pressure. 1—2 drops of this viscous solution was added to dioxane at 8—10°C to give a microcrystalline precipitate immediately. The main solution was seeded with this precipitate, left for 10—15 h then filtered. The precipitate was dried in a N_2-stream. This crude product was extracted six times with a mixture of ether (80 ml) and dioxane (8 ml). After drying, 5.1 g (14%) pure sodium cyanotripyrrolylborate-1.5 dioxane was obtained. IR(KBr): ν(C≡N), 2216.8

cm^{-1}. (Found: B, 2.86; Na, 6.04. $C_{19}H_{24}BN_4NaO_3$ calcd.: B, 2.77; Na, 5.89%.)

Preparation of $C_5H_5N \cdot BH(NC_4H_4)CN$

(a) From $NaBH(NC_4H_4)_2CN \cdot 3\ C_4H_8O_2$. To a stirred suspension of 1.12 g (96.6 mmol) $C_5H_5N \cdot HCl$ in THF (15 ml) was added 4.42 g (96.7 mmol) $NaBH(NC_4H_4)_2CN \cdot 3\ C_4H_8O_2$ in THF (30 ml). After 10 min, the mixture was filtered and the filtrate evaporated to dryness in a N_2-stream. The residue was triturated with ether (20 ml), and residue filtered off. The product was isolated from it by extraction with ether. Yield: 1.06 g (60%). IR(KBr): ν(B—H), 2462.8 cm^{-1}; ν(C≡N), 2207.2 cm^{-1}. (Found: B, 5.73; N, 21.87. $C_{10}H_{10}BN_3$ calcd.: B, 5.91; N, 22.96%.)

(b) From $KBH_2(NC_4H_4)CN \cdot 1.5\ C_4H_8O_2$. Using the above procedure, 0.90 g (41%) crystalline product was obtained from 1.39 g (12.0 mmol) $C_5H_5N \cdot HCl$ and 3.23 g (12.0 mmol) $KBH_2(NC_4H_4)CN \cdot 1.5\ C_4H_8O_2$. (Found: B, 5.80; N, 21.49%.)

Preparation of $4\text{-}CH_3\text{-}C_5H_4N \cdot BH(NC_4H_4)CN$

To a stirred suspension of 1.21 g (9.3 mmol) 4-picoline hydrochloride in THF (15 ml) was added in 6—8 minutes 4.16 g (9.1 mmol) $NaBH(NC_4H_4)_2CN \cdot 3\ C_4H_8O_2$ in THF (35 ml). The resulting solution was evaporated under reduced pressure, the gelatinous residue triturated with ether (40—50 ml) until it became crystalline. It was filtered off then extracted with ether (25 ml) and a crystalline product (0.78 g, 44%) was isolated from the extract. IR(KBr): ν(B—H), 2440.5 cm^{-1}; ν(C≡N), 2210.5 cm^{-1}. (Found: B, 5.56; N, 20.83. $C_{11}H_{12}BN_3$ calcd.: B, 5.49; N, 21.33%.)

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