Studies on the Reactivity of Dicyanodihydroborate with Some Lewis Base Hydrochlorides

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Synopsis. The reactions of sodium dicyanodihydroborate with various Lewis base hydrochlorides produce mainly the metathesis reaction products in contrast to those of sodium cyanotrihydroborate, which produces cyanoborane adducts. This has been established with the help of IR, ^{1}H and ^{11}B NMR data.

Although cyanotrihydroborate ion has been known as its lithium salt[1] for long time, its sodium salt[2] has been mostly used for its chemistry. On the other hand, dicyanodihydroborate ion has been reported only recently as its sodium salt,[3] which can be stabilized as its dioxane complex, $Na[BH_2(CN)_2]\cdot 0.65\,C_4H_8O_2$.[4] With the aim of devising a general synthesis of amine adducts of dicyanoborane similar to those of cyanoborane, a series of reactions between sodium dicyanodihydroborate and Lewis base hydrochlorides have been carried out and the results are reported here.

Results and Discussion

An important general synthesis of amine-cyanoboranes involves the reaction of $Na[BH_3CN]$ with amine hydrochlorides (Eq. 1).[5,6] In most cases the yields are

$$Na[BH_3CN] + R_{3-n}NH_n\cdot HCl \xrightarrow[66\,^\circ C]{THF} R_{3-n}NH_n\cdot BH_2CN + NaCl + H_2 \quad (1)$$

very high indicating that a path involving the metathesis of the two reactants to produce $[R_{3-n}NH_{n+1}][BH_3CN]$ is quite less favorable. This method is general even for Lewis bases having tertiary nitrogen, such as *N,N'*-tetramethylethylenediamine,[7] trialkylamines[6] and phosphines.[8] Accordingly, we have been interested in devising a general synthesis of amine-dicyanoboranes, $R_{3-n}NH_n\cdot BH(CN)_2$, by a similar method (Eq. 2a) starting from the dioxane complex, $Na[BH_2(CN)_2]\cdot 0.65C_4H_8O_2$, which is an air-stable solid.[4] The reactions of this complex have been investigated with several amine hydrochlorides.

$$Na[BH_2(CN)_2] + R_{3-n}NH_n\cdot HCl \longrightarrow \begin{cases} R_{3-n}NH_n\cdot BH(CN)_2 + NaCl + H_2 & (2a) \\ [R_{3-n}NH_{n+1}][BH_2(CN)_2] + NaCl & (2b) \end{cases}$$

In all cases the principal product was the metathesis product, a quarternary ammonium dicyanodihydroborate, as evident from the ^{11}B NMR spectra (vide infra). The amines have been varied from primary through secondary to tertiary with various groups on the nitrogen to find out whether changes in the basicity have any influence on the mode of reaction, that is, whether the path as in Eq. 2a or in Eq. 2b is the preferred one. Similarly, an amine oxide such as β-picoline oxide and a phosphine such as triphenylphosphine have been utilized for the same purpose. It has been observed that, in all cases, the primary product was the metathesis reaction product, although minor amounts of other products have been detected in some of these by the ^{11}B NMR spectra. This behavior is remarkable in that, with cyanotrihydroborate only amine-cyanoboranes have been reported, with no apparent formation of the metathesis products. Trimethylamine oxide has been reported to react with $NaBH_4$ to give $Me_3NO\cdot BH_3$ in solution, while trimethylphosphine oxide and triphenylphosphine oxide react with diborane to give materials of composition $R_3PO\cdot 0.5B_2H_6$.[9] Therefore, nonformation of amine-dicyanoborane from this reaction must be related to its extreme stability induced by the presence of an additional cyano group.

The products have been found to be highly soluble in water and organic solvents such as DMSO, DMF, and THF, and insoluble in aprotic nonpolar solvents. Conductance studies in water show them to be appreciably conducting. The Λ° for $Na[BH_2(CN)_2]$ in water is 84 ohm^{-1} cm^2 mol^{-1} giving Λ° for $[BH_2(CN)_2]^-$ to be 33.9 ohm^{-1} cm^2 equiv^{-1} at 25 °C. Complete conductance measurements on the products derived from one representative amine, viz., dibutylamine, β-picoline oxide, and triphenylphosphine show that for $[\beta\text{-picOH}][BH_2(CN)_2]$ the coordinated proton in $[\beta\text{-picOH}]^+$ begins to dissociate below the concentration of 10^{-4} mol dm^{-3} (Λ=56 ohm^{-1} cm^2 mol^{-1} at $c=0.9\times10^{-4}$ mol dm^{-3}, 66 ohm^{-1} cm^2 mol^{-1} at $c=0.7\times10^{-4}$ mol dm^{-3}, 132 ohm^{-1} cm^2 mol^{-1} at $c=0.7\times10^{-5}$ mol dm^{-3} and so on). But the protons in $[(n\text{-}C_4H_9)_2NH_2][BH_2(CN)_2]$ (Λ°=71 ohm^{-1} cm^2 mol^{-1}) and $[Ph_3PH][BH_2(CN)_2]$ (Λ°=58 ohm^{-1} cm^2 mol^{-1}) do not do so.

In the IR the ν(BH) and ν(CN) modes are found to occur, respectively, at 2422—2387 cm^{-1} and 2257—2193 cm^{-1} and the ν(NH) bands at 3413—3318 cm^{-1} as broad ones. For the compound derived from β-picoline oxide the ν(OH) of the cation occurs at 2587 cm^{-1} in consonance with that (2581 cm^{-1}) in the free hydrochloride. Similarly, the ν(PH) in the triphenylphosphine compound is found at 2612 cm^{-1}, that in the hydrochloride itself being 2608 cm^{-1}.

The ^{1}H NMR spectra confirm the presence of alkyl or aryl groups. The ^{11}B NMR signals are shown as triplets at δ −41.1 to −42.1 with $J(^{11}B\text{-}^1H)$ of 93—98.4 Hz, except for the products derived from β-picoline oxide and triphenylphosphine, for which the $\delta(^{11}B)$ are −45.8 (J=95 Hz) and −45.9 (J=93 Hz), respectively. The difference in the δ values with the cation has also been observed between the sodium and tetrabutylammonium salts.[3] Thus the spectra show the

presence of BH_2 groups in all the products, indicating the presence of $[LH][BH_2(CN)_2]$ instead of the expected $L \cdot BH(CN)_2$ species (L=amine, amine oxide, or phosphine). In addition to the signals for $[BH_2(CN)_2]^-$ which dominate in the spectra, there are signals at ca. −23 and/or ca. −19 ppm, which are not insignificant, in the products derived from the amines except for $(i\text{-}C_3H_7)_2NH$. This indicates that in addition to the metathesis reaction, at least two other reactions take place. Following $^{11}B\{^1H\}$ studies and considering that δ −23 region would correspond to a B_3 species, it is assumed that this signal may result from $[B_3H_7CN]^-$ or the like, while the signal at δ −19 region seems to result from H-free species. The signals at δ 0.78 region in **2** and **8** may be due to $L \cdot B(CN)_3$ species as no B-H coupling is present. The δ −17.7 signal in β-picoline oxide compound probably owes to the same species as that for the ca. −19 ppm signal in others. Thus the results show that the species $[LH][BH_2(CN)_2]$ dominate in the products of all the reactions, while secondary reactions also take place either simultaneously or on storing but the elusive $L \cdot BH(CN)_2$ are not formed.

Considering that the preferred route is Eq. 2b, the hydride hydrogen may no longer be available for reaction, it was thought worthwhile to compare their reducing behavior, if any, with those of amine-boranes,[10] cyanotrihydroborate,[2] and amine-cyanoboranes.[11] The results indicate that the ion $[BH_2(CN)_2]^-$ having two cyano groups—one additional with respect to the cyanotrihydroborate or amine-cyanoborane—fails to reduce even the most susceptible substrate 4-nitrobenzaldehyde with butylamine-cyanoborane.[11] Therefore, the presence of one additional cyano group gives extra stability so that the hydride hydrogen which would have been available for the generation of H_2 (Eq. 2a) is no longer available.

Experimental

$Na[BH_3CN]$(Aldrich) and Ph_3P (Riedel) were used without further purification. All amines were commercial products and were purified by standard procedures. β-Picoline oxide was prepared according to published procedure.[12] The Lewis base hydrochlorides were prepared by passing dry HCl through either ethereal[6] or ethanolic[13] solutions. $Na[BH_2(CN)_2] \cdot 0.65C_4H_8O_2$ was prepared by published method,[3,4] and was washed with ether repeatedly to remove the liberated aniline and adhering dioxane.

All initial operations were carried out under an atmosphere of dry N_2. IR spectra were recorded on a Perkin-Elmer 883 spectrophotometer as smears. Proton NMR spectra were recorded in DMSO-d_6 on a JEOL-JNM-100 spectrometer, with TMS as internal standard, and ^{11}B NMR were recorded on an IBM 200 SY, a Varian VXR-400, or a Bruker AP 200 spectrometer. Boron was estimated volumetrically,[14] and nitrogen by Kjeldahl's method.

Reactions of Lewis Base Hydrochloride with $Na[BH_2(CN)_2] \cdot 0.65C_4H_8O_2$. A mixture of $Na[BH_2(CN)_2] \cdot 0.65\ C_4H_8O_2$ (2.90 g, 0.02 mol), an appropriate Lewis base (amine, amine oxide, or phosphine) hydrochloride (0.02 mol) and THF (50 ml) was taken in a three-necked flask fitted with a reflux condenser, a magnetic stirring bar, and a N_2-inlet tube, the set-up having been previously flushed with dry N_2 and stirred for 30 min at room temperature, followed by refluxing for 24 h. There was no perceptible liberation of gas. On cooling the reaction mixture, the precipitated NaCl was removed by filtration and the solvent was evaporated on a rotary evaporator whereby colorless or light yellow viscous materials were obtained. The products were further washed with ether to ensure complete removal of dioxane and aniline, if any still present. The products along with their yields and physical and analytical data are collected below.

$[(C_2H_5)_2NH_2][BH_2(CN)_2]$ (1). (80%): ν(NH) 3408 m, br, ν(BH) 2394 s, ν(CN) 2200 s; $\delta(^1H)$=1.20 t, 2.92 q; $\delta(^{11}B)$=−42.0 (t, J=94 Hz), minor bands at −22.0, −19.5. Found: B, 7.89; N, 29.42%; Calcd for $C_6H_{14}N_3B$: B, 7.77; N, 30.22%.

$[(C_2H_5)_3NH][BH_2(CN)_2]$ (2). (81%): ν(NH) 3413 s, br, ν(BH) 2397 s, ν(CN) 2198 s; $\delta(^1H)$=1.16 t, 3.08 q; $\delta(^{11}B)$=−42.1 (t, J=94.4 Hz), minor bands at −23.6, +0.78. Found: B, 6.55; N, 24.86%; Calcd for $C_8H_{18}N_3B$: B, 6.47; N, 25.15%.

$[n\text{-}C_3H_7NH_3][BH_2(CN)_2]$ (3). (81%): ν(NH) 3382 m, br, ν(BH) 2396 s, ν(CN) 2200 s; $\delta(^1H)$=0.88 t, 1.08—1.80 m, 2.60—3.08 m; $\delta(^{11}B)$=−41.1 (t, J=93 Hz), minor bands at −23.1, −18.8. Found: B, 8.93; N, 33.14%; Calcd for $C_5H_{12}N_3B$: B, 8.65; N, 33.62%.

$[(i\text{-}C_3H_7)_2NH_2][BH_2(CN)_2]$ (4). (84%): ν(NH) 3382 s, br, ν(BH) 2392 s, ν(CN) 2202 s; $\delta(^1H)$=1.24 d, 3.32 m; $\delta(^{11}B)$=−41.9 (t, J=98.4 Hz). Found: B, 6.77; N, 24.78%; Calcd for $C_8H_{18}N_3B$: B, 6.47; N, 25.15%.

$[(n\text{-}C_3H_7)_3NH][BH_2(CN)_2]$ (5). (81%): ν(NH) 3375 m, br, ν(BH) 2380 s, ν(CN) 2193 m; $\delta(^1H)$=0.87 t, 1.70 m, 2.96 m; $\delta(^{11}B)$=−42.0 (t, J=94 Hz), minor bands at −23.6, −19.4. Found B, 5.06; N, 19.07%; Calcd for $C_{11}H_{24}N_3B$: B, 5.17; N, 20.09%.

$[s\text{-}C_4H_9NH_3][BH_2(CN)_2]$ (6). (74%); ν(NH) 3355 m, br, ν(BH) 2391 s, ν(CN) 2200 s; $\delta(^1H)$=0.88 t, 1.16 d, 1.52 m, 3.08 m; $\delta(^{11}B)$=−41.1 (t, J=95 Hz), minor bands at −23.1, −18.9. Found: B, 7.66; N, 29.64%; Calcd for $C_6H_{14}N_3B$: B, 7.77; N, 30.22%.

$[(n\text{-}C_4H_9)_2NH_2][BH_2(CN)_2]$ (7). (77%); ν(NH) 3318 s, br, ν(BH) 2393 s, ν(CN) 2200 s,; $\delta(^1H)$=0.88 t, 1.42 m, 2.88 t; $\delta(^{11}B)$=−41.1 (t, J=95 Hz), minor bands at −23.1, −18.9. Found: B, 5.81; N, 21.06%; Calcd for $C_{10}H_{22}N_3B$: B, 5.54; N, 21.53%. Λ°=71 ohm^{-1} cm^2 mol^{-1} (in water).

$[(i\text{-}C_4H_9)_2NH_2][BH_2(CN)_2]$ (8). (79%); ν(NH) 3356 m, br, ν(BH) 2387 s, ν(CN) 2200 s; $\delta(^1H)$=0.96 d, 2.02 m, 2.74 d; $\delta(^{11}B)$=−42.0 (t, J=93.6 Hz), minor bands at −19.2, +0.78. Found: B, 5.64; N, 21.19%; Calcd for $C_{10}H_{22}N_3B$: B, 5.54; N, 21.53%.

$[3\text{-}CH_3C_5H_4NOH][BH_2(CN)_2]$ (9). (82%); ν(OH) 2587 m, br, ν(BH) 2397 s, ν(CN) 2193 s; $\delta(^1H)$=2.34 s, 7.44 m, 7.6 m, 8.46 m; $\delta(^{11}B)$=−45.8 (t, J=95 Hz), minor band at −17.7. Found: B, 5.83; N, 23.81%; Calcd for $C_8H_{10}N_3OB$: B, 6.17; N, 24.01%. Λ°=58 ohm^{-1} cm^2 mol^{-1} (in water).

$[(C_6H_5)_3PH][BH_2(CN)_2]$ (10). (79%); ν(PH) 2612 m, br, ν(BH) 2422 s, 2388 s, ν(CN) 2257 s, 2196 s; $\delta(^1H)$=7.36 m, 7.60 m; $\delta(^{11}B)$=−45.9 (t, J=93 Hz). Found: B, 3.04: N, 8.15; P, 9.11%; Calcd for $C_{20}H_{18}N_2BP$: B, 3.29; N, 8.54; P, 9.44%. Λ°=52 ohm^{-1} cm^2 mol^{-1} (in water).

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