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PREPARATION AND PROPERTIES OF NOVEL CYANO AND ISOCYANO DERIVATIVES OF BORANE AND THE TETRAHYDROBORATE ANION

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Summary

Reaction of $NaBH_3CN$ with HCl in THF gave mainly $NaBH_3CNBH_2CN$, whereas in Me_2S quantitative formation of BH_2CN was observed. In dimethyl sulfide BH_2CN exists in monomeric or dimeric form as Me_2S complexes in an equilibrium with oligomers. These compounds are converted by amines into BH_2CN complexes in nearly quantitative yield, and treatment with lithium cyanide gives $LiBH_2(CN)_2$. The reaction of the Me_2S complexes of the corresponding bromoboranes with AgCN gives isocyanoborates $AgBH_n(NC)_{4-n}$ ($n = 1,2$), which can be easily converted into sodium salts, which are transformed into cyanoborates by thermal isomerization. The di- and tricyanohydroborates are extremely stable towards acids, and the $BH_3CNBH_2CN^-$ ion is significantly more stable than the BH_3CN^- ion. On bromine oxidation in the presence of N-bases $LiBH_2(CN)_2$ gives N-base · $BH(CN)_2$ complexes and $LiBH_2(CN)CNBH(CN)_2$. $NaBH(NC)_3$ is transformed into $C_5N_5N \cdot BH(NC)_2$ upon treatment with pyridin hydrochloride.

Introduction

Of the cyanohydroborates only the salts of monocyanotrihydroborate [1–4] and the CN-bridged $NaBH_3CNBH_3$ [5] have been synthesized up to now. Of the isocyanohydroborates, $NaBH_3NC$ has been observed but not isolated [2]. Except for $B(CN)_3$, only monosubstituted analogues of cyano- and isocyanoboranes are known, namely, THF · BH_2CN in tetrahydrofuran solution [6,7], $(BH_2CN)_n$ oligomers [8,9], amine and phosphine complexes of BH_2CN [7,10–15], $Me_3N \cdot BH_2NC$ [16], and several CN-bridged compounds (THF · BH_2CNBH_3 [17], amine · BH_2NCBH_3 [5,18]). To our knowledge the only dicyanohydroborate prepared previously is the $NaBH(CN)_2(NC_4H_4) \cdot 1{,}5C_4H_8O_2$ (where NC_4H_4 = pyrrolyl-1, $C_4H_8O_2$ = dioxane) [19].

Because of the presence of the strong electron-withdrawing CN group in cyanoboranes and cyanohydroborates the reactivity of the B–H bonding is signifi-

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cantly decreased towards protons and reducable organic groups. Consequently, $NaBH_3CN$ is stable in aqueous medium up to pH = 3, and it is widely utilized as a selective reducing agent in organic and biochemistry [21,22].

We describe below the preparation and study of the chemical properties of some novel cyano and isocyano derivatives of BH_3 and the BH_4^- anion.

Results and discussion

Previous studies [6,7] have established that reaction of $NaBH_3CN$ with HCl in THF gives $THF \cdot BH_2CN$. However, our investigations showed that after reaction of $NaBH_3CN$ with HCl in a 1/0.64–0.68 molar ratio (in 0.5–3.5 *M* solution) $NaBH_3CNBH_2CN$ could be isolated in 45–50% yield. In the light of the molar ratio found, it seems that 64–72% of the reaction takes the following course:

$$2NaBH_3CN + HCl \xrightarrow[0°C]{THF} NaBH_3CNBH_2CN + NaCl + H_2 \quad (1)$$

while 28–36% involves another process, corresponding to a 1/1 molar ratio of the reactants, and resulting in the formation of $(BH_2CN)_n$ as shown by IR spectroscopy. The addition of HCl causes an almost immediate evolution of H_2, but $NaBH_3CNBH_2CN$ is not further transformed even in the presence of excess HCl, indicating that the $CNBH_2CN$ group stabilizes the B–H bonding towards protolyses much better than the CN group.

The reaction of $NaBH_3CN$ with HCl in Me_2S involves a 1/1 molar ratio of the reactants and is accompanied by the evolution of a stoichiometrical amount of H_2:

$$NaBH_3CN + HCl \xrightarrow[0°C]{Me_2S} 1/n(BH_2CN)_n + NaCl + H_2 \quad (2)$$

The $(BH_2CN)_n$ was isolated in solid form with almost quantitative yield. Its IR spectrum in CCl_4 (Fig. 1, spectrum d) is very similar (ν(B–H) 2440, 2473; ν(C≡N) 2298 cm^{-1}) to that of the product formed from $NaBH_3CN$ with HCl in ether, which could be isolated in not more than 20% yield upon sublimation [9]. In addition to < 1% of $(BH_2CN)_4$ (*m/e* 152–156), only five (*m/e* 190–195) and six-membered oligomers (*m/e* 228–233) could be detected in the Me_2S solution of the product by GC/MS, and the amounts of $(BH_2CN)_5$ and $(BH_2CN)_6$ were ca. 86 and 14%, respectively. The *m/e* values indicate the isotope pattern for boron and loss of hydrogen from the molecular ion. On evaporation of a Me_2S solution of the sample in the test tube, or on using a solid sample, the corresponding 7–15 membered oligomers (for $(BH_2CN)_{15}$: *m/e* 575–583) could be also detected with gradually decreasing intensities.

In the light of the above IR and GC/MS data it is probable that the $(BH_2CN)_n$ which we isolated has a cyclic structure, similar to that of the cyanoborane oligomer obtained from ether [9]. On the other hand, the IR spectrum of $(BH_2CN)_n$ recorded in Me_2S or Me_2S/CCl_4 solutions shows two absorptions, at 2248 and 2216 cm^{-1}, in addition to that characteristic of the bridged CN group (at 2295 cm^{-1} in Me_2S); presumably, the former bands are to be assigned to the $Me_2S \cdot BH_2CN$ and/or $Me_2S \cdot BH_2CNBH_2CN$ complexes (Fig. 1, a, b, c). Compared with the band at 2295 cm^{-1}, the intensity of the two bands at lower wave numbers is increased by increasing the Me_2S/BH_2CN molar ratio, and is markedly decreased on dilution

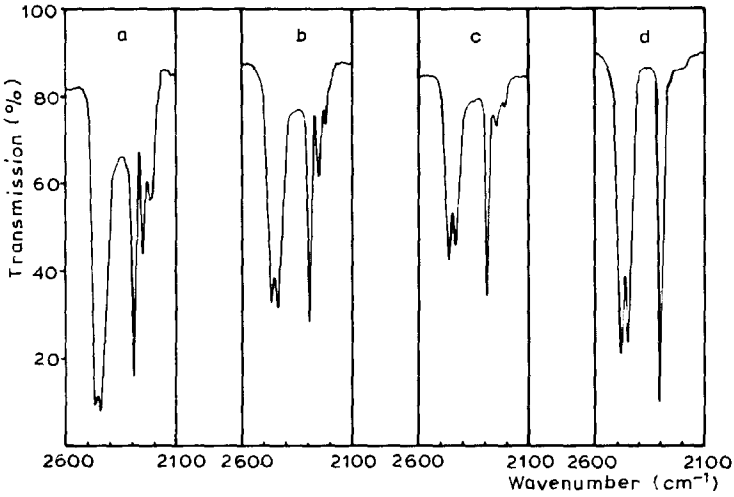

Fig. 1. Relevant parts of the IR spectrum of $(BH_2CN)_n$ in Me_2S at 1/120 BH_2CN/Me_2S molar ratio (a), in Me_2S at 1/30 BH_2CN/Me_2S molar ratio (b), in 1/1 Me_2S/CCl_4 at 1/30 BH_2CN/Me_2S molar ratio (c), and in CCl_4 (d).

with CCl_4 at a given molar ratio. This suggests that an equilibrium exists between $(BH_2CN)_n$ and the dimethyl sulfide complexes.

Reaction of $(BH_2CN)_n$ with $LiCN \cdot CH_3CN$ in dimethyl sulfide gave dicyanodihydroborate:

$$1/n(BH_2CN)_n + LiCN \cdot CH_3CN \xrightarrow[\text{reflux}]{Me_2S} LiBH_2(CN)_2 + CH_3CN \qquad (3)$$

Formation of only a small amount of $LiBH_2(CN)CNBH_2CN$ was detected. The product was isolated in 65–70% yield as a dioxane adduct $[LiBH_2(CN)_2 \cdot C_4H_8O_2]$, and this which under reduced pressure gives the dioxane-free borate, which upon treatment with pyridine gives a product of composition $LiBH_2(CN)_2 \cdot C_4H_8O_2 \cdot 0.5NC_5H_5$.

The bromoborane complexes $Me_2S \cdot BH_nBr_{3-n}$ ($n = 1,2$) do not react with LiCN or NaCN in Me_2S but can be transformed into isocyanohydroborates with AgCN:

$$Me_2S \cdot BH_nBr_{3-n} + (4-n)AgCN \xrightarrow[\text{room temp.}]{Me_2S} AgBH_n(NC)_{4-n} + (3-n)AgBr + Me_2S \qquad (4)$$

The silver isocyanohydroborates can be separated from AgBr by treatment with alkali cyanides in aqueous medium as they are appreciably soluble only in the presence of a large excess of cyanide ion.

The silver isocyanohydroborates can be transformed into the corresponding Na salts by treatment with sodium in the presence of benzophenone:

$$AgBH_n(NC)_{4-n} + Na \xrightarrow[Ph_2CO]{THF} NaBH_n(NC)_{4-n} + Ag \qquad (5)$$

The sodium salts are isolated as $NaBH(NC)_3 \cdot 2C_4H_8O_2$ or $NaBH_2(NC)_2 \cdot 3C_4H_8O_2$, which can be converted under reduced pressure (0.01 mbar) at 60°C, into

adducts containing 0.5 mol of dioxane. Boiling of suspensions of these adducts in n-dibutyl ether gives the corresponding cyanoborates by isomerization:

$$NaBH_n(NC)_{4-n} \cdot 0.5C_4H_8O_2 \xrightarrow[\text{reflux}]{Bu_2O} NaBH_n(CN)_{4-n} + 0.5C_4H_8O_2 \quad (6)$$

The isomerization of the triisocyanohydroborate and diisocyanodihydroborate requires 10–15 and 2 h, respectively.

The mode of bonding of the CN group in the above compounds was established from the $\nu(C{\equiv}N)$ frequency in the IR spectrum, and by considering their hydrolytic stability. The $\nu(C{\equiv}N)$ frequency of alkali cyanohydroborates was 50–70 cm^{-1} higher than that of the respective isocyanohydroborates (Table 1). This difference corresponds to the frequency-difference generally observed for coordinated cyanide and isocyanide ligands [23,24] and also for those in cyanotrihydro- and isocyanotrihydroborates [2] or $Me_3N \cdot BH_2CN$ and $Me_3N \cdot BH_2NC$ [16]. The $\nu(C{\equiv}N)$ frequencies are not significant different in the case of the corresponding silver salts (Table 1), and consequently, these values are not suitable for establishing of the mode of bonding.

It was previously found that $NaBH_3NC$ is markedly less stable towards hydrolysis than $NaBH_3CN$ [2]. An analogous large difference is observed in the hydrolytic stabilities of the prepared cyano- and isocyanohydroborates. Neither hydrolysis nor H–D exchange was observed in a ^1H NMR study of the cyanoborates in 50 g/g % deuterosulfuric acid solution even after one week. In 98% sulfuric acid evolution of H_2 was observed only at 100–120°C and was accompanied by the formation of SO_2. On the basis of these results the $BH_2(CN)_2^-$ and $BH(CN)_3^-$ ions seem to be the most hydrolytically stable tetrahydroborate derivatives known. These ions possess hydrolytic stability similar to or greater than the "aromatic" polyhedral $(B_nH_n)^{2-}$ ions, carboranes [25], or ions of the $BH_2(NR_3)_2^+$-type [34]. The hydrolytic stability of isocyanoborates is markedly lower. Like that of BH_3CN^- [20] and pyrrolylhydroborates [26], the hydrolysis of these isocyanoborates is a H^+-catalyzed process. The $BH_2(NC)_2^-$ ion and the $BH(NC)_3^-$ ion hydrolyze almost 3.5–4 and 2 orders of magnitude faster, respectively, as the BH_3CN^- ion [27]. On the other hand, the isocyanohydroborates are more stable than the hydroborates containing B–N(amino) bonding. For example the $BH_2(NC)_2^-$ ion is almost 4 orders of magnitude more stable than the $BH_2(NC_4H_4)_2^-$ ion [26], and the $BH(NC)_3^-$ ion is ca. 3 orders of magnitude more stable than the $BH(NC_4H_4)_3^-$ ion [26].

Comparison of the ^1H NMR data of the cyano- and isocyanohydroborates with relevant data in the literature [2,16] provides further confirmation of our conclusion regarding the CN bonding. The values of chemical shift (δ, ppm) and coupling constants (^1J(BH), Hz) in D_2O are: $BH_2(CN)_2^-$: 1.11, 96.0; $BH(CN)_3^-$: 1.94, 99.6; $BH_2(NC)_2^-$: 2.17, 106.4; $BH(NC)_3^-$: 2.58, 122.0.

Treatment of the Me_2S solution of $(BH_2CN)_n$ obtained on reaction 2 with amines gave the corresponding amine complexes which were isolated generally in 85–90% yield:

$$1/n(BH_2CN)_n + A \xrightarrow[\text{room temp.}]{Me_2S} A \cdot BH_2CN \quad (7)$$

(A = aniline, 4-chloroaniline, morpholine, piperidine, 4-cyanopyridine, 4-aminopyridine, 4-acetylpyridine, isonicotinic acid, *N*-methylnicotinic amide, pyrazole)

The preparation of amine-monocyanoboranes by reactions 2 and 7 is more convenient than the hitherto described general methods, which give low yields (ca. 30%) [7,10,13], or require prolonged reaction times (16–200 h) [14,15]. The complexes can be isolated in good yield even in the case of very weakly basic amines or amines containing a reducable group (C=O group).

The compounds $BH(CN)_2$ could not be made from dicyanodihydroborates and HCl because of the great stability of the $BH_2(CN)_2^-$ ion towards protons and so the possibility of the oxidative removal of the hydrogen with bromine in the presence of base was examined. No $BH(CN)_2$ was, in fact, produced in reactions in various solvents (Me_2S, THF, CH_3CN, CCl_4) and under various conditions. Less than the calculated amount of bromine reacted, and unchanged $LiBH_2(CN)_2$, base · $BH(CN)_2$ and a compound of composition $LiBH_2(CN)CNBH(CN)_2$ were isolated from the reaction mixtures. The last product was obtained in ca. 35% yield from the dioxane-free $LiBH_2(CN)_2$ by treatment with half molar equivalents of pyridine perbromide in acetonitrile:

$$2\ LiBH_2(CN)_2 + C_5H_5NBr_2 \xrightarrow[\text{room temp.}]{\text{MeCN}} LiBH_2(CN)CNBH(CN)_2 + LiBr + C_5H_5N \cdot HBr \qquad (8)$$

The pyridine and 4-cyanopyridine complexes of $BH(CN)_2$ were prepared in good yield by bromine oxidation:

$$LiBH_2(CN)_2 \cdot C_4H_8O_2 + A \cdot Br_2 + A \xrightarrow[\text{room temp.}]{\text{THF}} A \cdot BH(CN)_2 + LiBr + A \cdot HBr + C_4H_8O_2 \qquad (9)$$

(A = pyridine, 4-cyanopyridine)

The complexes of $BH(CN)_2$ with amines which do not form perbromides were obtained by exchange reaction with a complex of the weak base 4-cyanopyridine ($pK_a = 1.35$):

$$4\text{-}CNC_5H_4N \cdot BH(CN)_2 + A \xrightarrow[\text{room temp.}]{\text{THF}} A \cdot BH(CN)_2 + 4\text{-}CNC_5H_4N \qquad (10)$$

(A = piperidine, dimethylamine, 4-aminopyridine)

The synthesis of $BH(NC)_2$ from $NaBH(NC)_3$ and $NaBH_2(NC)_2$ with HCl, from $NaBH_2(NC)_2$ with bromine, and from $Me_2S \cdot BHBr_2$ with AgCN was also attempted, but with no success. The pyridine complex of $BH(NC)_2$ was synthesized by the following reaction:

$$NaBH(NC)_3 + C_5H_5N \cdot HCl \xrightarrow[\text{room temp.}]{\text{THF}} C_5H_5N \cdot BH(NC)_2 + NaCl + HCN \qquad (11)$$

Experimental

The experiments were carried out in dry, oxygen-free solvents under dry oxygen-free nitrogen using the Schlenk-technique [28]. The dimethyl sulfide complexes of the bromoboranes [29] and the base perbromides [30] were synthesized by published procedures. $LiCN \cdot CH_3CN$ was prepared in MeCN as described for LiCN [31].

(Continued on p. 24)

TABLE I

DETAILS OF PREPARATIONS AND YIELDS AND ANALYTICAL AND IR DATA FOR THE PRODUCTS

Compound	Method	Yield (%)	Analyses (Found (calcd.) (%))			IR data (cm^{-1})	
			B	H (attached to B)	CN (attached to B)	ν(B–H)	ν(C≡N)
$(BH_2CN)_n$	A2	98	27.61 (27.83)	4.97 (5.19)	67.25 (66.98)	2440, 2468	2298
$AgBH_2(NC)_2$	C2	83	6.04 (6.26)			2413	2189, 2215
$NaBH_2(NC)_2 \cdot 3DO$ [a]	D	69	3.18 (3.07)	0.584 (0.572)		2403	2151
$NaBH_2(NC)_2 \cdot 0.5DO$	D	66	8.05 (8.20)	1.50 (1.53)		2413	2165, 2155sh
$AgBH(NC)_3$	C1	59	5.35 (5.47)			2478	2192
$NaBH(NC)_3 \cdot 2DO$	D	60	3.85 (3.74)	0.339 (0.349)		2477	2158
$NaBH(NC)_3 \cdot 0.5DO$	D	58	6.80 (6.89)	0.646 (0.642)		2480	2161
$AgBH_2(CN)_2$	K	81	6.41 (6.26)			2386sh, 2412	2195
$LiBH_2(CN)_2$	B	74	14.84 (15.06)	2.83 (2.81)	72.06 (72.47)	2400	2214, 2223
$LiBH_2(CN)_2 \cdot DO$	B	77	6.83 (6.76)	1.22 (1.26)	32.11 (32.54)	2378, 2390	2218
$NaBH_2(CN)_2$	E	95	11.96 (12.31)	2.36 (2.30)	60.11 (59.23)	2392, 2408	2202
$NaBH_2(CN)_2 \cdot 1.5DO$	E	73	5.07 (4.91)	0.894 (0.916)	22.41 (23.65)	2392, 2410sh	2201, 2211
$AgBH(CN)_3$	K	86	5.19 (5.47)			2438	2218
$NaBH(CN)_3$	E	96	9.32 (9.58)	0.880 (0.893)	70.40 (69.16)	2427	2232
$NaBH(CN)_3 \cdot 1.5DO$	E	82	4.57 (4.41)	0.413 (0.411)	33.13 (31.86)	2400, 2425sh	2227
$NaBH_3CNBH_2CN \cdot 2DO$	A1	53	7.93 (7.78)			2378, 2410, 2425	2210, 2259

$LiBH_2(CN)CNBH(CN)_2 \cdot 1.5DO$	G	32	8.04 (8.07)			2388, 2456	2221, 2293
$C_6H_5NH_2 \cdot BH_2CN$	F	89	8.11 (8.19)	1.48 (1.53)	19.66 (19.71)	2392, 2401, 2426	
$4\text{-}ClC_6H_4NH_2 \cdot BH_2CN$	F	94	6.51 (6.50)	1.25 (1.21)	16.18 (15.63)	2413sh, 2433	2202
$O(CH_2CH_2)_2NH \cdot BH_2CN$ [b]	F	86	8.30 (8.58)	1.57 (1.60)	20.03 (20.66)	2404	2202
$C_5H_{10}NH \cdot BH_2CN$	F	57	8.53 (8.72)	1.66 (1.63)	20.44 (20.98)	2414	2201
$4\text{-}CNC_5H_4N \cdot BH_2CN$	F	91	7.64 (7.56)	1.39 (1.41)	17.86 (18.20)	2416, 2436	2193, 2243
$4\text{-}NH_2C_5H_4N \cdot BH_2CN$	F	92	7.95 (8.13)	1.46 (1.52)	19.05 (19.57)	2388, 2409	2185
$4\text{-}CH_3COC_5H_4N \cdot BH_2CN$	F	95	6.71 (6.76)	1.24 (1.26)	16.45 (16.26)	2417, 2445	2190
$3\text{-}CH_3(H)NCOC_5H_4N \cdot BH_2CN$ [c]	F	76	6.30 (6.18)	1.19 (1.15)	14.81 (14.87)	2422	2204
$C_3H_4N_2 \cdot BH_2CN$ [d]	F	85	10.07 (10.11)	1.83 (1.89)	23.90 (24.33)	2418, 2439	2207
$4\text{-}HOOCC_5H_4N \cdot BH_2CN$	F	92	6.39 (6.67)	1.20 (1.25)	16.78 (16.07)	2425, 2468	2213
$C_5H_5N \cdot BH(CN)_2$	H	56	7.16 (7.56)	0.664 (0.705)	35.61 (36.40)	2485	2218
$4\text{-}CNC_5H_4N \cdot BH(CN)_2$	H	61	6.18 (6.44)	0.573 (0.600)	30.71 (30.98)	2455	2218, 2254
$C_5H_{10}NH \cdot BH(CN)_2$	I	81	7.38 (7.26)	0.650 (0.677)	34.58 (34.92)	2446	2221
$(CH_3)_2NH \cdot BH(CN)_2$	I	93	10.28 (9.92)	0.953 (0.925)	46.94 (47.77)	2438sh, 2455	2218
$4\text{-}NH_2C_5H_4N \cdot BH(CN)_2$	I	95	7.09 (6.84)	0.632 (0.638)	32.20 (32.94)	2450	2214
$C_5H_5N \cdot BH(NC)_2$	J	24	7.27 (7.56)			2500	2136, 2144sh

[a] DO = dioxane. [b] $O(CH_2CH_2)_2NH$ = morpholine. [c] $3\text{-}CH_3(H)NCOC_5H_4N$ = *N*-Methylnicotinic amide. [d] $C_3H_4N_2$ = Pyrazole.

$NaBH_3CN$ (Aldrich) was purified by recrystallization from THF/CH_2Cl_2 [2].

The boron content of the prepared compounds was determined by acid-base titration in the presence of mannitol after fusion with NaOH. The percentage of hydrogen attached to boron was determined iodometrically [10,34]; in the case of isocyanoborates the determinations were carried out after treatment with $HgCl_2$. The content of cyanide attached to boron was also iodometrically determined by the Schulek method after conversion of the CN group into bromine cyanide with bromine and subsequent removal of the excess of bromine with phenol [33]. The IR and ^1H NMR spectra were recorded on Perkin–Elmer 283 and Bruker WP 200 SY instruments. Mass spectra were obtained with a VG-7035 GC-MS-COM instrument operation at 70 eV and an ion source temperature: 150°C. The GLC separation was performed with a HP-5710A GC apparatus, using a 4 ft long 1/4 diameter column packed with 3% OV-17 on 80/100 mesh Chromosorb W-HP; the flow rate of the He gas was 50 ml/min; heating program: 70–220°C with a rate of 2°C/min; injector temperature: 150°C. Details relevant to the isolation of the products and the analytical and IR data are summarized in Table 1.

A1. Reaction of $NaBH_3CN$ with HCl in THF

22.0 ml of 1.00 *M* HCl in THF was added dropwise with rapid stirring to a solution of $NaBH_3CN$ (2.19 g, 34.85 mmol) in THF (40 ml). The addition was then continued in 5 drop portions until H_2 evolution was no longer observed. The solution was evaporated under reduced pressure (0.1 mbar) and the residue was treated with dioxane (20 ml) and evaporated again under reduced pressure. The residue was shaken with dioxane (20 ml) then filtered off and washed with more dioxane (4×6–8 ml), then dried in N_2 stream. The crude product was purified by repeated extractions into ether (30 ml). The $NaBH_3CNBH_2CN \cdot 2C_4H_8O_2$ salt which gradually crystallized out of the extract was filtered off. The mother liquor from the filtration of the dioxane solution was concentrated under reduced pressure (10^{-2}–10^{-4} mbar); IR and ^1H NMR spectroscopy indicated that the residual sticky mass was mainly $(BH_2CN)_n$.

A2. Reaction of $NaBH_3CN$ with HCl in Me_2S

100 ml of 1.625 *M* HCl in Me_2S was dropwise added at 0°C to a suspension of $NaBH_3CN$ (10.52 g, 167.4 mmol) in Me_2S (50 ml). When H_2 evolution had ceased (3580 ml at NTP, 160.0 mmol) the solution was filtered and the NaCl remaining on the filter was washed with Me_2S (3×30 ml). The filtrate was evaporated at room temperature and the syrupy residue was kept under reduced pressure (0.01 mbar) for 1 h. Crystallization of the product was initiated by scratching and was completed within a few hours.

B. Reaction of $(BH_2CN)_n$ with $LiCN \cdot CH_3CN$ in Me_2S

A solution of $(BH_2CN)_n$ (130.0 ml, 0.74 *M* for BH_2CN, 96.2 mmol) (prepared by method A2) was added with stirring to a suspension of $LiCN \cdot MeCN$ (7.33 g, 0.99 mmol) in Me_2S (50 ml). The mixture was refluxed for 5 h then filtered, and dioxane (20 ml) was added to the filtrate. The crystalline product was filtered off and washed with ether (2×15 ml). The crude product was purified by repeated extractions into ether (70 ml) or dioxane (60 ml). The $LiBH_2(CN)_2 \cdot C_4H_8O_2$ which gradually precipitated out of the extract was filtered off, washed with ether (2×10 ml) and dried in N_2 stream.

The $LiBH_2(CN)_2 \cdot C_4H_8O_2$ complex completely loses its dioxane content in 2–3 h at 10^{-4}–10^{-5} mbar pressure and 220–245°C.

Pyridine (0.534 g, 6.75 mmol) was added with stirring to a suspension of $LiBH_2(CN)_2 \cdot C_4H_8O_2$ (1.08 g, 6.75 mmol) in Me_2S (12 ml). After 40 min the solid product was filtered off, washed with Me_2S (2 × 2 ml) and dried, to give a product of composition $LiBH_2(CN)_2 \cdot C_4H_8O_2 \cdot 0.5C_5H_5N$.

C1. Reaction of $Me_2S \cdot BHBr_2$ with AgCN in Me_2S

To a solution of AgCN (40.17 g, 300.0 mmol) in Me_2S (120 ml) a 2.00 *M* solution of $Me_2S \cdot BHBr_2$ (50.0 ml, 100.0 mmol) was added during 25 min with stirring and cooling with cold water. After a further 30 min stirring the mixture was filtered and the yellow coloured lower oily layer was separated and added dropwise to diglyme (200 ml) at 80–85°C during 2 h in a fast N_2 stream to remove Me_2S. The powdery product was filtered off, washed with ether (2 × 40 ml), dried and suspended in water (80 ml). To this suspension was added a solution of KCN (31.25 g, 479.9 mmol) in water (50 ml). The suspension was stirred for 15 min, filtered, dried in N_2 stream and kept under reduced pressure (0.01 mbar) for 1.5 h at 110°C to give $AgBH(NC)_3$.

C2. Reaction of $Me_2S \cdot BH_2Br$ with AgCN in Me_2S

A solution of AgCN (18.26 g, 136.38 ml) in Me_2S (20 ml) was added to a 2.80 *M* solution of $Me_2S \cdot BH_2Br$ (24.0 ml, 67.2 mmol) in Me_2S. The crystals which separated were filtered off, washed with Me_2S (2 × 4 ml), and dried. The filtrate was concentrated to 25 ml, and the solid which precipitated was filtered off, washed with Me_2S (2 × 4 ml), and dried. The filtrate was dropwise added to 300 ml of refluxing ether. The separated material was filtered off and dried. The combined solid product-fractions were suspended in water (25 ml) and then stirred with an aqueous solution (15 ml) of KCN (9.75 g, 150.0 mmol) with stirring. After 15 min the mixture was filtered, washed with water (5 × 10 ml), and dried under reduced pressure in a N_2 stream to constant weight, yielding $AgBH_2(NC)_2$.

D. Conversion of $AgBH_n(NC)_{4-n}$ (n = 1,2) into Na salts

To a mixture of Na (3.0 g, 130.5 mmol) in THF (40 ml) was added benzophenone (0.66 g, 3.6 mmol), and after the development of a violet colour $AgBH(NC)_3$ (7.20 g, 36.41 mmol) or $AgBH_2(NC)_2$ (6.29 g, 36.41 mmol) was added in portions with vigorous stirring. After 4 h stirring 0.33 g of benzophenone was added, and stirring was continued for a further one hour. The solution was then filtered. In the case of $AgBH(NC)_3$ the filtrate was treated dropwise with the THF solution (10 ml) of the violet ketyl compound prepared from benzophenone (0.33 g) and sodium, but when $AgBH_2(NC)_2$ was used this procedure was not necessary. The solution was evaporated under reduced pressure (0.01 mbar), the residue was dissolved in water (20 ml) and the solution was treated with active carbon, filtered, and concentrated under reduced pressure. 10 ml of dioxane was then added and the solution was evaporated. Dioxane (5 ml) and ether (20 ml) were added and the solid was filtered off, washed with ether (2 × 5 ml) and dried in a N_2 stream. The products obtained were $NaBH(NC)_3 \cdot 2C_4H_8O_2$ and $NaBH_2(NC)_2 \cdot 3C_4H_8O_2$. These compounds were converted into derivatives containing 0.5 mol of dioxane when kept under reduced pressure (0.01 mbar) as the temperature was gradually raised to 60°C.

E. Isomerization of $NaBH_n(NC)_{4-n}$ (n = 1,2) to cyanoborates

A suspension of $NaBH(NC)_3 \cdot 0.5C_4H_8O_2$ (1.57 g, 10.0 mmol) or $NaBH_2(NC)_2 \cdot 0.5C_4H_8O_2$ (1.32 g, 10.0 mmol) in n-dibutylether (25 ml) was refluxed for 30 min. The solvent which contained most of the dioxane was then decanted off and 20 ml of pure Bu_2O was added to the residue. In the case of triisocyanohydroborate and diisocyanodihydroborate refluxing was then continued for 15 and 1 h, respectively, and the powdery product was filtered off, and shown to be practically dioxane-free crude $NaBH(CN)_3$ or $NaBH_2(CN)_2$. For purification a solution of the product in water (10 ml), was treated with carbon, filtered and, evaporated under reduced pressure (0.01 mbar). The residue was taken up in dioxane (5 ml), and the solvent was evaporated off in vacuum, than ether (10 ml) and dioxane (2 ml), were added. The crystalline product was filtered off, washed with ether (2 × 3 ml), and dried in a N_2 stream to give $NaBH(CN)_3 \cdot 1.5C_4H_8O_2$ or $NaBH_2(CN)_2 \cdot 1.5C_4H_8O_2$.

F. Reaction of $(BH_2CN)_n$ with nitrogen bases

An Me_2S solution (5 ml) of the stoichiometrically required base was added to a solution of $(BH_2CN)_n$ in Me_2S (5 ml, 1.33 *M* for BH_2CN, 6.65 mmol) obtained by method A2. When isonicotinic acid or *N*-methylnicotinic amide were used the reactions were carried out in a 1/1 mixture of Me_2S and THF and the base was added in solid form to the solution of $(BH_2CN)_n$. After 20 min the solvent was evaporated off. In the case of morpholine, 4-aminopyridine, isonicotinic acid and *N*-methylnicotinic amide the residue was triturated with ether, filtered off, washed again with the same solvent (2 × 2 ml) and dried in a N_2 stream. For 4-chloroaniline, piperidine, 4-acetylpyridine and pyrazole ether was replaced by pentane. In the case of aniline and 4-cyanopyridine the product separated as crystals within 5–20 min and so the evaporation was unnecessary.

The complexes obtained with aniline, morpholine, 4-cyanopyridine, and 4-aminopyridine were purified by repeated extractions into ether. The 4-chloroaniline- and pyrazole complexes were recrystallized from ethereal solutions (2–3 ml) by addition of pentane (15–20 ml).

G. Reaction of $LiBH_2(CN)_2$ with pyridineperbromide

A solution of pyridine perbromide (2.40 g, 10.05 mmol) in acetonitrile (10 ml) was added with stirring to a suspension of $LiBH_2(CN)_2$ (1.44 g, 20.06 mmol) in acetonitrile (20 ml). Stirring was continued for a further 30 min, the mixture was filtered, the filtrate was evaporated under reduced pressure (0.01 mbar) and the oily residue was triturated with a mixture of dioxane (5 ml) and ether (25 ml). The solid, $LiBH_2(CN)CNBH(CN)_2 \cdot 1.5C_4H_8O_2$, was filtered off and purified further by repeated extractions into a mixture of dioxane (2 ml) and ether (30 ml).

H. Reaction of $LiBH_2(CN)_2 \cdot C_4H_8O_2$ with base perbromides in the presence of base

To a 0°C solution of $LiBH_2(CN)_2 \cdot C_4H_8O_2$ (1.60 g, 10.0 mmol) in THF (10 ml) was added a solution of $C_5H_5NBr_2$ (2.39 g, 10.0 mmol) and pyridine (0.79 g, 10.0 mmol) in THF (10 ml) or a solution of $4\text{-}CNC_5H_4NBr_2$ (2.64 g, 10.0 mmol) and 4-cyanopyridine (1.04 g, 10.0 mmol) in THF (10 ml). The mixture was then allowed to warm to room temperature. After stirring for a further 30 min, the solid was filtered off washed with THF (3 × 5 ml), and the filtrate was concentrated under reduced pressure (0.01 mbar). The residual resinous product was taken up in water

(12 ml), the solution was cooled to 0°C, and the crystalline product was filtered off and washed with cold (0°C) water (4 × 4 ml) and then dried in a N_2 stream under reduced pressure. $C_5H_5N \cdot BH(CN)_2$ can be purified by extraction into ether.

I. Base-exchange reactions with 4-cyanopyridine-dicyanoborane

A solution of the stoichiometric amount of the corresponding amine (0.254 g of piperidine, 0.134 g of dimethylamine or 0.280 g of 4-aminopyridine) in THF (5 ml) was added to a suspension of $4\text{-}CNC_5H_4N \cdot BH(CN)_2$ (0.50 g, 2.98 mmol) in THF (5 ml). After dissolution of the solid material the solution was evaporated, the residue was triturated with ether (6–10 ml), filtered off, washed with ether (3 × 5 ml) and dried in a N_2 stream.

J. Reaction of $NaBH(NC)_3 \cdot 0.5C_4H_8O_2$ with pyridine hydrochloride

A solution of $NaBH(NC)_3 \cdot 0.5C_4H_8O_2$ (0.98 g, 6.25 mmol) in THF (5 ml) was added to a suspension of $C_5H_5N \cdot HCl$ (0.72 g, 6.23 mmol) in THF (10 ml). After 10 min the mixture was filtered, the filtrate was evaporated to dryness, and the residue was extracted with ether (20 ml) and the extract was filtered, then evaporated to 5 ml. The needles which separated were filtered off, washed with ether (2 × 1 ml), and dried, to give $C_5H_5N \cdot BH(NC)_2$.

K. Preparation of $AgBH_n(CN)_{4-n}$ ($n = 1,2$)

To an aqueous solution (15 ml) of $LiBH_2(CN)_2 \cdot C_4H_8O_2$ (0.80 g, 5.0 mmol) or $NaBH(CN)_3$ (0.564 g, 5.0 mmol) was added a 1.0 *M* aqueous $AgNO_3$ solution (0.5 ml). After 0.5 h stirring the mixture was treated with carbon then filtered, and 1.0 *M* $AgNO_3$ solution (4.5 ml) was added to the filtrate. The precipitated Ag salts were filtered off, washed with water (3 × 3 ml), dried and purified, by extraction with MeCN.

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