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Preparation and Characterization of Alkali-Metal (α-Cyanoalkyl)trihydroborate–Dioxane Complexes

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The lithium (α-cyanoalkyl)trihydroborate–dioxane complexes $LiBH_3CH_2CN \cdot xC_4H_8O_2$, $LiBH_3C(CH_3)_2CN \cdot xC_4H_8O_2$, and $LiBH_3CHPhCN \cdot xC_4H_8O_2$ have been prepared by the reaction of acetonitrile anion and borane–tetrahydrofuran. The compounds are isolated as dioxane adducts; the purity is dependent on reagent ratios. The lithium salts may be converted into sodium and potassium salts, which are less hygroscopic and easier to handle. All compounds are characterized by IR and NMR spectroscopies.

Introduction

The importance of hydroborates in the development of organic[1] and inorganic[2] chemistry is well-known. Studies have shown that the reaction behavior of a hydroborate is substantially influenced by both steric and electronic effects. To date, a wide range of reactivity in hydroborates has been provided by substitution of different groups onto the boron itself.[3] Some examples of substituted hydroborates include trialkylhydroborates[1b,c] ($[R_3BH]^-$), dialkylhydroborates[3] ($[R_2BH_2]^-$), alkylhydroborates[1a,3] ($[RBH_3]^-$), and cyanotrihydroborate[4] ($[BH_3CN]^-$). Trialkylhydroborates are strong reducing agents whereas cyanotrihydroborate, a mild reducing agent, has been found to be an extremely useful reagent for the selective reduction of organic functional groups[4] particularly at low pH. Thus, attaching a CN group directly to boron has clearly resulted in useful and unusual behavior usually attributed to the electron-withdrawing effect of the cyano group. Structural modifications of the $[BH_3CN]^-$ anion have not been explored.

In this paper we report the synthesis and characterization of a new class of hydroborates, the (α-cyanoalkyl)trihydroborates, $[BH_3CRR'CN]^-$. The lithium (cyanoalkyl)trihydroborates are obtained as dioxane complexes in crystalline form. The moisture-sensitive lithium salts can be converted into the less hygroscopic sodium and potassium salts.

Experimental Section

Materials. All equipment was oven-dried at 120 °C and cooled under a stream of nitrogen gas. Reaction flasks were sealed with rubber septum stoppers. Solvents and reagents were transferred either via needle and syringe or by siphoning through a cannula using a positive pressure of dry nitrogen gas. All reactions were carried out under an atmosphere of dry nitrogen gas.

All solvents were purified prior to their use. THF and 1,4-dioxane were dried by allowing the solvent to stand for at least 12 h over solid KOH pellets followed by refluxing and distilling from sodium metal when dry (benzophenone indicator). Hexane solvent was purified by distillation from calcium hydride and was stored over 4-Å molecular sieves. Acetonitrile, isobutyronitrile, and phenylacetonitrile were obtained from Aldrich and distilled prior to use. The reagents *n*-butyllithium (2.5 M) and $BH_3 \cdot THF$ (1 M) were obtained from Aldrich and used directly from the bottle as fresh solutions.

The ^7Li and ^{11}B NMR spectra were recorded on a JEOL FX-90Q FT NMR spectrometer operating at 34.77 and 28.69 MHz, respectively. The ^7Li chemical shifts were measured with respect to external saturated aqueous LiCl; ^{11}B shifts were measured with respect to external $BF_3 \cdot OEt_2$. ^1H and ^{13}C NMR spectra were obtained on a Varian XL-300

spectrometer operating at 300 and 75.44 MHz, respectively. ^{13}C NMR spectra were referenced by using the ^{13}C resonance of the solvent as an internal standard but are reported with respect to SiMe₄. IR spectra were obtained as Nujol mulls on a Perkin-Elmer 599 FT spectrophotometer.

Preparation of $LiBH_3CH_2CN \cdot xC_4H_8O_2$ (3A). The following procedure is typical for the preparation of all three compounds except for differences in the molar ratios of the reagents and final purification steps, which are detailed later in the experimental portion.

A 500-mL dry round-bottom flask is charged with 70 mL of dry THF and sealed with a serum stopper having an N_2 inlet and outlet. A stream of nitrogen gas is passed through the flask, which is cooled to –78 °C in a dry ice/2-propanol cooling bath. A 0.2-mol sample of 2.5 M *n*-butyllithium is introduced into the flask by using a syringe. With the liquid maintained at –78 °C, 0.22 mol of acetonitrile is added slowly with a syringe to give an amber solution. This mixture is stirred for 1 h at –78 °C. During this time 0.18 mol of $BH_3 \cdot THF$ is syringed into a dry flask, which is sealed with a serum stopper and cooled to –78 °C while a slow stream of N_2 gas is passed through the apparatus. Following the 1-h mixing time, the precooled $BH_3 \cdot THF$ is transferred to the reaction mixture through a cannula with a positive pressure of nitrogen gas. The reaction mixture is slowly brought to room temperature while being stirred. The THF solvent is removed on a rotary evaporator to yield a viscous yellow oil. To this residue is added 50 mL of dry 1,4-dioxane, and the mixture is allowed to remain at room temperature for 48 h. A crystalline material generally separates out. If no solid is formed, dry hexane is added with stirring until a slight turbidity appears, which consequently should disappear on warming. When the solution is allowed to stand for 12–24 h, a crystalline material separates out, which is filtered with suction, rinsed with small portions of dioxane, and dried on a vacuum line at room temperature for 4 h at 1 mmHg; yield[5] 15.5 g (58%).

Preparation of $LiBH_3C(CH_3)_2CN \cdot xC_4H_8O_2$ (3B). Until the removal of THF and addition of 1,4-dioxane, the procedure is the same as described above using 0.60 mol of $HC(CH_3)_2CN$, 0.2 mol of *n*-BuLi, and 0.18 mol of $BH_3 \cdot THF$. When the reaction mixture is allowed to stand at room temperature for 48 h, a white crystalline product settles. If no solid is formed, hexane is added until a slight turbidity occurs, which becomes clear on warming. The reaction mixture is then left at room temperature overnight to give a white crystalline product, which is vacuum filtered under an N_2 atmosphere and dried at room temperature on a vacuum line for 4 h at 1 mmHg; yield[5] 25 g (78%).

Preparation of $LiBH_3CHPhCN \cdot xC_4H_8O_2$ (3C). Until the removal of THF and addition of dioxane, the procedure is the same as the earlier description using 0.27 mol of CH_2PhCN, 0.2 mol of *n*-BuLi, and 0.20 mol of $BH_3 \cdot THF$. After dioxane is added, the reaction mixture is stirred thoroughly and left overnight at room temperature. The solvent is then removed on a rotary evaporator, and the residue is dissolved in a minimum amount of dichloromethane (50 mL). Hexane is added to give a slight turbidity, which on warming disappears. The clear solution is left at room temperature for 24–48 h to give a white crystalline material, which is filtered and dried at room temperature under vacuum for 4 h at 1 mmHg; yield[5] 40 g (85%).

Conversion of $LiBH_3CRR'CN \cdot xC_4H_8O_2$ into $(Na/K)BH_3CRR'CN \cdot xC_4H_8O_2$: General Procedure. The lithium salt 3 (5 g) is dissolved in THF (50 mL) and cooled to –20 °C. Excess (5 equiv) 2 M NaF/KF aqueous solution is added while the solution is stirred. After the solution is warmed to room temperature, the solvent is removed on a rotary evaporator at 30 °C. Fresh THF is added (50 mL) to the residue, and the mixture is stirred thoroughly and then filtered to remove LiF and excess NaF/KF. The solution is concentrated to 25 mL, and dioxane is

(1) Examples include: (a) Brown, H. C.; Singaram, B. *J. Am. Chem. Soc.* **1984,** *106,* 1797 and references therein. (b) Krishnamurthy, S.; Brown, H. C. *J. Org. Chem.* **1983,** *48,* 3085 and references therein. (c) Walker, E. R. H. *Chem. Soc. Rev.* **1976,** *5,* 23.
(2) Examples include: (a) Marks, T. J.; Kolb, J. R. *Chem. Rev.* **1977,** *77,* 263. (b) Bommer, J. C.; Morse, K. W. *J. Chem. Soc., Chem. Commun.* **1977,** 137. (c) Bommer, J. C.; Morse, K. W. *Inorg. Chem.* **1978,** *17,* 3708. (d) Bommer, J. C.; Morse, K. W. *Inorg. Chim. Acta* **1983,** *74,* 25. (e) Egan, P. G.; Holah, D. G.; Morse, K. W. *Inorg. Chem.* **1984,** *23,* 2203. (f) Barton, R. J.; Holah, D. G.; Shengzhi, H.; Hughes, A. N.; Khan, S. I.; Robertson, B. E. *Inorg. Chem.* **1984,** *23,* 2391.
(3) Brown, H. C.; Krishnamurthy, S. *Tetrahedron* **1979,** *35,* 567.
(4) Hutchins, R. O.; Natale, N. R. *Org. Prep. Proceed. Int.* **1979,** *11*(5), 201–246.

(5) Yields are based on the amount of $BH_3 \cdot THF$ used.

Table I. IR and ^{11}B and ^{7}Li NMR Data

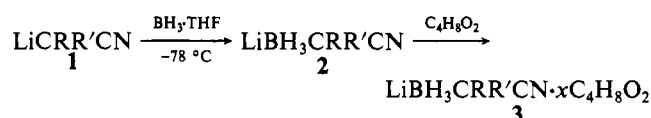| compd	IR (Nujol),[a] cm^{-1}	^{11}B NMR (THF),[b] ppm	^{7}Li NMR (THF), ppm
LiBH$_3$CH$_2$CN·xC$_4$H$_8$O$_2$ (3A)	2278, 2235 (B—H) 2206 (C≡N)	−30.5 (q, J_{BH} = 84.0) −28.4 (q of t, J_{BH} = 86.0, J_{BCH} = 4.6)[c]	−1.4 (s)
LiBH$_3$C(CH$_3$)$_2$CN·xC$_4$H$_8$O$_2$ (3B)	2264, 2220 (B—H) 2206 (C≡N)	−21.5 (q, J_{BH} = 85.0) −21.3 (q of spt, J_{BH} = 85.0, J_{BCCH} = 3.2)[c]	−1.4 (s)
LiBH$_3$CHPhCN·xC$_4$H$_8$O$_2$ (3C)	2278 (B—H) 2227 (C≡N) 1595 (C=C)	−23.5 (q, J_{BH} = 87)	−1.3 (s)
NaBH$_3$CH$_2$CN·xC$_4$H$_8$O$_2$ (4A)	2278 (B—H) 2220 (C≡N)	−30.6 (q, J_{BH} = 85.6)	
NaBH$_3$C(CH$_3$)$_2$CN·xC$_4$H$_8$O$_2$ (4B)	2264 (B—H) 2206 (C≡N)	−21.2 (q, J_{BH} = 85.0)	
NaBH$_3$CHPhCN·xC$_4$H$_8$O$_2$ (4C)	2278 (B—H) 2206 (C≡N) 1595 (C=C)	−23.5 (q, J_{BH} = 86.0)	
KBH$_3$CH$_2$CN·xC$_4$H$_8$O$_2$ (5A)	2271 (B—H) 2199 (C≡N)	−30.0 (q, J_{BH} = 86.0)	
KBH$_3$C(CH$_3$)$_2$CN·xC$_4$H$_8$O$_2$ (5B)	2242 (B—H) 2184 (C≡N)	−20.0 (q, J_{BH} = 86.0)	
KBH$_3$CHPhCN·xC$_4$H$_8$O$_2$ (5C)	2264 (B—H) 2206 (C≡N) 1593 (C=C)	−22.1 (q, J_{BH} = 86.0)	

[a] Only characterizing IR bands are given. [b] Abbreviations: q = quartet, s = singlet, t = triplet, spt = septet, J values are in Hz. [c] DMSO-d_6 solvent.

added until the solution shows slight turbidity, which disappears on warming. When it is allowed to stand for 2–3 h, the clear solution gives crystalline Na/K salts (dioxane adducts) in 75–80% yields.

Results and Discussion

Members of the (α-cyanoalkyl)trihydroborate–dioxane complexes of the general form LiBH$_3$CRR′CN·xC$_4$H$_8$O$_2$ (R, R′ = H, H; CH$_3$, CH$_3$; H, Ph) are synthesized by the generation of LiCRR′CN (1), which then is allowed to react in situ with borane–tetrahydrofuran (BH$_3$·THF) to form the product 2.[6] The dioxane adducts 3 are obtained by evaporating the solvent and treating 2 with 1,4-dioxane (Scheme I).

Scheme I

$$\text{LiCRR'CN} \xrightarrow[-78\,°C]{\text{BH}_3\cdot\text{THF}} \text{LiBH}_3\text{CRR'CN} \xrightarrow{\text{C}_4\text{H}_8\text{O}_2}$$
$$\quad\;\;\mathbf{1} \qquad\qquad\qquad\qquad\;\; \mathbf{2}$$
$$\text{LiBH}_3\text{CRR'CN}\cdot x\text{C}_4\text{H}_8\text{O}_2$$
$$\mathbf{3}$$

$$\text{R,R' = H, H (A); CH}_3\text{, CH}_3\text{ (B); H, Ph (C)}$$

The synthesis proceeds smoothly as a "one-pot" reaction. The reaction is carried out at −78 °C in order to prevent polymerization of the acetonitrilide anion. The mode of addition has no effect on the yield. For convenience, BH$_3$·THF is added to the anion mixture. However, it is necessary to precool BH$_3$·THF to −78 °C prior to its addition.

A major byproduct of this reaction can be the complex LiBH$_4$·xC$_4$H$_8$O$_2$. Its formation was minimized by selecting an optimum ratio of reactants determined by a series of experiments in which reactant ratios were varied. Thus, yields of desired products were maximized with appropriate reactant ratios: 3A (1/1.1/0.9 n-BuLi/CH$_3$CN/BH$_3$·THF); 3B (1/3/0.9 n-BuLi/HC(CH$_3$)$_2$CN/BH$_3$·THF) 3C (1/1.35/1 n-BuLi/PhCH$_2$CN/BH$_3$·THF). With use of the latter ratios, the products were either pure or were easily obtained pure by recrystallization.

The product dioxane adducts are characterized by ^{11}B, ^{1}H, and ^{13}C NMR and IR spectroscopies. The ^{11}B NMR spectra of the (α-cyanoalkyl)trihydroborate–dioxane complexes were each shown to appear as a quartet (Table I). Upon closer examination, the individual peaks of the quartet in the spectrum of 3A are split into a broad triplet by further coupling with the CH$_2$ protons (J_{BCH} = 4.6). In the spectrum of 3B each peak of the quartet is split into a septet by long-range coupling with the methyl groups (J_{BCCH}

(6) Reference to this compound is found in: Peters, J. L.; Norwood, V. M., III; Morse, K. W. *Inorg. Chem.* **1986**, *25*, 3713.

Table II. ^{1}H and ^{13}C NMR Data[a] (DMSO-d_6), ppm

compd	^{1}H NMR	^{13}C NMR
3A	0.51 (3 H, q of t, BH$_3$, J_{BH} = 85.6, J_{HCBH} = 6), 0.84 (2 H, m, CH$_2$), 3.59 (s, C$_4$H$_8$O$_2$)	1.8 (q, CH$_2$, J_{BC} = 32), 67.0 (s, C$_4$H$_8$O$_2$), 130.0 (CN)
3B	0.63 (3 H, q, BH$_3$, J_{BH} = 85.5), 1.10 and 1.01 (6 H, (CH$_3$)$_2$), 3.59 (s, C$_4$H$_8$O$_2$)	18.7 (q, C(CH$_3$)$_2$, J_{BC} = 36), 30.2 (s, (CH$_3$)$_2$), 66.6 (s, C$_4$H$_8$O$_2$), 135.0 (CN)
3C	0.80 (3 H, q, BH$_3$, J_{BH} = 86), 2.75 (1 H, br s, CHPh), 3.39 (s, C$_4$H$_8$O$_2$), 6.95 (1 H, m, ar), 7.10 (4 H, m, ar)	26.0 (br q, CHPh), 65.8 (s, C$_4$H$_8$O$_2$), 122.2, 125.4, 126.8, and 147.0 (ar), 129.0 (CN)
4A	0.51 (3 H, q of t, BH$_3$, J_{BH} = 85.6, J_{HCBH} = 6), 0.84 (2 H, m, CH$_2$), 3.59 (s, C$_4$H$_8$O$_2$)	1.4 (q, CH$_2$, J_{BC} = 32), 66.5 (s, C$_4$H$_8$O$_2$), 130.0 (CN)
4B	0.87 (3 H, q, BH$_3$, J_{BH} = 85), 0.81 and 0.80 (6 H, (CH$_3$)$_2$), 3.40 (s, C$_4$H$_8$O$_2$)	30.0 (s, (CH$_3$)$_2$), 66.1 (s, C$_4$H$_8$O$_2$), 135.0 (CN)
4C	0.80 (3 H, br q, BH$_3$, J_{BH} = 86), 2.70 (1 H, br s, CHPh), 3.50 (s, C$_4$H$_8$O$_2$), 6.93 (1 H, m, ar), 7.09 (4 H, m, ar)	27.0 (br q, CHPh), 66.5 (s, C$_4$H$_8$O$_2$), 123.0, 126.0, 128.0, and 148.0 (ar), 130.0 (CN)
5A	0.42 (3 H, q of t, BH$_3$, J_{BH} = 86, J_{HCBH} = 6), 0.76 (2 H, m, CH$_2$), 3.50 (s, C$_4$H$_8$O$_2$)	1.27 (q, CH$_2$, J_{BC} = 32), 66.5 (s, C$_4$H$_8$O$_2$), 130.0 (CN)
5B	0.42 (3 H, q, BH$_3$, J_{BH} = 85), 0.80 and 0.82 (6 H, (CH$_3$)$_2$), 3.40 (s, C$_4$H$_8$O$_2$)	18.4 (q, C(CH$_3$)$_2$, J_{BC} = 36), 30.0 ((CH$_3$)$_2$), 66.5 (s, C$_4$H$_8$O$_2$), 135.0 (CN)
5C	0.80 (3 H, q, BH$_3$, J_{BH} = 86), 2.74 (1 H, br s, CHPh), 6.93 (1 H, m, ar), 7.09 (4 H, m, ar)	26.6 (q, br, CHPh), 66.5 (s, C$_4$H$_8$O$_2$), 123.0, 126.0, and 127.5 (ar), 130.0 (CN)

[a] Abbreviations: s = singlet, t = triplet, q = quartet, m = multiplet, ar = aromatic, br = broad. J values are in Hz.

= 3.2). No discernible splitting is seen in the spectrum of 3C. The ^{1}H NMR spectra of all compounds (Table II) show a 1/1/1/1 quartet due to the coupling of hydrido hydrogens with ^{11}B. Further splitting, attributed to the CH$_2$, is observed only in

the case of **3A**. The expected septet due to the coupling of the hydrido hydrogens with ^{10}B is also observed except in **3C**. Except for the dioxane peak, integrations are consistent with the proposed formulation. The integration for dioxane peaks in ^{1}H NMR spectra can show a degree of variability, which is an artifact of the methods employed to purify these compounds. Excess solvent is removed from the precipitates by subjecting the solids to vacuum conditions for varying lengths of time. The dioxane also slowly evolves from the dried solid. For this reason, elemental analyses were generally not satisfactory. However, all other characterization data support the proposed structures.

Carbon adjacent to boron in all three compounds is observed in the ^{13}C NMR spectra as a quartet of very weak intensity, due to coupling with ^{11}B; coupling due to ^{10}B is not noticeable. Signals of other carbons in each compound are consistent with the proposed structures (Table II).

The IR spectra for the dioxane complexes of the (α-cyanoalkyl)trihydroborates are consistent with the proposed structures, showing peaks in the range of 2235–2278 cm^{-1} for B—H, 2200–2215 cm^{-1} for C≡N, and 1125–1140 cm^{-1} for the C—O bond of the dioxane molecule.

The lithium salts of (α-cyanoalkyl)trihydroborates are converted into their corresponding sodium (**4A–4C**) and potassium (**5A–5C**) salts by using aqueous sodium fluoride and potassium fluoride, respectively. Once formed, the dioxane adducts of the sodium and potassium salts are stable to moisture for relatively longer times, unlike their comparable lithium salts, which are moisture-sensitive.

The ^{11}B, ^{1}H, and ^{13}C NMR and IR spectra of these sodium and potassium (α-cyanoalkyl)trihydroborates are similar to those of the lithium salts. The ^{7}Li NMR spectra of the lithium salts of (α-cyanoalkyl)trihydroborate–dioxane complexes show a single sharp peak at −1.4 ppm for **3A** and **3B** and −1.3 ppm for **3C**. The ^{7}Li NMR spectra of the Na and K salts of (α-cyanoalkyl)trihydroborate–dioxane complexes obtained from the previous Li salts, recorded after a much longer accumulation time, did not show any signal due to the presence of the lithium salt as a contaminant.

The behavior of these compounds as reducing agents toward organic functional groups indicates they are intermediate in reducing power between tetrahydroborate and cyanotrihydroborate and also differ depending on the CRR′ substituents. These results will be reported in a subsequent paper as will the ability of the anions to complex to metals.

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Cocondensation Reaction between Phosphine and Fluorine: Matrix Infrared Spectra of PH₃F₂, PHF₂, and PH₂F

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Argon/F₂ and argon/PH₃ samples codeposited at 16 K yielded reaction product infrared absorptions identified as PH₃F₂, PHF₂, and the new molecule PH₂F. In contrast the analogous NH₃ and F₂ system gave only the NH₃--F₂ complex, which required photolysis to produce the NH₂F--HF complex. The phosphine–fluorine reaction apparently proceeds through a pentavalent activated complex. This activated complex either is relaxed by the matrix to give PH₃F₂ or dissociates to the PHF₂ or PH₂F products, which are trapped in the matrix.

Introduction

The increased reactivity of second-row hydrides compared to first-row hydrides can be illustrated with NH₃ and PH₃. Although each forms a symmetrical complex with ozone,[1] photolysis of the PH₃--O₃ complex proceeds with red light and gives an extensive array of products including H₂POH and the higher oxidation state oxide H₃PO and acid HOPO₂ whereas the NH₃--O₃ complex requires blue light for dissociation and gives only H₂NOH.[2,3] Although ammonia and fluorine react explosively in the gas phase at room temperature, when separate samples were condensed at 12 K with excess argon, only the NH₃--F₂ complex forms.[4] However, mercury arc photolysis converts this complex quantitatively to NH₂F--HF complexes and provides a means for synthesis of the elusive NH₂F species,[4] which has very recently been observed by microwave spectroscopy.[5] The analogous PH₃ and F₂ matrix reactions have been done in order to synthesize phosphinous fluoride, PH₂F, and to explore the greater reactivity of second-row hydrides. There is no previous experimental evidence for PH₂F, although a number of theoretical calculations have been performed on this subject molecule largely concerned with the barrier to inversion,[6,8] hybridization of phosphorus,[9] and ab initio calculation of force fields.[10]

Experimental Section

The cryogenic apparatus and experimental techniques have been described previously.[4] Fluorine (Matheson) was handled in a passivated stainless-steel vacuum system, and Ar/F₂ = 150/1 samples were passed through a U-tube immersed in liquid nitrogen to remove HF before deposition; however, traces of the usual volatile impurities CF₄, OCF₂, SiF₄, and NF₃ were found in these samples. Phosphine and PF₃ (Matheson), PD₃, and (CH₃)₃P were handled and prepared as described previously.[11,12] Argon-diluted samples of reagent (Ar/R = 200/1) and

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