Metal Tetrahydridoborates and Tetrahydroborato Metallates, 24[≠] Solvates of Sodium Bis(borane)dimethylamide

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The reaction of sodium metal with dimethylamine–borane in THF yields $Na[(H_3B)_2NMe_2]$ (**1**) which can be isolated as $\{Na[(H_3B)_2NMe_2]\}_5{\cdot}THF$ or as $Na[(H_3B)_2NMe_2]{\cdot}$15-crown-5 (**2**) and $Na[(H_3B)_2NMe_2]{\cdot}$benzo-15-crown-5 (**3**) after addition of the appropriate crown ether to the THF solution of **1**. Reaction of **1** with $ZrCl_4$ yields $Me_2HN–BH_2–NMe_2–BH_3$ (**4**), the structure of which has been determined. In THF solution, **1** reduces aldehydes, ketones, acyl chlorides, and esters to the corresponding alcohols. It also reacts slowly with nitriles and allylbenzene. Compound $(\mathbf{1})_5{\cdot}THF$ crystallizes in an extended three-dimensional lattice, in which the Na atoms are coordinated by 6–9 hydridic H atoms, while **3** is a molecular compound in the solid state. Only one hydrogen atom of each BH_3 group coordinates to the sodium center. On the other hand, **4** forms dimeric associates in the solid state through N–H···H–B interactions.

Introduction

As reducing agents, lithium dialkylamidotrihydridoborates, $Li(H_3BNR_2)$, have many advantages over MBH_4 compounds (M = Li, Na) and, in some respects, over $LiAlH_4$ as well.[2] The structures of the solvates of these amidotrihydridoborates $M(R_2NBH_3){\cdot}nL$ depend on the type and number of ligands L;[3] all of them are characterized by metal−nitrogen bonds as well as M···H−B interactions. A metal−nitrogen interaction is not possible in alkali metal salts of the anion $H_3B-NMe_2-BH_3^-$ because the nitrogen atom is tetracoordinated. However, the hydridic atoms of this anion with an alkali metal cation is of interest, particularly in comparison to solvates of alkali metal tetrahydridoborates.[1]

Synthesis

Compound $Na[H_3B-NMe_2-BH_3]$ (**1**) was first obtained by addition of NaH to $Me_2NB_2H_5$[4] according to Equation 1. It was isolated as a hemidioxanate. **1** is also formed when $NaBH_4$ is allowed to react with $Me_2NB_2H_5$ in diglyme, as described by Equation 2.[5] A possible synthesis from $NaNMe_2$ and $BH_3{\cdot}THF$ is difficult to perform because pure $NaNMe_2$ is not readily accessible. We now report an efficient synthesis starting from the readily available $Me_2NH{\cdot}BH_3$ and elemental sodium in the presence of THF. This process is described by Equation 3.

$$\mu\text{-}Me_2NB_2H_5 + NaH \rightarrow Na[H_3B-NMe_2-BH_3]\ (\mathbf{1}) \quad (1)$$

$$\mu\text{-}Me_2NB_2H_5 + 2\ NaBH_4 \rightarrow Na[H_3B-NMe_2-BH_3] + NaB_2H_7 \quad (2)$$

$$4\ Me_2NH{\cdot}BH_3 + 2\ Na \rightarrow 2\ Na[H_3B-NMe_2-BH_3] + H_2 + 2\ Me_2NH \quad (3)$$

Compound **1** slowly decomposes in THF solution with formation of $NaBH_4$ and dimeric dimethylaminoborane (Equation 4). In addition, small amounts of $(Me_2N)_2BH$ [$\delta^{11}B = 29.7$, $^1J(^{11}BH) = 132$ Hz][6] can be detected in the ^{11}B-NMR spectrum of the solution. Experimental evidence has shown that the faster the rate of formation of **1**, the lower the amount of by-products. A higher reaction rate can be achieved by providing an excess of sodium metal, if possible in a highly dispersed form. The shortest reaction times were achieved by using sodium metal dispersed on an Al_2O_3 support, which allowed the conversion of 0.1 mol of $Me_2NH{\cdot}BH_3$ into **1** within 30 min.

$$2\ \mathbf{1} \rightarrow 2\ NaBH_4 + [Me_2NBH_2]_2 \quad (4)$$

Following the dissolution of solid $\mathbf{1}{\cdot}n$THF in toluene, single crystals were obtained, which were shown to be $\{Na[H_3B-NMe_2-BH_3]\}_5{\cdot}THF$ by X-ray structure analysis. Addition of 15-crown-5 or benzo-15-crown-5 to the THF solution of **1** yielded the 1:1 solvates of the crown ethers $[Na(15\text{-crown-}5)][H_3B-NMe_2-BH_3]$ (**2**) and $[Na(benzo\text{-}15\text{-crown})][H_3B-NMe_2-BH_3]$ (**3**). Single crystals could only be obtained in the case of **3**.[7]

IR and NMR Spectra

While the IR spectra of covalently bonded BH_4 groups, particularly of mononuclear tetrahydroborates, usually provide conclusive evidence with regard to the bonding mode of the BH_4 ligand,[8] this is not the case if highly polar tetrahydridoborates are present, as would be expected for **1**.[9] Nevertheless, the IR spectra of 3 different compounds derived from **1**, depicted in Figure 1, show quite drastic differences in the B−H stretching region. Consequently, the

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structures of **1** in THF solution, in solid $(\mathbf{1})_5$·THF, and in **3** must be significantly different. We attribute the strong band of **1** seen at 2291 cm^{-1} to $\nu_{as}BH_3$, and the band of medium intensity at 2251 cm^{-1} to $\nu_{s}BH_3$.

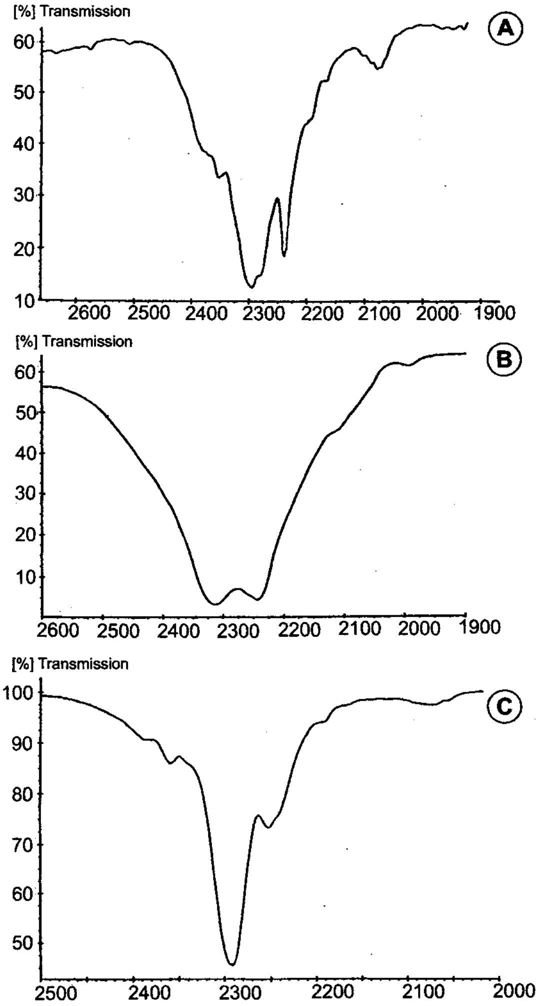

Figure 1. IR spectra in the B−H stretching band region of (A) solid $(\mathbf{1})_5$·THF, (B) **1** in THF solution, and (C) **3** in nujol

On the other hand, the IR spectrum of $(\mathbf{1})_5$·THF in nujol shows two strong bands at 2312 and 2244 cm^{-1}, along with shoulders, which cannot be unequivocally assigned. These observations suggest that the anion in **1** must have a different structure to that seen in THF solution. Compound **3** gives a better resolved IR spectrum. The three intense bands at 2294, 2281 and 2239 cm^{-1}, correspond to BH_3 groups in which a single hydrogen bond is present (ν_{MHB} = 2239 cm^{-1}), with the strongest bands being attributable to $\nu_{as}BH_3$. The presence of BH_3 groups in **1**−**3** is clearly demonstrated by 1:3:3:1 quadruplets in the ^{11}B-NMR spectrum with $^{1}J(^{11}B^{1}H)$ values ranging from 90 to 92 Hz, typical for tetracoordinated B atoms.

Reactions

Compound **1** may be a useful reducing agent having properties akin to those of $NaBH_4$. Some "standard" reductions were therefore tested, employing an acyl chloride, an aldehyde, two ketones, an ester and amide, as well as a nitrile, a carboxylic acid, and allylbenzene. Alcohols were obtained as reduction products of benzoyl chloride, benzaldehyde, acetophenone, and cyclohexanone. All other functional groups were reduced only slowly. Moreover, not all of the available hydride was utilized in the reactions (Table 1). The reaction of $ZrCl_4$ with **1** in a 1:4 molar reaction yielded small quantities of $Me_2NH{-}BH_2{-}NMe_2{-}BH_3$ (**4**). This compound is well known.[10] Its crystal structure has now been determined (vide infra).

X-ray Structures

The crown ether complex **3** was shown to be a molecular compound (or contact ion pair) in the solid state by X-ray crystallography. The compound crystallizes from THF solution in the monoclinic system, space group *Cc*, $Z = 8$.

Figure 2 shows that the anion $H_3B{-}NMe_2{-}BH_3^{-}$ coordinates to the sodium center through one hydridic H atom per BH_3 group. Thus, the coordination number at the sodium center is seven, resulting from two hydrogen and five oxygen atoms. The latter are arranged almost in a plane, and the Na atom resides above this plane with Na−O lengths ranging from 2.426(3) to 2.513(3) Å. Two different Na−B lengths [2.944(5) and 3.110(6) Å] indicate that the anion is not symmetrically coordinated to the metal center. On the other hand, the B−N−B bond angle is close to the ideal tetrahedral angle.

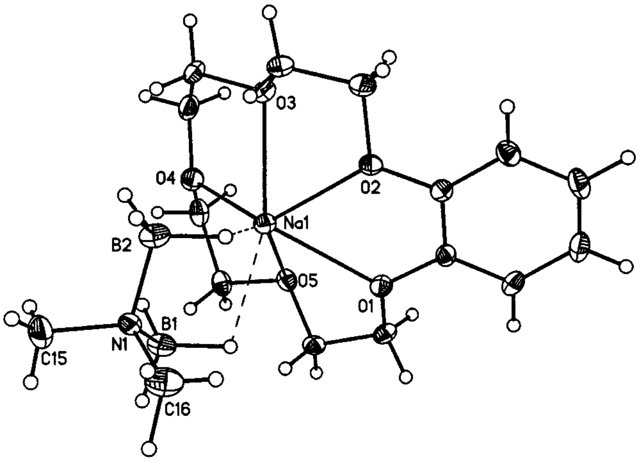

Figure 2. Molecular structure of **3** in the crystal; thermal ellipsoids represent a 25% probability; estimated standard deviations are shown in parentheses; selected atom distances [Å] and bond angles [°]: Na1−O1 2.469(3), Na1−O2 2.465(3), Na1−O3 2.449(3), Na1−O4 2.426(3), Na1−O5 2.513(3), Na1···B1 2.944(5), Na1···B2 3.110(6), N1−B1 1.580(6), N1−B2 1.580(6); O2−Na1−O1 63.9(1), O3−Na1−O2 65.9(1), O4−Na1−O3 68.0(1), O4−Na1−O5 67.64(9), O1−Na1−O5 65.29(1), B1−Na1−B2 51(1), C15−N1−C16 108.3(3), B1−N1−B2 110.9(3), B1−N1−C15 109.9(3), B2−N1−C15 109.2(3)

In contrast to **3**, the structure of compound $(\mathbf{1})_5$·THF is much more complex in the solid state. There are five different "molecules" of **1** in the asymmetric unit. This is represented in Figure 3, while Figure 4 shows a plot of the three-dimensional array.

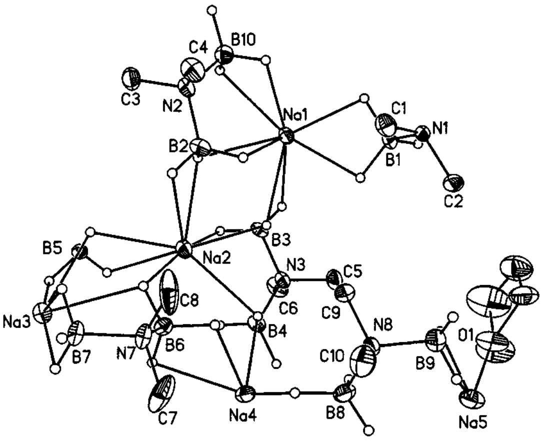

Figure 3. Atoms in the asymmetric unit of **(1)**$_5$·THF in an ORTEP representation with thermal ellipsoids at a 25% probability level; selected atom distances [Å] and bond angles [°]: Na1···B1 2.828(4), Na1···B2 2.899(3), Na1···B3 2.850(5), Na1···B10 2.888(5), Na2···B6 2.943(5), Na4···B6 2.970(5), Na5···B9 2.795(6), Na5−O1 2.310(4), N1−B1 1.588(5), N2−B2 1.581(6), N2−B10 1.588(5); B1−Na1−B3 107.6(2), B1−Na1−B2 124.5(2), B1−Na1−B10 118.5(2), B2−Na1−B10 53.4(2), B3−Na2−B2 88.7(2), B3−Na2−B6 135.9(1), B3−Na2−B5 119.5(2), B3−Na2−B4 51.4(1), B7−Na3−B7′ 86.9(1), B7−Na3−B5 135.6(1), B7−Na3−B4′ 120.2(1), B7−Na3−B6 51.7(1), B1′−Na4−B4 86.9(1), B1′−Na4−B6 122.5(1), Ba′−Na4−B8 86.2(1), B1′−Na4−B5′ 53.2, O1−Na5−B9 109.0(2), O1−Na5−B10′ 109.0(2), O1−Na5−B5′ 103.4(2), B9−Na5−B10′ 129.4(2), B3−N3−B4 110.7(3), B2−N2−B10 110.2(3), C3−N2−C4 108.9(3)

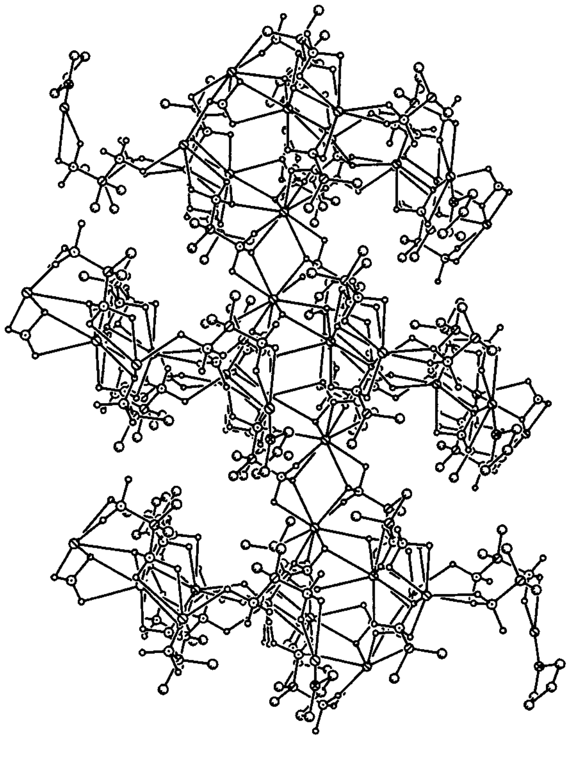

Figure 4. Plot of the three-dimensional array of the unit **(1)**$_5$·THF; view down the *b* axis

All hydrogen atoms of the BH_3 groups are involved in Na···H−B interactions; one shows contacts with two different Na atoms (as a $\mu^2{}_1$ bridge), while the other two H atoms coordinate either through a $\mu^1{}_1$ interaction to two different Na atoms or through a $\mu^1{}_2$ interaction to one Na center (see the "coordination polyhedra" in Figure 5). If we consider only the corresponding boron atoms ($NaOB_3$ polyhedron), then a slightly distorted tetrahedral array is observed with O−Na5−B bond angles ranging from 103.4(2)° to 109.0(2)°. Atom Na1 is surrounded by five boron atoms at distances of 2.828(4) to 2.899(5) Å, as well as by nine H atoms. Nine H atoms are associated with atom Na3, while Na4, like Na2, is coordinated by eight hydridic hydrogen atoms. In contrast, but in line with expectation, the B−N−B bond angles of all five different $H_3B-NMe_2-BH_3^-$ anions are close to the ideal tetrahedral bond angle, varying only from 108.9(3) to 110.2(3)°. Moreover, the B−N bond lengths are equal within the standard deviation, the average value being 1.58 Å, which is typical for a B−N single bond involving sp^3-type atoms (in cubic BN 1.56 Å[11]). Figure 4 depicts the three-dimensional array of atoms in the solid state of compound **(1)**5·THF. One must assume that this lattice is broken up into smaller units upon dissolution in solvents such as THF.

Figure 6 shows the molecular structure of two molecules of the amine−borane **4**. This species represents the BN analogue of 2,2,4,4-tetramethylbutane. The two terminal B−N bonds [1.600(2), 1.599(2) Å] have equal lengths, while the central B−N bond is slightly but significantly shorter [1.583(2) Å]. Interestingly, the B−N−B and the N−B−N bond angles are slightly wider than might be expected for tetracoordinated N and B atoms [113.4(1), 113.9(1)°].

N−C bond lengths in **4** lie in the expected range (1.477−1.487 Å) for single bonds.[12] The most interesting aspect of the structure of **4** in the solid state is its association. Crystallographically, there is a center of inversion between each pair of molecules, resulting in close contacts between the NH proton with two hydridic hydrogen atoms of the BH_3 group (H1−H3c 2.27 Å, H1a−H3b 2.38 Å; angle N1a−H1a−H3c 151°, N1a−H1a−H3b 135°) . This implies that the observed packing is a result of a dipolar interaction between hydrogen atoms of opposite polarization. Such interactions have previously been observed in the case of H_3N-BH_3,[13] and other amine−boranes[14] and have also been invoked as being responsible for determining the conformations of BH_3 adducts of triazacyclohexanes and heteroatom-azacyclohexanes $[S_{2-n}(NMe)_{n+1}(CH_2)_3]$.[15]

Discussion

Sodium bis(borane)dimethylamide is readily obtained in excellent yield by allowing elemental sodium to react with dimethylamine−borane in the presence of THF. Under similar conditions, elemental Li reacts with $Me_2NH\cdot BH_3$ with formation of $Li(Me_2NBH_3)$ but not of $Li(H_3B-NMe_2-BH_3)$.[16] It seems likely that $Na(Me_2NBH_3)$, which should be formed initially, is a very

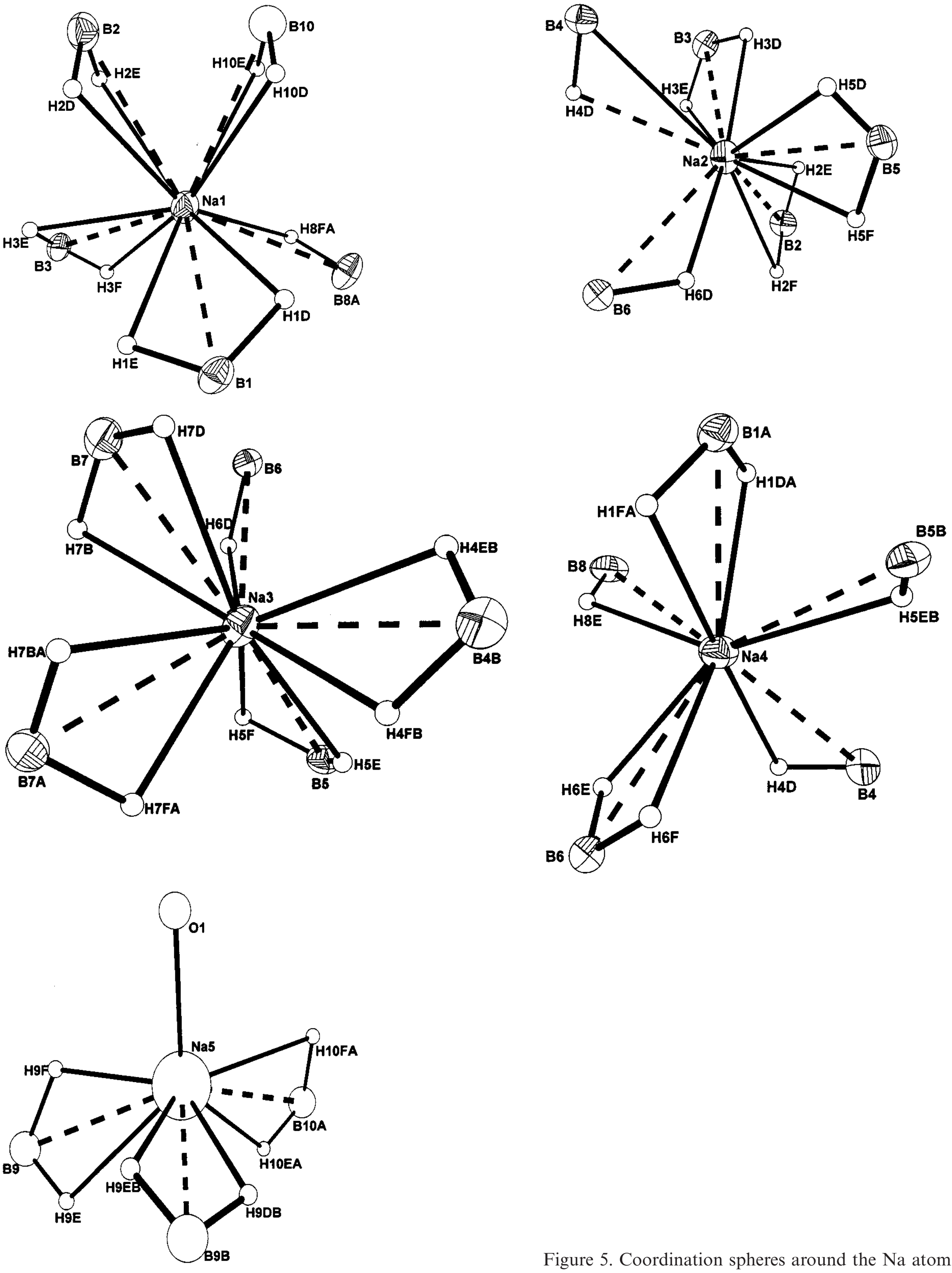

Figure 5. Coordination spheres around the Na atoms in $(\mathbf{1})_5$·THF

strong base and thus displaces Me_2NH from the amine−borane according to Equation 5.

$$\mathrm{Na(Me_2NBH_3) + Me_2NH{\cdot}BH_3 \rightarrow Na(H_3B{-}NMe_2{\cdots}BH_3) + Me_2NH} \quad (5)$$

Compound **1** is soluble in THF (up to 1.57 M at 25°C) and may be present in solution as an ion pair $(THF)_nNa(H_3B{-}NMe_2{-}BH_3)$, possibly with a structure similar to that adopted by the crown-ether solvate **3**. On the other hand, differences are seen in the IR spectra of a

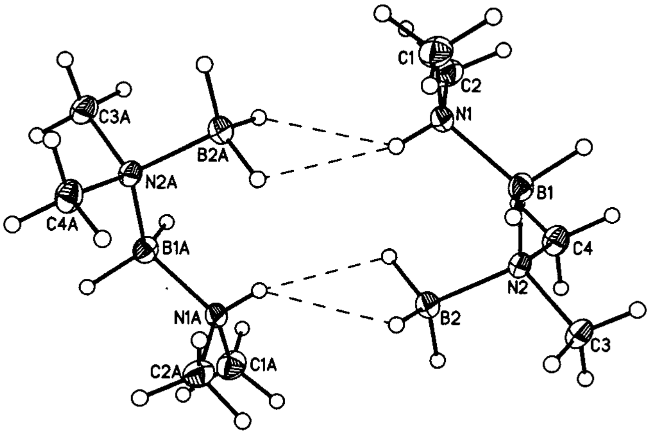

Figure 6. ORTEP plot of two molecules of **4**; thermal ellipsoids are depicted at a 25% probability level; selected bond lengths [Å] and bond angles [°]: B1−N1 1.599(2), B1−N2 1.589(2), B2−N2 1.600(2), N2−C3 1.488(2), N2−C4 1.481(2), N1−C2 1.477(2), N1−C1 1.483(2); N1−B1−N2 113.9(1), B2−N2−B1 113.4(1), C3−N2−B1 105.0(1), C3−N2−B2 108.3(1), C2−N1−B1 116.5(1)

THF solution of **1** and of the well-defined compound **3**. Nevertheless, these spectra are not too dissimilar when compared to that of (**1**)$_5$·THF.

The good solubility of **1** in THF is in remarkable contrast to the limited solubility of $NaBH_4$ in this solvent. Therefore, **1** in THF solution may represent a promising reducing agent, as has been shown for typical organic functional groups. Compared to $NaBH_4$, compound **1** is a stronger reducing agent in that it also reduces benzoic acid, benzamide, ethyl benzoate, and benzonitrile. It also acts as a mild hydroboration agent, for example attacking styrene. The structures of (**1**)5·THF and **3** have no precedent in the field of alkali metal hydridoborates. Thus, **3** is the first example where "single" M···H−B bridges are present, while (**1**)5·THF forms a three-dimensional array comprising 7−9 coordinated sodium atoms (taking into account only O and H atoms), involving all hydridic hydrogen atoms of the anion $H_3B-NMe_2-BH_3$. The bridging mode of the BH_3 units resembles that of BH_4 groups in dimeric $LiBH_4$·TMEDA[17] and in dimeric $NaBH_4$·PMDETA,[1] e.g. two hydrogen atoms bridge to two different Na centers, while one hydrogen atom connects to two metal centers.

Conclusion

Compound **1** is a nice example where changes in the coordination mode of the $H_3B-NMe_2-BH_3^-$ anion, as brought about by different ligands, can be studied. It is evident from the examples presented here that an expected three-dimensional structure of **1** (which is not yet known) breaks up into smaller units upon solvation. (**1**)$_5$·THF still retains the three-dimensional association, which most likely breaks down into ion pairs in THF solution or upon addition of a crown ether. This is in agreement with previous structural studies on Li(R_2NBH_3) ether solvates[3] and on $LiBH_4$ ether solvates.[9][18] Although $NaBH_4$ has been known for more than 40 years, its structural chemistry remains largely unexplored. Compound **1** would seem to represent another reducing agent that may compete with lithium amidohydridoborates as a convenient and easy to handle reagent.

Experimental Section

General: All experiments were performed under anhydrous conditions in flame-dried glassware using Schlenk techniques and N_2 as a protecting gas. − NMR spectra were recorded with a Bruker AC 200 or a JEOL GSX 270 instrument (^1H, ^{13}C: reference C_6D_6 or $SiMe_4$; ^{11}B: ext. BF3·OEt2; ^7Li ext. aq. LiCl). − IR: Nicolet 520 FT-IR spectrometer.

Preparation of a Solution of Sodium Bis(borane)dimethylamide (1) in THF: Sodium pieces (2.00 g, 87 mmol) were suspended in stirred THF (150 mL). Then, a concentrated solution of $Me_2NH\cdot BH_3$ (5.1 g, 87 mmol) in THF was added and the mixture was refluxed for 6 d. A turbid solution was formed and a gas was evolved, leaving sodium pellets. The solution showed the following ^{11}B-NMR signals: δ = −42.4 (very weak, $NaBH_4$), −12.5 [q, $^1J(^{11}B^1H)$ = 91 Hz, **1**], 6.3 [very weak t, $(Me_2NBH_2)_2$], 29.7 [d, $^1J(^{11}B^1H)$ = 128 Hz, $(Me_2N)_2BH$]. 1.0 g (43 mmol) of Na was recovered. All volatile materials were then removed from the solution in vacuo (down to 10^{-3} Torr). Yield: 3.8 g of **1** (ca. 92%) as a fine white powder. − Solubility: 1.57 M in THF at 25°C. − IR (cm^{-1}, BH region): ṽ = 2384 w, 2359 w, 2291 vs, 2251 m. − $C_2H_{12}B_2NNa$ (94.73): calcd. B 22.82, N 14.79, Na 22.99; found B 22.1, N 13.9, Na 20.5.

Pentakis[sodium bis(borane)dimethylamide]·Tetrahydrofuran [(1)$_5$·THF]: Prepared as described for **1**. All volatiles were removed at 10 Torr. The solid residue was then suspended in toluene (20 mL) and the suspension was heated to reflux. Insoluble material was then removed from the hot solution by filtration through a G3 glass frit. Pentane (10 mL) was added to the filtrate, which subsequently became turbid. After cooling to −20°C, crystals of m.p. 7°C were deposited. The supernatant solution was separated by means of a syringe. Further crystals separated from this solution. Although these were largely intergrown, single crystals could easily be separated. − ^{11}B NMR (THF): δ = −10.1 [q, $^1J(^{11}B^1H)$ = 91 Hz]. − ^1H NMR (C_6D_6): δ = 2.33 (s, 30 H), 3.56 (m, 8 H, THF). − IR (cm^{-1}, Nujol): ṽ = 2312 vs, 2244 vs, 1627 w, 1579 w, 1469 vs, 1445 m, 1427 w, 1398 w, 1384 w, 1370 w, 1214 vs, 1177 vs, 1159 vs, 1032 s, 1031 vs, 935 m, 914 m, 819 m. − $C_{14}H_{68}B_{10}N_5Na_5O$ (545.77): calcd. C 30.81, H 12.56, N 12.83; found C 30.62, H 12.52, N 12.65.

Sodium Bis(borane)dimethylamide·15-Crown-5 (2): (**1**)5·THF (1.1 g, 2.02 mmol) was dissolved in THF (10 mL) and 15-crown-5 (2 mL, 10 mmol) was added to the stirred solution by means of a syringe. The solution showed ^{11}B-NMR signals at δ = −9.4 [q, $^1J(^{11}B^1H)$ = 91 Hz, **1**] and −12.4 (s) in a 21:1 ratio. Crystals separated from the solution within 2 d at −14°C. They were extensively intergrown and no single crystal could be separated. Yield: 2.3 g of **2** (73%); m.p. 175°C. − ^{11}B NMR: δ = −7.6 [q, $^1J(^{11}B^1H)$ = 92 Hz] in DMF; δ = −9.2 [q, $^1J(^{11}B^1H)$ = 91 Hz] in glyme, besides very weak signals at δ = 21.0 and 11.9; δ = −9.3 [q, $^1J(^{11}B^1H)$ = 91 Hz] in toluene, δ = −9.4 [q, $^1J(^{11}B^1H)$ = 93 Hz] in diethyl ether; δ = −9.3 [q, $^1J(^{11}B^1H)$ = 90 Hz] in benzene. − IR (cm^{-1}, BH region): ṽ = 2340 s, 2293 vs, 2237 s, 2163 m. − $C_{12}H_{32}B_2NNaO_5$ (315.00): calcd. C 45.76, H 10.24, B 6.86, N 4.45; found C 47.30, H 10.45, B 6.50, N 3.93.

Sodium Bis(borane)dimethylamide·Benzo-15-crown-5 (3): The crown ether (1.34 g, 5 mmol) was dissolved in THF (20 mL) with stirring.

To this solution was added a solution of **1** in THF (3.36 mL, 1.49 M). After concentrating the solution in vacuo to a volume of ca. 10 mL, crystals separated within 2 months at −14°C, which were eventually isolated. Yield: 1.49 g of **2** (82%); m.p. 129°C (dec.). − ^{11}B NMR (DMSO): $\delta = -7.9$ [q, $^1J(^{11}B^1H) = 90$ Hz]. − IR (cm^{-1}, BH region): $\tilde{\nu}$ = 2295 vs, 2281 vs, 2239 vs, 2168 sh, 2194 sh. − $C_{18}H_{32}B_2NNaO_5$ (363.04): calcd. C 52.93, H 8.88, B 5.96, N 3.86; found C 53.12, H 8.91, B 5.74, N 3.44.

Reductions: To a 1.57 M solution of **1** in THF (32 mL, 50 mmol) was added the appropriate organic compound (usually 50 mmol). The mixture was refluxed for 2 h (5 min in the case of benzoyl chloride). After cooling to ambient temperature, 15 mL of a 6 M HCl solution was added, followed by NaOH until the solution was basic. The mixture was extracted with diethyl ether (3 × 15 mL), the combined extracts were dried with $MgSO_4$, and the reaction product was finally isolated by distillation. All compounds were characterized by their ^{1}H- and ^{13}C-NMR spectra.

Benzyl Alcohol from Benzoyl Chloride: From C_6H_5COCl (7.05 g, 50 mmol) was obtained $C_6H_5CH_2OH$. Yield: 4.49 g (83%); b.p. 93°C/10 Torr.

Table 1. Hydrogen consumptions for some reductions using **1** in THF solution

Substrate	Hydride equiv.	H_2 evolved	Hydride consumed
Ethyl benzoate	42	345 cm^3, 15.6 mmol	26.5 mmol
Benzamide	42	525 cm^3, 23.7 mmol	18.3 mmol
Benzonitrile	42	550 cm^3, 24.8 mmol	17.2 mmol
Benzoic acid	63	790 cm^3, 35.7 mmol	27.3 mmol
Allylbenzene	21	345 cm^3, 15.6 mmol	5.4 mmol

[a] $w^{-1} = \sigma^2F_o^2 + (xP)^2 + yP$; $P = (F_o^2 + 2F_c^2)/3$.

Benzyl Alcohol from Benzaldehyde: From C_6H_5CHO (5.30 g, 50 mmol) was obtained $C_6H_5CH_2OH$. Yield: 4.32 g (80%); b.p. 90−93°C/10 Torr.

1-Phenylethanol from Acetophenone: From $C_6H_5COCH_3$ (6.00 g, 50 mmol) was obtained $C_6H_5CH_2CH_2OH$. Yield: 4.58 g (75%); b.p. 95−97°C/10 Torr.

Cyclohexanol from Cyclohexanone: From $C_6H_{10}O$ (4.90 g, 50 mmol) was obtained $C_6H_{11}OH$. Yield: 3.81 g (76%); b.p. 58−62°C/10 Torr.

Hydride Consumption by Various Organic Compounds: A solution of **1** in THF (4.5 mL, 1.57 M) was placed in a two-necked flask. Then, the organic compound (20 mmol) was slowly added and the mixture was refluxed for 3 d. The hydrogen gas released after addition of 15 mL of a 6 M HCl solution was collected, the volume of which allowed the hydride consumption to be determined. The results of these experiments are collected in Table 1.

Dimethylamine−Dimethylaminoborane−Borane (4): $ZrCl_4$ (1.16 g, 5.00 mmol) was suspended in THF (80 mL). To the stirred brownish suspension was added a solution of **1** in THF (13.6 mL, 1.47 M, 20 mmol). A clear solution resulted, which was stored at −78°C. Crystals of **4** separated over a period of 2 weeks. The yield of **4** was not determined, but was rather low. − ^{11}B NMR (THF): $\delta = -13.2$ [q, $^1J(^{11}B^1H) = 198$ Hz], 2.0 [t, $^1J(^{11}B^1H) = 96$ Hz]. − ^{1}H NMR (C_6D_6): $\delta = 5.0$ (br., NH, 1 H) 2.3 (NMe, 6 H), 1.8 (Me_2NH, 6 H), 2.0 (q, $^1J = 108$ Hz), 1.95 (q, $^1J = 96$ Hz). − ^{13}C NMR (C_6D_6): $\delta = 52.4$ (NMe_2), 42.7 ($HNMe_2$). − IR (cm^{-1}, νBH region): $\tilde{\nu}$ = 2447 s, 2390 vs, 2353 vs, 2345 vs, 2315 vs, 2293 vs, 2283 s, 2253 s, 2165 m, 2109 m, 2084 m, 2061 m. − $C_4H_{18}B_2N_2$ (115.82): calcd. C 52.93, H 8.88, B 5.96, N 3.82; found C 53.12, H 8.91, B 5.74, N 3.44.

X-ray Structure Determinations: Crystals were transferred into cooled perfluoroether oil, a single crystal was selected and placed

Table 2. Summary of crystallographic data and information relating to data collection and refinement

Compound	**3**	(**1**)$_5$·THF	**4**
Empirical formula	$C_{16}H_{32}B_2NNaO_5$	$C_{14}H_{68}B_{10}N_5Na_5O$	$C_4H_{18}B_2N_2$
Formula mass	363.04	672.25	115.82
Crystal size	0.2×0.45×0.45	0.3×0.45×0.56	0.25×0.32×0.5
Crystal system	monoclinic	monoclinic	monoclinic
Space group	*Cc*	*P*2(1)/*c*	*P*2(1)/*n*
a [Å]	8.5440(10)	10.529(2)	6.2774(3)
b [Å]	29.262(5)	19.439(5)	10.0411(5)
c [Å]	9.1030(10)	20.101(4)	13.8360(6)
α [°]	90	90	90
β [°]	114.65(1)	100.24(1)	102.519(1)
γ [°]	90	90	90
V [Å^3]	2068.5(5)	4048.6(15)	851.38(7)
Z	4	4	4
ρ(calcd.) [Mg/m^3]	1.166	0.895	0.904
μ [mm^{-1}]	0.100	0.097	0.052
F(000)	784	1200	264
Index range	$-9 \le h \le 9$ $0 \le k \le 34$ $-10 \le l \le 10$	$0 \le h \le 12$ $-22 \le k \le 22$ $-23 \le l \le 22$	$-8 \le h \le 6$ $-12 \le k \le 12$ $-17 \le l \le 16$
2θ [°]	48.98	48.00	57.70
Temperature [K]	196	213	233
Refl. collected	3605	7066	4320
Refl. unique	3350	6209	1721
Refl. observed (4σ)	2835	3145	1342
R (int.)	0.0344	0.0569	0.0595
No. of variables	242	347	146
Weighting scheme[a] *x*/*y*	0.0753/3.1604	0.0607/1.7723	0.0813/0.1664
GOOF	1.033	1.033	1.125
Final *R* (4σ)	0.0504	0.0645	0.0462
Final *wR*2	0.1338	0.1332	0.1386
Largest res. peak [e/Å^3]	0.163	0.201	0.221

on top of a glass fibre, which was mounted on the goniometer head of the diffractometer. Most measurements were performed with a Siemens P4 diffractometer equipped with a graphite monochromator, an Mo-K_α tube, an LT2 low-temperature device, and an area detector. For one compound, a Siemens P3m diffractometer was employed. − Reflection data sets were collected either in the hemisphere mode (SMART program) with $\Delta\varphi = 0.3°$ per frame, or in the $\omega/2\Theta$ mode. Lorentz and polarization corrections were applied in the data reduction, but not an absorption correction. The structures were solved by direct methods (SHELXT programs). Non-hydrogen atoms were refined anisotropically, while all H atoms bound to boron atoms were refined isotropically in their found positions. Hydrogen atoms attached to carbon atoms were placed in calculated positions and included in the refinement as a riding model. The THF molecule in compound (**1**)$_5$·THF was found to be disordered; atoms were placed in split positions and SOFs were refined for two different sites. A summary of the relevant crystallographic data and information relating to the data collection, structure solution, and refinement is given in Table 2. − Additional data (except F_o/F_c tables) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-125203−125205 Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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