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Metal Tetrahydridoborates and Tetrahydridoborato Metalates. 23.[1] Amine Solvates of Lithium and Sodium Tetrahydridoborate[†]

Hans-Hermann Giese, Tassilo Habereder, Heinrich Nöth,* Werner Ponikwar, Steffen Thomas, and Marcus Warchhold

Institute of Inorganic Chemistry, University of Munich, Butenandtstrasse 5-13, Building D,
D-81 377 München, Germany

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A series of amine solvates of $LiBH_4$ and $NaBH_4$ have been prepared and characterized by IR and NMR spectroscopy as well as by X-ray single-crystal structure determinations. $LiBH_4$ crystallizes from pyridine as $LiBH_4{\cdot}3(py)$, **1**, in which the BH_4 anion acts as a bidentate ligand. However, in the structure of $LiBH_4{\cdot}3py^*$, **2** ($py^* =$ *p*-benzylpyridine), a tridentate BH_4 group is observed. In contrast, $LiBH_4{\cdot}2(coll)$, **3** (coll = 2,4,6-trimethylpyridine, collidine), possesses only a bidentate tetrahydridoborate group, while a tridentate BH_4 group is present in monomeric $LiBH_4{\cdot}PMDTA$, **4** (PMDTA = pentamethyldiethylenetriamine). In contrast, $NaBH_4{\cdot}PMDTA$, **6**, is dimeric in the solid state: three of the four H atoms of each BH_4 group coordinate to the Na atoms; two form a double bridge to two Na atoms while the third one is bonded only to one Na center. $LiBH_4{\cdot}TMTA$, **5** (TMTA = trimethylhexahydrotriazine), is also dimeric; however, only two of the nitrogen atoms of the TMTA ligand coordinate to Li. The BH_4 groups bridge the two Li centers each with one H atom coordinating to two Li atoms, and two bind to a single Li atom. A totally different situation exists for $NaBH_4{\cdot}TMTCN$, **7** (TMTCN = trimethyltriazacyclononane), which is tetrameric in the crystal. Only one hydrogen atom of the BH_4 group functions as a hydride bridge and binds to three Na centers. The molecule contains a Na_4B_4 heterocubane core. Thus, the different modes of the interaction of the BH_4 groups with the alkali metal atoms are determined by the number of donor atoms from the neutral amine ligand and the size of the cation. No definitive conclusion as to the structure of the amine solvates can be derived from IR and/or ^{11}B NMR spectra for the solution state. The crystallographic data are as follows. **1**: $a = 10.9939(5)$ Å, $b = 9.9171(4)$ Å, $c = 14.8260(8)$ Å, $\beta = 94.721(3)°$, $V = 1611.0(1)$ Å^3, monoclinic, space group $P2(1)/n$, $Z = 4$, $R_1 = 0.0823$. **2**: $a = 10.121(1)$ Å, $b = 12.417(2)$ Å, $c = 13.462(3)$ Å, $\alpha = 83.189(2)°$, $\beta = 86.068(3)°$, $\gamma = 69.166(4)°$, $V = 1369.3(5)$ Å^3, triclinic, space group $P\bar{1}$, $Z = 2$, $R_1 = 0.0689$. **3**: $a = 28.527(3)$ Å, $b = 10.858(1)$ Å, $c = 11.319(1)$ Å, $V = 3505.7(6)$ Å^3, orthorhombic, space group $Fdd2$, $Z = 8$, $R_1 = 0.0502$. **4**: $a = 7.591(3)$ Å, $b = 15.325(6)$ Å, $c = 8.719(4)$ Å, $\beta = 99.80(2)°$, $V = 999.5(7)$ Å^3, monoclinic, space group $P2(1)/c$, $Z = 4$, $R_1 = 0.0416$. **5**: $a = 14.68(1)$ Å, $b = 11.830(7)$ Å, $c = 16.960(8)$ Å, $V = 2946(3)$ Å, orthorhombic, space group $P2(1)2(1)2(1)$, $Z = 8$, $R_1 = 0.0855$. **6**: $a = 9.993(2)$ Å, $b = 10.008(3)$ Å, $c = 14.472(4)$ Å, $\beta = 93.55(2)°$, $V = 1444.6(7)$ Å^3, monoclinic, space group $P2(1)/n$, $Z = 4$, $R_1 = 0.0455$. **7**: cubic, $a = b = c = 13.859(5)$ Å, $V = 2662(2)$ Å^3, cubic, space group $I\bar{4}3m$, $Z = 8$, $R_1 = 0.0871$.

Introduction

Alkali metal tetrahydridoborates, and sodium tetrahydridoborate in particular, belong to an important class of hydridic reducing reagents of wide applicability.[2,3] One of the advantages of $NaBH_4$ is that it can be employed in aqueous or alcoholic solutions due to its comparatively good solvolytic stability in neutral and alkaline media, in contrast to $LiBH_4$, which requires an ether as a solvent. Solutions of $LiBH_4$ in various ether solvents contain contact ion pairs as exemplified by $LiBH_4{\cdot}3THF$ even for the solid state,[1] and various kinds of aggregations have recently been determined. For example, $LiBH_4{\cdot}OEt_2$ forms double-stranded chains.[1,4] A similar situation has been found for $LiBH_4{\cdot}O(Me)^tBu$,[1] and even extended three-dimensional arrays were observed.[1] The structure of these and other solvates depends both on the stoichiometry of the ether solvate and on the number of oxygen atoms of the ligand. Therefore, it was of interest to investigate more strongly complexing ligands than ethers. Here we report on the synthesis and on the structure determination of lithium and sodium tetrahydroborate complexes with ligands such as pyridines, pentamethyldiethylenetriamine (PMDTA), *N,N′,N″*-trimethylhexahydrotriazine (TMTA), and 1,4,7-trimethyl-1,4,7-triazacyclononane (TMTCN).

Experimental Section

All experiments were performed in an atmosphere of dry dinitrogen using Schlenk techniques. Solvents were made anhydrous by standard procedures and were kept in an atmosphere of N_2.

[†] Dedicated to Prof. Dr. M. F. Hawthorne, a pioneer in boron chemistry and a good friend, on the occasion of his 70th birthday.

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Materials. LiBH$_4$ and NaBH$_4$ were of commercial quality (Chemetall GmbH) and were crystallized from ether and diglyme, respectively. Coordinated ether was removed in vacuo. The amine ligands were also of commercial grade and were used as supplied or after drying liquids with zeolite beads. Elemental analyses were performed at the institute's microanalytical laboratory. The contents of alkali metal and amines were determined by acidimetric titration and/or by AAS.

Physical Measurements. IR spectra were recorded with a Perkin-Elmer FT 370 instrument using Nujol/Hostaflon suspensions. ^{1}H, ^{7}Li, ^{13}C, and ^{11}B resonances were determined with a Bruker AP 200 instrument (^{11}B), a JEOL X270 instrument (^{7}Li,^{11}B, ^{13}C), or a JEOL 400 instrument (^{1}H, ^{13}C). TMS was used as internal standard for ^{1}H and ^{13}C, while BF$_3$·OEt$_2$ served as external standard for ^{11}B, and an aqueous solution of LiCl (1 M) served as external standard for ^{7}Li.

LiBH$_4$·3NC$_5$H$_5$ (1). A saturated solution of LiBH$_4$ in pyridine (30 mL) was prepared to which cyclohexane (10 mL) was added. The precipitate which formed was removed by filtration. Cooling the solution to 0 °C yielded needles of **1**, mp 52−54 °C. Attempts to dissolve **1** in C$_6$D$_6$ gave a solution consisting of ~90% of H$_3$B·py and 10% of **1**. However, if **1** was dissolved in a mixture of C$_6$D$_6$ and pyridine (6:1), then **1** was the dominant species (>90%).

IR (cm^{-1}, ν-BH region): 2354sh, 2309s, 2279s, 2245s. NMR for **1** in C$_6$D$_6$/NC$_5$D$_5$ (6:1): δ^1H 1.4 (1:1:1:1 quartet, $^1J(^{11}B^1H) = 81$ Hz; septet, $^1J(^{10}B^1H) = 27$ Hz); δ^{11}B (pyridine) −41.9 (**1**, quintet, $^1J(^{11}B^1H) = 81$ Hz), −10.4 (H$_3$B·NC$_5$H$_5$, quartet, $^1J(^{11}B^1H) = 98$ Hz); δ^7Li (C$_6$D$_6$) 0.7.

Anal. Calcd for C$_{15}$H$_{19}$N$_3$BLi (259.08): C, 69.54; H, 7.39; N, 16.22; B, 4.17; H$^-$, 5.80. Found: C, 67.14; H, 7.33; N, 15.63; H$^-$, 5.86.

LiBH$_4$·3NC$_5$H$_4$(*p*-CH$_2$Ph) (2). LiBH$_4$ (0.200 g, 9.18 mmol) was suspended in toluene (10 mL), and *p*-benzylpyridine (10 mL) was added. Stirring was continued for 2 h and insoluble material removed by filtration. Colorless crystals of **2** separated from the filtrate on standing for 5 days at 8 °C. The yield was not determined. No H$_3$B·NC$_5$H$_4$(CH$_2$Ph), mp 42−45 °C dec, was detected in the solution by ^{11}B NMR. When **2** was dissolved in C$_6$D$_6$, *p*-benzylpyridine (4:1) about 40% of **2** had decomposed to give H$_3$B·NC$_5$H$_4$(CH$_2$Ph), δ^{11}B = −12.1.

IR (cm^{-1}, ν-BH region): 2331s, 2230s, 2209s, 2149sh. NMR (C$_6$D$_6$/*p*-benzylpyridine): δ^1H (400 MHz) 1.4 (quartet, $^1J(^{11}B^1H) = 81$ Hz; septet, $^1J(^{10}B^1H) = 27$ Hz); δ^{11}B −38.1 (quintet, $^1J(^{11}B^1H) = 81$ Hz), −12.1 (borane adduct, may be present); δ^7Li (C$_6$D$_6$) 2.4.

Anal. Calcd for C$_{36}$H$_{37}$N$_3$BLi (529.44): C, 81.67; H, 7.04; N, 7.94, H$^-$, 2.84. Found: C, 81.96; H, 7.16; N, 8.00; H$^-$, 2.68.

LiBH$_4$·2[2,4,6-(CH$_3$)$_3$NC$_5$H$_2$] (3). After preparation of a saturated solution of LiBH$_4$ in 2,4,6-trimethylpyridine and after removal of excess LiBH$_4$, methylcyclohexane (10 mL) was added to 50 mL of the LiBH$_4$ solution. The solid that precipitated was removed by filtration. On cooling the solution to −10 °C colorless prisms of **3** separated, mp 62−65 °C dec. On attempts to dissolve **3** in C$_6$D$_6$ only H$_3$B·NC$_5$H$_2$(Me)$_3$ was present in solution (δ^{11}B = −16.8).

IR (cm^{-1}, ν-BH region): 2421m, 2330s, 2268s. NMR (2,4,6-trimethylpyridine): δ^{11}B −35.9 (quintet, $^1J(^{11}B^1H) = 82$ Hz), −16.8 (quartet, $^1J(^{11}B^1H) = 98$ Hz, borane-coll. Adduct may be present).

Anal. Calcd for C$_{16}$H$_{26}$N$_2$BLi (264.14): C, 72.75; H, 9.92; N, 10.61. Found: C, 67.31; H, 9.61; N, 10.01.

LiBH$_4$·(Me$_2$NCH$_2$CH$_2$)$_2$NMe (4). LiBH$_4$ (0.45 g, 21 mmol) was suspended in hexane (20 mL). To the stirred suspension was added (Me$_2$NCH$_2$CH$_2$)$_2$NMe (4.31 mL, 21 mmol). Stirring was continued for 2 h, and then toluene (15 mL) was added and stirring continued for 1 h. After filtration, crystals of **4** separated from the solution within 1 week at a temperature of −14 °C. Yield: 2.78 g of **4** (68%).

IR (cm^{-1}, ν-BH region): (in Nujol) 2324vs, 2284s, 2210vs, 2198s, 2181vs, 2163vs, 2102m; (in THF) 2323vs, 2272s, 2211vs, 2162s. NMR (C$_6$D$_6$): δ^1H 1.79 (3H, NMe), 2.08 (12H, Me), 2.13 (8H, CH$_2$); δ^{13}C (THF) 44.6 (Me), 45.7 (Me), 53.4 (CH$_2$), 56.8 (CH$_2$); δ^{11}B (toluene-*d*$_8$) −38.8 (quintet, $^1J(^{11}B^1H) = 81$ Hz), −7.2 (quartet, amine-borane (ratio 1:20); in toluene/hexane the ratio was 6:1); in ether only δ^{11}B = −38.3 was observed.

Calcd for C$_6$H$_{19}$LiBN$_3$ (150.99): C, 47.73; H, 12.68; N, 27.83; Li, 4.60. Found: C, 46.73; H, 12.15; N, 26.57; Li, 4.23 (AAS).

IR (cm^{-1}): ν = 2154sh, 2225sh, 2271s, 2367s. NMR: (C$_6$D$_6$/TMS): δ^7Li 0.373; δ^{11}B −39.3 (quintet, $^1J(^{11}B^1H) = 81$ Hz).

LiBH$_4$·(MeNCH$_2$)$_3$ (5). LiBH$_4$ (0.66 g, 30 mmol) was suspended in xylene (20 mL), and 1,3,5-trimethylcyclohexahydrotriazine (4.26 mL, 30.3 mmol) was added to the stirred suspension. Stirring was continued for 2 h at ambient temperature. Then the suspension was kept at reflux for 2 h. All solid material was removed from the hot solution by filtration. On cooling the solution crystals of **5** separated (mp 89 °C dec). Yield: 2.4 g of **5** (53%).

IR (cm^{-1}, ν-BH region): 2154sh, 2225sh, 2271s, 2343s, 2367s. NMR (C$_6$D$_6$): δ^{11}B −39.3 (quintet, $^1J(^{11}B^1H) = 81$ Hz); δ^7Li (C$_6$D$_6$) 0.373.

Anal. Calcd for C$_6$H$_{19}$N$_3$BLi (150.99): C, 47.73; H, 12.68; N, 27.83; Li, 4.60. Found: C, 46.73; H, 12.15; N, 26.57; Li, 4.23.

NaBH$_4$·(Me$_2$NCH$_2$CH$_2$)$_2$NMe (6). To a stirred suspension of NaBH$_4$ (760 mg, 20 mmol) in hexane (20 mL) was added pentamethyldiethylenetriamine (4.18 mL, 20 mmol). After the suspension was heated to reflux for 10 min, toluene (15 mL) was added. This resulted in the formation of a turbid solution. Insolubles were removed 3 h later by filtration. Storing the solution at −14 °C yielded clear prismatic crystals as well as needles. Yield: 3.08 g of **6** (73%), mp 55 °C. Solubility at 20 °C: 1.25 mol/L in toluene, 0.004 mol/L in hexane.

IR (Nujol, cm^{-1}): 2316s, 2249vs, 2184s, 1852w, 1637w, 1507w, 1476s, 1393w, 1362w, 1331w, 1224m, 1179s, 1161s, 1140m, 1097s, 1076s, 1011s, 978m, 929s, 913s, 872w, 736w, 694w, 663w. The following ratios were observed by ^{11}B NMR spectroscopy. In hexane: −7.3 (borane adduct, quartet, $^1J(^{11}B^1H) = 91$ Hz) and −41.4 (**6**, quintet, $^1J(^{11}B^1H) = 81$ Hz); ratio = 1:1. In toluene: −7.4 (quartet, $^1J(^{11}B^1H) = 92$ Hz) and −41.4 (quintet, $^1J(^{11}B^1H) = 81$ Hz), ratio = 1:10. δ^1H (C$_6$D$_6$) 3.67 (t, 2H), 2.59 (m, 4H), 2.48 (m, 4H), 2.21 (BH$_4$); δ^{13}C 58.3 (*C*H$_2$), 56.9 (*C*H$_2$), 46.0 (NMe$_2$), 43.1 (NCH$_3$).

Anal. Calcd for C$_9$H$_{27}$N$_3$BNa (211.14): C, 51.20; H, 12.89; N, 19.90. Found: C, 51.04; H, 13.04; N, 19.62.

NaBH$_4$·(MeNC$_2$H$_4$)$_3$, 7. To NaBH$_4$ (0.13 g, 0.33 mmol) in THF (35 mL) was added (MeNCH$_2$CH$_2$)$_3$ (0.1 mL, 0.5 mmol). On reducing the volume of the solution to ~8 mL, crystals separated at 8 °C within several days. These were suitable for X-ray diffraction analysis. The prismatic crystals melted at 155−157 °C with decomposition. The yield was not determined.

IR (cm^{-1}, ν-BH region): 2398m, 2304s, 2227m. NMR (in THF-*d*$_8$): δ^1H −0.5 (1:1:1:1 quartet, $^1J(^{11}B^1H) = 81$ Hz; septet, $^1J(^{10}B^1H) = 27$ Hz), 2.3 (s, 9H, Me), 2.6 (s, 12H, CH$_2$); − δ^{13}C 46.9 (CH$_2$), 57.1 (CH$_3$); − δ^{11}B −41.9 (quintet, $^1J(^{11}B^1H) = 81$ Hz). Anal. Calcd for C$_9$H$_{25}$N$_3$BNa (209.14): C, 51.69; H, 12.05; N, 20.09; B, 5.17. Found: C, 51.31; H, 11.79; N, 19.75; B, 5.00.

Crystallography. Data collection was performed with Mo Kα radiation employing a graphite monochromator at 193 K on a Siemens P4 diffractometer equipped with a low-temperature device LT2 and a CCD area detector. Crystals were transferred from the cold mother liquor into precooled perfluoroether oil. The selected crystal was mounted on a glass fiber and rapidly put on the goniometer head cooled with a cold stream of N$_2$. The sizes of the unit cells were calculated from the reflections collected on 15 frames each per 5 different runs and setting angles by changing φ by 0.3° for each frame. Data were collected in the hemisphere mode of the program SMART[6] with 10 s/frame exposure time. Two different χ settings were used and φ changed by 0.3° per frame. Data on a total of 1290 frames for compounds **1**−**3**, **5**, and **7** were collected and reduced with the program SAINT.[7] Data for compounds **4** and **6** were collected on a Siemens R3m instrument in the $\omega/2\theta$ mode. The structures were solved by direct methods (SHELXTL).[8] Non-hydrogen atoms were refined anisotropically. All H atoms of the BH$_4$ groups were found in the difference Fourier map. They were freely refined, and in the final cycles most of them with fixed U_i parameters. Many crystals had only a weak diffraction power. In this case several crystals were used, and the result of the best data set is reported here.[9] Relevant crystallographic data and data referring to data collection and refinement are summarized in Table 1. In the case of compound **6** it was difficult to locate and refine

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(6) SMART, Siemens Analytical Instruments, version 4, 1996.
(7) SAINT, Siemens Analytical Instruments, version 4, 1997.
(8) SHELXTL, Siemens Analytical Instruments, version 5, 1994.

Table 1. Summary of Crystallographic Data as Well as Data Referring to Data Collection and Structure Refinement

	1	**2**	**3**	**4**	**5**	**6**	**7**
empirical formula	$C_{15}H_{19}N_3BLi$	$C_{36}H_{37}N_3BLi$	$C_{16}H_{26}N_2BLi$	$C_9H_{27}N_3BLi$	$C_6H_{19}N_3BLi$	$C_9H_{27}N_3BNa$	$C_9H_{25}BN_3Na$
fw	259.08	529.44	133.08	195.09	150.99	211.14	209.14
cryst size (mm)	0.15 × 0.2 × 0.45	0.17 × 0.3 × 0.33	0.20 × 0.20 × 0.20	0.4 × 0.5 × 0.7	0.3 × 0.3 × 0.35	0.3 × 0.3 × 0.4	0.2 × 0.3 × 0.35
cryst system	monoclinic	triclinic	orthorhombic	orthorhombic	monoclinic	monoclinic	cubic
space group	$P2(1)/n$	$P\bar{1}$	$Fdd2$	$P2(1)2(1)2(1)$	$P2(1)/c$	$P2(1)/n$	$I\bar{4}3m$
a, (Å)	10.9939(5)	10.121(1)	28.527(3)	14.683(12)	7.591(3)	9.993(2)	13.859(5)
b, (Å)	9.9171(4)	12.417(2)	10.8575(10)	11.830(7)	15.325(6)	10.008(3)	13.859(5)
c, (Å)	14.8260(8)	13.462(3)	11.3185(10)	16.960(8)	8.719(4)	14.472(4)	13.859(5)
α, (deg)	90	83.189(2)	90	90	90	90	90
β, (deg)	94.721(3)	86.068(3)	90	90	99.80(2)	93.55(2)	90
γ, (deg)	90	69.166(4)	90	90	90	90	90
V, (Å^3)	1610.96(13)	1569.3(5)	3505.7(6)	2946(3)	999.5(7)	1444.6(7)	2661.6(17)
Z	4	2	16	8	4	4	8
ρ(calcd) (Mg/m^3)	1.068	1.120	1.009	0.880	1.003	0.985	1.059
μ (mm^{-1})	0.063	0.064	0.057	0.051	0.059	0.084	0.091
F(000)	552	564	1168	880	336	484	952
index range	$-12 \leq h \leq 12$, $-6 \leq k \leq 6$, $-17 \leq l \leq 17$	$-7 \leq h \leq 12$, $-16 \leq k \leq 16$, $-16 \leq l \leq 16$	$-33 \leq h \leq 33$, $-13 \leq k \leq 13$, $-14 \leq l \leq 13$	$0 \leq h \leq 16$, $-13 \leq k \leq 0$, $-19 \leq l \leq 19$	$-9 \leq h \leq 10$, $-19 \leq k \leq 19$, $-10 \leq l \leq 10$	$-6 \leq h \leq 10$, $-1 \leq k \leq 11$, $-15 \leq l \leq 2$	$-15 \leq h \leq 15$, $-14 \leq k \leq 14$, $-15 \leq l \leq 15$
2θ (deg) max	49.40	55.40	52.74	47.14	57.82	46.10	46.40
temp (K)	193	193	193	223	193(2)	193	183(3)
reflns collected	7087	8950	4600	4823	5535	1828	5847
reflns unique	1990	4799	1710	4401	2018	1774	376
reflns obsd (4σ)	1256	1499	1416	1961	1723	1261	347
R (int)	0.0823	0.1535	0.0341	0.0788	0.0226	0.0267	0.0416
no. of variables	257	386	103	287	176	215	33
weighting scheme[a] x/y	0.0538/0.1860	0.04700/0.0000	0.0403/2.2556	0.0985/2.7116	0.0330/0.2711	0.0994/2.2820	0.1030/5.9645
GOF	1.057	0.834	1.165	0.982	1.164	1.132	1.169
final R1 (4σ)	0.0522	0.0689	0.0503	0.0855	0.0416	0.0527	0.0871
final wR2	0.1043	0.1285	0.1114	0.2029	0.0937	0.1170	0.2268
largest residual peak (e/Å^3)	0.130	0.238	0.109	0.202	0.172	0.322	0.239

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

the H atoms bonded to atom B2. Moreover, one $CH_2CH_2NMe_2$ unit of the PMDTA ligand is disordered. The disorder refined with SOF = 0.5 for two configurations. In Figure 6 only one configuration is represented.

Results and Discussion

Preparation. The amine complexes of $LiBH_4$ and $NaBH_4$ have been prepared by two different methods. The first method is to add the amine ligand to a suspension of MBH_4 (M = Li, Na) in a hydrocarbon. The suspension was then heated shortly to reflux, insoluble material was then removed by filtration, and the solvated MBH_4 crystallized from the solution at low temperature. When toluene was used as a solvent, the ^{11}B NMR spectrum showed the formation not only of $MBH_4{\cdot}nL$ but also of $L{\cdot}BH_3$ (quartet in the ^{11}B NMR spectrum). However, when the amine was used as a solvent, only small amounts of the borane adduct were noted. Thus, there are two competing reactions as shown by eqs 1 and 2. The second method starts

$$MBH_4 + nL \rightarrow (L)_nMBH_4 \qquad (1)$$

$$MBH_4 + L \rightarrow LiH + L{\cdot}BH_3 \qquad (2)$$

$$NaBH_4{\cdot}THF + nL \rightarrow L_nNaBH_4 + THF \qquad (3)$$

from $NaBH_4$ in THF. On addition of the amine the coordinated ether is replaced by the stronger amine base. Due to the negligible solubility of $NaBH_4$ in diethyl ether, THF had to be used, although the solubility of $NaBH_4$ in this solvent is also quite low.

The following compounds have been obtained: $LiBH_4{\cdot}3(py)$ (**1**), $LiBH_4{\cdot}py^*$ (**2**), $LiBH_4{\cdot}2(coll)$ (**3**), $LiBH_4{\cdot}PMDTA$ (**4**), $LiBH_4{\cdot}TMTA$ (**5**), $NaBH_4{\cdot}PMDTA$ (**6**), and $NaBH_4{\cdot}TMTACN$ (**7**) (py = NC_5H_5, py* = NC_5H_4-*p*-CH_2Ph, coll = 2,4,6-NC_5H_2-Me_3, PMDTA = $MeN((CH_2CH_2)NMe_2)_2$, TMTA = $(MeNCH_2)_3$, TMTACN = $(MeNCH_2CH_2)_3$).

Spectroscopic Data. Toluene solutions of the solvates **1**−**7** exhibit ^{11}B NMR signals with a 1:4:6:4:1 quintet structure as expected for the presence of a BH_4 group. There is little difference in the chemical shifts, $\delta^{11}B$ ranging from −35.9 (**3**) to −41.9 (**1** and **7**). This is somewhat unexpected considering the different bonding modes of the BH_4 group, the ligand, and the alkali metal atom, but would be in accord with a rather polar interaction of the tetrahydridoborate unit with the alkali metal cationic center. So, the bonding mode, which is truly different in the solid state (vide infra) is not reflected in $\delta^{11}B$ nor in the coupling constant $^1J(^{11}B^1H)$ for the solutions. In consonance with this observation is the fact that the coupling constant $^1J(^{11}B^1H)$ is 81(±1) Hz for all of the compounds investigated. For some of them, the ^1H resonance also detects B−H bonding by a 1:1:1:1 quartet for the $^{11}BH_4$ protons, and a septet for the $^{10}BH_4$ protons. Therefore, ^{11}B NMR as well as ^1H NMR spectroscopy is no probe for testing any M−H−B bridge bonding interactions. However, IR spectroscopy as a much better time-resolved method may be able to discern between the different modes of bonding between the BH_4 groups and the metal center as revealed by the structures in the solid state. Regarding the pyridine type solvates **1**−**3**, there is a close analogy between **1** and **3**, which both contain a $\mu^1{}_2$-BH_4 group: there are two strong bands at 2304 and 2272 cm^{-1}, while compound **2** with a $\mu^1{}_3$-BH_4 group features a different pattern which fits the prediction of three strong νBH bands (νBH_t, $\nu_{s,as}BH_3$). The IR spectrum of the mononuclear compound **4** resembles that of **2** with a $\mu^1{}_3$-BH_4 group. On the other hand, the IR bands in the BH stretching region of compounds **5** and **6** are quite different in spite of the fact that the BH_4 groups contact the alkali metal centers in the same manner ($2\mu^1{}_1,\mu^2{}_1$-BH_4) the bonding of the BH_4 group in compound **7** is exceptional (vide infra) and different, e.g., from compound **2**, both having a BH_4 group with approximate C_{3v} symmetry. For this case one expects three bands, and these are indeed found for **7**. We tentatively assign bands at 2390 and 2305 cm^{-1} to terminal BH bonds and the band at 2226 cm^{-1} to the $BHNa_3$ arrangement.

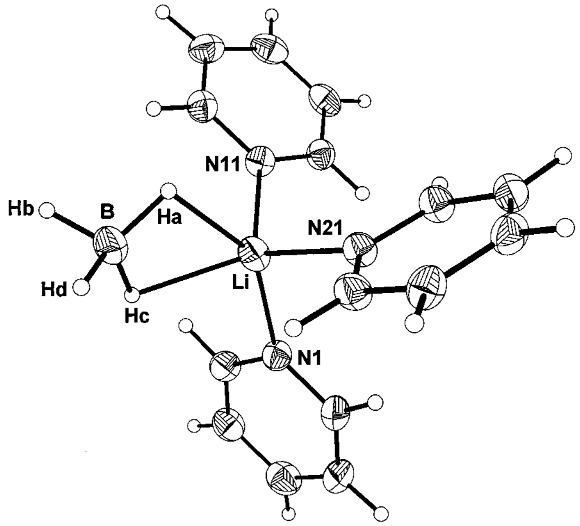

Figure 1. Molecular structure of compound **1** in the crystal. Thermal ellipsoids are depicted at the 25% probability level. Selected atom distances in Å: Li−N1 2.078(6), Li−N11 2.074(5), Li−N21 2.065(5), Li···B 2.401(7), Li−H(A) 2.06, Li−H(B) 1.90, B−H(A) 1.15, B−H(B) 1.07, B−H(C) 1.14, B−H(D) 1.11. Selected bond angles in deg: N1−Li−N11 102.8(2), N1−Li−N21 105.1(2), N11−Li−N21 112.6(2), N1−Li···B 117.8(2), N11−Li−B 108.6(2), N21−Li−B 109.8(2), H(A)−Li−H(C) 56.6, H(A)−Li−H(B) 108, H(B)−B−H(D) 97.4. Interplanar angles in deg: N1 to C6/N11 to C16 87.9, N1 to C6/N21 to C26 96.1, N11 to C16/N21 to C26 62.1.

Molecular and Crystal Structures. $LiBH_4{\cdot}3(py)$, **1**, crystallizes from hexane/pyridine or from pyridine. All BH hydrogen atoms were found in the difference Fourier synthesis, and those bonding to the boron atom were freely refined. Figure 1 depicts the structure of the molecule. There are no intermolecular interactions in the solid state besides van der Waals H···H contacts.

The three Li−N distances are equal within the 3σ limit of the esd (average 2.072 Å). As expected, the N−C bond lengths are shorter than the C−C bonds, and it is noticeable that the C−N−C bond angles are compressed (average 116.3°) while the N−C−C bond angles are enlarged (average 123.8°). This corresponds nicely with the bonding parameters of the free ligand (C−N 1.340(1) Å, C−C 1.395(1) Å, C−N−C 116.8°.[10] If we consider the BH_4 group as a halide imitator (BH_4^- is “isoelectronic” with F^-),[11] then the Li center is tetracoordinated by three N atoms and the B atom of the BH_4 group. However, the arrangement of the ligands around the Li center deviates

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(9) Supplementary data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC 124106−124112. Copies of the data may be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, U.K. E-mail: deposit@ccdc.cam.ac.uk.

(10) Bak, B.; Hansen-Kygard, L.; Restrup-Andersen, J. *J. Mol Spectrosc.* **1958**, *2*, 361.

(11) This analogy was drawn by M. J. S. Dewar.

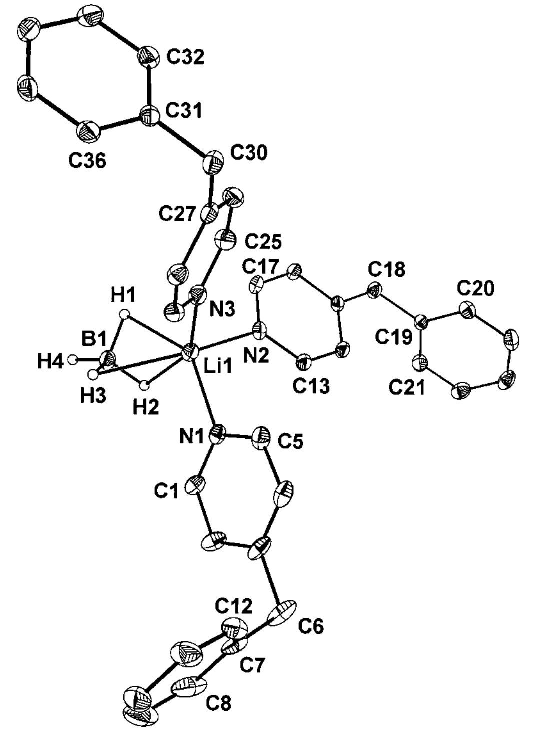

Figure 2. Molecular structure of compound **2** in the crystal. Thermal ellipsoids are represented at the 25% probability level. Selected atom distances in Å: N1−Li1 2.083(3), N2−Li1 2.107(3), N3−Li1 2.109(3), Li1···B1 2.279(4), B1−H1 1.15, B1−H2 1.11, B1−H3 1.12, B1−H4 1.23. Selected bond angles in deg: N1−Li1−N2 102.7(1), N1−Li1−N3 99.0(1), N2−Li1−N3 105.3(1), N1−Li1···B1 112.5(1), N2−Li1···B1 112.9(2), N3−Li1···B1 121.9(2), H1−B1−H2 106, H2−B1−H3 112, H3−B1−H4 114, H1−Li1−H2 52, H2−Li1−H4 40. Interplanar angles in deg: N1 to C5/N2 to C17 102.9; N1 to C5/N3 to C29 60.4; N2 to C17/ N3 to C29 69.9; N1 to C5/ C7 to C12 77.3; N2 to C13/C19 to C24 90.7; N3 to C25/C29 to C33 74.7.

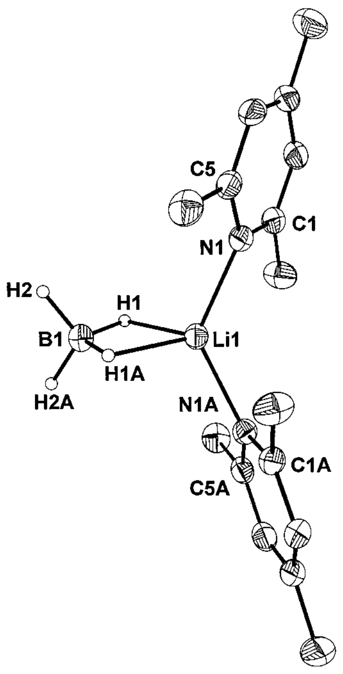

Figure 3. Molecular structure of compound **3** in the crystal. Thermal ellipsoids are shown at the 25% probability level. Selected atom distances in Å: Li1−N1 2.050(3), Li1···B1 2.252(6), B1−H1 1.17(2), B1−H2 1.13(3). Selected bond angles in deg: N1−Li1−N1A 128.2(2), N1−Li1−B1 115.9(1), N1−Li1−H1 105(1), H1−B1−H(1A) 108(2), H2−B1−H(2A) 110(3), H(1A)−B1−H(2A) 106(1), C1−N1−C5 117.9(2), N1−C1−C2 122.6(2), C1−C2−C3 120.1(2), C2−C3−C4 117.3 (2). Interplanar angles in deg: N1 to C5/N(1A) to C(5A) 51.9, H1−Li1−H1(1A)/N1 to C5 83.1, H1−Li1−H(1A)/N(1A) to C(5A) 96.9.

from the ideal tetrahedral angle; the largest deviation is the bond angle N1−Li−B1, 117.8(2)°. Thus, the BH_4 group is not symmetrically bonded to the Li center, due to the fact that the $Li(\mu\text{-}H)_2BH_2$ arrangement is asymmetric. The H−B−H bond angle for the bridging H atoms is 112.8°, while that for the terminal hydrogens is 97.4°. However, there is no clear correlation between the B−H bond lengths for bridging versus terminal hydrogens although the average B−H distance (1.09 Å) for the terminal hydrogen is 0.06 Å shorter than for the bridging hydrogen atoms (1.15 Å). This conclusion, however, must be taken with caution considering the inaccuracy of determining B−H bond lengths and H−B−H bond angles by X-ray diffraction.

One might expect that tris(*p*-benzylpyridine)lithium tetrahydroborate, **2**, may have the same coordination for the Li center as **1**. This is, however, not the case as shown in Figure 2, because the molecule possesses a μ^{1}_{3}-BH_4 group coordinating with three of its hydrogen atoms to the Li center. The average Li−N distance is 2.10 Å, slightly longer than in **1**, and the average C−N−C bond angle is 115.2°, slightly smaller than in **1**. It is somewhat surprising that the benzylpyridine ligands are rather asymmetrically arranged about the Li center, bond angles N−Li−N range from 99.0(1)° to 105.3(1)°, and consequently the N−Li−B angles are also not uniform. Angles between 112.9(1)° and 121.9(2)° have been found. Moreover, the BH_4 group does not bind symmetrically to the Li center, and the BH_4 group by itself is also not tetrahedral because the B−H bond lengths vary from 1.11 to 1.15 Å and the H−B−H angles from 105° to 113°. At least for **2**, there seems to be a correlation between B−H and Li−H bond lengths: the longer the B−H bond, the longer the Li−H distance: the corresponding data are 1.15 Å for B−H1 and 2.07 Å for Li−H1, 1.10 Å for B−H2 and 2.08 Å for Li−H2, and 1.13 Å for B−H4 and 2.26 Å for Li−H4. The terminal B−H3 bond is 1.12 Å long.

In accordance with the triply bridging BH_4 group,[12] a short Li−B atom distance is observed (2.279 Å). The interplanar angles of the *p*-benzylpyridine ligand may give an explanation why a μ^{1}_{2}-BH_4 function is realized in **1** and a μ^{1}_{3}-BH_4 group is present in **2**. These angles are 67.1°, 61.3°, and 103.9° (for planes between AC/CE/EA with A = pyridine N1, C = pyridine N2, E = pyridine N3). The asymmetry of the molecule **2** results not only from the asymmetry of the bonding of the BH_4 groups and the pyridines but particularly from the different orientation of the phenyl rings with respect to the pyridine ring. The values are 77.3° for pyridine N1, 90.7° for pyridine N2, and 74.7° for pyridine N3. These data indicate that the phenyl groups are differently oriented to their respective pyridine ring. However, this is a typical phenomenon for the packing, because in solution all benzylpyridine ligands are equivalent as disclosed by the NMR data. Nevertheless, these different orientations of the pyridine rings may be responsible also for the asymmetrically bonded BH_4 group.

While pyridine and *p*-benzylpyridine form 1:3 adducts with $LiBH_4$, only two molecules of collidine (2,4,6-trimethylpyridine) add to one molecule of $LiBH_4$. This seems to be caused by the steric effect of the two methyl groups in the 2,6-positions of the pyridine ring.

The molecular structure of compound **3** is depicted in Figure 3. It reveals that the molecule contains a μ^{1}_{2}-BH_4 group. This

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(12) Edelstein, N. *Inorg. Chem.* **1981**, *20*, 297.

is an unexpected result in light of the structure of **2** and because one might expect a $\mu^1{}_3$-BH$_4$ group because the number of N ligands is reduced to two.

Molecule **3** possesses a crystallographically imposed 2-fold axis with the Li and the B atoms lying in a C_2 axis. Its Li−N bond lengths (2.050(3) Å) fit well with many other Li−N distances of coordinative function.[13] In spite of the fact that the BH$_4$ group adopts a $\mu^1{}_2$-bonding fashion, the Li···B distance falls into the range of a Li($\mu^1{}_3$-BH$_4$) group.

A large asymmetry results for **3** because the N1−Li1−N1(A) bond angle is rather large, 128.2(2)°. However, if one considers the BH$_4$ anion as a halide imitator, then the coordination at the Li center is "trigonal planar". However, the question must be answered, why do we observe only a $\mu^1{}_2$-BH$_4$ instead of $\mu^1{}_3$-BH$_4$ group. There is a small difference of only 0.04 Å between the BH distance of bridging and terminal hydrogens, and in this case the H−B−H bond angle involving the bridging hydrogen atoms is smaller (108°) than for the terminal ones (110°). However, it is noticeable that the Li−H1 distance is only 1.83 Å, indicating a strong interaction.

Intermolecular contacts cannot be responsible for the $\mu^1{}_2$ function of the BH$_4$ group and two neutral ligand molecules. This suggests that the Li centers in **3** are sterically shielded, making a $\mu^1{}_3$-BH$_4$ group obsolete. Intermolecular Li···H contacts result for Li with H(6C) and H(6AA) (2.60 and 2.69 Å, respectively) as well as intermolecular contacts of Li to two H atoms of CH$_3$ groups (H(6AA) and H(6CA)) with distances of 2.69 and 2.60 Å. If we take this into account, then the atom Li1 adopts hexacoordination.

Figure 4 demonstrates the molecular structure of LiBH$_4$·PMDTA, **4**. There are two independent molecules in the asymmetric unit which differ not grossly in their molecular parameters but definitely by their configuration.

The coordination about the Li atoms is the same as in **1**, e.g., the Li atom is pentacoordinated (3N, 2H) or tetracoordinated considering the BH$_4$ group as a single ligand (3N, 1B). However, due to the bidentate nature of the amine, the N−Li−N bond angles are quite different, ranging from 83.8(6)° to 122.9(7)° for the Li1 molecule and from 84.7(6)° to 124.3(6)° for Li2. The coordination polyhedron is better described by a strongly distorted tetrahedron—taking the N and B atoms into account—than by a distorted trigonal bipyramid (considering H atoms as coordination partners). Moreover, the BH$_4$ groups differ considerably from a tetrahedral array because the H−B−H bond angles vary from 96(4)° to 124(5)° for molecule Li1, and from 92(4)° to 135(5)° for molecule Li2. It is particularly noticeable that the H−B−H bond angle for the bridging hydrogen atoms is larger (125(4)° and 119(4)°) than for the terminal hydrogen atoms (97(3)° and 92(4)°).

Li−N distances in molecule Li1 are on average the same (2.13 Å) as found for Li2 (2.12 Å), in contrast to the Li−B distances, which are 2.29(2) and 2.35(2) Å, respectively. The reason for this difference is not easily rationalized, but corresponds with shorter B−H (bridge) bonds for molecule Li1 (1.07, 1.07(4) Å) compared to molecule Li2 (1.31, 1.30(4) Å). This reversed situation holds also for the terminal B−H bonds (1.23, 1.21(4) Å vs 0.95, 0.94(4) Å). It is obvious that a more precise determination of BH bond lengths is needed.

Figure 4 shows the difference of configurations between the two independent molecules which results from the different orientation of the envelope conformations. The envelope atoms C3/C7 and C12/C16 adopt an opposite orientation with respect to the orientation of the MeN···Li(B) group. The central nitrogen atom is chiral, and therefore, two enantiomers had to be expected.

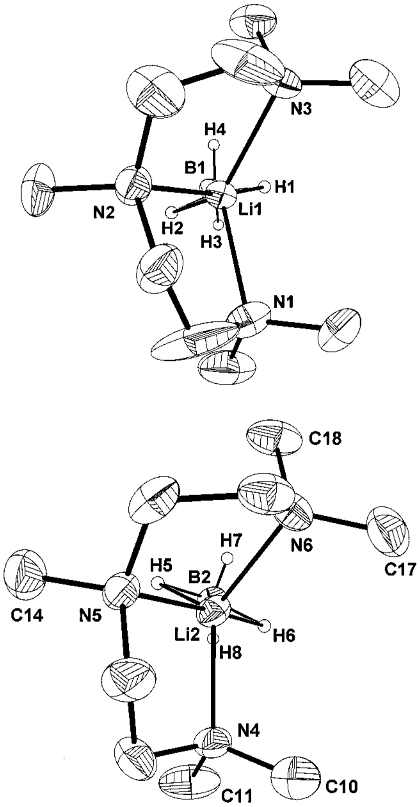

Figure 4. ORTEP plot of the molecular structure of **4**. Thermal ellipsoids are depicted at the 25% probability level. H atoms bound to carbon atoms are removed for the sake of clarity. Selected atom distances in Å: (molecule 1, top) Li1−N1 2.12(1), Li1−N2 2.14(2), Li1−N3 2.14(1), Li1···B1 2.29(2), Li1−H(1) 2.05(4), Li1−H(2) 2.04(4), B1−H(1) 1.07(4), B1−H(2) 1.07(4), B1−H(3) 1.22(4), B1−H(4) 1.21(4), N1−C1 1.40(1), N1−C2 1.44(1), N1−C3 1.47(1), N2−C5 1.446(9), N2−C4 1.48(1), N2−C6 1.48(1); (molecule 2, bottom) Li2−N4 2.11(2), Li2−N5 2.14(2), N2−N6 2.12(2), Li2−H(5) 1.92(4), Li2−H(6) 1.92(2), B2−H(5) 1.31(4), B2−H(6) 1.30(4), B2−H(7) 0.95(4), B2−H(8) 0.94(4), Li2···B2 2.35(2). Selected bond angles in deg: (molecule 1) N1−Li1−N2 85.5(6), N1−Li1−N3 122.9(7), N2−Li1−N3 83.8(6), N1−Li1−B1 110.3(7), N2−Li1−B1 140.0(7). N3−Li1−B1 113.5(7), H(1)−Li1−H(2) 55(2), H(1)−B1−H(2) 125(4), H(3)−Li1−H(4) 97(3); (molecule 2) N4−Li2−N5 85.1(6), N4−Li2−N6 124.3(7), N5−Li2−N6 84.7(6), N6−Li2−B2 110.7(8), N5−Li2−B2 139.2(7), N4−Li2−B2 112.3(7), H(5)−B2−H(6) 68(2), H(5)−B2−H(6) 110(3), H(7)−B2−H(8) 92(5).

Compound **5**, lithium tetrahydridoborate 1,3,5-trimethyl-1,3,5-triazacyclohexane (trimethylhexahydrotriazine = TMTA) crystallizes from a hot toluene solution. The X-ray structure analysis shows that it is dimeric in the solid state. Figure 5 represents an ORTEP representation of the molecule.

As can be noted from Figure 5, there is an inversion center in the molecule which is also a crystallographic inversion center situated at the midpoint between the two Li atoms. Most surprising is the fact that only two of the three nitrogen atoms of the TMTA molecules are used in coordination. The Li−N distances to the coordinated atoms N2 and N3 are 2.156(2) and 2.217(2) Å, respectively, while the distance to the noncoordinated atom N1 is 2.883(2) Å. There is also a comparatively short Li1−C6 distance of 2.489 Å. The N2−Li1−N3 bond angle is rather sharp, 64.49(7)°.

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(13) For a summary of data see chapters 8 and 9 in the following: Sapse, A.-M.; Schleyer, P. v. R. *Lithium Chemistry. Theoretical and Experimental Overview*; J. Wiley Interscience Inc.: New York, Toronto, Singapore, 1995.

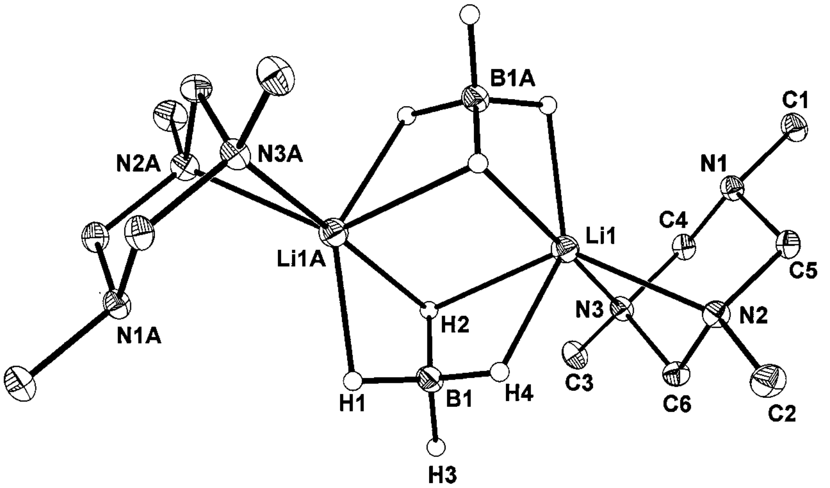

Figure 5. Molecular structure of the dimeric compound **5**. Thermal ellipsoids are drawn at the 25% probability level. Hydrogen atoms of the TMTA ligand are not shown for the sake of clarity. Selected atom distances in Å: Li1−N2 2.156(2), Li1−N3 2.217(2), Li1−H2 2.08(1), Li1−H4 2.02(2), Li1−H(2A) 2.19(1), Li1−H(1A) 1.92(2), Li1···C6 2.489(3), Li1···B(1A) 2.395(3), B1−H1 1.14(2), B1−H2 1.15(2), B1−H3 1.12(2), B1−H4 1.15(2). Selected bond angles in deg: N2−Li1−N3 64.49(7), N2−Li1−H4 90.8(4), N2−Li1−H2 132.1(4) N3−Li1−H4 104.5(4), N3−Li1−H2 91.3(4), N3−Li1−H(2A) 170.8(4), N3−Li1−H(1A) 121.2(5), Li1−B1−Li1A 80.49(9), B1−Li1−B1A 99.51(9), H3−B1−H1 110(1), H3−B1−H2 110(1), H3−B1−H4 111(1), H2−B1−H1 108(1), H2−B1−H4 109(1). Interplanar angles: N2−C6−N3/N2−C5−B3−C4 119.3, C4−N1−C5/N2−C5−N3−C4 127.5; N2−C6−C3/C4−N1−C5 8.0.

Two BH_4 groups bridge the two Li centers via six hydrogen atoms; each BH_4 unit acts as a $2\mu^{1}{}_{1},\mu^{2}{}_{1}$ ligand, one H atom per BH_4 group binds to two Li atoms via a single bridge, and two H atoms bind via a single bridge to one Li center. This bonding mode was first observed for $[LiBH_4{\cdot}TMEDA]_2$.[14] Bond angles at the boron atoms are very close to the tetrahedral angle. They range from 108(1)° to 111(1)°. Therefore, they are all equivalent. However, the bridging mode is reflected in this case by the B−H distances. The shortest bond is to the terminal H atom H3 (1.12(2) Å), the largest to the H atom that coordinates to two Li centers. However, all BH bonds can be considered to be of almost equal lengths, esd's being taken into account.

Bond angles at the Li atoms are, however, very different. Two are practically equal (H(1A)−Li1−H(2A), 53(6)°, and H(4)−Li−H(2), 54.2°) while the bond angles H(2)−Li1−H(2A) and H(2)−Li1−H(1) are 84.6(6)° and 108.5(6)°. In contrast, the bond angles H(2)−Li1−N3 and H(2)−Li1−N2 differ considerably, with 91.3(4)° and 132.1(4)°. Thus, the symmetry about the hexacoordinated Li center is highly asymmetric. Although there are little differences for the B−H bond lengths, the Li−H distances vary considerably. The largest distance is 2.19(2) Å (Li1−H(2A)); the shortest is 1.92(1) Å for Li1−H(1A).

Solvates of $NaBH_4$. In contrast to $LiBH_4$, it is much more difficult to grow single crystals of amine solvates of $NaBH_4$. So far only two $NaBH_4$ amine solvates, **6** and **7**, provided single crystals for an X-ray structure determination. Among these, only a single pair, $NaBH_4{\cdot}PMDTA$, **6**, and $LiBH_4{\cdot}PMDTA$, **4**, can be directly compared.

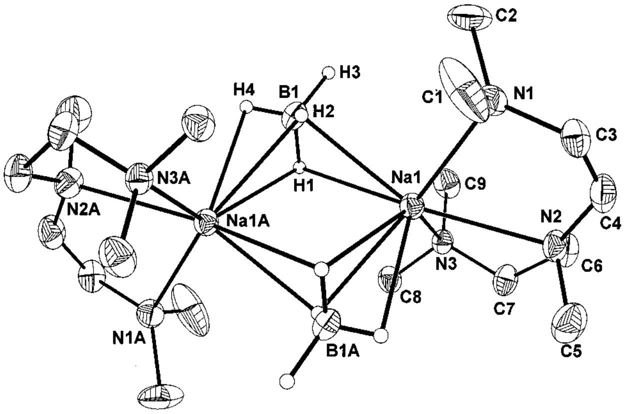

Figure 6. ORTEP representation of the molecular structure of dimeric **6**. Thermal ellipsoid are represented at the 30% probability level. Only the boron H atoms are depicted for the sake of clarity. Selected atom distances in Å: Na1−N1 2.510(3), Na(1A)−B1 2.727(4), Na1−N2 2.597(2), Na1−N3 2.498(2), Na1···B1 2.867(4), Na1−Na(1A) 3.639(2), Na1−H(1) 2.58(3), Na1−H(2) 2.51(3), Na1−H(4A) 2.54(3), Na1−H(2A) 2.49(3), Na1−H(1A) 2.49(3), B1−H(1) 1.10(3), B1−H(2) 1.13(3), B1−H(3) 0.97(3), B1−H(4) 1.07(3). Selected bond angles in deg: N1−Na1−N2 70.79(9), N1−Na1−N3 120.8(1), N2−Na1−N3 71.95(8), N1−Na1−H(1A) 103.3(7), N1−Na1−H(4A) 114.5(6), N1−Na1−H(2A) 145.8(7), N1−Na1−H(2) 84.8(7), N2−Na1−H(1) 152.0(6), N2−Na1−H(2) 155.2(6), N1−Na1−B1 97.4(1), N2−Na1−B1 154.4a(1), N3−Na1−B1 96.9(1), H(1)−B1−H(2) 110(3), H(1)−B1−H(3) 113(2), H(1)−B1−H(4) 103(2), H(2)−B1−H(3) 114(2), H(2)−B1−H(4) 104(2).

The amine solvate **6** crystallizes in the monoclinic space group $P2_1/n$, $Z = 4$. In the asymmetric unit there is only one molecule of $NaBH_4{\cdot}PMDTA$. This molecule is associated to dimers via a crystallographic inversion center which is found at the midpoint of the Na1−Na1A vector (3.639(2) Å) of the molecule which is depicted in Figure 6. As can be noted, the Na centers are coordinated to the three N atoms of the amine ligand and to hydrogen atoms of two bridging BH_4 groups. The Na−N bond to the central N atom of the ligand (N2) is *longer* (2.597(2) Å) than the Na1−N1 and Na1−N1A bonds (2.510(3) and 2.498(2) Å). In compound **6** the bridging B−H bond length is better discriminated than in the other amine solvates, as the terminal BH bonds (0.97 (3) Å) are shorter than the B−H bond to the bridge. Taking all close Na−X distances into account, the Na center is nonacoordinated.

The most surprising part of the structure of **6** is, at the moment, that it does not resemble $LiBH_4{\cdot}TMEDA$ because every BH_4 group binds with two of its hydrogen atoms to two sodium centers, and with one only to a single Na atom, while the reverse is true for the Li compound. So the BH_4 group has to be classified as $2\mu^{2}{}_{1},\mu^{1}{}_{1}$. The longest B−H bond (1.13(3) Å) is responsible for deviations from a tetrahedral array. Thus,

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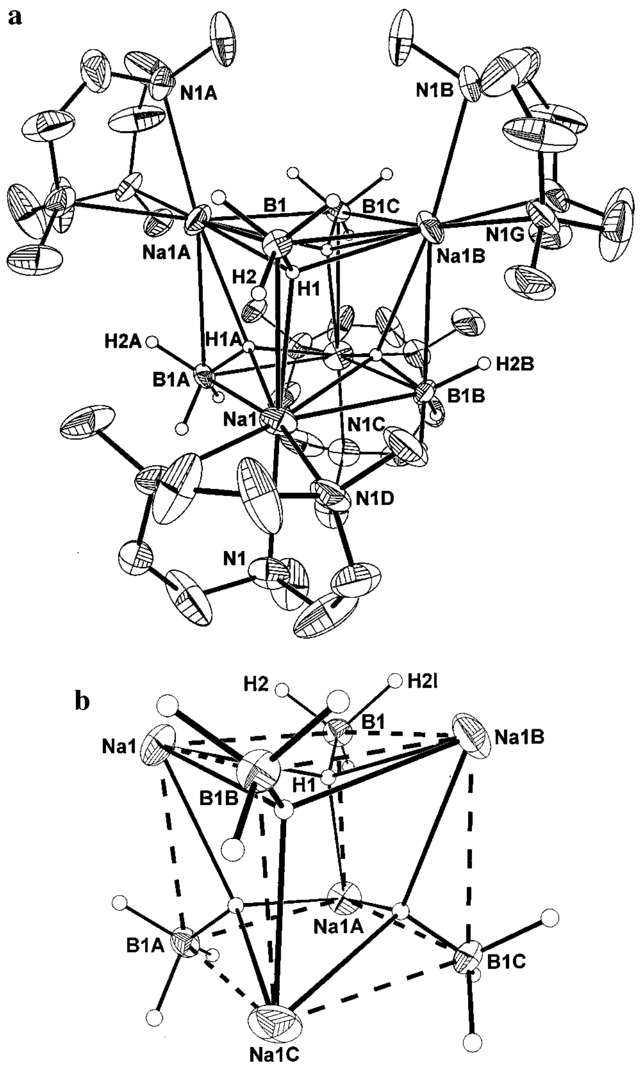

Figure 7. (a) The molecular structure of tetrameric **7** in the crystal. Only boron-bonded hydrogen atoms are depicted for the sake of clarity. The thermal ellipsoids are represented at the 20% probability level. Selected atom distances in Å: Na1−N1 2.607(6), Na1···B1 3.114(5), N1−C2 1.440(6), N1−C1 1.457(9), B1−H1 1.14, B1−H2 1.26. Selected bond angles in deg: Na(1A)−Na1−B1 166.3(2), B1−Na1−B(1A) 88.9(2), Na1−B1−Na(1C) 91.2(2), N1−Na1−N(1A) 68.0(2), N(1A)−Na1−B1 100.9(2), H1−B1−H2 115, H2−B1−H(2A) 104. (b) The core frame of tetrameric **7**.

Na1−H(1) is 2.58(3) Å, Na1−H(2) is 2.51(3) Å, and Na1−H(4A) is 2.53(4) Å. The longest Na−H distance is to the doubly bridging hydrogen atoms. However, the bonding of the two BH_4 groups to the Na center is different as demonstrated by Na−B distances of 2.727(4) and 2.867(4) Å (to Na1), respectively.

So far we were unable to prepare crystals of $NaBH_4$·TMTA in order to compare its structure with that of the Li analogue. However, sodium tetrahydridoborate 1,5,9-trimethyl-1,5,9-triazacyclododecane, **7**, was obtained as single crystals. The structure determination revealed that it is present as a tetramer in the solid state (Figure 7a). It is one of the few molecular alkali metal compounds that crystallize in the cubic system, in this case in space group $I\bar{4}3m$.

The most significant structural feature is that the Na and B atoms form a cubane core which is slightly distorted, Na−B distances being 3.114(6) Å while the Na−B−Na bond angles are 91.2(2)° and B−Na−B bond angles 88.9(2)°. Each sodium center is symmetrically coordinated by three nitrogen atoms with a Na−N distance of 2.607(6) Å, the "bite" angle N−Na−N being 68.0(2)°. N−Na−B bond angles range from 100.9(2)° to 166.43(2)°. A second, somewhat surprising feature can be recognized: the BH_4 group supplies only a single hydrogen atom for coordination to three Na centers. Thus, the BH_4 groups act as μ^{3}_{1}-bridging ligands. The other three H atoms of the BH_4 group are "terminal". If we consider the structure of **7** as derived from a cubane, then the bridging hydrogen atoms occupy places *inside* of the cubane.

Discussion

The seven structures of alkali metal tetrahydridoborates solvated by pyridines or tertiary amines display four different types of M···BH_4 interactions. Three types are already known, the BH_4 group coordinating as a μ^{1}_{2} and μ^{1}_{3} donor as well as a $\mu^{2}_{1},2\mu^{1}_{1}$ donor bridging two alkali metal centers. A new type is found in the sodium tetrahydridoborate complex **7** where only a single hydridic hydrogen atom is used for bridging to three sodium centers (μ^{3}_{1} mode). Another unusual coordination mode is observed in **5**, where the amine ligand uses only two of its three nitrogen centers for coordination with the Li atom.[15]

The effective radius of the BH_4 group is closer to that of a bromide than to that of a chloride.[16] Therefore, the observed structures for compounds **1**−**7** can be compared with those found for halides LiX·*n*L and NaX·L (X = Cl, Br; L = amine ligand). For this reason it is best to look at the BH_4^- anion as a halide imitator. If we do so, then the Li centers in **1** and **2** are tetracoordinated in contrast to **3** where the coordination number would be 3. The first situation is found for LiX·3(py),[17,18] LiX·3(2,6-dimethylpyridine),[19,20] and LiX-3-(4-*tert*-butylpyridine).[15]

While the Li−X distances (X = BH_4, Br, I) within each series of LiCl and LiBr adducts do not alter significantly, this is not the case for **1** and **2**, where the Li···B atom distance is significantly shorter in **2**, with its μ^{1}_{3}-BH_4 group, in contrast to **1**, which displays a μ^{1}_{2}-BH_4 unit. This shortening is in accord with Edelstein's rule,[12] and this is of course a good argument for considering the BH_4^- group not simply as a pseudohalide but rather as more than a "pseudohalide" and a rather specific ligand.[21,22] Lithium halide complexes of collidine have been reported only for LiBr and LiI, the coordination compounds having the composition $(LiX)_4$·6(coll).[18]

Moreover, the 2,6-lutidine (lut) adducts should also be considered because they should exert the same steric effect as 2,4,6-trimethylpyridine (collidine). Reported lithium halide complexes are $[LiBr]_4$·6(lut) and $[LiI]_4$·6(lut)[23] having a four-membered $(LiX)_2$ ring structure in contrast to those with a $(LiX)_4$ core. Thus, compound **3** has so far no pendant and is, at the present time, unique. Since the Li1···B atom distances can be determined much more accurately than Li−H and B−H distances, it is not easy to rationalize the observed Li···H bridges in compounds **1**−**3**. While it is readily understood that the Li···B

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atom distance is longer in **1** (2.402(7) Å for a $\mu^1{}_2$-BH_4 group) than in **2** ($\mu^1{}_3$-BH_4 group, 2.279(4) Å), we observe a Li···B atom distance of 2.252(6) Å in compound **3** which corresponds with that of **2**, suggesting a tridentate $\mu^1{}_3$-BH_4 group. However, in **3** there are only two collidine ligands presents; the coordination number, therefore, is smaller than in **1** and **2**; and since M−X bond length increases with increasing coordination numbers, the short Li···B distance observed for the $\mu^1{}_2$-BH_4 group in **3** can be rationalized. On the other hand, the Li···B distances of the two independent molecules of compound **4** suggest the presence of a $\mu^1{}_2$-BH_4 and a $\mu^1{}_3$-BH_4 group (2.29 and 2.35 Å) although the structure determination reveals asymmetrically bonded $\mu^1{}_2$-BH_4 groups. As far as we know, **4** is the first mononuclear molecular amine solvate of $LiBH_4$ so far reported. $LiBH_4$·TMEDA is a binuclear molecular compound,[14] where the two Li centers are bridged by $\mu^2{}_1,2\mu^1{}_1$-BH_4 units. This bridging mode is not observed for dimeric $NaBH_4$·PMDTA, **6**, which shows $2\mu^2{}_1,\mu^1{}_1$-BH_4 groups. Thus, the coordination number of Li in **4** is either 4 (3N, 1B) or 5 (3N, 2H), and that of Na in **6** is either 5 (3N, 2B) or 8 (3N, 5H), the higher coordination being the consequence of the larger cation radius of Na. On the other hand, the structure of $(LiBH_4$·$TMTA)_2$[31] resembles that of $(LiBH_4$·$TMEDA)_2$. However, due to the structure of the amine ligand, the N−Li−N bond angles in **5** are rather small (70.8°, 71.9°) compared to that in $(LiBH_4$·$TMEDA)_2$ (74.6°).[14] While compounds LiX·TMEDA are dimeric for X = Br, I, the chloride forms a compound $(LiCl)_6$-$(TMEDA)_2$ having a $(LiCl)_6$ core formed by boat-shaped $(LiCl)_3$ units staggered by Li···Cl interactions between two six-membered rings.[24] The Li−Br and Li−I complexes are counterparts for the structure of $LiBH_4$·TMEDA. However, in contrast to monomeric $LiBH_4$·PMDTA, the halide LiBr·PMDTA proved to be dimeric in the solid state.[25] The dimer of LiBr·PMDTA dissociates in the solution into the monomer; this monomer should be comparable with the $LiBH_4$ solvate **4**. Nevertheless, compound **4** has a simple structure in comparison to $(LiCl)_4$·3PMDTA, which contains a four-membered $(LiCl)_2$ ring in a chain structure.[17] This again demonstrates that the $LiBH_4$ complexes are better to be compared with the structures of LiBr·*n*L (L = amine ligand) than with LiCl·*n*L compounds.

The core of $[NaBH_4$·$TMTACN]_4$ consists of a Na_4B_4 cubane structure. Cubanes in alkali metal chemistry are not known for lithium halides[11] but are typical for alkali metal alkoxides $[MOR]_4$.[26−28] However, the compound most akin to **7** is $[NaHBMe_3]_4$, which possesses a Na_4H_4 core.[29] Its hydrogen atoms bridge to three Na centers as now found for **7**. This is, of course, electronically a favored arrangement fitting also with a Na_3H four-center two-electron bond. Nevertheless, there are considerable differences in the structures of **7** and $NaHBMe_3$. In compound **7** the sodium centers are hexacoordinated, and, therefore, this is a unique situation because only one out of four hydridic hydrogen atoms of the tetrahydroborate group is used in coordination.

Conclusions

Amine solvates of $LiBH_4$ with pyridine, pentamethyldiethylenetriamine, and trimethylhexahydrotriazine ligands are readily accessible. However, depending on their mode of preparation they lose a BH_3 component by formation of an amine·BH_3 adduct. This cleavage, considered to be characteristic for covalent tetrahydridoborates,[9] seems to be also a feature for ionic tetrahydridoborates. When these are transferred into small molecules, this cleavage is even observed for $NaBH_4$. For amine solvates of lithium halides as well as for lithium tetrahydridoborate, the resulting coordination number at Li is a balance between the ligand property of the BH_4^- anion, the number of N atoms of the amine ligands coordinating to Li, and the steric requirements of the amine ligand. The fewer nitrogen atoms coordinate, the more likely is it that the BH_4^- group bridges with three hydridic hydrogen atoms to the metal center or the compound dimerizes. In the latter case it seems that the BH_4 group in the bridging positions supplies two of its hydrogens for each metal center, making the BH_4 group a $\mu^2{}_1,2\mu^1{}_1$ ligand. However, other coordinating modes in oligo- and multinuclear metal tetrahydridoborates are possible as realized in the solid state structure of $Be(BH_4)_2$ with its terminal $\mu^1{}_2$-BH_4 and bridging $2\mu^1{}_2$-BH_4 groups.[30]

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Supporting Information Available: Listings of data referring to crystallography, structure solution and refinement, atomic coordinates, full list of bond distances, bond angles, and thermal parameters, in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org. Such files have also been deposited at the Cambridge Crystallographic Data Center in CIF format.[9]

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