

Tetraamine Me₆TREN Induced Monomerization of Alkali Metal Borohydrides and Aluminohydrides

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Dedicated to Professor Malcolm Chisholm on the happy occasion of his 70th birthday from his many friends at the University of Strathclyde.

Abstract

Monomeric 1:1 complexes of MEH₄ (M, E = Li, B, **1**; Na, B, **2**; Li, Al, **3**; Na, Al, **4**) and the tripodal tetradentate ligand (Me₂NCH₂CH₂)₃N (Me₆TREN) have been prepared in good yields by refluxing in THF and allowing the solutions to cool slowly. X-ray diffraction studies show that the BH₄ group binds to either Li or Na via three hydride bridges while the AlH₄ group connects to Li via a single hydride bridge. Surprisingly, Me₆TREN·LiAlH₄ represents the first monomeric contacted ion pair LiAlH₄ derivative to be structurally characterized. In every case the tetraamine coordinates via all four of its Lewis basic nitrogen atoms. A similar protocol using the alkyl-rich borohydride MBEt₃H also gives monomeric species (M = Li, **5**; Na, **6**). All complexes have been characterized in solution by multinuclear (¹H, ⁷Li, ¹¹B, ¹³C and ²⁷Al, where appropriate) NMR spectroscopy which reveals excellent textbook examples of ¹J coupling between B/Al and H in the cases of complexes **1-4** and between B and C in the cases of complexes **5** and **6**.

Introduction

The group 1 tetra(group 13) hydrides MEH₄ (M = Li, Na; E = B, Al) have long been studied due primarily to their effectiveness as reducing agents.[1-3] The borohydride derivatives in particular are attractive for such transformations as a consequence of

their selectiveness towards certain functionality. In general, the aluminohydrides are much less selective although their selectivity can be improved slightly by for example carrying out reactions in pyridine (py) so that an intermediary solvent separated ion pair complex, $[\text{Li}(\text{py})_4]^+ [\text{Al}(\text{1,4-dihydro-py})_4]^-$, [4-6] Lansbury's reagent, is generated which is more discerning in its reducing capability (figure 1). These tetrahydride materials have also garnered more recent interest in energy storage [7-9] on account of their high gravimetric hydrogen content which passes the threshold of the US Department of Energy recommendation of at least 6.5 mass% hydrogen for a material to be considered as a viable potential hydrogen storage material. [10]

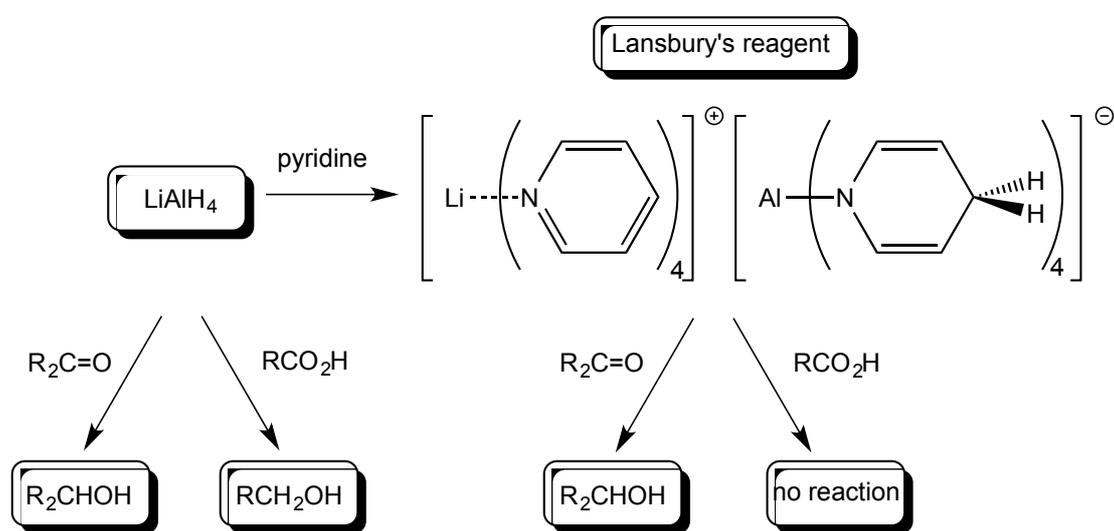


Figure 1 Modification of LiAlH_4 reactivity by treatment with excess pyridine to give Lansbury's reagent

Despite this extensive interest, surprisingly there does not appear to have been a single study of their molecular composition stabilized by a common Lewis donor so that a direct comparison can be made between the boron and aluminium congeners. We have recently utilized the tripodal tetraamine tris(*N,N*-dimethyl-2-aminoethyl)amine (Me_6TREN) as an effective donor for stabilizing highly reactive organometallic species and found that part of its appeal is its ability to alter its coordination profile to suit a particular metal, with the full set of η^1 , [11] η^2 , [11] η^3 [12, 13] and η^4 [14-16] coordination modes all identified. A further added benefit is that because Me_6TREN can cap a hemisphere of a metal's coordination sphere it can function as a 'monomerizing agent', stripping out any secondary oligomerizing interactions and allowing a study of the primary bonding interactions holding the

metal and its ligand(s) together. Our background in this area, coupled with our ongoing interest in group 1/group 13 ate chemistry,[17-22] prompted us to study the series of Me₆TREN solvated monomeric complexes of the group 1 tetra(group 13) hydride species mentioned above, which we have characterized in solution and where appropriate in the solid state and present herein.

Results and Discussion

Molecular structures of MEH₄ complexes

Crystalline complexes of the lighter alkali-metal borohydrides were obtained by refluxing them in THF solution in the presence of two molar equivalents of Me₆TREN. Slow cooling of this solution yielded X-ray quality colourless crystals which were confirmed as being contacted ion pair monomeric adducts of formula MBH₄·Me₆TREN (M = Li, **1**; Na, **2**) by X-ray crystallography (figure 2, pertinent bond parameters are in table 1).

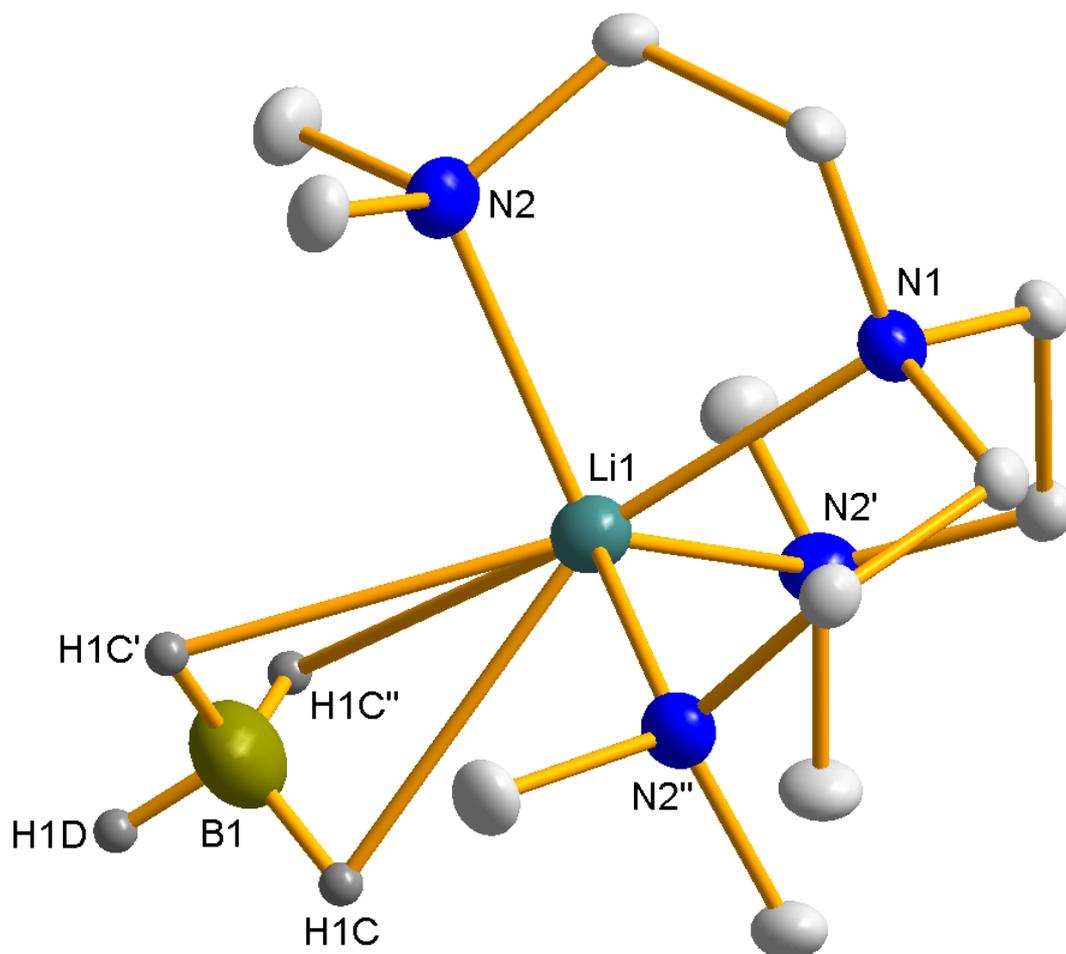


Figure 2 Molecular structure of $\text{LiBH}_4 \cdot \text{Me}_6\text{TREN}$ (**1**). Ellipsoids are displayed at 50% probability and all hydrogen atoms except those of borohydride are omitted for clarity. Symmetry operations to generate equivalent atoms labeled ‘: $1-x, x-y, z$; “: $1-x+y, 1-x, z$. Since $\text{NaBH}_4 \cdot \text{Me}_6\text{TREN}$ (**2**) is isostructural it is not shown for brevity. Symmetry operations to generate equivalent atoms labeled ‘: $1-y, 1+x-y, z$; “: $1-x+y, 1-x, z$.

Table 1 Selected bond lengths (\AA) and angles ($^\circ$) for complexes **1** ($M = \text{Li}$) and **2** ($M = \text{Na}$).

	1	2		1	2
M1-N1	2.268(5)	2.556(3)	N1-M1-N2	79.2(1)	71.98(4)
M1-N2	2.254(1)	2.495(1)	N2-M1-N2'	116.57(8)	110.89(4)
M1-H1C	2.65(4)	2.44(2)	N1-M1-B1	180.0	180.0
M1...B1	2.655(6)	2.612(4)	N2-M1-B1	100.8(1)	108.02(4)
B1-H1C	1.06(3)	1.11(2)	H1C-B1-H1C'	116(2)	108(1)
B1-H1D	0.92(7)	1.18(6)	H1C-B1-H1D	102(2)	111(1)
			Li1-H1C-B1	78(2)	86(1)

Both complexes crystallized in the hexagonal space group $P 6_3$, with the central nitrogen, alkali-metal and boron atoms all lying on a three-fold axis of symmetry. The tripodal tetraamine adopts a η^4 coordination to the alkali-metal. While there has been a considerable number of crystallographic studies on Lewis donor solvated LiBH_4 and a reasonable number on NaBH_4 , [23] this study provides an opportunity to make a direct comparison of the two in the presence of the same donor and in the same oligomerization state. In each case, the BH_4 moiety binds to the alkali-metal through three bridging hydride ligands, with only one occupying a terminal position, giving the alkali-metal a formal coordination number of seven ($4 \times \text{N}$, $3 \times \text{H}$). Monomeric examples containing three bridging hydrides between lithium and boron have been

witnessed previously with tripodal HC(3,5-Me₂pz)₃ (pz = pyrazolyl),[24] THF,[25] 4-benzylpyridine,[26] phenylamine,[27] 4-methylpyridine[28] and N-methylimidazole[29] all having been reported but in each case the lithium was only six coordinate (that is, only one tridentate/three monodentate ligands solvated the lithium). This coordination via three hydride bridges in **1** is perhaps surprising given that the less bulky tridentate N-donor ligand PMDETA gives a monomer with only two bridging hydrides (Li_{CN} = 5),[26] while we note that bidentate TMEDA is not sufficiently polydentate to monomerize LiBH₄, rather giving a dimeric complex with lithium having a coordination number of six.[30] To the best of our knowledge only a single example of this bonding motif for a NaBH₄ fragment has been reported, namely in that solvated by 15-crown-5,[28] giving a coordination number of 8 for sodium. It should be pointed out here though, that the BH₄ fragment was asymmetrically coordinated to Na with the three Na-H distances ranging from 2.28(2)-2.74(2) Å; whereas in **2** it is necessarily symmetric due to crystallographically imposed symmetry at 2.44(2) Å. The Na···B separation distance of 2.612(4) Å in **2** is only marginally shorter than in NaBH₄·15-crown-5 [2.659(3) Å], perhaps suggesting tetradentate tripodal Me₆TREN permits less steric crowding of the sodium cation than pentadentate (and more pseudoplanar) 15-crown-5. Interestingly, the Li···B separation distance in **1** [2.655(6) Å] is actually marginally longer than the Na···B distance in **2** (by more than 0.04 Å) and is considerably longer than the corresponding distances in the six-coordinate complexes mentioned earlier which range from 2.223(7) Å for the tris(pyrazolyl) complex to 2.381(4) Å for the imidazole complex.

The bond distances in **1** between lithium and the nitrogen atoms of the η⁴ Me₆TREN ligand [2.268(5) Å to the central nitrogen atom and 2.254(1) Å to the peripheral nitrogens] are at the long end of those previously recorded for η⁴ Me₆TREN bonds to lithium such as in the benzyllithium complex [2.162(3)-2.356(3) Å],[14] the 3,5-dimethylbenzyllithium complex [2.181(2)-2.302(2) Å][15] and the [Cl(Li·Me₆TREN)₂]⁺ cation [2.186(3)-2.257(3) Å],[31] perhaps reflecting the increased (seven) coordinate nature of lithium in **1**. The corresponding metal nitrogen distances in **2** [2.556(3)/2.495(1) Å] were in accord with previously published data for η⁴ Me₆TREN interactions to sodium including in complexes of benzylna⁺ [2.466(1)-2.535(1) Å],[14] 3,5-dimethylbenzylna⁺ [2.480(1)-2.542(1) Å] [15] and sodium mesityloxide [2.481(5)-2.559(5) Å].[12]

Applying the same synthetic procedure, equimolar mixtures of $\text{LiAlH}_4/\text{NaAlH}_4$ and Me_6TREN in THF solution deposited colourless crystalline products **3** and **4** respectively. In the former case, a single crystal X-ray diffraction study again revealed a monomeric complex, also in space group $P\bar{6}_3$, although this time the group 1 and group 13 metals are bridged by only a single hydride anion, with three terminal hydrides completing the tetrahedral coordination around aluminium (figure 3). Surprisingly given its prominent place in synthesis, crystallographic studies of LiAlH_4 are rare in the literature, with only bidentate N,N' donors giving dimeric structures (figure 4)[32-34] and a single bis-TMEDA solvated solvent-separated ion pair monomer[33] being reported. Thus, to the best of our knowledge, the structure of complex **3** represents the first example of a crystallographically characterized contacted-ion LiAlH_4 monomer.

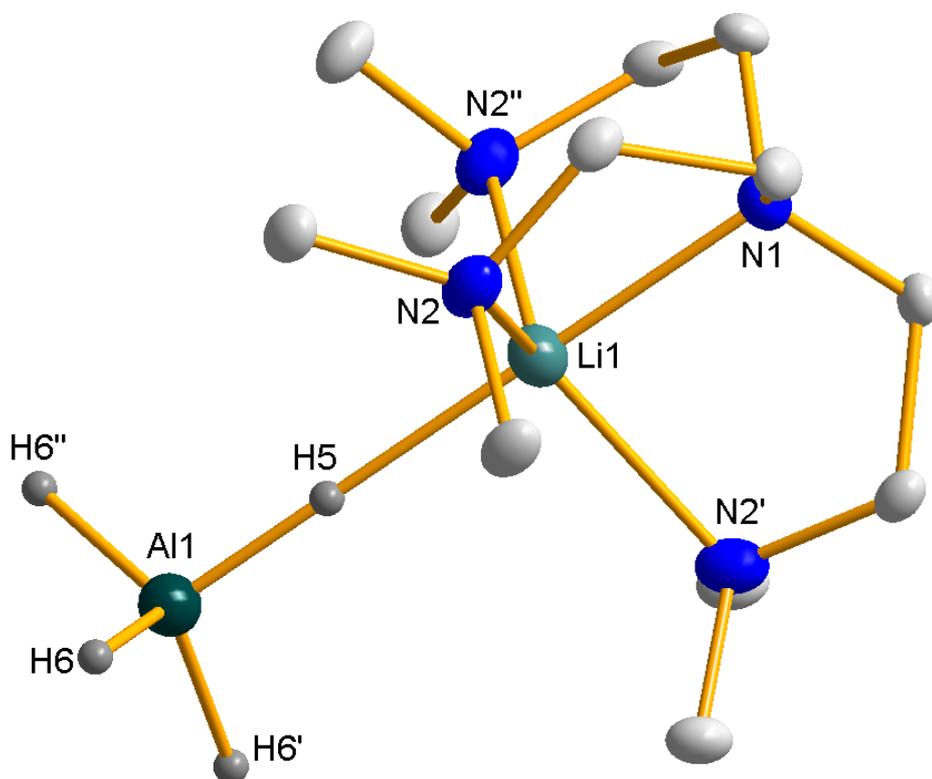


Figure 3 Molecular structure of $\text{LiAlH}_4 \cdot \text{Me}_6\text{TREN}$ (**3**). Ellipsoids are displayed at 50% probability and all hydrogen atoms except those of the aluminohydride are omitted for clarity. Symmetry operations to generate equivalent atoms labeled ‘: 1-y, x-y, z; ‘‘: 1-x+y, 1-x, z. Selected bond lengths (Å) and angles (°): Li1-N1, 2.107(6); Li1-N2, 2.205(1); Li1-H5, 1.96(6); Al1-H5, 1.46(6); Al1-H6, 1.54(2); Li1⋯Al1,

3.416(5); N1-Li1-N2, 83.7(1); N2-Li1-N2', 118.80(6); N2-Li1-H5, 96.3(1); H5-Al1-H6, 106.6(10), H6-Al1-H6', 112.1(14).

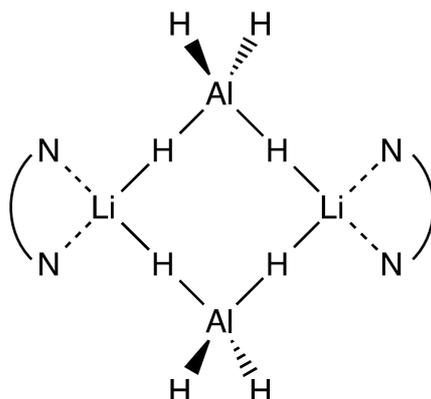


Figure 4 Generic structural motif of crystallographically characterized *N,N'*-bidentate donor solvated LiAlH₄ dimers. Bidentate donor = HN(*t*Bu)CH(*t*Bu)CH₂N(H)(*t*Bu) (A),[32] TMEDA (B),[33] HN(*t*Bu)CH(*t*Bu)CH=N(*t*Bu) (C).[34]

As in **1** and **2**, the Me₆TREN ligand in **3** again binds to lithium in a η^4 manner resulting in an overall coordination number of five within a trigonal bipyramidal environment. This geometry is defined by N2, N2' and N2'' in the equatorial sites with N1 and H5 positioned axially (N2-Li-N2' = 118.80(6) $^\circ$; N1-Li-H5 = 180 $^\circ$). The presence of only a single hydride bound to lithium allows the tetradentate donor closer access to Lewis acidic lithium, evidenced by shorter Li-N bonds in **3** [2.107(6)/2.205(1) Å] when compared to **1** [2.268(5)/2.254(1) Å]. The Li-H and Al-H_{bridging} distances in **3** [1.96(6) and 1.46(6) Å respectively] are in accord with those of complexes **A-C** [range from 1.66(9)-2.04(7) and 1.46(7)-1.59(3) Å respectively] although the Li-H-Al bond angle is different since it is necessarily 180 $^\circ$ in **3** but is 129 and 159 $^\circ$ in complex **A** for example, as a consequence of being in a lower symmetry dimeric framework with bulky donors capping each end lithium. The Al-H_{terminal} distance [1.54(2) Å] is also consistent with complexes **A-C** [1.42(8)-1.67(9) Å]. Interestingly, this value in **3** is longer than Al-H_{bridging} distance and is close to the Al-H distance in the polymeric unsolvated LiAlH₄ (average 1.55 Å).[35] The Li \cdots Al separation at 3.416(5) Å is longer than those reported for complexes **A** or **B** [3.13(1)/3.32(1) and 2.972 Å respectively] since the bridging hydride atoms in **A** or **B** are not perfectly linear. The difference in the coordination mode of the EH₄ moiety and Li in complexes **1** and **3** may have both a steric and electronic contribution.

Sterically, the longer E-H bonds in **3** would give a larger bite angle at Li, which would perhaps encroach into the space occupied by the NMe₂ groups of the tetraamine. Electronically, the electronegativity difference between Al (1.61) and B (2.04; note H is 2.20)[36] means that there is much more covalent character to the B-H bonds. On the other hand, the Al-H bonds have a more pronounced Al(δ^+)-H(δ^-) ionic character. Thus, one could perhaps describe **3** as containing a neutral AlH₃ fragment coordinated through its Lewis acidic Al centre to the hydride of a Li-H fragment via an electrostatic interaction, while the bridging hydrides in **1** are more like bent 3-centre-2-electron bonds typically seen in borane-type complexes.

An X-ray crystallographic study of **4** confirmed a monomeric complex, however disorder in the Me₆TREN ligand meant we were then unable to locate the hydride ligands so the bonding motif linking Na⁺ and (AlH₄)⁻ could not be discerned.

IR and NMR spectroscopic studies

IR spectra of complexes **1-4** were recorded as Nujol mulls (figure 5). In the cases of **1** and **2**, the B-H stretching region confirmed the presence of such functionality although the spectra themselves were somewhat different despite their comparable solid state bonding; complex **1** displaying only a broad band while complex **2** displayed better resolution. Likewise, the spectra of **3** and **4** differed with only a sharp single band seen for **3** while two bands were visible for **4**. Unfortunately, mirroring the work of Nöth, it was not possible to unequivocally assign a specific bonding motif between EH₄ and M based on IR data.

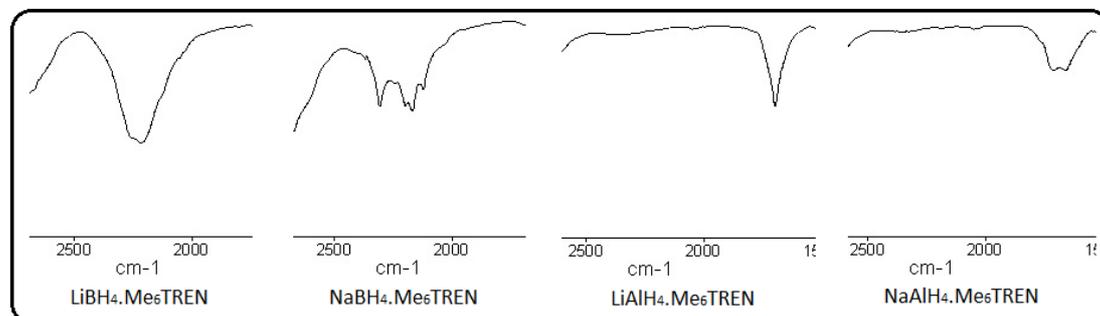


Figure 5 IR spectra of complexes **1 - 4** in Nujol; only the E-H stretching region is shown.

Table 2 Selected NMR spectral data, collected in C₆D₆ at 300 K, for complexes **1** – **4**.

	1	2	3	4	Me₆TREN
Hydride	0.59	0.65	3.86	3.93	-
CH ₂ §	1.94 (57.0)	2.10 (57.7)	1.58 (56.5)	1.64 (56.8)	2.67 (58.8)
CH ₂ §	1.90 (51.2)	2.10 (52.5)	1.58 (50.0)	1.63 (50.7)	2.42 (52.6)
CH ₃ §	2.11 (45.7)	2.10 (45.6)	2.03 (45.4)	1.98 (45.1)	2.14 (46.1)
¹ J(E-H) coupling	27.5 (¹⁰ B) 81.5 (¹¹ B)	27.2 (¹⁰ B) 82.3 (¹¹ B)	*	176.6 (²⁷ Al)	-
⁷ Li	0.29	-	0.11	-	-
¹¹ B	-39.5	-41.6	-	-	-
²⁷ Al	-	-	100.6	97.2	-

§ ¹H (¹³C in parentheses) * not resolved

The Me₆TREN resonances in the ¹H and ¹³C NMR spectra of complexes **1-4** were all shielded with respect to free Me₆TREN, indicative that it remained coordinated to the Lewis acidic alkali metal in solution. In the MAIH₄ complexes **3** and **4**, the ¹H resonances of the bridging ethylene groups were particularly shielded (by almost 0.5 ppm compared to the BH₄ complexes **1** and **2**) although this was not replicated in the CH₃ resonances.

Hydride resonances appeared between 0 and 1 ppm for BH₄ complexes **1** and **2**, and between 3.5 and 4.5 ppm for AlH₄ complexes **3** and **4**. Complexes **1** and **2** provided classical splitting patterns into a quartet and septet due to ¹J coupling to ¹⁰B and ¹¹B respectively, with coupling constants consistent with other Lewis donor solvated alkali-metal BH₄ complexes. Likewise, complex **4** displayed a sextet due to coupling to ²⁷Al, which has a nuclear spin of 5/2. The coupling was not resolved in complex **3**, with only a large broad resonance seen. This was confirmed as the hydride resonance in the ²⁷Al decoupled ¹H NMR spectrum by virtue of it collapsing to a sharp singlet centred at the same chemical shift. The concomitant splitting in the ¹¹B/²⁷Al NMR spectra were evident, with a quintet seen in all four cases consistent with the four hydride ligands being equivalent each time. The chemical shifts of these quintets were similar to those of previously reported MEH₄ complexes. Complex **2** also had its ¹H and ¹¹B NMR spectra recorded at -50°C in C₇D₈ solution which showed that the

bridging and terminal hydrides cannot be spectroscopically distinguished even at this low temperature.

Triethylborohydride complexes

Following the successful preparation and characterization of the lithium and sodium BH_4 and AlH_4 monomers, we turned our attention to the commercially available congeneric triethylborohydride reducing agents LiBEt_3H and NaBEt_3H . Despite their ready availability, there have been only a few studies probing their molecular structures and solution behavior.[37-40] When subjected to a molar equivalent of Me_6TREN in hexane/THF solution, each trialkylhydride formed a crystalline complex in good yield. X-ray crystallographic studies on each complex suggested monomeric complexes of general formula $\text{MBeEt}_3\text{H}\cdot\text{Me}_6\text{TREN}$ ($\text{M} = \text{Li}$, **5**; Na , **6**), although large amounts of disorder rendered the structures unreliable making the $\text{M}-\text{BEt}_3\text{H}$ bonding mode difficult to discern and hence they will not be discussed further.

Soluble in C_6D_6 solution, both complexes gave ^1H NMR spectra consistent with the expected 1:1 adducts with the exception of the hydride resonance, which could not be observed. Complex **5** revealed a sharp singlet in the ^7Li NMR spectrum and a broad resonance in the ^{11}B NMR spectrum at -11.3 ppm. In contrast, the ^{11}B NMR spectrum of **6** displays the expected doublet at a near identical chemical shift (-11.9 ppm) with a $^1J_{\text{BH}}$ coupling constant of 65.1 Hz. The corresponding coupling constant in the TMEDA solvated dimer $[\text{NaBEt}_3\text{H}\cdot\text{TMEDA}]_2$ was found to be solvent dependent, with values of 52.0 Hz noted in C_6D_6 and 70.6 Hz in dimethylsulfoxide (DMSO), which was attributed to retention of it in benzene but disruption of molecular structure in more polar DMSO.[38] The ^{13}C NMR spectra of both complexes were as predicted, although the CH_2 group bound directly to the boron centre was split into a well-resolved quartet with a $^1J_{\text{BC}}$ coupling constant of 41.5 Hz for **5** and 40.2 Hz for **6**. This coupling in alkyl borane functionality is often not resolved but instead only seen as a broad signal due to partially relaxed $^{13}\text{C}-^{11}\text{B}$ scalar coupling.[41] The values are consistent with other four coordinate boron complexes displaying an sp^3-sp^3 bond, such as LiBMe_4 (39.4 Hz)[42] and lower than sp^3-sp^2 bound complexes such as NaBPh_4 (49.5 Hz).[43] Mirroring the situation with complexes **1** and **2**, IR spectra of complexes **5** and **6** clearly displayed stretches consistent with B-H functionality but

there was nothing indicative of the specific bonding mode between the boron-centred complex anion and the alkali-metal cation.

Conclusions

The ability of the tripodal tetraamine Me₆TREN to stabilize monomeric derivatives of the lighter alkali-metal (Li, Na) complexes has been reinforced and exploited to isolate crystalline samples of the borohydride and aluminohydride anions BH₄, BEt₃H and AlH₄ in good yields. This represents a unique opportunity to analyze the bonding modes present in the absence of secondary oligomerizing interactions typical of this class of compound. X-ray crystallography shows that the BH₄ moiety binds to the alkali-metals via three hydride bridges with only one terminal B-H bond, which is in contrast to LiAlH₄ displaying a single bridging hydride and three terminal Al-H bonds. In the BH₄ examples the central alkali-metal is in an unusual seven coordinate environment. In solution NMR experiments, nicely resolved examples of coupling between B/Al and H are evident while the BEt₃H complexes also exhibit B-C coupling which is not generally seen in alkali-metal triethylborohydride complexes.

Experimental

General experimental

All reactions and manipulations were carried out under a protective dry argon atmosphere using standard Schlenk techniques. Products were isolated and NMR samples pre-prepared in an argon-filled glovebox. THF was dried by heating to reflux over sodium-benzophenone and distilled under nitrogen prior to use. Me₆TREN was prepared according to a literature method.[44] The solids LiBH₄, NaBH₄, LiAlH₄, NaAlH₄, LiBEt₃H (1.0 M in THF) and NaBEt₃H (1.0 M in toluene) were purchased from Aldrich and used as received. NMR spectra were recorded on a Bruker AVANCE 400 NMR spectrometer, operating at 400.13 MHz for ¹H, 155.5 MHz for ⁷Li, 128.3 MHz for ¹¹B, 100.6 MHz for ¹³C and 104.2 MHz for ²⁷Al. All ¹³C spectra were proton decoupled. ¹H and ¹³C spectra were referenced to the appropriate solvent signal. ⁷Li, ¹¹B and ²⁷Al spectra were referenced against LiCl in D₂O at 0.00 ppm,

BF₃·OEt₂ in CDCl₃ at 0.00 ppm and AlCl₃ in D₂O at 0.00 ppm respectively. Elemental analyses were carried out on a Perkin-Elmer 2400 elemental analyser. IR spectra were obtained on a Perkin-Elmer Spectrum 100 FT-IR spectrometer.

X-ray crystallography

Crystallographic data were collected on Oxford Diffraction instruments with Mo or Cu K α radiation. Structures were solved using *SHELXS-97*, while refinement was carried out on *F*² against all independent reflections by the full-matrix least-squares method using the *SHELXL-97* program. All non-hydrogen atoms were refined using anisotropic thermal parameters. For the BH₄ and AlH₄ anions all H atom positions were freely refined.

Table 3 Crystallographic data and refinement details for complexes **1-3**.

Compound	1	2	3
Formula	C ₁₂ H ₃₄ N ₄ LiB	C ₁₂ H ₃₄ N ₄ NaB	C ₁₂ H ₃₄ N ₄ LiAl
Formula weight	252.18	268.23	268.35
Crystal system	hexagonal	hexagonal	hexagonal
Space group	P 6 ₃	P 6 ₃	P 6 ₃
Wavelength/Å	1.54180	0.71073	0.71073
<i>a</i> /Å	9.9574(3)	10.1151(4)	10.2029(5)
<i>b</i> /Å	9.9574(3)	10.1151(4)	10.2029(5)
<i>c</i> /Å	10.1837(3)	10.1201(6)	10.4028(7)
Volume/Å ³	874.44(5)	896.72(7)	937.84(9)
<i>Z</i>	2	2	2
Reflns. collected	2460	3133	3243
Unique reflns.	825	1160	1039
R _{int}	0.0240	0.0280	0.0319

Obs. Reflns. [$I > 2\sigma(I)$]	818	1044	913
Goodness of fit	1.084	1.042	1.056
$R[F^2 > 2\sigma], F$	0.0379	0.0357	0.0334
R_w (all data), F^2	0.1092	0.0841	0.0755
Largest diff. peak/hole $e/\text{\AA}^{-3}$	0.207/-0.149	0.177/-0.166	0.138/-0.148

LiBH₄·Me₆TREN (1)

LiBH₄ (22 mg, 1 mmol) and Me₆TREN (0.52 mL, 2 mmol) were added to 5 mL of THF. This was heated to reflux for 1 hr at which point the heat and stirrer were turned off. Slow cooling of the solution yielded X-ray quality colourless crystals (40 mg, 16 %).

¹H NMR (400.1 MHz, C₆D₆, 300 K): δ 0.59 (s, 12H, Me₆TREN Me), 1.94, 1.90 (overlapping br s, 12H, Me₆TREN CH₂), 0.59 ppm (quartet/septet, 4H, BH₄, ¹J_{10BH} = 27.5 Hz, ¹J_{11BH} = 81.5 Hz).

¹³C NMR (100.6 MHz, C₆D₆, 300 K): δ 57.0 (CH₂), 51.2 (CH₂), 45.7 ppm (Me).

⁷Li NMR (155.5 MHz, C₆D₆, 300 K): δ 0.29 ppm.

¹¹B NMR (128.3 MHz, C₆D₆, 300 K): δ -39.5 ppm (quin, ¹J_{BH} = 81.2 Hz).

Elemental analysis (%) for C₁₂H₃₄N₄LiB: calcd: C 57.15, H 13.59, N 22.22; found: C 57.16, H 13.48, N 22.59.

NaBH₄·Me₆TREN (2)

The same procedure as **1** was followed using NaBH₄ (38 mg, 1 mmol) giving X-ray quality colourless crystals (176 mg, 66 %).

¹H NMR (400.1 MHz, C₆D₆, 300 K): δ 0.65 (br s, 30H, Me₆TREN Me + CH₂), 0.65 ppm (quartet/septet, 4H, BH₄, ¹J_{10BH} = 27.2 Hz, ¹J_{11BH} = 82.3 Hz).

^{13}C NMR (100.6 MHz, C_6D_6 , 300 K): δ 57.7 (CH_2), 52.5 (CH_2), 45.6 ppm (Me).

^{11}B NMR (128.3 MHz, C_6D_6 , 300 K): δ -41.6 ppm (quin, $^1J_{\text{BH}} = 81.2$ Hz).

Elemental analysis (%) for $\text{C}_{12}\text{H}_{34}\text{N}_4\text{NaB}$: calcd: C 53.73, H 12.78, N 20.89; found: C 53.28, H 12.71, N 20.58.

$\text{LiAlH}_4 \cdot \text{Me}_6\text{TREN}$ (**3**)

The same procedure as **1** was followed using LiAlH_4 (76 mg, 2 mmol) and Me_6TREN (0.52 mL, 2 mmol) giving X-ray quality colourless crystals (351 mg, 65 %).

^1H NMR (400.1 MHz, C_6D_6 , 300 K): δ 0.03 ppm (s, 4H, AlH_4), 1.58 ppm (s, 12H, Me_6TREN Me).

^{13}C NMR (100.6 MHz, C_6D_6 , 300 K): δ 56.5 (CH_2), 50.0 (CH_2), 45.4 ppm (Me).

^7Li NMR (155.5 MHz, C_6D_6 , 300 K): δ 0.11 ppm.

^{27}Al NMR (104.2 MHz, C_6D_6 , 300 K): δ 100.6 ppm (quin, $^1J_{\text{AlH}} = 170.3$ Hz).

Elemental analysis (%) for $\text{C}_{12}\text{H}_{34}\text{N}_4\text{LiAl}$: calcd: C 53.71, H 12.77, N 20.88; found: C 53.14, H 12.35, N 21.33.

$\text{NaAlH}_4 \cdot \text{Me}_6\text{TREN}$ (**4**)

The same procedure as **1** was followed using NaAlH_4 (108 mg, 2 mmol) and Me_6TREN (0.52 mL, 2 mmol) giving X-ray quality colourless crystals (314 mg, 55 %).

^1H NMR (400.1 MHz, C_6D_6 , 300 K): δ 0.93 ppm (s, 4H, AlH_4 , $^1J_{\text{AlH}} = 176.6$ Hz), 1.98 ppm (s, 12H, Me_6TREN Me), 1.64, 1.63 (overlapping s, 12H, Me_6TREN CH_2).

^{13}C NMR (100.6 MHz, C_6D_6 , 300 K): δ 56.8 (CH_2), 50.7 (CH_2), 45.1 ppm (Me).

^{27}Al NMR (104.2 MHz, C_6D_6 , 300 K): δ 97.2 ppm (quin, $^1J_{\text{AlH}} = 176.2$ Hz).

Elemental analysis (%) for C₁₂H₃₄N₄NaAl: calcd: C 50.68, H 12.05, N 19.70; found: C 50.37, H 11.75, N 19.37.

LiBEt₃H·Me₆TREN (**5**)

LiBEt₃H (1 mL, 1.0 M in THF, 1 mmol) and Me₆TREN (0.26 mL, 1 mmol) were added to 5 mL of hexane, precipitating a white powder. THF was slowly added dropwise with stirring until a homogeneous solution was obtained (approx. 3 mL). Cooling of the solution at -30°C yielded X-ray quality colourless crystals (225 mg, 67 %).

¹H NMR (400.1 MHz, C₆D₆, 300 K): δ 0.06 (s, 6H, Me₆TREN Me), 1.86 (t, 6H, ³J_{HH} = 4.95 Hz, Me₆TREN CH₂), 1.78 (t, 6H, ³J_{HH} = 4.95 Hz, Me₆TREN CH₂), 1.54 (t, 9H, ³J_{HH} = 7.43 Hz, BCH₂CH₃), 0.95 ppm (q, 6H, ³J_{HH} = 7.43 Hz, BCH₂CH₃).

¹³C NMR (100.6 MHz, C₆D₆, 300 K): δ 57.2 (Me₆TREN CH₂), 50.6 (Me₆TREN CH₂), 45.7 (Me₆TREN Me), 16.7 (m, ¹J_{BC} = 41.5 Hz, BCH₂CH₃), 14.2 ppm (BCH₂CH₃).

⁷Li NMR (155.5 MHz, C₆D₆, 300 K): δ -0.18 ppm.

¹¹B NMR (128.3 MHz, C₆D₆, 300 K): δ -11.3 ppm (broad singlet).

Elemental analysis (%) for C₁₈H₄₆N₄LiB: calcd: C 64.28, H 13.79, N 16.66; found: C 64.24, H 13.49, N 16.75.

NaBEt₃H·Me₆TREN (**6**)

The same procedure as **1** was followed using NaBEt₃H (1 mL, 1.0 M in toluene, 1 mmol). Toluene was added slowly to give a homogeneous solution (approx. 4 mL) which was cooled to -30°C giving X-ray quality colourless crystals (208 mg, 59 %).

¹H NMR (400.1 MHz, C₆D₆, 300 K): δ 0.00 (s, 6H, Me₆TREN Me), 1.70 (br, 12H, Me₆TREN CH₂), 1.57 (t, 9H, ³J_{HH} = 7.16 Hz, BCH₂CH₃), 0.89 ppm (q, 6H, ³J_{HH} = 7.36 Hz, BCH₂CH₃).

^{13}C NMR (100.6 MHz, C_6D_6 , 300 K): δ 57.0 ($\text{Me}_6\text{TREN CH}_2$), 50.8 ($\text{Me}_6\text{TREN CH}_2$), 45.3 ($\text{Me}_6\text{TREN Me}$), 16.1 (q, $^1J_{\text{BC}} = 40.2$ Hz, BCH_2CH_3), 12.0 ppm (BCH_2CH_3).

^{11}B NMR (128.3 MHz, C_6D_6 , 300 K): δ -11.9 ppm (d, $^1J_{\text{BH}} = 65.1$ Hz).

Elemental analysis (%) for $\text{C}_{18}\text{H}_{46}\text{N}_4\text{NaB}$: calcd: C 61.35, H 13.16, N 15.90; found: C 61.03, H 12.90, N 15.64.

Appendix A. Supplementary Data

CCDC 1413365 - 1413367 contains the supplementary crystallographic data for **1 - 3**. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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References

- [1] A. Hajos, *Complex Hydrides and Related Reducing Agents in Organic Synthesis*, Elsevier, Amsterdam, 1979.
- [2] M.V. Nora de Souza, T.R. Alves Vasconcelos, *Appl. Organomet. Chem.*, 20 (2006) 798-810.
- [3] J.S. Cha, H.C. Brown, *J. Org. Chem.*, 58 (1993) 4727-4731.
- [4] P.T. Lansbury, J.O. Peterson, *J. Am. Chem. Soc.*, 85 (1963) 2236-2242.
- [5] D.D. Tanner, C.-M. Yang, *J. Org. Chem.*, 58 (1993) 1840-1846.
- [6] K. Hensen, A. Lemke, T. Stumpf, M. Bolte, H. Fleischer, C.R. Pulham, R.O. Gould, S. Harris, *Inorg. Chem.*, 38 (1999) 4700-4704.
- [7] S.-i. Orimo, Y. Nakamori, J.R. Eliseo, A. Züttel, C.M. Jensen, *Chem. Rev.*, 107 (2007) 4111-4132.
- [8] U.B. Demirci, P. Miele, *Energy Environ. Sci.*, 2 (2009) 627-637.

- [9] J. Manna, M. Vashistha, P. Sharma, *Inter. J. Ener. Clean Env.*, 11 (2010) 65-97.
- [10] L. Schlapbach, A. Züttel, *Nature*, 414 (2001) 353-358.
- [11] T. Cadenbach, E. Hevia, A.R. Kennedy, R.E. Mulvey, J.-A. Pickrell, S.D. Robertson, *Dalton Trans.*, 41 (2012) 10141-10144.
- [12] D.M. Cousins, M.G. Davidson, C.J. Frankis, D. Garcia-Vivo, M.F. Mahon, *Dalton Trans.*, 39 (2010) 8278-8280.
- [13] S.D. Robertson, A.R. Kennedy, J.J. Liggat, R.E. Mulvey, *Chem. Commun.*, 51 (2015) 5452-5455.
- [14] M.G. Davidson, D. Garcia-Vivo, A.R. Kennedy, R.E. Mulvey, S.D. Robertson, *Chem. Eur. J.*, 17 (2011) 3364-3369.
- [15] D.R. Armstrong, M.G. Davidson, D. Garcia-Vivo, A.R. Kennedy, R.E. Mulvey, S.D. Robertson, *Inorg. Chem.*, 52 (2013) 12023-12032.
- [16] A.R. Kennedy, R.E. Mulvey, R.I. Urquhart, S.D. Robertson, *Dalton Trans.*, 43 (2014) 14265-14274.
- [17] B. Conway, A.R. Kennedy, R.E. Mulvey, S.D. Robertson, J. Garcia-Alvarez, *Angew. Chem. Int. Ed.*, 49 (2010) 3182-3184.
- [18] B. Conway, P. Garcia-Alvarez, A.R. Kennedy, J. Klett, R.E. Mulvey, S.D. Robertson, *New. J. Chem.*, 34 (2010) 1707-1712.
- [19] E. Crosbie, A.R. Kennedy, R.E. Mulvey, S.D. Robertson, *Dalton Trans.*, 41 (2012) 1832-1839.
- [20] B. Conway, E. Crosbie, A.R. Kennedy, R.E. Mulvey, S.D. Robertson, *Chem. Commun.*, 48 (2012) 4674-4676.
- [21] R. Campbell, E. Crosbie, A.R. Kennedy, R.E. Mulvey, R.A. Naismith, S.D. Robertson, *Aust. J. Chem.*, 66 (2013) 1189-1201.
- [22] D.R. Armstrong, E. Crosbie, E. Hevia, R.E. Mulvey, D.L. Ramsay, S.D. Robertson, *Chem. Sci.*, 5 (2014) 3031-3045.
- [23] F.H. Allen, *Acta Cryst.*, B58 (2002) 380-388.
- [24] D.L. Reger, J.E. Collins, M.A. Matthews, A.L. Rheingold, L.M. Liable-Sands, I.A. Guzei, *Inorg. Chem.*, 36 (1997) 6266-6269.
- [25] H.-H. Giese, H. Nöth, H. Schwenk, S. Thomas, *Eur. J. Inorg. Chem.*, (1998) 941-949.
- [26] H.-H. Giese, T. Habereeder, H. Nöth, W. Ponikwar, S. Thomas, M. Warchhold, *Inorg. Chem.*, 38 (1999) 4188-4196.
- [27] H.-H. Giese, T. Habereeder, J. Knizek, H. Nöth, M. Warchhold, *Eur. J. Inorg. Chem.*, (2001) 1195-1205.
- [28] J.C. Galvez Ruiz, H. Nöth, M. Warchhold, *Eur. J. Inorg. Chem.*, (2008) 251-266.
- [29] S. Leiner, P. Mayer, H. Nöth, *Z. Naturforsch.*, B64 (2009) 793-799.
- [30] D.R. Armstrong, W. Clegg, H.M. Colquhoun, J.A. Daniels, R.E. Mulvey, I.R. Stephenson, K. Wade, *J. Chem. Soc. Chem. Commun.*, (1987) 630-632.
- [31] A.R. Kennedy, R.E. Mulvey, C.T. O'Hara, G.M. Robertson, S.D. Robertson, *Angew. Chem. Int. Ed.*, 50 (2011) 8375-8378.
- [32] M.G. Gardiner, S.M. Lawrence, C.L. Raston, *Inorg. Chem.*, 35 (1996) 1349-1354.
- [33] M.M. Andrianarison, A.G. Avent, M.C. Ellerby, I.B. Gorrell, P.B. Hitchcock, J.D. Smith, D.R. Stanley, *J. Chem. Soc. Dalton Trans.*, (1998) 249-253.
- [34] M.G. Gardiner, S.M. Lawrence, C.L. Raston, *Inorg. Chem.*, 38 (1999) 4467-4472.
- [35] N. Sklar, B. Post, *Inorg. Chem.*, 6 (1967) 669-671.
- [36] L. Pauling, *The Nature of the Chemical Bond*, Cornell University Press, Ithaca, New York, 1960.
- [37] R. Köster, W. Schüßler, R. Boese, D. Bläser, *Chem. Ber.*, 124 (1991) 2259-2262.
- [38] J. Haywood, A.E.H. Wheatley, *Eur. J. Inorg. Chem.*, (2009) 5010-5016.

- [39] S. Krieck, H. Görls, M. Westerhausen, *Inorg. Chem. Commun.*, 13 (2010) 1466-1469.
- [40] N.A. Bell, H.M.M. Shearer, C.B. Spencer, *Chem. Commun.*, (1980) 711-712.
- [41] B. Wrackmeyer, *Prog. NMR. Spectrosc.*, 12 (1978) 227-259.
- [42] M. Yanagisawa, O. Yamamoto, *Org. Magn. Reson.*, 12 (1980) 76-77.
- [43] D.E. Axelson, A.J. Oliver, C.E. Holloway, *Org. Magn. Reson.*, 5 (1973) 255-256.
- [44] G.J.P. Britovsek, J. England, A.J.P. White, *Inorg. Chem.*, 44 (2005) 8125-8134.