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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, $[\text{Li(py)}_4]^+$ $[\text{Al(1,4-dihydro-py)}_4]^{-}$.[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$_6$TREN) 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 $\eta^1$,[11] $\eta^2$,[11] $\eta^3$ [12, 13] and $\eta^4$ [14-16] coordination modes all identified. A further added benefit is that because Me$_6$TREN 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 LiBH$_4$·Me$_6$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 NaBH$_4$·Me$_6$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 (Å) and angles (°) for complexes 1 (M = Li) and 2 (M = Na).

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<td>M1-N1</td>
<td>2.268(5)</td>
<td>2.556(3)</td>
<td>N1-M1-N2</td>
<td>79.2(1)</td>
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<tr>
<td>M1-N2</td>
<td>2.254(1)</td>
<td>2.495(1)</td>
<td>N2-M1-N2’</td>
<td>116.57(8)</td>
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<td>2.44(2)</td>
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<td>M1···B1</td>
<td>2.655(6)</td>
<td>2.612(4)</td>
<td>N2-M1-B1</td>
<td>100.8(1)</td>
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<tr>
<td>B1-H1C</td>
<td>1.06(3)</td>
<td>1.11(2)</td>
<td>H1C-B1-H1C’</td>
<td>116(2)</td>
</tr>
<tr>
<td>B1-H1D</td>
<td>0.92(7)</td>
<td>1.18(6)</td>
<td>H1C-B1-H1D</td>
<td>102(2)</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>Li1-H1C-B1</td>
<td>78(2)</td>
</tr>
</tbody>
</table>

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 x N, 3 x 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 (LiCN = 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 tetradeutate 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 benzylsodium [2.466(1)-2.535(1) Å],[14] 3,5-dimethylbenzylsodium [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 LiAlH₄/NaAlH₄ and Me₆TREN 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 6₃, 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 LiAlH₄ 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 LiAlH₄ monomer.

Figure 3 Molecular structure of LiAlH₄·Me₆TREN (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,
Figure 4 Generic structural motif of crystallographically characterized \(N,N'\)-bidentate donor solvated LiAlH\(_4\) dimers. Bidentate donor = HN(tBu)CH(tBu)CH\(_2\)N(H)(tBu) (A),[32] TMEDA (B),[33] HN(tBu)CH(tBu)CH=N(tBu) (C).[34]

As in 1 and 2, the Me\(_6\)TREN ligand in 3 again binds to lithium in a \(\eta^4\) 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); N1-Li-H5 = 180°). The presence of only a single hydride bound to lithium allows the tetradeinate 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\(_{\text{bridging}}\) 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° in 3 but is 129 and 159° 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\(_{\text{terminal}}\) 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 then Al-H\(_{\text{bridging}}\) distance and is close to the Al-H distance in the polymeric unsolvated LiAlH\(_4\) (average 1.55 Å).[35] The Li···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 EH\(_4\) 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.](image-url)
Table 2 Selected NMR spectral data, collected in C₆D₆ at 300 K, for complexes 1 – 4.

<table>
<thead>
<tr>
<th></th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>Me₆TREN</th>
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<tr>
<td>Hydride</td>
<td>0.59</td>
<td>0.65</td>
<td>3.86</td>
<td>3.93</td>
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<tr>
<td>CH₃§</td>
<td>1.94 (57.0)</td>
<td>2.10 (57.7)</td>
<td>1.58 (56.5)</td>
<td>1.64 (56.8)</td>
<td>2.67 (58.8)</td>
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<tr>
<td>CH₃§</td>
<td>1.90 (51.2)</td>
<td>2.10 (52.5)</td>
<td>1.58 (50.0)</td>
<td>1.63 (50.7)</td>
<td>2.42 (52.6)</td>
</tr>
<tr>
<td>CH₃§</td>
<td>2.11 (45.7)</td>
<td>2.10 (45.6)</td>
<td>2.03 (45.4)</td>
<td>1.98 (45.1)</td>
<td>2.14 (46.1)</td>
</tr>
<tr>
<td>†J(E-H) coupling</td>
<td>27.5 (¹⁰B) 81.5 (¹¹B)</td>
<td>27.2 (¹⁰B) 82.3 (¹¹B)</td>
<td>*</td>
<td>176.6 (²⁷Al)</td>
<td>-</td>
</tr>
<tr>
<td>†Li</td>
<td>0.29</td>
<td>-</td>
<td>0.11</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>†¹¹B</td>
<td>-39.5</td>
<td>-41.6</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>²⁷Al</td>
<td>-</td>
<td>-</td>
<td>100.6</td>
<td>97.2</td>
<td>-</td>
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</table>

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

The Me₆TREN resonances in the †H 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 †H 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 †J 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 †H 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 †H 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 congenic triethylborohydride reducing agents LiBEt$_3$H and NaBEt$_3$H. 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$_6$TREN 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 MBEt$_3$H·Me$_6$TREN (M = Li, 5; Na, 6), although large amounts of disorder rendered the structures unreliable making the M-BEt$_3$H bonding mode difficult to discern and hence they will not be discussed further.

Soluble in C$_6$D$_6$ solution, both complexes gave $^1$H 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 $^7$Li 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 $^1$J$_{BH}$ coupling constant of 65.1 Hz. The corresponding coupling constant in the TMEDA solvated dimer [NaBEt$_3$H·TMEDA]$_2$ was found to be solvent dependent, with values of 52.0 Hz noted in C$_6$D$_6$ 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 $^1$J$_{BC}$ 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 $^{13}$C-$^{11}$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 Kα radiation. Structures were solved using SHELXS-97, while refinement was carried out on F² 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.

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<td>C₁₂H₃₄Na₄LiAl</td>
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<td>b/Å</td>
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</tr>
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<td>Goodness of fit</td>
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<td>1.042</td>
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<td>0.207/-0.149</td>
<td>0.177/-0.166</td>
<td>0.138/-0.148</td>
</tr>
</tbody>
</table>

**LiBH\(_4\)·Me\(_6\)TREN (1)**

LiBH\(_4\) (22 mg, 1 mmol) and Me\(_6\)TREN (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 %).

\(^1\)H NMR (400.1 MHz, C\(_6\)D\(_6\), 300 K): \(\delta\) 1.94, 1.90 (overlapping br s, 12H, Me\(_6\)TREN CH\(_2\)), 0.59 ppm (quartet/septet, 4H, BH\(_4\), \(\^1J_{10BH} = 27.5\) Hz, \(\^1J_{11BH} = 81.5\) Hz).

\(^13\)C NMR (100.6 MHz, C\(_6\)D\(_6\), 300 K): \(\delta\) 57.0 (CH\(_2\)), 51.2 (CH\(_2\)), 45.7 ppm (Me).

\(^7\)Li NMR (155.5 MHz, C\(_6\)D\(_6\), 300 K): \(\delta\) 0.29 ppm.

\(^{11}\)B NMR (128.3 MHz, C\(_6\)D\(_6\), 300 K): \(\delta\) -39.5 ppm (quin, \(\^1J_{BH} = 81.2\) Hz).

Elemental analysis (%) for C\(_{12}\)H\(_{34}\)N\(_4\)LiB: calcd: C 57.15, H 13.59, N 22.22; found: C 57.16, H 13.48, N 22.59.

**NaBH\(_4\)·Me\(_6\)TREN (2)**

The same procedure as 1 was followed using NaBH\(_4\) (38 mg, 1 mmol) giving X-ray quality colourless crystals (176 mg, 66 %).

\(^1\)H NMR (400.1 MHz, C\(_6\)D\(_6\), 300 K): \(\delta\) 0.65 ppm (quartet/septet, 4H, BH\(_4\), \(\^1J_{10BH} = 27.2\) Hz, \(\^1J_{11BH} = 82.3\) Hz).

LiBH\(_4\)·Me\(_6\)TREN (1)

LiBH\(_4\) (22 mg, 1 mmol) and Me\(_6\)TREN (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 %).

\(^1\)H NMR (400.1 MHz, C\(_6\)D\(_6\), 300 K): \(\delta\) 1.94, 1.90 (overlapping br s, 12H, Me\(_6\)TREN CH\(_2\)), 0.59 ppm (quartet/septet, 4H, BH\(_4\), \(\^1J_{10BH} = 27.5\) Hz, \(\^1J_{11BH} = 81.5\) Hz).

\(^13\)C NMR (100.6 MHz, C\(_6\)D\(_6\), 300 K): \(\delta\) 57.0 (CH\(_2\)), 51.2 (CH\(_2\)), 45.7 ppm (Me).

\(^7\)Li NMR (155.5 MHz, C\(_6\)D\(_6\), 300 K): \(\delta\) 0.29 ppm.

\(^{11}\)B NMR (128.3 MHz, C\(_6\)D\(_6\), 300 K): \(\delta\) -39.5 ppm (quin, \(\^1J_{BH} = 81.2\) Hz).

Elemental analysis (%) for C\(_{12}\)H\(_{34}\)N\(_4\)LiB: calcd: C 57.15, H 13.59, N 22.22; found: C 57.16, H 13.48, N 22.59.

**NaBH\(_4\)·Me\(_6\)TREN (2)**

The same procedure as 1 was followed using NaBH\(_4\) (38 mg, 1 mmol) giving X-ray quality colourless crystals (176 mg, 66 %).

\(^1\)H NMR (400.1 MHz, C\(_6\)D\(_6\), 300 K): \(\delta\) 0.65 ppm (quartet/septet, 4H, BH\(_4\), \(\^1J_{10BH} = 27.2\) Hz, \(\^1J_{11BH} = 82.3\) Hz).
$^{13}$C NMR (100.6 MHz, C$_6$D$_6$, 300 K): $\delta$ 57.7 (CH$_2$), 52.5 (CH$_2$), 45.6 ppm (Me).

$^{11}$B NMR (128.3 MHz, C$_6$D$_6$, 300 K): $\delta$ -41.6 ppm (quin, $^1J_{BH} = 81.2$ Hz).

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

LiAlH$_4$·Me$_6$TREN (3)

The same procedure as 1 was followed using LiAlH$_4$ (76 mg, 2 mmol) and Me$_6$TREN (0.52 mL, 2 mmol) giving X-ray quality colourless crystals (351 mg, 65%).

$^1$H NMR (400.1 MHz, C$_6$D$_6$, 300 K): $\delta$ 4H, AlH$_4$, 0338s, Me$_6$TREN Me), 1.58 ppm (s, 12H, Me$_6$TREN CH$_2$).

$^{13}$C NMR (100.6 MHz, C$_6$D$_6$, 300 K): $\delta$ 56.5 (CH$_2$), 50.0 (CH$_2$), 45.4 ppm (Me).

$^7$Li NMR (155.5 MHz, C$_6$D$_6$, 300 K): $\delta$ 0.11 ppm.

$^{27}$Al NMR (104.2 MHz, C$_6$D$_6$, 300 K): $\delta$ 100.6 ppm (quin, $^1J_{AlH} = 170.3$ Hz).

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

NaAlH$_4$·Me$_6$TREN (4)

The same procedure as 1 was followed using NaAlH$_4$ (108 mg, 2 mmol) and Me$_6$TREN (0.52 mL, 2 mmol) giving X-ray quality colourless crystals (314 mg, 55%).

$^1$H NMR (400.1 MHz, C$_6$D$_6$, 300 K): $\delta$ 9339sex4H, AlH$_4$, 0303s, Me$_6$TREN Me), 1.64, 1.63 (overlapping s, 12H, Me$_6$TREN CH$_2$).

$^{13}$C NMR (100.6 MHz, C$_6$D$_6$, 300 K): $\delta$ 56.8 (CH$_2$), 50.7 (CH$_2$), 45.1 ppm (Me).

$^{27}$Al NMR (104.2 MHz, C$_6$D$_6$, 300 K): $\delta$ 97.2 ppm (quin, $^1J_{AlH} = 176.2$ Hz).
Elemental analysis (%) for C<sub>12</sub>H<sub>34</sub>N<sub>4</sub>NaAl: calcd: C 50.68, H 12.05, N 19.70; found: C 50.37, H 11.75, N 19.37.

LiBEt<sub>3</sub>H·Me<sub>6</sub>TREN (5)

LiBEt<sub>3</sub>H (1 mL, 1.0 M in THF, 1 mmol) and Me<sub>6</sub>TREN (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 -30ºC yielded X-ray quality colourless crystals (225 mg, 67 %).

<sup>1</sup>H NMR (400.1 MHz, C<sub>6</sub>D<sub>6</sub>, 300 K): δ 1.86 (t, 6H, <sup>3</sup>J<sub>HH</sub> = 4.95 Hz, Me<sub>6</sub>TREN CH<sub>2</sub>), 1.78 (t, 6H, <sup>3</sup>J<sub>HH</sub> = 4.95 Hz, Me<sub>6</sub>TREN CH<sub>2</sub>), 1.54 (t, 9H, <sup>3</sup>J<sub>HH</sub> = 7.43 Hz, BCH<sub>2</sub>CH<sub>3</sub>), 0.95 ppm (q, 6H, <sup>3</sup>J<sub>HH</sub> = 7.43 Hz, BCH<sub>2</sub>CH<sub>3</sub>).

<sup>13</sup>C NMR (100.6 MHz, C<sub>6</sub>D<sub>6</sub>, 300 K): δ 57.2 (Me<sub>6</sub>TREN CH<sub>2</sub>), 50.6 (Me<sub>6</sub>TREN CH<sub>2</sub>), 45.7 (Me<sub>6</sub>TREN Me), 16.7 (m, <sup>1</sup>J<sub>BC</sub> = 41.5 Hz, BCH<sub>2</sub>CH<sub>3</sub>), 14.2 ppm (BCH<sub>2</sub>CH<sub>3</sub>).

<sup>7</sup>Li NMR (155.5 MHz, C<sub>6</sub>D<sub>6</sub>, 300 K): δ -0.18 ppm.

<sup>11</sup>B NMR (128.3 MHz, C<sub>6</sub>D<sub>6</sub>, 300 K): δ -11.3 ppm (broad singlet).

Elemental analysis (%) for C<sub>18</sub>H<sub>46</sub>N<sub>4</sub>LiB: calcd: C 64.28, H 13.79, N 16.66; found: C 64.24, H 13.49, N 16.75.

NaBEt<sub>3</sub>H·Me<sub>6</sub>TREN (6)

The same procedure as 1 was followed using NaBEt<sub>3</sub>H (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 -30ºC giving X-ray quality colourless crystals (208 mg, 59 %).

<sup>1</sup>H NMR (400.1 MHz, C<sub>6</sub>D<sub>6</sub>, 300 K): δ 1.70 (br, 12H, Me<sub>6</sub>TREN CH<sub>2</sub>), 1.57 (t, 9H, <sup>3</sup>J<sub>HH</sub> = 7.16 Hz, BCH<sub>2</sub>CH<sub>3</sub>), 0.89 ppm (q, 6H, <sup>3</sup>J<sub>HH</sub> = 7.36 Hz, BCH<sub>2</sub>CH<sub>3</sub>).
$^{13}$C NMR (100.6 MHz, C$_6$D$_6$, 300 K): $\delta$ 57.0 (Me$_6$TREN CH$_2$), 50.8 (Me$_6$TREN CH$_2$), 45.3 (Me$_6$TREN Me), 16.1 (q, $^1$$J_{BC}$ = 40.2 Hz, BCH$_2$CH$_3$), 12.0 ppm (BCH$_2$CH$_3$).

$^{11}$B NMR (128.3 MHz, C$_6$D$_6$, 300 K): $\delta$ -11.9 ppm (d, $^1$$J_{BH}$ = 65.1 Hz).

Elemental analysis (%) for C$_{18}$H$_{46}$N$_4$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](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