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Complexes of lithium tetrahydroaluminate with *N*,*N*,*N*′,*N*′-tetramethylethane-1,2-diamine (tmen). Crystal structures of $[\{Li(tmen)(AlH_4)\}_2]$ and $[Li(tmen)_2][AlH_4]$ and the use of the ^6Li-$\{^1H\}$ nuclear Overhauser effect to study $LiAlH_4$ and $LiBH_4$ in donor solvents

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Two crystalline complexes (1 : 1 and 1 : 2) of $LiAlH_4$ with *N*,*N*,*N*′,*N*′-tetramethylethane-1,2-diamine (tmen) have been isolated. A crystal structure determination of the 1 : 1 complex showed that it formed centrosymmetrical dimers in which $[AlH_4]^-$ anions and $[Li(tmen)]^+$ cations are linked by μ-hydrogen bridges. Bond lengths and angles within the non-planar eight-membered rings are Al–H 1.55(3), Li–H 1.99(3) Å, H–Li–H 131(1) and H–Al–H 112(1)° and the exocyclic Al–H distance was 1.53(4) Å. Cryoscopic data indicated that the dimeric structure with Li–H–Al bridges was preserved in benzene solution and measurements of the ^6Li-$\{^1H\}$ nuclear Overhauser effect (NOE) showed the presence of $Li\cdots H$–Al interactions. The 1 : 2 adduct $[Li(tmen)_2][AlH_4]$ **2**, which crystallised with an ionic NaCl structure, was converted into **1** by heating under vacuum at 120 °C. The NOE measurements on solutions of **2** in benzene showed the presence of $Li\cdots H$–Al interactions even when a large excess of tmen was present. Aluminium-bound hydrogen was shown to be near to lithium in solutions of $LiAlH_4$ in diethyl ether, tetrahydrofuran, mono- and di-glyme $[MeO(CH_2)_2O(CH_2CH_2O)_nMe$, $n = 0$ or 1]. The NOE measurements on solutions of $LiBH_4$ in Et_2O and NMR spectra of partially deuteriated species suggested the formation of contact ion pairs, with $Li\cdots H_4B$ interactions which were fluxional on the NMR time-scale.

Lithium tetrahydroaluminate, $LiAlH_4$, finds widespread use in both inorganic and organic chemistry as a reducing agent and as a hydride or hydroaluminate transfer reagent.[1,2] It is usually added to a reaction mixture as a solution in diethyl ether (Et_2O) or tetrahydrofuran (thf) and the species in solution have been studied by a variety of techniques, *e.g.* conductance and ebullioscopic measurements on both Et_2O and thf solutions,[3,4] vibrational spectroscopy on samples in Et_2O, thf and monoglyme,[5,6] ^{27}Al[7–10] and ^7Li NMR spectroscopy[8,9] on Et_2O, thf, mono-, di- and tri-glyme $[MeO(CH_2)_2O(CH_2CH_2O)_nMe$ ($n = 0$, 1 or 2)] solutions, and dielectrometry in Et_2O.[6] Results in Et_2O have been interpreted as evidence for ion pairs in dilute solution with multiple-ion formation at higher concentrations.[3–5,8] It has not been established whether the ions within a pair are separated by solvent molecules or whether they are linked by hydrogen bridges as in $[(Et_2O)_2Li(\mu\text{-}H)_2AlH_2]$.[6] Solvent-separated ion pairs were thought to be the major species in thf[3–5,9] and glyme solvents.[5,9,10]

In this paper we describe the structural characterisation of *N*,*N*,*N*′,*N*′-tetramethylethane-1,2-diamine (tmen) complexes of $LiAlH_4$ $[\{Li(tmen)(AlH_4)\}_2]$ **1** and $[Li(tmen)_2][AlH_4]$ **2**, and the use of ^6Li-$\{^1H\}$ heteronuclear Overhauser effect spectroscopy to study their solutions in benzene. This last technique, which relies on the low quadrupole moment of ^6Li and the consequent domination of its relaxation by dipolar interaction with nearby protons, has been used previously in one-dimensional form to study, for example, lithium hydro[tris(trimethylsilyl)methyl] compounds of boron, aluminium, gallium and indium[11] and in two-dimensional form to study organolithium compounds.[12] We also describe ^6Li-$\{^1H\}$ nuclear Overhauser effect (NOE) measurements on solutions of $LiAlH_4$ in Et_2O, thf, mono- and di-glyme and solutions of $LiBH_4$ in Et_2O and compare the conclusions with those derived previously by other methods.

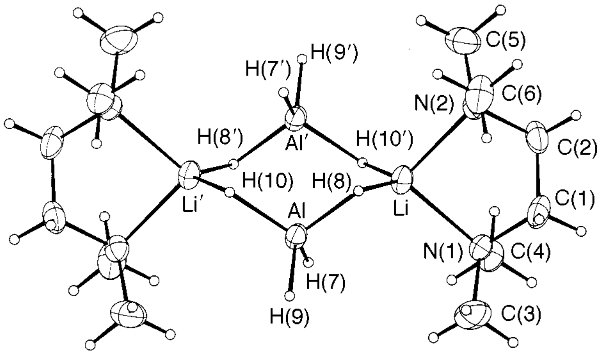

Fig. 1 Molecular structure of compound **1**

Results and Discussion

$LiAlH_4$–tmen complexes

The reaction between $LiAlH_4$ and 1 equivalent of tmen in thf gave, after recrystallisation from toluene, colourless, air-sensitive crystals of the known[13] adduct, $Li(tmen)AlH_4$ in good yield. A crystallographic study showed the structure to consist of centrosymmetric dimers **1** (Fig. 1) based on eight-membered rings similar to those observed in the structures of $Li[AlH_3\{C(SiMe_2Ph)_3\}]\cdot 2thf$ **3**,[14] $Li[AlH_3(C_6H_2Ph_3\text{-}2,4,6)]\cdot 1.5Et_2O$ **4**, $Li[AlH_3(C_6H_2Bu^t_3\text{-}2,4,6)]\cdot 2thf$ **5**, $Li[AlH_3\{N(SiMe_3)_2\}]\cdot 2Et_2O$ **6**[15] and $LiAlH_4\cdot HN(Bu^t)CH(Bu^t)CH_2N(Bu^t)H$ **7**, and suggested for that of $LiAlH_4\cdot HN(Bu^t)CH(Bu^t)CH{=}NBu^t$.[16] Discussion of bond lengths and angles (Table 1) is inevitably tentative because of the high standard deviations associated with bonds to hydrogen. However, the average Al–H bond length within the $Al_2H_4Li_2$ ring of compound **1**, 1.55(3) Å, is at the short end of the range found in the related hydroaluminate derivatives **3**–**7**[14–16] [*cf.* 1.62(4) in **3**, 1.62(4) in **4**, 1.57(4) in **5**,

Table 1 Bond lengths (Å) and angles (°) for $[\{Li(tmen)(AlH_4)\}_2]$ **1**

Al–H(7)	1.55(4)	Al–H(9)	1.50(3)
Al–H(8)	1.52(3)	Al–H(10)	1.59(3)
Li–N(2)	2.090(5)	Li–N(1)	2.095(5)
Li–H(8)	2.04(3)	Li–H(10′)	1.94(3)
H(7)–Al–H(9)	113(2)	H(7)–Al–H(8)	97(2)
H(9)–Al–H(8)	117(2)	H(7)–Al–H(10)	106(2)
H(9)–Al–H(10)	111(1)	H(8)–Al–H(10)	112(1)
N(2)–Li–N(1)	88.2(2)	N(2)–Li–H(8)	100.7(9)
N(1)–Li–H(8)	114.3(8)	N(1)–Li–H(10′)	104.6(8)
N(2)–Li–H(10′)	109.3(8)	H(8)–Li–H(10′)	131(1)

Symmetry transformation: ′ $-x, -y, -z$.

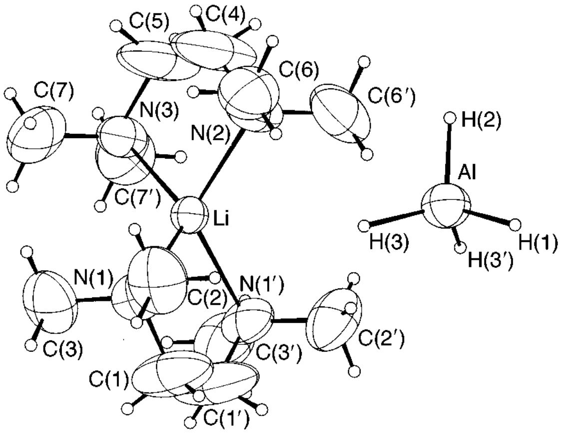

Fig. 2 Molecular structure of compound **2**

1.62(4) in **6** and 1.56(4) Å in **7**]. The average terminal Al–H bond length is 1.53(4) Å so that, as in **3**–**7**, terminal and bridging Al–H bond lengths are similar. The Li–H bond length in **1** [1.99(3) Å] is long [*cf.* 1.77(4) in **4**, 1.78(4) in **6**, 1.85(5) in **7**, 1.93(4) in **3** and 2.00(5) Å in **5**] and the Li–N bond lengths are normal. The ring in **1** is puckered with the two aluminium atoms 0.9 Å above and below, and the two lithium atoms 0.1 Å above and below, the plane defined by the ring hydrogen atoms. Similar puckered rings are found in **3**–**5** and **7** but the ring in **6** is planar. The endocyclic H–Al–H angle in **1** is 112(2)°. Other H–Al–H angles differ somewhat from this value but the mean [109(2)°] is close to those for **3** [105(1)], **4** [106(2)] and **5** [107(3)°] and not significantly different from the tetrahedral value. The H–Li–H angles [131(1) in **1**, 117(1) in **3**, 126(2) in **4**, 103(2) in **5**, 107(2) in **6** and 91(2)° in **7**] show much wider variation. These data suggest that within the dimers the $[AlH_4]^-$ ions retain their integrity so that the species **1** is best described as comprising two $[AlH_4]^-$ anions and two $[Li(tmen)]^+$ cations. The non-planarity of the ring in **3** was attributed to the presence of the large alkyl group attached to aluminium[14] but this steric constraint cannot apply to **1**. Here the puckering is probably associated with the narrow exocyclic N–Li–N angle imposed by the tmen ligand, which in turn affects the endocyclic H–Li–H angle. The structure of **1** differs from that of $[\{Li(tmen)(BH_4)\}_2]$ in which each $[BH_4]^-$ group bridges two lithium centres through three hydrogens (two μ, one μ_3) so that the metal atoms are six- not four-co-ordinate as in **1**.[17] This difference in structure is probably related to the greater size of aluminium as illustrated by the mean Li···B (2.464) and Li···Al (2.972 Å) distances.

The boron compound did not react with an excess of tmen but the reaction between $LiAlH_4$ and an excess of tmen in thf gave $LiAlH_4{\cdot}2tmen$ **2** in high yield. An X-ray study of the colourless, air-sensitive crystals showed that separate $[Li(tmen)_2]^+$ cations and $[AlH_4]^-$ anions (Fig. 2) were packed in a structure of the sodium chloride type (mean Li···Al 5.66 Å).

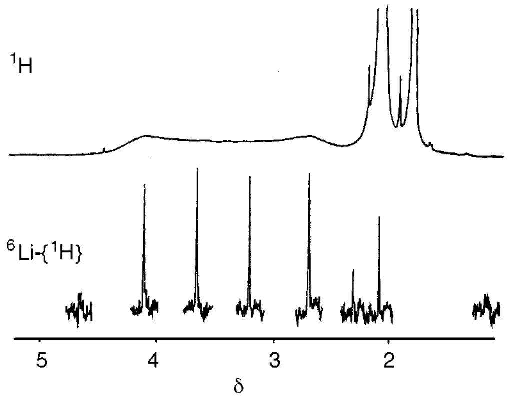

Fig. 3 Proton NMR spectrum of a 0.1 M solution of compound **1** in C_6D_6, and ^6Li-{^1H} difference spectra with signals placed at the positions of the selective irradiation in the ^1H spectrum

The tetrahydroaluminate anion has been structurally characterised previously as the $[NEt_4]^+$ [18] and $[AlH_2L]^+$ [19] salts (L = *N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine or 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane). The mean Al–H distance [1.52(7) Å] in **2** may be compared with values of 1.61(5) Å in $[NEt_4][AlH_4]$ and 1.55(3) Å in $LiAlH_4$.[20] Compound **2** was converted into **1** when it was heated to 120 °C under vacuum.

The dimeric structure of compound **1** in benzene was confirmed by cryoscopic measurements. Fig. 3 shows the ^1H NMR spectrum of a *ca.* 0.1 M solution in C_6D_6; the hydride resonance is exceedingly broad and even in spectra obtained from concentrated solutions only just visible above the baseline. The width of the ^{27}Al-{^1H} peak, 390 Hz, is somewhat broader than those found for $LiAlH_4$ in donor solvents (*ca.* 180 Hz in diethyl ether and as low as 14 Hz in diglyme).[8] The aluminium is thus in an environment similar to that in $[AlH_4]^-$, distorted enough from tetrahedral for ^{27}Al relaxation to broaden the ^1H signal but not enough to cause it to collapse to a single line. The ^6Li-{^1H} difference spectra show enhancements of *ca.* 50% on selective irradiation in the hydride region of the spectrum and *ca.* 38% in the NMe region but not elsewhere. They indicate that the lithium nuclei are close to hydrogen atoms of AlH_4 and NMe fragments. The NMR and cryoscopic data taken together are in accord with the presence in solution of species which are cyclic as in solid **1**. It is not possible to tell whether there is rapid exchange on the NMR time-scale of ionic fragments between rings.

The NMR data for compound **2** were similar to those for **1** and the NOE was strong in both the Al–H and N–Me regions. The ions present in the crystals of **2** cannot therefore be fully separated in solution since if this were the case the NOE in the hydride region would disappear, leaving only a weak enhancement near the NMe signal. Similar results were obtained from solutions of **2** in Et_2O. Since the concentration of solvent-separated ion pairs would be expected to be increased by the addition of base, samples containing a 10-fold excess of tmen were examined. Unfortunately the Al–H and tmen signals now overlapped so that separate enhancements could not be observed but an NOE could still be observed over the whole hydride region. Hence although the solid that separated from solution was the ionic compound **2**, significant Li···H–Al interactions persisted in the supernatant solution. The ionic compound **2** must therefore either dissociate into **1** and free tmen or give other species in which $[AlH_4]^-$ competes successfully with tmen for a place in the co-ordination sphere of lithium. Problems associated with the study of the co-ordination of tmen in solution have been reviewed: it seems that bonds between lithium and tmen can be broken in a wide range of solvent systems.[21]

Table 2 Peak widths of ^{1}H NMR resonances in concentrated solutions of $LiAlH_4$ in diethyl ether

Concentration/M	$\Delta\nu_{\frac{1}{2}}$/Hz
1.92	20
2.36	9.9
4.87	9.1
5.16	8.2
5.85	6.3

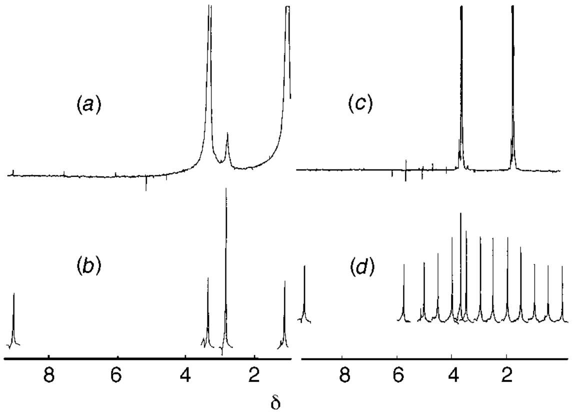

Fig. 4 (*a*) The ^{1}H NMR spectrum of a 1.0 M solution of $LiAlH_4$ in diethyl ether, (*b*) ^{6}Li-{^{1}H} spectra placed at positions of selective irradiation in the proton spectrum, (*c*) the ^{1}H spectrum of a 0.5 M solution of $LiAlH_4$ in thf, and (*d*) ^{6}Li-{^{1}H} spectra placed at positions of selective irradiation in the proton spectrum

Proton and ^{6}Li-{^{1}H} NOE spectra of $LiAlH_4$ in ethers

Diethyl ether. The relationship between solute concentration and ^{27}Al NMR signal widths for solutions of $LiAlH_4$ in Et_2O has been studied previously. The peak width, which is *ca.* 1 kHz at a concentration of 1.0 M, decreases in more dilute solutions so that Al–H coupling may be observed.[8] Conversely, signals from hydrogen atoms bound to aluminium are sharp at high concentrations but become broad upon dilution so that chemical shifts are difficult to determine. Data for a range of concentrations, wider than that reported previously, are given in Table 2. They show that in the more concentrated solutions the environment around aluminium is highly distorted from tetrahedral, the electric field gradient is large, and quadrupole relaxation is so fast that coupling to hydrogen is completely suppressed. At lower concentrations the aluminium environment is less distorted from tetrahedral and the ^{1}H signals are broadened by Al–H coupling. Fig. 4(*b*) shows ^{6}Li-{^{1}H} NMR spectra of $LiAlH_4$ in Et_2O obtained with selective irradiation at various frequencies in the proton spectrum [Fig. 4(*a*)]. The largest NOE (180%) resulted from irradiation of the hydrogen atoms attached to aluminium and there was only a small effect near the methylene and the methyl protons of the diethyl ether. This implies that the hydrogens on aluminium spend a significant proportion of their time close to lithium. In previous work,[8] the ^{7}Li NMR spectra were recorded for solutions of $LiAlH_4$ in Et_2O in the concentration range 3.75–0.0075 M. The linewidths (0.55–2.8 Hz) were concentration dependent but as they changed only negligibly (typically <0.1 Hz) on broad-band decoupling it was deduced that persistent Li–H–Al bridges were absent.[8] It is however notoriously difficult to observe Li–H coupling.[15] Our results suggest that although Li···H–Al interactions may not be stable over periods long enough for Li–H coupling constants to be measured they are sufficient to generate a significant NOE. The effect on ebullioscopic and conductimetric results has been described previously.[3,4]

Tetrahydrofuran. The ^{1}H NMR spectra of a 0.5 M solution of $LiAlH_4$ in thf [Fig. 4(*c*)] showed only solvent signals at δ 1.7 and 3.7; the hydrogen atoms attached to aluminium could not be directly observed, suggesting that the signals were broadened as a result of coupling to nearby aluminium nuclei in nearly tetrahedral environments. The ^{6}Li-{^{1}H} spectra are shown in Fig. 4(*d*). The largest NOE resulted from irradiation of the downfield α-methylene multiplet of thf. This showed that, in contrast to solutions of $LiAlH_4$ in Et_2O, the α-methylene protons of the solvent were close to the lithium. However, the NOE spectra also showed a large effect upon irradiation between the solvent signals in the region where Al–H resonances have been located.[22] The results provide direct evidence for the proximity of lithium and hydroaluminate ions and a method for the determination of values of δ_H for hydrogens attached to aluminium in a system in which direct observation is difficult or heteronuclear decoupling of aluminium is not possible. Although earlier ^{7}Li NMR studies[9] indicated that Li–H scalar coupling was absent, the NOE results show that Li···H–Al bridges are formed at least transiently in 0.5 M solution. When 1 mol equivalent of HCl was condensed into the thf solution at −78 °C the NOE near the α-protons of the solvent remained, and that over the hydride region was suppressed, showing that Li···H–Al interactions were absent. The species in solution were probably solvent-separated ion pairs $[Li(thf)_4][AlCl_nH_{4-n}]$ or chloride-bridged species, *e.g.* $(thf)_3LiClAlH_3$ in which electron-deficient Li–H–Al bridges have been replaced by stronger electron-precise Li–Cl–Al links.

Mono- and di-glyme. The ^{1}H NMR spectra of a 0.5 M solution of $LiAlH_4$ in monoglyme showed a weak sextet [δ 2.90, ^1J(Al–H) 172.8 Hz], resulting from coupling of hydrogen to aluminium nuclei ($I = \frac{5}{2}$), partly obscured by intense solvent signals between δ 3 and 4. In the ^{6}Li-{^{1}H} spectra the largest NOE arose from irradiation of the methylene protons of the solvent, but there was a slightly smaller effect from the hydrogens bound to aluminium with an approximate correlation with maxima at points expected if the signal were a sextet. As with solutions in thf, the NOE results showed that both the methylene protons of the solvent and the hydrogen atoms attached to aluminium were close to the lithium cations. The solutions in diglyme were similar [δ 3.10, ^1J(Al–H) = 173.5; lit.,[10] δ 3.08, ^1J(Al–H) 173 Hz]. Hence the $[AlH_4]^-$ anion is able to compete successfully with the glyme for a place in the lithium coordination sphere even when the aluminium environment is sufficiently symmetrical to allow the sextet in the ^{1}H spectrum to be observed.

Hydrogen–deuterium exchange between $LiBH_4$ and $LiBD_4$ in Et_2O

Solutions of $LiBH_4$ in Et_2O have been investigated by ebullioscopic and conductance measurements,[3] and by vibrational[6,23] and NMR[24] spectroscopy. It has been suggested that the species in solution are either contact ion pairs and multiple ions or hydride-bridged molecular species. Multinuclear NMR and NOE measurements allow a distinction between these two possibilities to be made. The ^{1}H spectra (see Fig. 5) from a 0.5 M solution of $LiBH_4$ in Et_2O show, besides solvent peaks, a sharp quartet due to hydrogens coupled to ^{11}B [^1J(^{11}B–H) = 81.25 Hz] and a less intense septet from hydrogens coupled to ^{10}B nuclei [^1J(^{10}B–H) = 26.6 Hz]. The NOE spectra show that the largest effect results from irradiation of the components of the hydridic quartet and septet, and that a smaller effect is produced upon irradiation of the downfield resonance of the solvent. These results suggest (a) that $LiBH_4$ in Et_2O gives species in which the lithium and hydrogen atoms are close and (b) that the $[BH_4]^-$ anion is not significantly distorted from tetrahedral. Further evidence comes from the isotope shifts in partly deuteriated $LiBH_4$. The ^{1}H NMR spectrum of a 1 : 1 mixture of $LiBH_4$ and $LiBD_4$ in Et_2O (Fig. 6) showed four major features

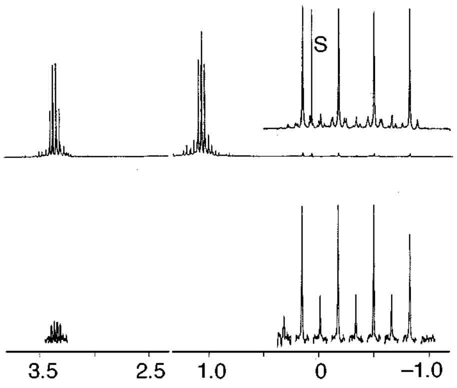

Fig. 5 (*a*) The ^{1}H NMR spectrum of a 0.5 M solution of $LiBH_4$ in Et_2O, (*b*) ^{6}Li-{H} difference spectra with irradiation at various positions in the proton spectrum. The peak marked S is attributed to silicone grease

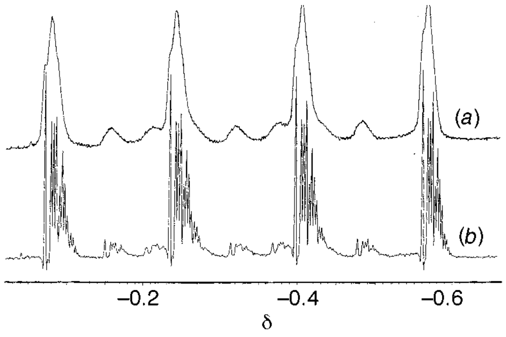

Fig. 6 Proton NMR spectra of a 1 : 1 mixture of $LiBH_4$ and $LiBD_4$ in Et_2O at (*a*) 243 and (*b*) 288 K

which could be assigned to the statistical mixture of isotopomers $[LiBH_{4-n}D_n]^-$ ($n = 0$–3) observed earlier.[24] If there were specific interactions *via* $(\mu\text{-H})_2$ or $(\mu\text{-H})_3$ bridges between lithium and boron there would be a non-uniform equilibrium isotope shift as hydrogen was replaced by deuterium and this non-uniformity would be expected to increase when the sample was cooled. If however the interactions were non-specific and largely electrostatic, only small secondary isotope shifts would be expected. Fig. 6 shows that the second alternative is observed. The resonance centres were shifted only 0.01 ppm to lower frequency for each increase in the value of *n* and although resolution was lost at −30 °C the spectrum had a very similar envelope to that at 25 °C showing that the effect of changing temperature was small. There was also an isotope effect on the coupling constant $^{1}J(^{11}\text{B–H})$, *viz.* $LiBH_4$ 81.3, $LiBH_3D$ 81.1, $LiBH_2D_2$ 80.9 and $LiBHD_3$ 80.6 Hz, corresponding to a monatonic decrease in the value of ^{1}J as *n* increased. The isotope effects on the coupling constant ^{2}J(H–D) (1.56 Hz) were too small to be measured. Similar results have been obtained for $NaBH_{4-n}D_n$ and $KBH_{4-n}D_n$ in ether solvents.[25]

An attempt to make a similar assessment of the specificity of the hydride bridges in the $LiAlH_4$–$LiAlD_4$ system was inconclusive. The ^{1}H-{^{27}Al} NMR spectra of samples of $LiAlH_4$ and $LiAlH_4$–$LiAlD_4$ (1 : 1) in Et_2O gave singlets with $\Delta\nu_{\frac{1}{2}}$ 7 Hz so that with reasonable estimates of the isotope shifts it was clear that the peaks were too broad for signals from individual isotopomers like those in the $LiBH_4$–$LiBD_4$ system to be observed. The asymmetry of the broad signals should however have been sufficient to show the presence of mixed species $LiAlH_nD_{4-n}$. We were surprised therefore to find that the ^{1}H signal in the $LiAlH_4$–$LiAlD_4$ mixture was symmetrical indicating that under our conditions (in Et_2O at 50 °C for 17 h) H–D exchange had not taken place. Hydrogen–deuterium exchange has been observed previously in strong donor solvents such as thf,[26] diglyme[9,26] or MeCN.[26]

Conclusion

The solid obtained from a toluene solution containing $LiAlH_4$ and an equivalent of tmen is the complex **1** in which Li and Al are joined by μ-H bridges. The solid that separates from a toluene solution of $LiAlH_4$ containing an excess of tmen is $[Li(tmen)_2][AlH_4]$ **2**. There are no specific bonds between the anion and cation in the solid **2** but ^{6}Li-{^{1}H} NOE measurements indicate that $[AlH_4]^-$ ions in solution are brought near to Li. Similar Li···H–Al contacts are detected in solutions of $LiAlH_4$ in ether solvents in the absence of amine donors. The Li···H–Al interactions are stronger in diethyl ether or thf than in mono- or di-glyme and apparently determine the structure of the solvent-free solid which crystallises from diethyl ether.[20] The NOE measurements in themselves are not sufficient to distinguish between hydride bridges between specific lithium and aluminiun atoms in well defined species such as **1** and less discriminate fluxional interactions within ion pairs. For $LiBH_4$ in Et_2O the interactions are of the second kind. For $LiAlH_4$ in Et_2O the nature of the interaction is still unclear. The NOE measurements appear to show that whereas the symmetry of the $[AlH_4]^-$ ions is significantly perturbed by the formation of hydrogen bridges, that of the $[BH_4]^-$ ion remains essentially tetrahedral. Although this observed difference between boron and aluminium may result from genuine differences in the nature of the hydride-bridged species, it may simply reflect the different sensitivities of the boron and aluminium nuclei to the symmetry of their environments. More work is required to resolve this problem. Interactions analogous to those described in this paper have been postulated in solutions of the complex $[Li(hmpa)_4][BF_4]$ [hmpa = hexamethylphosphoramide, $P(NMe_2)_3O$] in aromatic solvents.[27]

Experimental

All materials were manipulated by standard Schlenk techniques using a conventional vacuum manifold and argon as a blanket gas. Solvents were dried, by heating under reflux with $LiAlH_4$ for ethers and with sodium for toluene, and subsequently distilled. The compound $LiAlH_4$ (Aldrich) was used as received and tmen (Aldrich) was dried over CaH_2 and then distilled. Solutions of $LiAlH_4$ were made by heating 1 g under reflux in the relevant ether (20 cm^3), filtering through Celite, determining the concentration by decomposing aliquots in 1 M sulfuric or hydrochloric acid, measuring the dihydrogen evolved with a Sprengel pump,[28] and diluting to give the concentrations required. Melting points were measured on samples in sealed capillaries and IR spectra were recorded as Nujol mulls on a Perkin-Elmer 1720 FT spectrometer. For the H–D exchange reaction between $LiBH_4$ and $LiBD_4$ in Et_2O a solution of $LiBD_4$ (0.32 g, 12.5 mmol) and $LiBH_4$ (0.27 g, 12.5 mmol) in Et_2O (50 cm^3) was heated under reflux for 30 min in an atmosphere of argon, allowed to cool to room temperature, and filtered through a medium-porosity glass frit. All NMR spectra were recorded on samples in sealed glass tubes or tubes with rotationally symmetrical poly(tetrafluoroethylene) valves. The ^{1}H NMR spectra were recorded at 90, 250, 360 or 500 MHz using respectively Perkin-Elmer R32, Bruker AC 250, WM 360 or AMX 500 instruments. The ^{7}Li NMR spectra were recorded on a Bruker WP 80 FT spectrometer at 31.14 MHz, a Bruker AC 250 instrument at 73.6 MHz, or a Bruker WM 360 spectrometer at 139.9 MHz; chemical shifts are relative to external aqueous $LiNO_3$. The ^{6}Li NMR spectra were recorded on a Bruker WM 360 spectrometer at 52.99 MHz or an AMX 500 spectrometer at 73.59 MHz. The ^{6}Li NOE difference spectra were obtained by selectively irradiating a resonance in the ^{1}H spectrum for 14 s before obtaining a ^{6}Li spectrum using a 30° pulse and no decoupling during the 8.4 s acquisition period. The procedure was repeated with selective irradiation of an empty region of the ^{1}H spectrum and the two ^{6}Li spectra were subtracted to give the difference spectrum. The value of the NOE enhancement cited was obtained by absolute integration of the two ^{6}Li spectra; the theoretical maximum enhancement is 340%. The power level for the selective irradiation was the same as that used in the more familiar ^{1}H–^{1}H NOE experiment. The ^{27}Al NMR spectra were recorded on a Bruker WM 360 spectrometer at 93.8 MHz; chemical shifts are relative to external $[Al(H_2O)_6]^{3+}$.

Preparations

$LiAlH_4$·tmen 1. A mixture of tmen (0.8 cm^3, 5.3 mmol) and $LiAlH_4$ (0.2 g, 5.27 mmol) was stirred in thf (25 cm^3) for 24 h at 20 °C. Filtration through Celite followed by removal of solvent and crystallisation from toluene gave colourless crystals of compound **1** (0.57 g, 70%), m.p. 179 °C (Found: C, 46.7; H, 12.8; N, 17.7%; M = 310. $C_{12}H_{40}Al_2Li_2N_4$ requires C, 46.7; H, 13.1; N, 18.2%; M = 308). $\tilde{\nu}_{max}$/cm^{-1} (Al–H) 1660s (br) and 1730 (sh); $\delta_H(C_6D_6)$ 1.73 (4 H, CH$_2$) and 2.07 (12 H, CH$_3$); $\delta_C(C_6D_6)$ 46.0 (CH$_3$) and 56.5 (CH$_2$); $\delta_{Li}(C_6D_6)$ 0.47; $\delta_{Al}(C_6D_6)$ 103 [qnt, J(Al–H) 172 Hz, $\Delta\nu_{\frac{1}{2}}$ (^{27}Al-{^{1}H}) 391 Hz].

$LiAlH_4$·2tmen 2. A mixture of tmen (2.0 cm^3, 13.3 mmol) and $LiAlH_4$ (0.2 g, 5.27 mmol) was stirred at 60 °C in thf (25 cm^3) for 6 h. After cooling to 20 °C and filtration through Celite the solvent was removed to give a white solid. Crystallisation from toluene gave colourless crystals of compound **2** (1.28 g, 90%) (Found: C, 52.5; H, 13.1; Al, 10.0; Li, 2.7; N, 20.8. $C_{12}H_{36}AlLiN_4$ requires C, 53.3; H, 13.4; Al, 10.0; Li, 2.6; N, 20.7%). $\tilde{\nu}_{max}$/cm^{-1} (Al–H) 1651s (br); $\delta_H(C_6D_6)$ 2.0 (8 H, CH$_2$) and 2.07 (24 H, CH$_3$); $\delta_C(C_6D_6)$ 46.0 (CH$_3$) and 57.3 (CH$_2$); $\delta_{Li}(C_6D_6)$ 0.45; $\delta_{Al}(C_6D_6)$ 103 [qnt, J(Al–H) 171 Hz, $\Delta\nu_{\frac{1}{2}}$ (^{27}Al-{^{1}H}) = 365 Hz].

Crystallography

Crystal data. For **1**, $C_{12}H_{40}Al_2Li_2N_4$, M = 308.3, monoclinic, space group $P2_1/n$ (no. 14), a = 7.839(2), b = 15.802(5), c = 9.132(6) Å, β = 98.17(4)°, U = 1119.7(9) Å^3, Z = 2, D_c = 0.91 Mg m^{-3}, F(000) = 344. Colourless, air-sensitive block 0.4 × 0.3 × 0.3 mm, μ(Mo-Kα) = 0.13 mm^{-1}, T = 173 K.

Data collection and processing: CAD4 diffractometer, θ–2θ scan, Mo-Kα radiation, λ = 0.710 73 Å, $2 < \theta < 25°$, 1967 unique reflections giving 1400 with $I > 2\sigma(I)$, no absorption or decay correction. Structure analysis and refinement: direct methods (SHELXS 86),[29] full-matrix least-squares refinement on all F^2 using SHELXL 93,[30] all non-H atoms anisotropic, hydride H atoms located on a difference map and freely refined with isotropic thermal parameters, ligand H atoms included in riding mode with $U_{iso}(H) = 1.2\ U_{eq}(C)$ or $1.5\ U_{eq}(C)$ for methyl groups. $R1 = \Sigma(||F_o| - |F_c||)/\Sigma|F_o| = 0.049$ [for $I > 2\sigma(I)$], $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{\frac{1}{2}} = 0.138$, S = 1.03 (for all data).

For **2**, $C_{12}H_{36}AlLiN_4$, M = 270.4, orthorhombic, space group $Pnma$, a = 18.146(2), b = 11.616(5), c = 9.438(3) Å, U = 1989.4(11) Å^3, Z = 4, D_c = 0.90 Mg m^{-3}, F(000) = 608, colourless air-sensitive needle 1.0 × 0.4 × 0.15 mm (in a capillary), μ(Mo-Kα) = 0.10 mm^{-1}, T = 293 K, 1833 reflections, for $2 < \theta < 25°$, no absorption or decay correction.

Refinement on F^2 using SHELXL 93, non-H atoms anisotropic, hydride H atoms located on a difference map and positions refined, ligand H atoms in riding mode, $R1$ = 0.072 [for 502 reflections with $I > 2\sigma(I)$ and 98 parameters], $wR2$ = 0.367, S = 1.02 (for all data). Both the anion and cation lie on a crystallographic mirror plane, with consequent averaged positions for the disordered central CH_2CH_2 groups of the tmen ligands.

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