Dalton Trans

ARTICLE

Reactivity and Catalytic Activity of *tert*-Butoxy-Aluminium Hydride Reagents

Robert J. Less,* Hayley R. Simmonds and Dominic S. Wright*

The reactivity and catalytic activities of the *tert*-butoxy aluminium hydride reagents $[({}^{t}BuO)_{x}AlH_{3-x}]$ [x = 1 (**1**), 2 (**2**)] and $(L)Li[({}^{t}BuO)_{2}AlH_{2}]$ [L = THF (**3**), 1,4-dioxane (**4**)] are investigated. The structural characterisation of the novel compounds **3** and **4** shows that the nature of the hydridic species present is affected dramatically by the donor ligand coordinating the Li^{+} cation. Stoichiometric reaction of **1** with pyridine gives $[(1,4-H-pyrid-1-yl)_{4}Al]^{-}[(pyridine)_{4}AlH_{2}]^{+}$ (**5**) while reaction with the amine-borane $Me_{2}NHBH_{3}$ in the presence of PMDETA $[(Me_{2}NCH_{2}CH_{2})_{2}NMe]$ affords $[(PMDETA)AlH_{2}]^{+}[(BH_{3})_{2}NMe_{2}]^{-}$ (**6**). The reagents **1**, **2**, **3** and **4** catalyse the dehydrocoupling reaction of the amine-borane $Me_{2}NHBH_{3}$ into the ring compound $[Me_{2}NBH_{2}]_{2}$, with the activity descreasing in the order **1** $\gg$ **2** $\sim$ **3** > **4**. The greater reactivity of the neutral dihydride **1** provides the potential basis for future catalytic optimisation.

1. Introduction

Transition metal organometallics have played a central role in single-site heterogeneous catalysis across an immense spectrum of organic transformations.[1] However, recently it has become clear that molecular and catalytic activation may not be the sole domain of transition metals but that these attributes can be extended to main group elements, despite the lack of accessible *d*-orbitals in the valence shell. A leading example of this shift in perception is the remarkable activation of small molecules by completely non-metallic frustrated Lewis pairs and recent developments of this concept towards molecular catalysis.[2] More recently, direct parallels have even been seen between the catalytic behaviour of main group metal complexes and transition metals in some key reactions.[3] A case in point is the recent realisation that various main group metal complexes are active in the catalytic dehydrocoupling of element-H bonds into element-element bonds (Scheme 1).[4] This development is significant for a number of reasons, not least because main group metals are cheaper, more plentiful and in many cases more environmentally benign than transition metal counterparts (particularly commonly used 4*d* and 5*d* metals[5]). However, the most obvious problem which is still to be overcome in replacing transition metals by main group metals in heterogeneous catalysis is the generally lower activity of main group metals than the most active transition metal counterparts.

Our interest in this field has focused on the applications of *p*-block metal bases (*e.g.*, metal amides) as reagents for stoichiometric and catalytic homoatomic (P-H/P-H[6] or N-H/N-H[7]) and heteroatomic (B-H/N-H) dehydrocoupling.[8-10] Studies by ourselves and others have shown that there is a close relationship between the mechanism of transition metal-mediated dehydrocoupling and main group mediated counterparts.[8-10] In particular, hydride intermediates have been observed in both the main group and transition metal reactions.[4] For this reason we have switched from using main group bases as precatalysts in these systems (which are converted into the active metal hydrides *in situ*) to employing metal hydrides directly as the catalytic species.[8b,c]

$$E\text{-}H \ + \ H\text{-}E \ \longrightarrow \ E\text{-}E \ + \ H\text{-}H$$

Scheme 1 Dehydrocoupling of a *p*-block element-H bond to give the E-E bond and H_2.

As the most common metal in the Earth's crust and one which forms many stable hydride compounds, aluminium is a particularly attractive metal to use in this setting. We showed in a recent study that even $LiAlH_4$ functions as a catalyst in the dehydrogenation of the amine-borane Me_2NHBH_3 into $[Me_2NBH_2]_2$.[8c] However, relatively low activity was observed because of the low solubility of $LiAlH_4$ in most organic solvents. In the current study we have set out to explore the reactivity and catalytic activity of a series of Al^{III} hydrides containing ${}^{t}BuO$-substituents of the type $[({}^{t}BuO)_{x}AlH_{3-x}]$ [x = 1 (**1**), 2 (**2**)] and $(L)Li[({}^{t}BuO)_{2}AlH_{2}]$ [L = THF (**3**), 1,4-dioxane (**4**)]. The primary conclusion of this work is that of this series of compounds the neutral dihydride **1** exhibits superior catalytic activity and selectivity in the dehydrocoupling reaction with the amine-borane Me_2NHBH_3. This provides, to our knowledge,

the first confirmation that the catalytic activity of the Al^{III} hydride catalysts (or indeed of any other main group metal-based catalyst) is structure dependent, in the same way as transition metal based catalysts. This study therefore potentially opens the door to the optimisation of Al^{III} catalysts through ligand modification.

2. Results and Discussion

2.2 Aluminium Hydride Reagents

The aluminium (III) hydrides $(^tBuO)AlH_2$ (**1**) and $(^tBuO)_2AlH$ (**2**) were obtained from the reactions of AlH_3 (generated *in situ* from $LiAlH_4$ and $AlCl_3$) with ^tBuOH (1 or 2 equivalents for **1** and **2**, respectively) in THF using the literature procedures.[11] Both compounds have dimeric structures in the solid state, as shown in Figure 1. The new lithium salts $(THF)Li[(^tBuO)_2AlH_2]$ (**3**) and $(1,4\text{-dioxane})Li[(^tBuO)_2AlH_2]$ (**4**) were prepared by the reactions of ^tBuOH (2 equivalents) with $LiAlH_4$ (1 equivalent) in thf or 1,4-dioxane in crystalline yields of 33 and 50% yield, respectively (Scheme 2).†
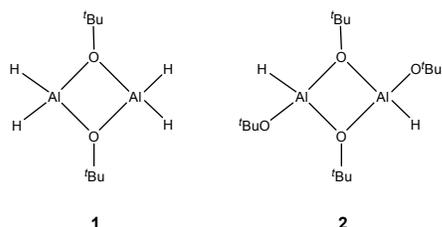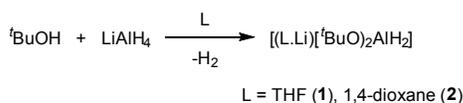

Figure 1 Structures of the aluminium hydride reagents **1** (left) and **2** (right).

$$^tBuOH + LiAlH_4 \xrightarrow[-H_2]{L} [(L{\cdot}Li)[^tBuO)_2AlH_2]$$

L = THF (**1**), 1,4-dioxane (**2**)

Scheme 2 Synthesis of the new Al^{III} hydrides **1** and **2**.

Since the unsolvated Mg compound $[Mg\{(^tBuO)_2AlH_2\}_2]$ has been reported previously, having a ion-paired dimeric molecular arrangement composed of Mg^{2+} cations and $[(^tBuO)_2AlH_2]^-$ anions,[12] we anticipated a similar composition for **3** and **4**. However, surprisingly the X-ray structures of both complexes revealed that their true nature is highly sensitive to the Lewis base ligand present. Rather than being composed of Lewis base solvated Li^+ cations and $[(^tBuO)_2AlH_2]^-$ anions **3** has the molecular formula $[(THF{\cdot}Li)_2(AlH_4)\{(^tBuO)_4Al\}]$ (**3**), consisting of AlH_4^- and $[(^tBuO)_4Al]^-$ anions, and can be regarded as an ionic tautomer of the expected formulation.‡ This is seen in the view of the asymmetric unit of **3** in which the formula units are associated *via* $Li{\cdots}H$ bonding (Figure 2a), the result of which is the formation of a complicated honeycomb lattice structure built from cyclic $[(THF{\cdot}Li)_2(AlH_4)(^tBuO)_2Al]_4$ fragments (Figure 2b). The $Li{\cdots}H$ interactions in **3** [range 1.90(3)-1.95(3)Å] are in a similar

range to those reported previously in lithium aluminium hydride derivatives.[13]

Although only relatively poor quality crystal data could be obtained for **4** despite repeated attempts, its structural arrangement is nonetheless unambiguous.‡ In contrast to the solid-state structure of **3**, the 1,4-dioxane complex **4** is constructed from the expected anion units, being composed of 1,4-dioxane-solvated Li^+ cations and $[(^tBuO)_2AlH_2]^-$ anions (Figure 3). The polymeric arrangement of **4** results exclusively from bridging of the 1,4-dioxane ligands between Li^+ centre, with no further $Li{\cdots}H$ interactions linking the zig-zagged chains together.
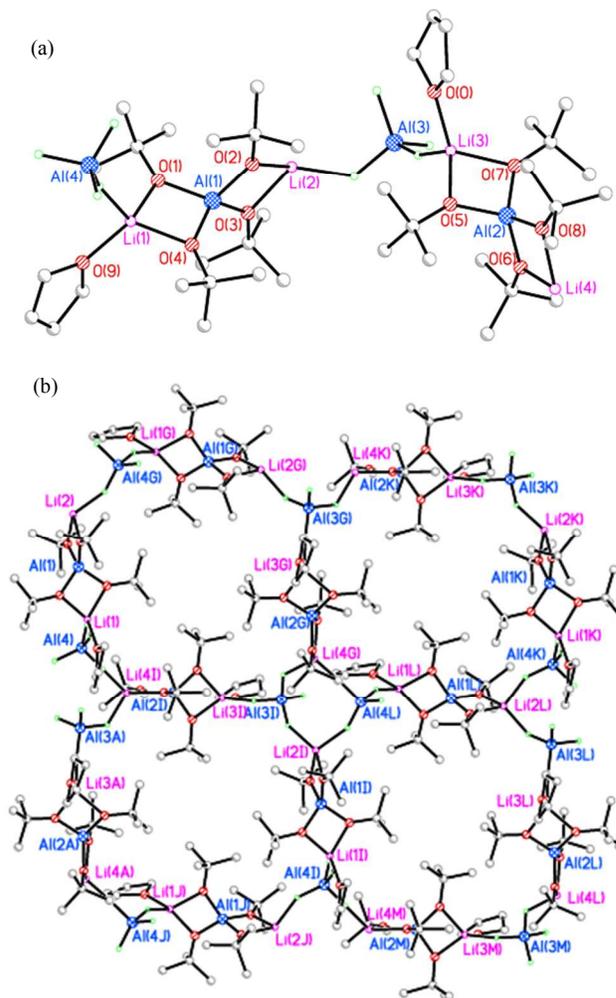

Figure 2 (a) The asymmetric unit in the structure of $(THF)Li[(^tBuO)_2AlH_2]$ (**3**) and (b) the polymeric structure formed by $H{\cdots}Li$ bridging. Selected bond lengths (Å) and angles (°): Al-O range 1.744(2)-1.752(2), Al-H range 1.51(4)-1.62(3), Li-O range 1.933(5)-1.960(5), $Li{\cdots}H$ 1.90(3)-1.95(3). Symmetry transformations used to generate equivalent atoms, A *x, y, z*, B *-x, -y, z* + $^1/_2$, C *x* + $^1/_2$, *-y* + $^1/_2$, *z*, D *−x* + 1/2, *y* + $^1/_2$, *z* + $^1/_2$.
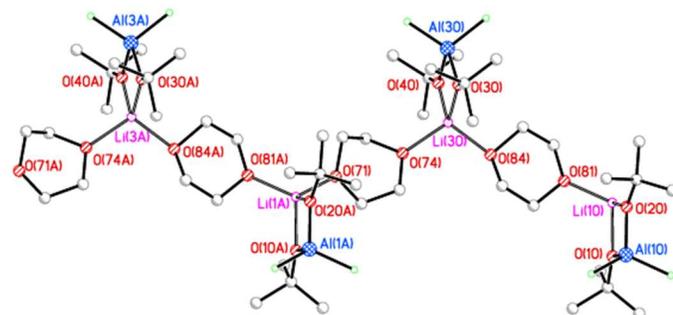
Figure 3 The zig-zagged chain polymer of (1,4-dioxane)Li[(^{t}BuO)$_2$AlH$_2$] (**4**). The extensive disordering of the C-atoms of the dioxane rings and of some of the ^{t}Bu groups has been omitted for clarity. Selected bond lengths (Å) and angles (°): Al-O range 1.745(7)-1.780(7), Li-O range 1.90(2)-2.01(2). Symmetry transformations used to generate equivalent atoms, A *x, y, z*, B -*x, y* + $^1/_2$, -*z*.

The view of **3** and **4** as representing 'ionic-isomers' is emphasized by the observation that both complexes can readily be interconverted (the notional equilibrium being shown in Scheme 3). If **3** is dissolved in 1,4-dioxane then **4** is crystallised (as shown by unit cell analysis). The ^{7}Li and ^{27}Al NMR spectra of **3** and **4** in THF are also identical, indicating that complete disproportionation of the [(^{t}BuO)$_2$AlH$_2$]$^-$ anion of **4** into [(^{t}BuO)$_2$AlH$_2$]$^-$ and AlH$_4^-$ occurs. The H-coupled ^{27}Al spectra of **3** or **4** in THF are particularly diagnostic, showing the presence of a broad resonance at *ca.* δ 107 for the [Al(O^{t}Bu)$_4$]$^-$ anion and a binomial quintet for the AlH$_4^-$ anion at δ 94.0. The observed influence of the ligand in dictating the structure of the tautomer in the case of **3** and **4** is related to previous studies of the coordination of multidentate nitrogen Lewis base ligands (L) to AlH$_3$·NMe$_3$ (which gives 'asymmetric-cleavage' salts of the type LAlH$_2^+$AlH$_4^-$; L = PMDETA [(Me$_2$NCH$_2$CH$_2$)$_2$NMe] and the cyclam [N(Me)CH$_2$CH$_2$]$_4$).[14] The well documented disproportionation of a range of salts of the type M[(RO)$_{4-x}$AlH$_x$] (M = Li, Na) in THF is also relevant.[15] However, it should be noted that our conclusion concerning the disproportionation of the [(^{t}BuO)$_2$AlH$_2$]$^-$ anion of **4** (Scheme 3) is at variance with that proposed by Nöth *et al.*, who suggested that redistribution of Li[(^{t}BuO)$_2$AlH$_2$] gives the monohydride Li[(^{t}BuO)$_3$AlH] and LiAlH$_4$. This conclusion appears to have resulted from the mis-assignment of the ^{27}Al resonance for glass (at *ca.* δ 75) to a third solution species, which was assumed to be the [(^{t}BuO)$_3$AlH]$^-$ anion (see ESI).[15]

$$Li_2[(^tBuO)_4Al][AlH_4] \rightleftharpoons 2\,Li[(^tBuO)_2AlH_2]$$

Scheme 3 The notional equilibrium between the 'ionic-isomers' found in complexes **3** and **4**.

A further, if not unexpected, property of these aluminium hydride reagents is their ability to undergo H-/D-exchange with pyridine.[16,17] The ^{1}H NMR spectrum of **1** in D$_5$-pyridine at room temperature initially shows a number of ^{t}BuO resonances in the region δ 1.3-1.6, in addition to a singlet for the hydride ligands of **1** (*ca.* δ 5.2) (Figure 4, ESI). After 48 h all of the Al-H ligands seen at *ca.* δ 5.2 have completely

exchanged for deuterium. After reflux for 1h it is clear from the aromatic region that a mixture of 2-, 3- and 4-H-deutero-pyridine has been formed (see the insert to Figure 4). These observations are similar to those made previously by Tanner *et al.* on the reaction of LiAlH$_4$ with pyridine, who found that the H/D-exchange process occurs through 1,2- and 1,4-dihydridopyrid-2-yl intermediates.[17]
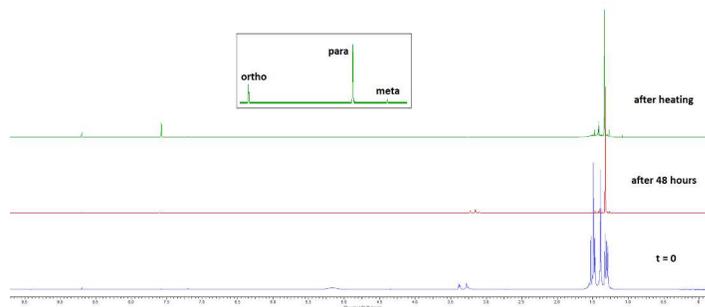

Figure 4 ^{1}H NMR spectra of **1** in D$_5$-pyridine (from bottom) after initial mixing (t = 0), 48 h and after brief reflux.

Crystallisation of the reaction of pyridine with **1** gave the new complex [(1,4-H-pyrid-1-yl)$_4$Al]$^-$[(pyridine)$_4$AlH$_2$]$^+$ (**5**)† whose single-crystal structure was obtained.‡ Compound **5** consists of octahedral Al^{III}-hydride cations and tetradehral Al^{III} 1,4-H-dihydridopyrid-2-yl anions (Figure 5). A persistent disorder in the cation of **5** is the presence of *ca.* 0.15 of an OH group superimposed at each of the hydride positions. This could not be eliminated even by using seemingly rigorously CaH$_2$-dried pyridine in the reaction and despite repeated data collections on different crystals from different batches of product. One possible explanation for this is that the -OH groups are generated by loss of propene from the ^{t}BuO groups initially present in the precursor **1** (Scheme 4). A radical pathway may be possible in this case as radical intermediates have been implicated in the reaction of AlH$_4^-$ with pyridine previously.[16,17]

Structurally characterised [LAlH$_2$]$^+$ cations like that seen in **5** have been reported previously, with the six-coordinate cyclam cation [(N(Me)CH$_2$CH$_2$)$_4$AlH$_2$]$^+$ being the closest relative.[14] In addition, the [Al(1,4-H-pyrid-1-yl)$_4$]$^-$ anion has been observed previously in the structure of [Li(pyridine)$_4$]$^+$[Al(4-H-pyrid-1-yl)$_4$]$^-$, obtained from the reaction of LiAlH$_4$ with pyridine.[18] The Al-N bond lengths present in the anion of **5** [Al(1)-N range 1.852(2)-1.855(2) Å] are identical to those reported in this previous example [1.863(4) Å] within the crystallographic errors, while the Al-N bonds within the cation of **5** are consistent with coordinative interactions [Al(2)-N range 2.085(2)-2.093(2) Å].[18]

The ^{1}H NMR spectrum of crystalline **5** in THF at room temperature is also entirely consistent with the proposed formulation, with two distinct sets of resonances being observed for the pyridine ligands (δ 7.5-9.0) and 1,4-H-dihydropyrid-1-yl anions (δ 3.0-6.0). The chemical shifts of the three resonances for the 1,4-H-dihydropyrid-1-yl are almost identical to those previously assigned for [Li(pyridine)$_4$]$^+$[Al(1,4-H-dihydropyrid-1-yl)$_4$]$^-$ in toluene [at δ 3.02 (4-H$_2$), 3.93 (3,5-H) and 5.90 (2,6-

H)].[17] However, unlike this previous report there is *no* sign of any 1,2-dihydropyrid-1-yl anions being present in equilibrium with the 1,4-H-dihydropyrid-1-yl anions for **5**.
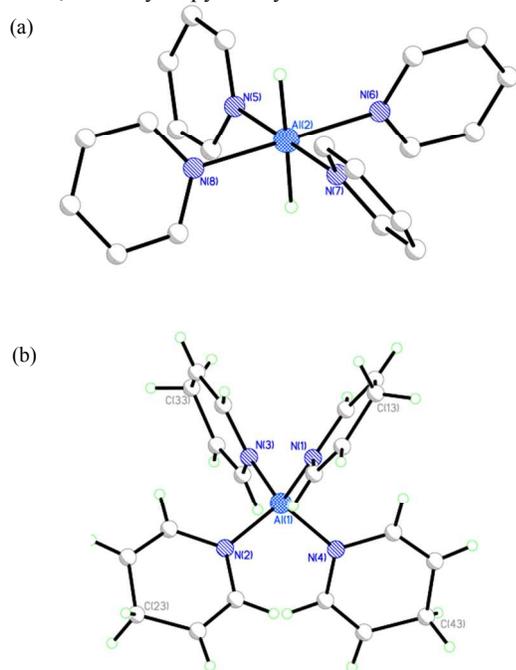

Figure 5 The structures of (a) the cation and (b) the anion in the ion separated structure of [(1,4-H-pyrid-1-yl)$_4$Al]$^-$[(pyridine)$_4$AlH$_2$]$^+$ (**5**). Selected bond lengths (Å) and angles (°); Al(1)-N range 1.852(2)-1.855(2), Al(2)-N 2.085(2)-2.093(2), N-Al(1)-N range 108.60(7)-110.09(7). H-atoms on the 4-H positions were directly located in the difference map. Symmetry transformations used to generate equivalent atoms, A *x, y, z*, B -*x, -y, -z*.
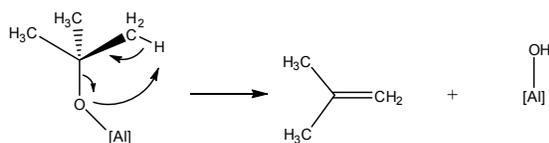
Scheme 4 Proposed formation of the Al-OH disorder *via* elimination of propene.

The previous solution and solid-state studies of **1**, **3** and **4** emphasised the importance of the choice of solvent in further studies of these species as catalysts in dehydrocoupling reactions.

2.3 Catalytic Studies of 1, 2, 3 and 4

The catalytic activities of **1**, **2**, **3** and **4** were assessed by monitoring the formation of the products of the reactions of each with the amine-borane Me$_2$NHBH$_3$ using *in situ* ^{11}B NMR spectroscopy in D$_8$-THF and D$_8$-toluene (using 10 mol% loading of the reagents to amine-borane) (ESI). This amine-borane has often been employed as a test substrate in this area since the main products have very diagnostic chemical shifts [i.e., the B$_2$N$_2$ ring compound [Me$_2$NBH$_2$]$_2$ (t., δ = 5.2, $^1J_{BH}$ = 108) and the short-chain compound (Me$_2$N)$_2$BH (d., δ = 28.6, $^1J_{BH}$ =130Hz].[8-10]

Since the solution species present in **3** and **4** are identical in THF (see previous discussion), catalytic studies in this solvent were only undertaken on **1**, **2** and **3**. The ^{11}B NMR spectroscopic studies in THF show that after stirring for up to 4 days at room temperature a variety of species are generated using **1**, **2** and **3** (depending on the reagent used), including the deprotonated amine-borane [Me$_2$NBH$_3$]$^-$ (lit. quart., δ -13.6[8c]), (Me$_2$N)$_2$BH (d., δ 28.6), [(BH$_3$)$_2$NMe$_2$]$^-$ (lit. quart., *ca.* δ -11.1[8c]), [H$_3$BN(Me$_2$)BH$_2$NMe$_2$]$^-$ (lit. t., δ 2.5, quart. δ -13.6[8c]) and BH$_4^-$ (lit. quint., δ -42.2[8c]). However, after reflux (16h) it is clear that the reaction of **3** is far from complete, with very little of the ring product [Me$_2$NBH$_2$]$_2$ being generated and with a significant amount of [(BH$_3$)$_2$NMe$_2$]$^-$ and BH$_4^-$ present.[8c] This situation is similar to the final reaction mixture produced after reflux in the case of **2**. In the case of **1**, however, *very* clean conversion of Me$_2$NHBH$_3$ into the ring compound [Me$_2$NBH$_2$]$_2$ is apparent after reflux and noticeably there is no chain product (Me$_2$N)$_2$BH, [(BH$_3$)$_2$NMe$_2$]$^-$ or BH$_4^-$ generated in the reaction at any time (Figure 6 and ESI). Although the activity of **1** is clearly much greater than that of **2** or **3** in THF, disappointingly, only *ca.* 33% conversion of Me$_2$NHBH$_3$ to [Me$_2$NBH$_2$]$_2$ occurs using **1** even after reflux so that under these conditions the reaction is at best sub-stoichiometric.

Changing the solvent from THF to toluene has a large effect on the activity of **1** with Me$_2$NHBH$_3$ (largely because of the higher temperature that can be reached). Figure 7 shows selected *in situ* ^{11}B NMR spectra of this reaction. Like the reaction in THF, after 4 days at room temperature the reaction mixture consists largely of the deprotonated amine-borane, [Me$_2$NBH$_3$]$^-$, with almost no other intermediates being found (ESI). After reflux, however, very clean and now almost completely quantitative formation of the ring compound [Me$_2$NBH$_2$]$_2$ is observed, with only trace amounts of the chain compound (Me$_2$N)$_2$BH and BH$_4^-$ being formed. This activity is *far* greater than that observed for **2**, **3** or **4** under the same conditions in toluene, with the overall order of activity being **1** >> **2** ~ **3** > **4** (*cf.* **1** >> **2** ~ **3** in THF). The particularly low reactivity of **4**, which exhibits almost no conversion into the ring [Me$_2$NBH$_2$]$_2$ product or chain product (Me$_2$N)$_2$BH in toluene, is partly due to its low solubility. The selectivity of **1** in toluene can be compared to that of **2** and **3** which produce a much broader range of products after reflux. In addition to the normal products of dehydrocoupling, [Me$_2$NBH$_2$]$_2$ and [(Me$_2$N)$_2$BH], two other minor species are observed which are not present in any of the other catalytic reactions of **1-4** in THF or toluene. These species were tentatively assigned to the oligomer [-Me$_2$NBH$_2$-]$_n$ (br. s., *ca.* δ 22)[19] and the heteroleptic chain compound [(^{t}BuO)(Me$_2$N)BH] (d., δ 26.8, $^1J_{BH}$ = 128 Hz).[20] The latter presumably arises from competing nucleophilic addition of Al-bonded ^{t}BuO groups to the B-atom of Me$_2$N=BH$_2$ (see the intermediate of the far right in Scheme 5, later).
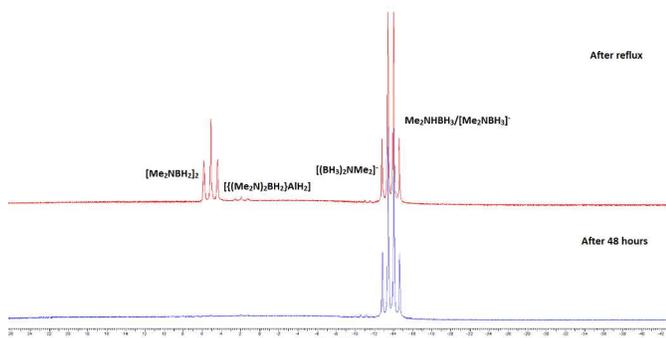
Figure 6 (a) *In situ* ^{11}B NMR spectra of the reaction of the amine-borane Me$_2$NHBH$_3$ with **1** in THF, (a) after 48 h at room temperature (in D$_8$-THF), (b) reflux for 16h.
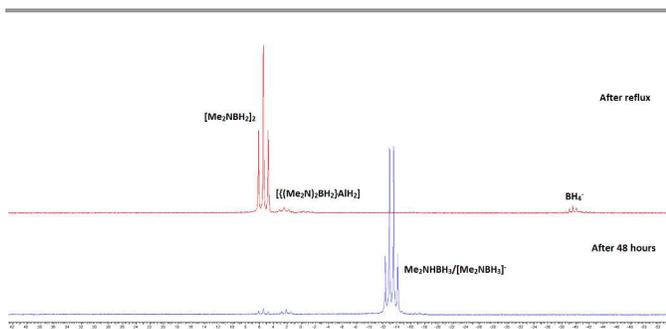

Figure 7 (a) *In situ* ^{11}B NMR spectra of the reaction of the amine-borane Me$_2$NHBH$_3$ with **1** in toluene, (a) after 48 h at room temperature (in toluene), (b) reflux for 16h.

The primary products and intermediates observed in the *in situ* NMR studies of the catalytic dehydrocoupling of Me$_2$NHBH$_3$ with **1**, **2**, **3** and **4** are similar to those found previously using LiAlH$_4$, and suggest that a similar mechanism and side-reactions are involved. Since no free Me$_2$N=BH$_2$ (t., δ 38.2)^{21} is observed in any of the *in situ* ^{11}B NMR spectroscopic studies of the catalytic or stoichiometric reactions using **1-4**, a mechanism involving metal-bonded Me$_2$N=BH$_2$ is most likely in the formation of the major product of the reaction [Me$_2$NBH$_2$]$_2$ (Scheme 5). The presence of the BH$_4^-$ and [(BH$_3$)$_2$NMe$_2$]$^-$ anions in the reactions involving **2**, **3** and **4** in in THF or **1**, **2**, **3** and **4** in toluene is explained by β-Al→B or δ-Al→B abstraction reactions of the [Me$_2$NBH$_3$]$^-$ or [H$_3$BMe$_2$BH$_2$NMe$_2$]$^-$ (Scheme 6).^{8c} Evidence in support of δ-Al→B is provided by the formation of [{H$_2$B(NMe$_2$)$_2$}AlH$_2$] in all of these reactions (δ 2.62) (Scheme 5, bottom reaction).^{8a,b} This species is also observed during and at the end of reactions involving **1** (see Figures 6 and 7). The presence of the [(H$_3$B)$_2$(NMe$_2$)]$^-$ anion was also supported by crystallisation of the 1 : 1 reaction of **1** with Me$_2$NHBH$_3$ in the presence of PMDETA [(Me$_2$NCH$_2$CH$_2$)$_2$NMe] which gave the new complex [(PMDETA)AlH$_2$]$^+$[(H$_3$B)$_2$(NMe$_2$)]$^-$ (**6**)† which was structurally characterised (Figure 8).‡ The [(PMDETA)AlH$_2$]$^+$ cation of **6** has been observed previously

in [(PMDETA)AlH$_2$]$^+$[AlH$_4$]$^-$ which was obtained by crystallisation of AlH$_3$·NMe$_3$ in the presence of PMDETA,^{14} while the only other structurally-authenticated example containing the [(H$_3$B)$_2$(NMe$_2$)]$^-$ anion is the unsolvated salt [Li[(H$_3$B)$_2$(NMe$_2$)].^{8c} The structural parameters found in the cation and anion of **6** are similar to those observed in these previous examples. Interestingly, like complex **5** (Figure 5) the ^{t}BuO ligands of **1** have been lost in this reaction.
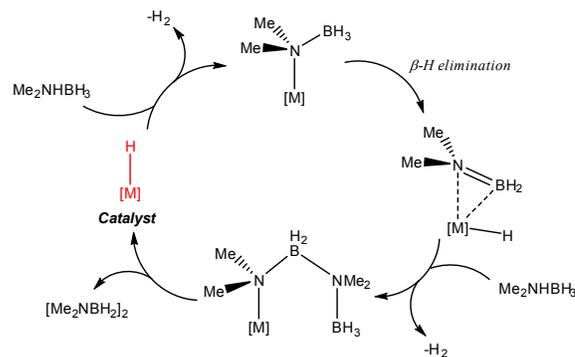
Scheme 5 General mechanism proposed for dehydrocoupling of amine boranes (the potential side reactions are not shown).
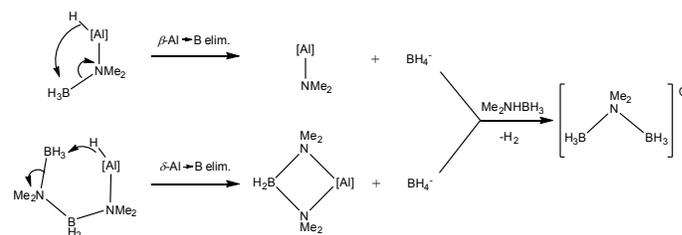
Scheme 6 Potential pathways to the formation of the [(H$_3$B)$_2$NMe$_2$]$^-$ anion in the reactions of **1**, **2** and **3** with Me$_2$NHBH$_3$. [Al] = a general Al centre coordinated by a variety of ligands.
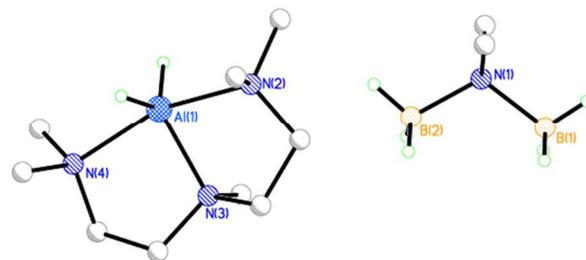

Figure 8 Structure of the salt [(PMDETA)AlH$_2$]$^+$[(H$_3$B)$_2$(NMe$_2$)]$^-$ (**6**). Non-hydridic H-atoms have been omitted for clarity. Selected bond lengths (Å) and angle (°); Al(1)-H range 1.46(3)-1.52(3), Al(1)-N(3) 2.018(2), Al(1)-N(2,4) range 2.145(2)-2.153(2), range, B(1)-N(1,2) range 1.581(4)-1.598(4), N(3)-Al(1)-N(2,4) 82.88(9)-82.0(1), B(2)-N(1)-B(1) 113.5(2). Symmetry transformations used to generate equivalent atoms, A *x, y, z*, B -*x, -y, -z*.

Conclusions

In the current study alkoxy-aluminium hydrides have been applied as stoichiometric and catalytic reagents, to our knowledge, for the first time. The solid-state structural and solution NMR studies of the new compounds **3** and **4** provide direct evidence of the influence of solvation on the nature of alkoxy aluminate anions, with these species representing ionic tautomers (*i.e.*, 2[(^{t}BuO)$_2$AlH$_2$]$^-$ vs. [(^{t}BuO)$_4$Al]$^-$ + AlH$_4$$^-$). This and the reactivity of reagent **1** with pyridine stress the importance of the choice of reaction solvents in the study of these species as catalysts.

Of all of the alkoxy aluminium hydrides investigated **1** exhibits by far the greatest activity in the catalytic dehydrocoupling reaction of [Me$_2$NHBH$_3$]. Perhaps the simplest but most important conclusion that can be made from the current study, which has compared the reactivity of a closely related series of alkoxy-aluminium hydrides, is that the catalytic activity of the Al^{III} hydride reagents is indeed structure dependent and can be drastically altered by changes in the number of alkoxide and hydride groups. There is therefore the potential to optimise the activity of main group metal systems further using the type of methodology that is already well established in the optimisation of transition metal catalysts.

Although we cannot provide a full explanation as to why **1** is the most active catalyst in the dehydrocoupling reaction investigated, based on the limited evidence available so far, it is clear from the current work that the catalytic activity of **1** with Me$_2$NHBH$_3$ is similar to that of LiAlH$_4$ but it is more selective in terms of the fewer side reactions/products generated.[8c] The premise on which our further studies in this area will develop is that dihydrides like **1** might offer an optimum balance between the number of hydridic groups available for reaction, the steric crowding of the Al^{III} centre and the tendency for completing β-Al$\rightarrow$B or δ-Al$\rightarrow$B abstraction. It is interesting to note in this respect that the dimeric structure of **1** (Figure 1) is very closely related to the highly active catalyst [(^{i}Pr$_2$N)AlH$_2$]$_2$ which has been identified in the dehydrocoupling reaction of Al(NMe$_2$)$_3$ with ^{i}Pr$_2$NHBH$_3$.[8b]

Notes and references

^{a} Chemistry Department, Cambridge University, Lensfield Road, Cambridge CB2 1EW (U.K.); E-mail dsw1000@cam.ac.uk, rjl1003@cam.ac.uk.

† **Synthesis of 3, 4, 5 and 6:** All syntheses were carried out on a vacuum-line under argon atmosphere. Products were isolated and handled with the aid of a N$_2$-filled glove box (Saffron type α). ^{1}H NMR spectra were recorded on a Bruker Advance 500 MHz spectrometer. Elemental analysis was obtained on a Perkin Elmer 240 Elemental Analyser.

Synthesis of [(THF)Li[(^{t}BuO)$_2$AlH$_2$] (**3**): A solution of ^{t}BuOH (7.7 g, 104 mmol) in 10 ml thf was added dropwise to a solution of LiAlH$_4$ (2.0 g, 52

mmol) in 25 ml thf at 0°C. The reaction mixture was allowed to warm to room temperature and was stirred for a further 2h. The solution was filtered through a glass sinter and the volume of solvent was decreased under reduced pressure until the onset of crystallisation occurred. The solution was heated to re-dissolve the crystals and then allowed to cool slowly to room temperature then to -30°C to complete the crystallisation. The white crystalline product was collected by filtration, washed with *n*-hexane (10 ml) then dried *in vacuo*. Yield 3.72 g, 33 %. ^{1}H NMR (500.1 MHz, +25ºC, D$_8$-THF), δ = 1.12 (mult., 9H, ^{t}BuO), 1.80 (mult., 4H, THF), 3.65 (mult., 4H, THF) (the Al-H resonance was not observed). ^{7}Li NMR (194.4 MHz, +25ºC, D$_8$-THF, rel. to saturated LiCl/D$_2$O), δ = -0.06 (s). ^{27}Al (proton coupled) NMR (130.3 MHz, +25ºC, D$_8$-THF, rel. to a 1.10 mol dm^{-3} Al(NO$_3$)$_3$ in D$_2$O), δ = *ca.* 107 (br. s, [(^{t}BuO)$_4$Al]$^-$), 94.0 (quint., $^1J_{Al-H}$ = 174.0 Hz, AlH$_4$$^-$ 22). Found %: C 55.0; H 11.9; C$_{40}$H$_{48}$Al$_2$Li$_2$O$_5$ requires: C 55.0; H 11.1.

Synthesis of (1,4-dioxane)Li[(^{t}BuO)$_2$AlH$_2$] (**4**): A solution of ^{t}BuOH (1.48g, 20 mmol) in 5 ml 1,4-dioxane was added dropwise to a suspension of LiAlH$_4$ (380 mg, 10 mmol) in 5 ml 1,4-dioxane at room temperature. The reaction mixture was heated under reflux for 2h then filtered through a glass sinter whilst still hot. Cooling of the solution to room temperature resulted in crystallisation of the product, which was collected by filtration and dried *in vacuo*. Yield 1.34 g, 50 %. ^{1}H NMR (500.1 MHz, +25ºC, D$_8$-THF), δ = 3.58 (mult., 8H, 1,4-dioxane), 1.76 (s, 2H, Al-H), 1.25 (mult., 18H, ^{t}BuO) (the Al-H resonance was not observed). ^{7}Li NMR (194.4 MHz, +25ºC, D$_8$-THF, rel. to saturated LiCl/D$_2$O), δ = -0.06 (s). ^{27}Al (proton-coupled) NMR (130.3 MHz, +25ºC, D$_8$-THF, rel. to a 1.10 mol dm^{-3} Al(NO$_3$)$_3$ in D$_2$O), δ = *ca.* 107 (br. s, [(^{t}BuO)$_4$Al]$^-$), 94.0 (quint., $^1J_{Al-H}$ = 174.0 Hz, AlH$_4$$^-$ 22). Found %: C 53.2; H 10.4; C$_{12}$H$_{28}$AlLiO$_4$ requires: C 53.3; H 10.4.

Synthesis of [Al(NC$_5$H$_6$)$_4$][AlH$_2$(NC$_5$H$_5$)$_4$] (**5**): Pyridine (3ml) was added to **1** (200 mg, 0.98 mmol) in a Schlenk tube which was cooled to -78°C. The mixture was allowed to warm to 0°C and the resulting yellow solution was stirred at this temperature for 5h. The volume of the solvent was decreased to *ca.* 1ml under reduced pressure and the mixture was transferred to a narrow (approx. 1 cm wide) crystallisation tube, carefully layered with 5 ml *n*-hexane and allowed to stand, undisturbed for 2d after which yellow plates had formed. The supernatant was removed *via* syringe and the product washed with 5 ml *n*-hexane. The yellow crystals were collected and allowed to dry on filter paper. Yield 80 mg, 18 %. ^{1}H NMR (500.1 MHz, +25ºC, D$_8$-THF), δ = 8.82 (s., 8H, *o*-C-H pyridine), 7.93 (mult., 8H, *p*-C-H pyridine), 7.53 (multi., 8H, *m*-C-H pyridine), 5.90 (mult., 8H, 2,6-C-H, 1,4-H-dihydropyrid-1-yl), 4.58 (br. s, 2H, Al-H), 3.93 (mult., 8H, 3,5-H, 1,4-H-dihydropyrid-1-yl), 3.02 (s., 8H, 4-H 1,4-H-dihydropyrid-1-yl). ^{27}Al NMR (130.3 MHz, +25ºC, D$_8$-THF, rel. to Al(NO$_3$)$_3$ in D$_2$O in D$_2$O), δ = 100.0 (s., Al-H). Found %: C 68.8; H 6.7; N 15.8; C$_{40}$H$_{46}$Al$_2$N$_8$ requires: C 69.4; H 6.7; N 16.2.

Synthesis of [(PMDETA)AlH$_2$]$^+$[(H$_3$B)$_2$(NMe$_2$)]$^-$ (**6**): In a narrow (approx. 1 cm diameter) Schlenk tube, PMDETA (0.24 ml, 1.15 mmol) was added to a stirred solution of ^{t}BuOAlH$_2$ (118 mg, 1.15 mmol) in 1ml toluene at 0°C. The mixture was stirred at this temperature for 1h, then Me$_2$NBH$_3$ (68 mg, 1.15 mmol) was added to the cooled mixture. The resulting effervescing solution was allowed to warm to room temperature and stirred for a further 16h. *n*-Hexane (5ml) was carefully layered onto the toluene solution and the tube allowed to remain undisturbed for 2d after which time needle-shaped crystals had formed. The supernatant liquid was removed *via* syringe and the crystals were collected and allowed to dry on a piece of filter paper. Yield 55 mg (17 %). ^{1}H NMR (500.1 MHz, +25ºC, D$_8$-THF), δ = 2.70 (s., 3H, NMe PMBETA), 2.53 (s., 12H, NMe$_2$ PMDETA), 2.20 (br. s., 8H, -CH$_2$-PMDETA), 2.18 (s., 6H, Me$_2$N [(BH$_3$)$_2$NMe$_2$]$^-$ anion), 1.55 (quart. (1:1:1:1), $^1J_{BH}$ = 90 Hz, 6H, BH$_3$ of anion) (the Al-Hs could not be clearly identified). ^{11}B NMR (160.48 MHz, +25ºC, D$_8$-THF, rel. to BF$_3$·Et$_2$O in CDCl$_3$), δ = −10.4 (quart., $^1J_{BH}$ = 96.3Hz). Found %: C 47.3, H 13.2, N 18.9; C$_{11}$H$_{37}$AlB$_2$N$_4$ requires: C 48.2, H 13.6, N 20.2.

‡ **X-ray Crystallographic Studies of 3, 4, 5 and 6**: All data were collected on a Nonius KappaCCD Diffractometer equipped with an Oxford Cryostream cooling device. Crystals were mounted directly from solution using perfuorohydrcarbon oil to prevent atmospheric oxidation, hydrolysis and solvent loss.[23] Data were solved by direct methods and refined by full-matrix least squares on F^2.[24] Details of the data collections and structural refinements are given in Table 1.

Table 1 Details of the data collections and structural refinements of (THF)Li[(^{t}BuO)$_2$AlH$_2$] (**3**), (1,4-dioxane)Li[(^{t}BuO)$_2$AlH$_2$] (**4**), [[(1,4-H-pyrid-1-yl)$_4$Al]$^-$ [(pyridine)$_4$AlH$_2$]$^+$ (**5**) and [(PMDETA)AlH$_2$]$^+$[(H$_3$B)$_2$(NMe$_2$)]$^-$ (**6**).

Compound*	3	4	5	6
Chemical formula	C$_{40}$H$_{96}$ Al$_4$Li$_4$O$_{10}$	C$_{36}$H$_{84}$Al$_3$Li$_3$O$_{12}$	C$_{40}$H$_{46}$Al$_2$N$_8$ O$_{0.30}$	C$_{11}$H$_{37}$Al B$_2$N$_4$
FW	872.85	810.79	697.61	274.05
Crystal system	Orthorhombic	Monoclinic	Triclinic	Triclinic
Space group	Pna2(1)	P21(n)	P-1	P-1
Unit cell dimensions				
a (Å)	17.6391(2)	15.7387(4)	10.6722(3)	6.0538(4)
b (Å)	20.0133(2)	11.7343(3)	13.5757(4)	12.6086(6)
c (Å)	16.0589(2)	15.7462(3)	13.6681(4)	13.3970(9)
α (°)	-	-	90.244(2)	114.250(2)
β (°)	-	112.603(2)	101.867(2)	93.497(2)
γ (°)	-	-	93.413(1)	99.234(3)
V (Å^3)	5669.06(11)	2684.68(11)	1934.2(1)	911.08(10)
Z	4	2	2	2
ρ_{calc} (Mg/m^3)	1.023	1.003	1.198	0.999
μ (Mo-Kα) (mm^{-1})	0.125	0.115	0.115	0.103
reflections collected	35011	25789	15742	8576
independent reflections (R_{int})	6952 (0.042)	2859 (0.018)	4994 (0.049)	4054 (0.087)
R1 [$I>2\sigma(I)$]	0.041	0.110	0.043	0.075
wR2 (all data)	0.112	0.331	0.106	0.170

* Additional data: λ = 0.70926; T = 180(2) K.

The hydridic H-atoms were all located in the structures of **3**, **4**, **5** and **6**. Three data sets were collected on **4**, all of which exhibit twinning (arising from the similarity of the *a* and *c* crystal axes). The data were refined using TWIN and BASF commands (final 0.43). If these commands are not used then a final R-factor of 28% is obtained. In addition, the three bridging 1,4-dioxane in the asymmetric unit and two of the ^{t}Bu groups are disordered (each of the disordered atoms being modelled over two 50 : 50 sites). Despite these problems, all six of the Al-H atoms were clearly visible in the difference map. Anisotropic displacement parameters were assigned to the Al and O atoms only. Each Li and C atom was assigned one of four common isotropic displacement parameters (one for the Li atoms, two for the ^{t}Bu groups and one for the dioxane rings), a process which reduced the total number of LS parameters to 316 and significantly improved the parameter to data ratio.

Electronic Supplementary Information (ESI) available: ^{1}H, ^{27}Al, ^{7}Li, ^{11}B NMR spectra of **3**, **4** , **5** and **6**. ^{1}H NMR study of the reaction of **1** with D$_5$-pyridine. Reactions of **1**, **2**, **3** and **4** with Me$_2$NHBH$_3$ in toluene and THF (10 mol% loading and 1:1 stoichiometric). CCDC numbers 981533-

981536 contain the crystallographic files for **3**, **4**, **5** and **6**. See DOI: 10.1039/b000000x/

1. J. P. Collman, L. S. Hegedus, J. R. Norton and R. C. Finke, *Principles and Applications of Organotransition Metal Chemistry*, University Science Books,U.S., Mill Valley, CA, 2nd edn., 1987.
2. D. W. Stephan, *Org. Biomol. Chem.*, 2008, **6**, 1535; D. W. Stephan and G. Erker, *Angew. Chem. Int. Ed.*, 2010, **49**, 46; G. Erker, *Pure and Appl. Chem.*, 2012, **12**, 2203; S. K. Ritter, *Chem. Eng. News*, 2012, **90**, 21.
3. P. P. Power, *Nature*, 2010, **463**, 171.
4. R. J. Less, R. L. Melen and D. S. Wright, *RSC Advances*, 2012, **2**, 2191.
5. C. W. Hamilton, R. T. Baker, A. Staubitz and I. Manners, *Chem. Soc. Rev.*, 2009, **38,** 279; A. Staubitz, A. P. M. Robertson, M. E. Sloan and I. Manners, *Chem Rev.*, 2010, **110**, 4023.
6. (a) R. J. Less, R. L. Melen, V. Naseri and D. S.Wright, *Chem. Commun.*, 2009, 4929; (b) V. Naseri, R. J. Less, M. McPartlin, R. E. Mulvey and D. S. Wright, *Chem. Commun.*, 2010, **46**, 5000.
7. R. J. Less, V. Naseri, M. McPartlin and D. S. Wright, *Chem. Commun.*, 2011, **47**, 6129.
8. B–H/N–H coupling; H. J. Cowley, M. S. Holt, R. L. Melen, J. M. Rawson and D. S. Wright, *Chem. Commun.*, 2011, **47**, 2682; (b) M. M. Hansmann, R. L. Melen and D. S. Wright, *Chem. Sci.*, 2011, **2**, 1554; (c) R. J. Less, H. R. Simmonds, S. B. J. Dane and D. S. Wright, *Dalton Trans.*, 2013, **42**, 6337.
9. For examples of dehydrocoupling involving Group 2 B–H/N–H coupling see, (a); J. Spielmann, G. Jansen, H. Bandmann and S. Harder, *Angew. Chem., Int. Ed.,* 2008, 47, 6290; (b) J. Spielman and S. Harder, *J. Am. Chem. Soc.*, 2009, **131**, 5064; (c) J. Spielmann, M. Bolte and S. Harder, *Chem. Commun.*, 2009, 6934; (d) D. J. Liptrot, M. S. Hill, M. F. Mahon and D. J. MacDougall, *Chem.–Eur. J.*, 2010, **16**, 8508; (e) J. Spielmann, D. F.-J. Piesik and S. Harder, *Chem.–Eur. J.*, 2010, **16**, 8307; (f) M. S. Hill, M. Hodgson, D. J. Liprot and M. F. Mahon, *Dalton Trans.*, 2011, **40**, 7783; (g) P. Bellham, M. S. Hill, D. J. Liptrot and D. J. MacDougall, M. F. Mahon, *Chem. Commun.*, 2011, **47**, 9060.
10. For an example involving Group 3 B–H/N–H coupling see, M. S. Hill, G. Kociok-Köhn and T. P. Robinson, Chem. Commun., 2010, **46**, 7587.
11. M. Veith, S. Faber, H. Wolfanger and V. Huch, *Chem. Ber.* 1996, **129**, 381.
12. M. Veith, A. Altherr and H. Wolfanger, *Chem. Vap. Deposition*, 1999, **5**, 87.
13. Search of the Cambridge Crystallographic Data Base (December, 2013), (Al-)H··Li range 1.53-2.80 (mean 1.94).
14. J. L. Atwood, K. D. Robinson, C. Jones and C. L. Raston, *Chem. Commun.*, 1991, 1697.
15. H. Nöth, A. Schlegel, J. Knizek, I. Krossing, W. Ponikwar and T. Seifert, *Chem. Eur. J.*, 1998, **4**, 2191. See Figure 2 of this paper.
16. P. T. Lansbury and J. O. Peterson, *J. Am. Chem. Soc.*, 1963, **85**, 2236.
17. D. D. Tanner and C.-M. Yang, *J. Org. Chem.*, 1993, **58**, 1840.
18. K. Hensen, A. Lemke, T. Stumpf, M. Bolte, H. Fleischer, C. P. Pulham, R. O. Gould and S. Harris, *Inorg. Chem.*, 1999, **38**, 4700.
19. K. A. Erickson, D. S. Wright and R. Waterman, *J. Organomet. Chem.*, in press.
20. P. Belham, M. S. Hill, G. Kociok-Köhn and D. J. Liprot, *Chem. Commun.*, 2013, **49**, 1960.

21. T. Beweries, H. Hansen, M. Kessler and M. Klahn, U. Rosenthal, *Dalton Trans.*, 2011, **40**, 7689.

22. Nuclear Magnetic Resonance, Specialist Periodical Reports, Ed. G. A. Webb, RSC, pp. 98.

23. T. Kottke and D. Stalke, *J. Appl. Crystallogr.* **1993**, *26*, 615.

24. G. M. Sheldrick, SHELX-97, Göttingen, 1997.

Graphical *Abstract*

Reactivity and Catalytic Activity of *tert*-Butoxy-Aluminium Hydride Reagents

R. J. Less, H. R. Simmonds and D. S. Wright
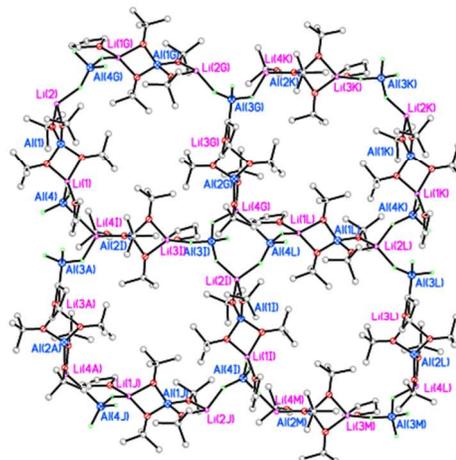
The reactivity and catalytic activity of the *tert*-butoxy aluminium hydride reagents $[(^tBuO)_xAlH_{3-x}]$ $[x = 1$ (**1**), 2 (**2**)] and $(L)Li[(^tBuO)_2AlH_2]$ [L = THF (**3**), 1,4-dioxane (**4**)] were investigated. These reagents exhibit interesting reactivity and catalyse the dehydrocoupling reaction of the amine-borane Me_2NHBH_3 into the ring compound $[Me_2NBH_2]_2$, with the activity in toluene decreasing in the order **1** >> **2** ~ **3** > **4**. The greater reactivity of the neutral dihydride **1** provides the potential basis for future catalytic optimisation.