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Dalton Transactions

ARTICLE

Multiple Deprotonation of Primary Aromatic Diamines by LiAlH$_4$

Robert J. Less,*[,a] Lucy. K. Allen,[a] Alexander Steiner[b] and Dominic S. Wright[a]

Reaction of LiAlH$_4$ with 1,2-phenylenediamine (**1**H$_4$) in THF results in formation of the metallocyclic amido-/imido complex [{Al(**1**H$_2$)}$_2${Al(**1**H)$_2$}$_2$][Li(THF)$_2$]$_4$ (**3**), while in the presence of various Lewis base ligands 1,8-diaminonaphthalene (**2**H$_4$) gives the amido-('ate') complexes [Al(**2**H$_2$)$_2$]$^-$[Li(LL')]$^+$ [L = THF, L' = PMDETA (*N,N,N',N',N''*-pentamethyldiethylenetriamine) (**4**); L = L' = TMEDA (*N,N,N',N'*-Tetramethylethylenediamine) (**5**)]. The latter complexes provide evidence of intermediates in the proposed reaction pathway for formation of the cyclic framework of the tetraanion [{Al(**1**H$_2$)}$_2${Al(**1**H)$_2$}$_2$]$^{4-}$ of **3**.

1. Introduction

Group 13 amido (R$_2$N$^-$) and imido (RN^{2-}) compounds are important classes of main group metal nitrogen compounds owing to their potential use in a number of synthetic and technologically-important applications, such as reagents for organic and inorganic transformations and single-source precursors for technologically important III/V semiconductor materials (*e.g.*, AlN and GaN).[1] More recent developments in lithium amido aluminate chemistry include derivatives based on TMP (2,2,6,6-tetramethylpiperidide) as reagents to effect the metalation of aromatic compounds.[2] Group 13 *amido* (R$_2$N$^-$) and *imido* (RN^{2-}) compounds have been obtained using a broad range of synthetic routes.[3]

One interesting class of these compounds are alkali metal primary-amido aluminium 'ate' complexes containing [Al(NHR)$_4$]$^-$ anions,[4] which can be employed as precursors for imido complexes *via* deprotonation of the Al-bonded RNH-groups with strong organometallic bases such as ^{n}BuLi.[5] This approach to imido aluminium compounds can, however, suffer from the drawback that the NH protons may not be reactive enough to effect deprotonation, with the result that the RNH functionality of the precursor is retained and the ^{n}BuLi base molecules are simply incorporated into the resulting cage structure.[6] Alternatively, separate studies by Roesky, Chivers and Nöth have shown that direct reactions of lithium and sodium aluminium hydride (MAlH$_4$; M = Li or Na) with secondary (R$_2$NH) and mono-functional primary amines (RNH$_2$) can be employed to produce a range of amido- and mixed amido/imido lithium 'ate' compounds.[7]

Our current focus on this area stems jointly from long standing interests in the synthesis and structural chemistry of main group metal imido complexes and their phosphanediide (RP^{2-}) counterparts[8] and from a more recent realization that key reagents which we have employed in their synthesis can be used to effect stoichiometric and catalytic dehydrocoupling of a range of bonds.[9] Pertinent to the current study, we have found that the reaction of the redox-active superbase mixture Sb(NMe$_2$)$_3$/^{n}BuLi with the 1,2-(PH$_2$)$_2$C$_6$H$_4$ results in the formation of the benzo-1,2,3-triphosphilide anion [C$_6$H$_4$P$_3$]$^-$ *via* a process involving a stepwise oxidative coupling of the P-H bonds (Scheme 1a), in combination with the reduction of Sb^{III} to a Zintl compound.[10] Remarkably, the same type of coupling occurs in the case of the reaction of the diamine analogue *o*-phenylene diamine, 1,2-(NH$_2$)$_2$C$_6$H$_4$, with the superbase mixture Sn(NMe$_2$)$_2$/^{n}BuLi at elevated temperature, which gives the benzo-1,2,3-triazolyl anion and Sn metal (Scheme 1b).[11]

(a)

(b)
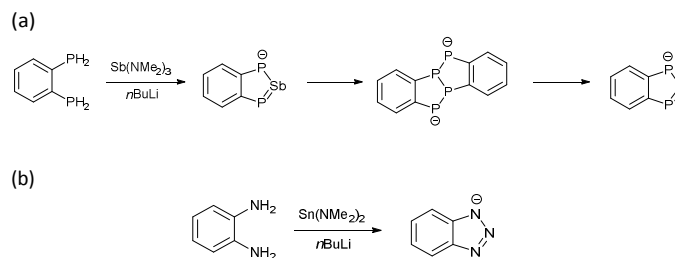
Scheme 1 Reactivity of 1,2-C$_6$H$_4$(EH$_2$)$_2$ (E = N, P) with *p*-block metal bases and ^{n}BuLi.

Such N-H/N-H coupling is extremely rare even in the case of transition metal-mediated reactions and may have broader scope in the synthesis of a range of nitrogen heterocycles.[12]

Most recently it was found that amides, like Al(NMe$_2$)$_3$, and hydrides, such as (^{t}BuO)AlH$_2$ and LiAlH$_4$, are effective pre-catalysts for N-H/B-H dehydrocoupling.[13] With this background in mind, we focus in the current study on the reactions of the most readily available reagent of this class (LiAlH$_4$) with aromatic diamines, with a view to exploring whether this simple reagent might also be capable of N-H/N-H dehydrocoupling.

2. Results and Discussion

Following on from previous studies in this area, we selected 1,2-phenylenediamine (**1**H$_4$) and 1,8-diaminonaphthalene (**2**H$_4$) as substrates for the current investigations (Fig. 1). Although **1**H$_4$ and **2**H$_4$ and anions derived from their deprotonation have been used extensively as ligands for a large number of transition metal complexes,[14,15] only three examples of Group 13 complexes containing the doubly-deprotonated [**1**H$_2$]$^{2-}$ ligand are known (*i.e.*, deprotonated at each of the NH$_2$ groups, see Scheme 2).[16] In addition, only one example of a main group metal complex containing the [**2**H$_2$]$^{2-}$ has been structurally characterized previously (*i.e.*, again with deprotonation at each of the NH$_2$ groups, see Scheme 3).[17]
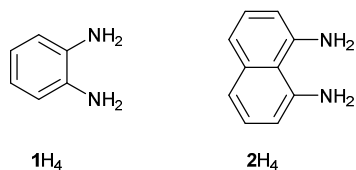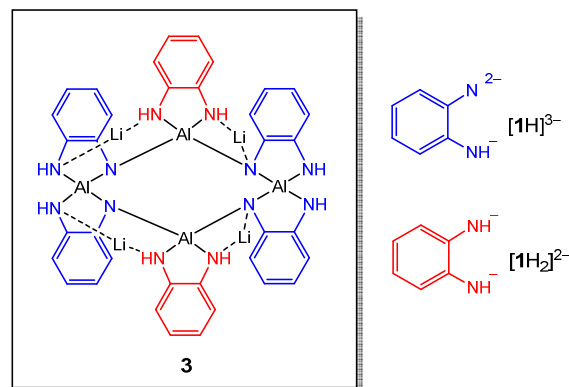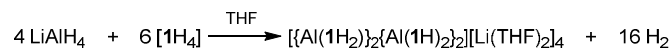

Fig. 1 Structures of the precursor diamines used in the current work **1**H$_4$ and **2**H$_4$.

Addition of solid LiAlH$_4$ to solutions of the diamines **1**H$_4$ or **2**H$_4$ using various stoichiometries in THF results in rapid exothermic reactions with the visible evolution of H$_2$ gas and the formation of colourless to light yellow solutions. Particular care had to be taken to ensure the rigorous exclusion of air from these reactions as the solutions generated react instantaneously with traces of atmospheric oxygen to give blue, purple or brown solutions (depending on the degree of contamination). Initially, a 1:1 ratio of the diamines to LiAlH$_4$ was employed in trial reactions, with the intention of fully deprotonating both amine groups to give the tetraanions [**1**]$^{4-}$ and [**2**]$^{4-}$. Unfortunately, in both cases the products of these reactions could not be isolated despite numerous attempts at crystallization. However, using a reduced ratio of LiAlH$_4$ with **1**H$_4$ (2 : 3, respectively) in THF allowed the isolation of highly air-sensitive colourless crystals of the new aluminium complex [{Al(**1**H$_2$)}$_2$[Al(**1**H)$_2$]$_2$][Li(THF)$_2$]$_4$ (**3**) in 48% yield, containing doubly and triply-deprotonated **1**H$_2$$^{2-}$ and **1**H^{3-} anions (Scheme 2).

The room-temperature ^{1}H NMR spectrum of crystalline **3** in D$_8$-THF (ESI) shows two distinct sets of aromatic C-H resonances for the [**1**H]$^{3-}$ [δ 6.16 (s) and 6.08 (s)] and [**1**H$_2$]$^{2-}$ [δ 5.0-6.5 (br. mult.)] ligands in the correct 1:1 ratio. However, the

NH protons of these anions are indistinguishable and only appear as a broad singlet (δ 3.08 ppm), but with the correct 24:8 ratio with respect to the total aromatic C-H protons. Reducing the temperature failed to resolve these resonances, possibly implying fast scrambling of the H-atoms between the [**1**H]$^{3-}$ and [**1**H$_2$]$^{2-}$ ligands.

$$4\ \text{LiAlH}_4 \quad + \quad 6\ [\mathbf{1H_4}] \quad \xrightarrow{\text{THF}} \quad [\{\text{Al}(\mathbf{1H_2})\}_2\{\text{Al}(\mathbf{1H})_2\}_2][\text{Li}(\text{THF})_2]_4 \quad + \quad 16\ \text{H}_2$$
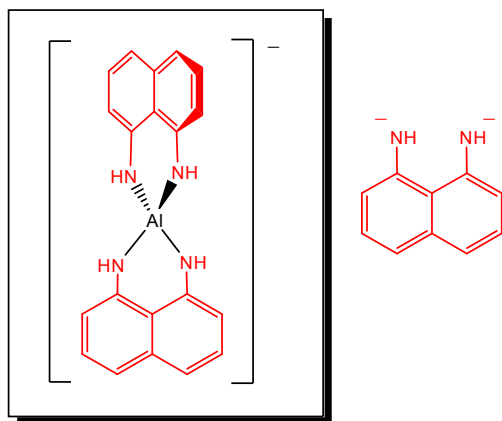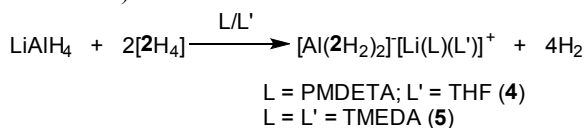

Scheme 2 The stoichiometry of the reaction producing **3**, showing the structure of the complex and the observed deprotonation pattern of the [**1**H$_4$] substrate.

A further feature of the ^{1}H NMR spectra of samples of **3**, which were dried under vacuum prior to transfer to a glove box for analysis, is the lower than expected integral of the THF ligands. This feature is probably largely responsible for the higher than expected N analysis found for isolated samples of the complex (found 14.3% *vs.* 12.5 %; although the C and H analyses were acceptable).

Double- and single-deprotonation of the NH$_2$ groups of monofunctional aliphatic and aromatic primary amines has been seen before using LiAlH$_4$.[7b,c] An example is the reaction of DippNH$_2$ (Dipp = 2,6-^{i}PrC$_6$H$_3$) which gives the dimer [Al{(DippNH)$_2$}$_2$(μ-NDipp)][Li(THF)]$_2$.[7b] However, to the best of our knowledge the current study represents the first investigation of the reactions of LiAlH$_4$ with aromatic diamines. The formation of the triply-deprotonated [**1**H]$^{3-}$ trianion in **3** is similar to that seen in the reaction of **1**H$_4$ with Sn(NMe$_2$)$_2$/^{n}BuLi at room temperature,[11] while the quadruple-deprotonation of **1**H$_4$ (to [**1**]$^{4-}$) only appears to occur in the presence of the more basic reagent mixture Sb(NMe$_2$)$_3$/^{n}BuLi.[18]

Reactions of **2**H$_4$ with LiAlH$_4$ proceeded in a similar manner to those with **1**H$_4$, but the products appeared to be much less sensitive to traces of oxygen. Although a variety of reaction conditions and different reactant stoichiometries were employed, only products resulting from double deprotonation of **2**H$_4$ could be isolated and only in the presence of chelating donor ligands. The new complexes [Al(**2**H$_2$)$_2$]$^-$[Li(PMDETA)(THF)]$^+$ (**4**) and [Al(**2**H$_2$)$_2$]$^-$[Li(TMEDA)$_2$]$^+$ (**5**) are obtained in highest yields (48% and 53%, respectively) from the 1:2 stoichiometric reactions of LiAlH$_4$ with **2**H$_4$ in THF, in presence of an excess of the Lewis base donor ligands PMDETA and TMEDA (respectively) (Scheme 3). Unlike the room temperature ^{1}H NMR spectrum of **3**, the ^{1}H NMR spectra

of **4** and **5** are well resolved in the aromatic region of the [**2**H$_2$]$^{2-}$ dianion ligands (ESI). The 1,8-naphthyl groups in both appear in the range δ 5.8-6.6, with the N-H protons being found at δ 3.8. The ^{1}H NMR spectra of **5** also show that a significant amount of residual THF is preserved in crystalline samples of the complex after isolation under vacuum. Both C, H and N analysis and integration of the ^{1}H NMR spectrum show that there are *ca.* three TMEDA molecules per THF normally found in solid samples (*i.e.*, 1 molecule of THF for every 1.5 molecules of **5**).

$$\text{LiAlH}_4 \ + \ 2[\textbf{2}\text{H}_4] \xrightarrow{\text{L/L'}} [\text{Al}(\textbf{2}\text{H}_2)_2]^-[\text{Li}(\text{L})(\text{L'})]^+ \ + \ 4\text{H}_2$$

L = PMDETA; L' = THF (**4**)
L = L' = TMEDA (**5**)

Scheme 3 The reactions producing the related ion-separated complexes **4** and **5**, showing the structure of the aluminate anion and the deprotonation pattern of **2**H$_4$.

1,8-diaminonaphthalene (**2**H$_4$), particularly in its doubly deprotonated form [**2**H$_2$]$^{2-}$, has been used extensively as a ligand in a number of transition metal complexes.[15] However, although a large number of complexes containing *N,N*-disubstituted ligands of the type [**2**R$_2$]$^{2-}$ (R = alkyl, aryl or silyl) have been reported for main group metals,[19] main group metal complexes containing the parent [**2**H$_2$]$^{2-}$ ligand are very rare[17] and there are no previously reported examples of Group 13 metal complexes containing the [**2**H$_2$]$^{2-}$ ligand.

Single-crystal X-ray diffraction studies of the new complexes **3**, **4** and **5** were undertaken at 180(2) K. Details of the structure refinements and data collections on **3** and **4** are collected in Table 1 (Experimental Section). Since the X-ray data for **5** was of poor quality [with lowest obtained $R(1) = 10.34\%$, despite repeated data collections] the structure of the complex is not discussed in detail here (see ESI).

[{Al(**1**H$_2$)}$_2${Al(**1**H)$_2$}$_2$][Li(THF)$_2$]$_4$ (**3**) crystallizes in monoclinic space group $P2_1/n$ and its molecular structure is illustrated in Fig. 2. The complex has an ion-paired structure resulting from the association of an aluminate [{Al(**1**H$_2$)}$_2${Al(**1**H)$_2$}$_2$]$^{4-}$ tetraanion with four [Li(THF)$_2$]$^+$ cations. A schematic of the structure is shown in the insert to Scheme 2. The [{Al(**1**H$_2$)}$_2${Al(**1**H)$_2$}$_2$]$^{4-}$ tetraanion is constructed (formally) from two [Al(**1**H)$_2$]$^{3-}$ and [Al(**1**H$_2$)]$^+$ subunits which form a cyclic arrangement composed of a

central eight-membered (*twist-chair*[20]) Al$_4$N$_4$ ring unit, using the imido-N atoms of the [Al(**1**H)$_2$]$^{3-}$ fragments.
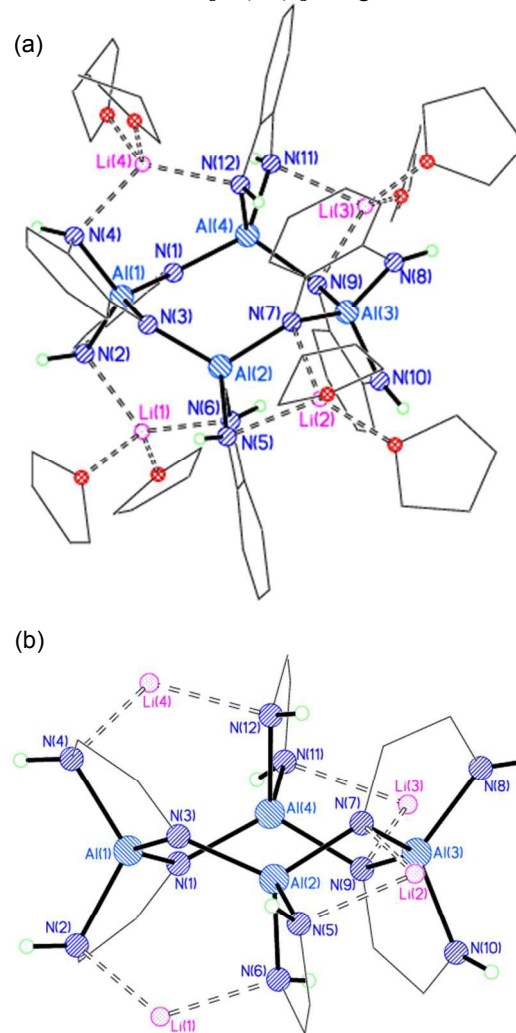
Fig. 2 (a) Molecular structure of [{Al(**1**H$_2$)}$_2${Al(**1**H)$_2$}$_2$][Li(THF)$_2$]$_4$ (**3**). C-bonded H-atoms and the disordered components of the THF ligands have been omitted for clarity. Selected bond lengths (Å) and angles (°): Al(1)-N(1) 1.846(3), Al(1)-N(2) 1.858(4), Al(1)-N(3) 1.843(3), Al(1)-N(4) 1.865(3), Al(3)-N(7) 1.869(3), Al(3)-N(8) 1.831(5), Al(3)-N(9) 1.880(3), Al(3)-N(10) 1.832(5), Al(2)-N(3) 1.818(3), Al(2)-N(5) 1.880(3), Al(2)-N(6) 1.874(3), Al(2)-N(7) 1.845(3), Al(4)-N(1) 1.826(3), Al(4)-N(9) 1.862(3), Al(4)-N(11) 1.880(3), Al(4)-N(12) 1.877(3), Li-N range 2.15(1)-2.25(1), N-Al-N (Al$_4$N$_4$ ring) range 117.3(2)-124.9(2), N-Al-N (chelate) range 87.2(9)-90.0(2), Al-N-Al (Al$_4$N$_4$ ring) range 119.4(2)-122.0(2); (b) The core structure of the complex, with the THF ligands and aromatic rings removed.
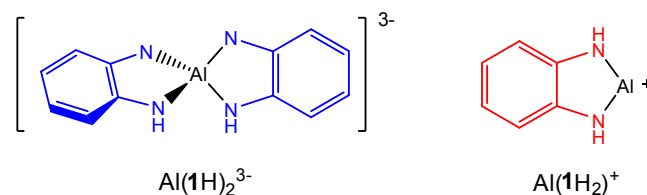
**Fig. 3** The [Al(**1**H)$_2$]$^{3-}$ and [Al(**1**H$_2$)]$^+$ subunits of **3**.

This arrangement results in two distinct Al-environments [Al(1)/Al(3) and Al(2)/Al(4)], each of which have pseudo-tetrahedral metal geometries with the Al centres being bonded

solely to N atoms. The Al-N bond lengths within **3** are in the range 1.818(3)-1.880(3) Å, with no significant differences between the amido N(-H)-Al and imido N-Al bonds being discernible.[21] The tetraanion of **3**, containing four Al-atoms, is the largest species of this type to be reported. Previously, amido/imido-aluminate anions containing a maximum of two Al atoms have been observed.[7b,c]

A surprising feature of the structural arrangement of **3** is the presence of two Li^+ coordination environments. Although all of the Li^+ cations are pseudo-tetrahedral, Li(1) and Li(4) are each bound to one amido N(H) atom of a $[Al(1H)_2]^{3-}$ and one of a $[Al(1H_2)]^+$ fragment, while Li(2) and Li(3) are bonded to the imido-N atom of a $[Al(1H)_2]^{3-}$ unit and an amido N(H) atom of a $[Al(1H)_2]^+$ unit. The N-Li bond lengths are in the range 2.15(1) - 2.25(1) Å, within the normal range observed previously.[21] The reason for the unsymmetrical coordination of the Li^+ cations in **3** can be traced to the disposition of the C_6H_4 rings of the $[Al(1H)_2]^{3-}$ subunits at either end of the $[\{Al(1H_2)\}_2\{Al(1H)_2\}_2]^{4-}$ tetraanion. As can be seen from Fig. 2b, showing the core structure of the complex, the $[Al(1H)_2]^{3-}$ subunits have virtual mirror symmetry with respect to the central Al_4N_4 ring, which limits the availability of the imido-N atoms to coordinate all of the Li^+ cations.
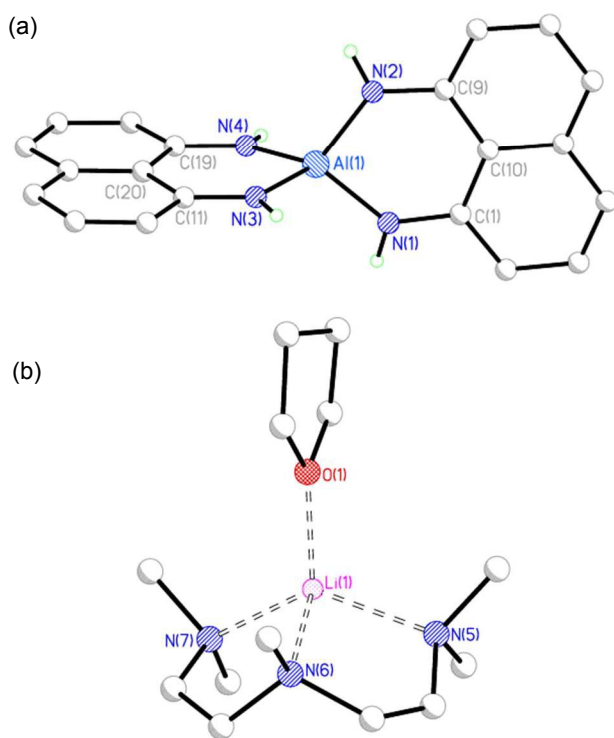

Fig. 4 Structure of (a) the anions and (b) the cation of $[Al(2H_2)_2]^-$ $[Li(PMDETA)(THF)]^+$ (**4**). C-bonded H-atoms have been omitted for clarity. Bound H atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): Al(1)-N(1) 1.821(3), Al(1)-N(2) 1.814(3), Al(1)-N(3) 1.831(3), Al(1)-N(4) 1.815(3), N-Al-N (chelate) range 95.2(1)-95.6(1), N-Al-N (between $[2H_2]^{2-}$ ligands) range 116.2(2)-118.3(2), C-N-Al range 127.6(2)-129.6(3).

$[Al(2H_2)_2]^-[Li(PMDETA)(THF)]^+$ (**4**) crystallizes in monoclinic space group $C2/c$ and its molecular structure is illustrated in Fig. 4. The complex is ion-separated and consists of $[Li(PMDETA)(THF)]^+$ cations and $[Al(2H_2)_2]^-$ anions. The structure of $[Al(2H_2)_2]^-[Li(TMEDA)_2]^+$ (**5**) (see ESI) only differs in the nature of the cation present. The formation of the $[Al(2H_2)_2]^-$ anion in **4** and **5** is similar to the outcome of the reactions of primary amines (RNH_2) with $MAlH_4$ (M = Li, Na) (1:4 equivalents) which give $[Al(NHR)_4]^-$ ions.[7c] The Al^{3+} cation of the anion of **4** has a highly distorted tetrahedral geometry, resulting from the sharp angles within the chelate rings [N-Al-N range 95.2(1) - 95.6(1)°; *cf*. range 116.2(2) - 118.3(2)° for the remaining N-Al-N angles]. The sharp chelate angles and the Al-N bond lengths [range 1.814(3) - 1.831(3) Å] are similar to those found in **3**. Despite the adoption of planar sp^2 hybridization at the N-atoms, there is no evidence for significant double-bond character in the C_{aryl}-N bonds, whose bond lengths are typical of those found in aromatic amines [range 1.359(5) - 1.384(5) Å]. Its simplicity apart, to our knowledge the anion of **4** is the only example of a mononuclear metal complex containing the $[2H_2]^{2-}$ ligand. In the context of the current study the $[Al(2H_2)_2]^-$ anion can be seen as representing a model precursor for the $[Al(1H_2)]^{3-}$ units found in complex **3**, resulting from further double deprotonation (see the conclusions section of this paper).

3. Conclusions

We have presented here the first study of the reactions of $LiAlH_4$ with primary diamines. The new compound $[\{Al(1H_2)\}_2\{Al(1H)_2\}_2][Li(THF)_2]_4$ (**3**) is especially interesting as contains the largest of this class of amido/imido aluminate anions, the tetraanion $[\{Al(1H_2)\}_2\{Al(1H)_2\}_2]^{4-}$.
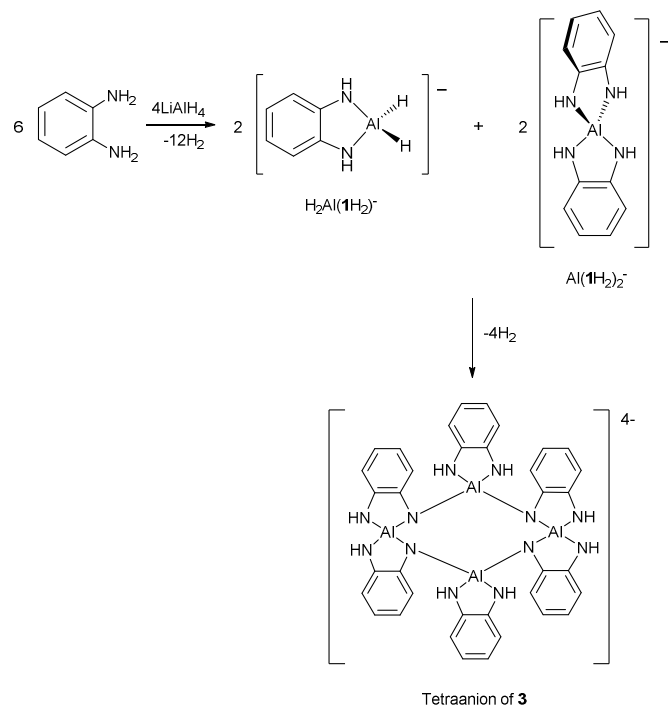
Scheme 4 Proposed reaction pathway of formation of the tetraanion of **3**.

The formation of the mononuclear anions in $[Al(2H_2)_2]^-$ $[Li(PMDETA)(THF)]^+$ (**4**) and $[Al(2H_2)_2]^-[Li(TMEDA)_2]^+$ (**5**) follows a more straightforward pathway that is similar to that seen previously in certain reactions of MAlH$_4$ (M = Li, Na).[7] The $[Al(2H_2)_2]^-$ anions in the latter give a clue to the way in which the tetraanion of **3** is formed (Scheme 4). It is likely, given the observed (2:3) stoichiometry of the reaction, that the AlH$_4^-$ ion will react to give a mixture of $[H_2Al(1H_2)]^-$ and $[Al(1H_2)_2]^-$ in the initial stage, which then further to give the anion of **3** directly. Finally, we have found in the current study that **3**, **4** and **5** are thermally stable at reflux in THF and do not appear to undergo oxidative coupling in a similar manner to that found previously in the case of **1**H$_4$ with Sn(NMe$_2$)$_2$/^{n}BuLi.[11] The reason for this is almost certainly the lack of a redox active metal species which will affect the N-H/N-H dehydrocoupling step.

Acknowledgements

Notes and references

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Electronic Supplementary Information (ESI) available: crystal and NMR data for compounds **3-5**. See DOI: 10.1039/b000000x/

Experimental

General Experimental Procedures

All compounds described in this paper are air and moisture sensitive. Preparations were performed on a double-manifold vacuum line under a nitrogen atmosphere. The products were isolated and stored with the aid of a nitrogen-filled glove box (Saffron type b), equipped with Cu and molecular sieve columns in order to remove O$_2$ and moisture, respectively. TMEDA and PMDETA (Aldrich) were distilled from Na and stored under argon. All ^{1}H and ^{13}C NMR spectra were recorded using a Brüker DPX 500 MHz NMR spectrometer. Elemental (C, H, N) analyses were obtained using an Exeter CE-440 Elemental Analyser. Samples for analysis (1‑2 mg) were placed in pre-weighed, airtight aluminium boats in the glove box prior to analysis.

*Synthesis of [{Al(1H$_2$)}$_2${Al(1H)}$_2$][Li(THF)$_2$]$_4$ (**3**):* LiAlH$_4$ (23 mg, 0.61 mmol) was added to a solution of 1,2-phenylenediamine (100 mg, 0.92 mmol) in 5 ml THF and the mixture stirred for 16h at room temperature. The solution was filtered into a crystallization tube (20 mm diameter) and the volume of solvent reduced *in vacuo* to approximately 1 ml. Hexane (10 ml) was then carefully layered onto the solution and the tube was sealed and allowed to remain undisturbed for one week after which time the product had solidified. The solvents were then decanted off and the solids collected and allowed to dry in the glove box. Yield 99 mg (48 %). Found (%): C 61.3, H 7.0, N 14.3; Calcd. for C$_{68}$H$_{96}$Al$_4$Li$_4$N$_{12}$O$_8$: C 60.7, H 7.2, N 12.5. ^{1}H NMR (400.1 MHz, 25 °C, D$_8$-THF), δ/ppm = 6.13 (br s, 8H, [ArH(NH)(N)]$^{3-}$), 6.05 (br s, 8H, [ArH(NH)(N)]$^{3-}$), 5.9-6.5 (br m, 8H, ArH(NH$_2$)$_2^{2-}$), 3.60 (m, THF), 3.05 (br s, 8H, NH), 1.77 (m, THF); ^{13}C{^{1}H} NMR (400.1 MHz, 25 °C, D8-THF), δ/ppm = 145.5 (br m, ArH), 114.5 (br m, ArH), 110.8 (br m, ArH), 68.2 (m, THF), 26.4 (THF).

*Synthesis of [Al(2H$_2$)$_2$]$^-$[Li(PMDETA)(THF)]$^+$ (**4**):* LiAlH$_4$ (12 mg, 0.32 mmol) was added to a solution of 1,8-diaminonaphthalene (100 mg, 0.63 mmol) in 5 ml THF containing 0.5 ml PMDETA (2.4 mmol). The mixture was heated to reflux for 1h and sufficient hot THF (approx. 3 ml) was added to dissolve the precipitate which had formed. The solution was filtered whilst hot and allowed to cool slowly to room temperature resulting in crystallization of the product. The mother liquor was decanted off and the crystals allowed to dry in the glove box. Yield 90 mg (48 %). Found (%): C 67.0, H 7.9, N 16.6; Calcd. for C$_{33}$H$_{47}$AlLiN$_7$O: C 67.0, H 8.0, N 16.6. ^{1}H NMR (400.1 MHz, 25 °C, D$_8$-THF), δ/ppm = 6.62 (t, J = 8.0 Hz, 4H, ArH), 6.33 (dd, J = 8.0, 1.2 Hz, 4H, ArH), 5.86 (dd, J = 8.0, 1.2 Hz, 4H, ArH), 3.81 (s, 4H, ArNH), 3.61 (m, 4H, THF), 2.39 (td, J = 6.8, 0.8 Hz, 4H, PMDETA CH$_2$), 2.28 (td, J = 6.8, 0.8 Hz, PMDETA CH$_2$), 2.19 (s, 3H, PMDETA CH$_3$), 2.14 (s, 12H, PMDETA CH$_3$). 1.76 (m, 4H, THF); ^{13}C{^{1}H} NMR (400.1 MHz, 25 °C, D8-THF), δ/ppm = 155.8

(Ar), 140.0 (Ar), 126.8 (Ar), 118.5 (Ar), 112.1 (Ar), 107.3 (Ar), 68.2 (THF), 58.7 (PMDETA), 56.8 (PMDETA), 46.1 (PMDETA), 43.5 (PMDETA), 26.4 (THF).

Synthesis of [Al(2H₂)₂]⁻[Li(TMEDA)₁.₅(THF)₀.₅]⁺ (**5**): LiAlH₄ (12 mg, 0.32 mmol) was added to a solution of 1,8-diaminonaphthalene (100 mg, 0.63 mmol) in 5 ml THF containing 0.5 ml TMEDA (3.6 mmol). The mixture was heated to reflux for 1h, filtered and the volume of solvent reduced *in vacuo* whilst hot until the onset of crystallization occurred. The solution was allowed to cool to room temperature to complete the crystallization whereupon the mother liquor was decanted off and the product collected and allowed to dry in the glove box. Yield 100 mg (53 %). Found (%): C 66.7, H 8.2, N 17.6; Calcd. for C₃₂H₄₈AlLiN₈·C₃₀H₄₀AlLiN₆O C 66.9, H 8.0, N 17.6. ¹H NMR (400.1 MHz, 25 °C, D8-THF), δ/ppm = 6.63 (t, *J* = 7.6 Hz, 4H, ArH), 6.34 (dd, *J* = 7.6, 0.8 Hz, 4H, ArH), 5.86 (dd, *J* = 7.6, 0.8 Hz, 4H, ArH), 3.82 (s, 4H, ArNH), 3.61 (m, THF), 2.30 (8H, s, TMEDA CH₂), 2.15 (s, 24H, TMEDA CH₃), 1.77 (m, THF); ¹³C{¹H} NMR (400.1 MHz, 25 °C, D8-THF), δ/ppm = 155.8 (Ar), 140.0 (Ar), 126.8 (Ar), 118.5 (Ar), 112.1 (Ar), 107.3 (Ar), 68.2 (THF), 58.9 (TMEDA), 46.2 (TMEDA), 26.4 (THF).

X-Ray Crystallography

Data for all complexes were collected on a Nonius KappaCCD diffractometer and solved by direct methods and refined by full-matrix least squares on *F*². All of the THF molecules in the structure of **3** [except those attached to Li(4)] exhibit site disorder in which the C-atoms of the backbone of the ligands were modelled over two 50:50 sites.

Table 1. Details of the data collections and structural refinements of **3** and **4**.

Compound	3	4
Chemical formula	C₆₈H₉₆Al₄Li₄N₁₂O₈·0.5(C₄H₈O)·0.5(C₆H₁₄)	C₂₀H₁₆AlN⁻ C₁₃H₃₁LiN₃O⁺
FW / g·mol⁻¹	1424.39	591.70
Crystal system	Monoclinic	Monoclinic
Space group	P2₁/n	C2/c
a / Å	15.8568(5)	34.6994(4)
b / Å	25.4155(9)	14.6711(2)
c / Å	20.1493(8)	30.4757(4)
β / °	101.022(2)	120.945(1)
V / Å³	7970.5(5)	13306.2(3)
Z	4	16
ρ_calcd / Mg·m⁻³	1.187	1.181
μ (MoKα) / mm⁻¹	0.118	0.097
Reflections collected	11879	12123
Independent reflections	7865	6898
*R*_int	0.042	0.097
*R*₁, w*R*₂ [*I* > 2σ(*I*)]	0.067, 0.157	0.081, 0.238
*R*₁, w*R*₂ (all data)	0.108, 0.181	0.127, 0.261

Data in common λ = 0.71070 nm, *T* = 180(2)K.

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21 Search of the Cambridge Crystallographic Data Base (October 2014), Al-N range 1.657-2.891 Å (mean 1.956 Å), N-Li range 1.352-2.767 Å (mean 2.077 Å).

Graphical Abstract

Multiple Deprotonation of Primary Aromatic Diamines by LiAlH$_4$

R. J. Less*, L. K. Allen, A. Steiner and D. S. Wright
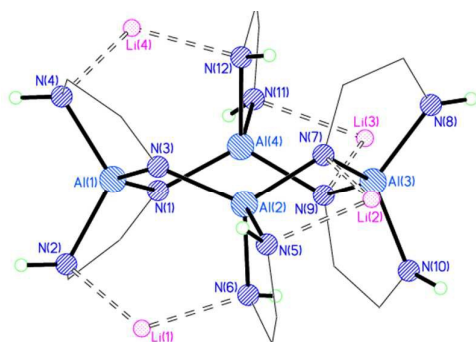
Reaction of LiAlH$_4$ with 1,2-phenylenediamine (**1**H$_4$) in THF gives **[**{Al(**1**H$_2$)}$_2${Al(**1**H)$_2$}$_2$**][**Li(THF)$_2$**]**$_4$, containing the largest aluminate of its type so far reported.