Preparation and Properties of a Series of Structurally Diverse Aluminium Hydrides Supported by β-Diketiminate and bis(amide) Ligands

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Abstract: The synthesis of a diverse series of hydride complexes of aluminium coordinated by N,N’-chelating ligands is reported. Reaction of [{2,6-iPr₂C₆H₃}NC(Me)CHC(Me)N(H)CH₂CH₂NMe₂] with either LiAlH₄ or Me₃N·AlH₃ allows isolation of the corresponding five-coordinate aluminium dihydride [κ₃-{(2,6-iPr₂C₆H₃)NC(Me)CHC(Me)NCH₂CH₂NMe₂}AlH₂] (2). The latter complex demonstrates trigonal bipyramidal geometry in the solid-state. Correlation of solid and n-hexane solution infrared spectroscopy data reveals that this coordination is retained in solution. To evaluate the observed coordination geometry, the dissociation of the pendant ligand of 2 was investigated by DFT methods conducted with the M06-2X functional and a hybrid 6,31G+(d,p)/Lanl2DZ basis-set. Reaction of Me₃N·AlH₃ with both N,N’-bis(di-iso-propylphenyl)ethylenediamine and N,N’-bis(mesityl)ethylenediamine gave [{κ²-(ArNCH₂)₂}AlH(NMe₃)] (Ar = Mes, 3a; Ar = 2,6-di-iso-propylphenyl, 3b) in moderate yields. Removal of NMe₃ from 3b by heating under dynamic vacuum allowed the isolation of cis-[AlH{µ-N(Ar)CH₂CH₂N(Ar)}] (Ar = 2,6-di-iso-propylphenyl, cis-4b₂) as a single diastereomer following crystallization. DFT studies in combination with infrared and NMR spectroscopy and single crystal X-ray diffraction data provide a weight of evidence consistent with the robust dimeric structure of cis-4b₂ remaining intact in solution. An unusual reaction in which the aluminium dihydride, [κ²-{(2,6-Me₂C₆H₃NHCH₂)₂CH}AlH₂], promotes the P–C bond cleavage of Ph₃PCH₂ is also reported.

Introduction

Since Hawthorne’s 1960 synthesis of a series of amine adducts of alane, the coordination chemistry of the heavier group 13 hydrides has blossomed. The use of kinetically stabilizing ligand sets has allowed the isolation and characterization of numerous hydride complexes of Al–In previously believed to be synthetically
inaccessible.\textsuperscript{2-3} During these studies, the characterization of aluminium hydrides by single-crystal X-ray diffraction has been extensive and an assortment of structures are now known.\textsuperscript{4-8} The low electronegativity of Al (\(\chi_p = 1.61\)) along with a tendency of the Al\textsuperscript{3+} ion to alleviate coordinative unsaturation by forming higher nuclearity species while expanding its coordination sphere beyond four to five- or, more rarely, six-coordinate explains the diverse number of coordination geometries observed in the solid-state.\textsuperscript{2-3} Despite these advances, there is little information on the solution structures of more complex aluminium hydrides.

Consider the adduct Me\textsubscript{3}N·AlH\textsubscript{3}. In the gas-phase this complex is monomeric as evidenced by electron diffraction studies,\textsuperscript{9} however it crystallizes as [Me\textsubscript{3}N·AlH\textsubscript{2}(\mu-H)]\textsubscript{2} a derivative of dialane that possess weakly bonded bridging hydride ligands.\textsuperscript{10} Molecular weight determinations in diethyl ether suggest a degree of aggregation in solution between monomeric and dimeric.\textsuperscript{1} The lack of studies correlating, often complex, solid-state data with solution data is surprising when considering that aluminium hydrides find applications as hydrogen storage materials, single-source precursors for chemical vapour deposition and are of fundamental interest to catalysis.\textsuperscript{11}

In this latter regard, we have previously reported [{(MesNCMe)\textsubscript{2}CH}AlH\textsubscript{2}] \textsuperscript{(1)} as a terminal reductant for the hydrodefluorination of fluoroarenes catalyzed by zirconocene dichloride.\textsuperscript{12a} Herein we disclose the synthesis and characterization of a five-coordinate \(\beta\)-diketiminate complex, including an investigation into its potential to isomerise to a four-coordinate analogue in solution. The synthesis of a single diastereomer of a dimeric \(\textit{bis}\)(amide) supported aluminium hydride is also reported along with an unusual P–C bond cleavage reaction of Ph\textsubscript{3}PCH\textsubscript{2} promoted by an aluminium dihydride.

\textbf{Experimental}

\textbf{General Experimental:} LiAlH\textsubscript{4} was purified by extraction in to THF (10g in approximately 50 mL), followed by filtration and removal of the solvent under reduced pressure. The mixture was heated to 45 °C to remove the last traces of solvent. \(N,N'\)-\textit{bis}(di-iso-propylphenyl)ethylenediamine,\textsuperscript{13} \(N,N'\)-\textit{bis}(mesityl)ethylenediamine,\textsuperscript{14} [{(2,6-Me\textsubscript{2}C\textsubscript{6}H\textsubscript{3}NCMe)\textsubscript{2}CH}AlH\textsubscript{2}]\textsuperscript{5f} \quad [{(MesNCMe)\textsubscript{2}CH}AlH\textsubscript{2}]\textsuperscript{5f} and \quad [{(2,6-
\( ^1 \text{Pr}_2 \text{C}_6 \text{H}_3 \text{NC} \text{(Me)} \text{CHC(Me)} \text{N(H)} \text{CH}_2 \text{CH}_2 \text{NMe}_2 \) were prepared by literature procedures. All other materials were purchased from Sigma-Aldrich and used without further purification. \( \text{AlH}_3 \cdot \text{NMe}_3 \) was synthesized by the procedure of Hawthorne and co-workers.\(^1\) Trimethylamine hydrochloride was purchased from Sigma-Aldrich and used without further purification.

**Synthesis of 2: Method A:** Under a purge of inert gas, \( \text{LiAlH}_4 \) powder (414 mg, 10.9 mmol, 1.2 equiv.) was added to a Schlenk tube, the Schlenk was cooled to -78 °C followed by careful addition of diethyl ether (20 mL). To this mixture was added a solution of \( [(2,6-\text{Pr}_2 \text{C}_6 \text{H}_3 \text{NC} \text{(Me)} \text{CHC(Me)} \text{N(H)} \text{CH}_2 \text{CH}_2 \text{NMe}_2] \) (3.0 g, 9.10 mmol) in diethyl ether (10 mL) via cannula. Once the addition was complete the cooling bath was removed. The reaction mixture was warmed to 25 °C and left to stir for 24h. The precipitated LiH (CARE: pyrophoric) was allowed to settle and the supernate isolated by cannula filtration. Slow reduction of the solvent volume to 10 mL under vacuum, followed by storage at -18 °C gave colourless crystals of 2 that were isolated by filtration (0.945g, 2.64 mmol, 29%). **Method B:** A solution of \( \text{AlH}_3 \cdot \text{NMe}_3 \) (0.27 g, 3.03 mmol, 1.2 equiv.) in toluene (20 mL) was cooled to -78 °C. A solution of the pro-ligand (0.83 g, 2.53 mmol) was added to this mixture via cannula. The reaction mixture was warmed to 25 °C and left to stir overnight (14 h). The solution was filtered by cannula and the solvent removed. The crude product was washed with \( n \)-hexane (30 mL) to give 2 as a pale yellow solid (0.57 g, 1.31 mmol, 52 %). \(^1\text{H} \) NMR \( (\text{C}_6 \text{D}_6, 400 \text{ Hz}, 298 \text{ K}) \) \( \delta \) 1.27 (d, 6H, \(^3\text{J}_{\text{H-H}} = 6.8 \text{ Hz}, \text{CHMe}_2), 1.69 (d, 6H, \(^3\text{J}_{\text{H-H}} = 6.8 \text{ Hz}, \text{CHMe}_2), 1.71 (s, 3H, \text{Me}), 1.72 (s, 3H, \text{Me}), 1.96 (s, 6H, \text{NMe}_2), 2.20 (t, 2H, \(^3\text{J}_{\text{H-H}} = 6.4 \text{ Hz}, \text{NCH}_2 \text{CH}_2), 2.76 (t, 2H, \(^3\text{J}_{\text{H-H}} = 6.4 \text{ Hz}, \text{NCH}_2), 3.67 \) (hept, 2H, \(^3\text{J}_{\text{H-H}} = 6.8 \text{ Hz}, \text{CHMe}_2), 4.87 (s, 1H, \text{CH}), 7.3 \) (m, 3H, \text{ArH}); \(^{13}\text{C} \) NMR \( (\text{C}_6 \text{D}_6, 100 \text{ MHz}, 298 \text{ K}) \) \( \delta \) 22.8, 23.5, 24.9, 25.7, 28.4, 43.5, 44.6, 54.8, 95.1, 124.3, 126.3, 142.9, 144.1, 167.7; Infrared (cm\(^{-1}\), solid) 1743; Infrared (cm\(^{-1}\), \( n \)-hexane) 1745; Elemental analysis calculated for \( \text{C}_{21} \text{H}_{36} \text{AlN}_3 = \text{C}: 70.55\%, \text{H}: 10.15\%, \text{N}: 11.75\% \) Found = C, 70.42%; H, 10.05%; N, 11.68%.

**Synthesis of 3a:** In a glovebox, \( N,N' \)-bis\( (\text{mesityl}) \) ethylenediamine (3.00 g, 10.12 mmol) and \( \text{AlH}_3 \cdot \text{NMe}_3 \) (0.900 g, 10.12 mmol) were weighed separately and transferred into separate Schlenk flasks. Each solid was dissolved in dry diethyl ether (20 mL) and both flasks were removed from the box. Following attachment to a vacuum line, under a
purge of inert gas the reaction mixtures were cooled to -78 °C. To the Schlenk containing the \( \text{AlH}_3\cdot\text{NMe}_3 \) solution, the diethyl ether solution of the pro-ligand was added dropwise and the mixture slowly warmed to 25 °C. The reaction was stirred at 25 °C for 16 h during which time gas evolution was observed. The solution was filtered to remove a small amount of fine white precipitate before the ether was removed in vacuo. The crude product was dissolved in n-hexane (10 mL). Storage of this solution at -20 °C gave a microcrystalline solid that was dried in vacuo, yielding **3a** as a colourless solid (1.51 g, 3.96 mmol, 39%). Crystals suitable for X-ray diffraction were grown from toluene solution at -20 °C. \(^1\text{H} \ \text{NMR} \) (400 MHz, C\(_6\)D\(_6\)) \( \delta \) 1.63 (s, 9H), 2.28 (s, 6H), 2.43 (br s, 6H), 2.80 (br s, 6H), 3.21-3.29 (m, 2H), 3.54-3.61 (m, 2H), 6.99 (s, 4H); \(^{13}\text{C} \ \text{NMR} \) (101 MHz, C\(_6\)D\(_6\), 298 K) \( \delta \) 20.6, 45.2, 53.8, 128.0, 129.5, 130.4, 134.7, 149.0; Infrared (solid, cm\(^{-1}\)) 1776; Elemental analysis calculated for C\(_{23}\)H\(_36\)AlN\(_3\) = C: 72.40%, H: 9.51%, N: 11.01% Found = C: 72.45%, H: 9.58%, N: 10.92%.

**Synthesis of 3b:** In a glovebox, \( \text{N',N'-bis(di-iso-propylphenyl)ethylenediamine} \) (2.02 g, 5.32 mmol) and \( \text{AlH}_3\cdot\text{NMe}_3 \) (0.47 g, 5.32 mmol) were weighed together into a Schlenk flask. The flask was removed from the box, attached to a vacuum line and under a purge of inert gas cooled to -78 °C. To the mixture of solids was added cold (-78 °C) diethyl ether (30 mL). The reaction mixture was allowed to slowly warm to 25 °C and stirred for 17 h during which time gas evolution was observed. The solvent was removed in vacuo, and the resulting crude solid was dissolved in toluene (10 mL). Storage of this solution at -20 °C gave a microcrystalline solid that was dried in vacuo, yielding **3b** as a colourless solid (1.19 g, 2.36 mmol, 45%). \(^1\text{H} \ \text{NMR} \) (C\(_6\)D\(_6\), 400 Hz, 298 K) \( \delta \) 1.25 (d, 6H, \( ^3J_{\text{HH}} = 7.2 \) Hz), 1.38 (d, 6H, \( ^3J_{\text{HH}} = 6.8 \) Hz), 1.47 (d, 6H, \( ^3J_{\text{HH}} = 7.2 \) Hz), 1.62 (d, 6H, \( ^3J_{\text{HH}} = 6.8 \) Hz), 1.71 (s, 9H), 3.32-3.40 (m, 2H), 3.63-3.70 (m, 2H), 3.84 (sept, 2H, \( ^3J_{\text{HH}} = 6.8 \) Hz), 4.32 (sept, 2H, \( ^3J_{\text{HH}} = 6.8 \) Hz), 7.18-7.23 (m, 4H), 7.27-7.32 (m, 2H); \(^{13}\text{C} \ \text{NMR} \) (101 MHz, C\(_6\)D\(_6\), 298 K) \( \delta \) 24.9, 25.1, 26.3, 26.7, 28.0, 28.9, 45.5, 56.9, 123.9, 124.1, 124.3, 147.5, 148.8; IR (cm\(^{-1}\)) 1829; Elemental analysis calculated for C\(_{29}\)H\(_{48}\)AlN\(_3\) = C: 74.79%, H: 10.39%, N: 9.01% Found = C: 74.62%, H: 10.26%, N: 9.13%.

**Synthesis of cis-4b\(_2\) by desolvation of 3b under dynamic vacuum:** In a glovebox, **3b** (0.220 g, 0.472 mmol) was weighed into a long, thin Schlenk flask. The flask was removed from the box and evacuated on a vacuum line. Once the internal pressure had
stabilised, the Schlenk flask was heated at 160 °C under dynamic vacuum for one hour until the internal pressure returned to its starting value. The resulting solid was dissolved in toluene (2 mL) and storage of this solution at -20 °C followed by drying in vacuo gave cis-4b₂ as a colourless solid (0.062 g, 0.076 mmol, 32%). ¹H NMR ¹H NMR (CD₆₂, 400 Hz, 298 K) δ 0.89 (d, 6H, 3/J_H-H = 6.5 Hz), 0.96 (d, 6H, 3/J_H-H = 6.0 Hz) 1.19 (d, 6H, 3/J_H-H = 6.5 Hz) 1.26 (d, 6H, 3/J_H-H = 7.0 Hz) 1.33 (d, 6H, 3/J_H-H = 6.5 Hz) 1.35 (d, 6H, 3/J_H-H = 7.0 Hz) 1.42 (d, 6H, 3/J_H-H = 6.5 Hz) 1.50 (d, 6H, 3/J_H-H = 7.0 Hz) 2.46 (sept, 2H, 3/J_H-H = 6.8 Hz), 2.91 (dd, 2H, 3/J_H-H = 10.5 Hz, 3/J_H-H = 4.5 Hz), 3.12 (dd, 2H, 3/J_H-H = 12.5 Hz, 3/J_H-H = 3.0 Hz), 3.64 (dt, 2H, 3/J_H-H = 12.0 Hz, 3/J_H-H = 3.0 Hz), 3.86 (sept, 2H, 3/J_H-H = 6.5 Hz), 3.95 (sept, 2H, 3/J_H-H = 6.5 Hz), 4.04 (sept, 2H, 3/J_H-H = 7.0 Hz), 4.31 (br, 2H), 4.96 (dt, 2H, 3/J_H-H = 12.0 Hz, 3/J_H-H = 4.5 Hz), 6.93-7.03 (m, 6H), 7.19-7.25 (m, 6H); ¹³C NMR (101 MHz, CD₆₂, 298 K) δ 23.3, 23.7, 25.6, 26.4, 27.3, 27.9, 28.6, 29.3, 30.9, 31.3, 54.1, 59.7, 124.0, 124.1, 125.1, 125.3, 126.5, 144.4, 145.6, 146.0, 146.4; IR (solid, cm⁻¹) 1903; Elemental analysis calculated for C₅₂H₇₆Al₂N₄ = C: 76.81%, H: 9.67%, N: 6.89% Found = C: 76.90 %, H: 9.84%, N: 6.75%.

Synthesis of 6: In a glovebox, triphenylphosphonium methyldi (0.332 g, 1.2 mmol) and [(2,6-Me₂C₆H₃NCMe₂)₂CH]AlH₂ (0.400 g, 1.2 mmol) were weighed and transferred to a Schlenk flask. The flask was sealed and removed from the box, on vacuum line CdH₆ (10 mL) was added and the mixture heated to 60 °C for 2 h. Removal of the solvent under reduced pressure gave an orange/red crystalline solid. Hot recrystallization from n-hexane gave 6 as colourless crystals (0.105 g, 0.26 mmol, 21 %). ¹H NMR (CD₆₂, 400 Hz, 298 K) δ 1.59 (s, 6H), 2.04 (s, 6H), 2.51 (s, 6H), 5.02 (s, 1H), 6.88 (d, 2H, 3/J_H-H = 7.6 Hz), 6.98 (d, 2H, 3/J_H-H = 7.6 Hz), 7.05 (d, 2H, 3/J_H-H = 7.6 Hz), 7.24-7.27 (m, 3H), 7.75-7.80 (m, 2H); ¹³C NMR (101 MHz, CD₆₂, 298 K) δ 19.2, 22.5, 97.1, 126.6, 127.1, 129.1, 129.2, 133.6, 134.2, 138.2, 143.0, 169.8; Elemental analysis calculated for C₂₇H₃₁AlN₄ = C: 78.99%, H: 7.61%, N: 6.82% Found = C: 78.87 %, H: 7.58%, N: 6.84%.

Crystallographic Data: Table S2 and S3 (see ESI) provide a summary of the crystallographic data for compounds 2, 3a, cis-4b₂ and 6. Data were collected using Oxford Diffraction Xcalibur 3 (2, 3a and 6) and Xcalibur PX Ultra (cis-4b₂) diffractometers, and the structures were refined based on F² using the SHELXTL and SHELX-97 program systems. The Al–H hydrogen atoms in all structures were located
from $\Delta F$ maps and refined freely. CCDC numbers 954263-954265 and 953189

Results and Discussion

A five-coordinate β-Diketiminate stabilised aluminium dihydride: Compound 2 could be prepared directly from the pro-ligand by reaction with either AlH$_3$·NMe$_3$ in toluene or LiAlH$_4$ in diethyl ether.$^5$ The former route gave 2 in 52% yield (Scheme 1).

***Scheme 1 here***

Structurally characterised five-coordinate aluminium dihydrides supported by anionic pincer ligands have been isolated previously.$^{16-17}$ Both $[\kappa^3\{2,6-(\text{Me}_2\text{NCH}_2)_2\text{C}_6\text{H}_3\}\text{AlH}_2]$ and $[\kappa^3\{2,5-(\text{Me}_2\text{NCH}_2)_2\text{C}_4\text{H}_2\text{N}\}\text{AlH}_2]$ display trigonal bipyramidal geometry at aluminium in the solid-state. The neutral L-type donors of the pincer occupy the axial sites. The preference for X-type ligands to occupy the equatorial sites in trigonal bipyramidal aluminium complexes is further underscored by the crystal structures of monomeric and polymeric complexes of empirical formulae [L$_2$AlH$_3$], in which the hydrides all sit in the trigonal plane (L = NMe$_3$, thf, quinuclidine, 1,3,5-trimethylhexahydro-1,3,5-triazine; L$_2$ = N-methylmorpholine, tmeda, $N,N',N'',N'''\text{-tetrathethylpropylenediamine, \text{Pr}_2\text{PCH}_2\text{CH}_2\text{P}\text{Pr}_2}$).$^{18}$ Related, five and six-coordinate dihydrides [L$_4$AlH$_2$]$^+$[AlH$_4^-$. (L$_3$ = $N,N',N'',N'''\text{-pentamethyldiethylenetriamine; L}_4$ = 1,4,8,11-tetramethyl-1,4,8,11-tetrazacyclotetradecane) have been synthesized by reaction of AlH$_3$·NMe$_3$ with the corresponding polydentate ligand in ether solvents.$^{19}$

Two independent molecules, 2-A and 2-B, exist within the unit cell of the crystal structure of 2. Metric parameters vary enough between the two to warrant reproduction of data for both in Table 2. Compound 2-A is represented in Figure 1. While both 2-A and 2-B display trigonal bipyramidal geometry at aluminium ($\tau = 0.8$ for 2-A),$^{20}$ the metal atoms in 2-A and 2-B sit ca. 0.18 Å and 0.36 Å out of the {N1,C1,C3,C4,N5} plane respectively. The pincer-type ligand occupies a plane incorporating a single equatorial and both axial positions. The remaining equatorial sites are occupied by the hydride ligands. As expected the Al–N(ax) bond lengths of Al–NMe$_2$ [2.1976(9), 2.1821(10) Å] and Al–N [2.0104(9), 2.0055(9) Å] are much larger than the Al–N(eq) bond lengths [1.9398(8) and 1.9359(10) Å]. The largest interatomic
distance in the coordination sphere of Al is that to the 1-NMe2 group. The NaN–Al–Nax bond angles of 172.64(4) and 171.38(4)° observed in 2-A and 2-B approach linearity. For comparison, the N–Al bond lengths in 1 are 1.893(1) and 1.887(2) Å. While [κ3-(2,6-{Me2NCH2})2C6H3]AlH2] displays a similar geometry to 2 in the solid-state the Al–Nax bond lengths of 2.233(5)–2.277(5) Å are longer than the longest Al–Nax bond in 2-A/2-B and the Nax–Al–Nax bond angle of 157.8(2)° is far more bent. Both differences may be attributed to tighter geometric constraints of the -NCN- pincer ligand. The carbon-carbon and carbon-nitrogen bond lengths within the backbone of the β-diketiminate ligand of 2 are suggestive of a localised bonding scheme. Hence, the C(2)–C(3) bond lengths for 2-A and 2-B are 1.4459(12) and 1.4121 Å respectively, while the C(3)–C(4) distances are 1.3855(14) and 1.3883(18) Å.

***Figure 1 here***

***Table 1 here***

1H NMR spectroscopy data taken across a 193 to 353 K range in toluene-d8 are consistent with retention of the pseudo mirror plane of 2, apparent in the solid-state data, in solution. The methylene protons of the pincer-ligand resonate as two sets of magnetically equivalent nuclei at δ = 2.20 (t, 2H, J = 6.4 Hz) and 2.67 (t, 2H, J = 6.4Hz) ppm at 298 K in C6D6. The NMR data alone, however, cannot exclude a solution structure in which the 1-NMe2 group has dissociated from the metal to form a four-coordinate complex. In order to probe this coordination mode, both solid-state and solution (n-hexane) infrared spectra were recorded at 298 K. Infrared data on compound 2 show Al–H stretches of 1746 cm⁻¹ and 1743 cm⁻¹ in n-hexane solution and the solid-state respectively. These values are similar to those of 1778 and 1797 cm⁻¹ reported for [κ3-{(2,5-{Me2NCH2})2C6H3}AlH2]. In contrast, the related four-coordinate complex 1 displays discernable asymmetric and symmetric Al–H vibrations at 1817 and 1775 cm⁻¹ in the solid-state and 1825 and 1775 cm⁻¹ in n-hexane solution.

DFT studies were also employed to investigate the potential for ligand isomerization. Calculations were conducted on 2-C, a model of 2 in which the iso-propyl groups have been replaced by hydrogen atoms. A series of functionals and basis-sets were investigated and the results compared to experimental data. The best correlation with experiment was obtained with the M06-2X functional and a hybrid 6,31+g(d,p)
(C,H,N) and Lanl2DZ (Al) basis-set. The calculated $\nu$(Al–H) = 1721, 1745 cm$^{-1}$ match well the experimental data $\nu$(Al–H) = 1743–1746 cm$^{-1}$ as do the bond lengths around the coordination sphere. While the smaller basis-sets fail to reproduce the infrared data accurately the B3LYP and BP86 functionals do not model the Al–NMe$_2$ bond length convincingly (see ESI for further details).$^{21}$

***Table 2 here***

A scan of the potential energy surface (PES) was conducted in which the Al–NMe$_2$ coordinate was varied systematically from 2.9 – 5.0 Å. A PES in which elongation of the Al–N bond gradually destabilizes the complex was recorded. Two four coordinate analogues of 2-C, 2-D and 2-E were located as shallow local minima on the PES.

Frequency calculations confirmed both to be a true (local) minimum and revealed Al–H stretches in the range 1758–1832 cm$^{-1}$, data which are comparable to those recorded for the analogue 1 (see above). In support of the spectroscopic studies on complex 2, both four-coordinate isomers are unstable with respect to the trigonal bipyramidal five-coordinate isomer 2-C. Hence, the Gibbs free energy for the isomerization of 2-C to 2-D and 2-C to 2-E are calculated as +12.3 and +11.4 kcal mol$^{-1}$ respectively. In combination with the experimental data, these results provide a weight of evidence for the integrity of the five-coordinate geometry of 2 in solution in the absence of exogeneous reagents.

**Dimeric bis(amide) stabilised aluminium hydrides:** Reaction of $N,N'$-bis(di-iso-propylphenyl)ethylenediamine or $N,N'$-bis(mesityl)ethylenediamine with AlH$_3$·NMe$_3$ in toluene followed by recrystallisation of the crude products from $n$-hexane gave the corresponding base-stabilised four-coordinate aluminium hydride complexes 3a or 3b in moderate yields (Scheme 2). A single crystal X-ray diffraction study on 3a revealed a four-coordinate complex in which Al is chelated by the bis(amide) ligand, additional coordination at the metal is supplied by a single hydride and neutral NMe$_3$ ligand (Table 2). Due to the lower coordination number, the Al–N bond lengths [Al–N, 1.8130(9) and 1.8224(9) Å; Al–NMe$_3$, 2.0253(10) Å] are significantly shorter than those of 2. These data are similar to the Al–N bond lengths [Al–N, 1.820(1) and 1.828(1) Å; Al–NMe$_3$, 2.024(2) Å] recorded for the related propylene bridged (bis)amide complex [κ$^2$-\{(ArNCH$_2$)$_2$CH$_2$\}AlH(NMe$_3$)] (Ar = 2,6-di-iso-propylphenyl).$^{22}$
the latter propylene bridged ligand of $106.52(6) ^\circ$ is less bent than that of $93.27(4) ^\circ$ recorded for $3a$.

Multinuclear NMR data on $3a$ and $3b$ suggest the retention of the $C_2$-symmetric structure observed in the solid-state in solution with hindered rotation occurring about the N–C$_{Ar}$ bonds. For both complexes, samples at 298 K display magnetically non-equivalent environments for the ortho-substituents on the aryl rings of the ligand. Warming of a $d_8$-toluene solution of $3a$ revealed a coalescence ($T_c = 308$ K) of the ortho-methyl environments corresponding to Gibbs activation energy of 15 kcal mol$^{-1}$. For $3b$, however, coalescence of the iso-propyl methyl resonances was not observed within the temperature limit of the experiment (383 K) and are consistent with a hindered rotation about the N–C$_{Ar}$ bond proceeding with a Gibbs activation energy $>$20 kcal mol$^{-1}$. The dimerization of $3a$ and $3b$ in solution can be discounted by considering the $^1$H NMR data of cis-$4b_2$ (see below).

The possibility of amine dissociation in bis(amide) complexes was investigated by calculations. DFT studies were undertaken on the adduct [κ$^2$-(PhNCH$_2$CH$_2$NPh)AlH(NMe$_3$)] ($5$$\cdot$NMe$_3$). A scan of the PES for the dissociation of Me$_3$N from $5$$\cdot$NMe$_3$ to form 5 was conducted; this reaction is endergonic. The PES displays a smooth curve from the ground-state to the ligand dissociation product. The Gibbs free energy of trimethylamine decoordination from $5$$\cdot$NMe$_3$ is calculated as +35.8 kcal mol$^{-1}$; thus decoordination of the amine to form a three-coordinate intermediate is considerably more energetically unfavorable than that from 2-C to form a four-coordinate intermediate. Nevertheless heating of samples of $3b$ under dynamic vacuum ($1 \times 10^{-2}$ mbar, 120 °C) until gas-evolution ceased (typically < 30 min) yielded the desolvated product cis-$4b_2$ as a colourless solid that could be purified by recrystallization from n-hexane (Scheme 2).

***Scheme 2 here***

Raston and coworkers have isolated aluminium(III) hydrides supported by diamide ligands.$^{23}$ Dependent upon the reaction conditions, both trans-[AlH{µ-N(‘Bu)CH$_2$CH$_2$N(‘Bu)}$_2$ or cis-[AlH{µ-N(‘Bu)CH$_2$CH$_2$N(‘Bu)}$_2$ may be isolated.$^{23}$ These complexes dimerize via bridging amide ligands, while related pyrrole(amine) supported alanes are known to adopt the same structure as the trans-diastereomer in the solid-
Furthermore, monomer reveal that following dimerisation doublets. Groups (present as four doublet resonances in (dt, 2H, 2.91 (dd, 2H, desymmetrise and hindered rotation around the N environment is observed, retention of a dimeric configuration can, however, result in the perturbation of the ground-state structure. For example, both [tmp]₂Al[µ-H]₂ and [(hmds)₂Al[µ-H]]₂ dimerise via bridging hydrides (tmp = 2,2',6,6'-tetramethylpiperidene, hmds = hexamethyldisilazane).

Single crystals of cis-4b₂ contain pseudo C₂-symmetric cis-4b₂ along with two molecules of toluene within the asymmetric unit (Figure 2, Table 2). The terminal Al–N bond lengths [1.8167(10) and 1.8163(11) Å] are longer than those observed in both trans-[AlH(µ-N('Bu)CH₂CH₂N('Bu)) and cis-[AlH(µ-N('Bu)CH₂CH₂N('Bu))] which lie within the range of 1.756(9)–1.781(7) Å. This observation may reflect the improved σ-donor ability of alkyl- over aryl-substituted amide ligands. The Al–N distances of the bridging ligands of the asymmetric Al₂N₂ core in cis-4b₂ are elongated with respect to the terminal ligands and range from 1.9692(10)–2.0345(10) Å. The Al–Al separation is 2.7800(5) Å and far exceeds the sum of the covalent radii, 2.42 Å.

***Figure 2 here***

¹H NMR data collected on cis-4b₂ in C₆D₆ solution are best explained by the retention of a dimeric configuration in solution. Hence, while a single ligand environment is observed, due to the presence of both terminal and bridging nitrogens and hindered rotation around the N–Ar bond, the backbone of the ligand in cis-4b₂ is desymmetrised. The now diastereotopic methylene protons are observed as four distinct resonances at 2.91 (dd, 2H, J = 12.0, 4.5 Hz), 3.12 (dd, 2H, J = 12.5, 3.0 Hz), 3.64 (dt, 2H, J = 12.0 Hz, 3.0 Hz), 4.96 (dt, 2H, J = 12.5 Hz, 4.5 Hz), while the iso-propyl methyl groups (present as four doublet resonances in 3b) now resonate as eight distinct doublets.

Calculations were undertaken to elucidate the possible isomeric reaction products following dimerisation of the high-energy intermediate 5 (Figure 3). Gibbs free energies reveal that cis-5₂ is considerably more stable than the hydride bridged dimer 5₂ and the monomer 5, being some 47-48 kcal mol⁻¹ lower in energy than these species. Furthermore cis-5₂ is 3.7 kcal mol⁻¹ lower in energy than trans-5₂ (See ESI for details).
more detailed computational study is required to comment on the selectivity of the dimerisation event. Based on the high energy of amine dissociation it remains possible that the formation of cis/trans-52 from 5•NMe3 could occur via a concerted mechanism or a stepwise associative process. It is noteworthy, however, that the model cis-52, predicted to be the thermodynamic product by DFT, is analogous to that observed experimentally upon heating of 3b under dynamic vacuum at 160 °C.

A series of additional experiments support the integrity of the structure of cis-4b2 in solution and are consistent with the non-reversible dimerization following loss of trimethylamine from 3b. Hence, reaction of cis-4b2 with an excess of triethylamine or N,N-dimethyl-p-toluidene in C6D6 at 80 °C for 1 week did not result in amine coordination as evidenced by 1H NMR spectroscopy. Similarly variable temperature NMR data recorded of a toluene-d8 solution of cis-4b2 and triethylamine across the temperature range 298 – 383 K revealed no evidence for reversible amine binding.

**Cleavage of a P–C bond of triphenylphosphonium methylide with an alane:** The cleavage of P–C bonds of phosphonium ylides with organometallic reagents has received recent attention.30 We have recently reported the dehydrocoupling of phenylsilane with Ph3PCH2,30c and speculated on the outcome of the reaction of a stabilised aluminium dihydride with this reagent. The reaction of a derivative of 1, [(2,6-Me2C6H3NHCH2)2CH]AlH2, with Ph3PCH2 proceeded at 60 °C in C6D6 to give clean conversion to the P–C bond cleavage product Ph2PMe and 6 within 2 h as evidenced by 1H and 31P NMR spectroscopy (Scheme 3, Figure 3). While complex 6, a mixed hydride/aryl complex, could be isolated in a low 21 % yield and fully characterised following a preparative scale reaction, the phosphine by-product was confirmed by spiking NMR scale experiments with authentic samples of Ph2PMe.

***Scheme 3 here***

***Figure 3 here***

**Conclusions**

A series of hydride complexes of aluminium supported by β-diketiminate and bis(amide) ligands have been synthesized and investigated by a suite of characterization
methods. The correlation of gas-phase DFT (M06-2X functional employing a hybrid 6,31G+(d,p)/Lanl2DZ basis-set) studies with data from X-ray crystallography and solution and solid-state spectroscopy has been used to investigate the persistence of solid-state structures in solution. Specifically the Al–H vibrations may be used to benchmark solution data against both solid-state data and gas-phase calculations and provide a means to probe the coordination geometry of structurally diverse alanes in solution.

**Acknowledgements**

We are grateful to the Royal Society for provision of a University Research Fellowship to MRC and Imperial College Department of Chemistry for support of a PhD studentship (AEN) and undergraduate project (SJG). Peter Haycock is thanked for assistance with NMR experiments. We are grateful to Nicole Schädel for developing the improved synthesis (Method B) for compound 2.

**References**


8. For synthesis and reactions of anilido-phosphinimine stabilised dihydrides see:


Figures, Schemes, Tables and Captions

Scheme 1. Synthesis of the five-coordinate aluminium dihydride 2

![Scheme 1](image)

Table 1. Selected bond angles (°) and bond lengths (Å) in 2, 3a and 4b

<table>
<thead>
<tr>
<th></th>
<th>2</th>
<th>3a</th>
<th>cis-4b₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al—Namide/eq</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A: 1.9398(8)</td>
<td>1.8130(9),</td>
<td>1.8167(10),</td>
<td>1.8163(11)</td>
</tr>
<tr>
<td>B: 1.9359(10)</td>
<td>1.8224(9)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al—Namine/ax</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A: 2.0104(9), 2.1976(9)</td>
<td>2.0253(10)</td>
<td>1.9848(10),</td>
<td>2.0261(10)</td>
</tr>
<tr>
<td>B: 2.0055(9), 2.1821(10)</td>
<td></td>
<td>1.9692(10),</td>
<td>2.0345(10)</td>
</tr>
<tr>
<td>N—Al—N</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A: 91.76(4), 80.93(3)</td>
<td>93.27(4)</td>
<td>91.90(4), 91.55(4)</td>
<td></td>
</tr>
<tr>
<td>B: 91.16(4), 81.00(4)</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Nax—Al—Nax</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A: 172.64(4)</td>
<td>—</td>
<td></td>
<td></td>
</tr>
<tr>
<td>B: 171.38(4)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 2. Comparison of Al—H stretches of with gas-phase calculated values in models.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Solution (Al—H) / cm⁻¹</th>
<th>Solid-state (Al—H) / cm⁻¹</th>
<th>Model</th>
<th>Calculated[a] (Al—H) / cm⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1825, 1775</td>
<td>1817, 1775</td>
<td>2-D</td>
<td>1790, 1758</td>
</tr>
<tr>
<td>2</td>
<td>1746[b]</td>
<td>1743[b]</td>
<td>2-E</td>
<td>1832, 1806</td>
</tr>
<tr>
<td>3a</td>
<td>1823</td>
<td>1776</td>
<td>2-C</td>
<td>1745, 1721</td>
</tr>
<tr>
<td>3b</td>
<td>1822</td>
<td>1829</td>
<td>5•NMe₃</td>
<td>1871</td>
</tr>
<tr>
<td>cis-4b₂</td>
<td>[c]</td>
<td>1903</td>
<td>cis-5₂</td>
<td>1910, 1906</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>trans-5₂</td>
<td>1878</td>
</tr>
</tbody>
</table>

[a] Non-corrected values calculated from frequency calculations on optimised geometries. [b] Distinct asymmetric and symmetric stretches not observed. [c] The low solubility of cis-4b₂ in n-hexane prevented the acquisition of solution IR data.
**Figure 1.** The crystal structure of 2-A. One of the two independent molecules present in the crystal of 2.

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**Scheme 2.** Synthesis of 3a-b and the desolvation of 3b to cis-4b

**Figure 2.** The crystal structure of cis-4b·(C₇H₈)₂. Toluene molecules omitted for clarity.
**Scheme 3.** Reaction of an aluminium dihydride with Ph₃PCH₂.

![Reaction Scheme]

**Figure 3.** DFT data on the stability of the isomers of 5₂ relative to two equivalents of 5

<table>
<thead>
<tr>
<th>Model</th>
<th>5 (x2)</th>
<th>5₂</th>
<th>trans-5₂</th>
<th>cis-5₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gibbs Free Energy / kcal mol⁻¹</td>
<td>0</td>
<td>-1.0</td>
<td>-45.2</td>
<td>-48.9</td>
</tr>
</tbody>
</table>

**Figure 4.** Crystal Structure of 6. Selected bond angles (°) and bond lengths (Å): Al–N 1.9018(10), Al–C 1.9833(17), N–Al–N 96.03(6), N–Al–C 115.72(4).