Preparation and Properties of a Series of Structurally Diverse Aluminium Hydrides Supported by β -Diketimate 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 $[(2,6\text{-}i\text{-Pr}_2\text{C}_6\text{H}_3)\text{NC}(\text{Me})\text{CHC}(\text{Me})\text{N}(\text{H})\text{CH}_2\text{CH}_2\text{NMe}_2]$ with either LiAlH_4 or $\text{Me}_3\text{N}\cdot\text{AlH}_3$ allows isolation of the corresponding five-coordinate aluminium dihydride $[\kappa^3\text{-}\{(2,6\text{-}i\text{-Pr}_2\text{C}_6\text{H}_3)\text{NC}(\text{Me})\text{CHC}(\text{Me})\text{NCH}_2\text{CH}_2\text{NMe}_2\}\text{AlH}_2]$ (**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 $\text{Me}_3\text{N}\cdot\text{AlH}_3$ with both *N,N'*-bis(di-iso-propylphenyl)ethylenediamine and *N,N'*-bis(mesityl)ethylenediamine gave $[\{\kappa^2\text{-}(\text{ArNCH}_2)_2\}\text{AlH}(\text{NMe}_3)]$ (Ar = Mes, **3a**; Ar = 2,6-di-iso-propylphenyl, **3b**) in moderate yields. Removal of NMe_3 from **3b** by heating under dynamic vacuum allowed the isolation of *cis*- $[\text{AlH}\{\mu\text{-N}(\text{Ar})\text{CH}_2\text{CH}_2\text{N}(\text{Ar})\}]$ (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, $[\kappa^2\text{-}\{(2,6\text{-Me}_2\text{C}_6\text{H}_3\text{NHCH}_2)_2\text{CH}\}\text{AlH}_2]$, promotes the P–C bond cleavage of Ph_3PCH_2 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.¹⁻³ 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.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.⁴⁻⁸ The low electronegativity of Al ($\chi_p = 1.61$) along with a tendency of the Al^{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.²⁻³ Despite these advances, there is little information on the solution structures of more complex aluminium hydrides.

Consider the adduct $\text{Me}_3\text{N}\cdot\text{AlH}_3$. In the gas-phase this complex is monomeric as evidenced by electron diffraction studies,⁹ however it crystallizes as $[\text{Me}_3\text{N}\cdot\text{AlH}_2(\mu\text{-H})]_2$ a derivative of dialane that possess weakly bonded bridging hydride ligands.¹⁰ Molecular weight determinations in diethyl ether suggest a degree of aggregation in solution between monomeric and dimeric.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.¹¹

In this latter regard, we have previously reported $[\{(\text{MesNCMe})_2\text{CH}\}\text{AlH}_2]$ (**1**) as a terminal reductant for the hydrodefluorination of fluoroarenes catalyzed by zirconocene dichloride.^{12a} Herein we disclose the synthesis and characterization of a five-coordinate β -diketiminato 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 *bis*(amide) supported aluminium hydride is also reported along with an unusual P–C bond cleavage reaction of Ph_3PCH_2 promoted by an aluminium dihydride.

Experimental

General Experimental: LiAlH_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'*-*bis*(di-*iso*-propylphenyl)ethylenediamine,¹³ *N,N'*-*bis*(mesityl)ethylenediamine,¹⁴ $[\{(\text{2,6-Me}_2\text{C}_6\text{H}_3\text{NCMe})_2\text{CH}\}\text{AlH}_2]$,^{5f} $[\{(\text{MesNCMe})_2\text{CH}\}\text{AlH}_2]$ ^{5f} and $[\{2,6-$

$i\text{-Pr}_2\text{C}_6\text{H}_3\}\text{NC}(\text{Me})\text{CHC}(\text{Me})\text{N}(\text{H})\text{CH}_2\text{CH}_2\text{NMe}_2]$ 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, LiAlH_4 powder (414 mg, 10.9 mmol, 1.2 equiv.) was added to a Schlenk tube, the Schlenk was cooled to $-78\text{ }^\circ\text{C}$ followed by careful addition of diethyl ether (20 mL). To this mixture was added a solution of $[\{2,6-i\text{-Pr}_2\text{C}_6\text{H}_3\}\text{NC}(\text{Me})\text{CHC}(\text{Me})\text{N}(\text{H})\text{CH}_2\text{CH}_2\text{NMe}_2]$ (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 $25\text{ }^\circ\text{C}$ 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 $-18\text{ }^\circ\text{C}$ 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 $-78\text{ }^\circ\text{C}$. A solution of the pro-ligand (0.83 g, 2.53 mmol) in toluene (10 mL) was added to this mixture *via* cannula. The reaction mixture was warmed to $25\text{ }^\circ\text{C}$ 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 %). ^1H NMR (C_6D_6 , 400 Hz, 298 K) δ 1.27 (d, 6H, $^3J_{\text{H-H}} = 6.8\text{ Hz}$, CHMe_2), 1.69 (d, 6H, $^3J_{\text{H-H}} = 6.8\text{ Hz}$, CHMe_2), 1.71 (s, 3H, *Me*), 1.72 (s, 3H, *Me*), 1.96 (s, 6H, NMe_2), 2.20 (t, 2H, $^3J_{\text{H-H}} = 6.4\text{ Hz}$, NCH_2CH_2), 2.76 (t, 2H, $^3J_{\text{H-H}} = 6.4\text{ Hz}$, NCH_2), 3.67 (hept, 2H, $^3J_{\text{H-H}} = 6.8\text{ Hz}$, CHMe_2), 4.87 (s, 1H, *CH*), 7.3 (m, 3H, *ArH*); ^{13}C NMR (C_6D_6 , 100 MHz, 298 K) δ 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 $\text{C}_{21}\text{H}_{36}\text{AlN}_3$ = C: 70.55%, H: 10.15%, N: 11.75% Found = C, 70.42%; H, 10.05%; N, 11.68%.

Synthesis of 3a: In a glovebox, *N,N'*-bis(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. ^1H NMR (400 MHz, C_6D_6) δ 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}C NMR (101 MHz, C_6D_6 , 298 K) δ 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 $\text{C}_{23}\text{H}_{36}\text{AlN}_3$ = 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, *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%). ^1H NMR (C_6D_6 , 400 Hz, 298 K) δ 1.25 (d, 6H, $^3J_{\text{H-H}} = 7.2$ Hz), 1.38 (d, 6H, $^3J_{\text{H-H}} = 6.8$ Hz), 1.47 (d, 6H, $^3J_{\text{H-H}} = 7.2$ Hz), 1.62 (d, 6H, $^3J_{\text{H-H}} = 6.8$ Hz), 1.71 (s, 9H), 3.32-3.40 (m, 2H), 3.63-3.70 (m, 2H), 3.84 (sept, 2H, $^3J_{\text{H-H}} = 6.8$ Hz), 4.32 (sept, 2H, $^3J_{\text{H-H}} = 6.8$ Hz), 7.18-7.23 (m, 4H), 7.27-7.32 (m, 2H); ^{13}C NMR (101 MHz, C_6D_6 , 298 K) δ 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 $\text{C}_{29}\text{H}_{48}\text{AlN}_3$ = C: 74.79%, H: 10.39%, N: 9.01% Found = C: 74.62%, H: 10.26%, N: 9.13%.

Synthesis of cis-4b₂ 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 (C₆D₆, 400 Hz, 298 K) δ 0.89 (d, 6H, ³J_{H-H} = 6.5 Hz), 0.96 (d, 6H, ³J_{H-H} = 6.0 Hz) 1.19 (d, 6H, ³J_{H-H} = 6.5 Hz) 1.26 (d, 6H, ³J_{H-H} = 7.0 Hz) 1.33 (d, 6H, ³J_{H-H} = 6.5 Hz) 1.35 (d, 6H, ³J_{H-H} = 7.0 Hz) 1.42 (d, 6H, ³J_{H-H} = 6.5 Hz) 1.50 (d, 6H, ³J_{H-H} = 7.0 Hz), 2.46 (sept, 2H, ³J_{H-H} = 6.8 Hz), 2.91 (dd, 2H, ²J_{H-H} = 10.5 Hz, ³J_{H-H} = 4.5 Hz), 3.12 (dd, 2H, ²J_{H-H} = 12.5 Hz, ³J_{H-H} = 3.0 Hz), 3.64 (dt, 2H, ²J_{H-H} = 12.0 Hz, ³J_{H-H} = 3.0 Hz), 3.86 (sept, 2H, ³J_{H-H} = 6.5 Hz), 3.95 (sept, 2H, ³J_{H-H} = 6.5 Hz), 4.04 (sept, 2H, ³J_{H-H} = 7.0 Hz), 4.31 (br, 2H), 4.96 (dt, 2H, ²J_{H-H} = 12.0 Hz, ³J_{H-H} = 4.5 Hz), 6.93-7.03 (m, 6H), 7.19-7.25 (m, 6H); ¹³C NMR (101 MHz, C₆D₆, 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 C₅₂H₇₈Al₂N₄ = 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 methylide (0.332 g, 1.2 mmol) and [{(2,6-Me₂C₆H₃NCMe)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 C₆H₆ (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 (C₆D₆, 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, ³J_{H-H} = 7.6 Hz), 6.98 (d, 2H, ³J_{H-H} = 7.6 Hz), 7.05 (d, 2H, ³J_{H-H} = 7.6 Hz), 7.24-7.27 (m, 3H), 7.75-7.80 (m, 2H); ¹³C NMR (101 MHz, C₆D₆, 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 *F*² using the SHELXTL and SHELX-97 program systems.¹⁵ The Al-H hydrogen atoms in all structures were located

from ΔF maps and refined freely. CCDC numbers 954263-954265 and 953189

Results and Discussion

A five-coordinate β -Diketiminato stabilised aluminium dihydride: Compound **2** could be prepared directly from the pro-ligand by reaction with either $\text{AlH}_3 \cdot \text{NMe}_3$ 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 $[\kappa^3\text{-}\{2,6\text{-(Me}_2\text{NCH}_2)_2\text{C}_6\text{H}_3\}\text{AlH}_2]$ and $[\kappa^3\text{-}\{2,5\text{-(Me}_2\text{NCH}_2)_2\text{C}_4\text{H}_2\text{N}\}\text{AlH}_2]$ 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 $[\text{L}_2\text{AlH}_3]$, in which the hydrides all sit in the trigonal plane ($\text{L} = \text{NMe}_3$, thf, quinuclidine, 1,3,5-trimethylhexahydro-1,3,5-triazine; $\text{L}_2 = N$ -methyldmorpholine, tmeda, N,N',N'',N''' -tetramethylpropylenediamine, $^i\text{Pr}_2\text{PCH}_2\text{CH}_2\text{P}^i\text{Pr}_2$).¹⁸ Related, five and six-coordinate dihydrides $[\text{L}_n\text{AlH}_2]^+[\text{AlH}_4]^-$ ($\text{L}_3 = N,N,N',N'',N'''$ -pentamethyldiethylenetriamine; $\text{L}_4 = 1,4,8,11$ -tetramethyl-1,4,8,11-tetrazacyclotetradecane) have been synthesized by reaction of $\text{AlH}_3 \cdot \text{NMe}_3$ 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-NMe₂ [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 -NMe_2 group. The $\text{N}_{\text{ax}}\text{-Al-N}_{\text{ax}}$ bond angles of $172.64(4)$ and $171.38(4)^\circ$ 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.^{5f} While $[\kappa^3\text{-}\{2,6\text{-(Me}_2\text{NCH}_2)_2\text{C}_6\text{H}_3\}\text{AlH}_2]$ displays a similar geometry to **2** in the solid-state the Al-N_{ax} bond lengths of $2.233(5)\text{--}2.277(5)$ Å are longer than the longest Al-N_{ax} bond in **2-A/2-B** and the $\text{N}_{\text{ax}}\text{-Al-N}_{\text{ax}}$ bond angle of $157.8(2)^\circ$ is far **more bent**. Both differences may be attributed to tighter geometric constraints of the -NCN- pincer ligand.¹⁶ The carbon-carbon and carbon-nitrogen bond lengths within the backbone of the β -diketiminato ligand of **2** are suggestive of a localised bonding scheme. Hence, the $\text{C}(2)\text{-C}(3)$ bond lengths for **2-A** and **2-B** are $1.4459(12)$ and 1.4121 Å respectively, while the $\text{C}(3)\text{-C}(4)$ 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- d_8 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 $\delta = 2.20$ (t, 2H, $J = 6.4$ Hz) and 2.67 (t, 2H, $J = 6.4$ Hz) ppm at 298 K in C_6D_6 . The NMR data alone, however, cannot exclude a solution structure in which the -NMe_2 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 $[\kappa^3\text{-}\{2,5\text{-(Me}_2\text{NCH}_2)_2\text{C}_4\text{H}_2\text{N}\}\text{AlH}_2]$.^{17a} 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 $\nu(\text{Al-H}) = 1721, 1745 \text{ cm}^{-1}$ match well the experimental data $\nu(\text{Al-H}) = 1743\text{--}1746 \text{ cm}^{-1}$ 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-NMe₂ 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-NMe₂ 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 AlH₃·NMe₃ 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 NMe₃ 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-NMe₃, 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-NMe₃, 2.024(2) Å] recorded for the related propylene bridged (*bis*)amide complex [κ^2 -{(ArNCH₂)₂CH₂}AlH(NMe₃)] (Ar = 2,6-di-*iso*-propylphenyl).²² The N-Al-N bite angle of

the latter propylene bridged ligand of 106.52(6)° is **less bent** than that of 93.27(4)° recorded for **3a**.

Multinuclear NMR data on **3a** and **3b** suggest the retention of the C_s -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 d₈-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 ¹H 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 -(PhNCH₂CH₂NPh)AlH(NMe₃)] (**5•NMe₃**). A scan of the PES for the dissociation of Me₃N from **5•NMe₃** 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 decooordination from 5•NMe₃ is calculated as +35.8 kcal mol⁻¹; thus decooordination 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 x 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(^tBu)CH₂CH₂N(^tBu)}]₂ or *cis*-[AlH{μ-N(^tBu)CH₂CH₂N(^tBu)}]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-

state.²⁴ Related aluminium alkyl complexes are known.²⁵⁻²⁶ The preference for amide supported aluminium complexes to aggregate *via* bridging amide ligands is further highlighted by the solid-state structures of $[(\text{Me}_2\text{N})(\text{H})\text{Al}(\mu\text{-NMe}_2)]_2$ and D_{2h} -symmetric $[(\text{H}_2\text{Al}\{\mu\text{-N}(\text{CH}_2)_5\})_2]$.²⁷ Increasing the steric demands of the nitrogen substituents on the amide ligands can, however, result in the perturbation of the ground-state structure. For example, both $[(\text{tmp})_2\text{Al}(\mu\text{-H})]_2$ and $[(\text{hmds})_2\text{Al}(\mu\text{-H})]_2$ dimerize *via* bridging hydrides (tmp = 2,2',6,6'-tetramethylpiperidene, hmds = hexamethyldisilazane).²⁸

Single crystals of *cis*-**4b₂** contain *pseudo* C_2 -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*- $[\text{AlH}\{\mu\text{-N}(\text{tBu})\text{CH}_2\text{CH}_2\text{N}(\text{tBu})\}]$ and *cis*- $[\text{AlH}\{\mu\text{-N}(\text{tBu})\text{CH}_2\text{CH}_2\text{N}(\text{tBu})\}]$ 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 Al_2N_2 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.²⁹

Figure 2 here

¹H NMR data collected on *cis*-**4b₂** in C_6D_6 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). A

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-*d*₈ 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 methyllide 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.

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Figures, Schemes, Tables and Captions

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

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

	2	3a		<i>cis</i> - 4b ₂
Al–N_{amide/eq}	A: 1.9398(8) B: 1.9359(10)	1.8130(9), 1.8224(9)	Al–N_{terminal}	1.8167(10), 1.8163(11)
Al–N_{amine/ax}	A: 2.0104(9), 2.1976(9) B: 2.0055(9), 2.1821(10)	2.0253(10)	Al–N_{bridging}	1.9848(10), 2.0261(10) 1.9692(10), 2.0345(10)
N–Al–N	A: 91.76(4), 80.93(3) B: 91.16(4), 81.00(4)	93.27(4)	N–Al–N	91.90(4), 91.55(4)
N_{ax}–Al–N_{ax}	A: 172.64(4) B: 171.38(4)	–	Al–Al	2.7800(5)
			Al–N–Al	88.17(4), 87.52(4)

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

Compound	Solution (Al–H) / cm ^{–1}	Solid-state (Al–H) / cm ^{–1}	Model	Calculated ^[a] (Al–H) / cm ^{–1}
1	1825, 1775	1817, 1775	2-D	1790, 1758
			2-E	1832, 1806
2	1746 ^[b]	1743 ^[b]	2-C	1745, 1721
3a	1823	1776	5·NMe₃	1871
3b	1822	1829		
<i>cis</i> - 4b ₂	– ^[c]	1903	<i>cis</i> - 5 ₂	1910, 1906
			<i>trans</i> - 5 ₂	1878

[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*-**4b**₂ 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**.

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

Figure 2. The crystal structure of *cis*-**4b**₂·(C₇H₈)₂. Toluene molecules omitted for clarity.

Scheme 3. Reaction of an aluminium dihydride with Ph_3PCH_2 .

Figure 3. DFT data on the stability of the isomers of 5_2 relative to two equivalents of **5**

5

5₂

trans-5₂

cis-5₂

Model	5 (x2)	5₂	<i>trans-5₂</i>	<i>cis-5₂</i>
Gibbs Free				
Energy / kcal mol ⁻¹	0	-1.0	-45.2	-48.9

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).