Introduction

Main group element-based molecules have been promoted as lower-cost and less toxic alternatives to some transition metals for bond transformations and catalysis. The lighter main group elements (rows 2 and 3) meet these desirable criteria and continue to be an area of intense study. An example is oxidative addition at a low-valent element such as in singlet carbenes, addition at a low-valent element such as in singlet carbenes, or singlet carbenes, and iminato ligands can be used as catalysts for a number of reactions including hydroboration of aldehydes, ketones, and dehydrocoupling of boranes with amines, including organoaluminum and aluminum-hydride chemistry, and continue to be interested in the reactivity of sterically bulky aluminum hydrides.

Recently, it has been shown that aluminum hydride complexes of β-diketiminato, diamidato, and imidazolin-2-iminato ligands can be used as catalysts for a number of reactions including hydroboration of aldehydes, ketones, and trimethylcyanide addition to aldehydes and ketones, and dehydrocoupling of boranes with amines, including organoaluminum and aluminum-hydride chemistry, and continue to be interested in the reactivity of sterically bulky aluminum hydrides. With the previously mentioned aluminum-based catalysis reactions in mind, we report the reactivity of aluminum β-diketiminato dihydride, L-AlH₂ (L = HC(MeCNDipp)₂), Dipp = 2,6-diisopropylphenyl), with two sterically bulky phenols (2,4,6-trimethylphenol, MesOH; 2,6-diisopropylphenol, DippOH) and an N-hydroxylamine (1-hydroxy-2,2,6,6-tetramethyl-piperidine, TEMPO-H) forms an Al–O bond with concomitant loss of hydrogen gas to give L-Al(H)OMes, L-Al(H)ODipp and L-Al(H)TEMPO, respectively. Reaction with 1 or 2 equivalents of benzaldehyde or 1 equivalent of benzenophenone results in insertion of carbonyl into the Al–H bond(s) to give the related benzylation and diphenylmethoxide products. Compounds L-Al(H)OMes, L-Al(H)ODipp, L-Al(H)TEMPO, L-Al(H)OBn, L-Al(OBn)₂, and L-Al(H)OCHPh₂ have been characterized by NMR spectroscopy, elemental analysis, infrared spectroscopy and single crystal X-ray diffraction. The reaction of L-Al(H)OBn with pinacol borane gives a complex mixture of unidentifiable products, providing evidence of the importance of the triflate group in the known aldehyde and ketone hydroboration catalyst L-Al(H)OTf (OTf = CF₃SO₂⁻).

Results and discussion

Reaction of sterically encumbered phenols, TEMPO-H, and organocarboxyl insertion reactions with L-AlH₂ (L = HC(MeCNDipp)₂, Dipp = 2,6-diisopropylphenyl)

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The reaction of L-AlH₂ (L = HC(MeCNDipp)₂, Dipp = 2,6-diisopropylphenyl) with sterically bulky phenols (2,4,6-trimethylphenol, MesOH; 2,6-diisopropylphenol, DippOH) and an N-hydroxylamine (1-hydroxy-2,2,6,6-tetramethyl-piperidine, TEMPO-H) forms an Al–O bond with concomitant loss of hydrogen gas to give L-Al(H)OMes, L-Al(H)ODipp and L-Al(H)TEMPO, respectively. Reaction with 1 or 2 equivalents of benzaldehyde or 1 equivalent of benzenophenone results in insertion of carbonyl into the Al–H bond(s) to give the related benzylation and diphenylmethoxide products. Compounds L-Al(H)OMes, L-Al(H)ODipp, L-Al(H)TEMPO, L-Al(H)OBn, L-Al(OBn)₂, and L-Al(H)OCHPh₂ have been characterized by NMR spectroscopy, elemental analysis, infrared spectroscopy and single crystal X-ray diffraction. The reaction of L-Al(H)OBn with pinacol borane gives a complex mixture of unidentifiable products, providing evidence of the importance of the triflate group in the known aldehyde and ketone hydroboration catalyst L-Al(H)OTf (OTf = CF₃SO₂⁻).
Dipp groups. There is also a slight widening of the N–Al–N angle (98.18(6)°) compared to that of L-AlH2 (96.41(5)°). The Al–O–C angle (151.28(11)°) is smaller than that in other aluminum compounds containing bulky phenolates; for example, three- and four-coordinate Al compounds containing the 2,6-BuC6H3O group have Al–O–C angles ranging from 157.51 Å to 177.21 Å.29 The hydrogen atom attached to aluminum was found in the difference map and refined to give an Al–H distance of 1.519(17) Å, which is the same as that found in L-AlH2 (1.512(2) Å and 1.518(19) Å). For compound 2, compared to 1, the aluminum atom is less distorted (average 0.51 Å) from the mean plane defined by the N–C–C–C–N ligand backbone. The Al–O–C angle (average 161.51°) is larger than that in 1, presumably due to less significant steric interactions between the phenoxide and the ligand N-Dipp groups. In addition, the N–Al–N angle (average 97.26°) is slightly larger than that in 1. Finally, there are no significant intermolecular interactions to report.

(90%) of compound 1, whereas the MesOH reaction had a poor isolated yield due to the high solubility of compound 2. Analysis of the crude reaction mixture of 2 revealed a mixture of 90% 2 and 10% starting material L-AlH2. 1H NMR spectroscopy revealed the expected signals for the ligand framework and the respective phenolates. However, the Al–H signal was not observable, presumably due to broadening and a relatively low intensity. The presence of the hydride was confirmed with IR spectroscopy; the Al–H stretch peaks appeared at 1850 cm⁻¹ (compound 1) and 1865 cm⁻¹ (compound 2) (Scheme 1).

X-ray quality crystals of compounds 1 and 2 were obtained from the pentane solutions after cooling to −35 °C. Compound 1 crystallized in the monoclinic space group P2₁/c with one equivalent of pentane. Multiple crystals of compound 2 were analysed (triclinic, P1) but we had difficulty obtaining good data; there were disordered units of co-crystallized pentane that had to be removed using the SQUEEZE routine in PLATON²⁷ to give a reasonable model. Structures are shown in Figs 1 and 2. The structure of compound 1 reveals the distortions to the six-membered aluminum chelate. The Al atom is 0.549(2) Å out of the plane defined by the N1–C3–C2–C1–N2 β-diketiminate backbone, on the side opposite the phenolate group. This is in contrast to the parent L-AlH2 where the Al atom is in the plane of the ligand backbone.²⁸ This distortion is necessary to accommodate the large Dipp-O group by reducing the interactions with the flanking β-diketiminate Dipp groups. There is also a slight widening of the N–Al–N angle (98.18(6)°) compared to that of L-AlH2 (96.41(5)°). The Al–O–C angle (151.28(11)°) is smaller than that in other aluminum compounds containing bulky phenolates; for example, three- and four-coordinate Al compounds containing the 2,6-BuC6H3O group have Al–O–C angles ranging from 157.51 Å to 177.21 Å.²⁹ The hydrogen atom attached to aluminum was found in the difference map and refined to give an Al–H distance of 1.519(17) Å, which is the same as that found in L-AlH2 (1.512(2) Å and 1.518(19) Å). For compound 2, compared to 1, the aluminum atom is less distorted (average 0.51 Å) from the mean plane defined by the N–C–C–C–N ligand backbone. The Al–O–C angle (average 161.51°) is larger than that in 1, presumably due to less significant steric interactions between the phenoxide and the ligand N-Dipp groups. In addition, the N–Al–N angle (average 97.26°) is slightly larger than that in 1. Finally, there are no significant intermolecular interactions to report.

Reaction of L-AlH2 with 2,4,6-tri-ℓ-butylyphenol or BHT resulted in no reaction, even under forcing conditions (110 °C, toluene). Attempts to react a second equivalent of DippOH with 1 under similar conditions resulted in only starting materials when analysed with 1H NMR spectroscopy. Reacting L-AlH2 with two equivalents of MesOH at room temperature gave a crop

![Dipp groups](image)
of crystals from cold pentane. None of the crystals gave a suitable diffraction pattern for crystallographic analysis. Curiously, when the $^1$H NMR spectrum was measured, it appeared that there was a 1 : 1 ratio of 2 and MesOH in the sample. Results from elemental analysis gave the correct values for 2 + MesOH in a 1 : 1 ratio, implying that this was a co-crystal of the two species. Since single crystal XRD was not possible, we measured the IR spectrum and noted that there were no changes in the Al–H stretching frequency, implying that the co-crystal does not include significant Al–H···H–O interactions between 2 and MesOH. We were unable to ascertain any change in the O–H stretch of the co-crystallized MesOH compared to free MesOH as these signals were quite broad.

**Reaction with TEMPO-H**

Originally, we attempted to react L-AlH$_2$ with TEMPO-H produced using methods from the literature, i.e. via reduction of TEMPO, (2,2,6,6-tetramethylpiperidin-1-yl)oxyl, with aqueous ascorbic acid. TEMPO-H is known to sublime in a 3 : 1 ratio and upon reaction of L-AlH$_2$ with anhydrous TEMPO-H we found that the resulting L-Al(H)TEMPO$_2$ (needle-like crystals, Fig. 3) was contaminated with L-Al(OH)TEMPO$_4$ (block-like crystals, Fig. 4) when grown from a cooled hexane solutions (Scheme 2). This prompted us to prepare TEMPO-H using anhydrous methods, and we have reported this elsewhere. The reaction of L-AlH$_2$ with anhydrous TEMPO-H proceeds smoothly at room temperature in hexanes with rapid evolution of gas. After normal workup, L-Al(H)TEMPO$_3$ was isolated as colorless, needle-like crystals in moderate isolated yield (59%, due to high solubility of 3). The $^1$H NMR spectrum has features containing both the β-diketiminate ligand and the TEMPO fragment, including a broad singlet at 1.20 ppm related to the ascorbic acid.

Compound 3 crystallizes as the monoclinic space group $P2_1/n$. The hydrogen atom bound to aluminum was found in the difference map and refined to give a typical distance of 1.51(3) Å. Similar to that in compounds 1 and 2, the aluminum atom in 3 is distorted out of the mean plane (N1–C1–C3–C4–N2) by 0.623(3) Å and the Al–O–N angle is 114.70(11)$^\circ$ to accommodate the bulky TEMPO ligand between the ligand-based N-Dipp groups. Finally, the N–Al–N angle of 94.60(11)$^\circ$ is more acute than that in 1, 2 and L-AlH$_2$, and the Al–O distance (1.745(2) Å) is considerably longer than that of 1 (1.7115(12) Å) and 2 (1.6955(18) Å).

Compound 4 crystallizes in the triclinic space group $P1$. Visually, compound 4 is similar to 3 except that the aluminum hydride has been replaced by an OH group. The Al–O1 distance of 1.7388(19) Å is similar to that in 3, whereas the N–Al–N angle of 94.90(9)$^\circ$ is slightly larger than that in 3. The Al atom is 0.596(3) Å out of the N1–C1–C3–C4–N2 mean plane, which is less than that in 3 and coincides with the larger Al–O–N angle (120.91(13)$^\circ$). The Al–O2 distance of 1.694(2) Å is considerably shorter than that of the Al–O1 distance; however, it is similar to the Al–O distances in NacNacAl(OH)$_2$ (1.6947(15) Å and 1.7107(16) Å). It should be noted that there are no intermolecular hydrogen bonding interactions of the O–H group with other atoms. This is in line with other β-diketinate-based terminal aluminum monohydrates in the literature.
that is hidden in the baseline; this has been tentatively assigned to the single aluminum hydride. Correspondingly, IR spectroscopy reveals an Al–H stretch at 1818 cm\(^{-1}\). In 6, the benzyl \(\text{CH}_2\) signal appears at \(\delta 4.82\) ppm and the symmetrical nature of the molecule is evident with only one septet and two doublets from the isopropyl groups.

In the solid state, mono-insertion product 5 crystallizes in the orthorhombic space group \(P2_1_2_1_2_1\), with one molecule of 5 in the asymmetric unit (Fig. 5). In order to minimize the steric interactions between the \(\text{OCH}_2\text{Ph}\) group and the flanking Dipp groups, the aluminum atom is pushed \(0.544(2)\) \(\text{Å}\) out of the plane defined by the N1–C1–C3–C4–N2 ligand backbone. Again, to minimize steric interactions, the Ph ring of the \(\text{OCH}_3\text{Ph}\) group is twisted so that it is nearly coplanar with the N–C–C–C–N ligand backbone at a dihedral angle of 8.68(12)° between the two planes. The N–Al–N angle 97.04° is slightly more obtuse than that observed in 3 or 4, and is more in line with the angles observed in compounds 1 and 2. In the solid state, double-insertion product 6 crystallizes in the \(P2_1/c\) space group with one molecule in the asymmetric unit (Fig. 6). One of the two \(\text{OCH}_3\text{Ph}\) groups exhibits a two component disorder in a 56 : 44 ratio. Due to the steric constraints of two \(\text{OCH}_3\text{Ph}\) groups on aluminum, the Al atom is only 0.388(2) \(\text{Å}\) out of the ligand N1–C1–C3–C4–N2 plane. In order to accommodate the two \(\text{OCH}_3\text{Ph}\) groups, one \(\text{OCH}_3\text{Ph}\) is twisted in a manner similar to that seen in compound 5, while the other is significantly twisted with the \(\text{CH}_2\text{Ph}\) moiety sandwiched between the isopropyl groups of the two Dipp groups. The N–Al–N angle (97.32(7)°) is similar to that in mono-insertion compound 5. The O–Al–O angle (115.3(5)°) is slightly more acute than that observed in compound 4.

Next, we looked at benzophenone as an example ketone for reactivity. Reaction of L–AlH\(_2\) with one equivalent of benzophenone proceeded smoothly at room temperature in pentane. Upon work up, the ketone insertion product, L–Al(\(\text{H}\))OCH\(_2\text{Ph}\), was isolated as colorless crystals from cold pentane. Analysis by IR spectroscopy revealed an Al–H stretch at 1814 cm\(^{-1}\), similar

Reactions with benzaldehyde and benzophenone

Aluminum hydrides are common stoichiometric reducing agents for organo-carbonyl groups, and recently they have been reported to act as catalysts in the hydroboration of acetylenes\(^{13,14}\) and organo-carbonyls.\(^{15-18}\) We were curious about the insertion of a carbonyl group into the Al–H bond as these products are postulated to be intermediates in the catalytic hydroboration process.\(^{15}\) Reaction of L–AlH\(_2\) with 1 or 2 equivalents of benzaldehyde in pentane at room temperature gave insertion products 5 or 6, respectively (Scheme 3). It should be noted that when only one equivalent of benzaldehyde is added, a mixture of compounds 5, 6, and L–AlH\(_2\) results, providing evidence that carbonyl insertion into the Al–H bond is competitive between L–AlH\(_2\) and the mono-insertion product 5. In 5, the characteristic benzyl \(\text{CH}_2\) signal appears at \(\delta 4.58\) ppm. The asymmetric nature of the molecule is clear with two sets of septets and two pairs of doublets arising from the isopropyl groups on the Al–H side or on the Al–OCH\(_2\text{Ph}\) side of the molecule. There is a very broad signal between 3.9 and 5.3 ppm

![Scheme 3 Reaction of L–AlH\(_2\) with benzaldehyde and benzophenone.](image-url)

![Molecular structure of compound 5, L–Al(\(\text{H}\))OCH\(_3\text{Ph}\), with thermal ellipsoids projected at the 50% probability level.](image-url)
to that for 5 (1818 cm\(^{-1}\)), but much lower than that in 1 and 2 (1850 and 1865 cm\(^{-1}\), respectively), presumably due to the stronger \(\sigma\)-withdrawing effects of the phenoxide derivatives. The \(^1\)H NMR spectrum reveals signals from the ligand that are typical of a complex that is unsymmetrical with respect to the top and bottom halves, as is expected for this complex. Most diagnostic is the methine signal of the alkoxide, which appears at \(\delta\) 5.79 ppm. Unfortunately, we were unable to observe the remaining Al–H signal in the \(^1\)H NMR spectrum, presumably due to the quadrupolar nature of the Al atom. Compound 7 crystallizes in the triclinic space group \(\text{P}1\) with one molecule in the asymmetric unit (Fig. 7). Just as with the other mono-substituted variants in this report, the aluminum atom in 7 is distorted out of the mean plane \((\text{N1}–\text{C1}–\text{C3}–\text{C4}–\text{N2})\) by 0.583(4) Å, and the Al–O–C angle is 123.9(3)° to maximize the distance between the OCHPh\(_2\) substituent and the Dipp groups. The N–Al–N angle (96.38(14)°) is similar to that in benzoaldehyde derivatives 5 and 6. Finally, addition of a second equivalent of benzophenone and heating to 100 °C in toluene showed no reaction when analysed with \(^1\)H NMR spectroscopy. Presumably this is due to the extreme steric bulk of the ligands surrounding the aluminum center.

We were curious to see if mono-benzylate derivative 5 would react with pinacol borate (HBpin) to eliminate PhCH\(_2\)OBPin and L-AlH\(_2\) in a manner similar to that observed in catalytic hydroboration using L-Al[H](O\(_3\)SCF\(_3\)). In an NMR tube, 5 and HBpin were combined in C\(_6\)D\(_6\). Unfortunately, a complex mixture of products was obtained, with none being either L-AlH\(_2\) or PhCH\(_2\)OBPin. This provides evidence that the trflate anion plays a key role in the hydroboration reaction when using L-Al(O\(_3\)SCF\(_3\))H as a catalyst.\(^{14}\)

**Conclusion**

The addition of bulky phenols (MesOH and DippOH) or bulky \(N\)-hydroxylamine (TEMPO-H) to L-AlH\(_2\) results in the mono-substitution of the aluminum center. All attempts to add a second equivalent of bulky phenols or TEMPO-H were unsuccessful, even at elevated temperatures, and provide evidence of how protected the aluminum hydride fragment is. Aldehyde and ketone insertion into the Al–H bond readily occurred at room temperature. With benzaldehyde, insertion occurs in both 1 : 1 and 1 : 2 ratios, giving the corresponding benzylate derivatives. In the case of benzophenone, only one equivalent inserts into the Al–H bond, even at elevated temperatures.

**Experimental**

**General synthetic procedures**

All reactions were performed in dry, O\(_2\)-free conditions under an atmosphere of N\(_2\) within an mBraun Labmaster SP inert atmosphere drybox or PTFE sealed reaction vessels using standard Schlenk techniques. L-AlH\(_2\) (ref. 26) and anhydrous TEMPO-H\(^{23}\) were prepared using procedures from the literature. All other reagents were purchased from Sigma-Aldrich and used as received, unless otherwise noted. Alumina and molecular sieves were pre-dried in a 150 °C oven before being dried at 300 °C \textit{in vacuo}. Solvents were purified using an Innovative Technology solvent purification system or purchased as...
Preparation of compound 1, L-(H)ODipp. To a stirred solution of L-AlH$_2$ [342 mg, 0.766 mmol] in 5 mL pentane, 2,6-dimethylphenol was added (136.5 mg, 0.766 mmol) in an additional 5 mL pentane. Immediate evolution of gas was noted and the mixture was subsequently stirred for 16 h. Removal of solvent in vacuo to approximately 3 mL and storage at −35 °C overnight yielded 433 mg (yield: 90%) of analytically pure colourless crystals with a m.p. of 164.9–165.7 °C. Anal. calc. for C$_{13}$H$_{18}$NAlO: C, 75.62; H, 10.23; N, 7.03. Found: C, 75.67; H, 10.21; N, 7.03. 1H NMR (C$_6$D$_6$, 300 MHz, 298 K): δ 8.84 (d, 3J$_{H,H}$ = 6.8 Hz, 6H, (CH$_3$)$_2$CH), 6.78 (d, 3J$_{H,H}$ = 6.8 Hz, 6H, (CH$_3$)$_2$CH), 1.16 (d, 3J$_{H,H}$ = 6.8 Hz, 6H, (CH$_3$)$_2$CH), 1.04 (s, 3J$_{H,H}$ = 6.8 Hz, 6H, (CH$_3$)$_2$CH). 13C{1H} NMR (75 MHz, 298 K): δ 77.54, 78.24, 124.8, 124.0, 129.3, 131.9, 185.0 ppm. IR (KBr, cm$^{-1}$): v 3062, 2922, 1458, 1431, 1381, 1310, 1248, 1156, 1121, 1087, 1049, 723, 694, 655, 618, 565. Rotation attempts to grow single crystals suitable for X-ray crystallography were unsuccessful. Crystal-like material that formed was analysed via 1H NMR spectroscopy and was determined to match the spectrum of compound 2 with one equivalent of MesOH present. Elemental analysis is in agreement with the formulation 2-MesOH. IR spectroscopy showed an Al–H stretch that matched that of 2, implying that the 2-MesOH co-crystal has no significant Al–H/MesOH interactions. Anal. calc. for C$_{14}$H$_{26}$N$_2$AlO$_2$: C, 78.73; H, 9.14; N, 3.92%. Found: C, 78.76; H, 8.95; N, 3.57.

Preparation of compound 4 L-Al(H)TEMPO. In a scintillation vial, 35.2 mg (0.223 mmol) of anhydrous 1-hydroxy-2,2,6,6-tetramethyl-piperidine (TEMPO-H) was added to a mixture of 100 mg (0.223 mmol) of L-AlH$_2$ dissolved in 10 mL of dry hexanes. After stirring for 12 h, the solution was filtered through a Celite plug and allowed to evaporate slowly yielding X-ray quality needle-like crystals. Yield: 80 mg (39%). Mp: 262–264 °C. Anal. calc. for C$_{13}$H$_{26}$AlO$_2$: C, 75.83; H, 10.05; N, 6.98. Found: C, 75.60; H, 10.23; N, 7.07. 1H NMR (C$_6$D$_6$, 500 MHz, 298 K) δ: 2.84 (d, 3J$_{H,H}$ = 6.8 Hz, 2H, (CH$_3$)$_2$CH), 1.01 (d, 3J$_{H,H}$ = 6.8 Hz, 6H, (CH$_3$)$_2$CH), 1.04 (s, 3J$_{H,H}$ = 6.8 Hz, 6H, (CH$_3$)$_2$CH), 1.52 (s, 3J$_{H,H}$ = 6.8 Hz, 2H, (CH$_3$)$_2$CH). 15N{1H} NMR (200 MHz, 298 K): δ: 24.33, 24.17, 24.69, 24.76, 24.83, 25.19, 26.71, 27.97, 29.07, 98.21, 119.27, 123.54, 124.24, 122.03, 137.29, 139.09, 143.71, 145.81, 152.63, 170.71 ppm. IR (KBr, cm$^{-1}$): v 1850 (Al–H).

Preparation of compound 2, L-(H)OMes. In a 20 mL scintillation vial, L-AlH$_2$ (400 mg, 0.896 mmol) was suspended in 5 mL pentane. Then, 2,4,6-trimethylphenol (122 mg, 0.896 mmol) dissolved in 5 mL pentane was added. The reaction mixture turned tan in colour and began to slowly evolve gas. The mixture was stirred for 16 h and the solvent was reduced to approximately 5 mL, after which the mixture was filtered and stored at −35 °C yielding 104 mg of analytically pure colourless crystalline solid (isolated yield: 20%). Analysis of crude reaction mixture was unsuccessful. Crystal-like material that formed was analysed via 1H NMR spectroscopy and was determined to match the spectrum of compound 2 with one equivalent of MesOH present. Elemental analysis is in agreement with the formulation 2-MesOH. IR spectroscopy showed an Al–H stretch that matched that of 2, implying that the 2-MesOH co-crystal has no significant Al–H/MesOH interactions. Anal. calc. for C$_{14}$H$_{26}$N$_2$AlO$_2$: C, 78.73; H, 9.14; N, 3.92%. Found: C, 78.76; H, 8.95; N, 3.57.

Preparation of compound 5, L-Al(H)OC$_6$H$_5$. L-AlH$_2$ (500 mg, 1.12 mmol) was added to a 20 mL scintillation vial containing 10 mL of pentane. To this slurry was added benzaldehyde (119 mg, 1.12 mmol), and the mixture was stirred for 16 h. The solution was filtered through Celite and the filtrate was subsequently dried in vacuo. The resulting solid contained approximately 5% of the di-substituted product 7, determined through 1H NMR spectroscopy. This crude solid was purified by

'Anhydrous' from Sigma-Aldrich. Solvents were then dried using KH and subsequently filtered through dry alumina and stored over previously dried 4 A molecular sieves. Glassware was dried at 150 °C overnight prior to experimentation. NMR spectra were recorded on a Bruker Avance 300 MHz or 500 MHz NMR spectrometer. Trace amounts of non- or partially-deuterated solvent were used as internal references for 1H NMR spectra and were referenced relative to tetramethylsilane. The deuterated solvent was used as an internal reference for 13C{1H} NMR spectra and were referenced relative to tetramethylsilane. Coupling constants are reported as absolute values. Melting points were recorded on an Electrotherm MEL-Temp 3.0 using glass capillaries sealed under inert conditions. Elemental analysis was performed by the Centre for Environmental Analysis and Remediation (CEAR) facility at Saint Mary’s University using a Perkin Elmer 2400 II series Elemental Analyser.
crystallization in pentane at −35 °C to yield analytically pure colourless crystals of the desired product (yield: 264 mg, 43%). Mp: 128.2–129.7 °C anal. calc. for $\text{C}_{30}\text{H}_{40}\text{N}_{2}\text{O}_{2}$: C, 78.22; H, 8.93; N, 5.07%. Found: C, 78.13; H, 9.00; N, 5.03%. $^1$H NMR (CD$_2$D$_2$, 300 MHz, 298 K): δ 1.13 (d, $^3$$J_{	ext{H-H}}$ = 7.1 Hz, 6H, (CH$_3$)$_2$CH), 1.15 (d, $^3$$J_{	ext{H-H}}$ = 7.1 Hz, 6H, (CH$_3$)$_2$CH), 1.32 (d, $^3$$J_{	ext{H-H}}$ = 7.1 Hz, 6H, (CH$_3$)$_2$CH), 1.37 (d, $^3$$J_{	ext{H-H}}$ = 7.1 Hz, 6H, (CH$_3$)$_2$CH), 1.57 (s, 6H, CH$_2$(CH$_2$CH$_2$)), 3.39 (sept, $^3$$J_{	ext{H-H}}$ = 7.1 Hz, 2H, (CH$_3$)$_2$CH), 3.42 (sept, $^3$$J_{	ext{H-H}}$ = 7.1 Hz, 2H, (CH$_3$)$_2$CH), 3.9–5.3 (broad s, 1H, AlH), 4.58 (s, 2H, OCH$_2$Ph), 4.90 (s, 1H, CH$_2$(CH$_2$CH$_2$)), 6.67 (m, 2H, OPh), 6.98 (m, 3H, OPh), 7.12–7.24 (m, 6H, Ar) ppm. $^{13}$C{1H} NMR (CD$_2$D$_2$, 75 MHz, 298 K): δ 23.0, 24.5, 24.6, 24.8, 25.9, 28.4, 28.8, 65.0, 96.6, 124.6, 124.7, 125.7, 126.0, 127.6, 128.0, 139.4, 144.4, 144.9, 145.4, 170.3. IR (KBr, cm$^{-1}$): v = 1818 (Al–H).

Preparation of compound 6, L-Al(OCH$_2$Ph)$_2$. To a stirred slurry of L-AlH$_2$ (500 mg, 1.12 mmol) in 10 mL pentane, 238 mg (2.24 mmol) of benzaldehyde was added. The reaction was stirred for 16 h, followed by removal of solvent in vacuo. This produced a crude product containing approximately 5% of the mono-substituted product that could be further purified by filtration and subsequent crystallization at −35 °C in pentane to yield 281 mg of analytically pure colourless crystals. Yield: 38%. Mp: 118.6–120.3 °C. Anal. calc. for $\text{C}_{34}\text{H}_{44}\text{AlN}_2\text{O}_2$: C, 78.8; H, 8.41; N, 4.45%. Found: C, 78.28; H, 8.49; N, 4.24%. $^1$H NMR (CD$_2$D$_2$, 300 MHz, 298 K): δ 1.12 (d, $^3$$J_{	ext{H-H}}$ = 7.1 Hz, 12H, (CH$_3$)$_2$CH), 1.20 (d, $^3$$J_{	ext{H-H}}$ = 7.1 Hz, 12H, (CH$_3$)$_2$CH), 1.60 (s, 6H, CH$_2$(CH$_2$CH$_2$)), 3.46 (sept, $^3$$J_{	ext{H-H}}$ = 7.1 Hz, 4H, (CH$_3$)$_2$CH), 4.82 (4H, OCH$_2$Ph), 4.96 (s, 1H, CH$_2$(CH$_2$CH$_2$)), 6.98–7.24 (m, 16H, Ar) ppm. $^{13}$C{1H} NMR (CD$_2$D$_2$, 75 MHz, 298 K): δ 23.4, 24.6, 25.0, 28.5, 65.2, 79.4, 124.6, 125.6, 125.9, 127.5, 140.4, 144.8, 145.7, 171.0.

Table 1. Crystallgraphic data for compounds 1–7

| Compound reference | Crystallographic data |
|--------------------|----------------------|
| 1                  | 2(C$_6$H$_5$AlN$_2$O)$_2$.C$_3$H$_8$ | 280.80 | Monoclinic | 12.59(8) | 14.73(9) | 22.23(3) | 90 | 90 | 4073.2(9) | 1(2) | MoKz |
| 2                  | 2(C$_6$H$_5$AlN$_2$O)$_2$.C$_3$H$_8$ | 601.87 | Triclinic | 12.12(5) | 20.092(4) | 2.297(6) | 90 | 947.55(2) | 125(2) | MoKz |
| 3                  | 2(C$_6$H$_5$AlN$_2$O)$_2$.C$_3$H$_8$ | 617.99 | Triclinic | 9.0846(18) | 11.936(3) | 1.976(3) | 90 | 93.894(3) | 293(2) | MoKz |
| 4                  | 2(C$_6$H$_5$AlN$_2$O)$_2$.C$_3$H$_8$ | 929.26(5) | Triclinic | 9.4096(9) | 17.610(5) | 98.473(4) | 90 | 104.305(4) | 125(2) | MoKz |
| 5                  | 2(C$_6$H$_5$AlN$_2$O)$_2$.C$_3$H$_8$ | 352.73 | C$_3$H$_8$N$_2$O$_2$.C$_3$H$_8$ | 532.73 | 185.13(5) | 90 | 100.237(4) | 125(2) | MoKz |
| 6                  | 2(C$_6$H$_5$AlN$_2$O)$_2$.C$_3$H$_8$ | 638.87 | C$_3$H$_8$N$_2$O$_2$.C$_3$H$_8$ | 630.86 | 10.598(2) | 90 | 90 | 90 | 4037.2(9) | 1(2) | MoKz |
| 7                  | 2(C$_6$H$_5$AlN$_2$O)$_2$.C$_3$H$_8$ | 10.598(2) | C$_3$H$_8$N$_2$O$_2$.C$_3$H$_8$ | 10.598(2) | 4037.2(9) | 90 | 90 | 90 | 4037.2(9) | 1(2) | MoKz |

X-ray crystallography

Crystals of compounds 1–7 were mounted from Paratone-N oil onto an appropriately sized MiTeGen MicroMount. The data were collected on a Bruker APEX II charge-coupled-device (CCD) diffractometer, with an Oxford 700 Cryocool sample cooling device. The instrument was equipped with graphite-monochromated Mo K$_\alpha$ radiation ($\lambda = 0.71073$ Å; 30 mA, 50 mV) and MonoCap X-ray source optics. For data collection, typically four $\omega$-scan frame series were collected with 0.5° wide scans, 5–60 second frames and 366 frames per series at varying
$\phi$ angles ($\phi = 0^\circ, 90^\circ, 180^\circ, 270^\circ$). Data collection, unit cell refinement, data processing and multi-scan absorption correction were applied using the APEX2 (ref. 43) or APEX3 (ref. 44) software packages. The structures were solved using SHELXT, and all non-hydrogen atoms were refined anisotropically with SHELXL using shelxl or OLEX2 (ref. 48) graphical user interfaces. Unless otherwise noted, all hydrogen atom positions were idealized and rode on the atom to which they were attached. The final refinement included anisotropic temperature factors on all non-hydrogen atoms. Details of crystal data, data collection, and structure refinement are listed in Table 1. All figures were made using ORTEP-3 for Windows. For compound 2, one of the iPr groups on the DippO ligand was modelled with a two-site disorder in a 57 : 43 ratio. For compound 6, one of the Bn groups was modelled with a two-site disorder in an 84 : 16 ratio. For compound 7, there were two badly disordered pentane molecules that could not be adequately modelled. The SQUEEZE routine as implemented in PLATON was used. The program removed 87 electrons from as asymmetric unit, which is roughly equivalent to two pentane molecules (42 electrons each). Additional details of the data collection and structure refinement and tables of bond lengths and angles are given in the ESI.

Conflicts of interest

There are no conflicts of interest to declare.

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