PAPER

Organoaluminum(III) complexes of the bis-N,N'-(2,6-diisopropylphenyl)imidazolin-2-imine ligand†

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The reaction of trimethylaluminum with the bis-N,N'-(2,6-diisopropylphenyl)imidazolin-2-imine (L–H) ligand **1** afforded several new organometallic aluminium complexes. Reaction in a 1 : 1 stoichiometry at room temperature afforded a Lewis acid–base adduct, whereas thermolysis resulted in the loss of methane and the formation of a dimer complex, (L-AlMe₂)₂, **3**. When reacted in a 1 : 2 ratio at 110 °C, the loss of two equivalents of methane yielded L₂AlMe, **5**, whereas when the reaction was performed at 60 °C, (L–H)AlMe₂(L), **4**, was found as an intermediate in the reaction. Compound **2** is, to the best of our knowledge, the first example of a structurally characterized primary imine coordinated to a triorganoaluminum(III) center. Attempts to form a two coordinate aluminum cation by CH_3^- abstraction are documented. All products were characterized *via* normal spectroscopic techniques and single crystal X-ray diffraction.
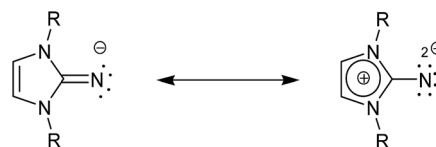
Introduction

Within the last several decades, the amido-based family of ligands including guanidinate $[R_2NC(NR')_2]^-$ systems have been extensively studied, primarily as ancillary ligands in the area of α-olefin polymerization in regards to catalytically active group 4 metal complexes.[1–3] Historically these molecules have functioned as building blocks in natural products[4–6] and have been utilized in the formation of pharmaceutical agents but they have garnered increasing attention in the field of small molecule activation.[7–9]

In addition to the synthesis of several group 4 catalysts, many series of lanthanide and actinide complexes have been reported for the use in effective homogeneous catalysts[7,10,11] and precursors for rare-earth oxide thin films.[7,12] The success of these ligands results mainly from their steric tunability and efficient π-donation that often exceeds conventional cyclopentadienyl ligands.[13]

Of particular interest is the closely related imidazolin-2-iminato family of ligands first developed by Kuhn et al.,[14] of which even, stronger electron donating capacity has been observed.[15,16] They have shown particular success as ancillary ligands in titanium-based olefin polymerization catalysis.[13,17–25] Due to the nature of these particular ligands, as anions, they can function as 2σ,2π-electron donors or as 2σ,4π-electron donors in a zwitterion form; these are effective at stabilizing early transition metal complexes or those of high oxidation states due to an increased contribution of the more polarized zwitterion shown in Scheme 1.[26,27] This feature has made this ligand a versatile replacement as it interacts in as similar fashion to phosphinimides, R_3PN^-,[28–30] and therefore can be utilized as monodentate alternatives to Cp-based ligands and has shown additional developments in the applications of catalytic dimerization of aldehydes,[31] lanthanide-based hydroamination catalysts,[15,26,32] ruthenium-based transfer hydrogenation[33–35] as well as copper[36] and palladium chemistry.[37,38]

Recently main group chemists have utilized the exceptional donating and steric properties of the title ligand to stabilize unique molecular frameworks. This is highlighted by the group 15 chemistry of Bertrand with the isolation of a carbene stabilized phosphorus mononitride,[39] a monomeric phosphinyl radical,[40] a singlet phosphinonitrene,[41] its protonated derivative[42] and metal complexes.[43] The imidazolin-2-iminato ligand has also been used by Inoue[44–48] and Rivard[49,50] to stabilize a number of group 13- and group 16-based molecules, in particular the remarkable isolation of the first molecule containing an Al=Te double bond.[46] The organo-aluminum chemistry of the title imidiazoline-2-iminato ligand is

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Scheme 1 Mesomeric forms of imidazolin-2-iminato ligands.

relatively understudied and has focussed on the aluminum hydrides.[47,48]

Our research group has had a long standing interest in the stabilization of unusual main group compounds.[51,52] These include the isolation and reactivity studies of a phosphinyl radical,[53,54] as well as the isolation of the first oxophosphonium cation.[55] Similarly, we have been interested in the isolation of low-valent and low-oxidation state aluminium complexes. Herein, we explore the reactivity of the bis-N,N′-(2,6-diisopropylphenyl)imidazolin-2-imine ligand (L–H, **1**) with trimethylaluminum in our quest of isolating new aluminium cations and aluminium(I) species. We report the isolation of a number of compounds that have been characterized by various methods including NMR spectroscopy and single crystal X-ray crystallography.

Results and discussion

Ligand **1** was reacted with trimethylaluminum in pentane at room temperature to give compound **2** as a beige colored powder in high yield (Scheme 2). The ^{1}H NMR spectrum revealed a singlet at δ −0.81 ppm that integrated to 9 hydrogen atoms and was assigned to the three methyl groups on aluminum. A broad singlet at δ 4.07 ppm was assigned to the imine proton. Combined, these indicated that a simple Lewis acid–base adduct was formed with the between aluminum and the imine nitrogen with no deprotonation of the imine. Although the molecule would be expected to have low symmetry, the presence of two doublets and a single septet related to the iPr groups indicate a dynamic process occurring at room temperature averaging out these signals. Presumably this is rotation about the imine N–C bond, implying that there is a reduced bond order between these atoms.

A Cambridge Structural Database search (CSD version 5.37 (April 2015)) reveals that this is the first structurally characterized primary imine coordinated to a triorganoaluminum(III) center (Fig. 1). The Al–N distance (1.9648(19) Å) is longer than nitrogen–AlMe₃ adducts such as Ph₃PN(H)AlMe₃ (1.672(4) Å)[56] and slightly shorter than the N–Al bond in the ammonia–AlMe₃ adduct (2.004(5) Å).[57] The imine N=C distance is 1.313(3) Å, slightly elongated compared to the parent imine with an N=C distance of 1.2888(17) Å.[58] The C1–N2 and C1–N3 distances (1.366(2) Å and 1.366(3) Å, respectively) are shorter than in the parent ligand (1.3815(15) Å, 1.4004(16) Å). This can be attributed to a significant contribution from the zwitterionic structure as shown in Scheme 1. The 1 : 1 reaction between ligand **1** and trimethylaluminum at elevated temperature (110 °C) in toluene gave compound **3** at moderate yields. Alternatively, the NMR-scale reaction of heating compound **2** to 50 °C in toluene-d₈ resulted in the slow formation of compound **3** and methane. The ^{1}H NMR spectrum revealed a peak at δ −1.50 ppm that integrated to six hydrogen atoms, confirming the loss of a methyl group. This along with the loss of the imine N–H signal supported the formation of a covalent bond between the nitrogen and aluminum.

Recrystallization of the product from hot heptane cooled to ambient temperature afforded crystals suitable for single crystal
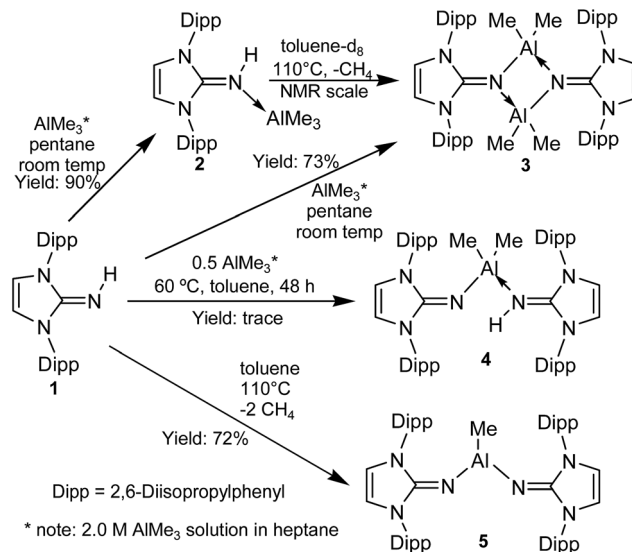
Scheme 2   Reactions of ligand **1** with trimethylaluminum.
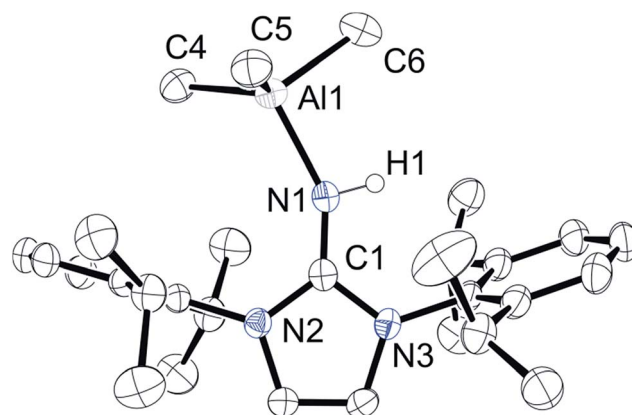

Fig. 1   Molecular structure of compound **2**, with thermal ellipsoids projected at the 50% probability level. Co-crystallized toluene and hydrogen atoms (except H1) have been omitted for clarity. Selected bond lengths (Å) and angles (°): Al1–N1 1.9648(19), N1–C1 1.313(3), N1–H1 0.86(2), N2–C1 1.366(2), N2–C2 1.400(3), N3–C1 1.366(3), N3–C3 1.394(2), C2–C3 1.332(3).

X-ray diffraction. This compound crystallized in the $P\bar{1}$ space group and revealed a dimerized product (Fig. 2). The four-membered Al–N–Al–N is planar; the N3–Al1–N6 and N3–Al2–N6 angles are 86.6(1)° and the Al1–N3–Al2 and Al1–N6–Al2 angles are 93.3(1)°. The C=N imine distances for C1–N3 (1.292(4) Å) and C28–N6 (1.302(4) Å) distances are statistically indistinguishable from the imine distance in **2**, indicating the important contribution of the zwitterionic form of the ligand (Scheme 1).

The reaction of ligand **1** in a 2 : 1 ratio with trimethylaluminum at 60 °C in toluene for two days gave a mixture of products as determined by ^{1}H NMR spectroscopy. A small amount of crystalline material was isolated from a hot heptane solution cooled to room temperature. Analysis by single crystal X-ray diffraction revealed compound **4** crystallized as neutral and anionic ligand **1** coordinated to an AlMe₂ fragment (Fig. 3).
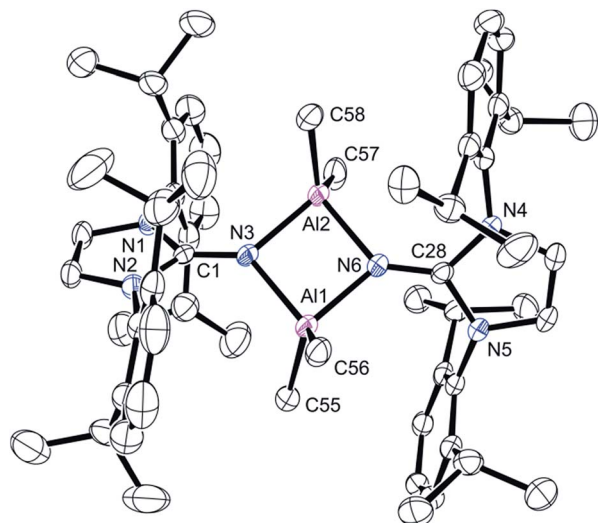
Fig. 2 Molecular structure of compound **3**, with thermal ellipsoids projected at the 50% probability level. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): Al1–N3 1.919(3), Al1–N6 1.923(2), Al2–N3 1.924(2), Al2–N6 1.919(3), N3–C1 1.292(4), N6–C28 1.302(4), N2–C1 1.403(3), C2–C3 1.329(5), C29–C30 1.322(5), N3–Al1–N6 86.6(1), N3–Al2–N6 86.6(1), Al1–N3–Al2 93.3(1), Al1–N6–Al2 93.3(1).
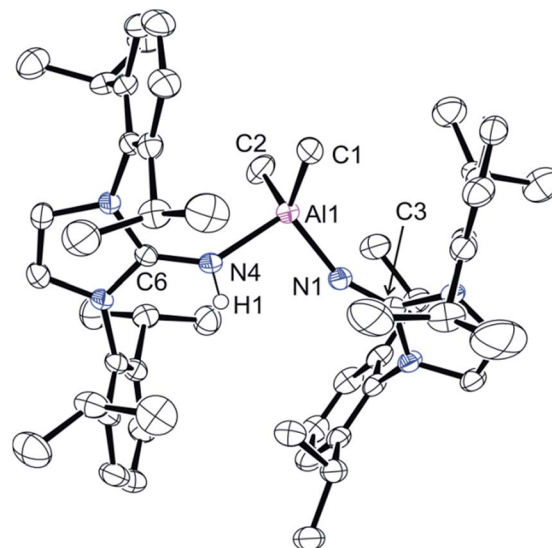

Fig. 3 Molecular structure of compound **4**, with thermal ellipsoids projected at the 50% probability level. Hydrogen atoms aside from H1 have been omitted for clarity. Selected bond lengths (Å) and angles (°): Al1–C1 1.967(2), Al1–C2 1.985(3), Al1–N1 1.822(2), Al1–N4 1.965(2), N1–C3 1.257(3), N4–C6 1.313(3), N4–H1 0.86(2), C1–Al1–C2 111.8(1), N1–Al1–N4 96.95(8), Al1–N1–C3 152.2(2), Al1–N4–C6 137.6(2).

The asymmetric nature of this compound is apparent in the aluminium–nitrogen distances; the adduct side had an Al1–N4 distance of 1.965(2) Å whereas the covalently bound ligand has a much shorter Al1–N1 distance of 1.822(2) Å. There is also a marked difference in the N=C imine bonds; the covalently bound ligand has an N4–C6 imine bond length of 1.313(3) Å, whereas the covalently bound ligand has a much shorter N1–C3 imine bond length of 1.257(3) Å. An attempt to prepare **4** by adding one equivalent of ligand **1** to dimer **3**, was unsuccessful. ^{1}H NMR spectroscopy showed no reaction at room temperature. Heating this mixture to 110 °C resulted in the loss of signals of the starting materials and gave a new Al–Me signal in the ^{1}H NMR spectrum at δ −1.49 ppm, integrating to three hydrogen atoms. This signal was assigned to compound **5**.

In a more direct approach, heating the 2 : 1 mixture of **2** and trimethylaluminum at 110 °C in toluene for two days gave a single product by ^{1}H NMR spectroscopy. The loss of two methyl groups from the trimethylaluminum and additional loss of the imine protons and resulting highly symmetrical ^{1}H NMR spectrum gave evidence towards the formation of **5**. Recrystallization of the isolated product from hot heptane yielded beige crystals suitable for single crystal X-ray diffraction. The product was found packed into a $P2_1/c$ space group and the formation of a complex between two coordinated ligands to trimethylaluminum was confirmed as shown in Fig. 4. The Al centre is trigonal planar with angles of N1–Al1–N4 119.73(7)°, N1–Al1–C1 117.77(8)° and N4–Al1–C1 122.45(8)°. Both imine carbon–nitrogen bonds (N1–C2 1.266(2) Å, N4–C29 1.265(2) Å) showed significant shortening compared to the neutral Lewis adducts. Compared to the synthesized adduct **2** (Al1–N1 1.965(2) Å) and dimer **3** (Al1–N3 1.919(3) Å and Al1–N6 1.923(2) Å), product **5** had significantly shorter Al–N distances of Al1–N1 1.759(2) Å and Al1–

N4 1.762(1) Å, reinforcing the covalent nature of these molecules. The imine C–N bonds in **5** (N1–C2 1.266(2) Å and N4–C29 1.265(2) Å) were found to be shorter than that in the free ligand. This shortening of the C=N imine bond indicates the stronger participation of the first mesomeric form shown as shown in Scheme 1.

Fig. 4 Molecular structure of compound **5**, with thermal ellipsoids projected at the 50% probability level. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): Al1–N1 1.759(2), Al1–N4 1.762(1), Al1–C1 1.950(2), N1–C2 1.266(2), N4–C29 1.265(2), C2–N2 1.413(2), C2–N3 1.400(2), N1–Al1–N4 119.73(7), C1–Al1–N1 117.77(8), C1–Al1–N4 122.45(8), Al1–N1–C2 140.8(1), Al1–N4–C29 143.4(1).
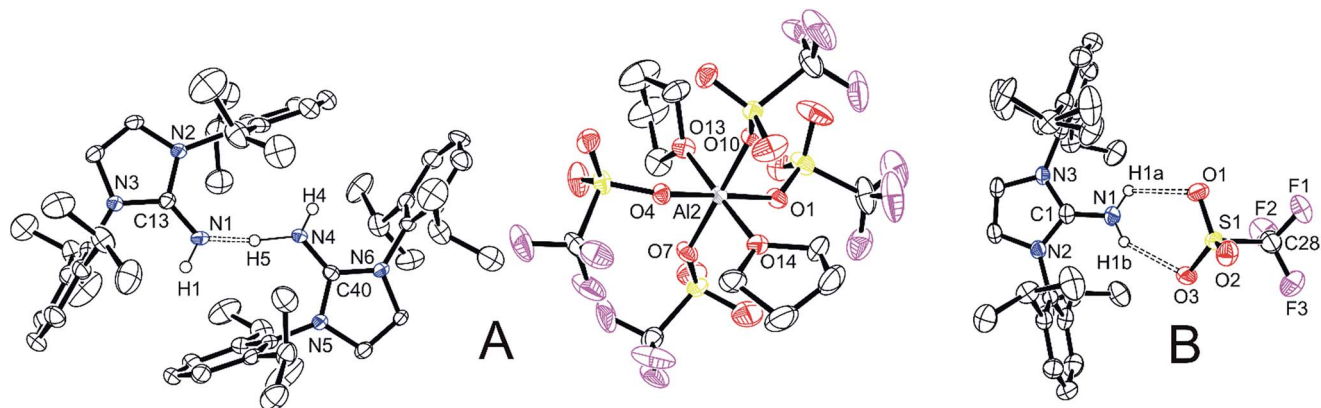
Fig. 5 Molecular structure of compounds **6** (A) and **7** (B), with thermal ellipsoids projected at the 50% probability level.

Recrystallization of the isolated product from hot heptane yielded beige crystals suitable for single crystal X-ray diffraction. The product was found packed into a $P2_1/c$ space group and the formation of a complex between two coordinated ligands to trimethylaluminum was confirmed as shown in Fig. 4. The Al centre is trigonal planar with angles of N1–Al1–N4 119.73(7)°, N1–Al1–C1 117.77(8)° and N4–Al1–C1 122.45(8)°. Both imine carbon–nitrogen bonds (N1–C2 1.266(2) Å, N4–C29 1.265(2) Å) showed significant shortening compared to the neutral Lewis adducts. Compared to the synthesized adduct **2** (Al1–N1 1.965(2) Å) and dimer **3** (Al1–N3 1.919(3) Å and Al1–N6 1.923(2) Å), product **5** had significantly shorter Al–N distances of Al1–N1 1.759(2) Å and Al1–N4 1.762(1) Å, reinforcing the covalent nature of these molecules. The imine C–N bonds in **5** (N1–C2 1.266(2) Å and N4–C29 1.265(2) Å) were found to be shorter than that in the free ligand. This shortening of the C=N imine bond

indicates the stronger participation of the first mesomeric form shown as shown in Scheme 1.
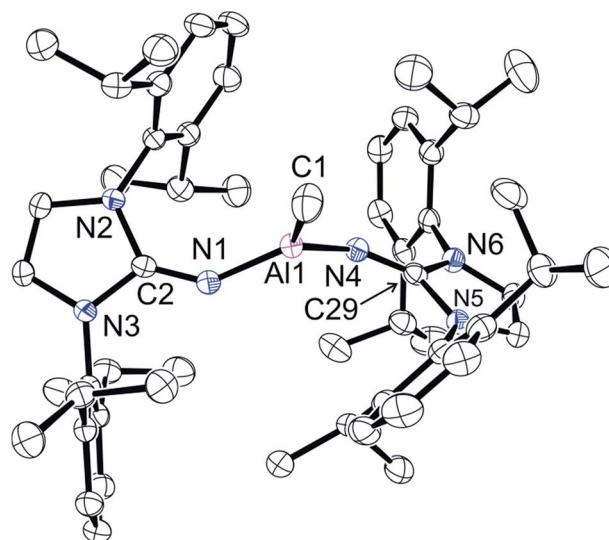
With significant quantities of compound **5** in hand, we tested it as a starting material with a two-coordinate aluminium cation as a target. Reaction of **5** with I_2 in toluene to exchange a methyl group with iodide (and loss of MeI) resulted in an intractable mixture. This is in contrast with the efficient exchange as seen with NacnacAlMe$_2$.[59] Attempted abstraction of the methyl group with the strong Lewis acid B(C$_6$F$_5$)$_3$ resulted in no reaction (or noticeable Al–Me–B interactions) by ^{1}H NMR spectroscopy. Thermolysis of the mixture resulted in no change. Similarly, there was no reactivity noted of **5** with the trityl borate [Ph$_3$C][B(C$_6$H$_2$(m-CF$_3$)$_2$)$_4$].

Adding triflic acid to a stirring mixture of **5** in pentane resulted in the evolution of a gas (presumably methane) with formation of a colourless precipitate. ^{1}H NMR spectroscopy of

Table 1 Crystallographic data for compounds **2–7**

Compound	2	3	4	5	6	7
Chemical formula	C$_{67}$H$_{100}$Al$_2$N$_6$	C$_{56}$H$_{79}$AlN$_6$	C$_{58}$H$_{84}$Al$_2$N$_6$	C$_{55}$H$_{75}$AlN$_6$	C$_{66}$H$_{91}$AlF$_{12}$N$_6$O$_{14}$S$_4$	C$_{28}$H$_{38}$F$_3$N$_3$O$_3$S
Formula mass	1043.48	863.23	919.27	847.19	1575.66	553.67
Crystal system	Triclinic	Monoclinic	Triclinic	Monoclinic	Monoclinic	Orthorhombic
a/Å	9.3542(18)	12.9094(10)	12.064(2)	22.0069(19)	12.6935(15)	10.5014(8)
b/Å	9.5893(18)	18.6830(14)	22.957(4)	11.7183(10)	16.0668(19)	14.0346(10)
c/Å	19.621(4)	21.6167(16)	24.196(4)	20.0358(17)	19.437(2)	20.5119(15)
α/°	90.186(3)	90	62.143(2)	90	90	90
β/°	96.123(2)	90.0500(10)	75.811(2)	99.4460(10)	102.1980(10)	90
γ/°	111.258(2)	90	89.463(2)	90	90	90
Unit cell volume/Å^3	1629.2(5)	5213.7(7)	5700.7(17)	5096.8(8)	3874.6(8)	3023.1(4)
Temperature/K	125(2)	125(2)	125(2)	125(2)	125(2)	125(2)
Space group	$P\bar{1}$	$P21/n$	$P\bar{1}$	$P2_1/c$	$P2_1$	$P2_12_12_1$
Z	1	4	4	4	2	4
Absorption coefficient, μ/mm^{-1}	0.086	0.080	0.091	0.081	0.225	0.157
No. of reflections measured	10 772	50 368	55 016	32 942	27 730	20 332
No. of independent reflections	5605	9160	19 990	8897	14 581	5314
R_{int}	0.0275	0.0893	0.0496	0.0290	0.0256	0.0282
Final R_1 values ($I > 2\sigma(I)$)	0.0536	0.0490	0.0641	0.0418	0.0456	0.0343
Final $wR(F^2)$ values ($I > 2\sigma(I)$)	0.1424	0.0998	0.1718	0.0996	0.1060	0.0763
Final R_1 values (all data)	0.0697	0.0945	0.0917	0.0566	0.0579	0.0399
Final $wR(F^2)$ values (all data)	0.1544	0.1207	0.1927	0.1083	0.1134	0.0798
Goodness of fit on F^2	1.148	1.009	1.112	1.024	1.022	1.032
CCDC number	1479384	1479388	1479389	1479386	1479385	1479387

the mixture showed loss of the methyl group, but otherwise was not diagnostic. Although we could not ascertain the exact composition of the bulk material, we were successful at obtaining a few single crystals from THF solutions. Analysis by single crystal X-ray crystallography (compound **6**, Fig. 5A) revealed a cation containing two equivalents of ligand **1** forming a dimer that is hydrogen bound to a central proton (no aluminum). More interesting is the anion; the central aluminum atom is in an octahedral configuration with two O-bound THF molecules in the axial positions and the four tri-flate ligands in the equatorial positions, each bound in a mon-odentate fashion. This is a rare example of aluminum containing four triflate anions acting as ligands; the only other example, $[Al(triglyme)_3][Al(OH_2)_2OTf_4]$, was recently reported.[60] From another reaction, another crystal was also analysed and was determined to be [**1**-H][OTf] (compound **7**, Fig. 5B). In this compound, two of the oxygens of the triflate are hydrogen bound to the NH_2^+ fragment of the cation, forming with donor–acceptor bond distances and N–H···O angles of 2.890(3) Å and 125(3)°, and 2.868(3) Å and 144(3)° for each.

Conclusions

In summary, a novel class of aluminium complexes based from the imidazolin-2-iminato ligand have been successfully syn-thesised and completely characterized *via* a number of methods including NMR spectroscopy, EA and single crystal X-ray diffraction. To the best of our knowledge, compound **2** is the first example of structurally characterized primary imine coor-dinated to a triorganoaluminum centre. Compound **5** was resistant to methyl abstraction reactions using highly Lewis acidic $B(C_6F_5)_3$ and trityl borates. Finally, addition of triflic acid to **5** resulted in the loss of Al–N bonds to form new products where ligand **1** acts as a Brønsted–Lowry base.

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 sealed reaction vessels using standard Schlenk techniques. Synthesis of ligand **1** was done *via* litera-ture procedure published by Tamm *et al.*[16] modified from the original synthesis by Kuhn *et al.*[14] All 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 bring dried at 300 °C *in vacuo*. Solvents were puri-fied using an Innovative Technology solvent purification system or purchased as 'anhydrous' from Sigma-Aldrich. Solvents were then dried using KH and subsequently filtered through dry alumina and stored over previously dried 3 Å molecular sieves. Glassware was dried at 150 °C overnight prior to experimenta-tion. NMR spectra were recorded on a Bruker Avance 300 MHz spectrometer. Trace amounts of non-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 ^{13}C {^1H} NMR spectra and

referenced relative to tetramethylsilane. Coupling constants are reported as absolute values. Melting points were recorded on an Electrothermal 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.

Preparation of (L–H)-AlMe₃ (2)

In a 100 mL round bottomed flask, ligand **1** (5.00 g, 12.4 mmol) was added to 50 mL pentane. 6.19 mL of a 2.0 M solution of trimethylaluminum in heptane (0.893 g, 12.4 mmol) was added to the resulting slurry. This mixture was then allowed to stir over 48 hours at ambient temperature. The solvent was subsequently removed *in vacuo* yielding the desired product as a beige solid pure by ^1H NMR (yield: 5.33 g, 90%). Analytically pure crystals were recovered by a second recrystallization in ambient temperature toluene layered with pentane. Mp 178 °C (decomp.); anal. calc. for $C_{30}H_{46}N_3Al$: C, 75.75; H, 9.75; N, 8.83%; found: C, 75.45; H, 9.68; N, 8.62%. ^1H NMR (300 MHz, C_6D_6): δ −0.81 (s, 9H, AlMe₃), 1.04 (d, $^3J_{H-H}$ = 6.9 Hz, 12H, $(CH_3)_2CH$), 1.36 (d, $^3J_{H-H}$ = 6.9 Hz, 12H, $(CH_3)_2CH$), 2.85 (sept, $^3J_{H-H}$ = 6.9, 4H, $(CH_3)_2CH$), 4.07 (s, 1H, N*H*), 5.79 (s, 2H, NC*H*NC*H*) and 7.07–7.23 (m, 6H, Ar) ppm. ^{13}C NMR (75 MHz, C_6D_6): δ −6.45, 23.46, 24.58, 29.11, 116.23, 125.19, 130.85, 131.46, 147.46, 152.87 ppm.

Preparation of (L-AlMe₂)₂ (3)

Ligand **1** (0.200 g, 0.496 mmol) and 0.243 mL of a 2.0 M solution of trimethylaluminium in heptane (0.035 g, 0.486 mmol) were combined in a sealed reaction vessel with 10 mL toluene. The resulting mixture was heated to 110 °C overnight where the solvent was then subsequently removed *in vacuo* (yield: 0.620 g, 73%). Analytically pure crystals were isolated by recrystalliza-tion in hot heptane cooled slowly to ambient temperature. Mp 320 °C (decomp.); anal. calc. for $C_{58}H_{84}Al_2N_6$: C, 78.16; H, 9.05; N, 9.89%; found: C, 75.35; H, 9.01; N, 8.96%; ^1H NMR (C_6D_6, 300 MHz): δ −1.50 (s, 12H, Al(CH_3)₂), 1.04 (d, $^3J_{H-H}$ = 6.8 Hz, 24H, $(CH_3)_2CH$), 1.46 (d, $^3J_{H-H}$ = 6.8 Hz, 24H, $(CH_3)_2CH$), 3.27 (sept, $^3J_{H-H}$ = 6.8 Hz, 8H, $(CH_3)_2CH$), 5.78 (s, 4H, NC*H*C*H*N), 7.15–7.22 (m, 12H, Ar) ppm. ^{13}C NMR (75 MHz, C_6D_6): δ −5.99, 23.64, 25.66, 28.69, 117.18, 124.61, 130.24, 135.38, 147.85, 150.66 ppm.

Isolation of (L–H)₂AlMe₂(L) (4)

A sealed reaction vessel fitted with a Teflon stopper containing ligand **1** (0.200 g, 0.496 mmol), 2.0 M AlMe₃ in heptane (0.124 mL, 0.248 mmol) and 15 mL toluene was heated to 60 °C for 48 h. The solvent was removed *in vacuo* leaving a colorless solid. Analysis by ^1H NMR showed a mixture of products. However, none of these matched with **1**, **2** or **5** and only trace amounts of **3** were detected. Crystallization from hot heptane gave a small amount of **4** suitable for analysis by single crystal X-ray diffraction. Multiple attempts to isolate bulk amounts of **4** by carefully monitoring the above reaction or adding ligand **1** to **3** were unsuccessful.

Preparation of L₂AlMe (5)

A sealed reaction vessel fitted with a Teflon stopper containing compound **2** (3.00 g, 6.32 mmol) and ligand **1** (2.55 g, 6.32 mmol) in 15 mL toluene was heated to 110 °C for 48 h. The solvent was removed *in vacuo* and the remaining solid was dissolved in hot heptane, which was slowly cooled to ambient temperature yielding the product as beige crystals (yield: 3.89 g, 72%). Analytically pure crystals were recovered by a second recrystallization in hot heptane cooled slowly to ambient temperature. Mp 226.9–228.4 °C. Anal. calc. for $C_{55}H_{75}AlN_6$: C, 78.16; H, 9.05; N, 9.89%; found: C, 77.99; H, 8.95; N, 9.89%. ^{1}H NMR (300 MHz, C_6D_6): δ −1.49 (s, 3H, $AlCH_3$), 1.12 (d, $^3J_{H-H}$ = 6.9 Hz, 24H, $(CH_3)_2CH$), 1.18 (d, $^3J_{H-H}$ = 6.9 Hz, 24H, $(CH_3)_2CH$), 3.11 (sept, $^3J_{H-H}$ = 6.9 Hz, 8H, $(CH_3)_2CH$), 5.97 (s, 4H, $NCHNCH$) and 7.13–7.29 (m, 12H, Ar) ppm. ^{13}C NMR (75 MHz, C_6D_6): δ −11.10, 23.37, 24.50, 28.74, 112.94, 124.00, 128.80, 135.37, 143.11, 148.09 ppm.

Reaction of 5 with triflic acid

(a) In a scintillation vial, triflic acid (0.010 mL, 0.12 mmol) dissolved in 5 mL of diethyl ether was added dropwise to a rapidly stirring solution of **5** (0.100 g, 0.12 mmol) in 5 mL of diethyl ether. A colorless precipitate rapidly formed and gas evolution (methane) was observed. After stirring for 15 minutes, the solvent was decanted from the solids and the solids were washed with diethyl ether. The residual solvent was removed from the solids *in vacuo*. ^{1}H NMR analysis of the solids revealed loss of the Al–Me signals. In order to partially determine the composition of the solid, a few X-ray quality crystals were grown from a THF solution layered with pentane. The analyzed crystal, compound **6**, matched the ^{1}H NMR data.

^{1}H NMR (300 MHz, THF-d_8): δ 1.23 (d, $^3J_{H-H}$ = 6.9 Hz, 24H, $(CH_3)_2CH$), 1.26 (d, $^3J_{H-H}$ = 6.9 Hz, 24H, $(CH_3)_2CH$), 1.79 (m, 8H, THF), 2.84 (sept, $^3J_{H-H}$ = 6.9 Hz, 8H, $(CH_3)_2CH$), 3.62 (m, 8H, THF), 6.94 (s, 4H, $NCHNCH$) and 7.33–7.47 (m, 12H, Ar) ppm. Note: protons attached to the imine functionality were not observed, presumably due to their rapid exchange with one another.

(b) In a second attempt, the reaction scale was multiplied 2.5×. Analysis of this material gave a slightly different ^{1}H NMR spectrum than in the smaller scale reaction, but was still not diagnostic. A few X-ray quality crystals were grown from a THF solution layered with pentane. Analysis of these crystals revealed the formation of compound **7**. ^{1}H NMR (300 MHz, THF-d_8): δ 1.22 (d, $^3J_{H-H}$ = 6.9 Hz, 12H, $(CH_3)_2CH$), 1.25 (d, $^3J_{H-H}$ = 6.9 Hz, 12H, $(CH_3)_2CH$), 2.74 (sept, $^3J_{H-H}$ = 6.9 Hz, 4H, $(CH_3)_2CH$), 7.02 (s, 2H, $NCHNCH$) and 7.33–7.45 (m, 6H, Ar) ppm. Note: the two protons attached to the imine functionality were not observed, presumably due to their rapid exchange between the imine and triflate anion.

X-ray crystallography

Crystals of compounds **2–7** were mounted from Paratone-N oil on 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 Kα radiation (λ = 0.71073 Å; 30 mA, 50 mV), with MonoCap X-ray source optics. For data collection, four ω-scan frame series were collected with 0.5° wide scans, 60 second frames and 416 frames per series at varying ϕ angles (ϕ = 0°, 90°, 180°, 270°). Data collection, unit cell refinement, data processing and multi-scan absorption correction were applied using the APEX II software package.[61] The structures were solved using direct methods[62] and all non-hydrogen atoms were refined anisotropically using the shelXle[63] graphical user interface and the SHELX suite of programs.[62] 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.[64] Additional details of the data collection and structure refinement and tables of bond lengths and angles are given in the ESI. CCDC 1479384–1479389 contain the supplementary crystallographic data for complexes **2–7**.†

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