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Reactivity studies and structural outcomes of a bulky dialkylaluminium amide in the presence of the N-Heterocyclic Carbene, ItBu

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In memory of Professor Malcolm Green, an inspiration to all organometallic chemists

Abstract

Aluminium reagent *i*Bu_2Al(TMP) (TMP is 2,2,6,6-tetramethylpiperidide) has previously shown interesting synergistic metallation chemistry when paired with alkali metal amides. Here its structural chemistry and reactivity is explored in the presence of the *N*-heterocyclic carbene, I*t*Bu, 1,3-di-tert-butylimidazol-2-ylidene. Abnormal a*t*Bu structures are obtained with *i*Bu_2Al(TMP) on its own and in the co-presence of LiTMP, NaTMP or KTMP. Reaction with phenol is stoichiometric dependent leading to the diphenolate $[I\textit{t}Bu(H)]^+$ $[(PhO)_2Al(\textit{i}Bu)_2]^-$ and triphenolate $[I\textit{t}Bu(H)]^+$ $[(PhO)_3Al(\textit{i}Bu)]^-$ ionic complexes. Dinuclear a*t*Bu(Ph)C=N[Al(*i*$Bu)_2$N=C(TMP)Ph]Al(*i*$Bu)_2$ was the surprising product from reaction with benzonitrile, displaying an imidoC- and (*i*$Bu)_2$Al- disubstituted imidazolium ring as well as a second imido unit made by addition of "non-nucleophilic" TMP across the benzonitrile triple bond. Potential insight into the mechanism of this intriguing complicated reaction was gained through the crystallographic characterisation of the ketamide [*i*Bu_2AlN=C(Ph)TMP]$_2$, a possible intermediate. Reaction with Ph_2CHCN, diphenylacetonitrile, proved more straightforward affording the ionic complex $[I\textit{t}Bu(H)]^+$ $[Ph_2C{=}C{=}N]^-$**.**

Keywords: Abnormal Carbene, Alkali-Metal, *N*-heterocyclic carbene, NMR studies, Organoaluminium compound

Introduction

Since their first isolation as stable crystalline solids by Arduengo in the early 1990s,[1] *N*-heterocyclic carbenes (NHCs) have been increasingly prominent in the landscape of organometallic chemistry as a consequence of their facile steric and electronic tuneability and their relative inertness, making them excellent neutral two-electron Lewis donors for a variety of applications.[2] NHC chemistry was initially studied mainly from a transition metal standpoint due to the dominant position of these metals within homogeneous catalysis on account of the convenience of oxidation state change possessed by the majority of them. However, the relationship between NHCs and main group metals has begun to blossom [3] as NHCs are excellent ligands for deaggregating and stabilizing otherwise reactive main group species [4] and supporting main group complexes which can operate in catalysis using non-redox pathways.[5] Replicating the chemistry of the transition metals with main group elements [6] is desirable due to many of these elements in general having a far greater natural abundance (making them cheaper and more sustainable in the long term) coupled with them often being more environmentally benign than many of the heavier transition metals.[7]

A strategy within main group chemistry that we have been developing is to construct new bimetallic systems in which the metals can cooperate together to produce synergistic reactivities that are not efficient or not possible at all via the monometallic precursors of the bimetallic compounds. These synergistic effects most commonly occurring when one of the metals is an alkali metal are becoming widespread in different areas of main group chemistry as recently showcased in a review.[8] Germane to the present study, we have incorporated the mononuclear aluminium reagent *i*Bu_2Al(TMP) (TMP = 2,2,6,6-tetramethylpiperidide, $C_9H_{18}N^-$) into bimetallic frameworks by pairing it with relatively strong alkali-metal bases such as Li(TMP),[9] in the aim of switching on alkali-metal mediated alumination (*AMMAl*) chemistry whereby the pairing might display the mutually beneficial properties of each individual component, that is the reactivity of the alkali-metal and the selectivity of the softer secondary metal aluminium.[8,10] What we actually discovered is that these specific two complexes cannot pair up on steric grounds so in deprotonative metalation reactions of aromatic substrates where both metals are present the bulky lithium amide first executes the deprotonation reaction before the aluminium reagent traps the resulting sensitive (and less bulky) carbanion.[11] As this is a special transmetallation reaction, we refer to it as trans-metal-trapping.[12]

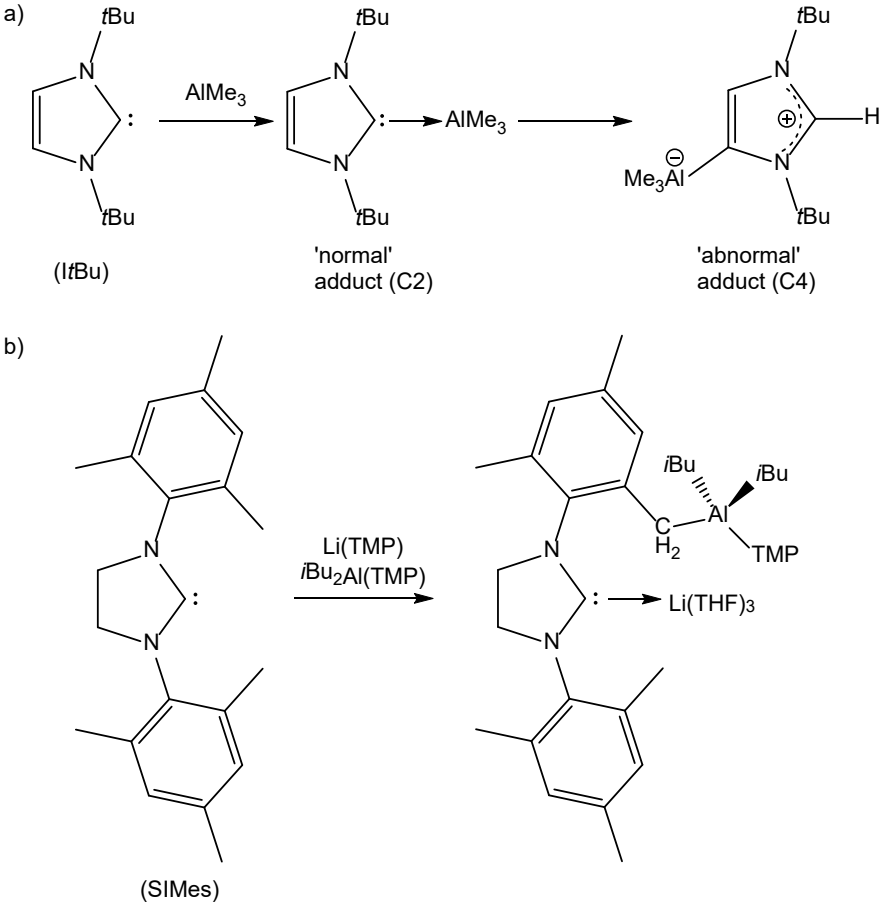


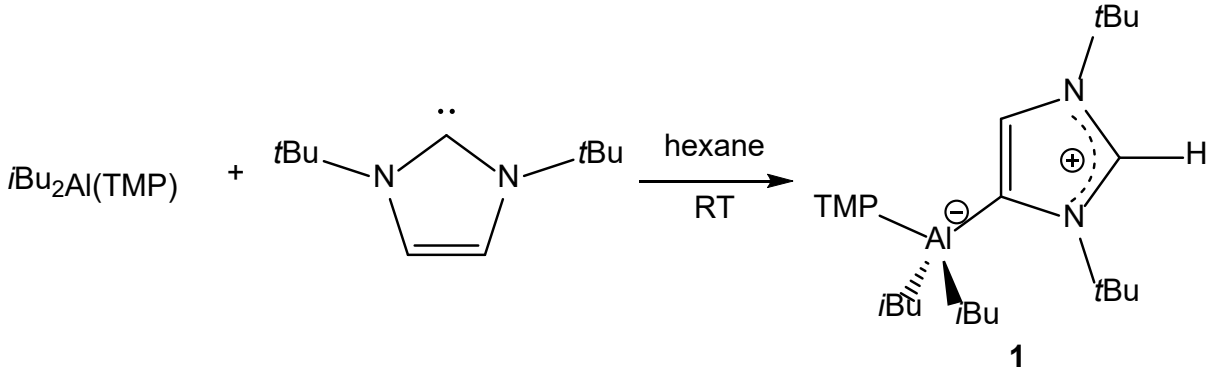
Figure 1 (a) conversion of Al-NHC complex from normal to abnormal; (b) surprising attack at lateral carbene site by Li/Al pairing

As mentioned earlier, one of the most attractive facets of NHCs is their relative inertness, although this is not always the case as the imidazole class have been shown to facilely convert from 'normal' (C2) binding to a metal to 'abnormal' or mesoionic (C4) binding under certain circumstances.[13] This transformation was clearly demonstrated within aluminium chemistry by Dagorne and co-workers

who reported the synthesis of a normal carbene complex of $AlMe_3$ and its subsequent conversion to the abnormal variant (figure 1a).[14] Hevia reported the lateral metalation of the aromatic-flanked NHC SIMes at the *ortho*-methyl arm of one of the mesityl groups by the aforementioned Li(TMP)/*i*Bu_2Al(TMP) pairing, with the (saturated) backbone remaining untouched (figure 1b).[15] With these two results particularly in mind, we were keen to continue our studies of alkali-metal/aluminium base pairings but with an aliphatically-flanked NHC, specifically I*t*Bu (1,3-di-tert-butylimidazol-2-ylidene) the outcomes of which we report herein.

Results and Discussion

We commenced the study by reacting an equimolar amount of the monomeric organometallic reagent *i*Bu_2Al(TMP) with the *N*-heterocyclic carbene I*t*Bu in hexane. This mixture produced a white precipitate the identity of which was suggested to be an abnormal carbene adduct of the aluminium reagent, *i*Bu_2Al(TMP)(a I*t*Bu) (**1**, scheme 1), by multinuclear NMR spectroscopy. Specifically, asymmetry in the carbene was evident in the ^{1}H NMR spectrum via two distinct singlets for the *t*Bu groups at 1.51 and 0.79 ppm and two ring C-H environments (doublets for H1 and H3 at 7.19 and 7.28 ppm respectively: note numbering as per the later described crystal structure). Likewise, the ring CH units (C1 and C3) resonate at 126.6 and 126.9 ppm respectively in the ^{13}C NMR spectrum; whereas the C2 position bound abnormally to Al resonates at 161.8 ppm, c.f., the carbene C of I*t*Bu bound in a normal fashion to Al resonates at 174.3 ppm.[14]



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Scheme 1

This coordination of the NHC ligand as well as the integrity of the *i*Bu_2Al(TMP) moiety were confirmed by an X-ray diffraction study on a single crystal generated by recrystallization of the white powder in THF (Figure 2), which crystallized with two independent molecules within the unit cell. There was no NMR spectroscopic evidence at any time of a normal adduct existing en route to abnormal complex **1**, contrasting with the case of the I*t*Bu complexes of the less sterically bulky aluminium species Me_3Al [14] and H_3Al [16] where normal to abnormal adduct isomerisation was observed, though the bulkier *i*Bu_3Al went straight to the abnormal complex.[14] A similar scenario has been reported for the related group 13 organometallic compound $Ga(CH_2SiMe_3)_3$ with I*t*Bu.[17] The direct synthesis of **1** is unsurprising given the greater bulk of the *i*Bu_2Al(TMP) system, even with respect to *i*Bu_3Al. The bulk on the N atoms of the carbene is also an important contributing factor since for example going to the less bulky IMes [18] with *i*Bu_3Al results in the normal adduct being formed exclusively with no apparent isomerization,[14] as is the case with the IPr adduct of *n*Bu_3Al.[19] Note that Stasch and co-workers have reported a family of aluminium hydride fragments which are simultaneously coordinated by a normal and an abnormal IDipp ligand.[20]

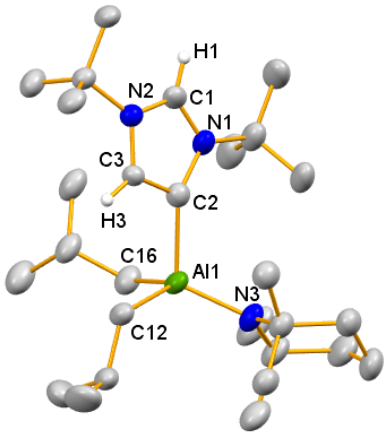


Figure 2 Molecular structure of one independent molecule of *i*Bu$_2$Al(TMP)(a*l*t*B*u) (**1**) with ellipsoids drawn at 50% probability. Disordered component of one *t*Bu group and hydrogen atoms other than those on the imidazole ring have been omitted for clarity.

Next we repeated the reaction producing **1** in the additional presence of the strong utility base Li(TMP).[21] We have shown previously that the components of the Li(TMP)/*i*Bu$_2$Al(TMP) pairing do not come together to form an observable bimetallic complex presumably for steric reasons,[11] but is effective for trans-metal-trapping [12] whereby the lithium reagent can execute a deprotonation reaction (even in very low yield, with the equilibrium lying considerably to the starting material side) and the aluminium reagent can sequester the resulting less bulky anion in the form of a lithium aluminate, thus dragging the equilibrium over to the desired product side. In searching for related systems we note that Camp and co-workers have deprotonated an imidazolium aluminate with KHMDS (HMDS = 1,1,1,3,3,3-hexamethyldisilazide) although the imidazolium ring was not bound to the aluminium centre in an abnormal fashion.[22]

The resulting white precipitate from this reaction of **1** was re-dissolved through addition of THF and the solution was cooled in a freezer to yield crystals, shown by XRD to be the bimetallic aluminate *i*Bu$_2$Al(TMP)(a*l*t*B*u)Li·2THF (**2**, figure 3). Similarly, reactions using the heavier alkali metal amides Na(TMP) and K(TMP) yielded the related complexes *i*Bu$_2$Al(TMP)(a*l*t*B*u)Na·4THF and *i*Bu$_2$Al(TMP)(a*l*t*B*u)K·4THF (**3** and **4** respectively). Though only complex **3** yielded single crystals suitable for a crystal structure determination (figure 3), the NMR spectra of complex **4** was essentially identical to those of **2** and **3** (table 1), giving confidence that the same type of reaction had occurred in all three cases. Specific diagnostic resonances include the metal-bound C2 and C4 (named C1 and C2 in the crystal structure of **3**) carbon atoms (197.7/155.2; 191.3/153.8; 199.2/153.5 for **2** – **4** respectively) and the individual ^{1}H and ^{13}C resonances for the *t*Bu groups which are indicative of asymmetry. Integration of the THF resonances, coupled with elemental analysis, suggest that four molecules of THF solvate the large potassium centre in **4**.

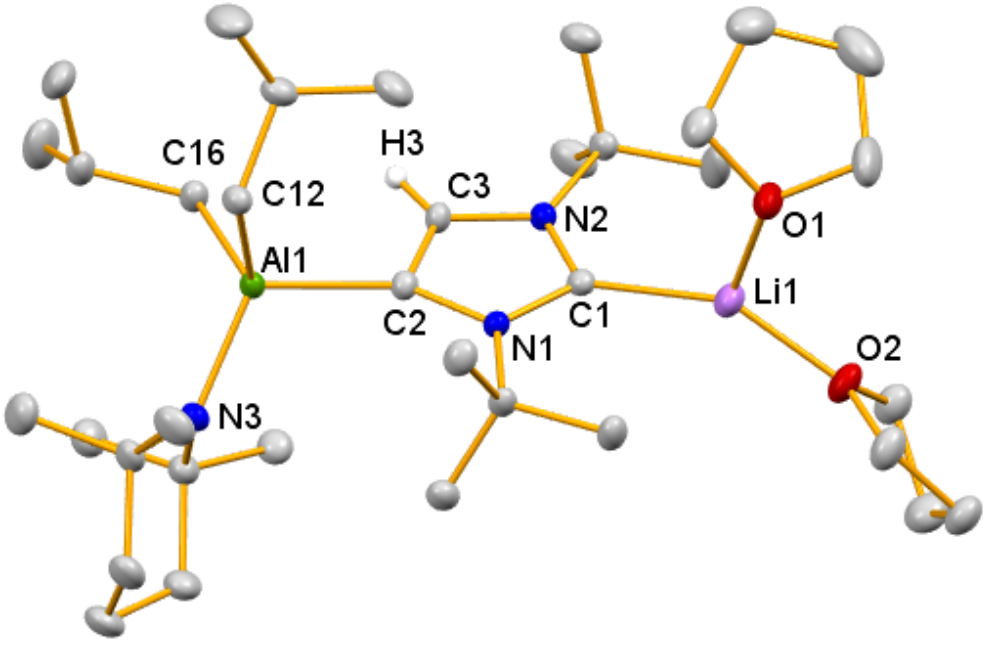
Table 1 Selected ^{1}H and ^{13}C NMR spectroscopic data of abnormal carbene complexes **1** – **4** in C_6D_6 at room temperature

	1		**2**		**3**		**4**	
C2	7.19	126.9	-	197.7	-	191.3	-	199.2

C4	-	161.8	-	155.2	-	153.8	-	153.5
C5	7.28	126.6	7.44	126.8	7.43	126.4	7.37	126.0
*t*Bu	0.79 1.51	29.3 31.3	1.31	31.3 32.5	1.83 1.90	33.9 35.5	1.39 1.88	31.5 34.2
*i*Bu CH_2	0.59 0.71	31.7	0.79	33.3	0.77	32.9	0.65	33.1
*i*Bu CH	2.33	27.8	2.50	28.2	2.49	28.2	2.48	28.1
*i*Bu CH_3	1.22 1.41	28.7 30.5	1.31 1.44	29.1 30.7	1.35 1.45	29.3 30.7	1.33 1.42	29.3 30.7

Each of these reactions can be considered as a selective deprotonation at the acidic C2 position of the imidazolium ring in complex **1**, replacing the hydrogen atom with a THF-solvated alkali-metal ion as reported previously by Dagorne in the reaction of Me_3Al(a*I*t*Bu*) with *n*BuLi.[14] That notwithstanding, it is also possible that alkali-metalation at C4 occurs initially, followed by ligand exchange of the newly formed carbanion to aluminium as reported previously by Robinson and co-workers in their seminal *N*-heterocyclic dicarbene paper.[23] Altering the order of addition of the three starting materials; specifically by reacting Na(TMP) with I*t*Bu first followed by addition of the Al reagent, or generation of **1** by reaction of iBu_2Al(TMP) with I*t*Bu prior to the introduction of Na(TMP) also produced complex **3** in similar yields (52 – 69%) each time.

Molecular structures of abnormal complexes 1 – 3



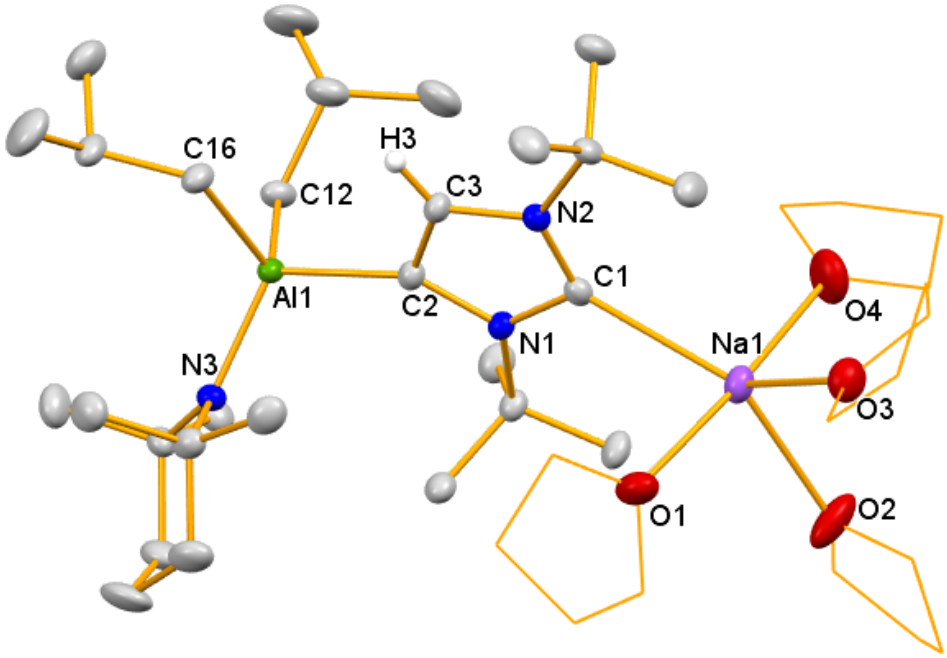


Figure 3 Molecular structures of *i*Bu$_2$Al(TMP)(a*I*t*B*u)Li·2THF (**2**, top) and *i*Bu$_2$Al(TMP)(a*I*t*B*u)Na·4THF (**3**, bottom) with ellipsoids drawn at 50% probability. Disordered THF groups of **3** are drawn as wire models and hydrogen atoms other than those on imidazole rings have been omitted for clarity.

Table 2 Selected bond lengths (Å) and angles (°) of abnormal carbene complexes **1** - **3**

	1 (M = H1)	**2** (M = Li1)	**3** (M = Na1)
C1-M	-	2.082(3)	2.583(1)
C1-N1	1.327(5)	1.369(2)	1.371(2)
C1-N2	1.312(5)	1.362(2)	1.362(2)
N1-C2	1.413(5)	1.426(2)	1.426(2)
N2-C3	1.383(5)	1.395(2)	1.395(2)
C2-C3	1.368(5)	1.364(2)	1.357(2)
C2-Al1	2.071(4)	2.071(1)	2.053(1)
Al1-C12	2.035(4)	2.042(1)	2.038(2)
Al1-C16	2.032(5)	2.044(1)	2.042(2)
Al1-N3	1.899(3)	1.912(1)	1.913(1)
M-O1	-	1.906(3)	2.406(1)
M-O2	-	1.915(3)	2.403(6)
M-O3	-	-	2.379(6)
M-O4	-	-	2.457(4)
C2-Al1-C12	101.4(2)	106.17(6)	105.93(6)
C2-Al1-C16	100.1(2)	102.37(6)	104.81(6)
C12-Al1-C16	105.1(2)	104.01(6)	103.91(7)
N3-Al1-C2	113.0(2)	112.66(5)	111.49(6)
N3-Al1-C12	113.5(2)	118.26(5)	119.09(6)
N3-Al1-C16	121.2(2)	111.85(6)	110.46(6)
Al1-C2-C3	115.7(3)	117.9(1)	117.9(1)
Al1-C2-N1	140.0(3)	139.2(1)	139.9(1)
C3-C2-N1	102.5(3)	101.8(1)	102.0(1)

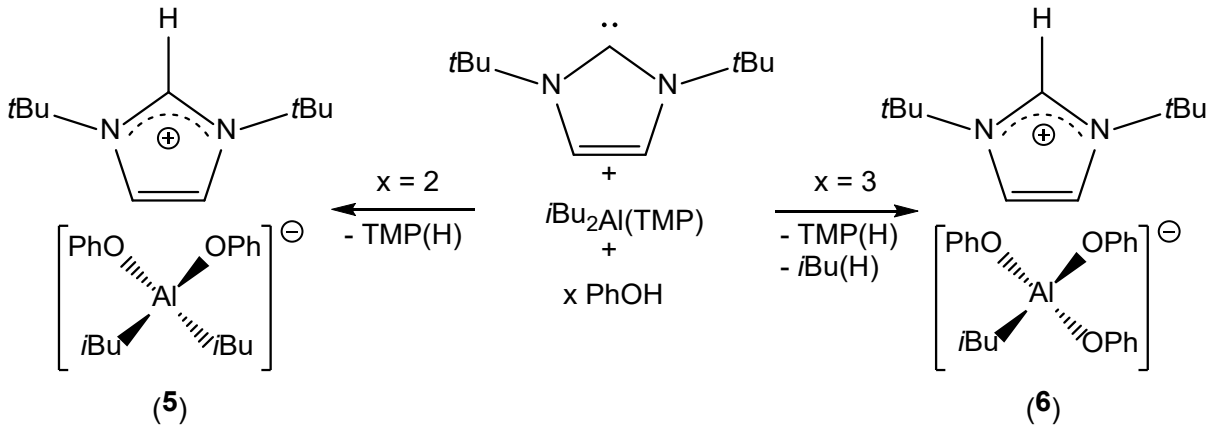
C2-C3-N2	110.6(3)	110.1(1)	109.9(1)
C1-N1-C2	110.0(3)	114.2(1)	114.3(1)
C1-N2-C3	106.9(3)	110.8(1)	111.2(2)
N1-C1-N2	110.0(3)	103.1(1)	102.5(1)
N1-C1-M	-	127.6(1)	126.3(1)
N2-C1-M	-	128.7(1)	127.9(1)
C1-M-O1	-	112.4(1)	85.0(4)
C1-M-O2	-	140.9(1)	140.5(1)
C1-M-O3	-	-	132.2(2)
C1-M-O4	-	-	89.2(1)
O1-M-O2	-	106.7(1)	94.2(3)
O1-M-O3	-	-	84.4(4)
O1-M-O4	-	-	174.0(3)
O2-M-O3	-	-	86.8(2)
O2-M-O4	-	-	89.4(2)
O3-M-O4	-	-	100.6(2)

As can be discerned from table 2, the local environment surrounding the Al centre in all three complexes (**1**-**3**) is largely unchanged as a function of the alkali metal atom coordinated to C2, with similar Al-ligand bond lengths and bond angles seen. Therefore while alkali metal effects are appearing more frequently in the literature, there appears to be no significance here on the identity of the alkali metal.[24] The presence of a metal at C2 (in **2** and **3**) rather than a hydrogen atom (in **1**) does cause deformation in the imidazolium ring, with the angles subtended at the nitrogen atoms noticeably smaller by approximately 4^{o} and the N-C-N angle around 7^{o} larger for complex **1**. This has been seen previously on transitioning from Me_3Al(aI*t*Bu) [25] to Me_3Al(aI*t*Bu)Li·2THF [14] (N-C-N = 109.7/102.5^{o} respectively). Likewise, the N-C distances in the N-C-N unit lengthen by approximately 0.05Å on replacing the imidazolium H atom with an alkali-metal. The lithium centre in **2** is solvated by two THF molecules in a distorted trigonal planar environment (Σ< = 360^{o}) while the sodium coordination geometry in **3** is best described as trigonal bipyramidal with O1 and O4 in the axial positions [174.0(3)^{o}] and O2, O3 and the carbene carbon in the equatorial positions (Σ< = 359.5^{o}). The Li-C bond length of **2** [2.082(3) Å] is consistent with that in other bimetallic carbene complexes such as $(Me_3SiCH_2)_3Ga$(aIDipp)Li·2THF [2.093(5) Å].[17] The Na-C bond length in **3** [2.583(1) Å] is noticeably longer than the corresponding bond in bimetallic *t*Bu_2Zn(aIDipp)Na·3THF [2.501(3) Å].[26] This elongation can be attributed to the higher coordination number in **3** as opposed to the difference in steric bulk at the ring heteroatoms as a similar disparity is seen on comparing related complexes with different coordination numbers at the alkali-metal namely in Ar_3B(aIDipp)Li·2THF and Ar_3B(aIMes)Li·3THF [2.100(3) and 2.198(2) Å respectively].[27] Likewise, the complexes $(C_6F_5)_3B$(aI*t*Bu)Li·2THF and $(C_6F_5)_3B$(aIDipp)Li·2THF show similar Li-C distances [2.092(2) and 2.094(3) Å respectively] despite having different *N*-bound groups but the same coordination number of three.[28]

Reactivity Studies of 1

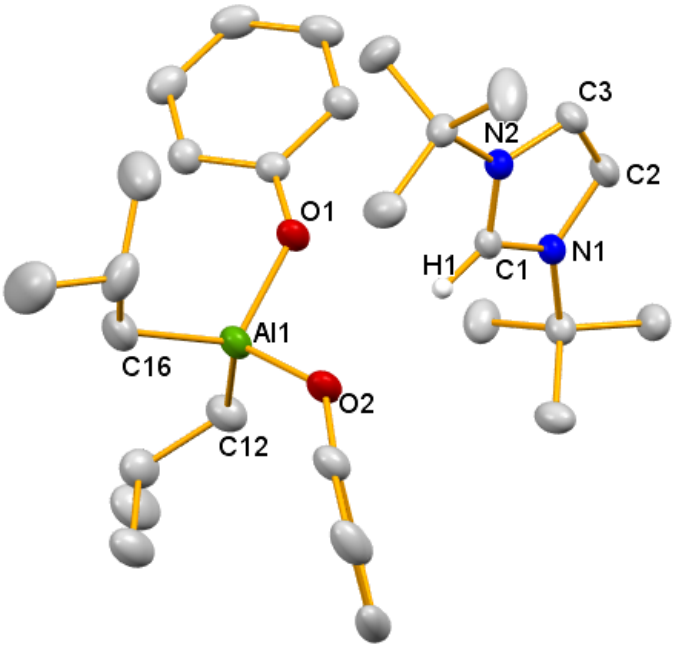
Next we studied the reactivity of the I*t*Bu/*i*Bu_2Al(TMP) pairing with the substrate phenol, which contains an acidic hydrogen to ascertain the ability of **1** to act as a base. I*t*Bu and then *i*Bu_2Al(TMP) were added sequentially to a hexane solution of phenol resulting in a cream suspension. Recrystallisation of this suspension from hexane/THF afforded crystals whose identity was confirmed by XRD from which it could be surmised that deprotonation of phenol had occurred. However, the

specific identity of these crystals was dependent on the stoichiometric amount of phenol present in the reaction solution. When two molar equivalents were utilized, the product was the ionic complex $[It\text{Bu(H)}]^+$ $[(PhO)_2Al(i\text{Bu})_2]^-$ (**5**, figure 4), where two molecules of phenol had been deprotonated via dual carbene/TMP basicity; while with four molar equivalents, $[It\text{Bu(H)}]^+$ $[(PhO)_3Al(i\text{Bu})]^-$ (**6**, figure 4), in which formally three-fold (carbene/TMP/*i*Bu) basicity has taken place (see scheme 2 for reactions). Such ratio-dependent deprotonation of phenol using $i\text{Bu}_3\text{Al}$ as the base has been seen previously by Holmes, with either 1 or 2 equivalents deprotonated.[29] Despite studying other reagent ratios, we were never able to isolate any products of single or four-fold basicity. Both complexes constitute imidazolium aluminates, with the differences being the ratio of phenoxy/alkyl ligands surrounding the distorted tetrahedral aluminium centre.



(**5**) (**6**)

Scheme 2 Synthesis of complexes $[It\text{Bu(H)}]^+$ $[(PhO)_2Al(i\text{Bu})_2]^-$ (**5**) and $[It\text{Bu(H)}]^+$ $[(PhO)_3Al(i\text{Bu})]^-$ (**6**)



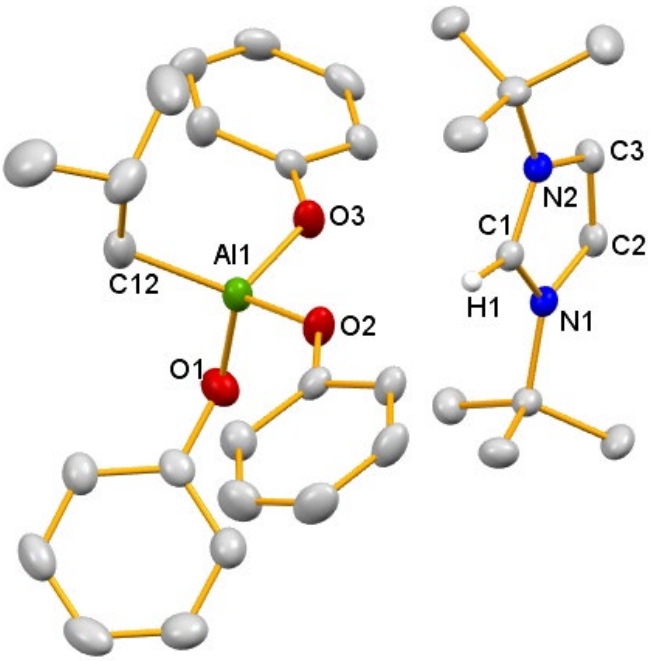


Figure 4 Molecular structures of [I*t*Bu(H)]$^+$ [(PhO)$_2$Al(*i*Bu)$_2$]$^-$ (**5**, top) and [I*t*Bu(H)]$^+$ [(PhO)$_3$Al(*i*Bu)]$^-$ (**6**, bottom) with ellipsoids drawn at 50% probability. Disordered component of one *i*Bu group of **5** and hydrogen atoms other than those on imidazole ring have been omitted for clarity.

Table 3 Selected bond lengths (Å) and angles (°) of imidazolium aluminate complexes **5** and **6**

	5	**6**		**5**	**6**
C1-N1	1.335(2)	1.331(2)	N1-C1-N2	109.1(1)	109.0(1)
C1-N2	1.331(2)	1.333(2)	C1-N1-C2	108.1(1)	108.2(1)
N1-C2	1.380(2)	1.384(2)	C1-N2-C3	108.0(1)	108.2(1)
N2-C3	1.381(2)	1.380(2)	N1-C2-C3	107.3(1)	107.1(2)
C2-C3	1.346(2)	1.349(3)	N2-C3-C2	107.5(1)	107.5(2)
Al1-O1	1.795(1)	1.763(1)	O1-Al1-O2	94.84(5)	110.15(7)
Al1-O2	1.783(1)	1.766(1)	O1-Al1-O3	-	102.27(7)
Al1-O3	-	1.765(1)	O1-Al1-C12	108.7(2)	112.60(8)
Al1-C12	2.021(6)	1.983(2)	O1-Al1-C16	114.40(7)	-
Al1-C16	1.981(2)	-	O2-Al1-O3	-	98.26(6)
C1(-H1)···O2	3.171(2)	3.228(2)	O2-Al1-C12	111.8(1)	111.84(8)
			O2-Al1-C16	109.62(7)	-
			O3-Al1-C12	-	120.47(8)
			C12-Al1-C16	115.7(1)	-

On first sight, both structures **5** and **6** appear to be separated ion pairs consisting of an imidazolium cation and a distorted tetrahedral aluminate anion. However, the C(H)···O separations between the imidazolium ring and one of the phenoxy ligands (denoted by O2) are both close to 3.2 Å which is right on the borderline between a 'moderate' and 'weak' hydrogen bond as described by Jeffrey.[30] For comparison, the C(H)···O separation in [IMe$_4$(H)]$^+$ [Al(OPh)$_4$]$^-$, where the donor is the less bulky 1,3,4,5-tetra-methylimidazolium cation, is 3.126(6) Å.[31] The bond parameters of the cation (table 3) are unsurprisingly similar to each other and are otherwise unremarkable. The aluminate centred anions are heavily distorted tetrahedral, with bond angles ranging from approximately 95-116 and 98-120°

respectively. The Al-O distances span the range 1.763(1)-1.795(1) Å, which is marginally longer than those typically seen in terminal Al-O (phenoxy) bonds in neutral aluminium complexes such as $Al_2(OPh)_6{\cdot}2THF$ [1.734(3) Å] [32] or ($tBu_2(OPh)Al)_2{\cdot}$(μ-4,4'-bipy) [1.719(5) – 1.755(4) Å].[33]

Their resulting NMR spectra in C_6D_6 are broadly similar (table S1), which is unsurprising given the close similarity between the two complexes in the crystal. The main differences lie in the integration values of the phenoxy and *iso*-butyl groups as well as the chemical shift of the 'normal' CH (9.47 and 9.03 ppm, respectively) which is likely a consequence of the different aluminate anion which is hydrogen bonded via this functionality.

Reaction with benzonitrile

Next, we studied the reactivity of the $iBu_2Al(TMP)$/I*t*Bu pairing with benzonitrile. The three reagents were stirred together in hexane in a 1:1:1 ratio, from which the solution yielded upon cooling a small crop of yellow crystals identified by X-ray crystallography as a*t*Bu(Ph)C=N[Al(iBu)$_2$N=C(TMP)Ph]Al(iBu)$_2$, **7**, (figure 5, scheme 3). Dinuclear complex **7** contains a disubstituted imidazolium ring with one position having an organic C-bound imido group (C20) and the other acting as a formally abnormal carbene bearing an Al(iBu)$_2$ fragment. The imido nitrogen (N3) then bridges between that aluminium centre Al1 and a second Al(iBu)$_2$ group containing Al2 to close up a fused five-membered ring, with the coordination sphere of Al2 completed by a second imide containing N4, this time formed by the addition of a TMP group across the benzonitrile triple bond. Functionalization of aromatic rings is known to proceed via M-TMP addition to a benzyne intermediate,[34] while addition of a Mg-TMP unit to an unsaturated isocyanate was recently reported.[35] The highly unusual central AlNCCNCNC fused system can be considered an aluminated derivative of the pyrrolo[3,4-d]imidazole class of compounds,[36] with the longer bonds of Al forcing the metal centre out of the plane of the organic fragment [0.371(1)Å with respect to the imidazole ring]. Both aluminium centres can be considered as mildly distorted from tetrahedral (τ_4 values [37] of 0.88 and 0.91, respectively), with more distortion at Al1 as a consequence of the strain imposed upon its angles by its incorporation in a five-membered ring. The reduction of the two nitrile groups is evidenced via their C=N bond lengths [1.286(3) and 1.246(3) Å] and the planarity at their imido sp^2-hybridised carbon atoms [Σ < = 359.17 and 359.83° at C20 and C35]. The distances of the imido(N-Al) bonds are unsurprisingly longer for bridging N3 [1.983(2) Å to Al1 and 2.017(2) Å to Al2] than terminal N4 [1.838(2) Å to Al2]. The C=C backbone [1.372(3) Å] is only marginally longer than those seen in complexes 1-3 [1.357(2) – 1.368(5) Å].

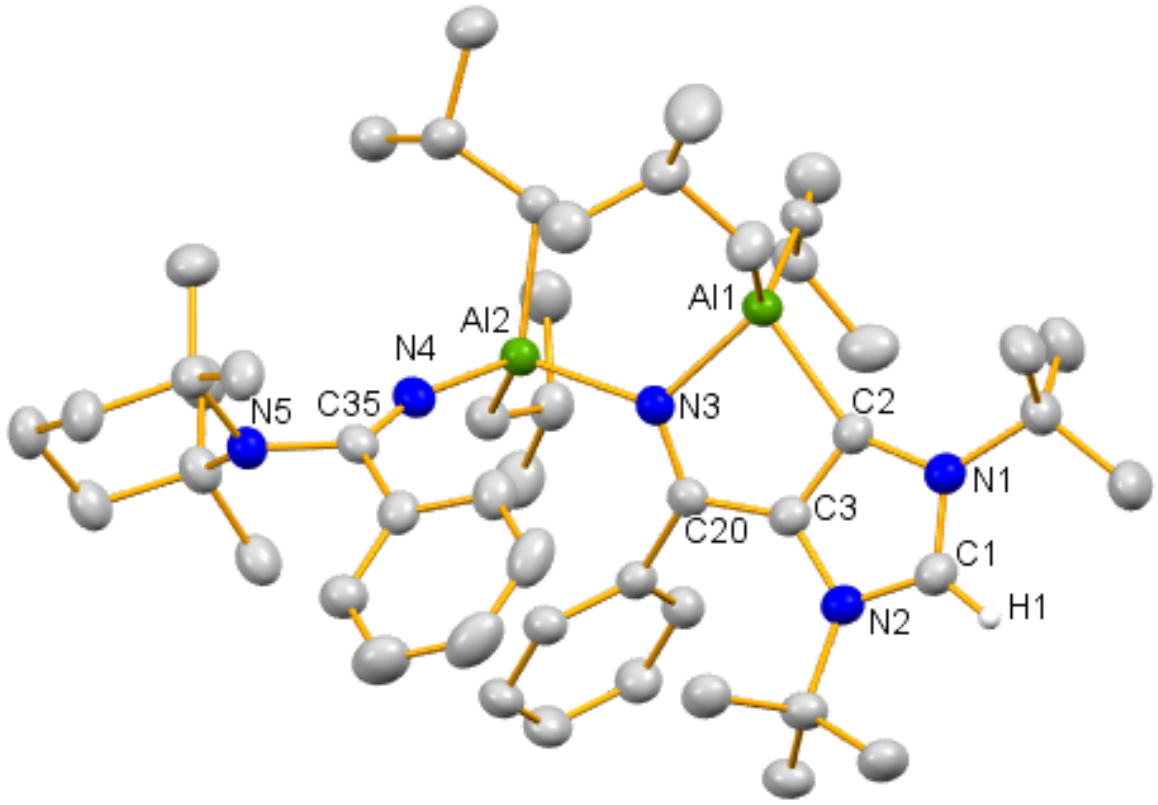
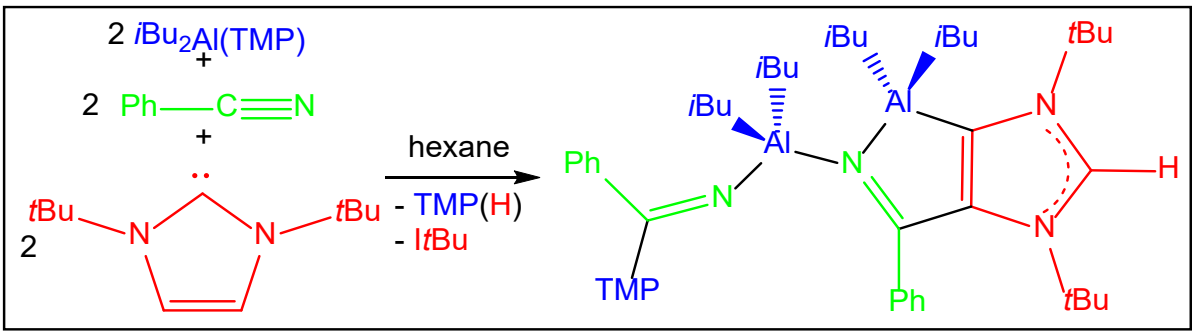


Figure 5 Molecular structure of a*l*tBu(Ph)C=N[Al(*i*Bu)$_2$N=C(TMP)Ph]Al(*i*Bu)$_2$, (**7**) with ellipsoids drawn at 50% probability and hydrogen atoms other than that on imidazole ring omitted for clarity. Selected bond lengths (Å) and angles (°): C1-N1, 1.330(3); C1-N2, 1.328(3); N1-C2, 1.387(3); N2-C3, 1.410(3); C2-C3, 1.372(3); C2-Al1, 2.041(2); Al1-N3, 1.983(2); C3-C20, 1.497(3); N3-C20, 1.286(3); Al2-N3, 2.017(2); Al2-N4, 1.838(2); N4-C35, 1.246(3); N5-C35, 1.455(3); N1-C1-N2, 111.2(2); C1-N2-C3, 105.5(2); N2-C3-C2, 109.2(2); C3-C2-N1, 104.9(2); C2-N1-C1, 109.2(2); C2-Al1-N3, 85.37(8); C2-Al1-C12, 114.02(9); C2-Al1-C16, 106.39(9); N3-Al1-C12, 110.70(8); N3-Al1-C16, 117.25(9); C12-Al1-C16, 118.4(1); N3-Al2-N4, 111.32(8); N3-Al2-C27, 100.61(8); N3-Al2-C31, 111.98(8); N4-Al2-C27, 109.82(9); N4-Al2-C31, 104.07(9); C27-Al2-C31, 119.19(9); Al1-N3-Al2, 121.26(8); Al2-N4-C35, 164.8(2).

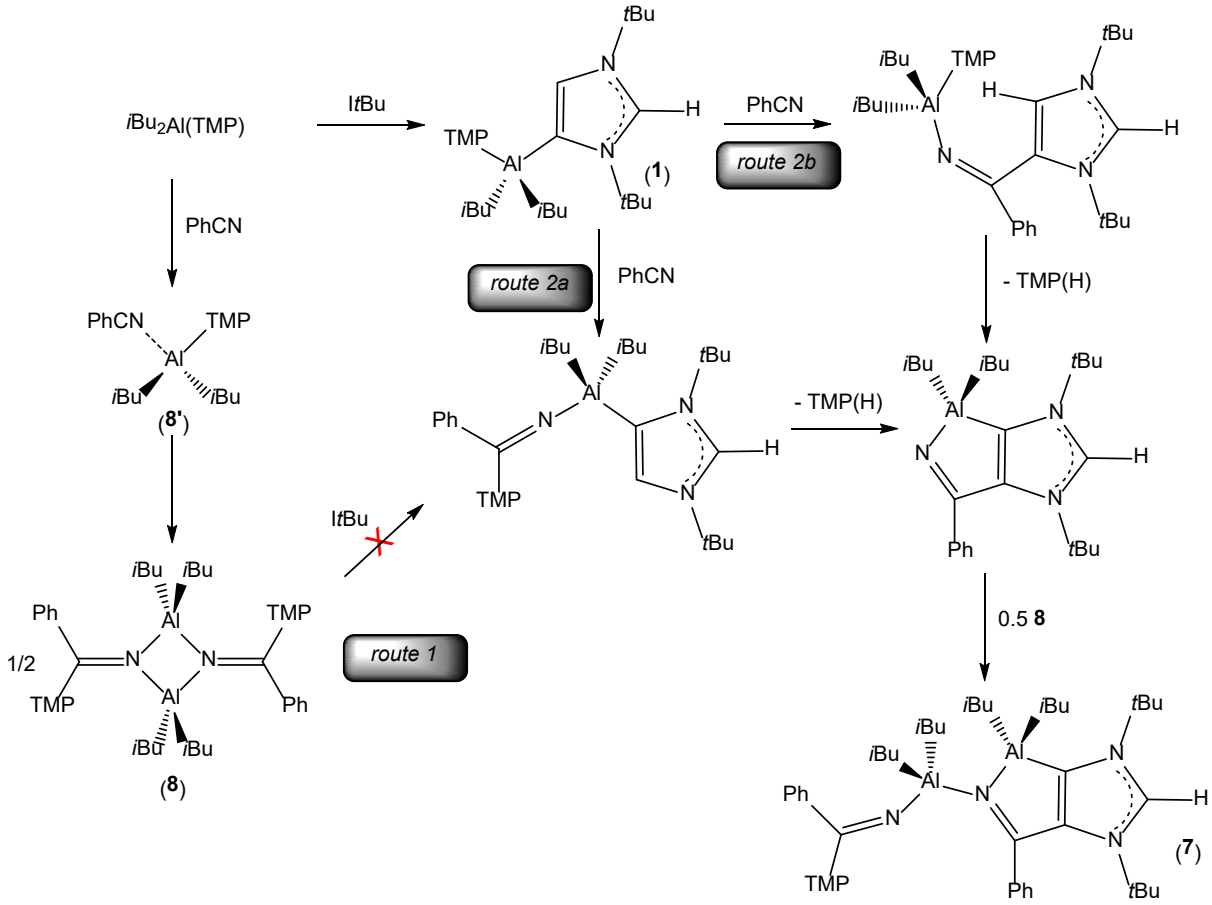


Scheme 3 Synthesis of complex **7**

Logic dictates that a number of steps must have occurred to assemble the structure of complex **7**. For example, the carbene can be considered abnormal (C1 is protonated), TMP(H) has been lost

(consistent with a deprotonation reaction at the C5 position of the intermediate) and Al-L addition across both nitrile groups has taken place (where L = al*t*Bu and TMP).

To probe the outcome of this reaction further, we identified some potential mechanistic pathways for the formation of **7** (scheme 4) and attempted to gain insight on them experimentally.



Scheme 4 Postulated mechanisms for formation of complex 7

The first step was postulated as the reaction of the aluminium reagent with either of the organic reagents PhCN (*route 1*) or I*t*Bu (*route 2*). We have already proven that reaction with I*t*Bu yields abnormal complex **1** (*vide supra*) so we commenced by probing *route 1*. In a 1:1 reaction, we were able to grow and isolate some crystals whose crystal structure showed that the nitrile functionality can insert into the Al-N(TMP) bond giving dimeric [*i*Bu$_2$AlN=C(Ph)TMP]$_2$, **8**. We were unable to identify any onward reaction of **8** with the carbene in hexane solution with only returned starting materials identified and no evidence of the dialkyl(imido)aluminium reagent forming a normal or abnormal carbene complex, suggesting that *route 1* was not viable. This is possibly due to the shorter, stronger Al-N bonds as part of the central four-membered ring of **8** being stable enough to prevent Lewis donor (carbene) access to Al. Unfortunately, we could not characterize **8** in solution via NMR spectroscopy as only a tiny amount of recrystallized material was obtained, although we do believe that the reaction passes through the nitrile solvated adduct *i*Bu$_2$Al(TMP)·NCPh (**8'**) as the ^{1}H and ^{13}C NMR spectra of the two reagents displayed all their original resonances with only very minor shifting. Of particular support to this hypothesis was the resonance at 119.2 ppm in the ^{13}C spectrum, consistent with retention of the nitrile functionality. Subsequently, we carried out an NMR scale reaction of **1** with PhCN in an attempt to shed light on whether *routes 2a* or *2b* were viable. NMR evidence was inconclusive with

several new resonances witnessed, none of which were particularly indicative of either pathway. Loss of TMP(H) was clear upon heating, as evidenced by a new singlet at 1.06 ppm (methyl groups) in the ^{1}H spectrum, although this is already known to occur and does not clarify which pathway is more plausible. We do consider pathway 2b to be more likely than 2a on the basis of the presence of an Al-TMP unit after reaction of **1** with PhCN, which is then still available to act as a base for the deprotonation of the remaining carbene backbone CH unit (C5 position), whereas if the TMP adds across the nitrile functional group first then it is likely to lose its basicity since it forms a more covalent Al-C bond.

Crystallographic authentication of complex 8

Previously we have inserted CO_2 into the Al-N bond of *i*Bu_2Al(TMP),[38] although delocalization of the negative charge over the OCO unit facilitated the formation of an 8-membered $[AlOCO]_2$ ring. Nöth has also seen CO_2 insertion into the Al-N bonds of the related heteroleptic alkyl/amido aluminium complexes *t*Bu_2Al(TMP) [39] and $MeAl(TMP)_2$,[40] while other examples of insertions into Al-amide units have also been documented.[41] In the solid state, complex **8** was found to dimerize with the newly formed aryl/amido imide ligand bridging between aluminium centres (figure 6) resulting in a non-planar four-membered Al_2N_2 ring (the two Al_2N planes lie at an angle of 15.21(4)^o from each other). Such a motif with bridging imides has been witnessed previously, formed via thermolysis of a larger aluminium complex,[42] deprotonation of an imine,[43] salt metathesis of a lithium imide with $AlCl_3$,[44] or addition of an Al-H,[45] or Al-Ph [46] unit across a nitrile group. Wade reported one of the earliest crystallographically characterised Al-N=C(imide) bonded structures in lithium tetrakis(di-*t*-butylmethyleneamine).[47] Woo, Richeson *et al.* have reported addition of one Al-NMe_2 bond of homoleptic $Al(NMe_2)_3$ across the CN triple bond of the related nitrile NC-NMe_2 to give $[(Me_2N)_2AlN=C(NMe_2)_2]_2$.[48] In **8**, the aluminium centres are in a heavily distorted tetrahedral environment caused by the strain of the four-membered ring (both approximately 84^o) while the bridging N atoms are trigonal planar (Σ = 359.99/359.82^o), reflecting their sp^2 hybridization, although again the four-membered ring (Al-N-Al both approximately 95^o) enforces variation in the individual angles. The bulky TMP groups lie trans with respect to one another, giving (non-crystallographic) C2 symmetry.

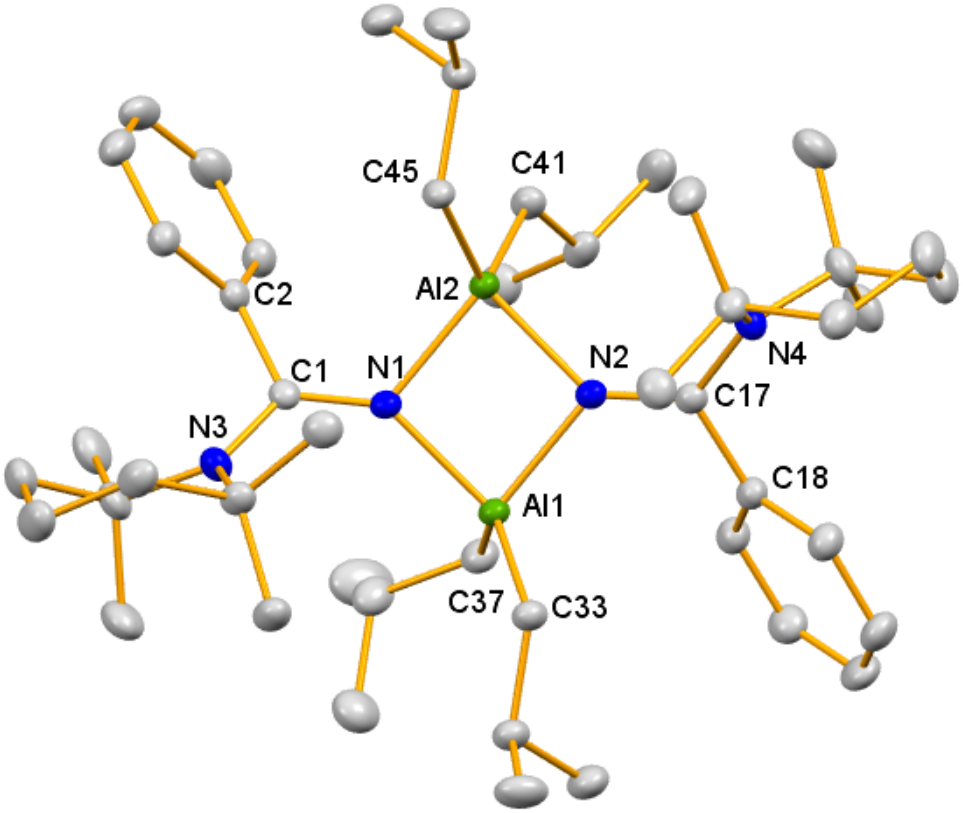


Figure 6 Molecular structure of [*i*Bu$_2$AlN=C(Ph)TMP]$_2$ (**8**) with ellipsoids drawn at 50% probability and hydrogen atoms omitted for clarity.

Table 4 Selected bond lengths (Å) and angles (°) of aluminium complex **8**

N1-Al1	1.946(1)	N2-Al2	1.947(1)	Al1-N1-Al2	95.09(4)	Al1-N2-Al2	95.02(4)
N1-Al2	1.966(1)	N2-Al1	1.967(1)	Al1-N1-C1	141.06(8)	Al1-N2-C17	127.88(8)
Al1-C33	1.992(1)	Al2-C41	1.991(1)	Al2-N1-C1	123.84(8)	Al2-N2-C17	136.92(8)
Al1-C37	1.998(1)	Al2-C45	1.997(1)	N1-Al1-N2	84.02(4)	N1-Al2-N2	84.03(4)
N1-C1	1.292(1)	N2-C17	1.286(1)	N1-Al1-C33	124.31(5)	N1-Al2-C41	126.08(5)
C1-C2	1.505(1)	C17-C18	1.508(1)	N1-Al1-C37	102.20(4)	N1-Al2-C45	105.00(4)
C1-N3	1.398(1)	C17-N4	1.409(1)	N2-Al1-C33	103.73(4)	N2-Al2-C41	104.78(4)
				N2-Al1-C37	115.62(5)	N2-Al2-C45	122.94(4)
				C33-Al1-C37	121.40(5)	C41-Al2-C45	112.64(5)
				N1-C1-C2	118.8(1)	N2-C17-C18	119.4(1)
				N1-C1-N3	125.6(1)	N2-C17-N4	124.5(1)
				C2-C1-N3	115.4(1)	C18-C17-N4	115.9(1)

Finally, we repeated the reaction of *i*Bu$_2$Al(TMP)/I*t*Bu with an alternative nitrile, namely diphenylacetonitrile, Ph$_2$CHCN, due to its potential for reactivity either at the acidic CH or at the CN triple bond. Hevia has previously reacted this nitrile with the Ga(CH$_2$SiMe$_3$)$_3$/I*t*Bu pairing and obtained the solvent-separated ion pair [I*t*Bu(H)]$^+$ [(Ph$_2$C=C=N)Ga(CH$_2$SiMe$_3$)$_3$]$^-$ where the carbene appears to function as a base to give an imidazolium cation, with the resulting ketenimide anion being trapped by the organogallium fragment.[49] While group 1 [50] and group 2 [51] complexes containing the Ph$_2$C=C=N ligand have also been characterized, to the best of our knowledge there are no known aluminium complexes, with the only other group 13 example being an indium complex.[50]

Stirring the three reagents in hexane yielded a crop of crystals suitable for XRD. The crystal structure of the recrystallised product revealed that the organometallic reagent does not appear to have been involved, with the final product consisting of an organic ion pair in the form of $[I\textit{t}Bu(H)]^+$ $[Ph_2C{=}C{=}N]^-$ (**9**, figure **7**). This confirms the enhanced steric crowding around the metal in $\textit{i}Bu_2Al(TMP)$ as it does not have enough space to accept the resulting ketenimide anion as less bulky $Ga(CH_2SiMe_3)_3$ does.

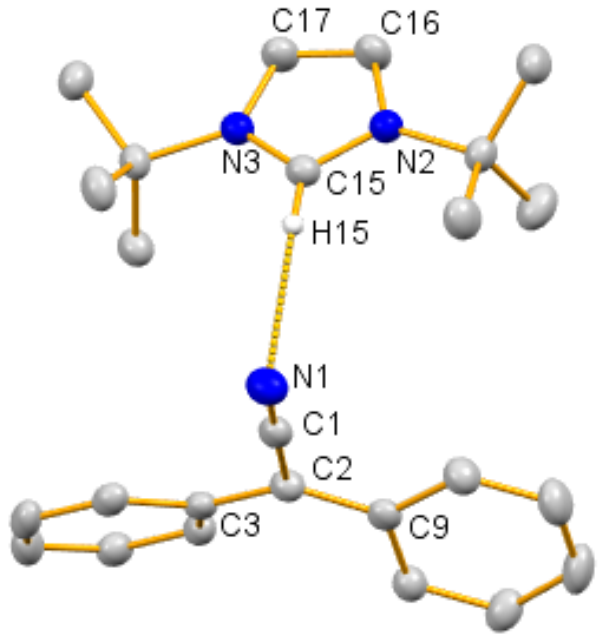


Figure 7 Molecular structure of $[I\textit{t}Bu(H)]^+$ $[Ph_2C{=}C{=}N]^-$ (**9**) with ellipsoids drawn at 50% probability and hydrogen atoms omitted for clarity. Selected bond lengths (Å) and angles (°): N1-C1, 1.161(3); C1-C2, 1.408(3); N1-C15, 3.278(3); C15-N2, 1.327(2); N2-C16, 1.379(3); C15-N3, 1.333(2); N3-C17, 1.375(3); C16-C17, 1.348(3); N1-C1-C2, 178.6(2); C1-N1-C15, 101.2(1); C1-C2-C3, 116.1(2); C1-C2-C9, 116.1(2); C3-C2-C9, 127.8(2); N2-C15-N3, 109.3(2); C15-N2-C16, 107.9(2); C15-N3-C17, 108.1(2); N2-C16-C17, 107.5(2); N3-C17-C16, 107.2(2).

In generating **9** the carbene has acted as a base,[52] deprotonating the nitrile which in turn adopts its preferred ketenimido tautomeric form. Subsequently, we repeated this reaction in the absence of $\textit{i}Bu_2Al(TMP)$, which yielded the same product in a high yield of 80%. Although **9** is formally considered to possess a C=C=N unit, its bond lengths [1.408(3)/1.161(3) Å] are intermediate between those of the free nitrile [1.470(2)/1.147(2) Å] and a complex such as $[Ph_2C{=}C{=}N)InMe_2{\cdot}THF]_2$ [average of two independent molecules = 1.354/1.194 Å].[50] These bond distances in **9** almost exactly mirror those of the ketenimide unit present in the metal-free separated ion in $2[I\textit{t}Bu(H)]^+$ $[N{=}C{=}C(CO_2)(CO_2H)]^{2-}$ [1.408(3)/1.162(2) Å].[53] That said, the sum of the angles at C2 (360°) suggests sp^2 hybridization and the angle at C1 [178.6(2)°] supports sequential double bonds. The N1···H15-C15 distance is similar to the hydrogen bond donor-acceptor distance in **5** and **6** and is consistent with a long-range hydrogen bond holding the two ions together. The C=C=N unit displayed a sharp band at 2095 cm^{-1} in the IR spectrum run in Nujol, which is similar to those reported for a series of alkaline earth ketenimide complexes,[51a] and close to our computed value of 2130 cm^{-1} (see SI for full details).

Conclusion

The reaction of the bulky monomeric bisalkylaluminium amide *i*Bu_2Al(TMP) with the imidazole-based NHC I*t*Bu yields exclusively an abnormal carbene adduct, which is shown to be the case regardless of whether it is H^+, Li^+, Na^+ or K^+ bound at the carbene C2 position. This aluminium/carbene pairing demonstrates reactivity with a variety of different substrates with a stoichiometric dependence towards the deprotonation of the acidic substrate phenol. An unusual multicomponent assembly is formed utilizing the unsaturated substrate benzonitrile via a complicated nucleophilic addition process, which establishes a new frontier for this organoaluminium reagent that augurs well for further development with a range of unsaturated substrates. Finally, I*t*Bu acts itself as a base in the deprotonation of diphenylacetonitrile with no contribution from the metallic component. The catalytic role of NHC Brønsted basicity in hydrophosphination has recently been elucidated [54] and further progress in non-metallic catalysis constitutes an interesting future endeavour for us.

Experimental

General Experimental

All reactions were performed under a protective argon atmosphere using standard Schlenk techniques. Solvents were dried by heating to reflux over sodium benzophenone ketyl and then distilled under nitrogen prior to use. *n*BuLi (1.6M in hexanes), *i*Bu_2AlCl, diphenylacetonitrile and phenol were obtained from commercial sources and used as received. TMP(H) and benzonitrile and were purchased commercially and stored over activated 4 Å molecular sieves; THF and hexane were distilled over sodium/benzophene and I*t*Bu,[55] *i*Bu_2Al(TMP),[9b] LiTMP,[56] NaTMP,[57] and KTMP,[58] were synthesised using known literature procedures. C_6D_6 was degassed by freeze-pump-thaw methods and stored over activated 4 Å molecular sieves. ^{1}H, ^{7}Li and ^{13}C NMR spectra were recorded on a Bruker AV400 MHz spectrometer operating at 400.13, 155.47 and 100.58 MHz respectively. Elemental (C, H, N) analyses were obtained using a Perkin Elmer 2400 elemental analyser. IR spectra were collected on a Perkin Elmer Spectrum 100 FT-IR Spectrometer.
Crystallographic data for **1-3** and **5-9** were collected on an Oxford Diffraction instrument using Mo-K_α radiation (λ = 0.71073 Å) or an Oxford Diffraction Gemini S instrument with graphite-mono-chromated Cu-K_α (λ 1.54184 Å) radiation. Structures were solved using OLEX2, while refinement was carried out on F^2 against all independent reflections by the full-matrix least-squares method by the Gauss-Newton algorithm using OLEX2.[59] All non-hydrogen atoms were refined using anisotropic displacement parameters. Selected crystallographic details and refinement details can be found in Table 5.

Synthesis of 1

To a solution of I*t*Bu (0.90 g; 5 mmol) in hexane (20 mL) was added *i*Bu_2Al(TMP) (1.40 g; 5 mmol) in hexane (5 mL) dropwise. The reaction was stirred for 2 hours at room temperature resulting in a white precipitate. The solid was isolated by filtration and washed with hexane (5 mL) then dried under vacuum to generate the desired product (1.50 g; 3.3 mmol; 65 % yield).
Elemental analysis (%) calculated for $AlN_3C_{28}H_{56}$ (found): C, 72.83 (72.51); H, 12.22 (12.47); N 9.10 (9.42). ^{1}H NMR (400.03 MHz; 300 K; C_6D_6): δ (ppm) 0.59 (d of d, *J* = 13.3 Hz, 7.7 Hz, 2H, C*H*$_2$CHMe$_2$); 0.71 (d of d, *J* = 13.5 Hz, 4.7 Hz, 2H, C*H*$_2$CHMe$_2$); 0.79 (s, 9H, *CH*$_3$ – *t*Bu); 1.22 (d, *J* = 6.58 Hz, 6H, CH$_2$CH(C*H*$_3$)$_2$); 1.41 (d, *J* = 6.58 Hz, 6H, CH$_2$CH(C*H*$_3$)$_2$); 1.51 (s, 9H, *CH*$_3$ – *t*Bu); 1.67 (s, 12H TMP *CH*$_3$); 1.68 – 1.73 (m, 4 H, TMP *βCH*$_2$); 1.92 – 1.99 (m, 2H, TMP γ*CH*$_2$); 2.33 (overlapping sept, *J* = 6.58 Hz, 2H, CH$_2$*CH*Me$_2$); 7.19 (d, *J* = 1.81 Hz, 1H, NC2(*H*)N); 7.28 (d, *J* = 1.81 Hz, 1H, imidazolium backbone *CH*). ^{13}C{^{1}H} NMR (100.59 MHz; 300 K; C_6D_6): δ (ppm) 19.7 (TMP *γC*H$_2$); 27.8 (CH$_2$*C*HMe$_2$); 28.7 (CH$_2$CH(*C*H$_3$)$_2$); 29.3 (I*t*Bu *t*Bu – *CH*$_3$); 30.5 (CH$_2$CH(*C*H$_3$)$_2$); 31.3 (I*t*Bu *t*Bu – *CH*$_3$); 31.7 (*C*H$_2$CH(CH$_3$)$_2$);

35.3 (TMP *CH₃*); 42.9 (TMP β*CH₂*); 53.2 (TMP *C*(CH₃)₂); 56.2 (I*t*Bu *C*(CH₃)₃); 59.6 (I*t*Bu *C*(CH₃)₃); 126.6 (N*CH*C(Al)N); 126.9 (N*C*N); 161.8 (*C*–Al – from HMBC).

Synthesis of 2

To a solution of TMP(H) (0.41 mL; 2.44 mmol) in hexane (10 mL) was added *n*BuLi (1.6 M in hexane; 1.5 mL; 2.44 mmol) and the reaction was allowed to stir for 30 minutes to generate LiTMP. *i*Bu₂Al(TMP) [(0.68 g; 2.44 mmol) in hexane (2 mL)] was added to this dropwise, followed by I*t*Bu (0.44 g; 2.44 mmol) via a solid addition tube. The resulting cream coloured suspension was allowed to stir for 2 hours at room temperature. The volatiles were then removed *in vacuo* and the residue re-dissolved in THF (5 mL) with hexane (10 mL) used as anti-solvent. Cooling the mixture at –33°C resulted in the formation of a white polycrystalline solid. The solid was isolated by cannula filtration, washed with hexane (5 mL) before being dried *in vacuo* to give the desired product as an off-white solid (0.61 g; 1.0 mmol, 40 % yield).
^{1}H NMR (400.03 MHz; 300 K; C_6D_6): δ (ppm) 0.79 (br. m, 4H, C*H₂*CH(CH₃)₂; 1.30 – 1.33 (m, 23H, overlapping resonances of CH₂CH(C*H₃*)₂ and I*t*Bu C(C*H₃*)₃); 1.44 – 1.45 (d, *J* = 4.25 Hz, 6H, CH₂CH(C*H₃*)₂); 1.85 (br. s, 24H, overlapping resonances of TMP βC*H₂*, TMP C*H₃*, and THF C*H₂*); 2.04 (m, 2H, TMP γC*H₂*); 2.50 (m, 2H, CH₂C*H*(CH₃)₂); 3.24 (t, *J* = 6.50 Hz, THF C*H₂*); 7.44 (s, N*CH*C(Al)N). ^{13}C{^{1}H} NMR (100.59 MHz; 300 K; C_6D_6): δ (ppm) 20.1 (TMP γ*C*H₂); 25.4 (THF CH₂); 28.2 (CH₂*C*H(CH₃)₂); 29.1 (CH₂CH(*C*H₃)₂); 30.7 (CH₂CH(*C*H₃)₂); 31.3 (I*t*Bu C(*C*H₃)₃); 32.5 (I*t*Bu *C*(CH₃)₃); 33.3 (*C*H₂CH(CH₃)₂); 35.4 (TMP *C*H₃); 43.3 (TMP β*C*H₂); 53.3 (TMP *C*(CH₃)₂); 57.2 (I*t*Bu *C*(CH₃)₃); 68.7 (s, THF OCH₂); 126.8 (N*C*HC(Al)N); 155.2 (NCH*C*(Al)N); 197.7 (*C:*–Li – from HMBC). ^{7}Li NMR (155.5 MHz, 300 K, C_6D_6, relative to LiCl in D_2O): δ (ppm) 0.60 (s).
Accurate elemental analyses could not be obtained.

Synthesis of 3

To a solution of I*t*Bu (0.18 g; 1.0 mmol) in hexane (10 mL) was added NaTMP (0.16 g; 1.0 mmol) via a solid addition tube followed by dropwise addition of *i*Bu₂Al(TMP) (0.28 g; 1.0 mmol) in hexane (2 mL) dropwise, resulting in a yellow solution and orange oil that over time became cloudy. After stirring the mixture for 2 hours the solvent was removed *in vacuo* and the residues dissolved in THF (3 mL) with hexane (6 mL) anti-solvent. Cooling to -15 °C produced a crop of colourless crystals. The crystals were isolated by cannula filtration and washed with aliquots of hexane (5 mL) before drying under vacuum (0.4 g; 0.52 mmol; 52 % yield).
Elemental analysis (%) calculated for $AlN_3C_{44}H_{87}NaO_4$ (found): C, 68.44 (68.52); H, 11.36 (11.19); N, 5.44 (5.69). ^{1}H NMR (400.13 MHz; 300 K; C_6D_6): δ (ppm) 0.77 (d, *J* = 6.11 Hz, 4H, *CH₂*CHMe₂); 1.35 (d, *J* = 6.49 Hz, 6H, CH₂CH(C*H₃*)₂); 1.40 (s, 12H, TMP C*H₃*); 1.41 – 1.45 (m, 8H, THF *CH₂*); 1.45 (d, *J* = 6.34 Hz, 6H, CH₂CH(C*H₃*)₂); 1.78 – 1.82 (m, 4H, TMP *βCH₂*); 1.83 (s, 9H, I*t*Bu *CH₃*); 1.90 (s, 9H, I*t*Bu *CH₃*); 2.00 – 2.08 (m, 2H, TMP *γCH₂*); 2.49 (sept, *J* = 6.78 Hz, 2H, CH₂*CH*Me₂); 3.39 (t, *J* = 6.78 Hz, 8H, THF O*CH₂*); 7.43 (s, 1H, N*CH*C(Al)N). ^{13}C{^{1}H} NMR (100.59 MHz; 300 K; C_6D_6): δ (ppm) 20.3 (TMP γ*CH₂*); 25.7 (THF *CH₂*); 28.2 (CH₂*CH*Me₂); 29.3 (CH₂CH(*C*H₃)₂); 30.7 (CH₂CH(*C*H₃)₂); 31.7 (TMP *C*H₃); 32.9 (*CH₂*CHMe₂); 33.9 (I*t*Bu *CH₃*); 35.5 (I*t*Bu *CH₃*); 43.6 (TMP β*CH₂*); 53.3 (TMP β*CH₂*); 53.7 (TMP CH₃); 56.8 (*t*Bu *C*(CH₃)₃); 68.2 (THF O*CH₂*); 126.4 (N*CH*C(Al)N); 153.8 (Al–*C* – from HMBC); 191.3 (*C:*–Na – from HMBC).

Synthesis of 4
A suspension of KTMP (0.18 g; 1.0 mmol) in hexane (10 mL) was cooled to 0°C and I*t*Bu (0.18 g; 1.0 mmol) was added via a solid addition tube, followed by dropwise addition of *i*Bu₂Al(TMP) (0.28 g; 1.0 mmol) in hexane (2 mL). THF (2 mL) was added and the reaction allowed to stir for 2 hours at 0°C, resulting in a dark solution and precipitate. The volatiles were removed *in vacuo* and the residues dissolved in THF (2 mL) with hexane (6 mL) added as anti-solvent. Cooling the mixture to -15°C resulted in a small crop of colourless crystals which were not suitable for X-ray crystallographic analysis.

Elemental analysis (%) calculated for $AlN_3C_{44}H_{87}KO_4$ (found): C, 67.04 (67.17); H, 11.12 (10.98); N 5.33 (5.70). ^{1}H NMR (400.13 MHz; 300 K; C_6D_6): δ (ppm) 0.60 – 0.69 (m, 4H, *CH*$_2$CHMe$_2$); 1.33 (d, *J* = 6.42 Hz, 6H, CH$_2$CH(*CH*$_3$)$_2$); 1.39 (s, 9H, C(*CH*$_3$)$_3$); 1.40 -1.44 (m, 8H, THF CH$_2$); 1.42 (overlapping resonances, 6H, CH$_2$CH(*CH*$_3$)$_2$); 1.80 (s, 12H, TMP *CH*$_3$); 1.80 – 1.82 (m, 4H, TMP β*CH*$_2$); 1.88 (s, 9H, C(*CH*$_3$)$_3$); 2.00 – 2.08 (m, 2H, TMP γ*CH*$_2$); 2.48 (sept, *J* = 6.26 Hz, CH$_2$*CH*(Me)$_2$); 3.38–3.46 (m, 8H, THF OCH$_2$); 7.37 (s, 1H, N*CH*=C(Al)N). ^{13}C{^{1}H} NMR (100.59 MHz; 300 K; C_6D_6): δ (ppm) 20.0 (TMP γ*CH*$_2$); 25.6 (THF CH$_2$); 28.1 (CH$_2$*CH*Me$_2$); 29.3 (CH$_2$CH(*CH*$_3$)$_2$); 30.7 (CH$_2$CH(*CH*$_3$)$_2$); 31.5 (C(*CH*$_3$)$_3$); 32.0 (*C*(CH$_3$)$_3$); 33.1 (*CH*$_2$CH(Me)$_2$); 34.2 (C(*CH*$_3$)$_2$); 35.3 (TMP *CH*$_3$); 43.3 (TMP β*CH*$_2$); 53.3 (TMP CH$_3$); 54.1 (TMP CH$_3$); 57.2 (*C*(CH$_3$)$_3$); 68.0 (THF OCH$_2$); 126.0 (s, N*CH*=C(Al)N)) 153.5 (s, NCH=*C(Al)*N, by HMBC); 199.2 (N*C:(K)*N).

Synthesis of 5

To a solution of PhOH (0.18 g; 2 mmol) in hexane (10 mL) was added I*t*Bu (0.18 g; 1 mmol) via a solid addition tube, giving a cream suspension. *i*Bu$_2$Al(TMP) (0.28 g; 1 mmol) in hexane (2 mL) was then added dropwise to this mixture. The reaction mixture was stirred for four hours then THF (5 mL) was added to generate a colourless homogeneous solution. Crystals were obtained at –15 °C (0.32 g, 0.63 mmol, 63 % yield).
Elemental analysis (%) calculated for $AlN_2C_{31}H_{49}O_2$ (found): C, 73.19 (72.53); H, 9.71 (9.24); N, 5.51 (6.10). ^{1}H NMR (400.13 MHz; 300 K; C_6D_6): δ (ppm) 0.63 (d, *J* = 6.9 Hz, 4H, *CH*$_2$CHMe$_2$); 1.10 (18H, I*t*Bu C*(CH*$_3$*)*$_2$); 1.42 (d, *J* = 6.52 Hz, 12H, CH$_2$CH*(CH*$_3$*)*$_2$); 2.48 (sept, *J* = 6.59 Hz, 2H, CH$_2$*CH*Me$_2$); 6.41 (d, *J* = 1.61 Hz, 2H, N*(H)C=C(H)*N); 6.77 (t of t, *J* = 7.25, 1.05 Hz, 2H aromatic *p*-CH); 7.01 (d of d, *J* = 8.63, 1.10 Hz, 4H, aromatic *o*-CH); 7.20 – 7.27 (m, 4H, aromatic *m*-CH); 9.47 (s, 1H, N*C(H)*N). ^{13}C{^{1}H} NMR (100.59 MHz; 300 K; C_6D_6): δ (ppm) 25.0 (*CH*$_2$CHMe$_2$); 27.6 (CH$_2$*CH*Me$_2$); 29.5 (I*t*Bu C(*CH*$_3$)$_3$); 29.5 (CH$_2$CH*(CH*$_3$*)*$_2$); 60.4 (*C*Me$_3$); 116.4 (*para CH* aromatics); 119.7 (N*C(H)=C(H)*N); 120.6 (*meta CH* aromatics); 129.5 (*ortho CH* aromatics); 132.7 (N*C(H)*N); 163.2 (*ipso* aromatics).

Synthesis of 6

To a solution of PhOH (0.376 g; 4 mmol) in hexane (10 mL) was added I*t*Bu (0.18 g; 1 mmol) via a solid addition tube, resulting in a cloudy solution. *i*Bu$_2$Al(TMP) (0.28 g; 1 mmol) in hexane (2 mL) was then added and the reaction mixture stirred for four hours. The volatiles were removed *in vacuo* and the residues were dissolved in THF (5 mL) and hexane (1 mL) was added as anti-solvent. Cooling to –15 °C produced a crop of crystals suitable for X-ray diffraction (0.28 g; 0.51 mmol, 51 % yield). Elemental analysis (%) calculated for $AlN_2C_{33}H_{45}O_3$ (found): C, 72.76 (72.39); H, 8.33 (7.80); N, 5.14 (5.36). ^{1}H NMR (400.13 MHz; 300 K; C_6D_6): δ (ppm) 0.65 (d, *J* = 6.91 Hz, 2H, *CH*$_2$CH(Me)$_2$); 1.06 (s, 18H, I*t*Bu C(*CH*$_3$)$_3$); 1.34 (d, *J* = 6.53 Hz, 6H, CH$_2$CH*(CH*$_3$*)*$_2$); 2.42 (sept, *J* = 6.54 Hz, 1H, CH$_2$*CH*(CH$_3$)$_2$); 6.60 (d, *J* = 1.74 Hz, 2H, N*C(H)=C(H)*N); 6.77 (t of t, *J* = 7.05, 1.28 Hz, 3H, *para CH* aromatics); 7.12 – 7.24 (m, 12H, *ortho CH* aromatics and *meta CH* aromatics); 9.03 (s, 1H, N*C(H)*N). ^{13}C{^{1}H} NMR (100.59 MHz; 300 K; C_6D_6): δ (ppm) 20.9 (*CH*$_2$CH(Me)$_2$); 27.1 (CH$_2$*CH*(Me)$_2$); 29.1 (CH$_2$CH*(CH*$_3$*)*$_2$); 29.4 (I*t*Bu C*(CH*$_3$*)*$_3$); 60.3 (*C*Me$_3$); 117.1 (*para CH* aromatics); 120.0 (N*C(H)=C(H)*N); 120.6 (*meta CH* aromatics); 129.6 (*ortho CH* aromatics); 132.4 (N*C(H)*N); 162.3 (*ipso* aromatics).

Synthesis of 7

To a solution of I*t*Bu (0.09 g; 0.5 mmol) in hexane (5 mL) was added benzonitrile (0.05 mL; 0.5 mmol) followed by dropwise addition of *i*Bu$_2$Al(TMP) (0.14 g; 0.5 mmol) in hexane (5 mL), resulting in a bright orange solution, with a small amount of dark orange oil observed after several minutes. The reaction mixture was stirred at room temperature for four hours before standing the solution at room temperature. A small crop of yellow crystals suitable for X-ray diffraction analysis were obtained.
Elemental analysis (%) calculated for $Al_2N_5C_{50}H_{83}$ (found): C, 74.31 (73.85); H, 10.35 (10.42); N 8.67 (8.79). The NMR spectra were highly complicated due to the asymmetric nature of the complex which resulted in overlapping resonances (see SI for ^{1}H Spectrum in d_8-THF).

Synthesis of 8

iBu_2Al(TMP) (0.28 g; 1.0 mmol) was dissolved in a mixture of hexane (10 mL) and benzonitrile (0.10 mL, 1.0 mmol) and was stirred for 5 hours. Removing the solvent *in vacuo* to approximately 3 mL and cooling the mixture to –30°C resulted in a small crop of crystals which were suitable for X-ray diffraction.
Elemental analysis (%) calculated for $AlN_2C_{24}H_{41}$ (found): C, 74.95 (73.81); H, 10.75 (10.80); N 7.28 (7.54). After repeated attempts to obtain the molecular structure there was not enough material remaining to obtain clear NMR spectra.

Synthesis of 8'
8' was obtained *in situ* in an NMR scale reaction by combining *i*Bu_2Al(TMP) and PhCN in C_6D_6. The solution immediately turned yellow upon addition of the nitrile.
^{1}H NMR (400.13 MHz; 300 K; C_6D_6): δ(ppm) 0.45 (d, *J* = 6.96 Hz, 4H, C*H*$_2$CH(CH$_3$)$_2$); 1.24 (d, *J* = 6.52 Hz, 12H, CH$_2$CH(C*H*$_3$)$_2$); 1.37 – 1.42 (m, 16H, TMP C*H*$_3$ and TMP β C*H*$_2$); 1.72 (m, 2H, TMP γC*H*$_2$); 2.18 (sept, *J* = 6.73 Hz, 2H, CH$_2$C*H*(CH$_3$)$_2$); 6.62 (t, *J* = 8.06 Hz, 2H, meta); 6.85 (t of t, *J* = 7.83 Hz, 1.24 Hz, 1H, para); 6.91 (d of d, *J* = 8.18 Hz, 1.33 Hz, 2H, ortho). ^{13}C{^{1}H} NMR (100.59 MHz; 300 K; C_6D_6): δ (ppm) 19.3 (TMP γ*CH*$_2$); 27.0 (CH$_2$*CH*(Me)$_2$); 28.8 (CH$_2$CH(*CH*$_3$)$_2$); 29.4 (*CH*$_2$CH(Me)$_2$); 33.7 (TMP Me); 41.5 (TMP β*CH*$_2$); 51.5 (TMP *C*(CH$_3$)$_2$); 108.5 (*ipso* aromatics); 119.2 (C≡N); 129.3 (*meta CH* aromatics); 132.5 (*ortho CH* aromatics); 134.5 (*para CH* aromatics).
As this was an in situ generated complex, no elemental analyses could be obtained.

Synthesis of 9

To a hexane (10 mL) solution of I*t*Bu (0.09 g; 0.50 mmol) was added diphenylacetonitrile (0.0965 g; 0.50 mmol) via a solid addition tube. This resulted in the immediate formation of a yellow precipitate. The reaction mixture was stirred for 10 minutes at room temperature before the yellow product was isolated by cannula filtration and washed with hexane (10 mL) before drying under vacuum (0.15 g; 0.4 mmol; 80 %). IR (nujol mull) ν (cm^{-1}): 2095 (s, N=C=C). We were unable to resolve any NMR spectra due to poor solubility in C_6D_6 and d_8-THF. Accurate elemental analyses could not be obtained.

Table 5 Selected crystallographic and refinement parameters

	1	**2**	**3**	**5**	**6**	**7**	**8**	**9**
Empirical formula	$C_{56}H_{112}N_6Al_2$	$AlLiO_2N_3C_{36}H_{71}$	$C_{44}H_{87}N_3O_4AlNa$	$C_{31}H_{49}O_2AlN_2$	$AlO_3N_2C_{33}H_{45}$	$C_{50}H_{83}Al_2N_5$	$Al_2N_4C_{48}H_{82}$	$C_{25}H_{31}N_3$
MW	923.47	611.87	772.13	508.70	544.69	808.17	769.13	373.53
Crystal system	Monoclinic	Triclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Orthorhombic
Space group	$P2_1$	P-1	$P2_1/n$	$P2_1/c$	$P2_1/c$	$P2_1/n$	$P2_1/n$	$P2_12_12_1$
a (Å)	11.8071(3)	11.8254(6)	10.8449(4)	9.8552(2)	9.6331(2)	15.9841(3)	13.8279(1)	9.9880(1)
b (Å)	24.6090(5)	12.2430(10)	16.9971(5)	18.0293(4)	27.9912(9)	14.0947(2)	15.2466(1)	10.4853(1)
c (Å)	11.8438(3)	14.5841(12)	26.5461(10)	17.2490(5)	11.5818(3)	22.2157(3)	22.5193(1)	20.5268(1)
α (°)	90	75.140(7)	90	90	90	90	90	90
β (°)	119.786(3)	79.893(6)	100.225(3)	90.594(2)	93.394(2)	99.809(2)	99.134(1)	90
γ (°)	90	75.019(6)	90	90	90	90	90	90
V ($Å^3$)	2986.70(15)	1958.0(3)	4815.6(3)	3064.7(3)	3117.46(15)	4931.83(14)	4687.51(5)	2149.71(4)
Z	2	2	4	4	4	4	4	4
λ (Å)	1.54184	0.71073	0.71073	0.71073	0.71073	1.54184	1.54184	1.54184
μ (mm^{-1})	0.709	0.083	0.091	0.094	0.099	0.799	0.811	0.519
Reflns. collected	17434	17526	74593	30325	25561	32993	73626	34945
Unique Reflns.	9298	10123	12710	8343	8368	9284	9330	4280
R_{int}	0.0366	0.0230	0.0508	0.0304	0.0328	0.0379	0.0403	0.0439

GooF	1.041	1.021	1.025	1.029	1.096	1.021	1.035	1.066
R[I>2σ(I)]	0.0520	0.0475	0.0577	0.0524	0.0652	0.0568	0.0421	0.0373
ωR2	0.1292	0.1174	0.1322	0.1311	0.1437	0.1563	0.1157	0.0978
CCDC	2093802	2093803	2093804	2093805	2093806	2093807	2093808	2093809

Appendix A Supplementary data

CCDC 2093802-2093809 contains the supplementary crystallographic data for complexes **1**-**9**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK; fax (+44) 1223-336-033; or email: deposit@ccdc.cam.ac.uk.

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