

Synthesis and structures of neutral and cationic 1-azaallyl-aluminium methyls†

Laurence Bourget, Peter B. Hitchcock and Michael F. Lappert*

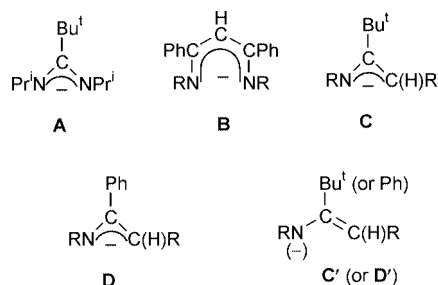
The Chemistry Laboratory, University of Sussex, Brighton UK BN1 9QJ.

E-mail: m.f.lappert@sussex.ac.uk

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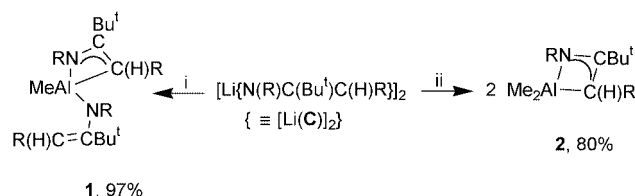
The 1-azaallylaluminium compounds $[\text{Al}\{\text{N}(\text{R})\text{C}(\text{Bu}^t)\text{C}(\text{H})\text{R}\}\{\text{N}(\text{R})\text{C}(\text{Bu}^t)=\text{C}(\text{H})\text{R}\}\text{Me}]$ (X-ray characterised), $\text{Al}\{\text{N}(\text{R})\text{C}(\text{Bu}^t)\text{C}(\text{H})\text{R}\}\text{Me}_2$, $\text{Al}\{\text{N}(\text{R})\text{C}(\text{Ph})=\text{C}(\text{H})\text{R}\}\text{Me}_2$ **3** and $\text{Al}\{\text{N}(\text{R})\text{C}(\text{Ph})=\text{C}(\text{H})\text{R}\}_2\text{Me}(\text{thf})$ were obtained from the appropriate methylaluminium chloride and 1-azaallyl-lithium; **3** with $\text{B}(\text{C}_6\text{F}_5)_3$ gave $[\text{Al}\{\text{N}(\text{R})\text{C}(\text{Ph})=\text{C}(\text{H})\text{R}\}-\text{Me}(\text{thf})(\text{OEt}_2)][\text{BMe}(\text{C}_6\text{F}_5)_3]$ ($\text{R} = \text{SiMe}_3$).

There is much current interest in bi- and tri-dentate nitrogen-centred spectator ligands, which often are a component of electrophilic neutral or cationic metal alkyls.¹ Aluminium complexes have become prominent, following the disclosure of Coles and Jordan that certain cationic amidinatoaluminium methyls, such as $[\text{Al}(\text{LL})\text{Me}][\text{B}(\text{C}_6\text{F}_5)_4]$ ($\text{LL} = \text{A}$), are active catalysts for the polymerisation of ethylene.² We recently described the synthesis and X-ray molecular structures of a series of neutral and cationic β -diketiminatoaluminium methyls $[\text{Al}(\text{LL})\text{Me}_2]$, $[\text{Al}(\text{LL})\text{Me}(\text{thf})][\text{BMe}(\text{C}_6\text{F}_5)_3] \cdot 0.5 \text{ thf}$ and $[\text{Al}(\text{LL})\text{Me}(\text{OEt}_2)][\text{B}(\text{C}_6\text{F}_5)_4] \cdot 0.5 \text{ Et}_2\text{O}$ ($\text{LL} = \text{B}$, $\text{R} = \text{SiMe}_3$), the latter two being the first crystallographically characterised cationic aluminium methyls.¹ The salt $[\text{Al}\{\text{N}(\text{Ar})\text{C}(\text{Me})\text{C}(\text{H})\text{C}(\text{Me})\text{N}(\text{Ar})\}\text{Bu}^t][\text{B}(\text{C}_6\text{F}_5)_4]$ has been mentioned ($\text{Ar} = \text{C}_6\text{H}_3\text{Pr}^t_2-2,6$).³ Molecular orbital calculations on $\text{Al}-\text{L}$ complexes ($\text{L} = \text{C}_6\text{H}_6$, $\text{C}_4\text{H}_4\text{O}$, C_5H_6 or $\text{C}_4\text{H}_4\text{NH}$) have been carried out.⁴ We now report on aluminium methyls containing the 1-azaallyl ligands C^5 and D^6 (or their tautomers C' and D'), which are skeletally isoelectronic with amidinates such as **A**.

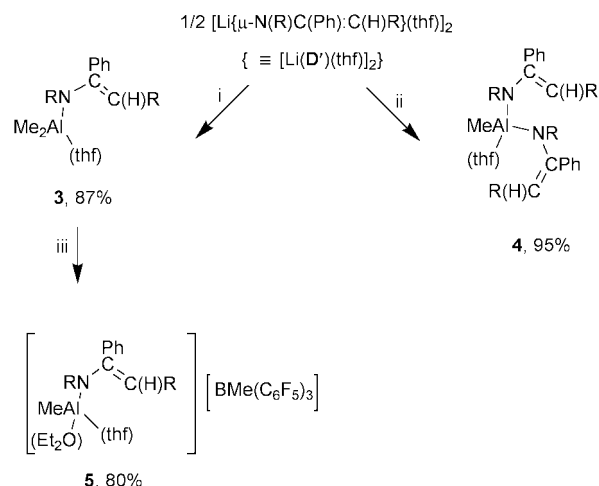


Treatment of the appropriate methylaluminium chloride with $[\text{Li}(\text{C})]_2$ ⁵ or $[\text{Li}(\text{D}')](\text{thf})_2$ ⁶ in the correct stoichiometry in hexane at low temperature afforded in high yield the 1-azaallylaluminium methyls **1**† and **2** (Scheme 1) or **3** and **4**† (i and ii in Scheme 2). From **3** and tris(pentafluorophenyl)borane, under the same conditions, the salt **5** was obtained (iii in Scheme 2), containing a 1-azaallyl(methyl)aluminium cation.

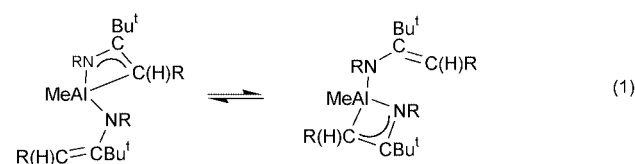
The pale yellow, crystalline complex **1** gave a satisfactory EI (70 eV) mass spectrum; the highest m/z peak corresponded to M^+ (4%), followed by $[M - \text{Me}]^+$ (44%). The multinuclear NMR spectra in toluene- d_8 showed (Table 1) that (i) the solution structure corresponded to that in the crystal (Fig. 1); (ii) the two 1-azaallyl ligands were tautomers $[\text{Al}(\text{C})(\text{C}')\text{Me}]$; (iii)



Scheme 1 Synthesis of the 1-azaallylaluminium methyls $[\text{Al}(\text{C})(\text{C}')\text{Me}]$ **1** and $\text{Al}(\text{C})\text{Me}_2$ **2**. Reagents and conditions: i) 1/2 $(\text{AlMeCl}_2)_2$, C_6H_{14} , -78°C ; ii) $(\text{AlMe}_2\text{Cl})_2$, C_6H_{14} , -78°C .



Scheme 2 Synthesis of the 1-azaallylaluminium methyls $\text{Al}(\text{D}')\text{Me}_2(\text{thf})$ **3**, $\text{Al}(\text{D}')_2\text{Me}(\text{thf})$ **4** and $[\text{Al}(\text{D}')\text{Me}(\text{thf})(\text{OEt}_2)][\text{BMe}(\text{C}_6\text{F}_5)_3]$ **5**. Reagents and conditions: i) 1/2 $(\text{AlMe}_2\text{Cl})_2$, C_6H_{14} , -78°C ; ii) 1/2 $(\text{AlMe}_2\text{Cl})_2$, C_6H_{14} , -78°C ; iii) $\text{B}(\text{C}_6\text{F}_5)_3$, C_6H_{14} , -78°C , then Et_2O .



the ligands **C** and **C'** exchanged rapidly on the NMR time scale, eqn. (1); and (iv) the ^1H NMR spectral coalescence temperature at $T_c = 302 \text{ K}$ [based on the $\text{C}(\text{CH}_3)$ signal at $\delta = 0.99$ at 302 K], corresponding to $\Delta G^\ddagger_{302 \text{ K}} = 60.7 \text{ kJ mol}^{-1}$.

The molecular structure of the crystalline complex **1** is illustrated in Fig. 1.† The aluminium atom is almost trigonally disposed with respect to the atoms C(25), C(2) and N(2) (the sum of the angles subtended by these atoms at $\text{Al} = 349.3^\circ$), the bond to N(1) completing the trigonal monopyramidal geometry about the four-coordinate metal atom. The two 1-azaallyl ligands differ in that one is of type **C** and the other **C'**. Thus, (i) the $\text{Al}-\text{N}(1)$ bond of $1.998(2) \text{ \AA}$ is only slightly longer than the average $\text{Al}-\text{N}$ bond length of $1.928(3) \text{ \AA}$ in the three-coordinate aluminium β -diketimate $[\text{Al}\{\text{N}(\text{R})\text{C}(\text{Ph})\text{C}(\text{H})\text{C}(\text{Ph})\text{N}(\text{R})\}-$

† No reprints available.

Table 1 Selected NMR spectroscopic chemical shifts (δ) and assignments

$\text{Me}_3\text{SiNC}_a(\text{Bu}^t \text{ or Ph})\text{C}_b(\text{H})\text{Si}_c\text{Me}_3$					
Compound (Ligand)	Assignment				T (K)/solvent
	C_a	C_b	H	$^{29}\text{Si}_c$	
1 { (Enamide) { $(\eta^3\text{-1-Azaallyl})$ }	174.0 221.0	116.4 45.2	4.78 2.09	−15.1 −1.6	203/ C_7D_8
2 (1-Azaallyl)	216.1	49.6	2.47	−1.0	333/ C_6D_6
3 (Enamide)	165.8	111.3	5.08	−11.7	298/ C_6D_6
4 (Enamide)	165.5	114.4	5.07	−11.6 ^a	333/ C_6D_6
5 (Enamide)	160.3	116.2	5.04	−10.3	298/ C_6D_6

^a At 298 K.

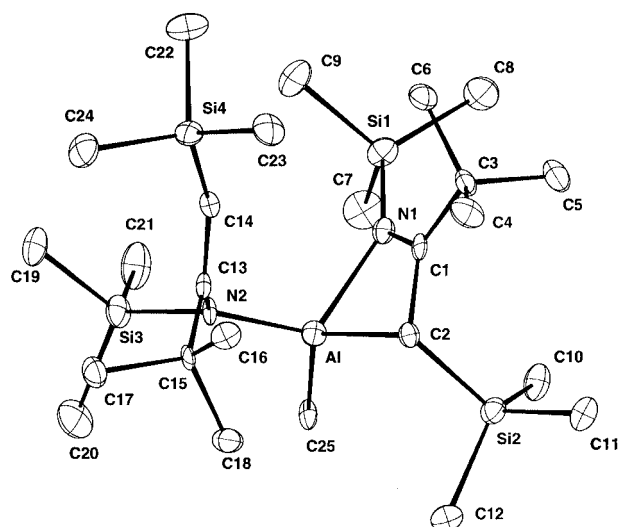


Fig. 1 Molecular structure of **1** with selected bond distances (Å) and angles (°): Al–N(1) 1.998(2), Al...C(1) 2.380(2), Al–C(2) 2.022(2), Al–C(25) 1.990(2), Al–N(2) 1.839(2), C(1)–C(2) 1.468(3), N(1)–C(1) 1.320(3), N(2)–C(13) 1.445(3), C(13)–C(14) 1.347(3) Å; N(1)–Al–C(2) 70.1(1), C(2)–Al–C(25) 122.1(1), C(25)–Al–N(2) 111.1(1), N(2)–Al–N(1) 112.5(1), N(1)–Al–C(25) 119.1(1), N(2)–Al–C(2) 116.1(1)°.

Me_2] **6**,¹ whereas the Al–N(2) bond of 1.839(2) Å is appreciably shorter; (ii) the Al–C(2) bond of 2.022(2) Å is only marginally shorter than the Al–C(25) bond of 1.990(2) Å, or the average Al–C bond length of 1.964(3) Å in **6**,¹ and is much shorter than the Al...C(13) distance of 2.816(2) Å; and (iii) the C(1)–C(2) bond of 1.468(3) Å is significantly longer than the C(13)–C(14) of 1.347(3) Å. The presence in a single crystalline molecule of two tautomeric 1-azaallyl ligands such as **C** and **C'** has previously been observed in $[\text{Sn}\{\text{N}(\text{R})\text{C}(\text{Ph})\text{C}(\text{H})\text{CR}_2\}\{\text{N}(\text{R})\text{C}(\text{Ph})=\text{CR}_2\}]$ **7**, in which the Sn–N and C(Ph)–CR₂ bond lengths were 2.288(4) and 2.153(4) and 1.461(6) and 1.365(3) Å, respectively.⁷ Moreover, the two ligands of **7** underwent rapid intramolecular exchange in toluene-*d*₈ down to −90 °C.

The assignment of structures for the complexes **2–5** rests at present on their multinuclear NMR spectra, as indicated for the 1-azaallyl ligands **C**, **C'**, **D** and **D'** in Table 1. The presence of an equivalent of thf in each of the complexes **3–5** and also of Et₂O in **5** is consistent with their ¹H NMR spectra. The ionic character of the salt **5** is borne out by the ¹¹B{¹H} NMR spectrum, $\delta = -14.6$ ($w_{1/2} = 90$ Hz), *cf.*, $\delta = -16.7$ for $[\text{Al}\{\text{N}(\text{R})\text{C}(\text{Ph})\text{C}(\text{H})\text{C}(\text{Ph})\text{N}(\text{R})\}\text{Me}(\text{thf})][\text{BMe}(\text{C}_6\text{F}_5)_3]$.¹ The

²⁷Al{¹H} NMR spectral signals for each of the complexes **1–5** was broad but distinct: δ 125 (**1**, 1.2), 141 (**2**, 2.4), 155 (**3**, 2.4), 128 (**4**, 3.8) and 167 (**5**, 4.0) (the second number in each bracket refers to $w_{1/2}$ in kHz). The difference in structures between the monomethylaluminium bis(azaallyls) **1** (**C**, **C'**) and **4** (**D'**), is attributed to the β -carbon substituent (Bu^t or Ph) rather than the influence for **4** of thf, since structure **1** was also found when **1** was prepared in thf. The bis(enamido)aluminium structure for **4** may have been preferred because of the conjugative effect.

Compounds related to the 1-azaallyls of aluminium, the 2-pyridylmethyls $[\text{Al}\{\text{C}(\text{R})_2(\text{C}_5\text{H}_4\text{N}-2)\}_2][\text{AlCl}_4]$ and $[\text{Al}\{\text{C}(\text{R})_2(\text{C}_5\text{H}_3\text{Me}-6)-2\}_n\text{Cl}_{3-n}]$ ($n = 1$ or 2) are known.⁸ The present results, together with those by Roesky and co-workers on the recently prepared neutral aluminium compounds containing the ligand $[\text{C}(\text{R})_2\text{C}(\text{Ph})\text{NR}]^-$,⁹ demonstrate the versatility of 1-azaallyl ligands in aluminium chemistry, which is now being explored more extensively.

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Notes and references

† *Synthesis of 1 and 4.* Methylaluminium dichloride (1.7 cm³ of a 1 mol dm^{−3} solution in hexanes, 1.7 mmol) was added dropwise to a solution of $[\text{Li}(\text{C})_2]$ (0.86 g, 1.72 mmol) in hexane (60 cm³) at −78 °C. The mixture was stirred for 12 h at ambient temperature, then filtered. Upon concentration and cooling at 4 °C, pale yellow crystals of **1** (0.87 g, 97%), mp 95–98 °C were obtained (Found: C, 56.6; H, 10.9; N, 5.40. $\text{C}_{25}\text{H}_{59}\text{AlN}_2\text{Si}_4$ requires C, 57.0; H, 11.2; N, 5.31%). In a similar fashion, from AlMeCl_2 (2.4 cm³ of a 1 mol dm^{−3} solution in hexanes, 2.4 mmol) and $[\text{Li}(\text{D}')(\text{thf})]_2$ (1.64 g, 2.4 mmol), there was obtained the pale orange solid **4** (1.4 g, 95%), mp 80–85 °C (Found: C, 59.4; H, 9.20; N, 4.46. $\text{C}_{33}\text{H}_{59}\text{AlN}_2\text{Si}_4$ requires C, 62.0; H, 9.25; N, 4.39%).

§ *Crystallographic data for 1:* $\text{C}_{25}\text{H}_{59}\text{AlN}_2\text{Si}_4$, $M = 527.19$, monoclinic, space group $P2_1/n$, $a = 11.360(4)$, $b = 20.099(5)$, $c = 15.366(8)$ Å, $\beta = 101.96(4)^\circ$, $U = 3432(2)$ Å³, $Z = 4$, $\lambda(\text{Mo-K}\alpha) = 0.71073$ Å, $\mu = 0.21$ mm^{−1}. Data were collected at 173(2) K on an Enraf Nonius CAD4 diffractometer in the $\omega - 2\theta$ mode for the range of $2 < \theta < 25^\circ$. The structure was solved by direct methods (SHELXS-97) and refined with full-matrix, least-squares on all F^2 (SHELXL-97).¹⁰ All non-hydrogen atoms were anisotropic, and hydrogen atoms were included in the riding mode with $U_{\text{iso}}(\text{H}) = 1.2 U_{\text{eq}}(\text{C})$ or $1.5 U_{\text{eq}}$ for Me groups. Final residual for 6033 independent reflections was $R_1 = 0.066$, $wR_2 = 0.110$ and for the 4592 with $I > 2\sigma(I)$, $R_1 = 0.043$, $wR_2 = 0.098$. CCDC reference number 186/1547. See <http://www.rsc.org/suppdata/dt/1999/2645/> for crystallographic files in .cif format.

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