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Synthesis and structures of neutral and cationic 1-azaallylaluminium methyls†

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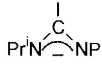
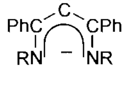
The 1-azaallylaluminium compounds [Al{N(R)C(Bu^t)C-(H)R}{N(R)C(Bu^t)=C(H)R}Me] (X-ray characterised), Al{N(R)C(Bu^t)C(H)R}Me_2, Al{N(R)C(Ph)=C(H)R}Me_2 3 and Al{N(R)C(Ph)=C(H)R}$_2$Me(thf) were obtained from the appropriate methylaluminium chloride and 1-azaallyllithium; 3 with $B(C_6F_5)_3$ gave [Al{N(R)C(Ph)=C(H)R}-Me(thf)(OEt_2)][BMe$(C_6F_5)_3$] (R = $SiMe_3$).

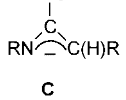
There is much current interest in bi- and tri-dentate nitrogen-centred spectator ligands, which often are a component of electrophilic neutral or cationic metal alkyls.[1] Aluminium complexes have become prominent, following the disclosure of Coles and Jordan that certain cationic amidinatoaluminium methyls, such as [Al(LL)Me][$B(C_6F_5)_4$] (LL = **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 [Al(LL)Me_2], [Al(LL)Me(thf)][BMe$(C_6F_5)_3$]·0.5 thf and [Al(LL)Me(OEt_2)]-[$B(C_6F_5)_4$]·0.5 Et_2O (LL = **B**, R = $SiMe_3$), the latter two being the first crystallographically characterised cationic aluminium methyls.[1] The salt [Al{N(Ar)C(Me)C(H)C(Me)N(Ar)}Bu^t]-[$B(C_6F_5)_4$] has been mentioned (Ar = $C_6H_3Pr^i_2$-2,6).[3] Molecular orbital calculations on Al^+–L complexes (L = C_6H_6, C_4H_4O, C_5H_6 or C_4H_4NH) 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**.



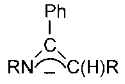
A



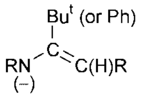
B



C



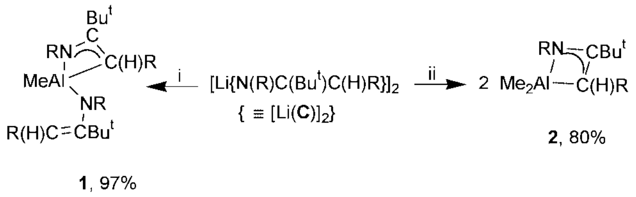
D



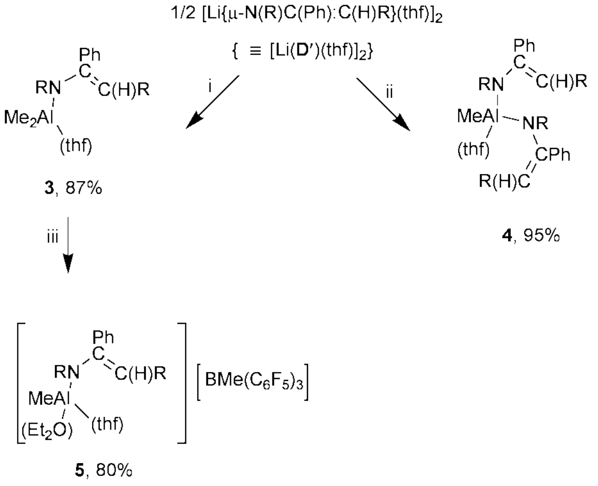
C′ (or **D′**)

Treatment of the appropriate methylaluminium chloride with [Li(**C**)]$_2$[5] or [Li(**D′**)(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.

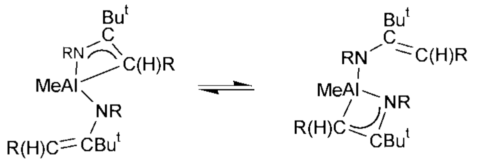
The pale yellow, crystalline complex **1** gave a satisfactory EI (70 eV) mass spectrum; the highest *m*/*z* peak corresponded to M^+ (4%), followed by $[M - \mathrm{Me}]^+$ (44%).The multinuclear NMR spectra in toluene-d_8 showed (Table 1) that (i) the solution structure corresponded to that in the crystal (Fig. 1); (ii) the two 1-azaallyl ligands were tautomers [Al(**C**)(**C′**)Me]; (iii) the ligands **C** and **C′** exchanged rapidly on the NMR time scale, eqn. (1); and (iv) the ^1H NMR spectral coalescence temperature at $T_c = 302$ K [based on the $C(CH_3)$ signal at $\delta = 0.99$ at 302 K], corresponding to $\Delta G^{\ddagger}_{302\,\mathrm{K}} = 60.7$ kJ mol^{-1}.



Scheme 1 Synthesis of the 1-azaallylaluminium methyls [Al(**C**)-(**C′**)Me] **1** and Al(**C**)Me_2 **2**. *Reagents and conditions*: i 1/2 $(AlMeCl_2)_2$, C_6H_{14}, −78 °C; ii $(AlMe_2Cl)_2$, C_6H_{14}, −78 °C.



Scheme 2 Synthesis of the 1-azaallylaluminium methyls Al(**D′**)-Me_2(thf) **3**, Al(**D′**)$_2$Me(thf) **4** and [Al(**D′**)Me(thf)(OEt_2)][BMe-$(C_6F_5)_3$] **5**. *Reagents and conditions*: i 1/2 $(AlMe_2Cl)_2$, C_6H_{14}, −78 °C; ii 1/2 $(AlMeCl_2)_2$, C_6H_{14}, −78 °C; iii $B(C_6F_5)_3$, C_6H_{14}, −78 °C, then Et_2O.



(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 Al = 349.3°), 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 Al–N(1) bond of 1.998(2) Å is only slightly longer than the average Al–N bond length of 1.928(3) Å in the three-coordinate aluminium β-diketiminate [Al{N(R)C(Ph)C(H)C(Ph)N(R)}-

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† No reprints available.

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

$Me_3SiNC_a(Bu^t$ or $Ph)C_b(H)Si_cMe_3$

Compound (Ligand)	Assignment C_a	C_b	H	$^{29}Si_c$	T (K)/ solvent
1 (Enamide)	174.0	116.4	4.78	−15.1	203/C_7D_8
1 (η^3-1-Azaallyl)	221.0	45.2	2.09	−1.6	
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.

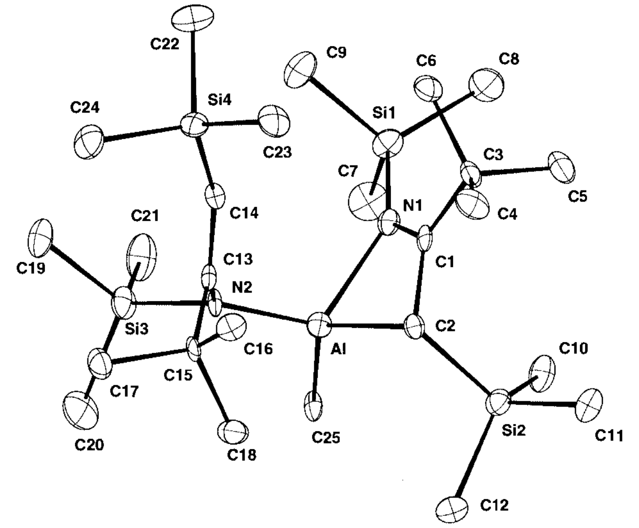

Fig. 1 Molecular structure of **1** with selected bond distances (Å) and angles (°): Al–N(1) 1.998(2), Al···C(1) 2.380(2), Al–C(2) 2.022(2), Al–C(25) 1.990(2), Al–N(2) 1.839(2), C(1)–C(2) 1.468(3), N(1)–C(1) 1.320(3), N(2)–C(13) 1.445(3), C(13)–C(14) 1.347(3) Å; N(1)–Al–C(2) 70.1(1), C(2)–Al–C(25) 122.1(1), 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 $[\overline{Sn\{N(R)C(Ph)C(H)C}R_2\}\{N(R)C(Ph){=}CR_2\}]$ **7**, in which the Sn–N and C(Ph)-CR_2 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 Et_2O in **5** is consistent with their ^1H NMR spectra. The ionic character of the salt **5** is borne out by the $^{11}B\{^1H\}$ NMR spectrum, $\delta = -14.6$ ($w_{1/2} = 90$ Hz), *cf.*, $\delta = -16.7$ for $[\overline{Al\{N(R)C(Ph)C(H)C(Ph)N}(R)\}Me(thf)][BMe(C_6F_5)_3]$.[1] The $^{27}Al\{^1H\}$ 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** ($\mathbf{D'}_2$), 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 $[\overline{Al\{C(R)_2(C_5H_4N}\text{-}2)\}_2][AlCl_4]$ and $[Al\{C(R)_2(C_5H_3Me\text{-}6)\text{-}2)\}_nCl_{3-n}]$ ($n = 1$ 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 $[C(R)_2C(Ph)NR]^-$,[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 cm^3 of a 1 mol dm^{-3} solution in hexanes, 1.7 mmol) was added dropwise to a solution of $[Li(\mathbf{C})]_2$ (0.86 g, 1.72 mmol) in hexane (60 cm^3) 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. $C_{25}H_{59}AlN_2Si_4$ requires C, 57.0; H, 11.2; N, 5.31%). In a similar fashion, from $AlMeCl_2$ (2.4 cm^3 of a 1 mol dm^{-3} solution in hexanes, 2.4 mmol) and $[Li(\mathbf{D'})(thf)]_2$ (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. $C_{33}H_{59}AlN_2Si_4$ requires C, 62.0; H, 9.25; N, 4.39%).

§ *Crystallographic data* for **1**: $C_{25}H_{59}AlN_2Si_4$, $M = 527.19$, monoclinic, space group $P2_1/n$, $a = 11.360(4)$, $b = 20.099(5)$, $c = 15.366(8)$ Å, $\beta = 101.96(4)°$, $U = 3432(2)$ Å^3, $Z = 4$, λ(Mo-Kα) = 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 $2 < \theta < 25°$. 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 $U_{iso}(H) = 1.2\ U_{eq}(C)$ or 1.5 U_{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.

1 F. Coslédan, P. B. Hitchcock and M. F. Lappert, *Chem. Commun.*, 1999, 705.
2 M. P. Coles and R. F. Jordan, *J. Am. Chem. Soc.*, 1997, **119**, 8125.
3 C. E. Radzewich, M. P. Coles and R. F. Jordan, *J. Am. Chem. Soc.*, 1998, **120**, 9384.
4 D. Stöckigt, *J. Am. Chem. Soc.*, 1999, **18**, 1050.
5 P. B. Hitchcock, M. F. Lappert and D.-S. Liu, *J. Chem. Soc., Chem. Commun.*, 1994, 2637.
6 R. Sablong, unpublished work; for the tmen complex, see P. B. Hitchcock, M. F. Lappert and M. Layh, *Chem. Commun.*, 1998, 201.
7 J. Hu, P. B. Hitchcock, M. F. Lappert, M. Layh and J. R. Severn, *Chem. Commun.*, 1997, 1189.
8 T. R. van den Ancker and C. L. Raston, *J. Organomet. Chem.*, 1995, **500**, 289.
9 C. Cui, H. W. Roesky, M. Noltemeyer, M. F. Lappert, H.-G. Schmidt and H. Hao, *Organometallics*, 1999, **18**, 2256.
10 G. M. Sheldrick, SHELXS-97 and SHELXL-97, Programs for crystal structure solution and refinement, University of Göttingen, 1997.

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