Synthesis and structures of neutral and cationic β-diketiminatoaluminium methyls†

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Trimethylaluminium with the β-diketimine H(LL) yields the aluminium complex $[\text{Al(LL)Me}_2]$, from which the salts $[\text{Al(LL)Me(thf)}][\text{BMe(C}_6\text{F}_5)_3]\cdot0.5\text{thf}$ and $[\text{Al(LL)Me(OEt}_2)][\text{B(C}_6\text{F}_5)_4]\cdot0.5\text{Et}_2\text{O}$ have been prepared, and crystallographically characterised.

There is much current interest in bi- or tri-dentate nitrogen-centered spectator ligands, which often are a component of electrophilic metal alkyl catalysts for olefin polymerisation or related reactions. Emphasis has been on Ti^{IV}, Zr^{IV}, Fe^{II}, Co^{II}, Ni^{II} or Pd^{II} complexes.[1] Attention is also now turning to Al compounds, triggered by the disclosure of Coles and Jordan in 1997 that certain cationic amidinatoaluminium methyls **A**–**C** are active catalysts for polymerisation of ethylene [**A** > **B** or **C**; LL = $\text{Bu}^t\text{C(NPr}^i)_2$ in **A** or **B**, but $\text{MeC(NPr}^i)_2$ in **C**];[2] as are compounds **D** (R = H, Ar = $\text{C}_6\text{H}_3\text{Pr}^i{}_2$-2,6 or $\text{C}_6\text{H}_2\text{Me}_3$-2,4,6; or, the least active, R = Me, Ar = $\text{C}_6\text{H}_3\text{Pr}^i{}_2$-2,6)[3] and **E** (LL = **G**),[4] while the X-ray-characterised **F** only showed only trace activity.[4]

$[\text{Al(LL)Me}][\text{B(C}_6\text{F}_5)_4]$

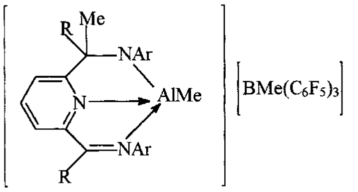
A

$[\{\text{Al(LL)Me}\}_2(\mu\text{-Me})][\text{BMe(C}_6\text{F}_5)_3]$

B

$[^+\text{Al(LL)(Me)}\ldots\text{MeB}^-\text{(C}_6\text{F}_5)_3]$

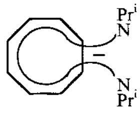
C



D

$[\text{Al(LL)R}][\text{B(C}_6\text{F}_5)_4]$

E (R = Et or Bu^i)



G

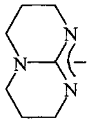
$[\{\text{Al(LL)Me}\}_2(\mu\text{-Me})][\text{B(C}_6\text{F}_5)_4]$

F

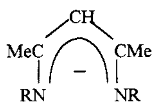
Nitrogen-centered, bidentate, monoanionic, four-electron spectator ligands $[\text{LL}]^-$ which form four-coordinate aluminium dimethyls $[\text{Al(LL)Me}_2]$ are the amidinates [LL = $\text{RC(NR}'\text{)}_2$],[2,5] guanidinates [LL = $\text{R}_2\text{NC(NR}'\text{)}_2$ or **H**],[6] aminotroponimate **G**[4,7] and the β-diketinimates **I**;[8] the thioureido complex $[\text{Al\{N(Ad)C(Me)S\}Me}_2]$ is a close relative (Ad = adamantyl).[9]

Tridentate, monoanionic ligands, such as those in **D**[2] or $[\text{R(H)N(CH}_2)_2\text{N(Me)(CH}_2)_2\text{NR}]$ (R = Me or SiMe_3)[10] have yielded five-coordinate AlMe_2 complexes. The diketiminatoaluminium compounds $[\text{Al(LL)Me}_2]$ (LL = **I**, R = $\text{C}_6\text{H}_4\text{Me}$-4) failed to furnish an isolable cationic complex with $\text{B(C}_6\text{F}_5)_3$.[8] The related compounds $[\text{Al(LL)R}'_2]$ (LL = **I** with R = $\text{C}_6\text{H}_3\text{Pr}^i{}_2$-2,6 and R′ = Et or Bu^i) with $[\text{Ph}_3\text{C}][\text{B(C}_6\text{F}_5)_4]$ and (for R′ = Et) then PhNMe_2 gave $[\text{Al(LL)Et(NMe}_2\text{Ph)}][\text{B(C}_6\text{F}_5)_4]$ or $[\text{Al(LL)Bu}^i][\text{B(C}_6\text{F}_5)_4]$ (structures based on ^{1}H and ^{13}C NMR spectral data).[11]

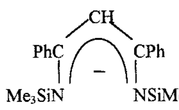
We now report the synthesis and structures of the crystalline β-diketiminatoaluminium compounds $[\text{Al(LL)Me}_2]$ **1**, $[\text{Al(LL)Me(thf)}][\text{BMe(C}_6\text{F}_5)_3]$ **2** and $[\text{Al(LL)Me(OEt}_2)][\text{B(C}_6\text{F}_5)_4]$ **3**, and of some related complexes based on the spectator ligand **J**.[12] Compounds **2** and **3** are the first X-ray-characterised, mononuclear, four-coordinate, cationic aluminium methyls. Preliminary experiments, to be reported in details elsewhere, show that **3** catalyses the conversion of MMA to syndiotactic PMMA of low polydispersity.



H



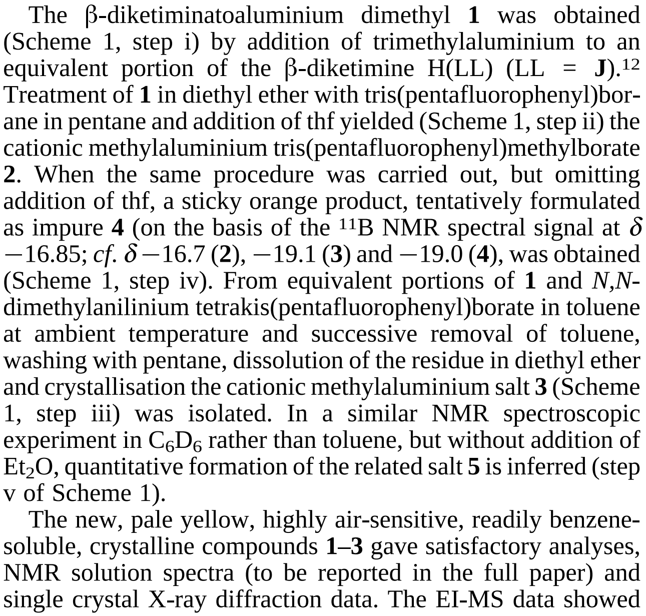
I (R = $\text{C}_6\text{H}_3\text{Pr}^i{}_2$ or $\text{C}_6\text{H}_4\text{Me}$-4)



J

The β-diketiminatoaluminium dimethyl **1** was obtained (Scheme 1, step i) by addition of trimethylaluminium to an equivalent portion of the β-diketimine H(LL) (LL = **J**).[12] Treatment of **1** in diethyl ether with tris(pentafluorophenyl)borane in pentane and addition of thf yielded (Scheme 1, step ii) the cationic methylaluminium tris(pentafluorophenyl)methylborate **2**. When the same procedure was carried out, but omitting addition of thf, a sticky orange product, tentatively formulated as impure **4** (on the basis of the ^{11}B NMR spectral signal at δ −16.85; *cf.* δ −16.7 (**2**), −19.1 (**3**) and −19.0 (**4**), was obtained (Scheme 1, step iv). From equivalent portions of **1** and *N*,*N*-dimethylanilinium tetrakis(pentafluorophenyl)borate in toluene at ambient temperature and successive removal of toluene, washing with pentane, dissolution of the residue in diethyl ether and crystallisation the cationic methylaluminium salt **3** (Scheme 1, step iii) was isolated. In a similar NMR spectroscopic experiment in C_6D_6 rather than toluene, but without addition of Et_2O, quantitative formation of the related salt **5** is inferred (step v of Scheme 1).

The new, pale yellow, highly air-sensitive, readily benzene-soluble, crystalline compounds **1**–**3** gave satisfactory analyses, NMR solution spectra (to be reported in the full paper) and single crystal X-ray diffraction data. The EI-MS data showed the highest *m/z* peak corresponded to $[\text{M} - \text{Me}]^+$ for **1** and $[\text{B(C}_6\text{F}_5)_3]^+$ for **2**.



Scheme 1 Synthesis of neutral and cationic, four-coordinate β-diketiminatoaluminium methyls. *Reagents and conditions*: i, AlMe_3 in C_6H_{14}, C_5H_{12}, −78 °C; ii, $\text{B(C}_6\text{F}_5)_3$ in C_5H_{12}, Et_2O, −78 °C, then thf at 20 °C; iii, $[\text{NHMe}_2\text{Ph}][\text{B(C}_6\text{F}_5)_4]$, PhMe, 20 °C; iv, $[\text{NHMe}_2\text{Ph}][\text{B(C}_6\text{F}_5)_4]$ in C_6D_6.

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† No reprints available.

Table 1 Selected geometric parameters for crystalline β-diketinimatoaluminium methyls

	Property				
Compound	av. Al–C/Å	av. Al–N/Å	C–Al–C′/°	N–Al–N′/°	Deviation (Å) of Al and CH from NC···C′N′ plane
[Al(LL)Me$_2$][8] (LL=**I**, R=$C_6H_3Pr^i_2$-2,6)	1.964(3)	1.928(2)	115.4(2)	96.18(9)	0.33, —
[Al(LL)Me$_2$][8] (LL=**I**, R=C_6H_4Me-4)	1.958(4)	1.906(3)	117.4(1)	94.72(14)	0.72, —
1	1.959(5)	1.921(4)	111.3(2)	97.1(2)	0.95, 0.12
2	1.868(4)	1.941(5)	—	100.8(2)	0.75, 0.13
3	1.872(4)	1.951(5)	—	102.6(2)	0.78, 0.13

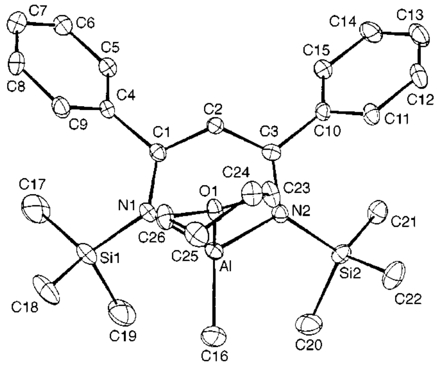

Fig. 1 Molecular structure of **2** with selected bond distances (Å) and angles (°) (see also Table 1). Cation: av. Si–N 1.787(3), Al–O(1) 1.875(3); N(2)–Al–C(16) 123.2(2), N(1)–Al–C(16) 122.9(2), av. N–Al–O 100.0(2), C–Al–O 103.4(2). Anion: B–C(27) 1.635(6), av. B–C(aryl) 1.656(6); C(28)–B–C(34) 104.4(3), C(28)–B–C(40) 112.2(3), C(28)–B–C(27) 114.7(3).

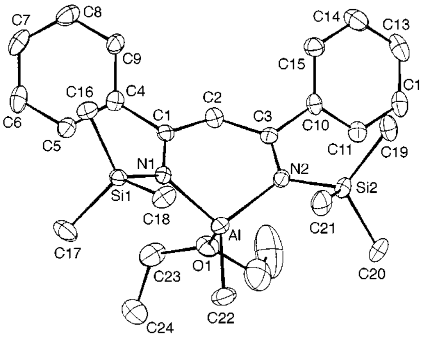

Fig. 2 Molecular structure of **3** with selected bond distances (Å) and angles (°) (see also Table 1). Cation av. Si–N 1.801(4), Al–O(1) 1.887(4); N(2)–Al–C(22) 123.7(2), N(1)–Al–C(22) 122.8(2), av. N–Al–O 101.6(2), C–Al–O 102.3(2). Anion av. B–C 1.653(4); C(27)–B–C(33) 113.5(4), C(27)–B–C(39) 113.8(4), C(27)–B–C(45) 102.4(4).

The molecular geometry of crystalline **1** (details to be published in the full paper) and the two compounds [Al(LL)Me$_2$] (LL = **I**)[8] are closely similar, Table 1. The AlNCCCN fragment in **1** has the boat conformation, as previously found *inter alia* in [Li(LL)]$_2$ and Sn(LL)Me$_3$,[12] although sometimes this β-diketiminatometal moiety is planar, as in [Co(LL)$_2$][13] (LL = **J**).

The molecular structures of the cations of the crystalline salts **2** and **3** are illustrated in Fig. 1 (**2**) and 2 (**3**); the anions will be described in the full paper. The four-coordinate aluminium atom in each cation has a distorted monopyramidal (TMP) geometry, with a similar distortion from tetrahedral to TMP. The Al–C distances are significantly shorter in each cation than in the neutral precursor **1**, but the Al–N bonds are slightly longer due to the widening of the N–Al–N′ angle in **2** or **3** compared with **1**, Table 1. The remaining geometric parameters of the β-diketiminato ligand are very similar in **1–3**. The sum of the angles at each nitrogen atom (of **1–3**) is close to 360°. There is no evidence of significant cation–anion interaction; the anion structures are unexceptional.[14]

The NMR spectra of compounds **1–3** in C_6D_6 (**1** and **3**) or $CDCl_3$ (**2**) indicate that the solution structures of **1–3** are identical to those in the crystal, except that in **1** there is only one ^1H or $^{13}C(^1H)$ signal for the two methyl groups, indicating that they undergo fast exchange.

The present results demonstrate once again [*e.g.*[15] the monomeric [Ce(LL)$_2$Cl] (LL = **J**)] that the β-diketiminato ligand **J** is exceptionally sterically demanding, having allowed us to prepare the well separated ion pairs in **2** and **3**; reactivity and catalytic studies are in hand. This ligand can be fine-tuned by varying the substituents in its skeleton.

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Notes and references

‡ *Crystallographic data* for **1**/**2**/**3**: $C_{23}H_{35}AlN_2Si_2/C_{45}H_{43}AlBF_{15}N_2OSi_2\cdot0.5(C_4H_{10}O)/C_{50}H_{42}AlBF_{20}N_2OSi_2\cdot0.5(C_4H_{10}O)$, M = 422.69/1043.8/1197.9, triclinic for all, space group $P\bar{1}$ for all, a = 6.335(2)/12.016(3)/13.503(5), b = 12.139(3)/13.439(5)/14.557(11), c = 17.103(4)/16.409(7)/15.403(7) Å, α = 78.55(2)/99.44(3)/69.39(5), β = 79.90(3)/91.80(3)/88.02(3), γ = 74.84(3)/108.31(7)/74.04°, U = 1233.6(6)/2472(2)/2718(3) Å^3, Z = 2/2/2, λ(Mo-Kα) = 0.71073 Å, μ = 0.19/0.19/0.19 mm^{-1}. Data were collected at 173(2) K on an Enraf Nonius CAD4 diffractometer in the ω–2θ mode for the range of $2 < \theta < 25°$. Final residuals for 4338/8664/9546 independent reflections were wR_2 = 0.235/0.201/0.214 and for the 3026/5806/6098 with $I > 2\sigma(I)$, R_1 = 0.079/0.053/0.067. CCDC 182/1181. See http://www.rsc.org/suppdata/cc/1999/705/ for crystallographic files in .cif format.

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