## Synthesis and structures of neutral and cationic $\beta$ -diketiminatoaluminium methyls $\dagger$

## Frédéric Coslédan, 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

Received (in Basel, Switzerland) 4th January 1999, Accepted 25th February 1999

There is much current interest in bi- or tri-dentate nitrogencentered spectator ligands, which often are a component of electrophilic metal alkyl catalysts for olefin polymerisation or related reactions. Emphasis has been on Ti<sup>IV</sup>, Zr<sup>IV</sup>, Fe<sup>II</sup>, Co<sup>II</sup>, Ni<sup>II</sup> or Pd<sup>II</sup> complexes.<sup>1</sup> 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 = Bu<sup>t</sup>C(NPr<sup>i</sup>)<sub>2</sub> in **A** or **B**, but MeC(NPr<sup>i</sup>)<sub>2</sub> in **C**];<sup>2</sup> as are compounds **D** (R = H, Ar = C<sub>6</sub>H<sub>3</sub>Pr<sup>i</sup><sub>2</sub>-2,6) or C<sub>6</sub>H<sub>2</sub>Me<sub>3</sub>-2,4,6; or, the least active, R = Me, Ar = C<sub>6</sub>H<sub>3</sub>Pr<sup>i</sup><sub>2</sub>-2,6)<sup>3</sup> and **E** (LL = **G**),<sup>4</sup> while the X-ray-characterised **F** only showed only trace activity.<sup>4</sup>



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

Tridentate, monoanionic ligands, such as those in **D**<sup>2</sup> or  $[R(H)N(CH_2)_2N(Me)(CH_2)_2\overline{N}R]$  (R = Me or SiMe<sub>3</sub>)<sup>10</sup> have yielded five-coordinate AlMe<sub>2</sub> complexes. The diketiminatoaluminium compounds  $[Al(LL)Me_2]$  (LL = **I**, R = C<sub>6</sub>H<sub>4</sub>Me-4) failed to furnish an isolable cationic complex with  $B(C_6F_5)_{3.8}$ The related compounds  $[Al(LL)R'_2]$  (LL = **I** with R = C<sub>6</sub>H<sub>3</sub>Pri<sub>2</sub>-2,6 and R' = Et or Bu<sup>i</sup>) with  $[Ph_3C][B(C_6F_5)_4]$  and (for R' = Et) then PhNMe<sub>2</sub> gave  $[Al(LL)Et(N-Me_2Ph)][B(C_6F_5)_4]$  or  $[Al(LL)Bu<sup>i</sup>][B(C_6F_5)_4]$  (structures based on <sup>1</sup>H and <sup>13</sup>C NMR spectral data).<sup>11</sup> We now report the synthesis and structures of the crystalline  $\beta$ -diketiminatoaluminium compounds [Al(LL)Me<sub>2</sub>] **1**, [Al(LL)-Me(thf)][BMe(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>] **2** and [Al(LL)Me(OEt<sub>2</sub>)][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] **3**, and of some related complexes based on the spectator ligand **J**.<sup>12</sup> 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.



The  $\beta$ -diketiminatoaluminium dimethyl 1 was obtained (Scheme 1, step i) by addition of trimethylaluminium to an equivalent portion of the  $\beta$ -diketimine H(LL) (LL = **J**).<sup>12</sup> 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 <sup>11</sup>B NMR spectral signal at  $\delta$ -16.85; cf.  $\delta$  -16.7 (2), -19.1 (3) and -19.0 (4), was obtained (Scheme 1, step iv). From equivalent portions of 1 and N,Ndimethylanilinium 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<sub>6</sub>D<sub>6</sub> rather than toluene, but without addition of Et<sub>2</sub>O, quantitative formation of the related salt 5 is inferred (step v of Scheme 1).

The new, pale yellow, highly air-sensitive, readily benzenesoluble, 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  $[M - Me]^+$  for 1 and  $[B(C_6F_5)_3]^+$  for 2.



Scheme 1 Synthesis of neutral and cationic, four-coordinate  $\beta$ -diketinimatoaluminium methyls. *Reagents and conditions*: i, AlMe<sub>3</sub> in C<sub>6</sub>H<sub>14</sub>, C<sub>5</sub>H<sub>12</sub>, -78 °C; ii, B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> in C<sub>5</sub>H<sub>12</sub>, Et<sub>2</sub>O, -78 °C, then thf at 20 °C; iii, [NHMe<sub>2</sub>Ph][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>], PhMe, 20 °C; iv, [NHMe<sub>2</sub>Ph][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] in C<sub>6</sub>D<sub>6</sub>.

<sup>†</sup> 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 <sub>6</sub> H <sub>3</sub> Pr <sup>i</sup> <sub>2</sub> -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 <sub>6</sub> H <sub>4</sub> Me-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<sub>2</sub>] (LL = **I**)<sup>8</sup> are closely similar, Table 1. The AlNCCCN fragment in **1** has the boat conformation, as previously found *inter alia* in [Li(LL)]<sub>2</sub> and Sn(LL)Me<sub>3</sub>,<sup>12</sup> although sometimes this β-diketiminatometal moiety is planar, as in [Co(LL)<sub>2</sub>]<sup>13</sup> (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  $\beta$ -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.<sup>14</sup>

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 <sup>1</sup>H or <sup>13</sup>C(<sup>1</sup>H) signal for the two methyl groups, indicating that they undergo fast exchange.

The present results demonstrate once again  $[e.g.^{15}$  the monomeric  $[Ce(LL)_2Cl]$  (LL = J)] that the  $\beta$ -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.

We thank EPSRC for support.

## Notes and references

‡ Crystallographic data for 1/2/3: C<sub>23</sub>H<sub>35</sub>AlN<sub>2</sub>Si<sub>2</sub>/C<sub>45</sub>H<sub>43</sub>AlBF<sub>15</sub>. N<sub>2</sub>OSi<sub>2</sub>·0.5(C<sub>4</sub>H<sub>10</sub>O)/C<sub>50</sub>H<sub>42</sub>AlBF<sub>20</sub>N<sub>2</sub>OSi<sub>2</sub>·0.5(C<sub>4</sub>H<sub>10</sub>O), M = 422.69/1043.8/1197.9, triclinic for all, space group  $P\overline{1}$  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,  $\alpha = 78.55(2)/99.44(3)/69.39(5)$ ,  $\beta = 79.90(3)/91.80(3)/88.02(3)$ ,  $\gamma = 74.84(3)/108.31(7)/74.04^{\circ}$ , U = 1233.6(6)/2472(2)/2718(3) Å<sup>3</sup>, Z = 2/2/2,  $\lambda$ (Mo-K $\alpha$ ) = 0.71073 Å,  $\mu = 0.19/0.19/0.19$  mm<sup>-1</sup>. Data were collected at 173(2) K on an Enraf Nonius CAD4 diffractometer in the  $\omega$ -2 $\theta$  mode for the range of  $2 < \theta < 25^{\circ}$ . 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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Communication 9/00003H