

# Formation of the lithium alkylaluminium secondary amide [Me<sub>2</sub>Al((PhCH<sub>2</sub>)<sub>2</sub>N)<sub>2</sub>Li · THF] by a methane elimination/amide insertion process<sup>1</sup>

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## Abstract

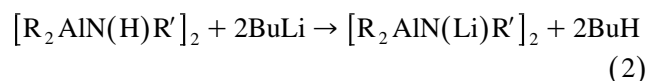
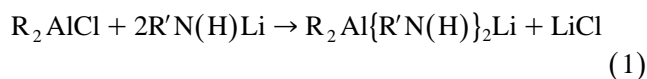
Synthesised by refluxing the amine adduct [Me<sub>3</sub>Al · (PhCH<sub>2</sub>)<sub>2</sub>NLi · HN(CH<sub>2</sub>Ph)<sub>2</sub>] in toluene/THF, the title compound has been structurally characterised by X-ray diffraction, and the methane elimination/amide insertion processes involved in its formation have been modelled theoretically through a series of ab initio MO calculations. © 1998 Elsevier Science S.A.

*Keywords:* Ab initio; X-ray diffraction; Heterobimetallics; Aluminium; Amide; Lithium

## 1. Introduction

Now that our understanding of the design principles involved in building lithium amide aggregates is well advanced [1,2], increasing attention is being paid to heterobimetallic compositions where a lithium amide molecule is attached to some other organometallic fragment [3]. In this regard, we recently synthesised [Me<sub>3</sub>Al · (PhCH<sub>2</sub>)<sub>2</sub>NLi · HN(CH<sub>2</sub>Ph)<sub>2</sub>], **1** [4], the structure of which contains monomeric fragments of (dimeric) trimethylaluminium and (trimeric) lithium dibenzylamide, mutually stabilising each other by complexation through N → Al and Me–Li interactions. There is an unusual secondary feature: the lithium amide component is solvated by its parent amine, dibenzylamine, which completes the structure. Here, in this paper, we show how this latter feature can be exploited to promote an intramolecular methane elimination/amide insertion process that generates the lithium alkylaluminium secondary amide [Me<sub>2</sub>Al{(PhCH<sub>2</sub>)<sub>2</sub>N}<sub>2</sub>Li · THF], **2**. This is the first reported compound of this specific formula-

tion. Three primary analogues, [<sup>t</sup>Bu<sub>2</sub>Al{Ph<sub>3</sub>C(H)N}<sub>2</sub>Li] and [Mes<sub>2</sub>Al{<sup>t</sup>Bu(H)N}<sub>2</sub>Li · (THF)<sub>n</sub>] (*n* = 1 or 2) [5–7], are known, but these were prepared by an alternative halide metathetical approach (Eq. (1)); while a deprotonation/lithiation procedure (Eq. (2)) was used to prepare a series of related imido derivatives [(R<sub>2</sub>Al(R'N)Li · (THF)<sub>n</sub>]<sub>2</sub>] [R, R' = Me, Ph (*n* = 2); Me, <sup>t</sup>Bu (*n* = 1); <sup>i</sup>Bu, Ph (*n* = 1); Me<sub>3</sub>Si, Ph (*n* = 2)] [5,6]. Though compounds of this type only emerged as recently as 1993 [5], they bear a close resemblance to the mixed lithium–aluminium ketimide, [LiAl{N=C(<sup>t</sup>Bu)<sub>2</sub>}]<sub>4</sub>, prepared by Wade from the corresponding lithium ketimide and aluminium trichloride over twenty years earlier [8].



## 2. Results and discussion

Methane evolution was accomplished by refluxing a toluene–THF (5:1 ratio) solution of the amine-solvate **1** (made as described previously [4]) for 24 h under a protective argon blanket. Grown by letting the solution cool to ambient temperature in a Dewar flask overnight,

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<sup>1</sup> Dedicated to Professor Ken Wade on the occasion of his 65th birthday in recognition of his sterling contribution to inorganic chemistry. REM adds his personal thanks in warm appreciation of two invaluable years spent working for, and learning from KW.

the colourless plates of **2** (m.p. 128–130°C) were obtained in 60% yield. Insoluble in toluene, the crystals were dissolved in  $d_5$ -pyridine solution to enable the recording of  $^1\text{H}$ ,  $^7\text{Li}$ ,  $^{13}\text{C}$  and  $^{27}\text{Al}$  NMR spectroscopic data which confirmed the identity of **2**. While this is a new strategy for preparing this particular type of compound, alkane elimination has been widely utilised in the preparation of other organonitrogenaluminium compounds, e.g., the amide  $[\{\text{Me}_2\text{AlN}(\text{H})\text{naphthyl}\}_2]$  [9], and the imide  $[\{\text{CpAlN}(2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3)\}_2]$  [10].

In the crystalline phase, **2** consists of discrete molecules which have no crystallographically imposed symmetry (Fig. 1). Its core ring,  $\text{AlN}(1)\text{LiN}(2)$ , is non-planar (mean deviation from the plane, 0.142 Å; sum of endocyclic bond angles, 355.8°). The mean bond angle at the distorted tetrahedral Al centre is 109.3°, with distortion most pronounced at  $\text{N}(1)\text{AlN}(2)$  [100.0(3)°] to allow chelation of the  $\text{Li}^+$  cation. Solvation by a THF molecule completes the  $\text{Li}^+$  cation's three-coordinate, pyramidal geometry (mean bond angle, 112.3°). Both N atoms occupy mean tetrahedral geometries, though the  $\text{AlN}(2)\text{C}(17)$  and  $\text{AlN}(1)\text{C}(3)$  bond angles must widen considerably [123.3(5) and 118.4(5)° respectively] to offset the sharp endocyclic corners. Reflecting its asymmetry, the central ring has long  $\text{Li}-\text{N}$  (2.09 Å) and short  $\text{Al}-\text{N}$  (mean, 1.912 Å) edges. Table 1 lists other important dimensions.

The same gross structural features are present in  $[\text{Mes}_2\text{Al}\{\text{tBu}(\text{H})\text{N}\}_2\text{Li}\cdot(\text{THF})]$  [5,6], where the increased steric bulk of the alkyl ligands (i.e., Mes cf. Me) is balanced by sterically less demanding primary amido bridges (cf. secondary ones in **2**): thus, dimensions are also similar (mean bond lengths,  $\text{Li}-\text{N}$ , 2.022 Å;  $\text{Al}-\text{N}$  1.910 Å). Though also based on an  $\text{AlNLiN}$  ring core, the structure of  $[\text{tBu}_2\text{Al}\{\text{Ph}_3\text{C}(\text{H})\text{N}\}_2\text{Li}]$  [7]

differs by not having a solvent ligand attached to the  $\text{Li}^+$  cation: in compensation, there are several short intramolecular  $\text{Li}\cdots\text{C}(\textit{ipso}, \textit{orthoPh})$  contacts (spanning 2.244–2.570 Å). Comparisons can also be made with a number of lithium tetrakis(amido) aluminate adducts that adopt  $\text{AlNLiN}$  ring motifs, e.g.,  $[(\text{C}_4\text{H}_8\text{NH})_2\text{LiAl}(\text{NC}_4\text{H}_8)_4]$  [11],  $[(\text{THF})_2\text{LiAl}(\text{NC}_5\text{H}_{10})_4]$  [11] and  $[(\text{THF})_2\text{LiAl}(\text{NMe}_2)_4]$  [12]. As in **2**, these rings deviate slightly from planarity, but the small and/or cyclic nature of their amido substituents leaves room for an additional solvent ligand, which leads to (distorted) tetrahedral, rather than pyramidal, geometries at Li. Note that all these alkyl-free amides were synthesised by treating  $\text{LiAlH}_4$  with the parent amine concerned.

Ab initio MO calculations [13–15] (set at the 6-31G\* level [16–18]) were carried out in order to shed light on the energetics involved in converting **1** to **2** and methane. For calculational simplicity,  $(\text{PhCH}_2)_2\text{N}$  was modelled by  $\text{Me}_2\text{N}$ . Scheme 1 summarises the relative energy changes along the reaction coordinate. The first step, solvating the Li centre of the mixed dimer with dimethylamine ( $\text{Me}_2\text{NH}$ ) to give the model for **1** (Fig. 2), is highly exothermic ( $-22.6 \text{ kcal mol}^{-1}$ ). This involves the formation of a new  $\text{Li}-\text{N}(\text{amine})$  bond (length, 2.075 Å) which raises the coordination number of Li from 2 to 3; as a secondary consequence the endocyclic  $\text{NLiC}$  bond angle sharpens from 102.1 to 96.3°, the  $\text{Li}-\text{N}(\text{amido})$  bond length increases from 1.928 to 1.969 Å, and the  $\text{Li}-\text{C}(\text{Me})$  bond length increases from 2.089 to 2.211 Å, with respect to the solvent-free mixed dimer. Changes in the dimensions of the Al coordination sphere are minimal. The activation barrier for methane elimination (step 2) is 61.9 kcal  $\text{mol}^{-1}$ . Fig. 2 shows the transition state (TS) associated

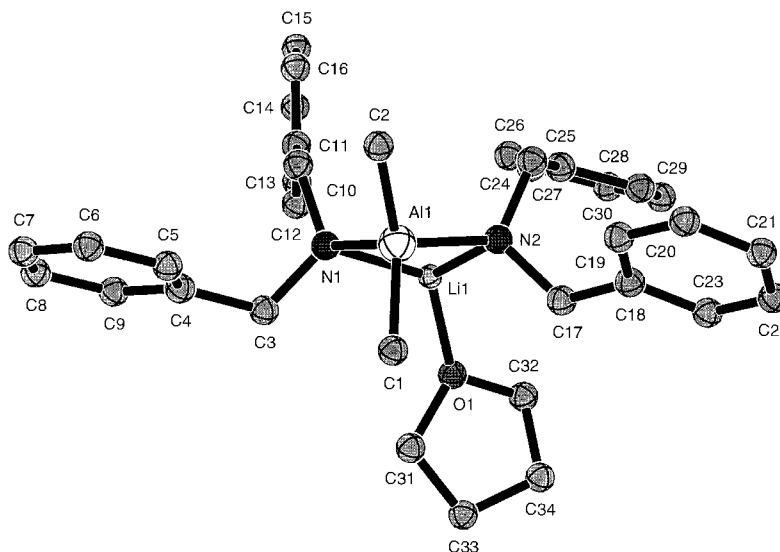


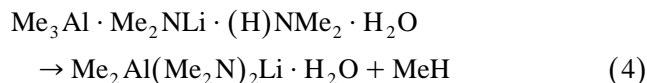
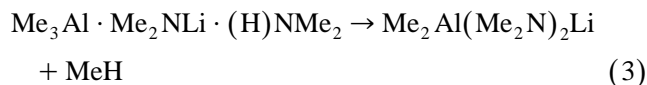
Fig. 1. Molecular structure of **2** showing atom-labelling scheme. Hydrogen atoms have been omitted for clarity.

Table 1  
Selected bond lengths (Å) and angles (°) for **2**

Parameter	Parameter	Parameter	Parameter
Al(1)–N(1)	1.927(6)	Al(1)–N(2)	1.896(6)
Al(1)–C(1)	1.989(9)	Al(1)–C(2)	1.973(9)
Al(1)–Li(1)	2.67(1)	Li(1)–N(1)	2.09(1)
Li(1)–N(2)	2.09(1)	Li(1)–O(1)	1.91(1)
N(1)–Al(1)–N(2)	100.0(3)	N(1)–Al(1)–C(1)	110.1(3)
N(1)–Al(1)–C(2)	112.0(3)	N(2)–Al(1)–C(1)	106.5(3)
N(2)–Al(1)–C(2)	112.3(3)	C(1)–Al(1)–C(2)	114.9(4)
Al(1)–N(1)–Li(1)	83.1(5)	Al(1)–N(2)–Li(1)	83.7(4)
N(1)–Li(1)–N(2)	89.0(6)	O(1)–Li(1)–N(1)	127.1(8)
O(1)–Li(1)–N(2)	120.5(8)		

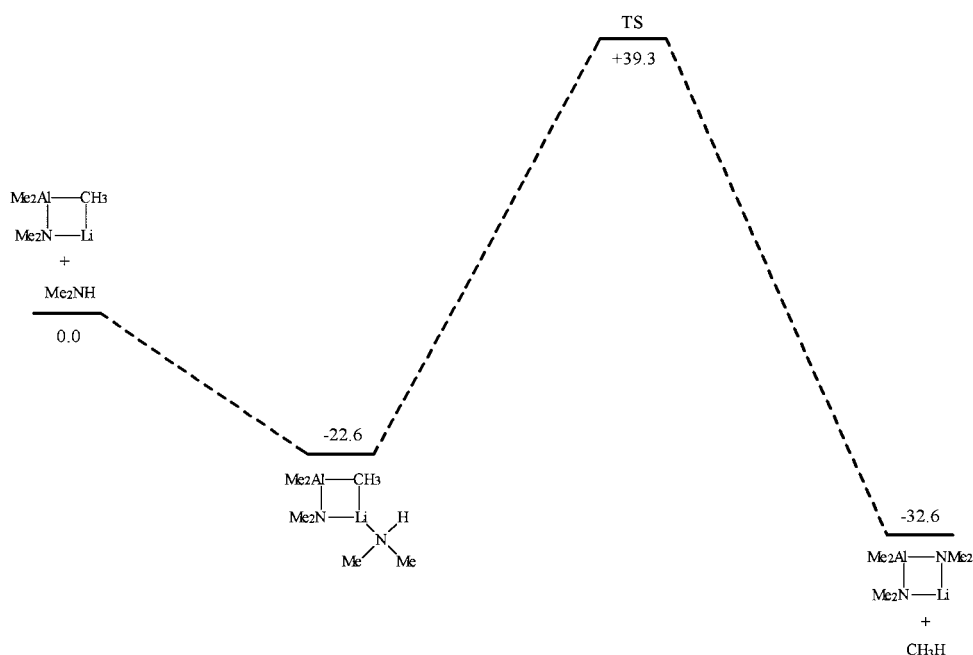
with this process (to obtain this, the structure was subjected to a frequency analysis and yielded one negative eigenvalue). With respect to the solvated dimer, the principal ‘movements’ in the TS are the elongation of the N–H bond (from 1.004 to 1.328 Å) and the development of a new N–H···C(H<sub>3</sub>) interaction (H···C length, 1.424 Å), the combination of which ultimately produces CH<sub>4</sub>. There are several other significant changes: the Al–C( $\mu$ Me) and Li–C bonds lengthen (from 2.092 to 2.964 Å and 2.211 to 2.303 Å respectively); the AlNLiC ring becomes lopsided, widening at both N (from 84.1 to 102.7°) and Li (from 96.3 to 101.3°), and narrowing at the other corners (at Al, from 100.5 to 85.7°; at C, from 75.4 to 70.3°). The enthalpy change on going from the TS to the products [the bis-amide, Me<sub>2</sub>Al(Me<sub>2</sub>N)<sub>2</sub>Li, and methane] in the final step is –71.9 kcal mol<sup>–1</sup>. This corresponds to an energy gain of –10 kcal mol<sup>–1</sup> for the reaction shown in Eq. (3). As in the experimental product **2**, the central AlNLiN ring in the model Me<sub>2</sub>Al(Me<sub>2</sub>N)<sub>2</sub>Li is buckled

slightly (sum of endocyclic angles, 357.9°); but overall the hypothetical structure is much more symmetrical (Al–N bond lengths, 1.969/1.970 Å; Li–N bond lengths, 1.958/1.959 Å; endocyclic bond angles at Al, 95.8°, at Li, 96.5°, at both N atoms, 82.8°) primarily because it lacks a solvent molecule (THF in **2**) at Li. When H<sub>2</sub>O is introduced into the calculation to mimic the effect of THF in **2** (Eq. (4)), a more realistic estimation of the energy gain on methane elimination is achieved: this is found to be –14.2 kcal mol<sup>–1</sup>.



### 3. Experimental

Characterisation of **2**: <sup>1</sup>H NMR (400 MHz,  $\delta$  in ppm, TMS at  $\delta = 0$ ) 0.06 (s, 6H, Me<sub>2</sub>Al), 1.70 (m, 4H, THF), 3.71 (m, 4H, THF), 4.64 (s, 8H, (PhCH<sub>2</sub>)<sub>2</sub>N), 7.22 (t, 4H, *para*Ph), 7.36 (m, 8H, *meta*Ph), 7.86 (d, 8H, *ortho*Ph). <sup>13</sup>C NMR (100.6 MHz,  $\delta$  in ppm, TMS at  $\delta = 0$ ) –6.1 (broad, Me<sub>2</sub>Al), 26.4 (THF), 54.2 ((PhCH<sub>2</sub>)<sub>2</sub>N), 68.5 (THF), 125.8 (*para*C), 128.4 (*meta*C), 130.0 (*ortho*C), 148.3 (*ipso*C). <sup>7</sup>Li NMR (139.95 MHz,  $\delta$  in ppm, external reference standard PhLi in *d*<sub>8</sub>-toluene) –0.1(s). <sup>27</sup>Al NMR (93.8 MHz,  $\delta$  in ppm, external reference standard Al(acac)<sub>3</sub> in *d*<sub>6</sub>-benzene) 136.1 (s,  $\omega_{1/2} = 800$  Hz). All spectra were recorded in *d*<sub>5</sub>-pyridine solution. <sup>1</sup>H/<sup>13</sup>C NMR spectra



Scheme 1.

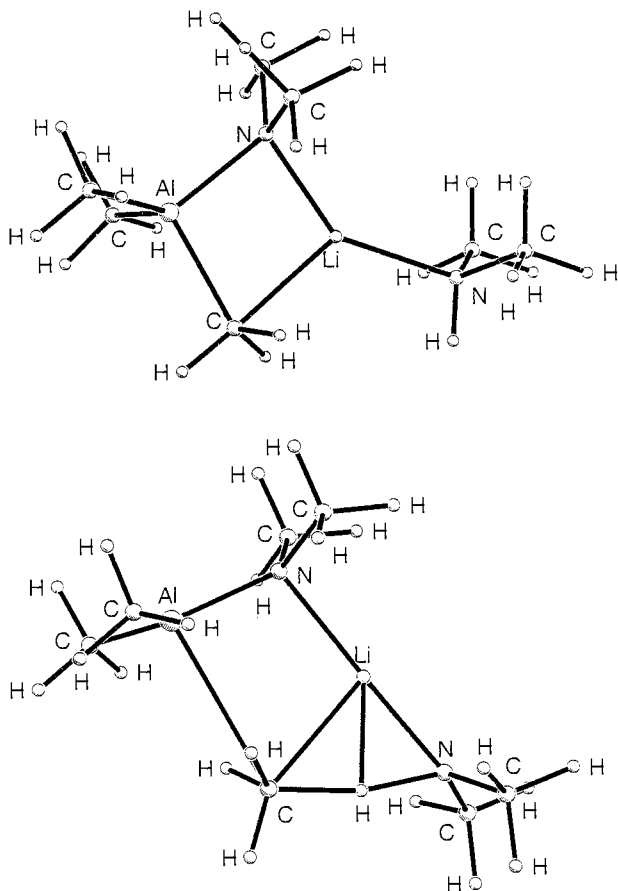


Fig. 2. Ab initio MO geometry optimised structures: (top) the starting amine adduct  $\text{Me}_3\text{Al}\cdot\text{Me}_2\text{NLi}\cdot(\text{H})\text{NMe}_2$ ; (bottom) the transition state in the methane elimination/amide insertion reaction.

were recorded on a Bruker AMX400 MHz spectrometer.  $^7\text{Li}/^{27}\text{Al}$  NMR spectra were recorded on a Bruker WH360 MHz spectrometer. Anal. Found: C, 77.2; H, 7.6; N, 5.4; Al, 4.9; Li, 0.9.  $\text{C}_{34}\text{H}_{42}\text{N}_2\text{AlLiO}$ . Calc.: C, 77.3; H, 8.0; N, 5.3; Al, 5.1; Li, 1.3; O, 3.0%.

X-ray crystallographic data:  $\text{C}_{34}\text{H}_{42}\text{N}_2\text{AlLiO}$ , fr. wt. = 528.6, orthorhombic, space group  $Pna2_1$ ,  $a = 25.226(6)$  Å,  $b = 11.430(8)$  Å,  $c = 10.750(7)$  Å,  $U = 3099(2)$  Å<sup>3</sup>,  $D_c = 1.133$  g cm<sup>-3</sup>, 4994 measured reflections, 4677 independent reflections, 1937 observed reflections, 231 parameters,  $w = 1/\sigma^2(F_o)$ ,  $R = 0.0583$ ,  $R_w = 0.0612$ ,  $S = 1.695$ , max.  $|\Delta\rho| = 0.25$  e Å<sup>-3</sup>. A colourless plate of dimensions  $0.70 \times 0.40 \times 0.20$  mm was mounted in a Lindemann capillary. Measurements were made at ambient temp. with graphite monochromated  $\text{MoK}_\alpha$  radiation. Reflections and their Friedel mates were collected to  $2\theta = 46^\circ$ . A linear decay correction of 2.0% was applied and equivalent intensities were averaged,  $R_m = 0.055$ . Reflections with  $I < 2\sigma(I)$  were excluded from further consideration. The structure was solved by direct methods [19]. The C atoms of the

phenyl rings were refined isotropically, as were the disordered sites of the THF ring (occupancy ratio 50:50). All other non-H atoms were refined anisotropically. H atoms were given idealised geometries. An isotropic extinction parameter,  $7.8(9) \times 10^{-7}$ , was included. The final full-matrix, least-squares refinement on F converged to give a maximum shift:esd ratio of 0.0004. All calculations were performed on a Silicon Graphics Indy R4600 with the teXsan set of programmes [20].

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