

Crystal Structure of a Representative Mixed Adduct of Trimethylaluminium and a Lithium Amide and a Theoretical MO Study on Model Systems

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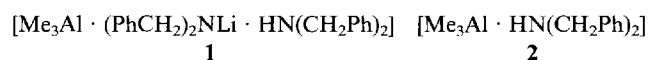
Reaction of the simple alane adduct $[\text{Me}_3\text{Al} \cdot \text{HN}(\text{CH}_2\text{Ph})_2]$ (**2**) with the lithium amide $[(\text{PhCH}_2)_2\text{NLi}]$ leads to the formation of the mixed adduct $[\text{Me}_3\text{Al} \cdot (\text{PhCH}_2)_2\text{NLi} \cdot \text{HN}(\text{CH}_2\text{Ph})_2]$ (**1**). The crystal structures of **1** and **2** are reported. Exhibiting a four-membered, mixed-metal, mixed-anion AlCLiN ring-core, the structure of **1** is unusual in containing a monomeric lithium dibenzylamide fragment. Such fragments generally convert to aza-allyl derivatives, so its

existence here can be attributed to the stabilising effect of the attached Me_3Al ligand. Crystalline **2** adopts the classical, distorted-tetrahedral arrangement of simple monomeric alane adducts. Ab initio MO calculations on model systems show that mixed adduct formation from Me_3Al and Me_2NLi is exothermic, while further reaction to give $\text{Me}_2\text{AlNMe}_2$ and MeLi (i.e., complete transmetallation) is endothermic.

Lithium dibenzylamide has been a key compound in the development of lithium amide structural chemistry. Its crystal structure (solvent-free)^[1] and those of a series of solvated derivatives (containing dioxane^[2], ether^[1], hexamethylphosphoramide^[1] or tetrahydrofuran^[2]) have contributed much to the understanding of how lithium amide structures self-assemble, for which there are now well-established principles^[3]. In addition, a novel form containing a phosphorus ylide molecule as a ligand has been characterised^[4]. Recently, we have introduced this lithium amide into the arena of heterobimetallic chemistry by synthesizing a mixed Group 1 (dilithium-disodium)^[5] and a pair of mixed Group 1-Group 2 (monolithium-monomagnesium and dilithium-monomagnesium)^[6] derivatives.

In this paper, we extend this heterobimetallic work to Group 3 in reporting the trimethylaluminium adduct $[\text{Me}_3\text{Al} \cdot (\text{PhCH}_2)_2\text{NLi} \cdot \text{HN}(\text{CH}_2\text{Ph})_2]$ (**1**), which contains the first example of dibenzylamine acting as a ligand in a lithium dibenzylamide structure. As described below, other examples of lithium amide · amine interactions are known. They are probably much more widespread than so far appreciated as conceivably they are formed but go undetected during the preparation of lithium amides from amines, either when the amine is genuinely in excess, or in equimolar reactions when the lithium reagent is added to the amine solution, a situation creating a temporary excess. Formally **1** was synthesised by insertion of the lithium amide into the $\text{N} \rightarrow \text{Al}$ dative bond of the simple amine adduct $[\text{Me}_3\text{Al} \cdot \text{HN}(\text{CH}_2\text{Ph})_2]$ (**2**), the crystal structure of which, for comparison, is also reported. Furthermore, the crystal structure of **1** demonstrates that trimethylaluminium can bind to the lithium amide through $\text{N} \rightarrow \text{Al}$ and $\text{Me} - \text{Li}$ interactions. In

addition, therefore, we have performed ab initio MO calculations on model compounds to determine the energies involved in the formation and break up of such mixed adducts and to compare the strengths of the distinct donor-acceptor bonds within them.



Results and Discussion

Syntheses, ¹H-NMR Spectroscopic Characterisation and Crystal Structures: The simple amine adduct **2**, in which trimethylaluminium acts only as an acceptor, was obtained merely by adding the two components together (in equimolar amounts) in hexane solution. Many simple alane adducts containing nitrogen donors have been made in this way^[7]. Forming as colourless, prismatic crystals, it melts sharply at 64 °C. Mixed adduct **1**, which illustrates the alane's dual bonding capacity (i.e., the Al centre behaves as a classical Lewis acid, while one of the methyl groups can interact in an electron-deficient manner with the Li centre), was produced by treating lithium dibenzylamide with a pre-prepared solution of **2** (1:1 stoichiometric ratio). Crystallising as colourless needles, **1** was found to melt higher than **2** at 82–83 °C. Satisfactory elemental analyses (Al, C, H, Li, N) were obtained for both new compounds, the empirical formulae of which were established by running ¹H-NMR spectra. Of note here, the dibenzylamine molecule in **1** and **2** could easily be recognised by the *NH* resonance, a quintet through coupling with the benzylic $\text{N}(\text{CH}_2)_2$ protons, which themselves appear as a doublet [³*J*(H,H) = 6–7 Hz]. The stronger Lewis acidity of Al versus Li (formally Al^{3+} versus Li^+) affects the chemical shifts of both of these

resonances; significantly for the benzylic protons (in **2**, $\delta = 3.55$; in **1**, 3.11), but dramatically so in the case of the NH protons (in **2**, $\delta = 2.36$; in **1**, 0.90) as these are directly attached to the donating atom. However, these values are also partly influenced by the different coordination spheres involved (i.e., distorted tetrahedral at Al, made up of the amine and three methyl groups; distorted trigonal-planar at Li, made up of the amine, one amido and one methyl group). In **1** only an averaged singlet resonance is observed (at ambient temperature) for the bridging and terminal methyl groups, located at $\delta = -0.30$. This represents a shift to higher frequency compared to the corresponding resonance in **2** (at $\delta = -0.45$), indicating a greater shielding of the methyl groups in **2**. Though amido anions are generally better donors than their parent amines, it can be reasoned here that in **1** [(PhCH₂)₂N⁻] has to compromise the amount of electron density it donates to Al as this is shared with the Li centre, whereas in **2** the (PhCH₂)₂NH molecule only donates to a single metal centre.

Experimental data for the X-ray crystallographic studies of compounds **1** and **2** are listed in Table 1. Having the VSEPR-predicted classical distorted-tetrahedral geometry (at the Al centre) common to many simple alane adducts, the crystal structure of **2** (Figure 1) merits only brief discussion. Its dative N–Al bond length [2.058(2) Å] is within experimental error of that in the quinuclidine analogue Me₃Al · NC₇H₁₃ [2.06(1) Å]^[8] and lies between that found in the acetonitrile analogue Me₃Al · N≡CMe [2.02(1) Å]^[9] and the trimethylamine analogue Me₃Al · NMe₃ [2.099(10) Å, gas-phase electron-diffraction structure^[10]]. The mean length of the normal covalent C–Al bonds in **2** is 1.968 Å (cf. 2.013, 1.987, and 2.013 Å, respectively, in the other adducts of trimethylaluminium). Other selected bond lengths and bond angles in **2** are given in Table 2.

The salient feature of the crystal structure of **1** (Figure 2) is the four-membered, bimetallic $\overline{\text{AlClLiN}}$ ring made up of four different atoms. As Figure 2 (bottom) emphasises this ring is not exactly planar [mean deviation from the plane, 0.100 Å; dihedral angle between N(1)C(1)Li(1) and Al(1)N(1)C(1) planes, 163.9°; sum of endocyclic ring angles, 358.1°]. Surrounded by the same four atoms as in **2**, the Al atom assumes a similar distorted-tetrahedral geometry. Bonding to one of the methyl carbon atoms attached to Al and to two N atoms, the three-coordinate Li atom occupies a distorted-trigonal planar coordination site. The bridging N atom [N(1)] belongs to the dibenzylamido anion, while the terminal one [N(2)] is part of the neutral dibenzylamine molecule [although no hydrogen atoms were refined; they were located in electron density difference syntheses].

There is a close similarity between **1** and the recently reported structure [Me₃Al · (Me₃Si)₂NLi]_∞ (**3**)^[11]. Both contain the same binuclear $\overline{\text{AlClLiN}}$ ring (note that the previously reported amido alane complex [(Me₃Si)₂NAIH₃Li · 2 Et₂O]₂)^[12] provides a contrast as its amido unit bonds to Al, and not to Li, while the two metal centres are linked by a bridging hydrogen atom; cf. the bridging Me group here). However, in **3** it is not discrete, but is associated into infinite chains held together by intermolecular C–Li inter-

Table 1. Crystallographic data and refinement details for the complexes **1** and **2**

Compound	1	2
formula	C ₃₁ H ₃₈ AlLiN ₂	C ₁₇ H ₂₄ AlN
formula weight	472.58	269.36
crystal system	monoclinic	triclinic
space group	P2 ₁ /n	P $\bar{1}$
a Å	14.030 (2)	9.943 (2)
b Å	11.237 (2)	10.007 (1)
c Å	19.279 (2)	9.730 (2)
α °		111.49 (1)
β °	107.05 (1)	107.44 (2)
γ °		93.06 (1)
U Å ³	2905.7 (6)	844.8 (2)
Z	4	2
D _c g cm ⁻³	1.08	1.06
crystal size mm	0.85 x 0.40 x 0.30	0.80 x 0.40 x 0.30
μ cm ⁻¹	7.42	9.33
2 θ range °	5 - 105	5 - 120
R merge	0.046	0.027
no. of reflections measured	3722	2682
unique data	3548	2512
observed data	1319	2246
no. of refined parameters	316	269
absorption range	0.81 - 1.00	0.81 - 1.00
R, R _w	0.045, 0.048	0.040, 0.060
max. $ \Delta\rho $ eÅ ⁻³	0.16	0.20

Table 2. Selected bond lengths [Å] and angles [°] for [Me₃Al · HN(CH₂Ph)₂] (**2**)

Al(1) - N(1)	2.058 (2)	Al(1) - C(1)	1.961 (2)
Al(1) - C(2)	1.966 (3)	Al(1) - C(3)	1.977 (3)
N(1) - C(4)	1.499 (2)	N(1) - C(11)	1.495 (3)
C(4) - C(5)	1.503 (3)	C(11) - C(12)	1.501 (3)
N(1) - Al(1) - C(1)	106.39 (9)	N(1) - Al(1) - C(2)	102.1 (1)
N(1) - Al(1) - C(3)	103.97 (9)	C(1) - Al(1) - C(2)	118.0 (1)
C(1) - Al(1) - C(3)	110.2 (1)	C(2) - Al(1) - C(3)	114.5 (1)
Al(1) - N(1) - C(4)	111.3 (1)	Al(1) - N(1) - C(11)	114.7 (1)
C(4) - N(1) - C(11)	110.8 (2)		

actions (i.e., a Li atom in one ring interacts with a C atom, terminally bound to Al, of another ring). This distinction is obviously caused by the lack of a solvent ligand in **3**. Hence, it is logical to presume that removing the dibenzylamine ligand from **1** would lead to the formation of a similar polymeric structure of formula [Me₃Al · (PhCH₂)₂NLi]_∞. This would continue the close structural relationship between the lithium amide components of **1** and **3**, [(PhCH₂)₂NLi]_n^[11] and [(Me₃Si)₂NLi]_n^[13], observed both in their unsolvated crystalline forms (where $n = 3$) and their crystalline ether and tetrahydrofuran solvates (where $n = 2$)^[14,15].

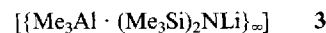
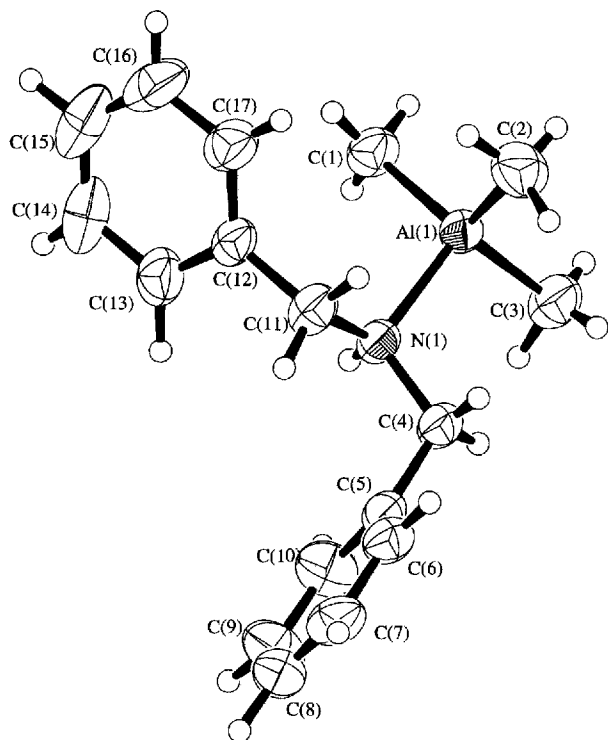


Table 3 lists selected bond lengths and bond angles within **1**. Comparison with those in **3** reveals that the most significant differences appear in the bond angles at the metal corners in the $\overline{\text{AlClLiN}}$ ring [i.e., at Li(1), 91.2(5)°, at Al(1), 103.1(3)°; cf. 96.0(3) and 114.6(2)°, respectively, in **3**]. The

Figure 1. Thermal ellipsoid plot (at 40% probability) of alane amine adduct **2** showing the atom numbering scheme



C–Al bond lengths in **1**, as in **3**, reflect whether the methyl group is terminally attached [C(2), C(3): mean length, 1.966 Å] or is bridging [C(1): length, 2.009(7) Å] [cf. in **3**: terminal, 1.974(4) Å; inter-bridging, 2.005(4), intra-bridging, 2.032(4) Å]. Mixed adducts **1** and **3** have similar N–Al bond lengths [1.902(5) and 1.944(3) Å, respectively] since they both involve amido ligands, whereas that in **2** is considerably longer [2.058(2) Å] since it involves an amine ligand. Note that the effect of the slight buckling of the AlCl₂N ring is to take the two sets of carbon atoms lying on opposite sides of the N–Al bond in **1** away from an eclipsing arrangement, only slightly in the case of C(2)AlN(1)C(4) [torsion angle, 7.6(6)°] but much more so with C(3)AlN(1)C(11) [torsion angle, 24.3(5)°]. On the basis of the longer C–Li bond length in **1** [2.25(1) Å, cf. 2.157(8) Å in **3**], it is evident that the amine is a more effective donor to Li than the intermolecularly bound methyl group in **3** (methyl H–Li distances in **3** were also deemed to be important, but unfortunately they cannot be considered in **1** as the H atoms were not refined). Though the standard deviations of the N–Li bonds in **1** are large, it is still discernible that the one involving the anion [N(1)–Li(1)] is shorter [2.04(1) Å] than the dative one [N(2)–Li(1), 2.08(1) Å], as would be expected. Dative lithium amide · parent amine coordinations have been observed in other structures, e.g., in the piperidine derivative [$\{CH_2(CH_2)_3NLi \cdot HN(CH_2)_3CH_2\}_4$]^[16] and the anilinopyridine derivative [Ph(2-Pyr)NLi · HN(2-Pyr)Ph · HMPA]^[17]. Such complexes are generally formed by the lithiation of the amine substrate, the dative (amine) coordinations of which are usually, but not necessarily, induced by having a stoichiometric

Figure 2. Top: Thermal ellipsoid plot (at 40% probability) of mixed adduct **1** showing the atom numbering scheme. Carbon-attached hydrogen atoms have been omitted for clarity. Bottom: Alternative view focusing on the orientation of the ligands with respect to the slightly buckled AlCl₂N ring

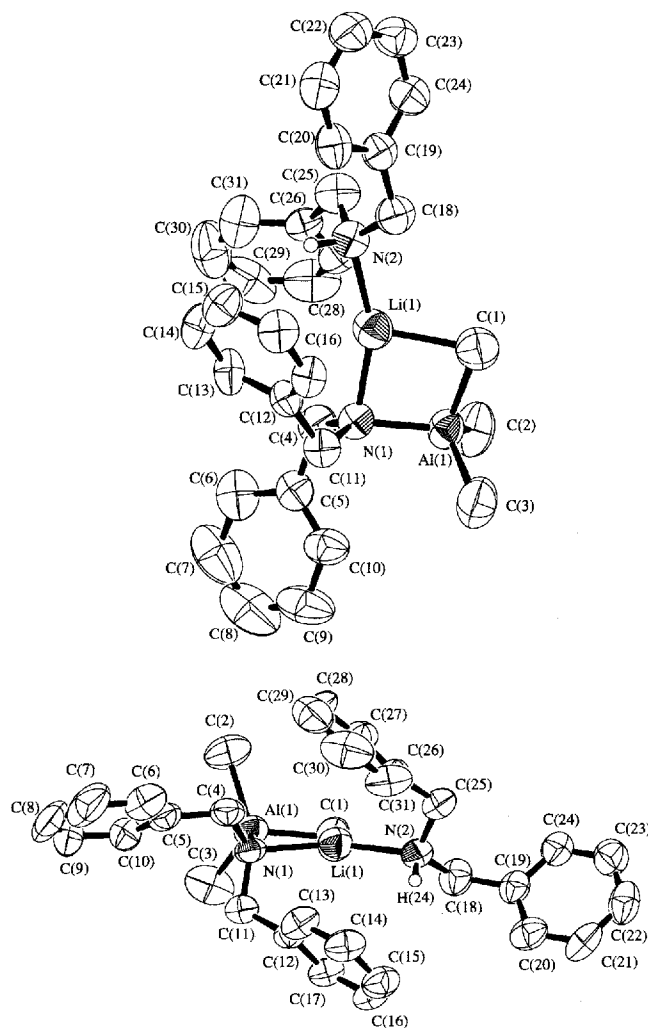


Table 3. Selected bond lengths [Å] and angles [°] for [Me₃Al · (PhCH₂)₂NLi · HN(CH₂Ph)₂] (**1**)

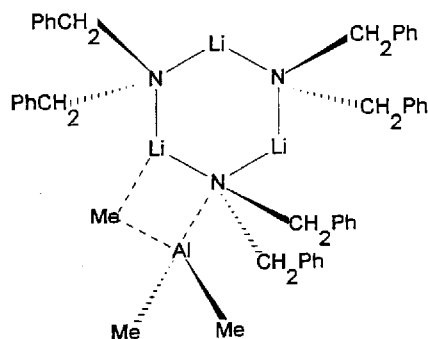
Al(1) - N(1)	1.902 (5)	Al(1) - C(1)	2.009 (7)
Al(1) - C(2)	1.963 (7)	Al(1) - C(3)	1.971 (8)
Li(1) - N(1)	2.04 (1)	Li(1) - N(2)	2.08 (1)
Li(1) - C(1)	2.25 (1)	N(1) - C(4)	1.465 (7)
N(1) - C(11)	1.469 (6)	N(2) - C(18)	1.482 (7)
N(2) - C(25)	1.451 (7)		
N(1) - Al(1) - C(1)	103.1 (3)	N(1) - Al(1) - C(2)	110.1 (3)
N(1) - Al(1) - C(3)	112.0 (3)	C(1) - Al(1) - C(2)	109.4 (3)
C(1) - Al(1) - C(3)	106.9 (3)	C(2) - Al(1) - C(3)	114.7 (3)
N(1) - Li(1) - N(2)	156.4 (6)	N(1) - Li(1) - C(1)	91.2 (5)
N(2) - Li(1) - C(1)	110.6 (5)	Al(1) - N(1) - Li(1)	85.9 (4)
Al(1) - C(1) - Li(1)	77.9 (4)	Al(1) - N(1) - Li(1) - C(1)	-10.2 (4)
Al(1) - C(1) - Li(1) - N(1)	9.9 (3)	N(1) - Al(1) - C(1) - Li(1)	-10.8 (4)
C(1) - Al(1) - N(1) - Li(1)	11.7 (4)	Al(1) - C(1) - Li(1) - N(2)	179.4 (5)
C(1) - Al(1) - N(1) - C(4)	124.2 (5)	C(1) - Al(1) - N(1) - C(11)	-90.2 (5)
C(2) - Al(1) - N(1) - C(4)	7.6 (6)	C(2) - Al(1) - N(1) - C(11)	153.2 (5)

excess of the nitrogen acid in the reaction mixture. The manner of the formation of the (H)N→Li coordination in **1** is therefore novel, in that the coordinating amine must

transfer from Al to which it is initially attached in the precursor **2**. One factor driving this process is the stronger Lewis acidity of Al^{3+} , cf. Li^+ , for in the product the Al binds to four anionic centres, whereas the Li binds to only two: in these terms, **1** can be interpreted as a lithium aluminate having a contact ion pair structure of formula $[\text{Li} \cdot \text{HN}(\text{CH}_2\text{Ph})_2]^+ [\text{Me}_3\text{Al} \cdot \{\text{N}(\text{CH}_2\text{Ph})_2\}]^-$. Formally, mixed adduct **1** can be considered as the product of inserting a monomeric fragment of lithium dibenzylamide “ $[(\text{PhCH}_2)_2\text{NLi}]$ ” (note that it usually exists as a trimer^[1]) into the dative $\text{N} \rightarrow \text{Al}$ bond of the amine adduct **2**. It is thought that lithium dibenzylamide cannot exist intact as a monomeric entity (solvated by conventional Lewis base donor molecules) as the stereochemistry of which sets up a process whereby the dibenzylamido anions spontaneously convert to a 1,3-diphenyl-2-azaallyl $[\{\text{PhC}(\text{H})=\text{N}=\text{C}(\text{H})\text{Ph}\}^-]$ system, with loss of H_2 ^[2]. The same conversion is observed for the sodium and potassium congeners^[2]. Hence, the existence of the monomeric lithium dibenzylamide unit in **1** can be attributed to the presence of, and more specifically to the dual bonding character (i.e., through both Al and Me centres) of, trimethylaluminium. Conventional Lewis base solvents (e.g., amines, ethers) perhaps fail to stabilise this unit presumably because they function only one way, as donors. Though the mechanism of the reaction producing **1** is, as yet, unknown, the fact that no aza-allyl product is observed, implies that “free” lithium dibenzylamide monomer does not form at any stage during the process (however, it does not completely rule this possibility out). Therefore, it can be reasonably postulated that the reaction proceeds by attack of trimethylaluminium on trimeric lithium dibenzylamide (its normal aggregated form in the absence of coordinating solvent). This would be preceded by dissociation of **2** into trimethylaluminium and the free amine by breaking the $\text{N} \rightarrow \text{Al}$ dative link. From crystal structure evidence, coordination of monodentate donor solvents (e.g., ether, tetrahydrofuran) to the Li centres is known to reduce the trimer to a dimer. Here, however, coordination of a methyl group to a Li centre can be accompanied by coordination of the amido anion to an Al centre, as depicted by the model shown in Figure 3. There is a precedent for the dibenzylamido anion being five-coordinate by μ_3 -bonding to metal atoms in this way: the heterobimetallic ladder structure of $[\{(\text{PhCH}_2)_2\text{N}\}_4\text{Li}_2\text{Na}_2 \cdot 2\text{Et}_2\text{O}]^{[5]}$ exhibits $\mu_3\text{N}-\text{Li}_2\text{Na}$ interactions (cf. the $\mu_3\text{N}-\text{Li}_2\text{Al}$ one in the model). All three N–Li units of the trimer could participate in such $[2 + 2]$ cycloadditions with Me–Al units of three trimethylaluminium molecules, inevitably leading to its fragmentation. Previously released from the Al centre in **2**, a dibenzylamine molecule could then coordinate to the open Li centre in the monomeric fragment to complete the structure of **1**.

Theoretical Calculations: Ab initio MO calculations were performed on a model system of the crystalline mixed adduct **1** to supplement the X-ray crystallographic results^[18]. In the hypothetical mixed adduct $\text{Me}_3\text{Al} \cdot \text{Me}_2\text{NLi}$ (**4**), for calculational simplicity the $(\text{PhCH}_2)_2\text{N}$ unit was modelled by an Me_2N one and the Li centre was left unsolvated. Fig-

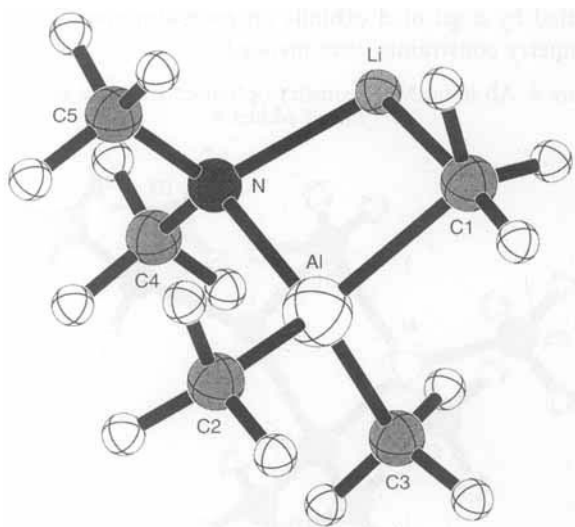
Figure 3. Schematic representation showing how Me_3Al might attach to the trimeric amide, as a prerequisite to mixed adduct formation



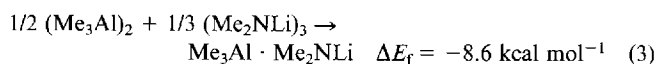
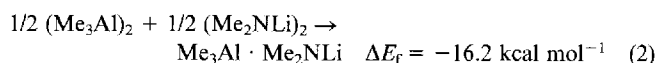
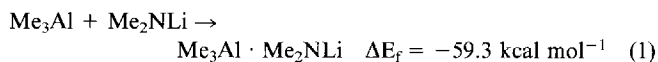
ure 4 shows the geometry-optimised structure of **4** as determined at the MP2/6-31G* basis set. Reassuringly, as found in the crystal structure, the energy minimum structure obtained on combining trimethylaluminium with the lithium amide is founded on a four-membered AlClLiN ring which is slightly buckled. Necessary to prevent eclipsing of the Me_2 substituents attached to Al with those attached to N, the non-planar nature of the ring can be gauged by the Li–N–Al–C torsion angle of 17.8° and the sum of the endocyclic ring angles of 354.6° . However, this buckling constitutes a very small contribution to the overall stability of **4**, for repeating the calculation on a model with an imposed, strictly-planar ring geometry leads to an increase in the total energy (destabilisation) of less than 1 kcal mol^{-1} . Of slightly more significance is the orientation of the μ_2 -bonding methyl [C(1)] group. In **4**, two of its three attached hydrogen atoms lie toward the C–Li edge of the AlClLiN ring setting up short $\text{Li} \cdots \text{H}$ contact lengths of 2.084 and 2.177 Å. Rotating this group such that one C–H bond lies close to the Li centre reduces the stability of the system by $2.16 \text{ kcal mol}^{-1}$. As in the crystal structure, in **4** the bridging methyl group forms a decidedly longer bond to Al (2.093 Å) than do the terminal methyl groups (1.984 and 1.990 Å), but both the C–Li and N–Li bonds are artificially shorter (2.048 and 1.923 Å, respectively) than their counterparts in the crystal [2.25(1) and 2.04(1), respectively] due to the lack of a solvating ligand. Completing the AlClLiN ring in **4**, the N–Al bond length is 1.973 Å, while the endocyclic bond angles are 98.3, 74.6, 101.5, and 80.2° at Al, C, Li and N, respectively. The C–N bond lengths associated with the Me_2N unit are 1.464 and 1.469 Å.



In order to explore the thermodynamics of such mixed adduct formation, each of the molecules highlighted in Equations (1)–(3) were optimised (at the same MP2/6-31G* level) in turn, and their total energies computed, from which the energy of formation (ΔE_f in kcal mol^{-1}) of **4** in each reaction could be calculated. Equation (1) considers the simplest system, where the aggregation phenomena of the reactants are completely disregarded. Mixed-adduct formation is in this case energetically favourable, but the scale of the energy gain involved (amounting to 59.3

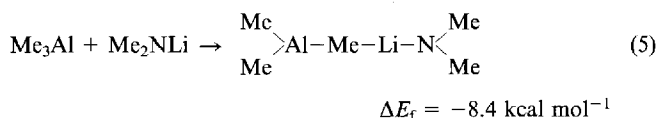
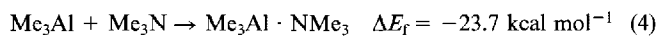
Figure 4. Ab initio MO geometry-optimised structure of hypothetical mixed adduct **4**

kcal mol⁻¹) is highly exaggerated by the crudeness of the models employed. Taking the dimeric nature of trimethylaluminium into account [in Equation (2)] leads to a considerably smaller energy gain of 16.2 kcal mol⁻¹. In the most realistic system [in Equation (3)], where both trimethylaluminium and the lithium amide (lithium dibenzylamide) are in their normal aggregated forms (dimeric and trimeric, respectively), the energy gain decreases further (to 8.6 kcal mol⁻¹), but again mixed-adduct formation is exothermic. It should be noted that the model lithium amide used here, lithium dimethylamide, is of course a known compound. However, its crystal structure^[19] and degree of aggregation have not yet been ascertained, though characteristics such as amorphousness and poor arene-solubility hint at a polymeric constitution. In view of this likelihood, it may be that the exothermicity of mixed-adduct formation is overestimated in the case of this particular (sterically undemanding) lithium amide given that ΔE_f decreases sequentially as aggregation increases [i.e., as shown by Equations (1)→(2)→(3)]. Indeed, it is conceivable that combining trimethylaluminium and lithium dimethylamide experimentally would lead to a product other than the dinuclear adduct **4**. That notwithstanding, the calculated ΔE_f in Equation (3) should be a reliable guide to the actual heat of formation of the crystalline adduct **1** as its more sterically demanding amide precursor (lithium dibenzylamide) is genuinely trimeric.

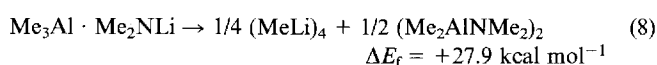
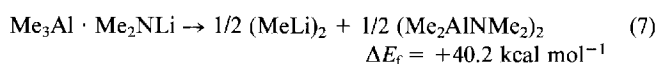
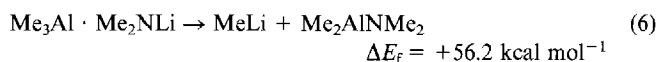


As highlighted earlier, trimethylaluminium interacts simultaneously through the Al and Me centres to the lithium amide moieties in the mixed adducts **1** and **3** (and in

their theoretical counterpart **4**). Therefore, in order to attempt to quantify, in approximate terms, the relative importance of each of these roles to the stability of the mixed adducts, calculations were carried out on simple model compounds that exhibit one or the other of these roles, but not both. The simple amine adduct $\text{Me}_3\text{Al} \cdot \text{NMe}_3$ was chosen to allow estimation of the energy associated with the N→Al dative interaction (i.e., where the alane acts as an acceptor). Equation (4) shows its formation is exothermic by 23.7 kcal mol⁻¹. Consideration of an isomeric structure of the mixed adduct **4**, in which adduct formation occurs through a single Me→Li contact (i.e., unlike **4**, no N→Al contact is present), enabled a similar estimate of the energy associated with the alane functioning as a “donor”. This required the geometry of the structure to be constrained so that excluding hydrogen atoms the molecule is planar, and the Al–C–Li–N unit is linear. Again, as Equation (5) reveals, the formation of this structure from its two components was found to be exothermic, but by a considerably smaller margin of 8.4 kcal mol⁻¹. Hence, on the basis of this comparison it is the Lewis acidity of Al which clearly dominates when trimethylaluminium acts as a “donor-acceptor” ligand in lithium amide chemistry.



Mixed adduct **4** can be formally regarded as an intermediate in the transmetallation reaction of trimethylaluminium and lithium dimethylamide, the final products of which would be methyl lithium and dimethylaluminium dimethylamide. To shed light on why this transmetallation does not occur in practice, the energetics of the hypothetical reactions shown in Equations (6)–(8) were calculated. As suspected, breaking up the mixed adduct in this manner is an endothermic process. When aggregation is ignored, the energy loss is considerable (i.e., +56.2 kcal mol⁻¹). However, more realistically, when the reactants are tetrameric methyl lithium and dimeric dimethylaluminium dimethylamide [Equation (8)], this drops to +27.9 kcal mol⁻¹. Clearly, irrespective of the margin of energy loss, there appears to be no thermodynamic compulsion for transmetallation to proceed to completion. Of course, it is also conceivable that the reaction stops at the intermetallic, intermediate stage for kinetic reasons with the mixed adduct being the least soluble species in solution (the steric bulk of the amido ligand may be a factor here), and therefore the first to crystallise. Studies are in hand to check whether more forcing reaction conditions will bring about transmetallation.



Ab initio MO calculations were also performed on $\text{Me}_3\text{Al} \cdot \text{NMe}_2\text{H}$ (**5**) (Figure 5), a model system of the crystalline adduct **2**. The geometry optimisation procedure at the MP2 level using the 6-31G* basis set revealed that for this species the organic groups are present in a staggered conformation about the Al–N dative bond. The calculated Al–N bond length, 2.094 Å, is close to the experimental value found for $\text{Me}_3\text{Al} \cdot \text{NMe}_3$ (2.099 Å)^[9] and moreover is longer (and weaker) than the aforementioned value (1.973 Å) for **4**, the lithiated derivative. The Al–C bonds span 1.990–1.992 Å which is expected when the organic groups are terminal and the C–Al–N angles lie between 100 and 102°. The donor-acceptor energy of the adduct with respect to the monomeric forms of the reactants amounts to $-32.4 \text{ kcal mol}^{-1}$ which can be compared to the corresponding value of $-59.3 \text{ kcal mol}^{-1}$ when lithium is present in place of the amido hydrogen. The extra stabilisation of the latter reflects that there is an extra channel of donor-acceptor interactions present (i.e., $\text{Me} \rightarrow \text{Li}$).

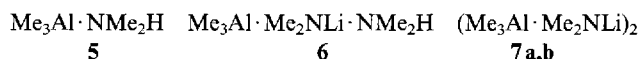
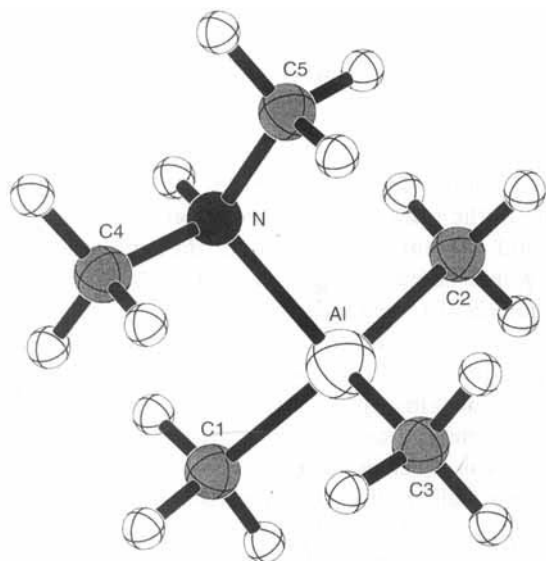


Figure 5. Ab initio MO geometry-optimised structure of amine adduct **5**



Finally, calculations were performed on model compounds $\text{Me}_3\text{Al} \cdot \text{Me}_2\text{NLi} \cdot \text{NMe}_2\text{H}$ (**6**) and $(\text{Me}_3\text{Al} \cdot \text{Me}_2\text{NLi})_2$ (**7a**, **7b**) to try to rationalise why **1** prefers a solvated monomeric state over two possible associated states one of which is found in **3** in the absence of solvent molecules. Thus **6** consists of a model solvent, NMe_2H , coordinated to **4** at lithium (Figure 6). The stepladder structure of **7a** could be thought of as a dimer of **4** with dimerisation occurring through a central four-membered ring of Li–N bonds (Figure 7). Alternatively, it could be viewed as a complex formed by the addition of two AlMe_3 species to the dimer $(\text{LiNMe}_2)_2$. Figure 8 shows **7b** which, in contrast, models the bonding in **3** whereby the monomeric units combine chain-like via the lithium on one moiety interacting with a terminal methyl group of the AlMe_3 portion of the

second ring. These geometry optimisation calculations were carried out at the SCF level using a 6-31G basis set augmented by a set of d orbitals on each aluminium, and no symmetry constraints were invoked.

Figure 6. Ab initio MO geometry-optimised structure of solvated mixed adduct **6**

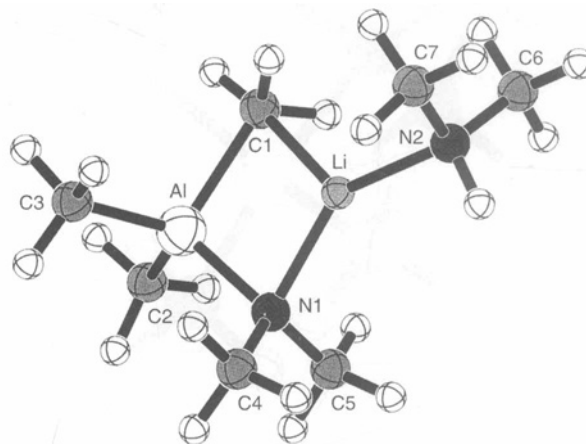
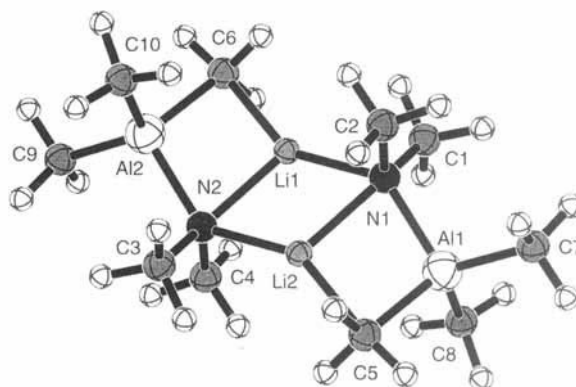


Figure 7. Ab initio MO geometry-optimised stepladder structure of aggregated mixed-adduct **7a**



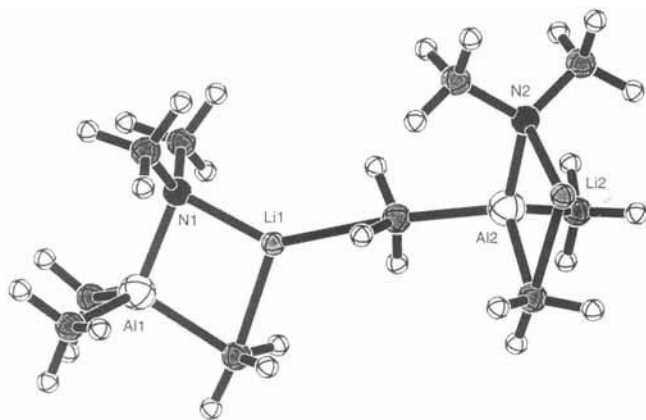
The calculations on **6** reveal that the extra stabilisation due to solvation of **4** amounts to $24.5 \text{ kcal mol}^{-1}$. The energy of dimer association for **7a** is $22.1 \text{ kcal mol}^{-1}$ i.e., there is an extra $11.1 \text{ kcal mol}^{-1}$ stabilisation energy for *each* unit of **4**. The energy of the intermolecular association for **7b** is $12.5 \text{ kcal mol}^{-1}$ and this latter value is for the intermolecular interaction between the two rings. In the infinite chain of **3** there will be two of these interactions per ring, and so the energy stabilisation per monomeric unit in such an infinite chain will be of the order of $12.5 \text{ kcal mol}^{-1}$. These values suggest that in the presence of a donor solvent the mixed adduct will preferentially form a coordination bond to the solvent rather than undergo self association. In the absence of a coordinating solvent the chain-like interaction present in **3** and **7b** will be preferred over dimeric association based on a four-membered ring of Li–N bonds as found in **7a**. Steric effects will also favour association via intermolecular $\text{Li} \cdots \text{H}_3\text{C}-\text{Al}$ interactions over a stepladder structure where bulky groups will adversely affect the formation of the central four-membered ring.

The calculations on **6** also reveal the effect (on the ring geometry of **4**) due to the donor molecule bound at lithium. The ring angle at lithium decreases by 6° as a result of the extra coordination bond present while the ring itself remains non-planar with a Li–N–Al–C torsion angle of 16.8° . The additional bonding at Li causes the Li–C and Li–N bond lengths to increase (by 0.129 and 0.046 Å, respectively), while a secondary effect is the shortening of the ring bonds emanating from Al as the relative attraction of the ring atoms N and C to lithium decreases.

Although the dimeric structure **7a** was input into the geometry optimisation procedure with C_1 symmetry, the resulting optimised geometry converged on C_i symmetry. The structure presented in Figure 7 is best described as having a stepladder framework^[20] built around a four-membered LiNLiN ring whose bonds are almost equal [Li(1)–N(1) = 2.077, Li(1)–N(2) = 2.076 Å]. The outer rings have an architecture similar to the monomeric adduct **4** with the only noteworthy difference being a lengthening of the Li–C bond to 2.49 Å.

The calculated structure of **7b** is presented in Figure 8. This clearly shows the linkage between the adducts is by a further Li...H₃C–Al interaction. The new Li–C bond spans 2.39 Å while the three Li...H bond distances are 2.26, 2.31, and 2.31 Å. The basis of this bonding interaction is electrostatic between the relatively electron-rich methyl group (the Me group in AlMe₃ carries a -0.28 charge) and the positively charged lithium. The creation of the bond only slightly perturbs the geometry of the four-membered ring of the adduct **4**.

Figure 8. Ab initio MO geometry-optimised chain-like structure of aggregated mixed adduct **7b**



We thank the EPSRC for funding a studentship (to F. J. C.) and the University of Strathclyde for funding the purchase of a diffractometer.

Experimental

All solvents were dried by standard techniques, and reagents were purchased from the Aldrich Chemical Co. All manipulations were carried out under a protective argon blanket either in a double-manifold argon/vacuum line or in an argon-filled recirculating dry box. – ¹H and ¹³C NMR: recorded at room temp., Bruker AMX 400. – Elemental analyses: Perkin-Elmer 240. – Lithium

and aluminium analyses: atomic absorption spectroscopy, PU 9100 and PU 9400 Philips Spectrophotometer, respectively.

[Me₃Al · (PhCH₂)₂NLi · HN(CH₂Ph)₂] (**1**): Dibenzylamine (1.92 ml, 10 mmol) was added dropwise to chilled *n*BuLi (10 mmol in hexane, 6.9 ml of a 1.45 M solution) in hexane (4 ml) to prepared lithium dibenzylamide. Warming to room temp. deposited a pink solid which was dissolved completely on addition of toluene (6 ml) and heating. [Me₃Al · HN(CH₂Ph)₂] (**2**), suspended in hexane (6 ml), was slowly added by means of a syringe to lithium dibenzylamide, and the mixture was stirred overnight. All solvents were removed under vacuum and the remaining red precipitate recrystallised from hexane (4 ml)/petroleum ether (1 ml). Crystals were deposited at room temp. overnight which were isolated, washed with chilled toluene (3 ml) and dried under vacuum: yield 3.02 g (64%), m.p. 82–83°C. – ¹H NMR (400 MHz, [D₆]benzene, 25°C, TMS): δ = –0.30 (br, 9H; CH₃), 0.90 (quint, 1H; NH), 3.11 (d, 4H; PhCH₂ amine), 3.80 (s, 4H; PhCH₂ amido), 6.82 (d, 4H; *o*-H_{amine}), 7.01–7.24 (m, 12H, *m*-, *p*-H_{amine} + amido), 7.23 (d, 4H, *o*-H_{amido}). – ¹³C NMR (100.6 MHz, [D₆]benzene, 25°C, TMS): δ = –6.9 (CH₃), 52.2 (PhCH₂ amine), 52.6 (PhCH₂ amido), 127.1–129.7 (*o*-, *m*-, *p*-C_{amine} + amido), 137.9 (*i*-C_{amine}), 143.9 (*i*-C_{amido}). – C₃₁H₃₈AlLiN₂ (472.6): calcd. C 78.8, H 8.1, Al 5.7, Li 1.5, N 5.9; found C 78.4, H 8.1, Al 5.5, Li 1.2, N 5.5.

[Me₃Al · HN(CH₂Ph)₂] (**2**): Dibenzylamine (1.92 ml, 10 mmol) was added to chilled Me₃Al (10 mmol in hexane, 5.0 ml of a 2 M solution) with the immediate precipitation of a white solid which dissolved with the addition of hexane (4 ml) and slight heating. Slow cooling of the solution deposited colourless crystals which were isolated, washed with hexane (3 ml) and dried under vacuum: yield 2.01 g (75%), m.p. 64°C. – ¹H NMR (400 MHz, [D₆]benzene, 25°C, TMS): δ = –0.45 (br, 9H; CH₃), 2.36 (quint, 1H; NH), 3.55 (d, 4H; PhCH₂), 6.67–7.03 (m, 10H; *o*-, *m*-, *p*-H). – ¹³C NMR (100.6 MHz, [D₆]benzene, 25°C, TMS): δ = –7.7 (CH₃), 52.1 (PhCH₂), 128.7–129.6 (*o*-, *m*-, *p*-C), 136.2 (*i*-C). – C₁₇H₂₄AlN (269.4): calcd. C 75.9, H 9.0, Al 10.0, N 5.2; found C 75.9, H 9.2, Al 9.8, N 4.8.

Crystallography: Crystal samples were mounted in Lindemann capillaries in a dry box. Crystal data, data collection and refinement parameters are given in Table 1, selected bond lengths and angles in Tables 2 and 3.

Data Collection and Processing: Measurements were made at ambient temp. with Cu-*K*_α X-rays, λ = 1.5418 Å, on a Rigaku AFC7S diffractometer fitted with a graphite monochromator. Cell dimensions were based on 20 reflections with 17.0 < Θ < 22.5 in the case of **1** and on 25 reflections with 47.0 < Θ < 50.0 in the case of **2**. Intensities, *I*, were derived from ω/2Θ scans, and corrections were applied for Lorentz and polarisation factors and also for absorption based on averaging several azimuthal scans. The data from **1** was also subjected to a linear decay correction of 5.11%. Equivalent intensities were then averaged and unobserved reflections with *I* < 2σ(*I*) excluded from further consideration.

Structure Analysis and Refinement: Both structures were solved by direct methods^[21] and the examination of subsequent difference syntheses. All non-hydrogen atoms were refined anisotropically. H atoms in **2** were treated isotropically. H atoms in **1** were located in difference syntheses, but only those of the bridging methyl group were placed as found. Other H atoms were placed in calculated positions (N– or C–H = 0.95 Å). All H atoms in **1** were given fixed isotropic thermal parameters 1.2 · Beq of their parent atom. For **2** an isotropic extinction parameter (1.29 · 10³) was also refined. Final full-matrix, least-squares refinements were on *F* with *w* = 1/σ²(*F*) and converged to give a maximum shift/esd ratio of

0.004. All calculations were performed on Silicon Grapics Indy R4600 with the teXan set of programmes^[22] and used published scattering factors^[23].

Further details of the crystal structure investigations are available from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany), on quoting the depository number CSD-405498 and -405499, the names of the authors, and the journal citation.

Theoretical Calculations: The ab initio MO calculations were performed on the GAMESS computational package^[24]. Preliminary calculations were performed on all the molecules with no symmetry constraints at the SCF level using the 6-31G basis set^[25] augmented by a set of d orbitals for aluminium. The final calculations on the monomeric species were done at the MP2 level^[26] (including all the core electrons) using the 6-31G* basis set^[25] and any symmetry found in the preliminary calculations. Intermediate calculations on the monomeric species were also done at SCF level using the 6-31G** basis set^[25] to investigate if a better representation of the hydrogens would alter the findings. The general conclusions were not altered, and so these calculations were not reported.

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