

# Reaction of *N,N'*-bis(mesityl)ethylenediamine with triethylaluminium. Formation of ten-membered aluminium amide heterocycles

James R. Gardinier and François P. Gabbaï\*

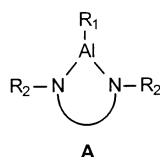
Chemistry Department, Texas A&M University, 3255 TAMU, College Station, TX77843-3255, USA.  
E-mail: francois.gabbaï@tamu.edu; Fax: +1 979 845 4719

Received (in Montpellier, France) 19th July 2001, Accepted 29th August 2001

First published as an Advance Article on the web

Reaction of *N,N'*-bis(mesityl)ethylenediamine with triethylaluminium in benzene leads to the formation of an aluminium diamide derivative of formula  $[\text{AlEt}(\mu\text{-MesNCH}_2\text{CH}_2\text{NMes})]_n$  (**1**) (Mes = 2,4,6-Me<sub>3</sub>C<sub>6</sub>H<sub>2</sub>). Upon treatment with pyridine or THF, compound **1** is converted into dinuclear aluminium amide derivatives of general formula  $[\text{AlEt}(\mu\text{-MesNCH}_2\text{CH}_2\text{NMes})]_2 \cdot 2\text{L}$  with L = pyridine (**2**) and THF (**3**), respectively. Compounds **1**, **2** and **3** have been characterized by <sup>1</sup>H, <sup>13</sup>C and <sup>27</sup>Al NMR spectroscopy as well as by elemental analysis. Single crystal X-ray analysis indicates that the two adducts exist as ten-membered heterocycles with tetracoordinated aluminium centers.

Owing to their fundamentally appealing structural diversity<sup>1–3</sup> and their use as AlN single source precursors,<sup>4</sup> aluminium amides have been the subjects of numerous investigations. For the most part, previous achievements have been concerned with aluminium derivatives of monofunctional amines. The chemistry of organoaluminium compounds with chelating bifunctional amido ligands (**A**) has been less extensively investigated. Despite their rarity, a series of applications identified in the general area of catalysis substantiate the extensive importance of such derivatives. In particular, these compounds have proved useful for the Lewis acid activation of organic reactions<sup>5–8</sup> as well as for the polymerization of olefins.<sup>9</sup> The Lewis acidity and hence, the ability of these compounds<sup>5</sup> to complex incoming nucleophiles, is a crucial parameter that dictates the catalytic properties of such derivatives. Interestingly, while the formation of Lewis adducts has often been proposed, very few studies have focused on the structural characterization of such adducts. In fact, it seems surprising that only one Lewis adduct of these derivatives, namely  $\text{AlMe}\{\text{N}(\text{SO}_2\text{CF}_3)\text{-CH}(\text{Pr})\text{CH}_2\}_2\text{N}(\text{CH}_2\text{Ph})\} \cdot \text{DMF}$ , has been isolated and structurally characterized.<sup>8</sup> In this contribution we report on the preparation of one organoaluminium bifunctional amide derivative,  $[\text{AlEt}(\mu\text{-MesNCH}_2\text{CH}_2\text{NMes})]_n$  (**1**) and two compounds of general formula  $[\text{AlEt}(\mu\text{-MesNCH}_2\text{CH}_2\text{NMes})]_2 \cdot 2\text{L}$  [L = pyridine (**2**), tetrahydrofuran (**3**)] that are derived from the reactions between **1** and the appropriate Lewis base.

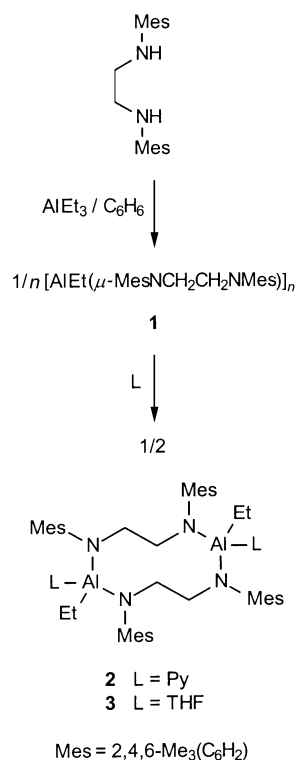


## Results and discussion

### Synthesis and characterization of $[\text{AlEt}(\mu\text{-MesNCH}_2\text{CH}_2\text{NMes})]_n$ (**1**)

The ethylaluminium diamide **1** is obtained in 76% yield by stirring and refluxing a benzene solution containing equimolar

amounts of AlEt<sub>3</sub> and the diamine (Scheme 1). Compound **1** is soluble in benzene, toluene, and chloroform, but only slightly soluble in aliphatic solvents and diethyl ether.



Scheme 1

A number of spectroscopic features indicate that **1** oligomerizes in solution. First, the <sup>27</sup>Al NMR spectrum of **1** in benzene solution consists of a single resonance at  $\delta$  63.3 ( $\omega^{1/2}$  = 3853 Hz). This resonance clearly differs from that typically observed for tricoordinate aluminium species with two amido ligands<sup>10</sup> and falls at the lower end of the range usually considered for tetracoordinate species.<sup>11</sup> In fact, the <sup>27</sup>Al NMR resonance observed for **1** compares favorably with

those of tetracoordinate Lewis adducts of bis(alkoxide) aluminium derivatives<sup>12</sup> and suggests tetracoordination of the metal center. The <sup>1</sup>H NMR spectral data presented in Table 1 support this view and can be conveniently interpreted by considering an associated solution structure. In benzene-d<sub>6</sub>, there are six resonances of equal intensity for protons in the mesityl-CH<sub>3</sub> region of the spectrum, which is consistent with the presence of two magnetically distinct and non-freely rotating mesityl groups. Accordingly, four resonances are observed in the aromatic region of the <sup>1</sup>H NMR spectrum of **1**. The N-methylene region of the <sup>1</sup>H NMR spectrum reflects an ABCD spin system due to the presence of two magnetically distinct methylene units with diastereotopic protons. Homonuclear decoupling experiments were used to verify this assignment and in particular the coupling pattern and magnitude of the coupling constants for the four equally intense resonances at δ 4.92 (ddd), 3.56 (ddd), 2.95 (dd), and 2.80 (dd) in C<sub>6</sub>D<sub>6</sub>. The resonances for the ethyl group protons appear as a triplet for the methyl protons and a pair of doublets of quartets for the symmetrically nonequivalent methylene protons,<sup>13</sup> as determined by acquiring the spectra at different frequencies (500, 300 MHz) and by selective homonuclear decoupling experiments. Finally, only a slight line broadening but no other significant changes were detected in the <sup>1</sup>H NMR spectrum of **1** as a benzene solution upon increasing temperature from 20 to 80 °C, indicating a retention of the structure.

While the molecularity of **1** was not ascertained beyond doubt, it is reasonable to assume that it exists as a dimer similar to the related derivative [AlH(<sup>t</sup>BuNCH<sub>2</sub>CH<sub>2</sub>N<sup>t</sup>Bu)]<sub>2</sub>.<sup>14</sup> We note that a trimeric species has been observed for a derivative containing the less sterically hindered N-phenylethylenediamine ligand.<sup>15</sup> The <sup>13</sup>C NMR spectral data for **1** are collected in Table 2 and are consistent with the proposed oligomeric nature of **1**. Whereas assignments of the chemical shifts for the resonances in the AlEt and NCH<sub>2</sub> regions of the spectrum were made by comparison with the spectroscopic characteristic of known compounds,<sup>16</sup> the resonances in the aromatic and Mes-CH<sub>3</sub> regions could not be unequivocally assigned. Two resonances for chemically distinguishable N-methylene carbons were observed. The low-field resonance was attributed to the methylene carbon bound to the tetracoordinate nitrogen whereas the high-field resonance was assigned to the methylene carbon bound to tricoordinate nitrogen. Similar assignments have been made for related group 13 azatranes and for cationic group 13 amidinate complexes on the basis of quadrupole effects of <sup>14</sup>N–<sup>13</sup>C interactions.<sup>16</sup> In the case of **1**, such assignments also appear

reasonable when comparing the chemical shift values of the N-methylene carbon resonances with that of the free diamine that possesses two three-coordinate nitrogen atoms. In accord with the different chemical environments about the N-methylene carbon atoms in **1**, there are two sets of nine resonances each for carbon atoms of the mesityl groups. Finally, only two resonances for aluminium ethyl carbon atoms were observed, which indicates a single environment for this ligand.

#### Synthesis and structure of [AlEt(μ-MesNCH<sub>2</sub>CH<sub>2</sub>NMes)]<sub>2</sub> · 2py (**2**) and [AlEt(μ-MesNCH<sub>2</sub>CH<sub>2</sub>NMes)]<sub>2</sub> · 2THF (**3**)

When compound **1** is dissolved in either pyridine or THF and heated at 60 °C for 1 h formation of adducts **2** and **3**, respectively, is observed (Scheme 1). The identity of **2** and **3** was confirmed by elemental analyses, <sup>1</sup>H, <sup>13</sup>C, and <sup>27</sup>Al NMR spectroscopic studies, as well as X-ray single crystal analysis.

Each compound crystallizes in the space group *P*2<sub>1</sub>/*c* with two molecules per unit cell (Table 3). The molecular structures of these derivatives (Fig. 1 and 2) present the following common features. The diamide ligands bridge the two aluminium centers, thereby forming a 1,6-diala-2,5,7,10-tetraazacyclodecane ring that has a chair conformation. The mesityl groups are in equatorial positions whereas the Lewis bases occupy axial positions. The coordination geometry about the aluminium centers in both compounds is best described as being distorted trigonal pyramidal where the C(1), N(1), and N(2) atoms define the basal plane while the Lewis donor atom [N(3) for **2**, O(1) for **3**] resides in the apical position (Fig. 3). In both compounds the aluminium atom is displaced by 0.39 Å above the basal plane in the direction of the apical atom. The distance between aluminium and Lewis donor atoms is 2.05 Å for Al–N(3) in **2** and 1.95 Å for Al–O(1) in **3**. These and all other bond distances are unexceptional and can be compared to typical values found for organoaluminium Lewis adducts and organoaluminium amido compounds.<sup>1b,17</sup>

The NMR spectral data of either **2** in pyridine-d<sub>5</sub> or **3** in THF-d<sub>8</sub> indicate the conformational flexibility of their structures (Tables 1 and 2). In particular, rather than giving rise to an AA'BB' spin system, which would be expected if the chair conformation observed in the solid state structure was retained in solution, a single proton resonance at δ 3.60 for **2** and δ 3.54 for **3** is observed for the N-methylene units. Accordingly, the mesityl substituents give rise to two CH<sub>3</sub> and one aromatic CH resonances in the expected intensity ratio. The <sup>27</sup>Al NMR

**Table 1** <sup>1</sup>H NMR spectral data for diamine and ethylaluminium derivatives

Compound (solvent)	MesH	NH	NCH <sub>2</sub>	<i>o</i> -MesCH <sub>3</sub>	<i>p</i> -MesCH <sub>3</sub>	AlCH <sub>3</sub>	AlCH <sub>2</sub>
[NH(Mes)CH <sub>2</sub> ] <sub>2</sub> (C <sub>6</sub> D <sub>12</sub> )	6.69	3.11	3.02	2.19	2.15	—	—
(C <sub>6</sub> D <sub>6</sub> )	6.79	3.10	2.93	2.19	2.18	—	—
(CDCl <sub>3</sub> )	6.94	3.33	3.26	2.40	2.35	—	—
(C <sub>5</sub> D <sub>5</sub> N)	6.87	3.94	3.25	2.35	2.23	—	—
Compound <b>1</b> (C <sub>6</sub> D <sub>6</sub> )	6.96 (× 2 <sup>a</sup> ), 6.68	—	4.92 (ddd) <sup>b</sup>	2.83, 2.62, 2.48, 2.29, 2.03, 2.00 <sup>e</sup>	—	0.93 (t) <sup>c</sup>	0.31 (dq) <sup>d</sup>
	6.53	—	3.56(ddd) <sup>f</sup> 2.95 (dd) <sup>g</sup> 2.80 (dd) <sup>h</sup>	—	—	—	0.18 (dq) <sup>d</sup>
Compound <b>1</b> (CDCl <sub>3</sub> )	6.92, 6.90	—	4.91 (ddd)	2.82, 2.46 (× 2), 2.28, 2.20, 1.97 <sup>e</sup>	—	0.60 (t) <sup>c</sup>	0.03 (dq) <sup>d</sup>
	6.84, 6.70	—	3.53 (ddd) 2.98 (× 2 dd)	—	—	—	−0.12 (dq) <sup>d</sup>
Compound <b>2</b> (C <sub>5</sub> D <sub>5</sub> N)	6.97	—	3.60	2.43	2.27	0.88 (t) <sup>c</sup>	0.32 (q) <sup>d</sup>
Compound <b>3</b> (C <sub>4</sub> D <sub>8</sub> O)	6.68	—	3.54	2.34	2.11	0.16 (t) <sup>c</sup>	−0.58 (q) <sup>d</sup>

<sup>a</sup> (×2) refers to intensity relative to other resonances in same region of the spectrum. <sup>b</sup> *J* = 13, 12, 5 Hz.; <sup>c</sup> *J* = 8 Hz. <sup>d</sup> *J* = 15, 8 Hz. <sup>e</sup> Assignment of chemical shifts to particular methyl group proton resonances was not attempted. <sup>f</sup> *J* = 12, 11, 3 Hz. <sup>g</sup> *J* = 11, 5 Hz. <sup>h</sup> *J* = 13, 3 Hz.

**Table 2**  $^{13}\text{C}$  NMR spectral data for diamine and ethylaluminium derivatives

Compound (solvent)	<i>i</i> -C <sub>ar</sub> N	<i>p</i> -C <sub>ar</sub>	<i>o</i> -C <sub>ar</sub>	<i>m</i> -C <sub>ar</sub>	NCH <sub>2</sub>	<i>p</i> -CH <sub>3</sub>	<i>o</i> -CH <sub>3</sub>	AlCH <sub>3</sub>	AlCH <sub>2</sub>
[NH(Mes)CH <sub>2</sub> ] <sub>2</sub> (C <sub>6</sub> D <sub>12</sub> )	144.15	131.30	130.23	130.02	49.98	20.84	18.55	—	—
(C <sub>6</sub> D <sub>6</sub> )	144.35	131.70	130.36	130.26	49.81	21.10	18.85	—	—
(CDCl <sub>3</sub> )	143.53	131.58	129.91	129.66	49.34	20.69	18.55	—	—
Compound <b>1</b> (C <sub>6</sub> D <sub>6</sub> )	148.86 148.45	(136.95 136.64)	(135.46 134.81 133.91 132.80)	(131.47 <sup>a</sup> 131.38 130.93 130.46)	61.46 52.72	22.85 21.59	21.44 21.15 20.72 20.63	10.81	5.32 (br)
Compound <b>1</b> (CDCl <sub>3</sub> )	148.43 147.83	(136.65 136.46)	(135.14 134.59 133.62 132.54)	(130.97 <sup>a</sup> 130.69 130.28 129.62)	61.06 52.19	22.43 20.99	20.86 20.77 20.51 20.35	10.04	4.57 (br)
Compound <b>2</b> (C <sub>5</sub> D <sub>5</sub> N)	149.63	136.58	130.95	129.97	54.34	21.28	20.20	9.68	0.19 (br)
Compound <b>3</b> (C <sub>4</sub> D <sub>8</sub> O)	150.17	137.48	131.52	129.84	57.74	21.04	20.70	8.80	0.51 (br)

<sup>a</sup> Assignment of chemical shifts in parentheses to particular mesityl group resonances was not attempted.

**Table 3** Crystal data, data collection, and structure refinement for **2** and **3**

	<b>2</b>	<b>3</b>
Formula	C <sub>54</sub> H <sub>72</sub> Al <sub>2</sub> N <sub>6</sub>	C <sub>52</sub> H <sub>78</sub> Al <sub>2</sub> N <sub>4</sub> O <sub>2</sub>
<i>M</i> <sub>r</sub>	859.14	845.14
<i>T</i> /K	110(2)	110(2)
Crystal system	Monoclinic	Monoclinic
Space group	<i>P</i> 2(1)/ <i>c</i>	<i>P</i> 2(1)/ <i>c</i>
<i>a</i> /Å	8.9097(6)	8.5899(5)
<i>b</i> /Å	16.3759(11)	17.0806(9)
<i>c</i> /Å	16.7141(11)	16.3606(9)
$\beta$ /°	94.0710(10)	95.1310(10)
<i>V</i> /Å <sup>3</sup>	2432.5(3)	2390.8(2)
<i>Z</i>	2	2
$\mu$ /mm <sup>−1</sup>	0.102	0.104
Measured refl.	15 955	16 327
Independent refl.	4275	4211
<i>R</i> <sub>int</sub>	0.0384	0.0827
<i>R</i> <sub>1</sub> <sup>a</sup>	0.0642	0.0894
<i>wR</i> <sub>2</sub> <sup>b</sup> [ <i>I</i> > 2σ( <i>I</i> )]	0.1948	0.2180
<i>R</i> <sub>1</sub> <sup>a</sup>	0.0679	0.1330
<i>wR</i> <sub>2</sub> <sup>b</sup> (all data)	0.2016	0.2583

<sup>a</sup>  $R_1 = \sum(F_o - F_c)/\sum F_o$ . <sup>b</sup>  $wR_2 = \{[\sum w(F_o^2 - F_c^2)^2]/[\sum w(F_o^2)^2]\}^{1/2}$ ;  $w = 1/[\sigma^2(F_o^2) + (ap)^2 + bp]$ ;  $p = (F_o^2 + 2F_c^2)/3$ ;  $a = 0.1405$  (**2**), 0.1626 (**3**);  $b = 0.8217$  (**2**), 0.00 (**3**).

spectrum of each compound has one resonance at  $\delta$  57 for **2** and  $\delta$  59 for **3**, which is comparable to that found for **1**. In light of the results of the single crystal X-ray analyses of **2** and **3**, the similarity of the  $^{27}\text{Al}$  NMR chemical shifts of **1**, **2** and **3** supports the tetracoordinated nature of the aluminium center in **1**.

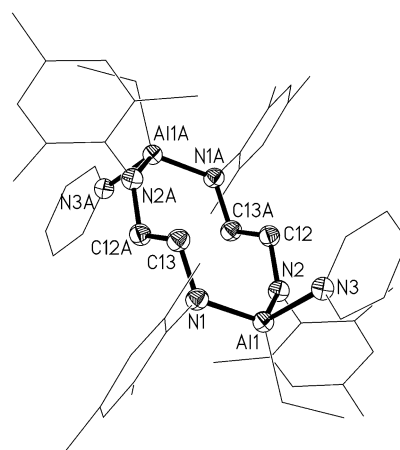
## Conclusions

The aluminium bifunctional amide **1** has been prepared in good yield by an alkane elimination reaction. The NMR spectral data indicated an associated solution structure. Compound **1** acts as a Lewis acid toward pyridine and THF; the corresponding products **2** and **3** contain tetracoordinate aluminium as part of a ten-member heterocycle, as indicated by X-ray diffraction analyses.

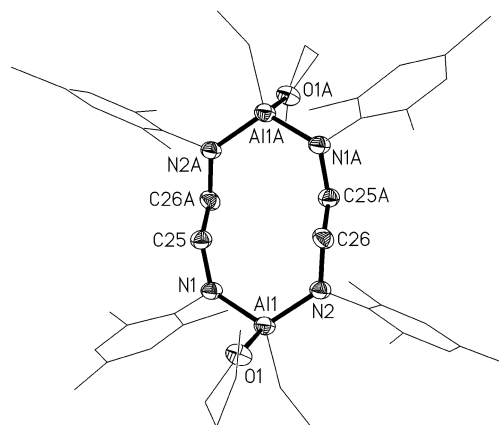
## Experimental

### General comments

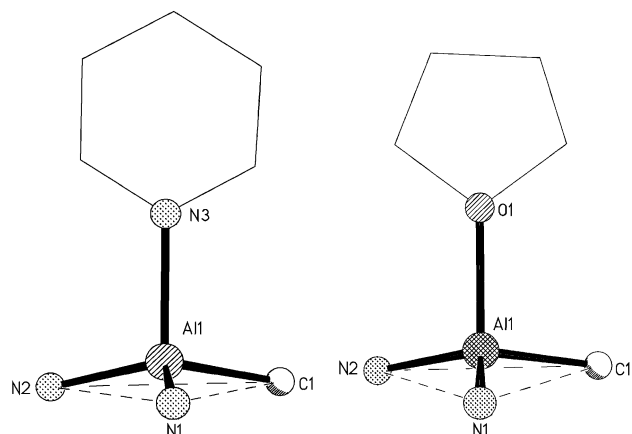
Due to the high air and water sensitivity of triethylaluminium and amido derivatives, all manipulations involving these



**Fig. 1** Molecular structure of **2** in the crystal. Selected bond length (Å) and angles (°): Al(1)–N(2) 1.8352(18), Al(1)–N(1) 1.8499(18), Al(1)–C(1) 1.975(2), Al(1)–N(3) 2.0255(18); N(2)–Al(1)–N(1) 117.08(8), N(2)–Al(1)–C(1) 113.62(9), N(1)–Al(1)–C(1) 116.83(8), N(2)–Al(1)–N(3) 104.08(8), N(1)–Al(1)–N(3) 100.88(8), C(1)–Al(1)–N(3) 100.83(8).



**Fig. 2** Molecular structure of **3** in the crystal. Selected bond length (Å) and angles (°): Al(1)–N(2) 1.832(3), Al(1)–N(1) 1.845(3), Al(1)–O(1) 1.946(3), Al(1)–C(1) 1.973(4); N(2)–Al(1)–N(1) 117.62(14), N(2)–Al(1)–O(1) 102.18(14), N(1)–Al(1)–O(1) 103.63(14), N(2)–Al(1)–C(1) 114.03(16), N(1)–Al(1)–C(1) 115.93(17), O(1)–Al(1)–C(1) 99.82(15).



**Fig. 3** Perspectives emphasizing the coordination environment of the aluminium centers in **2** and **3**. Sum of the angles:  $[N(2)-Al(1)-N(1)+N(2)-Al(1)-C(1)+N(1)-Al(1)-C(1)] = 347.5^\circ$  for **2** and  $347.6^\circ$  for **3**.

compounds were carried out either in a drybox under a purified  $N_2$  atmosphere or by using standard Schlenk techniques. The solvents were commercially available, purified by conventional means, and distilled immediately prior to use.  $AlEt_3$  was used as purchased from Aldrich. The diamine 1,2-[N(H)(Mes)] $_2$ C $_2$ H $_4$  was prepared according to a literature procedure.<sup>18</sup> Atlantic Microlab Inc. (Norcross, GA) performed all elemental analyses. Samples for melting point determinations were contained in flame-sealed capillaries and the reported temperatures are uncorrected. The NMR spectra were recorded by using either Varian Unity 500, Varian Unity Plus 300 ( $^1H$  300 MHz;  $^{13}C\{^1H\}$  75.24 MHz) or Varian Unity Inova 400 ( $^{27}Al$  104.14 MHz) spectrometers. Chemical shifts are reported in ppm and were referenced either to the solvent resonances as internal standards ( $^1H$ ,  $^{13}C$ ) or to 0 ppm for the resonance of a 0.1 M  $AlCl_3$  solution in  $D_2O$  as an external standard.

## Syntheses

**[AlEt( $\mu$ -MesNCH $_2$ CH $_2$ NMes)] $_n$  (**1**).** In the drybox, a 100 mL Schlenk flask fitted with a magnetic stir bar was charged with a solution of 0.569 g (1.92 mmol) of diamine in 30 mL  $C_6H_6$ . Then, 0.222 g (1.94 mmol) of  $AlEt_3$  dissolved in 5 mL  $C_6H_6$  was added by pipette. After the resulting solution had been stirred for 15 h at room temperature, the flask was attached to the Schlenk line by a reflux condenser and drying tube and was consequently heated to reflux for 22 h. Solvent was then removed by vacuum distillation at room temperature to leave a light tan solid. The product was washed with two 5 mL portions of pentane and 0.512 g (76.2% yield based on diamine) of **1** was isolated as a colorless pentane-insoluble solid. Mp: 201–205 °C dec./gas evol. Anal. calc. (found) for  $C_{44}H_{62}N_4Al_2$ : C, 75.39 (74.93); H, 8.91 (8.89); N, 7.99 (7.64%).  $^{27}Al$  NMR ( $C_6D_6$ )  $\delta$  63.3 ( $\omega_{1/2}$  = 3179 Hz). See Tables 1 and 2 for  $^1H$  and  $^{13}C$  NMR spectral data, respectively.

**[AlEt( $\mu$ -MesNCH $_2$ CH $_2$ NMes)] $_2$ ·2py (**2**) and [AlEt( $\mu$ -MesNCH $_2$ CH $_2$ NMes)] $_2$ ·2THF (**3**).** In a typical preparation, a 10 mL Schlenk tube was charged with a magnetic stir bar, approximately 40 mg of **1** and 3 mL of Lewis base. Afterwards, the flask was stoppered with a septum and placed in a 60 °C oil bath for 1 h. Solvent was then removed by vacuum distillation to give either **2** as a bright yellow solid or **3** as a colorless solid in yields greater than 90% based on **1**.

**Compound 2.** Soluble in pyridine, slightly soluble in either benzene or chloroform, insoluble in pentane. Crystals of **2** suitable for X-ray structural studies could be grown either by

slow diffusion of benzene into or by slow evaporation of a pyridine solution of **2**. Mp: 170–175 °C dec., 195 °C gas evol. Anal. calc. (found) for  $C_{54}H_{72}N_6Al_2$ : C, 75.49 (75.55); H, 8.45 (8.35); N, 9.78 (9.65%).  $^{27}Al$  NMR (Py- $d_5$ )  $\delta$  57.4 ( $\omega_{1/2}$  = 2622 Hz). See Tables 1 and 2 for  $^1H$  and  $^{13}C$  NMR spectral data, respectively.

**Compound 3.** Moderately soluble in THF, insoluble in either benzene or pentane. Crystals of **3** suitable for X ray structural studies could be grown either by slow diffusion of pentane into or by slow evaporation of a THF solution of **3**. Mp: 208–212 °C dec. Anal. calc. (found) for  $C_{52}H_{62}D_{16}N_4O_2Al_2$ : C, 72.52 (72.83); H, 9.13 (9.18); N, 6.51 (6.69%).  $^{27}Al$  NMR (THF- $d_8$ )  $\delta$  58.6 ( $\omega_{1/2}$  = 2555 Hz). See Tables 1 and 2 for  $^1H$  and  $^{13}C$  NMR spectral data, respectively.

## Single crystal X-ray analysis

X-Ray data for **2** and **3** were collected on a Bruker SMART-CCD diffractometer using graphite monochromated Mo-K $\alpha$  radiation ( $\lambda$  = 0.71073 Å). The crystals selected for analysis were mounted on a glass fiber. The data were collected using 0.3° wide  $\omega$  scans with a crystal-to-detector distance of 5.0 cm. No absorption corrections were applied. The remaining important crystallographic data is collected in Table 3. The structure was solved by direct methods,<sup>19</sup> which successfully located most of the non-hydrogen atoms. Subsequent refinement<sup>20</sup> on  $F^2$  allowed location of the remaining non-hydrogen atoms. All non-hydrogen atoms were refined anisotropically and the hydrogen atoms were included in calculated positions using a standard riding model.

CCDC reference numbers 167783 and 167784. See <http://www.rsc.org/suppdata/nj/b1/b106488f/> for crystallographic data in CIF or other electronic format.

## Acknowledgements

Financial support from the CONDEA Vista Company is gratefully acknowledged. We also thank the Department of Chemistry at Texas A&M University for making this work possible. The purchase of the X-ray diffractometer was made possible by a grant from the National Science Foundation (CHE-9807975).

## References

- 1 C. C. Chang and M. S. Ameerunisha, *Coord. Chem. Rev.*, 1999, **189**, 199.
- 2 S. J. Schauer and G. H. Robinson, *J. Coord. Chem.*, 1993, **30**, 197.
- 3 P. J. Brothers and P. P. Power, *Adv. Organomet. Chem.*, 1996, **39**, 15.
- 4 For leading references see: S. T. Barry, R. G. Gordon and V. A. Wagner, *Mater. Res. Soc. Symp. Proc.*, 2000, **606**, 83; D. C. Bradley, I. S. Harding, I. A. Maia and M. Motevalli, *J. Chem. Soc., Dalton Trans.*, 1997, 2969; Z. Jiang, L. V. Interrante, D. Kwon, F. S. Tham and R. Kullnig, *Inorg. Chem.*, 1991, **30**, 995.
- 5 E. J. Corey and S. Sarshar, *J. Am. Chem. Soc.*, 1992, **114**, 7938; E. J. Corey, S. Sarshar and D.-H. Lee, *J. Am. Chem. Soc.*, 1994, **116**, 12089.
- 6 N. Imai, H. Takahashi and S. Kobayashi, *Chem. Lett.*, 1994, 177.
- 7 N. Emig, H. Nguyen, H. Krautschied, R. Reau, J.-B. Cazaux and G. Bertrand, *Organometallics*, 1998, **17**, 3599; N. Emig, R. Reau, H. Krautschied, D. Fenske and G. Bertrand, *J. Am. Chem. Soc.*, 1996, **118**, 5822.
- 8 S. G. Nelson, B.-K. Kim and T. J. Peelen, *J. Am. Chem. Soc.*, 2000, **122**, 9318.
- 9 M. Corbellini and A. Balducci, *U.S. Pat.*, 3781318, 1971. D. R. Click and J. G. Watkin, *World Pat. Appl.*, WO1998US06857, 1998.
- 10 K. Knabel, I. Krossing, H. Nöth, H. Schwenk-Kircher, M. Schmidt-Amelunxen and T. Seifert, *Eur. J. Inorg. Chem.*, 1998, **8**, 1095.

- 11 R. Benn, E. Janssen, H. Lehmkuhl and A. Rufinska, *J. Organomet. Chem.*, 1987, **333**, 155; R. Benn, A. Rufinska, H. Lehmkuhl, E. Janssen and C. Kruger, *Angew. Chem., Int. Ed. Engl.*, 1983, **22**, 779.
- 12 A. R. Barron, *Polyhedron*, 1995, **14**, 3197.
- 13 A very similar pattern was reported for [EtAlN(CH<sub>2</sub>Ph)(μ-CH<sub>2</sub>Ph)]<sub>2</sub>; E. K. Styron, C. H. Lake, C. L. Watkins, L. K. Krannich, C. D. Incarvito and A. L. Rheingold, *Organometallics*, 2000, **19**, 3253.
- 14 M. G. Gardiner, S. M. Lawrence and C. L. Raston, *J. Chem. Soc., Dalton Trans.*, 1996, 4163.
- 15 S. J. Trepanier and S. Wang, *J. Chem. Soc., Dalton Trans.*, 1995, 2425.
- 16 J. Pinkas, B. Gaul and J. G. Verkade, *J. Am. Chem. Soc.*, 1993, **115**, 3925; S. Dagorne, I. A. Guzei, M. P. Coles and R. F. Jordan, *J. Am. Chem. Soc.*, 2000, **122**, 274.
- 17 T. Krossing, H. Nöth and H. Swenk-Kircher, *Eur. J. Inorg. Chem.*, 1998, 927; H. Hoberg, V. Gotor, A. Milchereit, C. Kruger and J.C. Sekutowski, *Angew. Chem., Int. Ed. Engl.*, 1977, **16**, 539.
- 18 H. Chen, R. A. Bartlett, H. V. Rasika Dias, M. M. Olmstead and P. P. Power, *Inorg. Chem.*, 1991, **30**, 2487.
- 19 G. M. Sheldrick, SHELXS97, Program for Automatic Solution of Crystal Structures, University of Göttingen, Germany, 1991.
- 20 G. M. Sheldrick, SHELXL97, Program for Crystal Structure Refinement, University of Göttingen, Germany, 1997.