Syntheses and Structures of a Four-co-ordinate Monomeric Dialkylaluminium Complex and a Cyclic Trimeric Alkylaluminium Propeller Complex with a Bidentate Amide Ligand, $\mathrm{Al(PhNCH_2CH_2NH_2)Me_2}$ and $\mathrm{[Al(\mu\text{-}PhNCH_2CH_2NH)Me]_3}$†

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The reaction of $\mathrm{AlMe_3}$ with *N*-phenylethylenediamine in toluene at 0 °C yielded a mononuclear complex $\mathrm{Al(PhNCH_2CH_2NH_2)Me_2}$ **1** as the major product and a trinuclear cyclic complex $\mathrm{[Al(\mu\text{-}PhNCH_2CH_2NH)Me]_3}$ **2** as a minor product. The trinuclear complex was obtained as the major product when the reaction was carried out at 25 °C. The crystal structure of **1** and a *cis* isomer of **2**, where all three methyl groups on the aluminium centres occupy the *cis*-axial positions of a chair conformation, have been determined by single-crystal X-ray diffraction analysis. Compound **1** can be converted into **2** either by heating or by allowing the solution to stand at 23 °C for a few days. Crystal data: **1**, orthorhombic, space group $P2_12_12_1$, $a = 10.304(3)$, $b = 13.172(5)$, $c = 8.552(3)$ Å, $Z = 4$; **2**, trigonal, space group $P\bar{3}$ (no. 147, hexagonal setting), $a = b = 16.441(7)$, $c = 11.184(3)$ Å, $Z = 2$.

There is much current interest in organoaluminium amido and imido complexes due to their versatile structural and bonding features and their potential applications in materials and catalysis.[1] Most previously characterized alkylaluminium amido and imido complexes involve monodentate amide and imide ligands. The few known complexes with polydentate amide and imide ligands are limited to aliphatic amine ligands such as ethylenediamine and diethylenetriamine.[2] We have been interested in building polynuclear alkylaluminium complexes by using polydentate primary or secondary amines containing an aromatic amino or pyridyl group because we believe that these complexes could display unusual structural and electronic properties, in contrast to the organoaluminium complexes with aliphatic amines only.[3] In this report the reactions of *N*-phenylethylenediamine with trimethylaluminium are described. The synthesis and structure of a new mononuclear complex $\mathrm{Al(PhNCH_2CH_2NH_2)Me_2}$ and its conversion into a novel cyclic trinuclear complex $\mathrm{[Al(\mu\text{-}PhNCH_2CH_2NH)Me]_3}$ are presented.

Experimental

All reactions were performed under a dry nitrogen atmosphere by using the standard Schlenk-line techniques. Crystallization and crystal mounting were carried out in an inert-atmosphere dry-box. Solvents were freshly distilled over the appropriate drying reagent under nitrogen prior to use. Trimethylaluminium and *N*-phenylethylenediamine were obtained from Aldrich. Proton NMR spectra were recorded on a Brüker AC-300 spectrometer. Elemental analyses were performed by Canadian Microanalytical Service, Delta, British Columbia.

Synthesis of $\mathrm{Al(PhNCH_2CH_2NH_2)Me_2}$ **1**.—A 2.0 mol dm^{-3} solution of $\mathrm{AlMe_3}$ (2.0 cm^3, 4.0 mmol) in toluene was added to *N*-phenylethylenediamine (544 mg, 4.0 mmol) dissolved in toluene (10 cm^3) at 0 °C. After the mixture had been stirred for 0.5 h at 0 °C, the solvent was removed *in vacuo* and a white solid **1** was obtained (650 mg, 3.39 mmol, yield 85%). ^{1}H NMR ($\mathrm{C_6D_5CD_3}$): δ −0.58 (s, 6 H, Al–CH$_3$), 0.67 [t, br, 2 H, NH$_2$, $J(\mathrm{H_x{-}H_a}) = 6$], 1.98 [qnt, 2 H, CH$_{2\mathrm{a}}$, $J(\mathrm{H_x{-}H_a}) = J(\mathrm{H_a{-}H_b}) = 6$ Hz], 2.63 (t, 2 H, CH$_{2\mathrm{b}}$), 6.68 (m, 3 H, CH) and 7.24 (m, 2 H, CH) (Found: C, 60.55, 60.90; H, 8.75, 8.30; N, 14.55, 14.00. Calc. for $\mathrm{C_{10}H_{17}AlN_2}$: C, 62.50; H, 8.85; N, 14.55%). Repeated analyses on crystalline samples from different batches of syntheses produced similar results. Although low carbon contents in aluminium amido and imido complexes have frequently been observed previously and attributed to the incomplete combustion of the sample,[4] it is not clear yet to us why a reasonable analytical result was obtained for **2** but not for **1**.

Conversion of Compound **1** *to* $\mathrm{Al_3(\mu\text{-}PhNCH_2CH_2NH)_3Me_3}$ **2**.—A solution of compound **1** (0.28 g, 1.45 mmol) in toluene (10 cm^3) was heated at 80 °C for 1 h. Upon cooling a microcrystalline solid **2** precipitated (dry weight 0.18 g, 0.34 mmol, yield 70%). ^{1}H NMR of crystals of the *cis* isomer characterized by single-crystal X-ray diffraction analysis ($\mathrm{C_6D_5CD_3}$, 297 K): δ −0.62 (s, 3 H, Al–CH$_3$), 0.14 [dd, 1 H, NH, $J(\mathrm{H_x{-}H_a}) = 14$, $J(\mathrm{H_x{-}H_{a'}}) = 4$], 2.13 [m, 1 H, CH$_\mathrm{a}$, $J(\mathrm{H_a{-}H_b}) = 11$, $J(\mathrm{H_a{-}H_{a'}}) = 12$, $J(\mathrm{H_a{-}H_{b'}}) = 6$], 2.46 [m, 1 H, CH$_\mathrm{b}$, $J(\mathrm{H_b{-}H_{b'}}) = 11$, $J(\mathrm{H_b{-}H_{a'}}) = 5$ Hz] and 2.77–2.82 [m, 2 H, CH$_{\mathrm{a'}}$ and CH$_{\mathrm{b'}}$, $J(\mathrm{H_{a'}{-}H_{b'}})$ is believed to be 2–3 Hz, but could not be determined due to the overlap of CH$_{\mathrm{a'}}$ and CH$_{\mathrm{b'}}$], 6.50 (d, 2 H, CH), 6.83 (m, 1 H, CH) and 7.30 (m, 2 H, CH) (Found: C, 61.95; H, 7.45; N, 15.40. Calc. for the vacuum-dried sample $\mathrm{C_{27}H_{39}Al_3N_6}$: C, 61.35; H, 7.40; N, 15.90%). Compound **2** can also be obtained from the direct reaction of $\mathrm{AlMe_3}$ with *N*-phenylethylenediamine at 25 °C for a few hours.

X-Ray Crystallographic Analysis.—A colourless plate crystal of compound **1** obtained from a concentrated toluene solution was mounted in a 0.5 mm capillary. Compound **2** cocrystallizes with a toluene solvent molecule and the crystal undergoes rapid decomposition upon isolation from the solution due to the loss of this molecule. The colourless hexagonal crystal of **2** was

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.

therefore sealed in the capillary along with the mother-liquor. Data were collected at 23 °C over the range 2θ 3–50° for **1** and 3–45° for **2** on a Rigaku AFC6S diffractometer with graphite-monochromated Mo-Kα radiation, operated at 50 kV and 35 mA. Three standard reflections were measured every 147. The crystal of compound **2** had lost about 6% intensity at the end of data collection while no significant decay was observed for **1**. The total number of unique reflections collected was 1219 for **1** and 2075 for **2**. Data were processed on a Silicon Graphics computer using the TEXSAN crystallographic package[5a] and corrected for decay and Lorentz-polarization effects. Neutral-atom scattering factors were taken from Cromer and Waber.[5b]

The crystal of compound **1** belongs to the orthorhombic space group $P2_12_12_1$ (no. 19) uniquely determined by the systematic absences ($h00$, $h = 2n + 1$, $0k0$, $k = 2n + 1$, $00l$, $l = 2n + 1$). The crystal of **2** belongs to the trigonal crystal system. The data for **2** were collected by using the unit-cell parameters of the hexagonal setting. No systematic absences were observed for **2** in accord with both space group $P3$ (no. 143) and $P\bar{3}$ (no. 147). Based on a statistical analysis of the intensity distribution, the centrosymmetric space group $P\bar{3}$ was chosen. The correctness of this choice was also confirmed by the successful solution and refinement of the structure. Both structures were solved by direct methods. Full-matrix least-square refinements minimizing the function $\Sigma w(|F_o| - |F_c|)^2$ were applied. Owing to the limitation of data the metal atom and some of the nitrogen and carbon atoms in **1** were refined anisotropically while only metal atoms and nitrogen atoms in **2** were refined anisotropically. Only about 20% reflections $[I \geqslant 2\sigma(I)]$ were observed for **2**. To reduce the number of parameters, the toluene solvent molecule in **2** was refined as a rigid body. The methyl group [C(16)] appeared to have some degree of disorder as evidenced by its large thermal parameter. However, this disorder could not be modelled because of insufficient data. The positions of hydrogen atoms were either located directly from the Fourier-difference maps or calculated, except those bonded to the methyl group [C(16)] of the toluene solvent molecule in **2**. The high R factor for compound **2** could be attributed to the insufficient number of observed reflections. The crystallographic data are given in Table 1.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Results and Discussion

Synthesis and Structure of $Al(PhNCH_2CH_2NH_2)Me_2$ **1**.—The reaction of *N*-phenylethylenediamine with 1 equivalent of $AlMe_3$ at 0 °C produces a mononuclear compound, $Al(PhNCH_2CH_2NH_2)Me_2$ **1**, in a nearly quantitative yield with the formation of methane. The *N*-phenylethylenediamine ligand has two potentially reactive sites toward the $AlMe_3$ complex, the primary amino group NH_2 and the secondary amino group NHPh. Only one NH resonance integrating for two hydrogen atoms was observed in the ^1H NMR spectrum of **1**. By comparing with the ^1H NMR spectrum of the free amine which shows clearly two distinct NH resonances corresponding to NH_2 and NHPh, respectively, this NH signal was attributed to the primary NH_2 group. The ^1H NMR result therefore implied that the proton of the NHPh group had been eliminated in compound **1**. This was further confirmed by the X-ray diffraction analysis. An ORTEP[6] drawing of the crystal structure of **1** is shown in Fig. 1. Atomic coordinates are listed in Table 2, selected bond lengths and angles in Table 3.

The aluminium atom in compound **1** is co-ordinated by two methyl ligands and two nitrogen atoms in an approximately tetrahedral environment. The Al–N and Al–C bond distances are in the usual ranges. The Al–N(2) bond length of 1.89(1) Å, however, is substantially shorter than that of Al–N(1) [1.98(1) Å], consistent with the N(2) atom being part of an amide ligand, since an amido nitrogen atom usually forms a shorter Al–N bond than does an amino nitrogen atom, owing to its relatively high affinity for Al^{III}. The formation of the N(2) amido group is further evidenced by its planar geometry [Al–N(2)–C(4) 113.1(8), Al–N(2)–C(5) 127.4(8), C(4)–N(2)–C(5) 119(1)°] and the short N(2)–C(5) bond length [1.35(1) Å], indicative of the lone-pair conjugation with the phenyl ring. The preferential deprotonation of the N(2) site can be attributed to the higher acidity of the proton on the N(2) atom ($pK_a \approx 5.0$), relative to that on N(1) ($pK_a \approx 10.5$).[7] To understand further the structure of **1** an extended-Hückel molecular orbital (EHMO) calculation was performed using the crystallographic coordinates.[8] The calculation results agree with the presence of significant π-orbital overlaps between N(2) and C(5) which is about 30% greater than that between N(2) and C(4) where no significant π bonding is expected. The net overlap population between N(2) and Al is about 16% greater than that between N(1) and Al, consistent with the shorter Al–N(2) bond. The net charge on N(2) is −0.96, twice that on N(1) (−0.49), in agreement with atom N(2) being from an amide ligand.

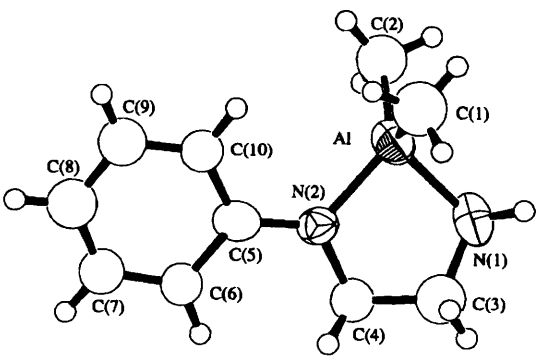


Fig. 1 An ORTEP diagram for compound **1** with 50% thermal ellipsoids and labelling scheme

Alkylaluminium amido complexes usually exist as polynuclear species such as dimers and trimers due to the bridging tendency of the amido group.[1–3] It has been demonstrated previously by Power and co-workers[9] that mononuclear three-co-ordinate alkylaluminium complexes with a monodentate amide ligand can be obtained when bulky alkyl ligands or amide ligands with bulky substituents are employed.[9] The four-co-ordinate structure displayed by **1** was proposed by Beachley and Racette[10] nearly two decades ago for mononuclear dialkylaluminium complexes with bidentate diamines $RHNCH_2CH_2NR'_2$, where R and R′ are aliphatic substituents. To our knowledge, compound **1** is the only structurally characterized example of a mononuclear dialkylaluminium complex with a bidentate amide ligand. Certain monomeric $Al(R'NCH_2CH_2NR''_2)R_2$ complexes have been shown to be in equilibrium with the dimeric species $[Al(R'NCH_2CH_2NR''_2)R_2]_2$ in solution where steric and electronic factors have been found to play an important role.[10] The crystal structure of **1** has no symmetry, the two methyl groups being in different environments. However, in solution only one methyl resonance was detected in the ^1H NMR spectrum in the temperature range 180–298 K. The chemical shifts of the protons on the methylene groups and the NH group displayed a typical XA_2B_2 pattern and experienced little change with temperature. No new resonances were observed at low temperature. Compound **1** is only slightly soluble in benzene or toluene ($\approx 4.4 \times 10^{-2}$ mol dm^{-3} in toluene at 25 °C). Nevertheless, the NMR spectra of a saturated solution and a dilute solution of **1** were examined at various temperatures and no concentration-dependent phenomena were observed. The presence of a monomer–dimer interconversion was therefore considered to be unlikely. The ^1H NMR spectra could be best explained by the existence of a rapid fluctuation beween two puckered five-membered rings which averages the chemical environments of the two methyl groups

Table 1 Crystallographic data

Compound	**1**	**2**
Formula	$C_{10}H_{17}AlN_2$	$C_{27}H_{39}Al_3N_6\cdot 3C_7H_8$
M	192.2	805.0
Crystal system	Orthorhombic	Trigonal
Space group	$P2_12_12_1$ (no. 19)	$P\bar{3}$ (no. 147, hexagonal setting)
a/Å	10.304(3)	16.441(7)
b/Å	13.172(5)	16.441(7)
c/Å	8.552(3)	11.184(3)
U/Å^3	1160.7(6)	2618(1)
Z	4	2
D_c/g cm^{-3}	1.10	1.02
Crystal size/mm	0.10 × 0.20 × 0.20	0.20 × 0.30 × 0.40
μ(Mo-Kα)/cm^{-1}	1.35	1.07
2θ Range/°	3–50	3–45
Reflections measured, observed	$+h, +k, +l$, 1219, 387 [$I > 3.00\,\sigma(I)$]	$\pm h, +k, +l, h + k \geqslant 0$, 2075, 373 [$I > 2.00\,\sigma(I)$]
No. of parameters refined	73	77
Largest shift/e.s.d. in final cycle	0.00	0.02
Largest electron-density peak/e Å^{-3}	0.23	0.23
R^a	0.057	0.105
R'^b	0.039	0.067

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2]^{\frac{1}{2}}$, $w = 1/\sigma^2(F_o)$.

Table 2 Positional parameters

Atom	*x*	*y*	*z*
Compound **1**			
Al	0.9798(4)	0.0711(3)	0.1728(5)
N(1)	1.031(1)	0.1031(7)	0.391(1)
N(2)	1.078(1)	−0.0494(7)	0.197(1)
C(1)	0.792(1)	0.052(1)	0.159(2)
C(2)	1.060(1)	0.173(1)	0.036(1)
C(3)	1.062(1)	0.005(1)	0.465(1)
C(4)	1.137(1)	−0.059(1)	0.350(1)
C(5)	1.111(1)	−0.1168(9)	0.084(1)
C(6)	1.204(1)	−0.197(1)	0.104(1)
C(7)	1.231(1)	−0.260(1)	−0.022(2)
C(8)	1.167(1)	−0.253(1)	−0.159(2)
C(9)	1.076(1)	−0.178(1)	−0.183(2)
C(10)	1.051(1)	−0.1112(8)	−0.064(1)
Compound **2**			
Al	0.5561(7)	0.3489(7)	0.0530(7)
N(1)	0.681(1)	0.448(1)	0.017(2)
N(2)	0.506(1)	0.386(1)	−0.066(2)
C(1)	0.671(2)	0.473(2)	−0.112(3)
C(2)	0.578(2)	0.462(2)	−0.132(2)
C(3)	0.526(2)	0.342(2)	0.226(2)
C(4)	0.417(2)	0.357(2)	−0.097(3)
C(5)	0.385(2)	0.395(2)	−0.187(2)
C(6)	0.288(3)	0.352(2)	−0.207(2)
C(7)	0.224(2)	0.285(3)	−0.148(3)
C(8)	0.248(3)	0.237(2)	−0.059(3)
C(9)	0.347(3)	0.281(2)	−0.032(3)
C(10)	1.005(2)	0.235(2)	0.672(2)
C(11)	0.930(1)	0.257(1)	0.624(1)
C(12)	0.957(1)	0.342(1)	0.567(1)
C(13)	0.889(2)	0.361(1)	0.523(1)
C(14)	0.794(1)	0.296(2)	0.537(1)
C(15)	0.767(1)	0.211(1)	0.595(2)
C(16)	0.835(2)	0.191(1)	0.638(1)

and the protons of the methylene group. We believe that the lack of a monomer–dimer equilibrium is caused by the conjugation of the lone pair of the amido N(2) atom with the aromatic ring which prevents it from forming the additional Al–N bond, thus stabilizing the mononuclear structure. The structures of the mononuclear four-co-ordinate aluminium complexes Al(H)-Cl(Bu^{t}NCH$_2$CH$_2$NHBu^t)[11a] and AlCl$_2$(EtNCH$_2$CH$_2$N-Me$_2$)[11b] were reported previously, and are apparently stabilized by the electron-withdrawing chloride ligand.

Table 3 Selected bond lengths (Å) and angles (°)

Compound **1**			
Al–N(1)	1.98(1)	C(3)–C(4)	1.51(2)
Al–N(2)	1.89(1)	N(1)–C(3)	1.47(1)
Al–C(1)	1.96(1)	N(2)–C(4)	1.45(1)
Al–C(2)	1.96(1)	N(2)–C(5)	1.35(1)
N(1)–Al–N(2)	86.2(4)	N(1)–C(3)–C(4)	108(1)
N(1)–Al–C(1)	110.3(6)	N(2)–C(4)–C(3)	109(1)
N(1)–Al–C(2)	107.6(5)	N(2)–C(5)–C(6)	125(1)
N(2)–Al–C(1)	115.5(5)	N(2)–C(5)–C(10)	120(1)
N(2)–Al–C(2)	114.2(5)	C(1)–Al–C(2)	118.0(6)
Al–N(1)–C(3)	106.2(7)	Al–N(2)–C(4)	113.1(8)
Al–N(2)–C(5)	127.4(8)	C(4)–N(2)–C(5)	119(1)
Compound **2***			
Al–N(1)	1.92(2)	C(6)–C(7)	1.27(4)
Al–N(1′)	1.92(3)	C(7)–C(8)	1.45(6)
Al–N(2)	1.83(2)	C(8)–C(9)	1.44(6)
Al–C(3)	1.99(3)	N(1)–C(1)	1.53(4)
N(2)–C(2)	1.42(3)	N(2)–C(4)	1.34(4)
C(1)–C(2)	1.48(5)	C(4)–C(5)	1.43(5)
C(4)–C(9)	1.40(4)	C(5)–C(6)	1.40(5)
N(1)–Al–N(1′)	107(1)	N(2)–C(4)–C(9)	117(3)
N(1)–Al–N(2)	92(1)	C(5)–C(4)–C(9)	116(3)
N(1)–Al–C(3)	112.5(9)	C(4)–C(5)–C(6)	118(2)
N(1′)–Al–N(2)	112(1)	C(5)–C(6)–C(7)	127(4)
N(1′)–Al–C(3)	105(1)	C(6)–C(7)–C(8)	121(4)
N(2)–Al–C(3)	126(1)	C(7)–C(8)–C(9)	114(3)
Al–N(1)–Al′	124(1)	C(4)–C(9)–C(8)	124(3)
Al–N(1)–C(1)	102(1)	C(2)–N(2)–C(4)	118(3)
Al′–N(1)–C(1)	116(2)	N(1)–C(1)–C(2)	110(2)
Al–N(2)–C(2)	111(2)	N(2)–C(2)–C(1)	113(3)
Al–N(2)–C(4)	131(2)	N(2)–C(4)–C(5)	127(2)

* Atoms related by the C_3 symmetry operation are labelled with a prime.

Synthesis and Structure of [Al(μ-PhNCH$_2$CH$_2$NH)Me]$_3\cdot$3C$_6$H$_5$Me **2**.—Compound **2** was isolated initially from the reaction of AlMe$_3$ with *N*-phenylethylenediamine in a 1 : 1 ratio in toluene at 25 °C. The structural characterization of compound **2** proved to be quite challenging because of the cocrystallization of the toluene solvent molecule. The crystals of compound **2** collapse rapidly upon isolation from the solution. Fortunately after many attempts we were able to carry out an

X-ray diffraction analysis for one of the crystals and determined its composition as $[Al(\mu\text{-}PhNCH_2CH_2NH)Me]_3\cdot3C_6H_5Me$. Atomic positional parameters are listed in Table 2, selected bond lengths and angles in Table 3. As shown in Figs. 2 and 3, compound **2** has a cyclic propeller structure and C_3 symmetry. The three aluminium atoms are linked together *via* three primary amido nitrogen atoms. The six-membered Al_3N_3 ring has a chair conformation with the three methyl groups occupying the *cis*-axial positions. As observed in **1**, the secondary amido N(2) atom has a planar geometry [sum of the three angles around N(2) is 358°] and co-ordinates to one aluminium only. The short N(2)–C(4) bond length of 1.34(4) Å again suggests the presence of a significant conjugation of the lone pair with the phenyl ring. The N(1) atom in **2** functions as a bridging amide ligand. The Al–N bond lengths are shorter than those in **1** while the Al–C bond length is comparable to those in **1**. The proton on the N(1) atom, although not located by X-ray diffraction analysis, is believed to occupy the *cis*-equatorial positions of the six-membered ring with respect to the three methyl groups, as evidenced by the pyramidal geometry of N(1). The ideal position of this proton was calculated by assuming a tetrahedral geometry of N(1). No significant π interactions between the toluene solvent molecule and the ligand in **2** were observed in the X-ray diffraction analysis. The cocrystallization of the toluene molecules could be attributed to the packing requirement of the crystal lattice. Several cyclohexane-like trinuclear aluminium amido complexes have been reported previously which involve monodentate amide ligands only.[12] Compound **2** is the first example of a trinuclear alkylaluminium complex with a bidentate amide ligand and a cyclic propeller structure.

The solution behaviour of the *cis* isomer was examined by ^{1}H NMR spectroscopy. The spectrum shows one methyl resonance, a double doublet NH signal, and four resonances owing to the CH_2 protons. The coupling patterns displayed by these protons are consistent with a XAA′BB′ system and the crystal structure. Homodecoupling experiments were performed which unambiguously established the chemical shifts of NH_x, CH_a and CH_b, and the coupling constants of $J(H_x\text{–}H_a)$, $J(H_x\text{–}H_{a'})$, $J(H_a\text{–}H_b)$, $J(H_a\text{–}H_{a'})$, $J(H_b\text{–}H_{b'})$, $J(H_a\text{–}H_{b'})$ and $J(H_b\text{–}H_{a'})$. The chemical shifts of $CH_{a'}$ and $CH_{b'}$ and $J(H_{a'}\text{–}H_{b'})$ could not be determined accurately by NMR experiments because of the overlap of the $CH_{a'}$ and $CH_{b'}$ resonances. Nevertheless, the spectra confirmed that compound **1** retains its cyclic structure in solution. When a solution of **2** was kept for an extended period at 25 °C, although compound **2** was still dominant other species appeared to form along with a weak methane signal, as monitored by NMR spectroscopy. The new species have not yet been characterized. It is, however, possible that compound **2** underwent further elimination of methane to form higher-nuclearity species such as $[Al(NPhCH_2CH_2N)]_6$.

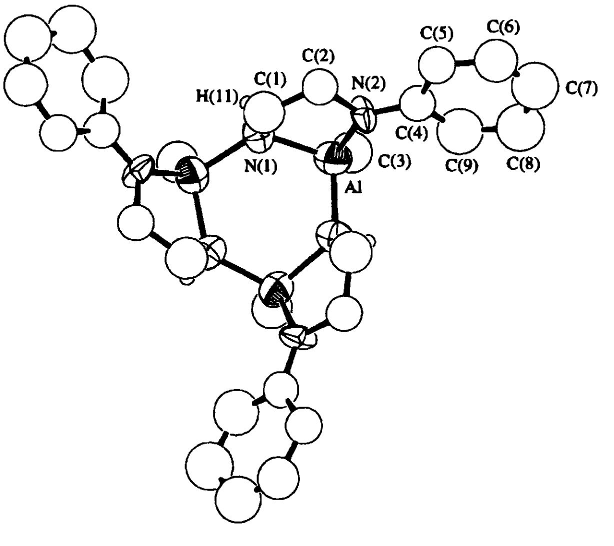


Fig. 2 An ORTEP diagram for compound **2** with 50% thermal ellipsoids and labelling scheme

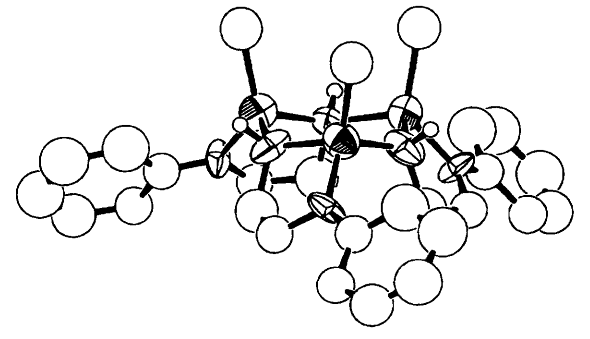
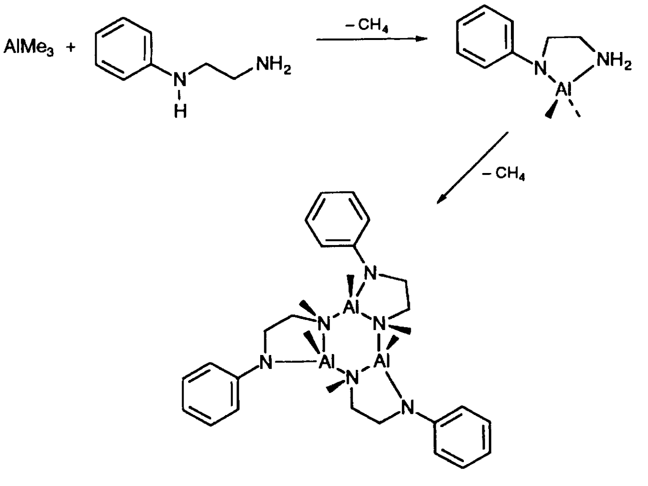


Fig. 3 Side view and conformation of compound **2**

Since both compounds **1** and **2** were obtained from similar reactants, but at different temperatures, we anticipated that compound **1** may be the precursor to **2**. The behaviour of **1** in solution was therefore examined by ^{1}H NMR spectroscopy. There was no apparent change in the spectrum immediately after dissolution in the solvent at 23 °C. At elevated temperature or prolonged standing at 23 °C, however, methane formation was detected with a gradual decrease in the Al–CH_3 signal of **1** and the appearance of the Al–CH_3 signal of compound **2**. Complete conversion of **1** into **2** can be achieved after prolonged heating of **1** at 80 °C (Scheme 1). In the Al–CH_3 region, in addition to the dominant signal of the characterized *cis* isomer of **2**, several new Al–CH_3 resonances were also observed. A similar spectral pattern was also observed after the solution of **1** was kept at 23 °C for several days. The results of elemental analysis on the sample obtained by heating **1** to 80 °C agree with the formula of **2**. We therefore believe that these new signals are likely caused by the formation of other stereoisomers of **2**. If only the relative positions of the three protons on the amido nitrogen atoms and the three methyl groups on the aluminium centres are considered, there are ten non-equivalent stereoisomers. In fact most of the crystals obtained from the conversion of **1** into **2** have a hexagonal shape, determined by X-ray diffraction to be the *cis* isomer of **2**. Among them a few rectangular-shaped crystals were also observed, which also contain toluene solvent molecules and collapse rapidly upon isolation from solution. We believe that these are likely to be one of the unidentified isomers of **2**. Unfortunately, attempts to characterize them by X-ray diffraction analysis were unsuccessful. As a consequence of the lack of crystal



Scheme 1

information, a conclusive ^{1}H NMR assignment for the structurally unidentified compounds cannot be achieved at this time. Efforts are being made to identify other stereoisomers of **2** and the possible high-nuclearity products in this system.

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