Synthesis and Characterization of New Dimeric Aminoalanes†

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The dimeric aminoalanes $[Me_2AlN(C_6H_{11})_2]_2$ **1**, $(Me_2AlNBu^i_2)_2$ **2**, $[(2,4,6\text{-}Me_3C_6H_2)_2AlNH_2]_2$ **4**, $[Cl_2AlN(C_6H_{11})_2]_2$ **5**, $(Me_2AlNHCH_2C_5H_4N\text{-}2)_2$ **6** and the ammonia adduct $(2,4,6\text{-}Me_3C_6H_2)_3Al{\cdot}NH_3$ **3** have been prepared by the reaction of substituted alanes with different amines. They have been fully characterized by elemental analyses, IR, NMR and mass spectrometry. The crystal structures of **1**, **5** and **6** have been determined. Those of **1** and **6** display slightly folded four-membered rings with alternating aluminium and nitrogen atoms, while **5** consists of a square-planar Al_2N_2 ring system.

The first aminoalane, dimeric $(Me_2AlNMe_2)_2$, was prepared in 1942 by Davidson and Brown.[1] The interest in aminoalanes $(R_2AlNR'_2)_n$ increased in the last decade due to their use in material chemistry as precursors for generating thin layers of aluminium nitride.[2] A major reaction in the synthesis of such compounds is that of organo-substituted alanes with primary or secondary amines. Another route is the salt elimination of organoaluminium halides with lithiated amines.[3] Most aminoalanes are dimeric, but trimers and higher aggregated species are also known.[4] In the case of large groups like cyclohexyl and 2-pyridylmethyl on aluminium monomeric Al–N systems might be expected. However, the driving force for dimerization is electronic in origin and the preferred co-ordination numbers of aluminium and nitrogen in such systems are four. Recently Power and co-workers[5] published the first structurally characterized monomeric aminoalanes with sterically demanding groups at both the metal and the nitrogen atoms. Another trend is represented by intramolecular adduct-stabilized aminoalanes, *e.g.* $AlCl(H)(Bu^tHNCH_2CH_2NBu^t)$.[6]

Herein we report on the synthesis, characterization and molecular structures of different types of aminoalanes. $[Me_2AlN(C_6H_{11})_2]_2$ and $(Me_2AlNBu^i_2)_2$ were prepared by the reaction of $AlMe_3$ with $NH(C_6H_{11})_2$ and $NHBu^i_2$, respectively; $[(2,4,6\text{-}Me_3C_6H_2)_2AlNH_2]_2$ was isolated from the thermolysis of the adduct $(2,4,6\text{-}Me_3C_6H_2)_3Al{\cdot}NH_3$; treatment of $AlCl_3$ with $Li[N(C_6H_{11})_2]$ afforded $[Cl_2AlN(C_6H_{11})_2]_2$, an example of a structurally characterized halide-substituted aminoalane. An example of an aminoalane stabilized by intramolecular adduct formation is $(Me_2AlNHCH_2C_5H_4N\text{-}2)_2$ which has been prepared by the reaction of $AlMe_3$ with 2-pyridylmethylamine.

Experimental

General Procedures.—All experiments were performed using Schlenk techniques under a dry nitrogen atmosphere due to the extreme sensitivity of the reactants and products towards moisture and air. Solvents were freshly distilled from sodium under nitrogen and degassed prior to use. Trimethylalane was obtained from Aldrich Chemical Co. Ammonia was dried over sodium prior to use. The amines $NH(C_6H_{11})_2$ and $NHBu^i_2$ were purified by distillation from CaH_2 under reduced pressure. The compound $Al(C_6H_2Me_3\text{-}2,4,6)_3$ was prepared by the literature method.[7]

Physical Methods.—Infrared spectra were recorded on a Bio-Rad FTS 7 FT-infrared spectrometer as Nujol mulls in the range 4000–400 cm^{-1}, electron-impact (EI) mass spectra on Finnigan MAT 8230 or Varian CH 5 instruments and ^1H NMR spectra on Bruker AM 250 or AM 400 spectrometers externally referenced to tetramethylsilane. Elemental analyses were performed by the Analytisches Labor des Instituts für Anorganische Chemie der Universität Göttingen.

Syntheses.—$[Me_2AlN(C_6H_{11})_2]_2$ **1**. A solution of $AlMe_3$ (13.1 cm^3, 45 mmol, 25% in hexane) was added dropwise to a solution of $NH(C_6H_{11})_2$ (9.1 g, 50 mmol) in pentane (50 cm^3) at −78 °C. After warming to room temperature and stirring for 2 h the solvent was removed under reduced pressure and the precipitated white solid was heated for 10 min at 170 °C. Methane evolution was apparent. Crystallization of the residue from hexane led to 7.5 g (31.5 mmol) colourless crystals of compound **1** (70%), m.p. 239 °C. ^1H NMR (C_6D_6): δ 3.22 [tt, *J*(HH) 10, *J*(HH) 2 Hz, 4 H, NCH], 2.15–0.88 (m, 40 H, C_6H_{11}) and −0.23 (s, 12 H, $AlCH_3$) (Found: C, 70.1; H, 11.7; N, 5.7. Calc. for $C_{28}H_{56}Al_2N_2$: C, 70.8; H, 11.8; N, 5.9%). IR: 1263m, 1192s, 1161m, 1085m, 1050m, 1021m, 970m, 942s, 900s, 835m, 792m, 777m, 732vs, 682vs, 662s, 622m, 562m and 449m cm^{-1}. Mass spectrum: *m*/*z* (relative intensity) 474 (*M*, 8), 459 (*M* $-CH_3$, 100) and 237 (*M*/2, 50).

$(Me_2AlNBu^i_2)_2$ **2**. A solution of $AlMe_3$ (30 cm^3, 0.1 mol) in hexane was added dropwise to a solution of $NHBu^i_2$ (17.2 cm^3, 0.1 mol) in pentane (50 cm^3). After warming to room temperature and stirring for 2 h the solvent was removed under reduced pressure and the precipitated white solid was heated for 10 min at 130 °C. Methane evolution was apparent. Crystallization of the residue from hexane led to 24.8 g (67 mmol) of colourless crystals of compound **2** (67%), m.p. 68 °C. ^1H NMR (C_6D_6): δ 3.45–3.15 (m, 8 H, NCH_2), 2.00–1.75 (m, 4 H, CH), 1.25–0.75 (m, 24 H, CH_3) and −0.21 to −0.30 (m, 12 H, $AlCH_3$) (Found: C, 61.8; H, 12.9; N, 6.5. Calc. for $C_{20}H_{48}Al_2N_2$: C, 64.6; H, 12.9; N, 7.5%). IR: 1260s, 1200s, 1118vs, 1020s, 983m, 920m, 890m, 799s, 742vs and 682s cm^{-1}. Mass spectrum: *m*/*z* 370 (*M*, 22) and 355 (*M* − CH_3, 100).

$(2,4,6\text{-}Me_3C_6H_2)_3Al{\cdot}NH_3$ **3**. A two-fold excess of ammonia was condensed on to a solution of $Al(C_6H_2Me_3\text{-}2,4,6)_3$ (7.4 g, 19.2 mmol) in hexane (50 cm^3) at −196 °C. After warming to room temperature and stirring for 2 h the solution was reduced in volume to 20 cm^3. Cooling overnight in a refrigerator at −25 °C gave 5.6 g (14 mmol) of colourless crystals of compound **3** (73%), m.p. (decomp.) 147 °C. ^1H NMR (C_6D_6): δ 6.85 (s, 6 H, aryl H), 2.25 (s, 18 H, *o*-CH_3), 2.23 (s, 9 H, *p*-CH_3) and 1.63 (br s, 3 H, NH_3) (Found: C, 79.2; H, 9.3; N, 3.5. Calc.

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

for $C_{27}H_{36}AlN$: C, 80.7; H, 9.0; N, 3.5%). IR: 3378m, 3358m, 3279m, 1599m, 1246vs, 1222m, 1093s, 1031s, 845m, 800s, 719m and 652s cm^{-1}. Mass spectrum: *m/z* 384 (*M* − NH_3, 100), 264 (*M* − $C_6H_3Me_3$, 80) and 120 ($C_6H_3Me_3$, 20).

$[(2,4,6\text{-}Me_3C_6H_2)_2AlNH_2]_2$ **4**. Adduct **3** (2.8 g, 7 mmol) was dissolved in hexane (40 cm^3) and refluxed overnight. The solution was reduced in volume to 20 cm^3. Cooling in a refrigerator at −25 °C gave compound **4** as colourless crystals, yield 1.5 g (5.3 mmol, 76%), m.p. (decomp.) 194 °C. ^1H NMR (C_6D_6): δ 6.76 (s, 8 H, aryl H), 2.20 (s, 24 H, *o*-CH_3), 2.18 (s, 12 H, *p*-CH_3) and 1.75 (br s, 4 H, NH_2) (Found: C, 76.8; H, 8.5; N, 4.9. Calc. for $C_{36}H_{48}Al_2N_2$: C, 76.9; H, 8.7; N, 4.1%). IR: 3398m, 3340m, 1600s, 1261s, 1223m, 1095s, 1054s, 1035s, 838vs, 802s, 715s and 664vs cm^{-1}. Mass spectrum: *m/z* 442 (*M* − $C_6H_3Me_3$, 10), 323 (*M* − $2C_6H_3Me_3$, 20), 120 ($C_6H_3Me_3$, 40) and 105 ($C_6H_3Me_3$ − CH_3, 100).

$[Cl_2AlN(C_6H_{11})_2]_2$ **5**. *n*-Butyllithium (18.8 cm^3, 30 mmol) in hexane was added to a stirred solution of $NH(C_6H_{11})_2$ (5.44 g, 30 mmol) in hexane (20 cm^3) at −78 °C. After warming to room temperature stirring was continued for 2 h. To this solution $AlCl_3$ (4 g, 30 mmol) was added at −78 °C. Warming to room temperature and stirring for 12 h completed the reaction. The precipitated LiCl was filtered off and the solvent removed *in vacuo*. Recrystallization of the residue from hexane afforded 7.16 g (86%) of compound **5** as colourless crystals, m.p. 165 °C. ^1H NMR (C_6D_6): δ 3.75–0.75 (m, 44 H, C_6H_{11}) (Found: C, 51.4; H, 7.6; N, 5.1. Calc. for $C_{24}H_{44}Al_2Cl_4N_2$: C, 51.8; H, 7.9; N, 5.0%). IR: 1261s, 1163m, 1149m, 1110s, 1057vs, 1025s, 977m, 899m, 801vs, 735s, 646m, 597m, 531m, 461m and 437m cm^{-1}. Mass spectrum: *m/z* 556 (*M*, 20), 473 (M − C_6H_{11}, 35) and 277 (*M*/2 − H, 100).

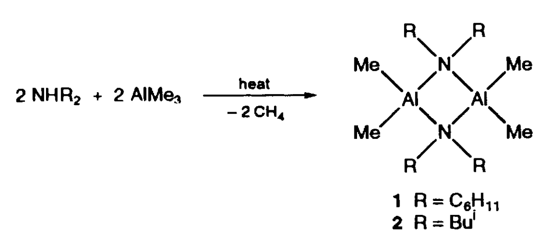
$(Me_2AlNHCH_2C_5H_4N\text{-}2)_2$ **6**. Trimethylalane (25 cm^3, 50 mmol) in hexane was added slowly to a solution of 2-pyridylmethylamine (5.41 g, 50 mmol) in hexane (10 cm^3) at 0 °C. Frothing occurred due to the evolution of methane, and the reaction mixture turned red. Stirring overnight completed the reaction. The solvent was removed *in vacuo*. Recrystallization from hexane gave the product **6** as pink crystals: yield 8.0 g (97%), m.p. (decomp.) 160 °C. ^1H NMR (C_6D_6): δ 8.30 [d, ^3J(HH) 4, 2 H, C_5H_4N], 6.81–6.31 (m, 6 H, C_5H_4N), 3.76 [d, ^3J(HH) 2, 4 H, CH_2], 0.48 [t, ^3J(HH) 2 Hz, 2 H, NH] and −0.31 (s, 12 H, $AlCH_3$) (Found: C, 57.4; H, 7.7; N, 17.1. Calc. for $C_{16}H_{26}Al_2N_4$: C, 58.5; H, 7.9; N, 17.1%). IR: 3274m, 1603s, 1457vs, 1345s, 1280m, 1183vs, 1147m, 1044vs, 1013s, 946m, 885s, 764m, 667s and 529vs cm^{-1}. Mass spectrum: *m/z* 149 (*M*/2 − Me, 100).

Single-crystal X-Ray Determination of Compounds **1**, **5** *and* **6**.—The intensities were measured on a Stoe-Siemens AED four-circle diffractometer with monochromated Mo-Kα radiation (λ = 0.710 73 Å). The crystals were mounted on a glass fibre in a rapidly cooled polyfluoropolyether.[8] All structures were solved by direct methods with SHELXS 90[9] and refined on F^2 by full-matrix least squares using SHELXL 93.[10] The hydrogen atoms were added in calculated positions and refined by a 'riding' model on their respective carbon atoms. In **1** one cyclohexyl group is disordered and was refined by using similar and ADP (anisotropic displacement parameter) restraints.

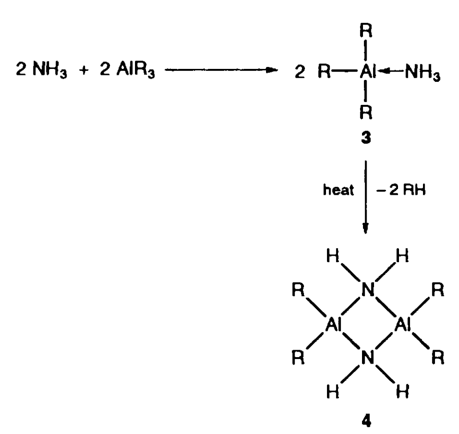
Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Results and Discussion

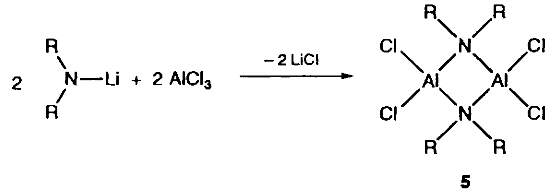
The reactions of $NH(C_6H_{11})_2$ and $NHBu^i_2$, respectively, with $AlMe_3$, involving the elimination of methane led directly to the dimeric aminoalanes $[Me_2AlN(C_6H_{11})_2]_2$ **1** and $(Me_2AlNBu^i_2)_2$ **2** as white solids sensitive to moisture and air (Scheme 1). Treatment of $Al(C_6H_2Me_3\text{-}2,4,6)_3$ with an excess of ammonia afforded the adduct **3**. Thermolysis of **3** resulted in precipitation of $[(2,4,6\text{-}Me_3C_6H_2)_2AlNH_2]_2$ **4** as demonstrated in Scheme 2. Compound **4** is one of the rare examples of a dimeric aminoalane containing NH_2 groups. Thus far, only the structures of the silicon-containing aminoalanes $[(Me_3Si)_2AlNH_2]_2$[11] and $\{[(Me_3Si)_2N]_2AlNH_2\}_2$[12] have been determined. Crystals of **4** contained disordered solvent molecules, making a final crystallographic refinement impossible.



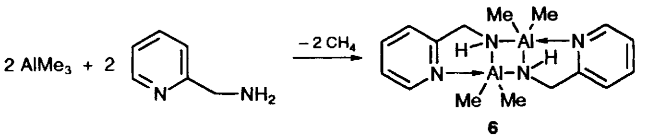
Scheme 1



Scheme 2 R = $C_6H_2Me_3$-2,4,6



Scheme 3 R = C_6H_{11}



Scheme 4

The reaction was monitored by IR spectroscopy. Characteristic bands are the stretching vibrations of the amino group in the range 3400–3100 cm^{-1}. For the adduct **3** three characteristic signals at 3378, 3358 and 3279 cm^{-1} have been detected in contrast to two for the NH_2 group in **4** at 3398 and 3340 cm^{-1}.

Compound **5** can be synthesized by salt elimination in the reaction of $Li[N(C_6H_{11})_2]$ with $AlCl_3$ at −78 °C (Scheme 3). Only two structurally characterized aminoalanes with two chlorine atoms at the aluminium are known thus far, $(Me_2NAlCl_2)_2$[13] and $(Bu^tHNAlCl_2)_2$.[14] These aminoalanes are of general interest as starting materials, due to the presence of the halides at aluminium, *e.g.* in reactions with lithium or magnesium organic reagents.

An example of an intramolecular donor-stabilized aminoalane is compound **6**, prepared at 0 °C by reaction of 2-pyridylmethylamine with $AlMe_3$, and elimination of methane

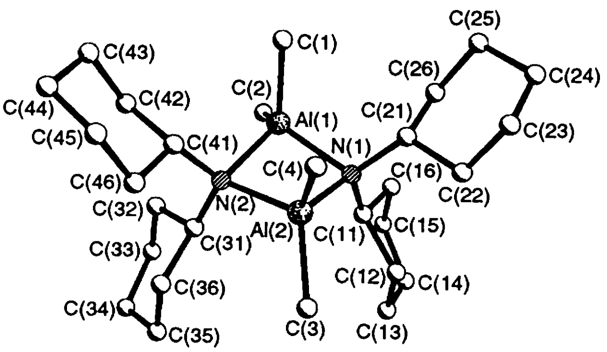


Fig. 1 Molecular structure of compound **1**

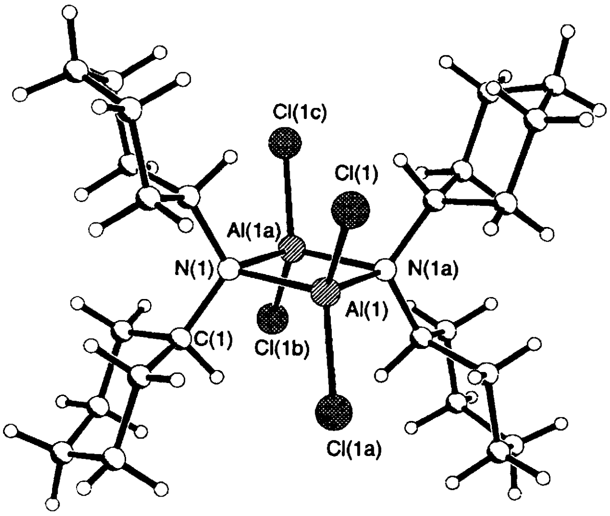


Fig. 2 Molecular structure of compound **5**

(Scheme 4). Normally, the metal atoms in aminoalanes prefer a co-ordination number of four. The stabilization of aminoalanes is a new trend in the chemistry of organoaluminium nitrogen compounds, *e.g.* Atwood *et al.*[6] reported on compounds $AlH_2(Bu^tHNCH_2CH_2NBu^t)$ and $AlCl(H)(Bu^tHNCH_2CH_2NBu^t)$ having intramolecular stabilization of the metal atom.[6]

Surprisingly, compound **6** is a pink solid, in contrast to the normally colourless aminoalanes. A possible explanation is that it is an intramolecular charge-transfer complex. Aluminium in the oxidation state +III has a s^0 electronic configuration. The only possibility for electron transfer is a ligand-to-metal charge transfer. Such complexes have already been obtained with other main group metals.[15] Solutions of **6** in different solvents have different colours. That in hexane is fluorescent red-orange, with characteristic absorptions in the UV/VIS spectra at 218, 528 and 568 nm. In polar acetonitrile the solution is dark green with absorptions at 260, 575, 606 and 678 nm. The colours of these solutions disappear on contact with air.

Single-crystal Structures.—$[Me_2AlN(C_6H_{11})_2]_2$ **1**. Crystal data for all the structures are given in Table 4, atomic coordinates in Table 5. The molecular structure of compound **1** is apparent from Fig. 1, which also shows the atom numbering scheme, while selected bond lengths and angles are given in Table 1. Compound **1** crystallizes in the monoclinic space group *C*2/*c*. It is remarkable that the central Al_2N_2 ring is folded. The plane described by Al–N–Al is tilted at an angle of 27.4(1)° out of the plane described by a planar four-membered Al_2N_2 ring. [Deviation from plane 27.4(1)°.] No reason for this behaviour could be detected. The Al–N bond lengths are on average 2.00(3) Å and comparable with those in other aminoalanes, for example $(Me_2AlNMe_2)_2$ (1.96 Å). The average angle in the ring is 88(1)°.

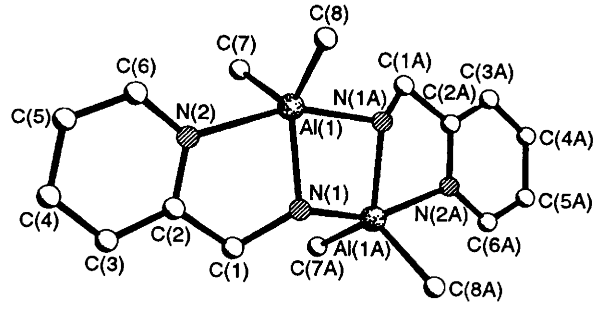


Fig. 3 Molecular structure of compound **6**

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

Al(1)–N(1)	1.995(2)	Al(1)–N(2)	2.006(2)
Al(2)–N(1)	2.004(2)	Al(2)–N(2)	1.999(2)
Al(1)–C(1)	1.975(3)	Al(2)–C(3)	1.966(3)
Al(1)···Al(2)	2.767(1)	N(1)–C(11)	1.540(14)
C(2)–Al(1)–C(1)	109.7(2)	N(1)–Al(1)–N(2)	89.25(8)
C(1)–Al(1)–N(1)	110.86(11)	C(2)–Al(1)–N(1)	117.13(12)
Al(1)–N(1)–Al(2)	87.56(8)	C(3)–Al(2)–C(4)	109.8(2)

Table 2 Selected bond lengths (Å) and angles (°) for compound **5**

Al(1)–N(1)	1.962(2)	N(1)–C(1)	1.521(3)
Cl(1)–Al(1)	2.117(1)	C(1)–C(2)	1.530(3)
C(2)–C(3)	1.532(3)	C(3)–C(4)	1.515(3)
N(1)–Al(1)–N(1a)	91.75(14)	Al(1)–N(1)–Al(1a)	88.25(14)
N(1)–Al(1)–Cl(1)	113.16(4)	C(1)–N(1)–Al(1a)	111.95(8)
Cl(1)–Al(1)–Cl(1a)	111.22(9)	C(1a)–N(1)–C(1)	117.2(3)
N(1)–C(1)–C(2)	116.25(13)	C(2)–C(1)–C(2a)	107.9(2)
C(1)–C(2)–C(3)	108.6(2)	C(4)–C(3)–C(2)	111.0(2)
C(3)–C(4)–C(3a)	112.6(3)		

Table 3 Selected bond lengths (Å) and angles (°) for compound **6**

Al(1)–N(1)	1.964(2)	Al(1)–N(1a)	2.028(3)
Al(1)–N(2)	2.226(3)	N(1)–C(1)	1.455(4)
Al(1)–C(7)	1.981(3)	Al(1)–C(8)	1.985(3)
N(1)–H(10)	0.770(4)	C(1)–C(2)	1.505(4)
N(1)–Al(1)–N(1a)	80.06(11)	N(1a)–Al(1)–N(2)	156.94(9)
Al(1)–N(1)–Al(1a)	97.47(11)	N(1)–Al(1)–C(7)	120.33(11)
C(1)–N(1)–Al(1)	114.8(2)	C(7)–Al(1)–C(8)	118.96(12)
C(7)–Al(1)–N(1a)	100.01(12)	C(8)–Al(1)–N(1a)	97.53(12)
C(7)–Al(1)–N(2)	92.20(11)	C(8)–Al(1)–N(2)	93.45(11)

$[Cl_2AlN(C_6H_{11})_2]_2$ **5**. Compound **5** crystallizes in the tetragonal space group *P*4$_2$/*mcm* as cuboidal crystals. The molecular structure is shown in Fig. 2 and selected bond lengths and angles are given in Table 2. The structure is highly symmetric. The central unit consists of a planar four-membered ring with alternating aluminium and nitrogen atoms. The structures of the other two structurally characterized aminoalanes with halides, at the metal atom also consist of planar Al_2N_2 rings.[13,14] The co-ordination number of the aluminium and nitrogen atoms is four. Within the Al_2N_2 ring the angles are close to 90° [N(1a)–Al(1)–N(1) 91.75(14), Al(1a)–N(1)–Al(1) 88.25(14)°]. The Al–N bond lengths are 1.96(2) Å, comparable to the average in aminoalanes with four-membered Al_2N_2 rings [1.94(4) Å].[16]

$(Me_2AlNHCH_2C_5H_4N\text{-}2)_2$ **6**. Single crystals suitable for X-ray analysis were obtained from hexane. Fig. 3 depicts the

Table 4 Crystallographic data for compounds **1**, **5** and **6**

	1	**5**	**6**
Formula	$C_{28}H_{56}Al_2N_2$	$C_{24}H_{44}Al_2Cl_4N_2$	$C_{16}H_{26}Al_2N_4$
M_r	474.71	556.37	328.37
Crystal system	Monoclinic	Tetragonal	Monoclinic
Space group	*C*2/*c*	$P4_2/mcm$	*C*2/*c*
a/Å	25.576(7)	8.885(2)	18.398(6)
b/Å	9.1070(10)	8.885(2)	7.741(3)
c/Å	25.960(7)	18.128(7)	16.443(5)
β/°	90.990(10)	90	128.76(2)
U/Å^3	6046(2)	1431.1(7)	1826.0(11)
Z	8	2	4
D_c/Mg m^{-3}	1.043	1.291	1.194
F(000)	2112	592	704
Crystal size/mm	0.5 × 0.5 × 0.8	0.4 × 0.15 × 0.15	0.3 × 0.2 × 0.2
μ/mm^{-1}	0.113	0.491	0.161
θ Range/°	3.53–22.51	4.50–27.59	4.27–29.98
h,*k*,*l* Ranges	−27 to 27, −9 to 9, −26 to 27	−11 to 9, −11 to 9, −19 to 23	−24 to 22, −10 to 10, −5 to 23
Unique reflections	3942	931	2601
Restraints	443	0	0
Parameters	348	45	106
$R[I > 2\sigma(I)]^a$	0.0487	0.0444	0.0660
wR2 (all reflections)^b	0.1348	0.1109	0.1953
$g1^c$	0.0613	0.0551	0.1070
$g2^c$	7.2299	0.3306	0.5503

^{a} $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. ^{b} $wR2 = \{[\Sigma w(F_o^2 - F_c^2)^2]/[\Sigma w(F_o^2)^2]\}^{\frac{1}{2}}$. ^{c} $w^{-1} = \sigma^2(F_o)^2 + [(g1)P]^2 + (g2)P$, where $P = (F_o^2 + 2F_c^2)/3$.

Table 5 Atomic coordinates (× 10^4)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Compound **1**							
Al(1)	775(1)	771(1)	6207(1)	C(16′)	1905(7)	2723(22)	6153(8)
Al(2)	1335(1)	−1460(1)	6684(1)	C(21)	1325(1)	1399(3)	7170(1)
N(1)	1421(1)	724(2)	6647(1)	C(22)	1719(1)	999(4)	7596(1)
N(2)	871(1)	−1372(2)	6057(1)	C(23)	1487(2)	1366(4)	8120(1)
C(1)	149(1)	1067(3)	6629(1)	C(24)	1340(2)	2956(4)	8152(1)
C(2)	763(1)	2155(3)	5624(1)	C(25)	980(1)	3424(3)	7707(1)
C(3)	1971(1)	−2662(4)	6645(1)	C(26)	1217(1)	3033(3)	7188(1)
C(4)	931(1)	−2036(4)	7294(1)	C(31)	1169(1)	−1686(3)	5571(1)
C(11)	1889(5)	1291(20)	6338(9)	C(32)	932(1)	−1164(3)	5062(1)
C(12)	2426(6)	732(15)	6514(6)	C(33)	1344(2)	−1140(4)	4646(1)
C(13)	2824(5)	997(17)	6091(6)	C(34)	1598(1)	−2622(4)	4581(1)
C(14)	2856(7)	2579(21)	5939(8)	C(35)	1787(2)	−3248(4)	5086(1)
C(15)	2327(8)	3251(17)	5829(7)	C(36)	1368(1)	−3239(3)	5492(1)
C(16)	1938(7)	2949(18)	6255(7)	C(41)	363(2)	−2180(3)	6130(1)
C(11′)	1912(6)	1193(22)	6391(9)	C(42)	−74(1)	−1815(3)	5745(1)
C(12′)	2430(6)	994(19)	6683(6)	C(43)	−595(1)	−2392(4)	5938(2)
C(13′)	2886(6)	1161(20)	6316(8)	C(44)	−568(1)	−4029(4)	6031(2)
C(14′)	2878(7)	2626(24)	6048(9)	C(45)	−119(1)	−4427(4)	6392(2)
C(15′)	2352(8)	2875(24)	5773(7)	C(46)	398(1)	−3842(3)	6192(1)
Compound **5**							
Cl(1)	2039(1)	2039(1)	4036(1)	C(2)	−3419(2)	1450(3)	5865(1)
Al(1)	1087(1)	1087(1)	5000	C(3)	−3732(3)	1726(2)	6685(1)
N(1)	−1121(3)	1121(3)	5000	C(4)	−3319(3)	3319(3)	6902(2)
C(1)	−1751(2)	1751(2)	5716(2)				
Compound **6**							
Al(1)	4126(1)	8004(1)	2389(1)	C(4)	4715(2)	7344(4)	5763(2)
N(1)	5467(1)	8380(3)	3493(2)	C(5)	3808(2)	7606(4)	4886(3)
N(2)	4285(1)	7797(3)	3843(2)	C(6)	3621(2)	7821(4)	3947(2)
C(1)	5854(2)	7538(4)	4480(2)	C(7)	3622(2)	5629(4)	1953(2)
C(2)	5167(2)	7547(3)	4690(2)	C(8)	3244(2)	9973(4)	1845(2)
C(3)	5406(2)	7311(4)	5663(2)				

structure of a single molecule of **6** and selected bond lengths and angles are given in Table 3. Compound **6** crystallizes in the monoclinic space group *C*2/*c*. The structure displays a four-membered ring with alternating aluminium and nitrogen atoms. Each Al–N unit is also part of a five-membered ring, involving a carbon atom of a methylene group and the nitrogen atom of the pyridylmethyl ligand. The co-ordination number of aluminium is five, and the geometry is distorted trigonal bipyramidal [N(1)–Al(1)–C(7) 120.33(11), N(2)–Al(1)–C(7) 92.20(11)°]. It is remarkable that two different Al–N bond lengths are present within the Al_2N_2 ring, a shorter one [Al(1)–N(1) 1.964(2) Å] and a longer one [Al(1)–N(1a) 2.028(3) Å], due to the intramolecular donor stabilization of the pyridylmethyl ligand. The distance between the aluminium atom and the pyridylmethyl nitrogen atom is 2.226(3) Å. The nitrogen atoms can be considered to bind the aluminium atoms through the lone-pair electrons. Owing to the connected ring systems the whole molecule is strained. This seems to be the reason for the folded Al_2N_2 ring in **6**.

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