

A comparative study of the behaviour of *N*-trimethylsilyl and *N*-neopentyl-anilines and 1,2-diaminobenzenes towards trimethylalane; X-ray structures of nine Al–N compounds

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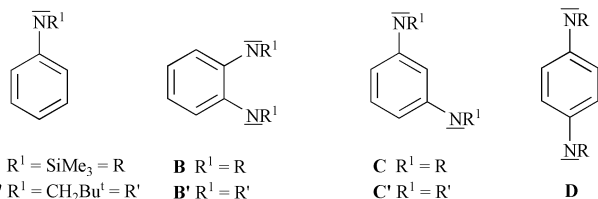
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The reactions of a pair each of monosubstituted anilines PhNHR^1 and disubstituted 1,2-diaminobenzenes $\text{C}_6\text{H}_4(\text{NHR}^1)_2$ -1,2 ($\text{R}^1 = \text{SiMe}_3 = \text{R}$, or $\text{R}^1 = \text{CH}_2\text{Bu}^t = \text{R}'$) with 1 or 2 equivalents of trimethylalane have been investigated. The trimethylsilyl derivatives were more reactive than the neopentyl analogues. The following crystalline compounds were obtained at ambient temperature or (1) gentle heating: *trans*- $[\text{AlMe}_2(\mu\text{-NRPh})]_2$ **1**, $[\text{AlMe}_3\text{-}\{\text{NH}(\text{R}')\text{Ph}\}]_2$ **2**, $[\text{AlMe}_2]_2\{\mu\text{-}(\text{NR})_2\text{C}_6\text{H}_4\text{-1,2}\}$ **4**, $[\text{AlMe}_2]\{\mu\text{-}(\text{NR}')_2\text{C}_6\text{H}_4\text{-1,2}\}$ **5**, $[\text{AlMe}\{\text{N}(\text{R})\text{C}_6\text{H}_4\text{NR}\text{-}\mu\text{-1,2}\}]_2$ **6** and $[\text{AlMe}_2\{\text{N}(\text{R}')\text{C}_6\text{H}_4\text{N}(\text{H})\text{R}'\}]_2$ **7**, while prolonged heating was required in order to obtain $[\text{AlMe}_2(\mu\text{-NR}'\text{Ph})]_2$ **3** and $[\text{AlMe}\{\text{N}(\text{R}')\text{C}_6\text{H}_4\text{NR}'\text{-}\mu\text{-1,2}\}]_2$ **8**. The amine adducts **2** and **7**, were identified as intermediates to **3** and **8**, respectively. Treatment of $\text{C}_6\text{H}_4(\text{NHR}')_2$ -1,2 with successively 2 LiBu^n and 2 AlCl_3 afforded $[\text{AlCl}\{\text{N}(\text{R}')\text{C}_6\text{H}_4\text{NR}'\text{-}\mu\text{-1,2}\}]_2$ **9**. The diamine adduct $[\text{C}_6\text{H}_4\{\text{N}(\text{H})\text{R}'(\text{AlMe}_3)\}_2\text{-1,3}]$ **10** was obtained from $\text{C}_6\text{H}_4(\text{NHR}')_2$ -1,3 and 2 AlMe_3 ; while the same diamine with successively 2 LiBu^n , 2 AlClMe_2 and 2 *tmen* yielded a compound tentatively formulated as $[\text{C}_6\text{H}_4\{\text{N}(\text{R}')\text{AlMe}_2(\text{tmen})\}_2\text{-1,3}]$ **11**. The X-ray structures of **1–7**, **9** and **10** are presented.

Introduction

We have a long standing interest in the chemistry of metal and metalloid amides.¹ Our most recent publications in this area relate to complexes of the *N*-mono-substituted anilides $\text{N}(\text{R}^1)\text{Ph}$ (**A**: $\text{R}^1 = \text{SiMe}_3 = \text{R}$, or **A'**: $\text{R}^1 = \text{CH}_2\text{Bu}^t = \text{R}'$) and the *N,N'*-disubstituted 1,2-, 1,3- and 1,4-benzenediamides $\{\text{N}(\text{R}^1)\}_2\text{C}_6\text{H}_4$ (**B** ($\text{R}^1 = \text{R}$), **B'** ($\text{R}^1 = \text{R}'$), **C** ($\text{R}^1 = \text{R}$) and **C'** ($\text{R}^1 = \text{R}'$)) and **D**, including the X-ray-characterised complexes $[\text{Li}(\text{A})]_4$,² $[\text{Li}\{\mu\text{-A}\text{-trans}\}(\mu\text{-tmen})]_2$,³ $[\text{Li}(\mu\text{-A}')(\text{OEt}_2)]_2$,³ $[\text{Li}_2(\mu\text{-B})(\text{thf})_2\{\mu\text{-Li}(\text{thf})\}_2]_2$,⁴ $[\{\text{Li}(\text{tmen})\}_2(\mu\text{-B})]_2$,⁴ $[\text{Li}(\text{thf})(\mu\text{-B})\text{-Li}(\text{thf})]_2$,⁴ $[\{\text{Li}(\text{tmen})\}_2(\mu\text{-B}')]_2$,⁴ $[\text{Li}(\mu\text{-B}')(\text{thf})_2(\mu\text{-Li})]_2$,⁴ $[\{\text{Li}(\text{thf})\}_2(\mu\text{-C})]_2$,⁵ $[\text{Mg}(\mu\text{-B})(\text{OEt}_2)]_2$,⁶ $[\{\text{Zr}(\text{B})(\text{NMe}_2)(\mu\text{-NMe}_2)\}_2]_2$,⁷ $[\text{Zr}(\text{B})\text{Cl}_2(\text{tmen})]_2$,⁷ $[\text{Sn}(\text{B})(\text{tmen})]_2$,⁸ $[\text{Sn}(\text{B}')_2]_2$,⁸ $[\{\text{Zr}(\text{NMe}_2)_3\}_2(\mu\text{-C})]_2$,⁹ $[\{\text{Zr}(\text{NMe}_2)_2\}_2(\mu\text{-C})]_2$,⁹ $[\text{Sn}(\text{C})]_2$,¹⁰ $[\text{Sn}_3(\text{C})_2]_2$,¹⁰ $[\{\text{Zr}(\text{NMe}_2)_3\}_2(\mu\text{-D})]_2$,⁹ $[\{\text{Zr}(\text{NMe}_2)_2\}_2(\mu\text{-D})]_2$,⁹ $[\{\text{Ge}(\text{NR}_2)_2\}_2(\mu\text{-D})]_2$,¹¹ $[\{\text{Sn}(\text{NR}_2)_2\}_2(\mu\text{-D})]_2$,¹¹ $[\{\text{Sn}(\text{OC}_6\text{H}_4\text{Bu}^t\text{-2,6-Me-4})\}_2(\mu\text{-D})]_2$,¹¹ and $[\{\text{SnCl}_2(\text{NR}_2)\}_2(\mu\text{-D})]_2$.¹¹ The ligand **B'** has had a central role in the development of the chemistry of the first X-ray-characterised silylene $\text{Si}(\text{B}')$,^{12a,b} for a review of some of its chemistry, see ref. 12c. The ligands **B** and **B'** have also featured in the following compounds: $[\text{Ga}(\text{B})]_2$,¹³ $[\text{Ge}(\text{B})]_2$,¹⁴ $[\text{MCl}n(\text{B})\{\eta^5\text{-C}_5\text{H}_3(\text{SiMe}_3)_2\text{-1,3}\}]$ ($n = 1$ and $\text{M} = \text{Zr}$ or Hf ; or $n = 2$ and $\text{M} = \text{Ta}$),¹⁵ $[\{\text{Mo}(\text{B})(\text{NPh})(\mu\text{-NPh})\}_2]_2$ ¹⁶ and various complexes containing the $\text{W}(\text{B})(\text{NPh})$ moiety.¹⁷



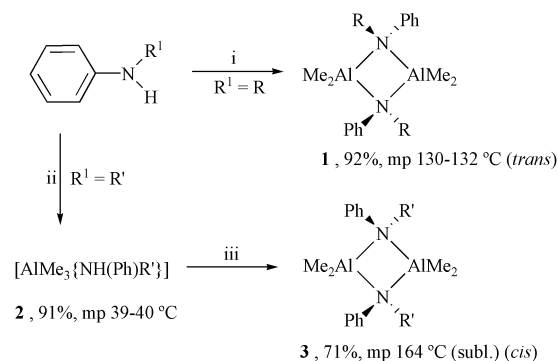
In this paper, we focus on the amides **A** and **A'** and the diamides **B**, **B'** and **C'** of aluminium and on some amine–alane adducts. Amides of aluminium have long been studied,¹ but recent interest in Al–N chemistry has been regenerated in part by the disclosure of Coles and Jordan in 1997 that certain cationic amidinatoaluminium methyls are catalysts for the

polymerisation of ethylene.¹⁸ We recently reported on the synthesis and structures of neutral and cationic aluminium 1-aza-allyls,¹⁹ β -diketiminates,²⁰ and on an amidinate^{21a} (see also ref. 21b).

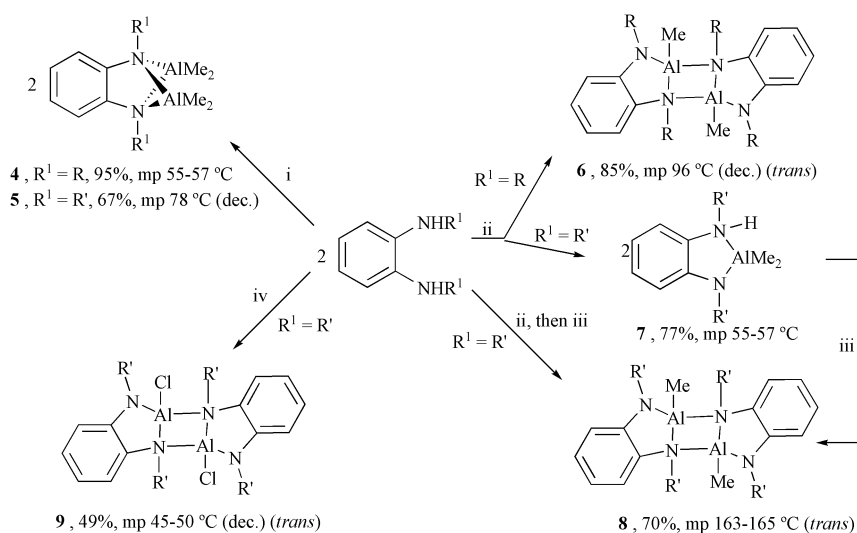
Results and discussion

An objective of the present work was to prepare and characterise a range of Al–N compounds derived from the amines $\text{HN}(\text{Ph})\text{R}^1$ and the diamines 1,2- and 1,3- $\text{C}_6\text{H}_4[\text{N}(\text{R}^1)\text{H}]_2$ ($\text{R}^1 = \text{SiMe}_3 = \text{R}$, or $\text{R}^1 = \text{CH}_2\text{Bu}^t = \text{R}'$). As a corollary, it was anticipated that some generalisations might emerge regarding the relative reactivities of the trimethylsilyl *versus* neopentyl derivatives.

The syntheses in good yields of the crystalline compounds **1–3** based on the anilines **HA** (**1**) or **HA'** (**2,3**) are summarised in Scheme 1. Whereas equivalent portions of trimethylalane and *N*-trimethylsilyl-²² or *N*-neopentyl-¹-aniline under mild conditions (gentle heating for **HA**, or ambient temperature for **HA'**) yielded the crystalline dimeric *trans*-*N*-trimethylsilyl-anilinodi(methyl)alane **1** (see also ref. 23, in which a 23% yield was recorded and the much lower mp of 77–80 °C) from **HA** (**i** in Scheme 1), with **HA'** the product was the 1 : 1-adduct **2**



Scheme 1 Synthesis of the crystalline compounds **1–3**. Reagents and conditions: i, AlMe_3 , *n*- C_6H_{14} , 0 °C and then <60 °C *in vacuo*; ii, AlMe_3 , *n*- C_6H_{14} , 20 °C; iii, *n*- C_6H_{14} , reflux, 16 h.

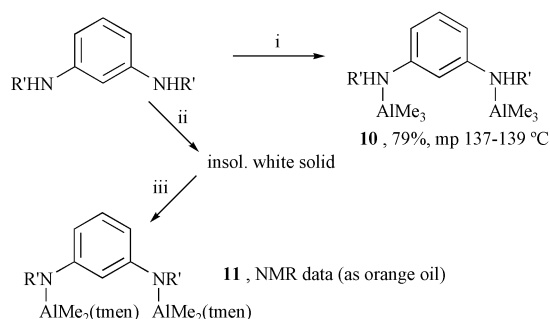


Scheme 2 Synthesis of the crystalline compounds **4–8**. *Reagents and conditions:* i, 4 AlMe₃, *n*-C₆H₁₄, 20 °C; ii, 2 AlMe₃, *n*-C₆H₁₄, 20 °C; iii, PhMe, 100 °C, 2 d; iv, 4 LiBuⁿ, PhMe, 20 °C, then 2 AlCl₃ at –78 to 20 °C, 16 h.

(ii in Scheme 1). Prolonged heating of **2** was required in order to complete the methane-elimination reaction leading (iii in Scheme 1) to the dimeric *cis*-*N*-neopentylanilinodi(methyl)alane **3**, an analogue of **1** but of opposite stereochemistry.

The syntheses in good (**4–8**) or moderate (**9**) yields of the crystalline compounds **4–9** derived from the 1,2-diaminobenzenes H₂B (**4** and **6**) and H₂B' (**5** and **7–9**) are outlined in Scheme 2. Treatment of the appropriate diamine and two equivalents of trimethylalane yielded (i in Scheme 2) the dinuclear chelated diamino-bis(trimethylalane)s **4** and **5**. By contrast, with one equivalent of AlMe₃, likewise at ambient temperature, the outcome (ii in Scheme 2) for the two diamines was different, the product being the bis(amido) compound **6** from H₂B but the amido(amine) compound **7** from H₂B'. However, thermolysis of **7** yielded (iii in Scheme 2) the neopentyl analogue **8** of **6**. The dimeric chloro compound **9**, related to the dimeric methyl compound **8**, was obtained (iv in Scheme 2) from H₂B' and successively dilithiation and reaction with AlCl₃. From 1,2-C₆H₄(NH₂)₂ and AlMe₃ in toluene the crystalline complex [(Me₂Al)₂AlMe{C₆H₄(NH)₂}₂·AlMe₃] was obtained.²⁴

1,3-Di(neopentylamino)benzene H₂C' (bp 165–167 °C / 5 Torr) was obtained by Li[AlH₄] reduction of 1,3-bis(dipivaloylamino)benzene (mp 195–198 °C), prepared from 1,3-diaminobenzene. Treatment of H₂C' with two equivalents of trimethylalane and brief heating in toluene afforded (i in Scheme 3) after concentration and cooling, the crystalline diamine-bis(trimethylalane) **10** in good yield. An attempt was made to gain access to a bis(amino)dialane by first converting H₂C' into Li₂C'(tmen)₂ and then adding 2 equivalents of dimethyl(chloro)alane (ii in Scheme 3). This yielded a white solid, insoluble in hydrocarbons or dichloromethane; in order to characterise it, tmen (2 equivalents) in thf was added. Removal



Scheme 3 Synthesis of the crystalline complex **10** and the oil **11**. *Reagents and conditions:* i, 2 AlMe₃, *n*-C₆H₁₄, 20 °C, 2 h, then PhMe and heated to dissolve; ii, 2 LiBuⁿ, 2 tmen, *n*-C₆H₁₄, 0 °C, 1 h, then 2 AlClMe₂, *n*-C₆H₁₄, 20 °C; iii, 2 tmen, thf, 20 °C.

of volatiles provided (iii in Scheme 3) an orange oil in a yield appropriate to the quantitative formation of the material tentatively formulated as **11**. This assignment was consistent with ¹H NMR spectral data in C₆D₆. The insoluble white solid may well have been a polymer or oligomer of 1,3-C₆H₄[N(R')-AlMe₂]₂, which with 2 tmen reverted to the soluble monomer **11**.

The reactions summarised in Schemes 1–3 lead us to the following conclusions regarding the relative behaviour of the trimethylsilyl *versus* neopentyl anilines or 1,2-diaminobenzenes: (i) the neopentylamines are less prone to deprotonation than the trimethylsilyl analogues, and (ii) it may be that the latter are able to yield stereoselective products.

As for (i), we note that (a) HA' formed a 1 : 1-adduct **2** with AlMe₃ at ambient temperature which only upon prolonged heating eliminated methane to form the amide **3**, whereas AlMe₃ with HA afforded the amide **1** at ambient temperature; (b) H₂B' with AlMe₃ under these conditions eliminated only one equivalent of methane to give the aminometal amide **7** (the second CH₄ loss occurred at elevated temperature to yield the diamidoaluminium compound **8**), whereas H₂B lost the two equivalents of CH₄ at 20 °C yielding the (SiMe₃)₂ analogue of **8**. Regarding (ii), it is inappropriate to generalise, but on the basis of the experiments leading to [AlMe₂(μ-A or μ-A')]₂ (**1** or **3**), we note that **1** was stereospecifically the *trans*-isomer even in benzene solution, whereas the neopentyl analogue **3** was a mixture of *cis* and *trans* (although the crystals were of the *cis*-isomer).

The ambient temperature ¹H NMR spectrum of **1** in benzene-*d*₆ revealed that the *trans*-structure observed in the solid state (*vide infra*) was maintained in solution. The neopentyl analogue **3**, while *cis* in the crystal, was a mixture of *ca.* 3(*cis*) : 2(*trans*) in solution (*cf.*, the ¹H NMR spectra). The NMR spectra of the compounds **2**, **4–7**, **9** and **10** were consistent with their solid state structures, which in the case of **4** and **5** was manifested by the appearance in both ¹H and ¹³C NMR spectra of two sets of AlMe₂ signals.

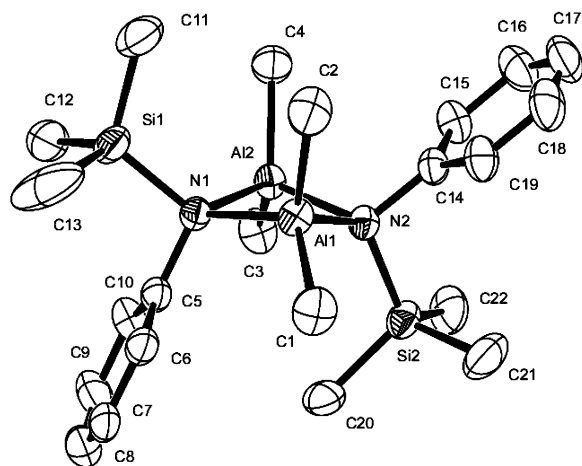
Crystal structures of compounds **1–7**, **9** and **10**

Each pair of the phenyl and trimethylsilyl groups adopts a *trans*-disposition around the Al₂N₂ non-planar ring (torsion angle 18.3°) of the dinuclear, C₁-symmetric, crystalline aluminium amide **1** (Fig. 1). The other geometric data (Table 1) are unexceptional, as may be judged by comparison with those for [AlMe₂(μ-NMe₂)₂], in which Al–N and Al–C bond lengths range from 1.955 to 1.972 Å, respectively, the Al...Al' distance is 2.815 Å, and the endocyclic bond angles vary from 88.4(3) to 91.6(3)°. ²⁵ A large number of complexes of formulae

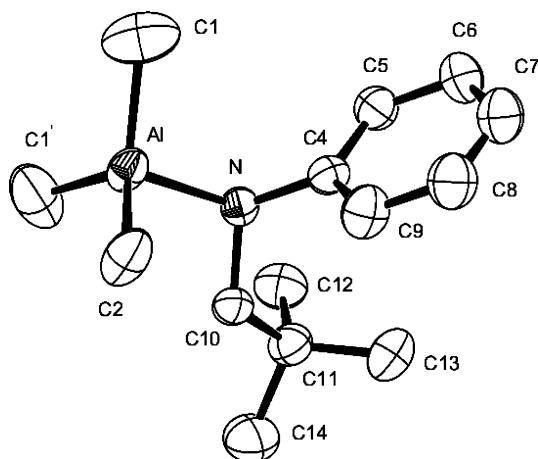
Table 1 Selected bond lengths (Å) and angles (°) for **1**

Al(1)···Al(2)	2.7895(12)	Al(1)–C(2)	1.957(4)
Al(1)–C(1)	1.958(3)	Al(2)–C(4)	1.963(3)
Al(2)–C(3)	1.967(3)	Al(1)–N(2)	2.002(2)
Al(1)–N(1)	2.020(2)	Al(2)–N(2)	1.987(2)
Al(2)–N(1)	2.019(2)		
C(2)–Al(1)–C(1)	110.01(16)	C(2)–Al(1)–N(2)	112.18(14)
C(1)–Al(1)–N(2)	113.22(14)	C(2)–Al(1)–N(1)	110.66(13)
C(1)–Al(1)–N(1)	120.50(14)	N(2)–Al(1)–N(1)	88.76(10)
C(4)–Al(2)–C(3)	108.42(15)	C(4)–Al(2)–N(2)	112.83(13)
C(3)–Al(2)–N(2)	114.33(13)	C(4)–Al(2)–N(1)	110.91(13)
C(3)–Al(2)–N(1)	120.19(13)	N(2)–Al(2)–N(1)	89.20(10)
Al(2)–N(1)–Al(1)	87.37(9)	Al(2)–N(2)–Al(1)	88.72(10)

[AlR₂(μ-NR²R³)₂]₂ have been crystallographically characterised.^{26–28} Most are of C₁ symmetry, have an almost square (AlN)₂ ring, but in some cases this is slightly puckered, as in [AlMe₂{μ-N(CH₂Ph)₂}]₂ which has a fold angle of 4.0° about the N–N' vector. The transoid geometry, if R² ≠ R³, is largely dominant, as in [AlMe₂{μ-N(H)Prⁱ}]₂,^{29a} or [AlMe₂{μ-N(SiMe₃)(CH₂C₄H₉O-2)}]₂,^{29b} but *cis*-complexes are encountered, particularly for higher AlR₂ homologues, as in [AlBu^t₂{μ-N(H)C₆H₄Ph-4}]₂,^{30a} but see also [AlMe₂{μ-N(CH₂Ph)Prⁱ}]₂.^{30b}

**Fig. 1** Molecular structure of *trans*-[(AlMe₂)(μ-A)]₂ **1**.

The AlMe₃ group of the crystalline compound [AlMe₃·H(A')] **2** (Fig. 2) lies on the mirror plane, with the rest of the molecule disordered across this plane. The geometric parameters are unexceptional (Table 2), as evident from a comparison with those (by gas electron diffraction) for [AlMe₃(NMe₃)], having Al–N, Al–C and N–C bond lengths of 2.099(10), 1.987(5) and 1.474(3) Å, respectively and C–Al–N and C–N–Al bond angles of 102.3(3) and 109.3(3)°, respectively.³¹

**Fig. 2** Molecular structure of [(AlMe₃)·H(A')] **2**.**Table 2** Selected bond lengths (Å) and angles (°) for **2**

Al–C(1)	1.953(3)	Al–C(2)	1.978(3)
Al–N	2.067(4)	N–C(4)	1.459(9)
C(1)–Al–N	107.8(2)	Al–N–C(4)	115.1(5)
C(2)–Al–N	106.14(16)	C(4)–N–C(10)	115.7(4)
Al–N–C(10)	108.5(4)		

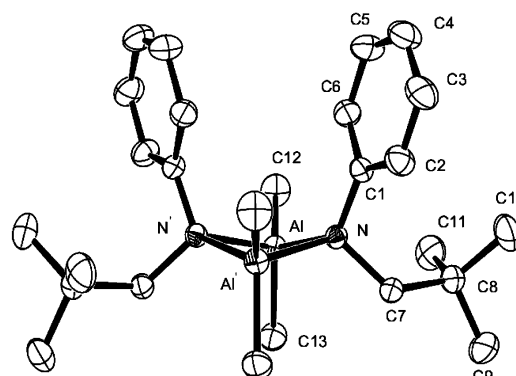
Symmetry transformations to generate equivalent atoms: ' *x*, *–y* + 1/2, *z*.

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

Al···Al'	2.792(1)	Al–C(13)	1.968(2)
Al–C(12)	1.970(2)	Al–N	1.984(2)
Al–N'	2.029(2)		
C(13)–Al–C(12)	109.90(11)	C(13)–Al–N	111.15(9)
C(12)–Al–N	122.61(10)	C(13)–Al–N'	107.71(9)
C(12)–Al–N'	115.02(9)	N–Al–N'	88.17(7)
Al–N–Al'	88.15(7)		

Symmetry transformations used to generate equivalent atoms: ' *–x*, *y*, *–z* + 1/2.

The crystalline [AlMe₂(A')]₂ **3** molecule (Fig. 3) lies on a two-fold rotation axis orthogonal to the Al–Al' vector. It also differs from **1** in its *cisoid* arrangement of substituents at the N- and N'-atoms of the puckered AlNAl'N' ring (torsion angle 20.1°). The other geometric parameters (Table 3) are similar to those of compound **1**.

**Fig. 3** Molecular structure of *cis*-[(AlMe₂)(μ-A')]₂ **3**.

The crystalline [(AlMe₂)₂(μ-B)] **4** molecule (Fig. 4) lies on a two-fold rotation axis, perpendicular to the Al–Al' vector. The two distorted tetrahedral nitrogen atoms N and N' of the ligand **B** are members of the strongly puckered AlNAl'N' ring

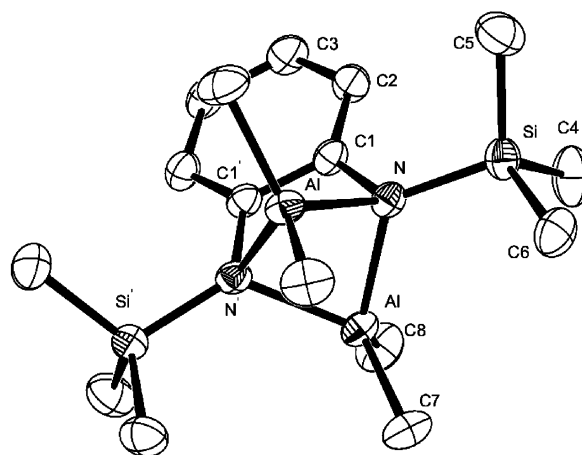
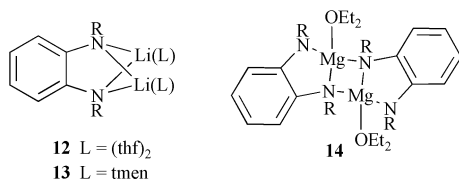
**Fig. 4** Molecular structure of [(AlMe₂)₂(μ-B)] **4**.

Table 4 Selected bond lengths (Å) and angles (°) for **4**

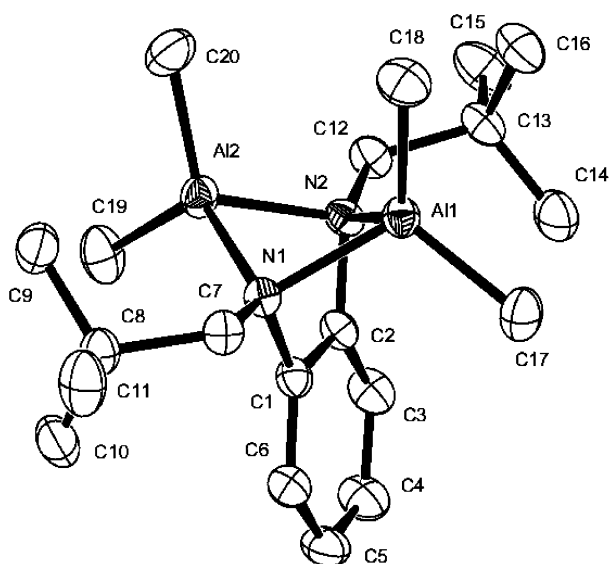
Al...Al'	2.8242(12)	Al-C(7)	1.959(3)
Al-C(8)	1.964(3)	Al-N	2.0041(19)
Al-N'	2.0043(19)	N-C(1)	1.462(3)
C(7)-Al-N	115.79(10)	C(7)-Al-C(8)	114.06(12)
C(7)-Al-N'	117.94(10)	C(8)-Al-N	113.93(11)
N-Al-N'	77.62(9)	C(8)-Al-N'	112.67(10)
C(1)-N-Al'	94.05(12)	C(1)-N-Al	94.14(12)
Al-N-Si	123.70(10)	Al-N-Al'	89.59(8)
C(1)-C(1)-N	112.20(10)	Al'-N-Si	125.56(10)

Symmetry transformations used to generate equivalent atoms: ' $-x + 1/2, y, -z + 1/2$.

(torsion angle 37.1°). The angles at the endocyclic aluminium atoms are more acute than those at the nitrogen atoms, Table 4. The ligand **B** is both chelating and bridging; in that respect the structure of **4** is similar to those of $[\{\text{Li}(\text{L})\}_2(\mu\text{-B})]_2$ [**L** = (thf)₂ **12**, **L** = tmen **13**], in which the Li-N distances range from 1.971(8) to 2.102(7) Å (**12**) and 2.056(7) to 2.078(7) Å (**13**).⁴ The Al...Al, Al-N and Al-CH₃ distances are very similar to those of **1** and **5**.



There are two independent C₁-symmetric molecules in the unit cell of crystalline $[\text{AlMe}_2(\mu\text{-B}')]$ **5** with essentially the same geometry (Fig. 5); hence data for only one are listed in Table 5. The structure is very similar to that of **4**, but the torsion angle of the $\overline{\text{Al1N1Al2N2}}$ puckered ring of 39.1° is slightly wider than the corresponding angle in **4**. The spread of the four N-Al-CH₂Bu^t angles [155.32(16) to 133.04(6)°] is much greater than that of the Al(Al')-N-Si angles [123.70(10), 125.56(10)°].

**Fig. 5** Molecular structure of $[(\text{AlMe}_2)_2(\mu\text{-B}')]_2$ **5**.

The crystalline $[\text{AlMe}(\mu\text{-B})]_2$ **6** molecule (Fig. 6) lies across an inversion centre, the mid-point of the central almost square $\overline{\text{AlNAl}'\text{N}'}$ ring. It comprises an array of three aluminium-containing fused rings in a ladder-type structure with a chair-like transoid disposition of the terminal five-membered rings

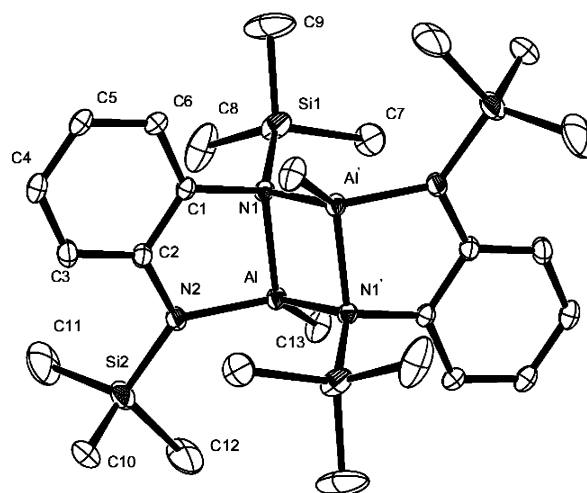
Table 5 Selected bond lengths (Å) and angles (°) for **5**

Al(1)...Al(2)	2.823(1)	Al(1)-C(18)	1.954(3)
Al(1)-C(17)	1.957(3)	Al(2)-C(19)	1.959(3)
Al(2)-C(20)	1.959(3)	Al(1)-N(2)	2.003(2)
Al(1)-N(1)	2.011(2)	Al(2)-N(1)	1.977(2)
Al(2)-N(2)	1.990(2)	N(1)-C(1)	1.450(3)
N(2)-C(2)	1.447(3)		
C(18)-Al(1)-C(17)	115.53(14)	C(19)-Al(2)-C(20)	116.63(14)
C(18)-Al(1)-N(2)	119.63(12)	C(17)-Al(1)-N(2)	115.38(12)
C(18)-Al(1)-N(1)	114.08(12)	C(17)-Al(1)-N(1)	110.10(12)
N(2)-Al(1)-N(1)	75.11(8)	N(1)-Al(2)-N(2)	76.17(9)
C(1)-N(1)-Al(2)	98.18(14)	C(1)-N(1)-Al(1)	94.81(14)
C(2)-N(2)-Al(2)	96.78(15)	C(2)-N(2)-Al(1)	95.71(14)
Al(2)-N(1)-Al(1)	90.10(9)	Al(2)-N(2)-Al(1)	89.95(9)
C(2)-C(1)-N(1)	110.5(2)	C(1)-C(2)-N(2)	111.1(2)
C(7)-N(1)-Al(2)	129.81(6)	C(12)-N(2)-Al(1)	133.04(6)
C(12)-N(2)-Al(2)	115.32(16)		

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

Al-N(2)	1.8358(19)	Al-C(13)	1.948(2)
Al-N(1)'	1.9621(18)	Al-N(1)	1.9799(18)
N(1)-C(1)	1.478(2)	N(2)-C(2)	1.401(3)
N(2)-Al-C(13)	119.39(11)	N(2)-Al-N(1)'	115.99(9)
N(2)-Al-N(1)	91.83(8)	C(13)-Al-N(1)	121.90(11)
C(13)-Al-N(1)'	113.10(10)	C(1)-N(1)-Si(1)	111.58(13)
N(1)'-Al-N(1)	89.62(7)	C(1)-N(1)-Al	102.76(12)
C(1)-N(1)-Al'	108.12(12)	C(2)-N(2)-Al	109.40(14)
Al'-N(1)-Al	90.38(7)	C(1)-C(2)-C(3)	116.9(2)
C(2)-C(1)-N(1)	117.30(17)		

Symmetry transformations used to generate equivalent atoms: ' $-x + 1/2, -y + 1/2, -z + 1$.

**Fig. 6** Molecular structure of $\text{trans}-[(\text{AlMe})(\mu\text{-B})]_2$ **6**.

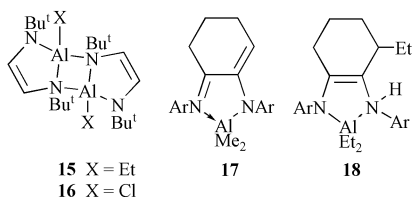
around the central $\overline{\text{AlNAl}'\text{N}'}$. The atoms Al and Al' from each of the terminal rings is *ca.* 0.2 Å out of the NCCN plane of the $\overline{\text{AlNCCN}}$ moiety. The two nitrogen atoms of the ligand **B** differ in that the four-coordinate N1 (or N1') atom bridge the two aluminium atoms Al and Al', while the three-coordinate N2 (or N2') is bonded to Al (or Al') in a terminal fashion; hence the Al-N1 and N1-C1 bonds are significantly longer than the Al-N2 and N2-C2 bonds (Table 6).

The skeletal structure of the fused trinuclear ring system of **6** is very similar to that of $[\text{Mg}(\mu\text{-B})(\text{OEt}_2)]_2$ **14**, in which the corresponding Mg-N1, Mg-N2, N1-C1 and N2-C2 distances are 1.997(7), 2.082(7), 1.371(11) and 1.472(11) Å, respectively,⁶ and the ladder has the chair conformation. This feature has also been found in **15** and **16**, having the following geometric parameters [**16** in square brackets]: Al-N1 1.985(2) [1.966(2)],

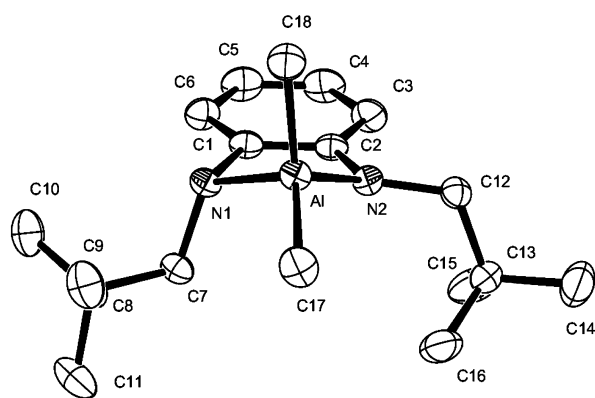
Table 7 Selected bond lengths (Å) and angles (°) for **7**

Al–N(2)	1.8655(12)	Al–C(17)	1.9590(15)
Al–C(18)	1.9643(15)	Al–N(1)	2.0234(12)
N(1)–C(1)	1.4765(16)	N(2)–C(2)	1.3782(17)
N(1)–C(7)	1.5169(17)	N(2)–C(12)	1.4555(18)
C(1)–C(6)	1.3804(19)	C(1)–C(2)	1.411(2)
N(2)–Al–N(1)	85.62(5)	C(17)–Al–C(18)	115.09(7)
C(2)–N(2)–Al	109.83(9)	C(1)–N(1)–Al	101.62(8)
N(2)–C(2)–C(1)	115.98(12)	C(2)–C(1)–N(1)	115.13(11)

Al–N 1.949(2) [1.812(2)], Al–N' 1.975(2) [1.940(2)], N1–C1 1.465(3) [1.479(3)], N2–C2 1.383(3) [1.386(3)] Å; N1–Al–N1' 86.83(8) [87.73(7)], and Al–N–Al' 93.47(8) [92.27(7)]°. ³² By contrast, the corresponding saturated compound with X = H (*i.e.*, with –NCH₂CH₂N– in place of –NCH=CHN–) was obtained both in the chair (*trans*-) and the boat (*cis*-) form. ³³ This type of isomerisation has been discussed in related gallium compounds. ³⁴ The structure of [(AlMe₂)₂{μ-*trans*-N(R)(C₆H₁₁-c)}] has recently been reported. ³⁵



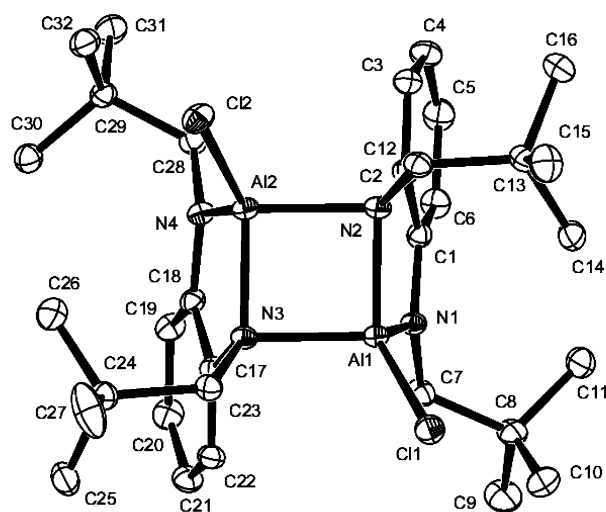
The 2-aminophenylamidodi(methyl)aluminium compound [AlMe₂{μ-H(B')}] **7** (Fig. 7) crystallised in a mononuclear C₁-symmetric fashion. The chelating ligand H(B') has Al–N and contiguous N–C bonds shorter for the three-coordinate (N2) than for the four-coordinate (N1) nitrogen atoms (the NH hydrogen atom was not located), Table 7. The torsion angle between the N1–Al–N2 and the 1,2-NC₆H₄N plane is 30.24(5)°. The aluminium atom is 0.706 Å out of the latter plane. The endocyclic bond angles of the $\overline{\text{AlN1C1C2N2}}$ ring range from 85.62(5)° at Al to 115.98(12)° at C2. The Al–CH₃ bond lengths are similar to those in **1** or **3**. Compound **7** has some structural similarity to the complexes **17** and **18**, which have Al–N distances of 1.968(11) and 1.897(2) Å (**17**) and 2.045(4) and 1.856(4) Å (**18**) for the dative and covalent bonds, respectively. ³⁶

**Fig. 7** Molecular structure of *trans*-[(AlMe₂)(μ-HB')] **7**.

Crystals of [AlMe(μ-B')]₂ **8** diffracted poorly, but the data were adequate to establish that its dimeric structure was similar to that of **6**. However, X-ray quality single crystals of the corresponding C₁-symmetric chloride [AlCl(μ-B')]₂ **9** were obtained (Fig. 8). In its three fused ladder-type aluminium containing rings it resembles those of **6**, but in **9** there is a boat-like cisoid disposition [*cf.* ref. 33) of the terminal five-membered rings around the almost rhomboidal (torsion angle 10.1°) (rather

Table 8 Selected bond lengths (Å) and angles (°) for **9**

Al(1)···Al(2)	2.721(1)	Al(1)–N(1)	1.812(2)
Al(1)–N(2)	1.925(2)	Al(1)–N(3)	1.977(2)
Al(1)–Cl(1)	2.107(1)	Al(2)–N(4)	1.811(2)
Al(2)–N(3)	1.920(2)	Al(2)–N(2)	1.973(2)
Al(2)–Cl(2)	2.105(1)	N(1)–C(1)	1.398(3)
N(1)–C(7)	1.471(3)	N(2)–C(2)	1.467(3)
N(2)–C(12)	1.507(3)	N(3)–C(17)	1.470(3)
N(3)–C(23)	1.508(3)	N(4)–C(18)	1.405(3)
N(4)–C(28)	1.469(3)	C(1)–C(2)	1.415(4)
C(17)–C(18)	1.412(4)		
N(1)–Al(1)–N(2)	90.71(10)	N(2)–Al(1)–N(3)	90.47(9)
N(4)–Al(2)–N(3)	91.10(9)	N(3)–Al(2)–N(2)	90.74(9)
N(1)–Al(1)–N(3)	115.69(10)	N(4)–Al(2)–N(2)	115.28(10)
C(1)–N(1)–Al(1)	111.58(17)	C(2)–N(2)–Al(1)	105.98(15)
Al(1)–N(2)–Al(2)	88.52(9)	C(17)–N(3)–Al(2)	106.09(16)
C(17)–N(3)–Al(1)	103.32(15)	Al(2)–N(3)–Al(1)	88.53(9)
C(18)–N(4)–Al(2)	110.98(17)	N(1)–C(1)–C(2)	116.1(2)
C(1)–C(2)–N(2)	115.3(2)	C(18)–C(17)–N(3)	115.0(2)

**Fig. 8** Molecular structure of [(AlCl)(μ-B')]₂ **9**.

than square, as in **6**) central $\overline{\text{AlN2AlN3}}$ core. The latter has endocyclic bond angles at N2 and N3 which are slightly narrower than those at the Al1 and Al2 atoms, Table 8. The aromatic rings are almost parallel and staggered. As in **6**, the Al–N and contiguous N–C bonds of each $\overline{\text{AlNCCN}}$ ring are longer for those involving the four- (N2, N3) rather than the three- (N1, N4) coordinate nitrogen atoms.

In the five complexes **4–7** and **9** containing a 1,2-*N,N'*-disubstituted ligand **B** or **B'**, the C1–C2 bond of the C₆ ring is invariably the longest, ranging from 1.407(4) Å in **4** to 1.418(4) Å in **5**. The shortest bonds are the C3–C4, C4–C5 and C5–C6, which vary from 1.37 to 1.39 Å.

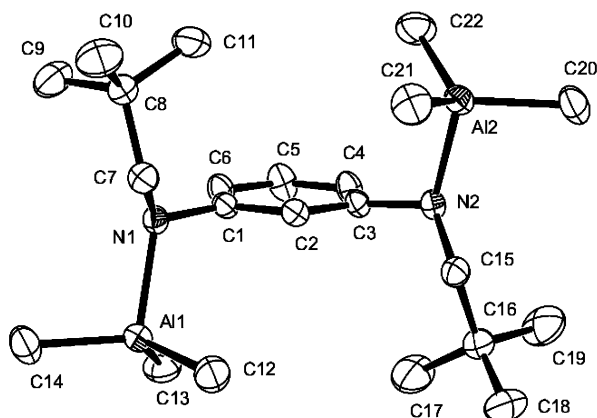
The crystalline C₁-symmetric molecule [(AlMe₃)₂·H₂(C')] **10** (Fig. 9), like **2**, has a four-coordinate tetrahedral environment about each aluminium atom, with Al–CH₃ and Al–N bond lengths (Table 9) very slightly longer than those of **2** and C–Al–N angles significantly narrower (by *ca.* 2 to 6°) than those of **2** (Table 1).

Experimental

All manipulations were carried out under argon or *in vacuo* using standard Schlenk techniques. Solvents were pre-dried over sodium, distilled from sodium (toluene), sodium–potassium alloy (pentane, hexane) or sodium–benzophenone (diethyl ether, tetrahydrofuran) and stored over a potassium mirror or molecular sieves (4 Å). Deuterated solvents were

Table 9 Selected bond lengths (Å) and angles (°) for **10**

Al(1)–C(12)	1.9714(19)	Al(1)–C(13)	1.9744(19)
Al(1)–C(14)	1.9756(18)	Al(2)–C(22)	1.9641(19)
Al(2)–C(21)	1.9670(18)	Al(2)–C(20)	1.9794(18)
Al(1)–N(1)	2.0864(13)	Al(2)–N(2)	2.0811(13)
N(1)–C(1)	1.4532(17)	N(2)–C(3)	1.4544(18)
C(13)–Al(1)–N(1)	101.43(7)	C(12)–Al(1)–N(1)	104.05(7)
C(22)–Al(2)–N(2)	103.44(7)	C(14)–Al(1)–N(1)	102.10(7)
C(20)–Al(2)–N(2)	99.84(7)	C(21)–Al(2)–N(2)	104.32(7)
C(3)–N(2)–Al(2)	110.34(9)	C(1)–N(1)–Al(1)	110.42(9)

**Fig. 9** Molecular structure of $[(\text{AlMe}_2)_2 \cdot \text{H}_2(\text{C}')] \mathbf{10}$.

likewise stored over such molecular sieves and degassed prior to use. Triethylamine, chloro(trimethyl)silane, lithium aluminium hydride, pivaloyl chloride, AlMe_3 , AlCl_3 and *n*-butyllithium in hexanes (1.6 mol dm^{-3} , FMC corporation) were commercial samples used without further purification. The NMR solution spectra were recorded on Bruker DPX 300 (for ^1H and ^{13}C) or AMX 500 (for ^{29}Si and ^{27}Al) instruments and referenced externally (using aqueous $\text{Al}(\text{OH})_3$ with a D_2O lock for ^{27}Al or SiMe_4 for ^{29}Si) or internally (^1H , ^{13}C) to the residual solvent resonances; chemical shift data in δ . Unless otherwise stated, all NMR spectra were examined at 293 K in C_6D_6 and, except for ^1H , were proton decoupled. Electron impact mass spectra were taken on a Kratos MS 80 RF instrument. Elemental analyses (empirical formulae shown) were carried out by Medac Ltd, UK., Brunel University. Melting points were taken in sealed capillaries and are uncorrected.

Preparations

1,3-Bis(pivaloylamino)benzene. A solution of pivaloyl chloride (45.0 g, 373 mmol) in thf (100 cm^3) was added dropwise at *ca.* 20 °C to a solution of 1,3-diaminobenzene (20.0 g, 185 mmol) and triethylamine (38 g, 374 mmol) in thf (900 cm^3). The resulting thick white suspension was stirred overnight. Volatiles were removed *in vacuo* and the resulting solid was washed several times with water, dried and crystallised from hot ethanol, to give 1,3-bis(pivaloylamino)benzene as a white solid (34.6 g, 68%) (Found: C, 69.6; H, 8.70; N, 10.14. $\text{C}_{16}\text{H}_{24}\text{N}_2\text{O}_2$ requires C, 69.7; H, 8.80; N, 10.07%), mp 195–198 °C. ^1H NMR (CDCl_3): δ 1.32 (s, 18H, Me), 7.23–7.35 (m, 3H, Ph), 7.93 (s, 1H, Ph), 7.46 (br s, 2H, NH); ^{13}C NMR (CDCl_3): δ 27.9 (CH_3), 40.0 (CCH_3), 111.7, 115.8, 129.7, 138.9 (Ph), 177.2 (CO). EI-MS (m/z , %): 276 {43, $[\text{M}]^+$ }, 57 {100, $[\text{Bu}]^+$ }.

1,3-Bis(neopentylamino)benzene $\text{H}_2(\text{C}')$. Solid 1,3-bis(pivaloylamino)benzene (34.3 g, 124 mmol) was added to a cooled (0 °C) suspension of $\text{Li}[\text{AlH}_4]$ (19.0 g, 500 mmol) in thf (400 cm^3). After 2 h at *ca.* 25 °C and 12 h at reflux, the grey suspension was carefully hydrolysed at 0 °C by a mixture of water and

thf and filtered. The filtrate was concentrated. Distillation of the residue under reduced pressure gave $\text{H}_2(\text{C}')$ as a colourless crystalline solid (22.4 g, 73%) (Found: C, 77.6; H, 11.29; N, 11.41. $\text{C}_{18}\text{H}_{28}\text{N}_2$ requires C, 77.4; H, 11.29; N, 11.29%), bp 165–167 °C/5 Torr. ^1H NMR (CDCl_3): δ 1.04 (s, 18H, Me), 2.92 (s, 4H, NCH_2), 3.85 (br s, 2H, NH), 6.0–7.05 (m, 4H, Ph); ^{13}C NMR (CDCl_3): δ 28.2 (Me), 32.1 (CCH_3), 56.5 (NCH_2), 97.7, 103.2, 130.3, 150.4 (Ph), EI-MS (m/z , %): 248 {83, $[\text{M}]^+$ }, 191 {100, $[\text{M} - \text{Bu}]^+$ }.

$[\text{AlMe}_2(\mu\text{-A})]_2 \mathbf{1}$. A solution of AlMe_3 (11 cm^3 of a 2.0 mol dm^{-3} solution in hexanes, 22 mmol) was added dropwise at *ca.* 0 °C to a solution of $\text{H}(\text{A})$ (3.55 g, 21.5 mmol) in hexane (10 cm^3). The colourless solution was stirred for 1 h at *ca.* 20 °C. Volatiles were removed *in vacuo* and the resulting oil was briefly heated *in vacuo* at <60 °C until a white solid had formed. Crystallisation from hexane at –25 °C yielded colourless needles of compound **1** (4.08 g, 92%) (Found: C, 57.6 (duplicate analyses); H, 8.80; N, 6.11. $\text{C}_{22}\text{H}_{40}\text{Al}_2\text{N}_2\text{Si}_2$ requires C, 59.7; H, 9.11; N, 6.33%), mp 130–132 °C. ^1H NMR: δ –0.07 (s, 6H, AlMe), 0.09 (s, 9H, SiMe), 7.0–7.33 (m, 5H, Ph); ^{13}C NMR: δ 0.4 (AlMe), 2.6 (SiMe), 125.2–144.1 (Ph); ^{27}Al NMR: δ 164.5 (br s, $\Delta w_{1/2}$ 5.8 kHz); ^{29}Si NMR: δ 14.2.

$[\text{AlMe}_3 \cdot \text{H}(\text{A}')] \mathbf{2}$. A solution of AlMe_3 (5 cm^3 of a 2.0 mol dm^{-3} solution in hexanes, 10.0 mmol) was added dropwise at *ca.* 0 °C to a solution of $\text{H}(\text{A}')$ (1.58 g, 9.68 mmol) in hexane (20 cm^3), then stirred for 1 h at *ca.* 20 °C. Volatiles were removed *in vacuo* and the resulting white solid was crystallised from pentane at –25 °C, yielding colourless needles of compound **2** (2.07 g, 91%) (Found: C, 68.1; H, 10.93; N, 5.80. $\text{C}_{14}\text{H}_{26}\text{AlN}$ requires C, 71.5; H, 11.14; N, 5.95%), mp 39–40 °C. ^1H NMR: δ –0.47 (s, 9H AlMe), 0.46 (s, 9H, CMe_3), 2.96 (d, $^3J_{\text{HH}} = 5.8$, 2H, NCH_2), 3.80 (t, $^3J_{\text{HH}} = 5.8$ Hz, 1H, NH), 6.56–7.15 (m, 5H, Ph); ^{13}C NMR: δ –8.7 (AlCH_3), 27.6 (CCH_3), 32.7 (CCH_3), 60.9 (NCH_2), 121.2–144.1 (m, Ph); ^{27}Al NMR: δ 183.6 (br s, $\Delta w_{1/2}$ 4.5 kHz).

$[\text{AlMe}_2(\mu\text{-A}')]_2$ (*cis* **3 + *trans*).** A solution of **2** (2.06 g, 8.75 mmol) in hexane (20 cm^3) was refluxed for 16 h. Upon cooling, colourless crystals of **3** were obtained (1.37 g, 71%) (Found: C, 69.5; H, 10.10; N, 6.53. $\text{C}_{26}\text{H}_{44}\text{Al}_2\text{N}_2$ requires C, 71.2; H, 10.11; N, 6.39%), mp 164 °C (subl.). ^1H NMR: δ –0.29 (s, 6H, AlMe of *cis*), –0.20 (s, 12H, AlMe of *trans*), –0.03 (s, 6H, AlMe of *cis*), 3.30 s, (4H, NCH_2 of *trans*), 3.36 (4H, NCH_2 of *cis*), 6.81–7.43 (m, 20H, Ph); ^{13}C NMR: δ –4.1 (AlMe of *cis*), –3.5 (AlMe of *trans*), –1.7 (AlMe of *cis*), 29.9 (CCH_3 of *cis*), 30.0 (CCH_3 of *trans*), 34.0 (CCH_3), 61.8 (NCH_2 of *cis*), 63.8 (NCH_2 of *trans*), 124.5–148.2 (Ph); ^{27}Al NMR: δ 173.2 (br s, $\Delta w_{1/2}$ 6 kHz). MS (m/z , %): 57 (84, $[\text{C}(\text{CH}_3)_3]^+$), 162 (100, $[\text{PhNCH}_2\text{-Bu}]^+$), 204 (73, $[\text{PhN}(\text{CH}_2\text{Bu})\text{AlMe}]^+$), 219 (66, $[\text{PhN}(\text{CH}_2\text{-Bu})\text{AlMe}_2]^+$), 423 (30, $[\{\text{PhN}(\text{CH}_2\text{Bu})\text{AlMe}_2\}_2 - \text{Me}]^+$).

$[\text{AlMe}_2(\mu\text{-B})]_2 \mathbf{4}$. Compound $\text{H}_2(\text{B})$ (1.21 g, 4.80 mmol) was dissolved in hexane (100 cm^3) at 0 °C and AlMe_3 (5 cm^3 of a 2.0 mol dm^{-3} solution in hexanes, 10.0 mmol) was added dropwise over 5 min. The solution was set aside for 30 min at 0 °C, then 2 h at *ca.* 20 °C. Hexane was partially removed *in vacuo* and the clear solution left at 0 °C for crystallisation, yielding colourless crystals of compound **4** (1.67 g, 95%) (Found: C, 51.8 (duplicate analyses); H, 9.67; N, 7.13. $\text{C}_{16}\text{H}_{34}\text{Al}_2\text{N}_2\text{Si}_2$ requires C, 52.7; H, 9.40; N, 7.68%), mp 55–57 °C. ^1H NMR: δ –0.97 (s, 6H, AlMe), 0.06 (s, 6H, AlMe), 0.21 (s, 18H, SiMe_3), 6.76 (m, 2H, *m*- C_6H_4), 6.88 (m, 2H, *o*- C_6H_4); ^{13}C NMR: δ –10.5 and –2.9 (AlMe), 0.3 (SiMe_3), 118.8 (*m*-H), 123.2 (*o*-H), 142.4 (*ipso*-C); ^{27}Al NMR: δ 171.1 (br $\Delta w_{1/2}$ 2.3 kHz); ^{29}Si NMR: δ –8.84. MS (m/z , %): 584 (20, $[\text{AlMe}(\text{B})]_2^+$), 364 (10, $[\text{Al}_2\text{-Me}_4(\text{B})]^+$), 349 (100, $[\text{Al}_2\text{Me}_3(\text{B})]^+$), 292 (100, $[\text{AlMe}(\text{B})]^+$), 277 (65, $[\text{Al}(\text{B})]^+$), 261 (15, $[\text{Al}(\text{B}) - \text{MeH}]^+$), 73 (55, $[\text{SiMe}_3]^+$).

[(AlMe₂)₂(μ-B')] 5. A solution of AlMe₃ (6.1 cm³ of a 2.0 mol dm⁻³ solution in hexanes, 12.2 mmol) was added dropwise at ca. 0 °C to a solution of H₂(B) (1.50 g, 6.05 mmol) in hexane (30 cm³). The pale orange solution was stirred for 1 h at ca. 20 °C. The volume of the reaction mixture was reduced to ca. 10 cm³. Cooling at 0 °C yielded large colourless crystals of compound **5** (1.44 g, 67%) (Found: C, 65.9; H, 10.41; N, 7.64. C₂₀H₃₈Al₂N₂ requires C, 66.6; H, 10.62; N, 7.77%), mp 78 °C (decomp.). ¹H NMR: δ -0.90 (s, 6H, AlMe), -0.08 (s, 6H, AlMe), 0.90 (s, 18H, CMe), 2.92 (s, 4H, NCH₂), 6.73–6.85 (m, 4H, Ph); ¹³C NMR: δ -11.1 (AlMe), -5.4 (AlMe), 29.4 (CCH₃), 33.7 (CCH₃), 56.6 (NCH₂), 114.1–142.8 (Ph); ²⁷Al NMR: δ 167.4 (br s, Δ*w*_{1/2} 10 kHz).

[(AlMe)(μ-B)]₂ 6. Compound H₂(B) (1.32 g, 5.23 mmol) was dissolved in hexane (100 cm³) at 0 °C and AlMe₃ (2.6 cm³, of a 2.0 mol dm⁻³ solution in hexanes, 5.2 mmol) was added dropwise over 5 min. The solution was set aside for 30 min at 0 °C, then 2 h at ca. 20 °C. Hexane was partially removed *in vacuo* and the clear solution left at 0 °C for crystallisation, yielding colourless crystals of compound **6** (1.32 g, 85%) (Found: C, 52.3 (duplicate analyses); H, 8.60; N, 8.89 (duplicate analyses). C₂₆H₅₀Al₂N₂Si₂ requires C, 53.4; H, 8.61; N, 9.58%), mp 95 °C (decomp.). ¹H NMR: spectrum appears to be that of a mixture of three isomers ([AlMe)(μ-B)]₂ **I**, 50%; [(AlMe)(μ-B)]₂ **II**, 37% and [μ-Al(Me)(B)]₂ **III**, 13%): δ -0.47 (s, **I**), -0.42 (s, **III**) and 0.10 (s, **II**) [total 6H, AlMe], 0.11 (2d, **I**), 0.31 (2s, **III**), 0.38 (2s, **II**) [total 36H, SiMe₃], 6.48 (t), 6.58 (t) 6.62–6.66 (m), 6.85–7.07 (4 m) [total 8H, C₆H₄]; ¹³C NMR: δ -4.9 (m, AlMe), 1.4, 2.0 (2 s, SiMe₃), 115.4–119.3 (6s), 125.9, 126.3, 135.2, 135.6, 149.7, 150.7 (Ph); ²⁷Al NMR: δ 153.0 (br Δ*w*_{1/2} = 8 kHz); ²⁹Si NMR: δ -0.56, -1.4. MS (*m/z*, %): 584 (35, [AlMe(B)]₂⁺), 569 (10, [Al(B) - H]₂⁺), 292 (100, [AlMe(B)]⁺), 277 (55, [Al(B)]⁺), 261 (15, [Al(B) - MeH]⁺), 247 (50, [Al(B) - 2Me]⁺), 73 (55, [SiMe₃]⁺).

[(AlMe₂)₂(μ-(H)B')] 7. A solution of AlMe₃ (4.23 cm³ of a 2 mol dm⁻³ solution in hexanes, 8.47 mmol) was added to a solution of H₂(B') (2.1 g, 8.47 mmol) in hexane (30 cm³), at -40 °C. The solution was slowly warmed to ambient temperature and stirred for 3 h, then reduced to about 15 cm³ and cooled to -25 °C to afford colourless crystals of compound **7** (1.98 g, 77%) (Found: C, 69.4; H, 10.82; N, 9.11. C₁₈H₃₃AlN₂ requires C, 71.0; H, 10.92, N, 9.20%), mp 55–57 °C. ¹H NMR: δ -0.26, -0.21 (2 s, 6H, AlMe), 0.69, 1.19 (2 s, 18H, Bu^t), 2.32 (d, 1H, NH), 3.29 (s, 2H, CH₂), 3.19, 3.23, 3.25 (AB-type, partly overlapped with other CH₂ signal, 2H, CH₂), 6.53–6.58, 6.76–6.79, 6.9–6.93, 7.21–7.27 (m, 4H, Ph); ¹³C NMR: δ -9.5, -8.28 (AlMe), 27.36, 28.87 (CMe₃), 30.78, 34.52 (CMe₃), 57.86, 64.67 (CH₂), 112.27, 112.5, 123.76, 129.48, 131.71, 153.69 (Ph); ²⁷Al NMR: δ 169.5, Δ*w*_{1/2} 6 kHz. MS (*m/z*, %): 304 (7, [M]⁺), 289 (11, [M - Me]⁺).

[(AlMe)(μ-B')] 8. Compound **7** (1.6 g, 5.26 mmol) was dissolved in toluene (30 cm³) and heated for 2 d at 100 °C. The solvent was removed and the residue extracted into hexane. After filtration and cooling of the filtrate at -25 °C colourless crystals of compound **8** were obtained (1.05 g, 70%) (Found: C, 70.1; H, 10.16; N, 9.81. C₃₄H₅₈Al₂N₄ requires C, 70.8; H, 10.13; N, 9.71%), mp 163–165 °C. Alternatively, **8** was synthesised directly from H₂(B') and AlMe₃ by heating an equimolar mixture in toluene for 2 d at 100 °C. ¹H NMR: δ -0.2 (br s, 3H, AlMe), 0.88 (br s, 18H, Bu^t), 2.75, 2.8, 3.12, 3.17 (AB-type, 4H, CH₂), 6.63–6.68 (m, 4H, Ph); ¹³C NMR (338 K): δ -9.4 (AlMe), 29.9 (CMe₃), 34.3 (CMe₃), 58.7 (CH₂), 116.9, 119.5, 143.0 (Ph); ²⁷Al NMR (338 K): δ 75 Δ*w*_{1/2} 3.2 kHz. MS (*m/z*, %): 576 (11, [M]₂⁺), 288 (100, [M]⁺).

[(AlCl)(μ-B')] 9. A solution of LiBuⁿ (15.37 cm³ of a 1.6 mol dm⁻³ solution in hexane, 24.6 mmol) was added to a solution of

Table 10 Crystal data and refinement for the compounds 1–7, 9 and 10

	1	2	3	4	5	6	7	9	10
Formula	C ₂₂ H ₄₀ Al ₂ N ₂ Si ₂	C ₁₄ H ₂₆ AlN	C ₂₆ H ₄₄ Al ₂ N ₂	C ₁₆ H ₃₄ Al ₂ N ₂ Si ₂	C ₂₀ H ₃₈ Al ₂ N ₂	C ₂₆ H ₅₀ Al ₂ N ₂ Si ₂	C ₁₈ H ₃₃ AlN ₂	C ₃₂ H ₅₂ Al ₂ Cl ₂ N ₄	C ₂₂ H ₄₆ Al ₂ N ₂
Crystal system	Tetragonal	Orthorhombic	Monoclinic	Monoclinic	Triclinic	Monoclinic	Triclinic	Monoclinic	Triclinic
Space group	<i>P</i> 4 ₂ <i>c</i> (No. 114)	<i>P</i> mma (no. 62)	<i>C</i> 2/c (no. 15)	<i>P</i> 2 ₁ / <i>n</i> (no. 13)	<i>P</i> 1 (no. 2)	<i>C</i> 2/c (no. 15)	<i>P</i> 1 (no. 2)	<i>P</i> 2 ₁ / <i>n</i> (no. 14)	<i>P</i> 1 (no. 2)
<i>a</i> /Å	17.2628(3)	11.7498(6)	23.0800(7)	9.9516(3)	7.9936(2)	17.1014(5)	9.6526(5)	12.0101(7)	9.8445(2)
<i>b</i> /Å	17.2628(3)	15.3318(14)	9.1565(4)	10.0786(3)	10.0922(2)	11.6579(3)	9.7157(5)	14.8750(9)	10.7407(4)
<i>c</i> /Å	18.0235(5)	8.6902(8)	15.8407(4)	11.4394(3)	28.6783(6)	17.7117(5)	10.6710(6)	20.3163(10)	13.0190(4)
<i>a</i> ^o	90	90	90	90	86.587(1)	90	90.773(3)	90	98.740(2)
<i>β</i> ^o	90	90	126.852(2)	100.846(2)	86.748(1)	100.098(2)	96.342(3)	106.504(3)	99.440(2)
<i>γ</i> ^o	90	90	90	90	85.995(1)	90	102.991(3)	90	97.884(2)
<i>U</i> /Å ³	5371.1(2)	1565.5(2)	2678.7(2)	1126.86(6)	2300.6(1)	3476.4(2)	968.40(9)	3480.0(3)	1323.50(7)
<i>Z</i>	8	4	4	2	4	4	2	4	2
<i>ρ</i> (Mo-Kα)/mm ⁻¹	0.21	0.11	0.12	0.24	0.13	0.24	0.10	0.26	0.12
Unique reflections, <i>R</i> _{int}	4738, 0.063	1410, 0.071	3181, 0.050	1962, 0.041	8008, 0.061	4117, 0.048	4542, 0.051	4566, 0.045	6225, 0.032
Reflections with <i>I</i> > 2σ(<i>I</i>)	3976	1193	2625	1817	6742	3225	3879	3780	5143
Final <i>R</i> indices for <i>I</i> > 2σ(<i>I</i>)	<i>R</i> ₁ = 0.043, <i>wR</i> ₂ = 0.092	<i>R</i> ₁ = 0.061, <i>wR</i> ₂ = 0.124	<i>R</i> ₁ = 0.053, <i>wR</i> ₂ = 0.134	<i>R</i> ₁ = 0.043, <i>wR</i> ₂ = 0.183	<i>R</i> ₁ = 0.056, <i>wR</i> ₂ = 0.141	<i>R</i> ₁ = 0.057, <i>wR</i> ₂ = 0.143	<i>R</i> ₁ = 0.047, <i>wR</i> ₂ = 0.123	<i>R</i> ₁ = 0.045, <i>wR</i> ₂ = 0.106	<i>R</i> ₁ = 0.048, <i>wR</i> ₂ = 0.122
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.059, <i>wR</i> ₂ = 0.099	<i>R</i> ₁ = 0.075, <i>wR</i> ₂ = 0.129	<i>R</i> ₁ = 0.067, <i>wR</i> ₂ = 0.140	<i>R</i> ₁ = 0.046, <i>wR</i> ₂ = 0.186	<i>R</i> ₁ = 0.067, <i>wR</i> ₂ = 0.147	<i>R</i> ₁ = 0.076, <i>wR</i> ₂ = 0.158	<i>R</i> ₁ = 0.057, <i>wR</i> ₂ = 0.131	<i>R</i> ₁ = 0.057, <i>wR</i> ₂ = 0.115	<i>R</i> ₁ = 0.060, <i>wR</i> ₂ = 0.131

H₂(B') (3.05 g, 12.3 mmol) in toluene (50 cm³). The suspension was stirred for 1 h, cooled to -78 °C and AlCl₃ (1.64 g, 12.3 mmol) was added. The mixture was slowly warmed to ambient temperature and stirred for 16 h. The precipitate was filtered off and the solvent removed from the filtrate *in vacuo*. The remaining solid was dissolved in hexane and first frozen in liquid N₂ and then stored at -25 °C for several days to afford **9** as a beige solid (1.85 g, 49%) (it was too labile for elemental analysis), mp 45–50 °C (decomp.). ¹H NMR: δ 0.89 (s, 9H, Bu'), 3.05 (vbr quartet, 4H, CH₂), 6.49–6.54 (m, 4H, Ph); ¹H NMR (343 K): δ 0.92 (s, 9H, Bu'), 2.99, 3.02, 3.12, 3.15 (AB-type, 4H, CH₂), 6.54–6.59 (m, 4H, Ph); ¹³C NMR (343 K): δ 29.83 (CMe₃), 34.17 (CMe₃), 59.52 (CH₂), 117.8, 120.75, 140.93 (Ph); ²⁷Al NMR: δ 115.2 Δ*w*_{1/2} 3 kHz. MS (*m/z*, %): 273 (6%, [M - Cl]⁺).

[AlMe₃]₂·H₂(C') **10**. A solution of AlMe₃ (8.5 cm³ of 2.0 mol dm⁻³ solution in hexanes, 17.0 mmol) was added dropwise at ca. 0 °C to a solution of H₂(C') (2.00 g, 8.06 mmol) in hexane (30 cm³). The pale green suspension was stirred for 2 h at ambient temperature. Toluene (40 cm³) was added and the reaction mixture was heated until complete dissolution was achieved. Upon cooling, colourless crystals of compound **10** formed (2.50 g, 79%) (Found: C, 65.9; H, 11.88; N, 7.18. C₂₂H₄₆Al₂N₂ requires C, 67.3; H, 11.81; N, 7.14%), mp 137–139 °C. ¹H NMR: δ -0.55 (s, 18H, AlMe), 0.55 (s, 18H, CMe), 3.30 (d, ³J_{HH} = 5.7, 4H, NCH₂), 3.83 (t, ³J_{HH} = 5.7 Hz, 2H, NH), 6.62–6.73 (m, 4H, Ph); ¹³C NMR: δ -8.6 (AlMe), 27.7 (CCH₃), 32.8 (CCH₃), 61.2 (NCH₂), 113.7–145.5 (Ph); ²⁷Al NMR: δ 190.6 (br s, Δ*w*_{1/2} 11 kHz).

[{AlMe₃(tmen)}₂(μ-C')] **11**. A solution of LiBuⁿ (12.0 cm³ of a 1.6 mol dm⁻³ solution in hexane, 19.2 mmol) was added to a solution of H₂(C') (2.23 g, 9.0 mmol) and tmen (2.30 g, 19.8 mmol) in hexane (20 cm³). The suspension was stirred 1 h at ca. 25 °C, then added at ca. 0 °C to a solution of AlClMe₂ (19.0 cm³ of a 1.0 mol dm⁻³ solution in hexanes, 19.0 mmol). The beige suspension was stirred for 2 h at ca. 25 °C, then filtered. Volatiles were removed from the filtrate *in vacuo*. The residual white solid was washed with hexane and dried *in vacuo* to give compound **10** (3.16 g, 97%), which was not soluble in hydrocarbons or chlorinated solvents and was not characterised. Addition of 2 equivalents of tmen in thf, followed by removal of volatiles under moderate vacuum, produced the adduct **11**, as an orange oil in quantitative yield. ¹H NMR: δ -0.39 (s, 12H, AlMe), 1.02 (s, 18H, CMe₃), 1.98 (s, 24H, NMe₃), 2.37 (s, 8H, NCH₂ of tmen), 3.42 (s, 4H, NCH₂), 6.59–7.20 (m, 4H, Ph).

Crystallography

Diffraction data were collected on a Enraf-Nonius Kappa-CCD diffractometer at 173(2) K, using monochromated Mo-Kα radiation, λ = 0.71073 Å. Crystals were mounted on the diffractometer under a stream of cold nitrogen gas at 173 K. The structures were refined on all F² with H atoms in riding mode, using SHELXL-97.³⁷ Further details for are found in Table 10.

CCDC reference numbers 202056–202064.

See <http://www.rsc.org/suppdata/dt/b3/b300957m/> for crystallographic data in CIF or other electronic format.

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