N,N′-Di-*tert*-Butylethylenediamine–$\mathrm{Cl}_n\mathrm{H}_{3-n}\mathrm{AlNMe_3}$ Derivatives: Alane-rich $[(\mathrm{H_2Al})_2\{\mu\text{-}\mathrm{N(Bu^t)CH_2}\}_2]$ and Stable, Intramolecular Secondary Amine Alane Complexes $[\mathrm{Cl}_n\mathrm{H}_{2-n}\overline{\mathrm{Al\{N(H)(Bu^t)CH_2CH_2N}}\mathrm{Bu^t}]$, n = 0,1

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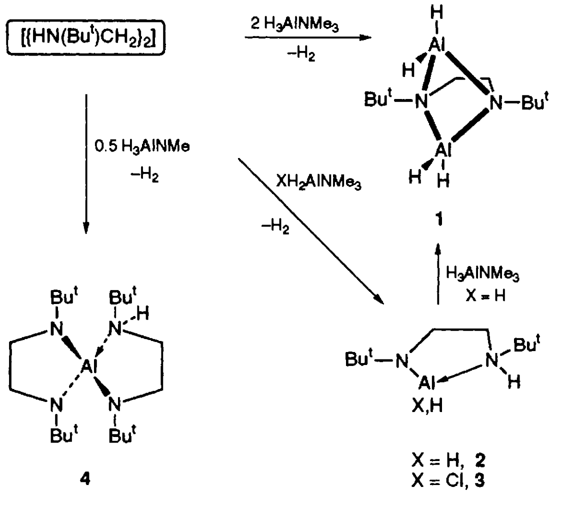
Treatment of *N,N′*-di-*tert*-butylethylenediamine with two equivalents of $\mathrm{H_3AlNMe_3}$ in diethyl ether affords a novel alane-rich amido species $[(\mathrm{H_2Al})_2\{\mu\text{-}\mathrm{N(Bu^t)CH_2}\}_2]$ **1**, whereas with one equivalent a stable, intramolecularly coordinated secondary amine adduct of aluminium dihydride results, $[\mathrm{H_2}\overline{\mathrm{Al\{N(H)(Bu^t)CH_2CH_2N}}\mathrm{Bu^t}]$ **2**; the monochloro analogue $[\mathrm{Cl(H)}\overline{\mathrm{Al\{N(H)(Bu^t)CH_2CH_2N}}\mathrm{Bu^t}]$ **3** is accessible using $\mathrm{ClH_2AlNMe_3}$, as a mixture of diastereoisomers in solution.

The only well characterised amidoalane complexes are (*i*) trimeric $[\{\mathrm{H_2Al}(\mu\text{-}\mathrm{NMe_2})\}_3]$,[1–3] and dimeric $[\{\mathrm{HAl}(\mu\text{-}\mathrm{NMe_2})(\mathrm{NMe_2})\}_2]$[3] and $[\{\mathrm{H_2Al}\{\mu\text{-}\mathrm{N(CHMeCH_2)_2CH_2}\}\}_2]$,[4] possessing either four- or six-membered $[\mathrm{AlN}]_n$ ring systems, and (*ii*) trimeric $[\{\mathrm{H}(\mu\text{-}\mathrm{H})\mathrm{Al}\{\mathrm{N(CHMeCH_2)_2CH_2}\}\}_3]$ and dimeric $[\{(\mu\text{-}\mathrm{H})\mathrm{Al}\{\mathrm{N(CMe_2CH_2)_2CH_2}\}_2\}_2]$ where the bulky amido groups circumvent N-bridging, and association is *via* H-bridges.[4] While this type of association is unknown for amidogallanes, a more extensive range of structural types have been established, including dimeric $[\{\mathrm{H_2Ga}(\mu\text{-}\mathrm{NMe_2})\}_2]$[5] (*cf.* trimeric for the aluminium analogue), trimeric $[[\mathrm{H_2Ga}\{\mu\text{-}\mathrm{N(CH_2)_2}\}]_3]$[6] and $[\{\mathrm{H_2Ga}(\mu\text{-}\mathrm{NH_2})\}_3]$,[7] $[(\mathrm{H_2Ga})_2\{\mu\text{-}\mathrm{N(Bu^t)CH_2}\}_2]$,[8] and the bis-amido species $[(\mathrm{HGa})_2\{(\mathrm{NPr^iCH_2})_2\}_2]$ and $[\mathrm{H_5Ga_3}\{(\mathrm{NMeCH_2})_2\}_2]$.[9]

In developing the bis-amido chemistry for alane we find that *N,N′*-di-*tert*-butylethylenediamine is readily metallated by $\mathrm{H_3AlNMe_3}$ affording three isolable amido species. Two of these are exceptional, notably the alane-rich $[(\mathrm{H_2Al})_2\{\mu\text{-}\mathrm{N(Bu^t)CH_2}\}_2]$ **1**, and the remarkably stable, intramolecularly coordinated secondary amine-amidoalane complex $[\mathrm{H_2}\overline{\mathrm{Al\{N(H)(Bu^t)CH_2CH_2N}}\mathrm{Bu^t}]$ **2**. We also report (*i*) the synthesis of the corresponding chlorohydrido species $[\mathrm{Cl(H)}\overline{\mathrm{Al\{N(H)(Bu^t)CH_2CH_2N}}\mathrm{Bu^t}]$ **3**, as a mixture of two diastereoisomers, with chirality at the metal and $\mathrm{N_{amine}}$ centres, (*ii*) the X-ray structure determination of one of these isomers as a means of substantiating the structure of **2**, as well as structurally authenticating a new class of compounds outright, and (*iii*) the X-ray structure determination of compound **1**.

Synthetic details are summarised in, Scheme 1.† A 2 : 1 ratio of $\mathrm{H_3AlNMe_3}$ to bis-amine favours compound **1**, whereas for a 1 : 1 ratio compound **2** is isolated. Increasing the amine component further removes all hydrido groups, affording compound **4**. Compound **3** was isolated from a 1 : 1 reaction of $\mathrm{ClH_2AlNMe_3}$ and the amine, as a 1 : 1 mixture of two diastereoisomers. The high stability of **2** (and **3**) with respect to hydrogen elimination (decomp. >215 °C) suggests that the formation of compound **1** possibly proceeds *via* **2**, which then binds $\mathrm{H_3Al}$ at the amido centre prior to the second metallation, and the formation of three-coordinate $\mathrm{HAl\{N(Bu^t)CH_2\}_2}$ is unlikely (such a species would bind $\mathrm{NMe_3}$ or diethyl ether solvent, or form hydrido bridges like those found in $[\{(\mu\text{-}\mathrm{H})\mathrm{Al}\{\mathrm{N(CMe_2CH_2)_2CH_2}\}_2\}_2]$[4]). The gallium analogue of **1** is conveniently formed *via* hydrometallation



Scheme 1 *Conditions*: OEt₂, −80 °C

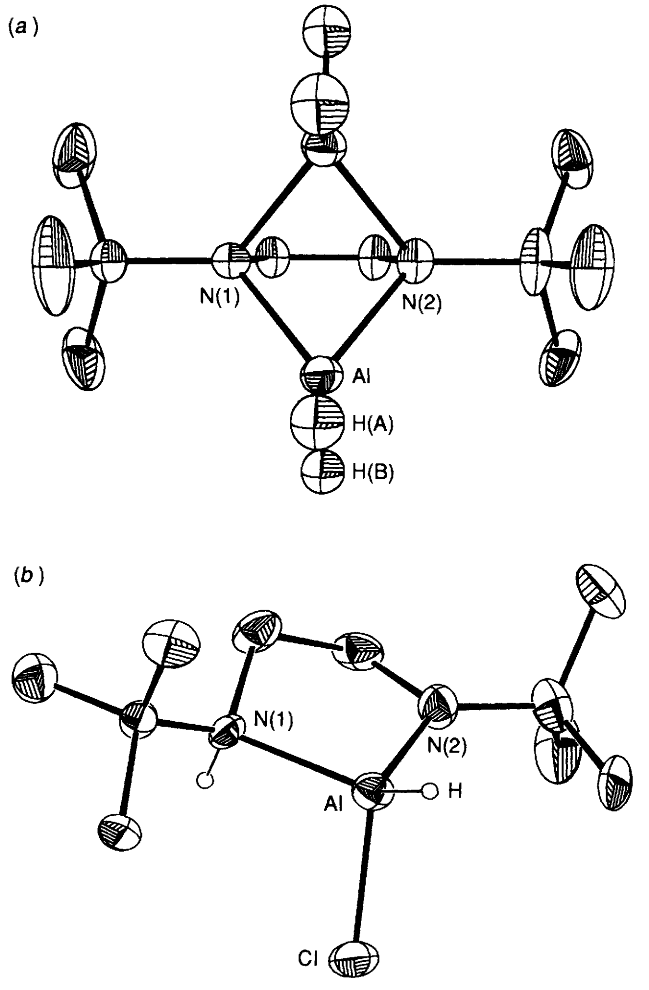


Fig. 1 Projections of (*a*) $[(\mathrm{H_2Al})_2\{\mu\text{-}\mathrm{N(Bu^t)CH_2}\}_2]$ **1**, and (*b*) $[\mathrm{Cl(H)Al\{N(H)(Bu^t)CH_2CH_2NBu^t}]$ **3**, with 20% thermal ellipsoids (arbitrary radii for H-atoms in **3**). Selected bond distances (Å) and angles (°): **1** Al–N(1,2) 1.941(7), 1.944(7); Al–H(A,B) 1.42(6), 1.37(7); Al···Al 2.726(5); Al–N(1)–Al 89.2; H(A)–Al–H(B) 113(4). **3** Al–H 1.60, Al–Cl 2.176(6), Al–N(1,2) 2.00(1), 1.80(1); H–Al–N(1,2) 127, 115; Cl–Al–N(1,2) 101.5(4), 116.5(4); N(1)–Al–N(2) 90.6(6); H–Al–Cl 106.

involving the appropriate diazabutadiene and $\mathrm{H_3GaNMe_3}$.[8] Interestingly, the corresponding diazabutadiene reaction involving $\mathrm{H_3AlNMe_3}$ affords a paramagnetic species, $[\{\mathrm{CH(Bu^t)N}\}_2\mathrm{Al}\{\mathrm{N(Bu^t)CH_2}\}_2]$,[10] rather than **1**.

Results of the X-ray structure determinations of **1** and **3**‡ are presented in Fig. 1. The asymmetric unit in **1** is half a molecule, the other half being generated by C_s symmetry with the N atoms and adjacent C atoms in the mirror plane, although the overall molecular symmetry is close to C_{2v}; molecules of **3** have only identity symmetry and the diastereoisomer isolated in the solid has the chloro group and N-proton on the same side of the plane of the chelate ring. Four-fold coordination of aluminium is achieved in **1** by way of bridging amido centres which is common for amidoaluminium species, except for (*i*) the hydrido bridging species $[\{(\mu\text{-H})\mathrm{Al}\{\mathrm{N(CMe_2CH_2)_2CH_2}\}_2\}_2]$,[4] (*ii*) the aluminates $[\{(\mathrm{Et_2O})_2\mathrm{Li}(\mu\text{-H})_2\mathrm{Al(H)N(SiMe_3)_2}\}_2]$ and $[\{(\mathrm{Et_2O})_2\mathrm{Li}(\mu\text{-H})_2\mathrm{Al}\{\mathrm{N(SiMe_3)_2}\}_2]$,[11] and (*iii*) monomeric **3** and $[\mathrm{H_2Al(NMe_3)}\{\mathrm{N(CMe_2CH_2)_2CH_2}\}]$[12] which involve neutral donor groups.

The four-membered $\mathrm{Al_2N_2}$ ring system in **1** is a common structural unit for dimeric amidoaluminium species.[3,13] They tend to be planar, for example in $[\{\mathrm{HAl}(\mu\text{-NMe_2})(\mathrm{NMe_2})\}_2]$,[3] unless steric buttressing intervenes,[14] where the $\mathrm{Al_2N_2}$ ring is puckered, as in the present case, but here it is a consequence of the geometrical requirements of the chelate rings. The angle between the two $\mathrm{AlN_2}$ planes, 126.7°, is a measure of the puckering, which is similar to the corresponding value in the isostructural gallium analogue, 123.7°,[8] noting aluminium and gallium have similar covalent radii. The Al–N distances at 1.943 Å are similar to those in structures with planar $\mathrm{Al_2N_2}$ rings, *e.g.* 1.966(2) Å in $[\{\mathrm{HAl}(\mu\text{-NMe_2})(\mathrm{NMe_2})\}_2]$,[3] and as expected are longer than where the amido centre is terminally bound, as in **3**, 1.80(1) Å, $[\mathrm{H_2Al(NMe_3)N(CMe_2CH_2)_2CH_2}]$, 1.838(2) Å,[12] $[(\mu\text{-H})\mathrm{Al}\{\mathrm{N(CMe_2CH_2)_2CH_2}\}_2]$,[4] 1.836 Å, and $[\{(\mathrm{Et_2O})_2\mathrm{Li}(\mu\text{-H})_2\mathrm{Al(H)N(SiMe_3)_2}\}_2]$ and $[\{(\mathrm{Et_2O})_2\mathrm{Li}(\mu\text{-H})_2\mathrm{Al}\{\mathrm{N(SiMe_3)_2}\}_2]$,[11] 1.86 Å. The Al–H distances in **1** and **3**, and the Al–Cl,$\mathrm{N_{amine}}$ distances in **3** are unexceptional.

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Footnotes

† Compound **1**: *N,N'*-di-*tert*-butylethylenediamine (0.15 g, 0.84 mmol) in $\mathrm{Et_2O}$ (10 ml) was added to a solution of $\mathrm{H_3AlNMe_3}$ (0.15 g, 1.69 mmol) in $\mathrm{Et_2O}$ (20 ml) over 15 min at −80 °C. After 2 h at room temperature the solution was filtered and concentrated *in vacuo* to *ca.* 10 ml affording colourless crystals on storing at −30 °C for 3 days (0.11 g, 60%); mp 158–159 °C, decomp. 215 °C (grey); ^{1}H NMR (250 MHz, $\mathrm{C_6D_6}$, 25 °C): δ 1.06 (s, 8H, $\mathrm{CCH_3}$), 2.78 (s, 4H, $\mathrm{CH_2}$), 4.30 (br, AlH); ^{13}C NMR (62.8 MHz, $\mathrm{C_6D_6}$, 25 °C): δ 29.3 (C*C*$\mathrm{H_3}$), 39.1 (*C*$\mathrm{H_2}$), 52.1 (*C*$\mathrm{CH_3}$); IR: ν/cm^{-1} 1860, 1752 (br, AlH).

Compound **2**: *N,N'*-di-*tert*-butylethylenediamine (0.75 g, 4.39 mmol) was added to a solution of $\mathrm{H_3AlNMe_3}$ (0.39 g, 4.39 mmol) in $\mathrm{Et_2O}$ (40 ml) at −80 °C. After 1 h at *ca.* 20 °C the solution was filtered and concentrated *in vacuo* to *ca.* 20 ml affording colourless crystals after 7 days at −26 °C (0.74 g, 85%); mp 197.6 °C, decomp. 292 °C (orange); ^{1}H NMR (200 MHz, $\mathrm{C_6D_6}$, 25 °C): δ 1.04 (1H, s, NH), 1.30, 1.32 (2 × 9H, s, $\mathrm{CH_3}$), 2.6 (2H, m, $\mathrm{CH_2}$), 2.8 (1H, m, $\mathrm{CH_2}$), 3.5 (1H, m, $\mathrm{CH_2}$); ^{13}C NMR (50.2 MHz, $\mathrm{C_6D_6}$, 25 °C): δ 29.9, 31.1 (C*C*$\mathrm{H_3}$), 45.4, 45.8 ($\mathrm{CH_2}$), 51.7, 55.5 (*C*$\mathrm{CH_3}$); ^{27}Al NMR (52.11 MHz, $\mathrm{C_6D_6}$, 25 °C): δ 134.87 ($w_{\frac{1}{2}}$ 2084 Hz); IR: ν/cm^{-1} 1840 (br, AlH). Found: C, 60.2; H, 12.4; N, 14.1. Calc. for $\mathrm{C_{10}H_{25}N_2Al}$: C, 60.0; H, 12.5; N, 14.0%).

Compound **3**: as for the synthesis of **2**; $\mathrm{ClH_2AlNMe_3}$ (0.19 g, 1.54 mmol) gave a white solid which was recrystallised from hexane (15 ml) at −30 °C for 10 days (0.23 g, 58%); mp 113.5–114.5 °C, decomp. 265 °C (yellow); ^{1}H NMR (200 MHz, $\mathrm{C_6D_6}$, 25 °C): δ 0.84, 0.87 (9H, s, $\mathrm{CH_3}$), 1.38, 1.39 (9H, s, $\mathrm{CH_3}$), 2.3, 2.8 (4H, m, $\mathrm{CH_2}$) 2.75; ^{13}C NMR (50.2 MHz, $\mathrm{C_6D_6}$, 25 °C): δ 27.5, 27.7, 30.2, 30.5 (C*C*$\mathrm{H_3}$), 41.4, 42.4, 44.2, 44.9 (*C*$\mathrm{H_2}$), 51.0, 51.3, 54.9, 55.9 (*C*$\mathrm{CH_3}$); IR: ν/cm^{-1} 1840.5 (br, AlH).

Compound **4**: *N,N'*-di-*tert*-butylethylenediamine (0.775 g, 4.49 mmol) was added to a solution of $\mathrm{H_3AlNMe_3}$ (0.20 g, 2.25 mmol) in $\mathrm{Et_2O}$ (50 ml) at −80 °C. After 30 min at −80 °C then 2.5 h at *ca.* 20 °C the solution was filtered and volatiles were removed *in vacuo*. The pale yellow powder was recrystallised from hexane (15 ml) at −30 °C over 9 days (0.74 g, 89.2%); mp 174.7 °C, decomp. 279 °C (orange); ^{1}H NMR (200 MHz, $\mathrm{C_6D_6}$, 25 °C): δ 1.03, 1.27, 1.37, 1.39 (3 9H, s, $\mathrm{CH_3}$), 2.3 (2H, m, $\mathrm{CH_2}$(, 2.65 (3H, m, $\mathrm{CH_2}$), 3.1 (1H, m, $\mathrm{CH_2}$), 3.2 (2H, m, $\mathrm{CH_2}$); ^{13}C NMR (50.2 MHz, $\mathrm{C_6D_6}$, 25 °C): δ 28.9, 30.0, 30.8, 31.0 (C*C*$\mathrm{H_3}$), 42.42, 43.91, 45.86, 46.04 (*C*$\mathrm{H_2}$), 51.2, 51.5, 51.5, 54.6 (*C*$\mathrm{CH_3}$); IR: ν/cm−1 3246 (s, NH).

‡ *Crystal structure determinations* (T = 296 K; Enraf-Nonius CAD4 diffractometer, crystals mounted in capillaries): compound **1**, $\mathrm{C_{10}H_{26}Al_2N_2}$, M = 228.3, orthorhombic, space group, *Pnma*, a = 12.818(7), b = 10.693(3), c = 10.834(3) Å, U = 1485 Å^3, $F(000)$ = 504; Z = 4, D_c = 1.021 g cm^{-3}, Mo-Kα, λ = 0.71069 Å, μ(Mo-kα) = 1.24 cm^{-1}. specimen 0.20 × 0.20 × 0.25 mm, 1222 unique reflections, 520 with $I > 3\sigma(I)$ used in the refinement, $2\theta_{\max}$ = 46°. Compound **3**, $\mathrm{C_{10}H_{24}AlClN_2}$, M = 234.8, orthorhombic, space group *Pbca*, a = 12.019(1), b = 12.922(1), c = 18.802(2) Å, U = 2920 Å^3, $F(000)$ = 1024; Z = 8, D_c = 1.068 g cm^{-3}, Mo-Kα, λ = 0.71069 Å, μ(Mo-Kα) = 1.2 cm^{-1}, specimen 0.20 × 0.25 × 0.40 mm, 1465 unique reflections, 675 with $I > 3\sigma(I)$ used in the refinement, $2\theta_{\max}$ = 50°.

The structures were solved by direct methods and refined by full-matrix least-squares using SHELX. For **1** H atoms attached to Al and the methylene H atoms were located and refined in x,y,z, U_{iso}; for **3** the analogous H atoms were included as invariants. Unit weights were used and the final residuals were R = 0.070, 0.076, R_w = 0.077, 0.085, for **1** and **3** respectively. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

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