# Polydentate Tertiary Amine Aluminium Hydride Adducts: Monomeric *versus* Polymeric Species

Jerry L. Atwood,*[a] Frederick R. Bennett,[b] Cameron Jones,[b] George A. Koutsantonis,[b] Colin L. Raston*[b] and Kerry D. Robinson[a]

[a] *Department of Chemistry, University of Alabama, Tuscaloosa, Alabama, 35487, USA*
[b] *Division of Science and Technology, Griffith University, Nathan, Brisbane, Queensland, 4111, Australia*

Treatment of $H_3AlNMe_3$ with 1,3,5-trimethylhexahydro-1,3,5-triazine (tmtz) yields trigonal bipyramidal, monomeric $[H_3Al(tmtz)_2]$, **1**, or polymeric $[H_3Al(tmtz)]_\infty$, **2**, which undergo $N-CH_2$ cleavage at *ca.* 123 °C; nitrogen-atoms in **1** and **2** are in apical positions, as also established for polymeric $[H_3Al(N,N,N',N'$- tetramethylpropylenediamine)$]_\infty$, in accordance with *ab initio* molecular orbital calculations on the model system $H_3Al(NH_3)_2$.

Tertiary amine aluminium hydride adducts are versatile reagents in synthesis,[1] and as precursors for delivering aluminium metal to surfaces.[2–5] Recently we established that the ubiquitous trimethylamine adduct, $H_3AlNMe_3$, and some other unidentate amine adducts, are dimeric in the solid, possessing unsymmetrical hydride bridges,[6] in contrast with monomeric $H_3AlNMe_3$ in the gas phase.[7] The availability of more than one tertiary amine centre can result in (*i*) five-coordinate species, *e.g.* $H_3Al(NMe_3)_2$,[8] polymeric $H_3Al(tmeda)$[9] (tmeda = $N,N,N'N'$-tetramethylethylene-

diamine) (based on incomplete X-ray structure determinations), and dimeric $H_3Al(tmeda)$ (vapour phase),[10] and (*ii*) ionic species for higher polydentate tertiary amines, $[H_2Al(N,N,N',N'',N''$-pentamethyldiethylenetriamine)$]^+[AlH_4]^-$, and *trans*-$[H_2Al(N,N',N'',N'''$-tetramethyl-cyclam)$]^+[AlH_4]^-$.[11]

1,3,5-Trimethylhexahydro-1,3,5-triazine (tmtz) is potentially a tridentate tertiary amine, but because of steric strain in any derived four-membered chelate rings oligomeric species are more likely, in which the metal forms a polymeric network
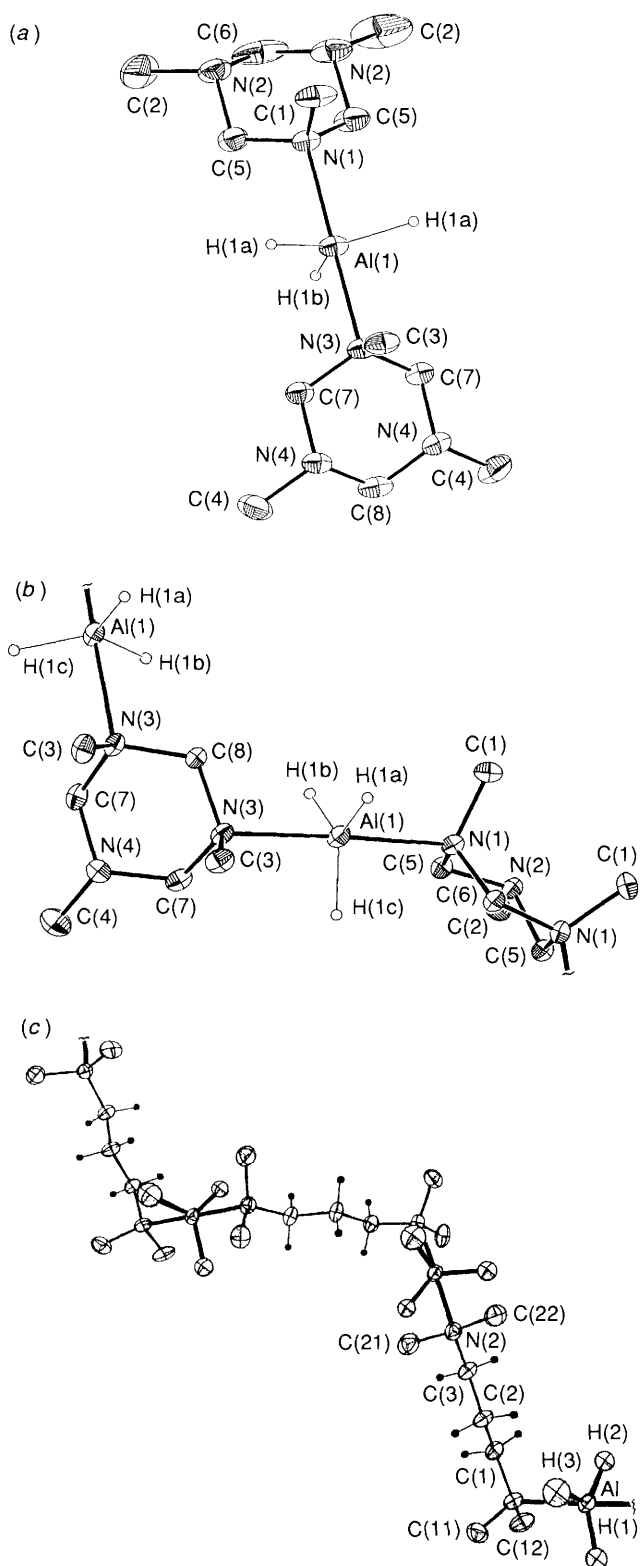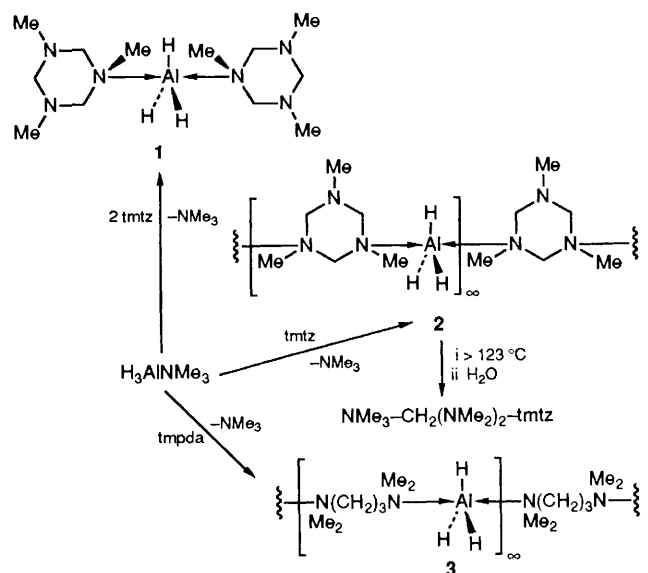
**Scheme 1**

**Fig. 1** Projections of (a) [H₃Al(tmtz)₂], **1**, (b) [H₃Al(tmtz)]∞, **2**, and (c) [H₃Al(tmpda)]∞, **3**, with 20% thermal ellipsoids for non-hydrogen atoms and arbitrary radii for hydrogen atoms shown, hydrides for **3** excepted. Selected bond distances (Å) and angles (°): **1** Al(1)–N(1, 3) 2.188(4), 2.187(4), Al(1)–H(1a, b) 1.64(4), 1.70(6), N(1)–Al(1)–N(3) 177.4(2); N(1)–Al(1)–H(1a, b) 90(1), 91(2), N(3)–Al(1)–H(1a, b) 89(1), 92(2), H(1a)–Al(1)–H(1b) 120(1), H(1a)–Al–H(1a)′ 120(2). **2** Al(1)–N(1, 3) 2.231(5), 2.198(6), Al(1)–H(1a, b, c) 1.61, 1.51, 1.48; N(1)–Al(1)–N(3) 174.9(2), N(1, 3)–H(1a, b, c) 84–93. **3** Al(1)–N(1, 2) 2.217(4), 2.200(4), Al(1)–H(1, 2, 3) 1.61(4), 1.47(4), 1.62(5); N(1)–Al(1)–H(1, 2, 3) 88(2), 93(2), 87(2), N(2)–Al(1)–H(1, 2, 3) 92, 94, 95, N(1)–Al(1)–N(2) 177.9(1), H(1)–Al(1)–H(2, 3) 114(2), 124(3), H(2)–Al(1)–H(3) 122 (3).

with the metal centres connected to two different tmtz units, as for the related ligand hexamethylenetetramine.[12] We report that tmtz forms neutral rather than ionic species, monomeric, [H₃Al(tmtz)₂], **1**, and polymeric, [H₃Al(tmtz)]∞ **2**, and that the 1:1 adduct of aluminium hydride with N,N,N′,N′-tetramethylpropylenediamine (tmpda), viz. [H₃Al(tmpda)]∞, **3**, is also polymeric in the solid, although it is dimeric in benzene.[13] Connectivity has been established using X-ray diffraction data and the resulting refinements represent the first complete structure determinations of five-coordinate aluminium hydride species. We also report a high level theoretical study on the model compound, H₃Al(NH₃)₂.

Synthesis of **1**, **2** and **3**,[13] involved treating H₃AlNMe₃ with the corresponding amine in the appropriate ratio, Scheme 1.† No further uptake of aluminium hydride from H₃AlNMe₃ is evident on the formation of **2** despite the availability of a nitrogen lone pair on each tmtz moiety (see below). Compound **1** decomposes thermally to **2** then undergoes N–CH₂ cleavage at ca. 123 °C yielding on hydrolysis NMe₃ and CH₂(NMe₂)₂, and some tmtz. The aluminium hydride adduct of CH₂(NMe₂)₂ also undergoes N–CH₂ cleavage but at ambient temperature.[14] All other aluminium hydride tertiary

amine adducts,[6,10,11] including **3** and those based on tmeda and $N,N,N',N'$-tetramethylbutylenediamine (tmbda),[15] decompose to free amine, metal and hydrogen, at typically >100 °C.

Results of the X-ray structure determinations of **1–3**‡ are presented in Fig. 1. Molecules in **1** have $m$-crystallographic symmetry whereas in **2** two tmtz ligands have $m$-crystallographic symmetry, and in **3** the asymmetric unit is AlH₃ and one diamine. In all three structures, and also in polymeric H₃Al(tmbda),[15] the metal centres are trigonal planar with the nitrogens in apical positions and Al–N distances (mean), **1**, 2.188, **2**, 2.217, **3**, 2.208 Å. These distances are significantly longer than in monomeric mono-tertiary amine aluminium hydride derivatives, 2.063(8) for H₃AlNMe₃ (gas phase),[7] and 2.088(2) and 2.082(4) Å for weakly associated [(H₃AlL)₂], L = benzyldimethylamine and 1-methyltetrahydropyridine,[6] reflecting greater solvation at the metal centres. The earlier defined Al–N distances in H₃Al(NMe₃)₂[8] and H₃Al(tmeda)[9] are similar, at 2.18(1) and 2.21 Å, respectively. In **2** the one dimensional polymeric strand results in a congested metal free N-centre, thus accounting for the lack of additional uptake of aluminium hydride. Five-coordinate adducts of aluminium hydride have also been structurally authenticated for phosphine and mixed phosphine–amine aluminium hydride adducts.[16]

Collectively, structural information on bis(amine) aluminium hydride adducts clearly establish the preference for the AlH₃ entity to be planar even if a chelate ring is likely to be relatively unstrained as would be the case in monomeric adducts of tmpda. *Ab initio* molecular orbital calculations§

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‡ *Crystal structure determinations* ($T$ = 296 K; Enraf-Nonius CAD4 diffractometer, crystals mounted in capillaries): compound **1**, $C_{12}H_{33}AlN_6$, $M$ = 288.4, monoclinic, space group $I2/m$, $a$ = 10.906(8), $b$ = 12.784(5), $c$ = 13.58(1) Å, $\beta$ = 99.99(4)°, $U$ = 1865 Å³, $F(000)$ = 640; $Z$ = 4, $D_c$ = 1.034 g cm⁻³, Mo-Kα λ = 0.71069 Å, μ(Mo-Kα) = 1.14 cm⁻¹, specimen 0.25 × 0.30 × 0.30 mm, 1714 unique reflections, 1043 with $I$ > 2.5σ($I$) used in the refinement, $2\theta_{max}$ = 50°. Compound **2**, $C_6H_{18}AlN_3 \cdot (OEt_2)$ 0.5, $M$ = 196.3, orthorhombic, space group $Pmnn$, $a$ = 11.569(1), $b$ = 12.606(1), $c$ = 15.532(2) Å, $U$ = 2265 Å³, $F(000)$ = 768; $Z$ = 8, $D_c$ = 1.15 g cm⁻³, Mo-Kα λ = 0.71069 Å, μ(Mo-Kα) = 1.47 cm⁻¹, specimen 0.15 × 0.25 × 0.40 mm, 2102 unique reflections, 1272 with $I$ > 2.5σ($I$) used in the refinement, $2\theta_{max}$ = 50°. Compound **3**, $C_7H_{21}AlN_2$, $M$ = 160.2, orthorhombic, space group $Pbca$, $a$ = 12.265(1), $b$ = 12.499(2), $c$ = 14.272(1) Å, $U$ = 2188 Å³, $F(000)$ = 720; $Z$ = 8, $D_c$ = 0.98 g cm⁻³, Cu-Kα λ = 1.5418 Å, μ(Cu-Kα) = 11.7 cm⁻¹, specimen 0.20 × 0.25 × 0.35 mm, 1236 unique reflections, 1030 with $I$ > 3σ($I$) used in the refinement, $2\theta_{max}$ = 110°.

The structures were solved by direct methods and refined by full-matrix least-squares refinement using SHELX and XTAL programmes. Hydrogen atoms attached to Al were located and refined in $x, y, z, U_{iso}$, **1**, or $x, y, z$, **2** and **3**; hydrogens attached to carbon were included as invariants. Unit weights were used and the final residuals were $R$ = 0.053, 0.077, 0.058, $R'$ = 0.053, 0.077, 0.062, **1**, **2** 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.

§ Calculation used the Hondo/7 package[19] on the Convex platform. To investigate the effects of polarization on the Al–N bonds the DZ basis sets were augmented with $d$-functions (DZP) on Al and N (exponents of $d$-functions were 0.3 and 0.8, respectively);. A comparison with earlier work on H₃AlNH₃[6] shows that the Al–N bond length increases by only 0.017 Å, when the ECP approximation is implemented, and therefore, the ECP approximation represents a good compromise between economy and accuracy for this study.

were carried out on H₃Al(NH₃)₂ at the Hartree Fock (HF) level of theory using a double-zeta (DZ) then double-zeta plus polarisation (DZP), both with an effective core potential (ECP) for Al.[17] HF/DZP-ECP calculations converged with $D_{3h}$ symmetry, Al–N 2.220, Al–H 1.611 Å, N–Al–H 90.0° (N–H 1.005 Å, Al–N–H 110.9°) which is close to the structures of **1–3**. Starting with geometries for the isomeric $C_{2v}$ and $C_s$ trigonal bipyramidal structures for H₃Al(NH₃)₂ resulted in fragmentation to H₃AlNH₃ and NH₃ which collectively are only 10.74 kcal mol⁻¹ (1 cal = 4.184 J) less stable than H₃Al(NH₃)₂. This is consistent with equilibrium between H₃Al(NMe₃)₂ and H₃AlNMe₃–NMe₃,[18] and overall represents an energy inequality: $C_{2v}$ and $C_s$ H₃Al(NH₃)₂ < H₃AlNH₃–NH₃ < $D_{3h}$ H₃Al(NH₃)₂.

## References

1 E. M. Marlett and W. S. Park, *J. Org. Chem.*, 1990, **55**, 2968 and references cited therein; F. G. N. Cloke, C. I. Dalby, M. J. Henderson, P. B. Hitchcock, C. H. L. Kennard, R. N. Lamb and C. L. Raston, *J. Chem. Soc., Chem. Commun.*, 1990, 1394; B. M. Bulychev, *Polyhedron*, 1990, **9**, 387; E. M. Marlett, US Pat. 4474743, 1984.

2 D. L. Schmidt and R. Hellmann, US Pat. 3462288, T. E. G. Daenen, UK Pat. GB 2021646, 1979.

3 W. L. Gladfelter, D. C. Boyd and K. F. Jensen, *Chem. Mater.*, 1989, **1**, 339 and references cited therein; A. T. S. Wee, A. J. Murrell, N. K. Singh, D. O'Hare and J. S. Ford,. *J. Chem. Soc., Chem. Commun.*, 1990, 11.

4 T. H. Baum, C. E. Larson and R. L. Jackson, *Appl. Phys. Lett.*, 1989, **55**, 1264.

5 T. P. Whaley and V. Norman, US Pat. 3206326, 1965; D. R. Carley and J. H. Dunn, US Pat. 3375129, 1968.

6 J. L. Atwood, F. R. Bennett, F. M. Elms, C. Jones, C. L. Raston and K. D. Robinson, *J. Am. Chem. Soc.*, 1991, **113**, 8183.

7 A. Almenningen, G. Gundersen, T. Haugen and A. Haaland, *Acta Chem. Scand.*, 1972, **26**, 3928.

8 C. W. Heitsch, C. E. Nordman and P. W. Parry, *Inorg. Chem.*, 1963, **2**, 508.

9 G. Palenick, *Acta Crystallog.*, 1964, **17**, 1573.

10 J. M. Davidson and T. Wartik, *J. Am. Chem. Soc.*, 1960, **82**, 5506.

11 J. L. Atwood, C. Jones, C. L. Raston, and K. D. Robinson, *J. Chem. Soc., Chem. Commun.*, 1991, 1697.

12 B. F. Abrahamas, B. F. Hoskins, J. Liu and R. Robson, *J. Am. Chem. Soc.*, 1991, **113**, 3045.

13 R. Archer, H. Young and R. Ehrlich, *Inorg. Chem.*, 1965, **4**, 1358.

14 N. N. Greenwood, B. P. Straughan and B. S. Thomas, *J. Chem. Soc. A*, 1968, 1248.

15 J. L. Atwood, C. Jones, C. L. Raston and K. D. Robinson, unpublished results.

16 F. R. Bennett, F. M. Elms, M. G. Gardiner, G. A. Koutsantonis, C. L. Raston and N. K. Roberts, *Organometallics*, in the press; F. R. Bennett, C. Jones, G. A. Koutsantonis and C. L. Raston, unpublished work.

17 W. R. Wadt and J. Hay, *J. Chem. Phys.*, 1985, **82**, 284.

18 C. W. Heitsch, *Nature*, 1962, **195**, 995.

19 M. Dupuis, J. D. Watts, H. O. Villar and G. J. B. Hurst, Hondo Version 7.0, IBM, Kingston, New York, 1987.