A Thermally Stable Alane–Secondary Amine Adduct: $[H_3Al(2,2,6,6\text{-Tetramethylpiperidine})]$

Jerry L. Atwood,[a] **George A. Koutsantonis,**[b] **Fu-Chin Lee**[b] **and Colin L. Raston***[b]

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

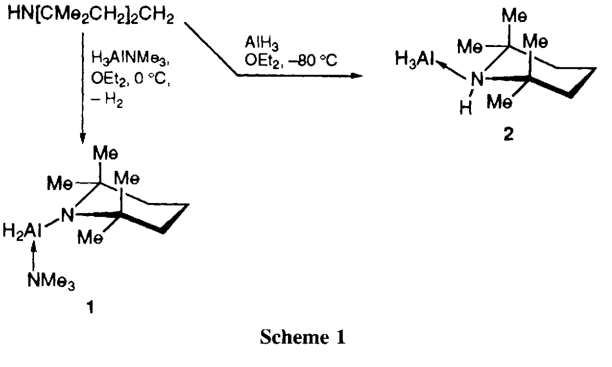
Metallation of 2,2,6,6-tetramethylpiperidine, $HN[CMe_2CH_2]_2CH_2$ (=HL), by H_3AlNMe_3 in diethyl ether affords a monomeric, Lewis base-stabilised amidoalane Me_3NAlH_2L,**1** [Al–N_{amido}, N_{amine} 1.838(2), 2.058(2) Å], whereas treating AlH_3 generated *in situ* with the same amine in diethyl ether yields a remarkably stable secondary amine adduct of alane $H_3Al(HL)$, **2** (decomp. > 115 °C), also as a monomer in the solid [Al–N_{HL} 2.04(1) Å].

Tertiary amine alane adducts show a remarkably diverse range of structural types. The trimethylamine adduct, H_3AlNMe_3, and some other unidentate amine adducts are dimeric in the solid possessing unsymmetrical hydride bridges.[1] This is in contrast to monomeric H_3AlNMe_3 in the gas phase,[2] and $H_3Al(quinuclidine)$[3] and $H_3AlNBu^n{}_3$[4] in the solid state. Polydentate tertiary amines yield oligomeric five-coordinate species[5,6] or ionic species.[7] All these compounds thermally decompose yielding aluminium metal, except adducts of 1,3,5-trimethylhexahydro-1,3,5-triazine, where N–C bond scission prevails.[6]

Secondary amines are usually rapidly metallated in the presence of alane above *ca.* −20 °C, affording amidometal species.[8] We find that H_3AlNMe_3 rapidly reacts with the bulky amine 2,2,6,6-tetramethylpiperidine ($HN[CMe_2CH_2]_2CH_2$, HL) at *ca.* 0 °C affording the monomeric Lewis base-stabilised amidoalane Me_3NAlH_2L **1**. However, the reaction of diethyl ether-solvated alane, generated *in situ* from $LiAlH_4$ and HCl, with the same amine yields the secondary amine adduct of alane, $H_3Al(HL)$, **2**, which has remarkably high thermal stability, Scheme 1.† Interestingly Klein *et al.* recently reported that the reaction of $LiAlH_4$ with HL·HCl affords $[\{H(\mu\text{-}H)Al\{N[CMe_2CH_2]_2CH_2\}\}_3]$ as a trimeric H-bridged species, and that H_3AlNMe_3 with two equivalents of HL results in dimeric $[\{(\mu\text{-}H)Al\{N[CMe_2CH_2]_2CH_2\}_2\}_2]$, also associated *via* H-bridges.[9] Amidoalane complexes are usually associated *via* N-bridges as in $[\{H_2Al(\mu\text{-}NMe_2)\}_3]$,[10,11] $[\{HAl(\mu\text{-}NMe_2)(NMe_2)\}_2]$,[11] $[\{H_2Al\{\mu\text{-}N[CHMeCH_2]_2CH_2\}\}_2]$,[9] and $[(H_2Al)_2\{\mu\text{-}N(Bu^t)CH_2\}_2]$,[12] except (*i*) where there is Lewis base stabilisation of the monomer, as in **1**, and $[H_2Al\{N(H)(Bu^t)CH_2CH_2NBu^t\}]$,[12] or (*ii*) for aluminate species, notably $[\{(Et_2O)_2Li(\mu\text{-}H)_2Al(H)N(SiMe_3)_2\}_2]$ and $[\{(Et_2O)_2Li(\mu\text{-}H)_2AlN(SiMe_3)_2\}_2]$.[13]

If the primary process for the formation of **1** is complexation of the bulky amine, then subsequent metallation without loss of trimethylamine may be favoured by release of steric strain and formation of a four-coordinate species. In the absence of trimethylamine any weakly bound diethyl ether may dissociate at the expense of complexation of the secondary amine. Seemingly here there is no steric impetus for elimination of hydrogen from the four-coordinate species, **2**, with stabilisation of any amidoalane by amido bridging being sterically suppressed. Compounds **1** and **2** decompose to grey metallic powders at 160 and 165 °C respectively, which are in the upper decomposition temperature range established for tertiary amine adducts of alane.[1,6] Compound **2** initially melts at 115–117 °C with evolution of a gas, presumably arising from hydrogen elimination and amidometal formation.

Results of the X-ray structure determinations‡ of **1** and **2** are presented in Fig. 1. Both structures consist of four-coordinate molecules of C_s-symmetry, which is crystallographi-



Scheme 1

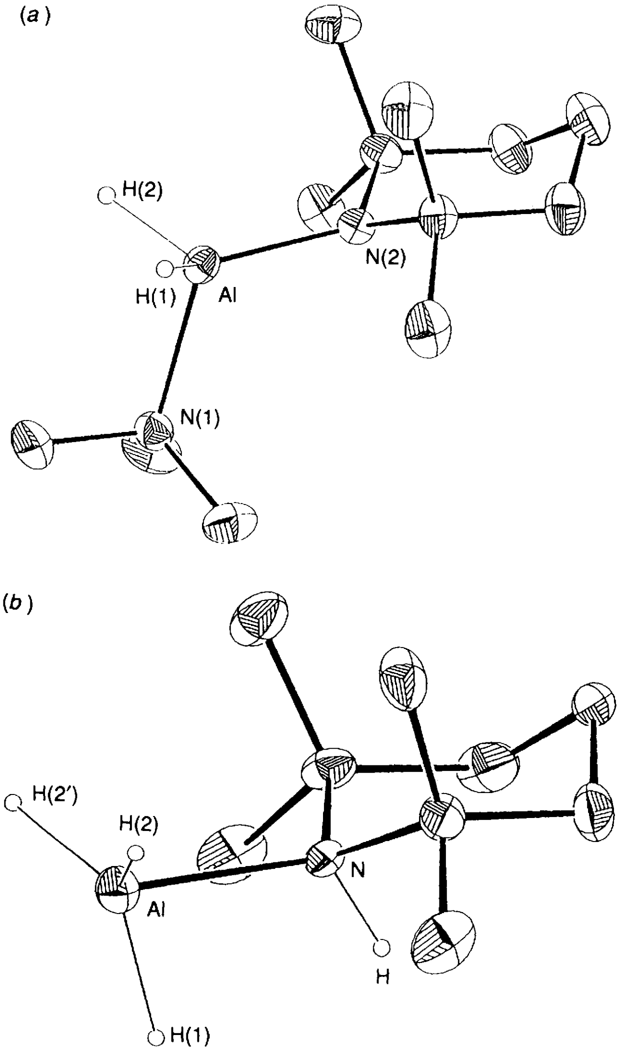


Fig. 1 Projections of (*a*) Me_3NAlH_2L **1**, and (*b*) $[H_3Al(HL)]$ **2**, with 20% thermal ellipsoids for non-hydrogen atoms and arbitrary radii for hydrogen atoms where shown. Selected bond distances (Å) and angles (°): **1** Al–N(1) 2.058(2), Al–N(2) 1.838(2), Al–H(1) 1.61(2), Al–H(2) 1.56(3), N(1)–Al–N(2) 114.4(1), N(1)–Al–H(1) 99.1(9), N(1)–Al–H(2) 99(1), N(2)–Al–H(1) 115.8(9), N(2)–Al–H(2) 116(1), H(1)–Al–H(2) 109(1); **2** Al–N 2.04(1), Al–H(1,2) 1.44(9), 1.60(7), N–H 1.03(8), H···H(1) 2.3(2), N–Al–H(1, 2) 79(4), 104(2), H(1)–Al–H(2) 116(3), H(2)–Al–H(2′) 124(3), Al–N–H 118(5), Al–N–C(1) 114.7(6).

cally imposed for **2**. The Al–N$_{amido}$ distance in **1**, 1.838(2) Å, is similar to that found in [{(μ-H)Al{N[CMe$_2$CH$_2$]$_2$CH$_2$}$_2$}$_2$], 1.836 Å,[9] and [{(Et$_2$O)$_2$Li(μ-H)$_2$Al(H)N(SiMe$_3$)$_2$}$_2$] and [{(Et$_2$O)$_2$Li(μ-H)$_2$AlN(SiMe$_3$)$_2$}$_2$], 1.86 Å,[13] and in three-coordinate dialkylamidoaluminium species.[14] A significant departure from a trigonal planar N$_{amido}$ centre in **1** ($\Sigma_{\text{dihedral angles}}$ = 353.7°, *cf.* 344.4° for the corresponding angles at the N$_{amine}$ centre in **2**) most likely results from minimisation of the non-bonding interaction between the associated methyl groups, and hydrides on the metal centre, Fig. 1. However, this is a dynamic structure in solution on the NMR time scale. The Al–N$_{amine}$ distance in **1**, 2.058(2) Å, compares with the Al–N$_{amine}$ distance in **2**, 2.04(1) Å, and is within the realms of that established for related structures, *viz.* 1.991(4) Å in H_3Al(quinuclidine),[1] 2.063(8) Å, for H_3AlNMe_3 (gas phase),[2] and 2.088(2) and 2.082(4) Å for weakly associated $(H_3AlL)_2$, L = benzyldimethylamine and 1-methyltetrahydropyridine.[1]

The novelty of the structure of **2** is the presence of adjacent $N{-}H^{\delta+}\cdots{}^{\delta-}H{-}Al$ groups with H···H(1) at 2.31 Å, Fig. 1(*b*). While this is at the van der Waal's limit, and despite the relative inaccuracy of the structure determination, it represents a transition state prior to dihydrogen evolution *en route* to an amidometal species. Further credence for this is the eclipsed geometry of the H_3Al entity with respect to the ligand, along the AlN bond. All structures of alane amine species to date have exhibited a staggered arrangement about this bond, and in theoretical calculations involving H_3Al and NH_3 the eclipsed geometry represents a first-order transition state.[15]

We thank the Australian Research Council for a Grant and the Department of Industry, Technology and Commerce (Australia) for support of this work. We also thank Karl Byriel, Colin Kennard and Kerry Robinson for collection of some diffraction data.

Received, 3rd August 1993; Com. 3/04661C

Footnotes

† Compound **1**: 2,2,6,6-tetramethylpiperidine (1 ml, 5.93 mmol) was added to an ethereal solution (25 ml) of H_3AlNMe_3 (0.53 g, 5.93 mmol) at 0 °C with immediate evolution of a gas. After stirring for 2 h at room temperature, the solvent was removed *in vacuo* and the resulting white solid recrystallised from toluene (yield 0.61 g, 45%), mp 98–100 °C; ^{1}H NMR (250 MHz, C_6D_6, 25 °C): δ 1.91 (s, 9H, NCH$_3$), 1.63 (s, 12H, CCH$_3$), 1.55 (t, 4H, ^3J 6.0 Hz, NCCH$_2$), 1.75 (m, 2H, NCCCH$_2$) and 3.58 (br, 2H, AlH); ^{13}C NMR (62.8 MHz, C_6D_6, 25 °C): δ 18.9 (NCC*C*H$_2$), 35.5 (NC*C*H$_3$), 43.2 (NC*C*H$_2$), 48.7 (N*C*H$_3$) and 52.2 (N*C*); ^{27}Al NMR (52.11 MHz, tetrahydrofuran, 25 °C): δ 135.5, peak width half height 2062 Hz; IR: ν/cm^{-1} 1768 (br, AlH). Compound **2**: 2,2,6,6-tetramethylpiperidine (1 ml, 5.93 mmol) was added to an ethereal solution (25 ml) of alane (5.93 mmol) at −80 °C. After 2 h at room temperature the solution was filtered, concentrated and cooled to −30 °C to afford colourless crystals 0.53 g, yield 53%), mp 115–117 °C; ^{1}H NMR (250 MHz, C_6D_6, 25 °C): δ 1.15 (s, 12H, CCH$_3$), 0.92 (t, 4H, ^3J 6.0 Hz, NCCH$_2$), 1.50 (m, 2H, NCCCH$_2$), 4.43 (br, 3H, AlH) and 1.43 (br, 1H, NH); ^{13}C NMR (62.8 MHz, C_6D_6, 25 °C): δ 18.3 (NCC*C*H$_2$), 32.0 (NC*C*H$_3$), 38.5 (NC*C*H$_2$) and 52.4 (N*C*); ^{27}Al NMR (52.11 MHz, tetrahydrofuran, 25 °C): δ 139.8, peak width half height 1928 Hz; IR: ν/cm^{-1} 1773 (br, AlH) and 3150 (s, NH). Satisfactory analytical data have been obtained on both compounds.

‡ *Crystal structure determinations* (T = 296 K; Enraf-Nonius CAD4 diffractometer, crystals mounted in capillaries). Compound **1**, $C_{12}H_{29}AlN_2$, M = 228.4, monoclinic, space group $P2_1/n$, a = 6.241(3), b = 15.783(3), c = 15.537(7) Å, β = 95.89(2)°, U = 1522.4 Å^3, F(000) = 512; Z = 4, D_c = 0.996 g cm^{-3}, μ(Mo-Kα) = 1.16 cm^{-1}, specimen 0.25 × 0.30 × 0.30 mm, 2678 unique reflections, 1951 with $I > 2.5\sigma(I)$ used in the refinement, $2\theta_{max}$ = 50°. Compound **2**, $C_9H_{22}AlN$, M = 171.3, hexagonal, space group $P6_3/m$, a = 12.384(6), c = 13.378(4) Å, U = 1777 Å^3, F(000) = 864; Z = 6, D_c = 0.96 g cm^{-3}, μ(Mo-Kα) = 1.19 cm^{-1}, specimen 0.20 × 0.25 × 0.40 mm, 2392 unique reflections, 472 with $I > 3\sigma(I)$ used in the refinement, $2\theta_{max}$ = 50 °. The structures were solved by direct methods,[14] and refined by full-matrix least-squares using SHELX and XTAL programmes. Hydrogen atoms attached to Al were located and refined in x,y,z, U_{iso}, as was the amine H atom in **2**; hydrogens attached to carbon were included as invariants. Unit weights were used and the final residuals were R = 0.042, 0.113, R_w = 0.045, 0.114, for **1** and **2** respectively. The unique methylene C atom in **2** is disordered across the mirror plane and only one half is shown in Fig. 1. 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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