Structures of $(C_5H_5N)_3Al(N_3)_3$, $[Me_2N(CH_2)_3]_2Al(N_3)$ and $Me_2(N_3)Al(H_2NBu^t)$. Low-temperature OMVPE of AlN in the absence of ammonia[†]

Roland A. Fischer,*[a] Alexander Miehr,[a] Harald Sussek,[a] Hans Pritzkow,[a] Eberhardt Herdtweck,[b] Jens Müller,[c] Oliver Ambacher[d] and Thomas Metzger[e]

[a] *Anorganisch-chemisches Institut, Ruprecht-Karls-Universität Heidelberg, Im Neuenheimer Feld 270, D-69120 Heidelberg, Germany*
[b] *Anorganisch-chemisches Institut, Technischen Universität München, Lichtenbergstraße 4, D-85747 Garching, Germany*
[c] *Institut für Anorganische Chemie der Technischen Hochschule Aachen, Professor-Pirlet-Str. 1, D-52056, Aachen, Germany*
[d] *Walter-Schottky-Institut, Technische Universität München, Am Coulombwall, D-85748, Garching, Germany*
[e] *Lehrstuhl für Angewandte Mineralogie und Geochemie Technische, Universität München, Lichtenbergstraße 4, D-85747, Garching, Germany*

New Lewis-base stabilized monomeric azido alanes are synthesized by salt metathesis from the corresponding chloro alanes and an excess of sodium azide; thin films of crystalline AlN are grown by OMVPE at 400–850 °C *in vacuo.*

GaN and the ternary systems with Al and In are very promising materials for advanced microelectronic and optoelectronic devices.[1] OMVPE of these materials is currently achieved by the copyrolysis of ER_3 (E = Al, Ga, In; R = alkyl) with a large excess of ammonia at very high temperatures (> 900 °C).[2] Alternative molecular precursors based on the concept of preformed direct E–N bonds in the precursor molecule may open up new possibilities for optimized growth processes. Recently, we reported on some organogallium azides $(N_3)_{3-x}GaR_xL$ (x = 1, 2; R = alkyl; L = thf, NR_3, py, *etc.*), which serve as sources for OMVPE of GaN thin films.[3,4] Lewis-base stabilized complexes, $Ga(N_3)_3L_m$ (m = 1–3), were used as precursors for solid-state synthesis to yield either polycrystalline films (spin-on-pyrolysis) or nanocrystalline GaN powders.[5] A recent communication in this journal by Cowley and coworkers[6] on a different synthesis and the molecular structure of $Ga(N_3)_3(py)_3$, a compound we previously synthesized, also characterized structurally, and reported on various occasions,[3–5] prompted us to present here a preliminary account on our collaborative effort to study the related aluminium azides and the corresponding materials chemistry.

Treatment of pyridine solutions of $AlCl_3$ with an excess of sodium azide afforded the trispyridine complex of triazidoaluminium[7].[‡] The molecular geometry of complex **1** (Fig. 1) is similar to its gallium congener,[5,6] with the exception, that one additional molecule of non-coordinated pyridine is incorporated into the crystal lattice.[§] In contrast to the related gallium chemistry,[3,4] $Cl_2Al[(CH_2)_3NMe_2]$ reacts with sodium azide to yield the monoazide **2**. Other azido alanes, *e.g.* $(N_3)_2Al[(CH_2)_3NMe_2]$, were not present as judged from the solution IR and ^{27}Al NMR spectra. The γ-aminoalkyl groups of **2** show dynamic behaviour in solution. At 25 °C, the NMe units give two broad and one sharp ^{13}C NMR signals. The ^{27}Al NMR resonance at δ 111 indicates a four-coordinate Al centre.[8] Interestingly, **2** is a five-coordinate monomer in the solid state (Fig. 2).[§]

Compound **3** (Fig. 3) shows that four-coordinate monomeric azido alanes without intramolecular adduct formation are also accessible.[§] With reference to matrix isolation experiments of monomeric azido alanes started recently, we calculated the equilibrium geometry of **3** on the RHF/6-31G* level of theory.[¶] The optimized geometry (C_1 point group) is comparable to that determined by X-ray crystallography; nevertheless, there are two main differences. First, the azido group of the calculated molecule is not, as in the solid state, tilted to the side [torsion angle: N(2)–N(1)–Al–N(4) 179.3° (calc.), 116.0° (exptl.)]. Secondly, the calculated Al–N 'donor-bond length' of 207.8 pm is significantly longer than the measured value of 198.3 pm [Al–N(4)]. This large difference is probably a medium effect and mainly due to crystal dipolar field interactions (calc. dipole moment of 7.12 D).[9] The reaction enthalpy of the adduct fission of the model compound $Me_2(N_3)Al{\cdot}NH_2Me$ was calculated to be 139 kJ mol^{-1}, which agrees well with the data of $Me_3Al{\cdot}NH_2Me$ (calc. 119 kJ mol^{-1}, exptl. 126 kJ mol^{-1} in hexane)[10] and $Me_3Al{\cdot}NH_3$ (109 kJ mol^{-1}).[11] These results show that azido groups favour amine alane adduct formation which is important in stabilizing monomeric molecular structures.

Using compounds **2** and **3**, AlN layers were grown on sapphire substrates *in vacuo* (isothermal hot wall reactor) without carrier gasses or additional nitrogen sources (*e.g.* ammonia). The low decomposition temperatures of the precursors (270–350 °C by TG–DSC) allowed the growth of very

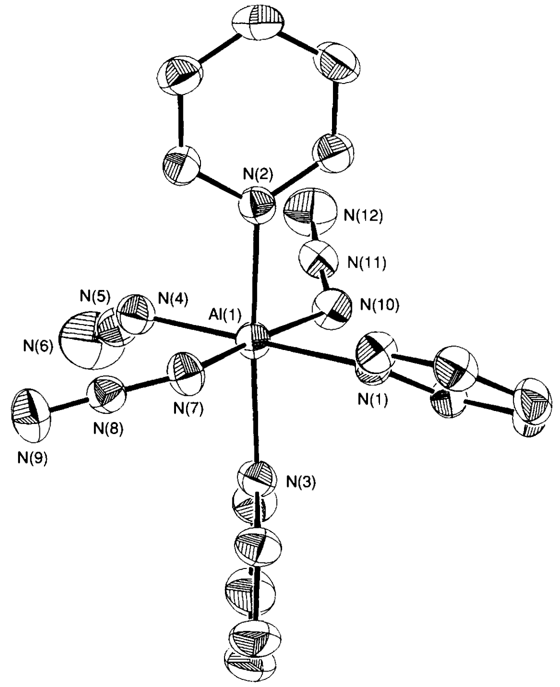

Fig. 1 Solid-state molecular structure of **1** (ORTEP with 50% probability thermal ellipsoids). Selected distances (pm): Al–N(1) 208.5(2), Al–N(2) 206.9(3), Al–N(3) 208.0(3), Al–N(4) 200.7(3), Al–N(7) 195.2(3), Al–N(10) 195.3(2).

smooth, amorphous AlN films (growth rate > 5 μm h^{-1}) even below 400 °C. Substrate temperatures > 800 °C gave epitaxial films with a surface roughness of 1–3 nm (AFM; almost pseudo-two-dimensional growth). The FWHM of the rocking curve of the (002) reflection is 0.16°. REM–EDX analysis showed C and O impurities close to the detection limit (0.5 atom%). The AlN films were also characterized by thermal gas effusion. Epitaxial films grown at 850 °C were stable up to 980 °C (the binding energy of the N atoms was 359 kJ mol^{-1}). Only traces of surface impurities were detected as desorbing fragments at 400 °C.[3b,12] These results add to our previously published studies on growth of GaN[4] and InN[12] films from related single sources.

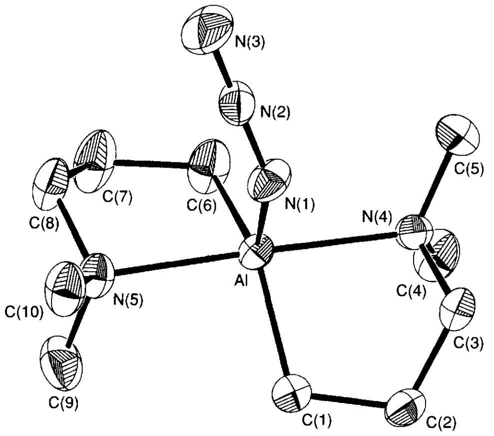

Fig. 2 Solid-state molecular structure of **2** (ORTEP with 50% probability thermal ellipsoids). Selected distances (pm): Al–N(1) 189.7(2), Al–N(4) 216.7(1), Al–N(5) 219.9(1), Al–C(1) 198.2(2), Al–C(6) 199.1(2), N(1)–N(2) 119.1(2), N(2)–N(3) 114.5(2).

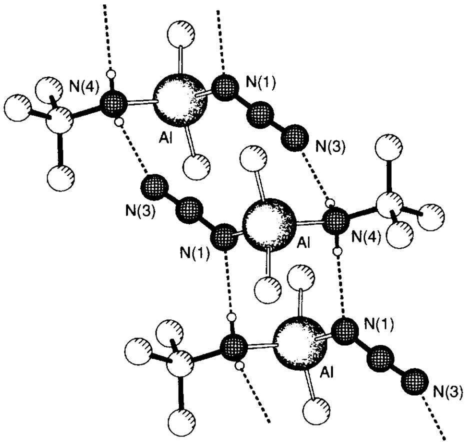

Fig. 3 Solid-state molecular structure of **3** (SCHAKAL). Selected distances (pm): Al–N(1) 190.1(1), Al–N(4) 198.3(1), Al–C(1) 195.5(2), Al–C(2) 194.9(2), N(1)–N(2) 120.2(2), N(2)–N(3) 113.9(2). Hydrogen bonds parallel to the *a*-axis of the unit cell: N(4)–H(1)–N(1′) 173(2), N(4)···N(1′) 308.6(2); N(4)–H(2)–N(3′) 160(2), N(4)···N(3′) 312.1(2).

Footnotes

† Molecular Precursors for Group 13 Nitrides, 5th Communication; 4th communication see ref. 5.

‡ *Experimental*: see references 3(*b*) and (*c*).

§ *Crystal data*: **1**·C_5H_5N; $C_{20}H_{20}AlN_{13}$, M = 469.47, orthorhombic, space group $P2_1cn$, a = 1.0645(5), b = 1.1983(6), c = 1.8688(9) nm, U = 2.384(2) nm^3, Z = 4, D_c = 1.308 g cm^{-3}, $F(000)$ = 976, T = 203(2) K, 3640 independent reflections (2.02 < θ < 30°), μ = 1.22 cm^{-1}; data were corrected for absorption, $wR2$ = 0.134, $R1$ = 0.052, GOF = 1.059 [$I > 2\sigma(I)$].

2: $C_{10}H_{24}AlN_5$, M = 241.32, monoclinic, space group $P2_1/n$ (no. 14), a = 0.7234(1), b = 1.1236(1), c = 1.7525(3) nm, β = 100.409(12)°, U = 1.4010(3) nm^3, Z = 4, D_c = 1.144 g cm^{-3}, $F(000)$ = 528, T = 160(1) K, 12795 data collected, 2466 unique (2.16 < θ < 25.56°), $R1$ = 0.0507, $wR2$ = 0.0916, GOF = 1.024.

3: $C_6H_{17}AlN_4$, M, = 172.21, monoclinic, space group $P2_1/n$ (no. 14), a = 0.7134(1), b = 1.5779(2), c = 0.9864(2) nm, β = 91.59(1)°, U = 1.1099(5) nm^3, Z = 4, D_c = 1.031 g cm^{-3}, $F(000)$ = 376, T = 163(3) K, ω-scans (2.44 < θ < 26.00°), μ = 1.4 cm^{-1}; 2125 unique data, $R1$ = 0.0380, $wR2$ = 0.0948, GOF = 1.068. The data collections for **1** and **2** were performed on an Enraf-Nonius CAD 4 diffractometer using graphite-monochromated Mo-Kα radiation (71.703 pm). Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/276.

¶ All calculations were conducted with the GAUSSIAN 94 software package Revision C.3. The reaction enthalpies were calculated on the RMP2(fc)/6-31G* level with the inclusion of zero-point vibrational energies scaled by 0.93.

References

1 D. A. Neumayer and J. G. Ekerdt, *Chem. Mater.*, 1996, **8**, 9.

2 S. Nakamura, N. Iwasa and T. Mukai, *Jpn. J. Appl. Phys.*, 1992, **31**, 1258.

3 (*a*) A. Miehr, M. R. Mattner and R. A. Fischer, *Organometallics*, 1996, **15**, 2053; (*b*) A. Miehr, Dissertation, Technische Universität München, 1996; (*c*) H. Sussek, Diploma Thesis, Universität Heidelberg, 1996.

4 A. Miehr, O. Ambacher, T. Metzger, E. Born and R. A. Fischer, *Chem. Vap. Deposition*, 1996, **2**, 51.

5 R. A. Fischer, A. Miehr, E. Herdtweck, M. R. Mattner, O. Ambacher, T. Metzger, E. Born, S. Weinkauf, C. R. Pulham and S. Parsons, *Chem. Eur. J.*, 1996, **2**, 101.

6 C. J. Carmalt, A. H. Cowley, R. D. Culp and R. A. Jones, *Chem. Commun.*, 1996, 1453.

7 E. Wiberg and H. Michaud, *Z. Naturforsch., Teil B*, 1954, **9**, 495.

8 R. Benn and A. Rufinska, *Angew. Chem., Int. Ed. Engl.*, 1986, **25**, 861.

9 H. Jiao and P. v. R. Schleyer, *J. Am. Chem. Soc.*, 1994, **116**, 7429 and references therein.

10 C. H. Henrickson, D. Duffy and D. P. Eyman, *Inorg. Chem.*, 1968, **7**, 1047; J. Müller, unpublished work.

11 J. Müller, *J. Am. Chem. Soc.*, 1996, **118**, 6370.

12 R. A. Fischer, A. Miehr, T. Metzger, E. Born, O. Ambacher, H. Angerer and R. Dimitrov, *Chem. Mater.*, 1996, **8**, 1356.

Received, 15th July 1996; Com. 6/04932J