Synthesis and crystal structure of the tris(pyridine) complex of gallium tris(azide)

Claire J. Carmalt, Alan H. Cowley,* Robert D. Culp and Richard A. Jones

Department of Chemistry and Biochemistry, The University of Texas at Austin, Austin, Texas, 78712, USA

Gallium tris(dimethylamide) reacts with trimethylsilylazide in the presence of pyridine to form the tris(pyridine) complex of gallium tris(azide), the structure of which is established by X-ray crystallography.

Interest in new molecular approaches to gallium nitride is heightening because of potential applications as blue light-emitting diodes and lasers, optical storage systems, and high-temperature electronics.[1] Although gallium nitride can be formed by thermolysis of mixtures of ammonia and gallium trialkyls, the reaction temperatures are very high (> 900 °C).[2] Accordingly, attention has turned to the development of single-source precursors that feature preformed gallium–nitrogen bonds and labile leaving groups in the hope of lowering the thermal budget. It was also considered important to avoid the use of gallium–carbon bonds in such precursors in order to minimise carbon incorporation. Recently we reported[3] the preparation of $[(Me_2N)(N_3)Ga(\mu\text{-}NMe_2)]_2$ **1** *via* the metathetical reaction of $(Me_2N)_2GaCl$ with NaN_3. Whilst **1** does indeed produce gallium nitride at 580 °C, a disadvantage of this precursor is the modest volatility which stems, in part, from the fact that the solid state comprises a polymer of dimeric units. With a view to developing mononuclear, monomeric gallium precursors, we treated **1** with an excess of pyridine at 25 °C. Surprisingly, work-up of the reaction mixture afforded a 32% yield of the tris(azide), $[Ga(N_3)_3(py)_3]$ **2**.† It is presumed that **2** arises from the following redistribution reaction [eqn. (1)]. A more straightforward and higher yield (79%) synthesis of **2** can

$$3\ [(Me_2N)(N_3)Ga(\mu\text{-}NMe_2)]_2 \xrightarrow{py} 2\ [Ga(N_3)_3(py)_3] + 4\ [Ga(NMe_2)_3(py)_x] \qquad (1)$$

be effected by treatment of $Ga(NMe_2)_3$ with Me_3SiN_3 in pyridine solution at 25 °C.† Interestingly, regardless of whether a 1 : 1, 1 : 2, or 1 : 3 $Ga(NMe_2)_3 : Me_3SiN_3$ reactant mole ratio is employed, the sole isolated solid product is **2** [eqn. (2)].

$$\underset{x\,=\,1\text{–}3}{Ga(NMe_2)_3 + x\ Me_3SiN_3} \xrightarrow{py} \underset{\mathbf{2}}{[Ga(N_3)_3(py)_3]} + x\ Me_3SiNMe_2 \qquad (2)$$

A correct elemental analysis was obtained for **2** and the ^1H and ^{13}C NMR spectra‡ revealed the presence of coordinated pyridine molecules. Terminal azide moieties were evident in the IR spectrum (2046, 2074 cm^{-1}). The highest peak in the $CI(CH_4)$ mass spectrum (positive mode) appeared at *m/z* 311 and corresponds to $[Ga(N_3)_2(py)_2]^+$. However, in the negative mode, the molecular ion was detected (*m/z* 432), along with fragmentation peaks corresponding to $[GaN(py)_3]$ (*m/z* 322) and $[Ga(N_3)_3]$ (*m/z* 195).

In order to confirm the structure of **2**, an X-ray crystallographic study was undertaken.§ The solid-state structure comprises individual molecules and there are no unusually short intermolecular contacts (Fig. 1, 2). The metrical parameters for the azide moieties are typical of those reported for a variety of covalent azides, *viz.* a *trans*-bent configuration [average

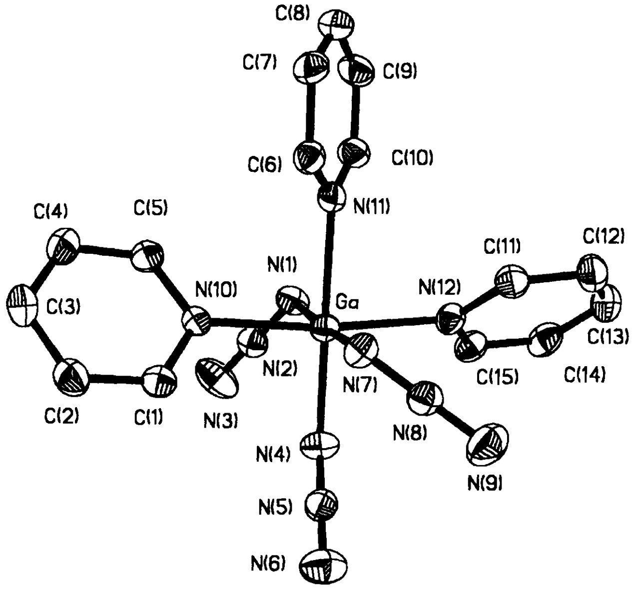

Fig. 1 Molecular structure of **2** showing the atom numbering scheme. Selected distances (Å) and angles (°): Ga–N(1) 2.005(4), Ga–N(4) 2.007(4), Ga–N(7) 2.007(4), Ga–N(10) 2.117(4), Ga–N(11) 2.132(4), Ga–N(12) 2.143(4), N(1)–N(2) 1.194(5), N(2)–N(3) 1.142(6), N(4)–N(5) 1.199(6), N(5)–N(6) 1.145(6), N(7)– N(8) 1.208(5), N(8)–N(9) 1.158(6), N(1)–Ga–N(10) 90.3(2), N(1)–Ga–N(4) 89.5(2), N(1)–Ga–N(11) 86.03(14), N(1)–Ga(1)–N(12) 89.4(2), N(7)–Ga–N(4) 94.2(2), N(7)–Ga–N(10) 88.9(2), N(7)–Ga–N(11) 90.29(14), N(7)–Ga–N(12) 91.0(2), N(1)–Ga–N(7) 176.27(14), N(10)–Ga–N(12) 172.90(13), N(4)–Ga–N(11) 175.16(14).

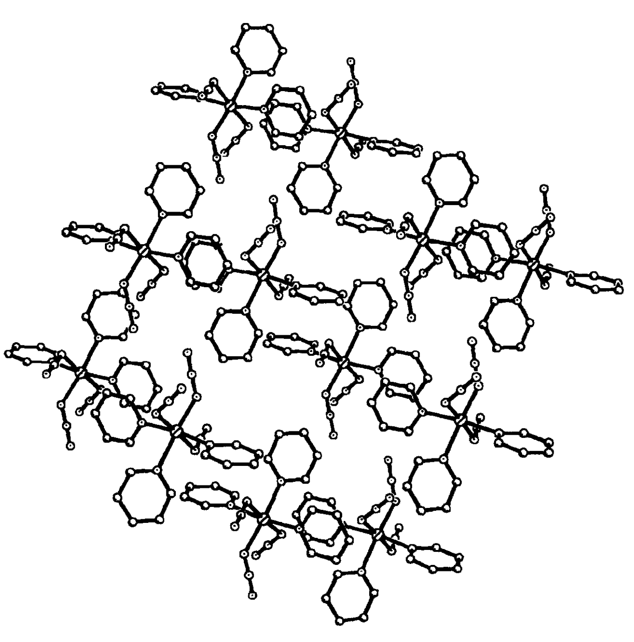

Fig. 2 View of the packing arrangement of molecules of **2**

N–N–N bond angle 177.4(5)°] and two significantly different N–N bond distances [1.200(6), 1.148(6) Å].[6] The average Ga–N_3 distance in **2** [2.006(4) Å] is slightly longer than that in a bulky aryl-substituted bis(azide) of gallium [1.921(4) Å].[4]

Interestingly, a product analysing as $GaH_{0.2}(N_3)_{2.8}$ was isolated from the reaction of GaH_3 with hydrazoic acid by Wiberg and Michaud over 40 years ago.[5,6] However, no further characterisation of this material has been published subsequently.

In view of the fact that the empirical lower limit for the explosivity of covalent nitrogen is 25% by mass of azide nitrogen,[7] we have exercised due caution when handling **2** because the % by mass of azide nitrogen is 29.1% in this case [and 64% in base-free $Ga(N_3)_3$]. We have, however, encountered no difficulties so far in manipulating samples of **2** which melts without decomposition at 58–60 °C. The ability of pyridine and other nitrogen bases to stabilise halogen azides has been observed previously.[6,8].

Preliminary experiments indicate that **2** serves as a thermal source of gallium nitride *via* loss of pyridine and dinitrogen. Detailed studies are in progress and will be reported elsewhere.

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Footnotes

† *Experimental procedure*: $[(Me_2N)(N_3)Ga(\mu\text{-}NMe_2)]_2$ **1**[3] (0.500 g, 2.51 mmol) was dissolved in pyridine (5 cm^3) which resulted in a pale yellow solution. Cooling of this solution to −20 °C overnight afforded a 32% yield (0.350 g) of colourless crystalline **2**.

Me_3SiN_3 (0.5 cm^3, 3.77 mmol) was added dropwise to a stirred pale yellow solution of $Ga(NMe_2)_3$ (0.379 g, 1.88 mmol) in pyridine (40 cm^3) at room temp. A darker yellow solution resulted and was stirred for 2 h, following which the solvent and volatiles were removed under reduced pressure. The white solid residue was redissolved in pyridine (15 cm^3) and cooled to −20 °C overnight which afforded a 79% yield (0.650 g) of colourless crystalline **2** (mp 58–60 °C).

‡ *Selected spectroscopic data* for **2**: ^1H NMR (CD_2Cl_2, 300 MHz, 298 K) δ 8.75–8.73 (m, 6 H, *o*-H of py), 7.97–7.91 (m, 3 H, *p*-H of py), 7.56–7.52 (m, 6 H, *m*-H of py). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 300 MHz, 298 K) δ 148.58 (s, *o*-C of py), 139.26 (s, *p*-C of py), 125.23 (s, *m*-C of py).

§ *Crystal data* for **2**: $C_{15}H_{15}GaN_{12}$, $M = 433.11$, triclinic, space group $P\bar{1}$, $a = 8.994(2)$, $b = 9.923(2)$, $c = 12.601(4)$ Å, $\alpha = 99.84(2)$, $\beta = 103.59(2)$, $\gamma = 115.76(2)°$, $U = 935.4(4)$ Å^3, $Z = 2$, $D_c = 1.538$ g cm^{-3}, $F(000) = 440$, $T = 298$ K. 3260 independent reflections were collected on an Enraf Nonius CAD 4 diffractometer using graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å, $2.56 < \theta < 24.97°$, $\mu = 15.0$ cm^{-1}. Data were corrected for absorption and extinction. $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{\frac{1}{2}} = 0.1398$ (3260 independent reflections), $R = \Sigma|F_o - F_c|/\Sigma F = 0.0495$ for reflections with $I/2\sigma(I) > 2.0$. 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 182/89.

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