

Reactivity of GaX₃ with silylamines and thermal decomposition of the compounds [Cl₂Ga{NH(SiMe₃)₂}]₂ and [Cl₃Ga{NH(SiMe₃)₂}]

Claire J. Carmalt,^{a*} John D. Mileham,^a Andrew J. P. White^b and David J. Williams^b

^a Department of Chemistry, Christopher Ingold Laboratories, University College London, 20 Gordon Street, London, UK WC1H 0AJ. E-mail: c.j.carmalt@ucl.ac.uk

^b Department of Chemistry, Imperial College London, South Kensington Campus, London, UK SW7 2AZ

Received 8th July 2003, Accepted 3rd September 2003

First published as an Advance Article on the web 22nd September 2003

The Lewis acid/base adducts [X₃Ga{NH(R)(R')}]} (X = Cl, R = R' = SiMe₃ (1), SiMe₂Ph (2) and R = Bu^t, R' = SiMe₃ (3); X = Br, R = R' = SiMe₃ (4) or SiMe₂Ph (5)) were synthesised by the 1 : 1 reaction of GaX₃ with NH(R)(R') in hexane solution at room temperature. Dimeric complexes, of the type [X₂Ga{NH(R)}]}₂ (X = Cl, R = SiMe₃ (6), R = SiMe₂Ph (7) and R = Bu^t (8); X = Br, R = SiMe₃ (9)) were prepared by the 1 : 1 reaction of GaX₃ with NH(R)(R') in CH₂Cl₂ solution. Compounds 1 and 8 have been structurally characterised. Polycrystalline GaN was obtained from the pyrolysis of compounds 1 and 6 under inert conditions (N₂, vacuum) above 500 °C, as shown by the X-ray powder diffraction patterns.

Introduction

Gallium nitride (GaN) is suitable for use in a range of optoelectronic devices, such as blue-light emitting diodes because of its semiconducting properties (GaN has a band gap of 3.4 eV).^{1,2} GaN can be prepared by reaction of R₃Ga (R = Me, Et),¹ Ga₂O₃³ or Ga⁴ metal with a large excess of NH₃ at high temperatures. Alternatively, single-source precursors, which contain pre-formed Ga–N bonds, have been used to prepare GaN.^{1,5} Possible advantages of the single-source route include lower deposition temperatures, removal of the inefficient use of ammonia and reduced contamination from other species (e.g. carbon). A further advantage of single-source precursors is the possibility of forming unusual phases, for example cubic GaN.⁶ A number of single-source precursors to GaN have been reported previously,¹ for example [H₂GaNH₂]}₂,⁶ [N₃{Me₂N}]}₂-Ga{μ-NMe₂]}₂,⁷ [Ga(N₃)₃(py)]₃,⁸ [Ga{N(SiMe₃)₂}(OSiMe₃)₂-py]}₉ [(N₃)₂Ga{(CH₂)₃NMe₂]}₁₀ and [H₂GaN₃]}₁₁.

Dehalogenosilylation reactions (*i.e.* the elimination of Me₃-SiX; X = halide) have been employed in the synthesis of relatively pure samples of GaAs and InAs at low temperatures.¹² Thus, the reaction of MX₃ and E(SiMe₃)₃ (M = Ga, In; X = Cl, Br, I; E = P, As) in solution resulted in the formation of ME or the isolation of intermediates such as [X₃M{E(SiMe₃)₃]} or [X₂M{μ-E(SiMe₃)₂}]₂.¹² This method has also been extended to dehydrosilylation reactions (involving the elimination of Me₃SiH) for the preparation of GaP, GaAs, AlP and AlAs nanoparticles.¹³ Recently, Fischer *et al.* described the synthesis and characterisation of the Lewis acid/base adducts [X₃M{N(SnMe₃)₃]} (X = Cl, Br; M = Al, Ga, In).¹⁴ Polycrystalline powders of AlN, GaN and InN were obtained by prolonged pyrolysis under inert conditions above 350 °C.¹⁵ However, the powders obtained were contaminated with metallic tin as shown by the X-ray powder diffraction patterns.^{14,15} Organometallic precursors, of the type [Cl₂(Me)M{N(SnMe₃)₃]} (M = Al, Ga), were also investigated.^{14,15}

We have previously reported the synthesis and characterisation of some new gallium silylamido complexes.¹⁶ We also described the reaction between GaCl₃ and N(SiMe₃)₃ and showed that the methyl transfer product [MeGaCl₂]}₂ was isolated rather than the adduct [Cl₃Ga{N(SiMe₃)₃}]₁₆. As discussed recently by Fischer *et al.*,¹⁵ the formation of an adduct of the type [X₃M{N(SiMe₃)₃}] is unlikely due to steric reasons and the strong N–Si bond. These factors reduce the Lewis base properties of N(SiMe₃)₃, when compared with E(SiMe₃)₃ (E = P, As), and in turn decrease the stability of any potential adducts.

However, we have previously found that the trimethylsilyl group is very labile and can lead to materials with no silicon contamination.¹⁷ Whereas adducts of the type [X₃M{N(SiMe₃)₃}] have not been isolated, the related Lewis acid/base adducts [X₃M{NH(SiMe₃)₂}] have been described.¹⁸

We were interested in investigating in detail the synthesis and characterisation of adducts, of the type [X₃M{NH(R)(R')}]} (X = Cl, R = R' = SiMe₃ or SiMe₂Ph, R = Bu^t, R' = SiMe₃; X = Br, R = R' = SiMe₃ or SiMe₂Ph), all of which have a silyl group attached to the nitrogen atom. These adducts are compared to the dimeric complexes [X₂Ga{NH(R)}]}₂ (X = Cl, R = SiMe₃, SiMe₂Ph or Bu^t; X = Br, R = SiMe₃), which are intermediates in the formation of GaN from [X₃M{NH(R)(R')}]} *via* the elimination of R'X (R' = SiMe₃ or SiMe₂Ph). The crystal structures of [Cl₃Ga{NH(SiMe₃)₂}] and [Cl₂Ga(μ-NH(Bu^t))]₂ are described. The pyrolysis of [Cl₂Ga{NH(SiMe₃)₂}] and [Cl₃Ga{NH(SiMe₃)₂}] were investigated in order to evaluate complexes of this type as precursors to GaN.

Results and discussion

Synthesis of precursors

The Lewis acid/base adducts [X₃Ga{NH(R)(R')}]} (X = Cl, R = R' = SiMe₃ (1), SiMe₂Ph (2), R = Bu^t, R' = SiMe₃ (3); X = Br, R = R' = SiMe₃ (4), SiMe₂Ph (5)) were formed by the 1 : 1 reaction of GaX₃ with NH(R)(R') in hexane at room temperature (Scheme 1).

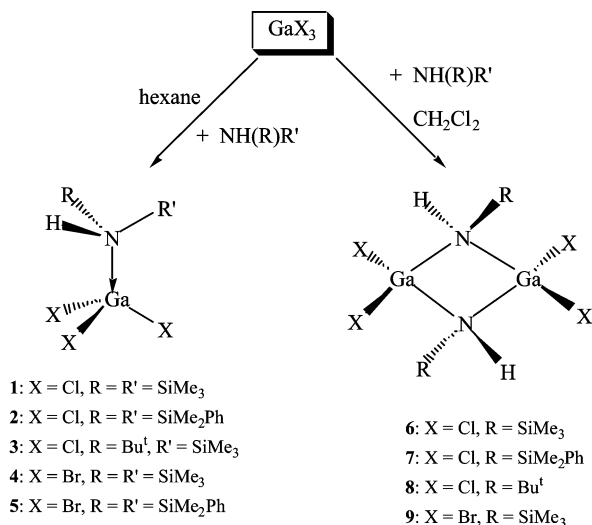
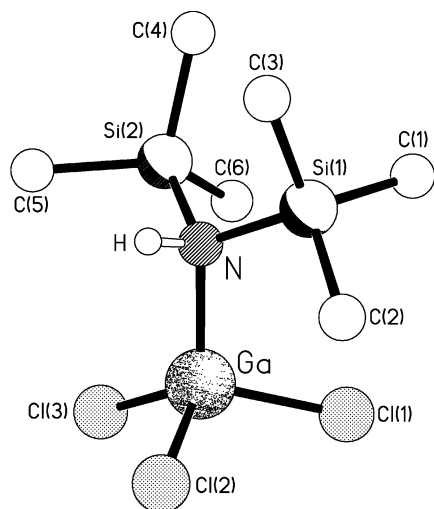
Compounds 1–5 were precipitated as white solids immediately upon addition of the relevant amine. All the compounds are stable in the solid state at room temperature. X-Ray quality crystals of compound 1 were grown from a concentrated CH₂Cl₂ solution at –20 °C. The structure of 1 (Fig. 1) is isomorphous with that of the aluminium analogue.¹⁹ Departures from tetrahedral geometry at gallium are small, the bond angles being in the range 106.07(12)–115.07(15)°, Table 1. There is a noticeable flattening of the geometry at the nitrogen centre with the sum of the 'basal' angles subtended at nitrogen by the metal and the two silicon atoms being 345° (*cf.* 328.5° for tetrahedral), a value the same as seen in, for example, the closely related gallium complex [Cl₃Ga{NH(Prⁱ)}]₂₀. The Ga–N bond length [2.011(4) Å] is the same within statistical significance as seen, for example, in [Cl₃Ga{NH(Prⁱ)}]₂₀ and in [Ga(OBu^t)₃{NH(Me₂)}]₂₁. Centrosymmetrically related pairs of molecules are linked by N–H ⋯ Cl(2) hydrogen bonds; N–H 3.39, H ⋯ Cl 2.49 Å, N–H ⋯ Cl 175°.

Table 1 Selected bond lengths (Å) and angles (°) for **1**

Ga–Cl(1)	2.169(2)	Ga–Cl(2)	2.1869(18)
Ga–Cl(3)	2.099(2)	Ga–N	2.011(4)
Si(2)–N–Si(1)	118.2(2)	Si(2)–N–Ga	112.0(2)
Si(1)–N–Ga	114.8(2)	N–Ga–Cl(3)	115.07(15)
N–Ga–Cl(1)	106.54(14)	Cl(3)–Ga–Cl(1)	112.18(13)
N–Ga–Cl(2)	107.56(14)	Cl(3)–Ga–Cl(2)	106.07(12)
Cl(1)–Ga–Cl(2)	109.27(10)		

Table 2 Selected bond lengths (Å) and angles (°) for **2**

Ga–Cl(1)	2.1579(9)	Ga–Cl(2)	2.1408(9)
Ga–N	1.977(2)	Ga–N'	1.973(2)
N'–Ga–N	86.82(10)	N'–Ga–Cl(2)	110.33(8)
N–Ga–Cl(2)	118.81(8)	N'–Ga–Cl(1)	119.44(8)
N–Ga–Cl(1)	109.89(8)	Cl(2)–Ga–Cl(1)	110.26(4)
C(1)–N–Ga'	125.4(2)	C(1)–N–Ga	124.3(2)
Ga–N–Ga'	93.18(10)		

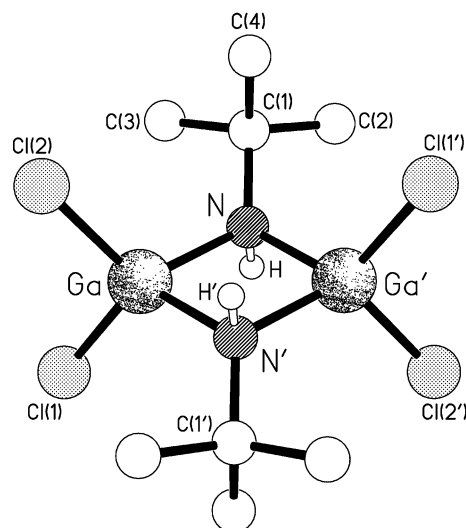
**Scheme 1****Fig. 1** The molecular structure of **1**.

Analytical data were obtained for compounds **1–5**. The carbon and hydrogen analyses for **1–5** were satisfactory. However, for most of the compounds (**1**, **2**, **4** and **5**) the nitrogen analyses were consistently low by 0.7–1.4%. This observation is most likely due to the formation of GaN during the thermal decomposition stage of the microanalysis procedure. Attempts at improving the microanalysis by using a combustion aid were unsuccessful. The ¹H and ¹³C NMR (CDCl₃ or CD₂Cl₂) data for **1–5** indicated that complexes of formulation [X₂Ga{NH(R)}₂] (X = Cl, R = SiMe₃ (**6**), R = SiMe₂Ph (**7**), R = Bu^t (**8**); X = Br, R = SiMe₃ (**9**)) have formed in solution. Presumably, the 1 : 1 adducts are decomposing in the NMR solvent, due to the formation of Me₃SiX or Me₂PhSiCl and a number of peaks corresponding to the silyl group (–SiMe₃ or –SiMe₂Ph) are observed in the ¹H NMR. A similar decomposition was observed for the 1 : 1 Lewis acid/base adducts [X₃M{N(SnMe₃)₃}] and it was suggested that these complexes decomposed *via* the elimination of Me₃SnX.¹³ However, the

adducts with N(SnMe₃)₃ decompose at room temperature and are more unstable than **1–5**. Compounds **6–9** can be prepared directly in good yield as described below.

The 1 : 1 reaction between GaX₃ and NH(R)(R') in CH₂Cl₂ (rather than hexane solution) resulted in the formation of the dimeric complexes [X₂Ga{NH(R)}₂] (**6–9**). Spectroscopic and analytical data for **6–9** were consistent with the proposed formula, [X₂Ga{NH(R)}₂]. The NMR data for compounds **6–9** indicated that in solution mixtures of *trans*-[X₂Ga{NH(R)}₂] and *cis*-[X₂Ga{NH(R)}₂] were present (*trans* : *cis* 1 : 1). Similar *trans/cis* isomerisations were reported for the dimeric silylamidogallanes described previously.^{16,22}

We have previously reported the structure of **7**¹⁶ and Nutt *et al.* published the structures of **6** and **9** (formed from the reaction of GaX₃ and NH(R)(R') in refluxing diethyl ether).^{22,24} X-Ray quality crystals of [X₂Ga{NH(Bu^t)₂}]₂ **8** were obtained by cooling a concentrated CH₂Cl₂ solution to –20 °C for 24 hours. The X-ray structure of **8** (Fig. 2) showed it also to be isomorphous with its aluminium analogue.²³ The planar central four-membered ring has a small rhombic distortion, having effectively the same Ga–N distances [1.977(2) and 1.973(2) Å] but with one angle that is acute, N–Ga–N' 86.82(10)°, and the other, Ga–N–Ga', obtuse [93.18(10)°], Table 2. The Ga–N bond lengths are the same as those seen for example in the structure of [Cl₂Ga{μ-NH(SiMe₃)₂}]₂²⁴ though the *trans*-annular metal ⋯ metal separation in this latter structure (2.810 Å) is significantly shorter than that we observe in **8** [2.8695(8) Å]; the Ga ⋯ Ga distance in the related complex, [Cl₂Ga{μ-NH(SiMe₂Ph)}]₂ is also shorter at 2.803 Å.¹⁶ There is a similar flattening of the geometry at the nitrogen to that seen in **1** with the sum of the C–N–Ga and Ga–N–Ga angles being 342.9°. Symmetry related pairs of molecules are loosely linked by weak N–H ⋯ Cl(1) hydrogen bonds; N–H 3.61, H ⋯ Cl 2.72 Å, N–H ⋯ Cl 171°.

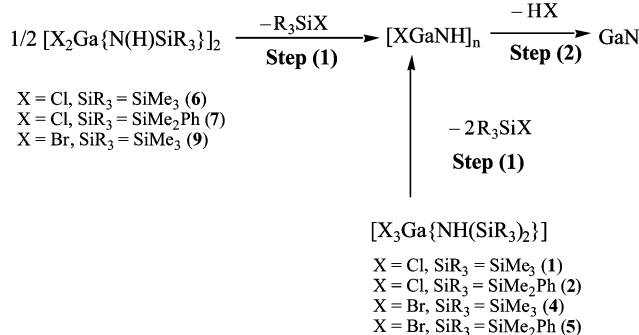
**Fig. 2** The molecular structure of the C₁ symmetric complex **8**.

Thermal analysis and pyrolysis

The thermogravimetric analysis (TGA) under N₂ at atmospheric pressure shows that at 500 °C, the precursors had lost

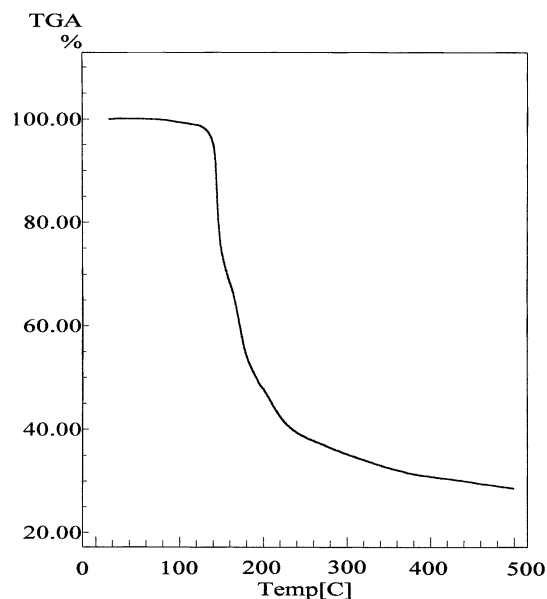
Table 3 Thermogravimetric analysis data for the decomposition of 1–9

Compound	Found % mass loss at 500 °C	Calc. % mass loss for GaN	Calc. % mass loss for [XGaNH] _n
1 [Cl ₃ Ga{NH(SiMe ₃) ₂ }]	71	75	64
2 [Cl ₃ Ga{NH(SiMe ₂ Ph) ₂ }]	82	82	74
3 [Cl ₃ Ga{NH(Bu ^t)(SiMe ₃) ₂ }]	53	74	63
4 [Br ₃ Ga{NH(SiMe ₃) ₂ }]	65	82	65
5 [Br ₃ Ga{NH(SiMe ₂ Ph) ₂ }]	69	86	72
6 [Cl ₂ Ga{NH(SiMe ₃) ₂ }] ₂	52	63	47
7 [Cl ₂ Ga{NH(SiMe ₂ Ph) ₂ }] ₂	70	71	59
8 [Cl ₂ Ga{NH(Bu ^t) ₂ }] ₂	67	61	44
9 [Br ₂ Ga{NH(SiMe ₃) ₂ }] ₂	67	74	48

**Scheme 2**

between 50 and 80% of weight depending on the sample (Table 3). Precursors of the type [X₃Ga{NH(SiR₃)₂}] (compounds 1, 2, 4 and 5) and [X₂Ga{NH(SiR₃)₂}]₂ (compounds 6, 7 and 9) are expected to decompose *via* loss of R₃SiX (two or one equivalents, respectively) to form an intermediate material of formulation [XGaNH]_n (Scheme 2). Indeed, theoretical investigations into the reaction of R₃M (M = Al, Ga; R = Cl, Me or Et) and NH₃ have been reported and showed that [RMNH]_n (n = 4–6) forms initially.^{25–27} The final step in the formation of GaN from compounds 1, 2, 4, 5–7 and 9 would be the loss of HX (Scheme 2). The TGA data indicate that for most of the compounds elimination of R₃SiX has occurred with incomplete loss of HX (Fig. 3 and 4). The TGA set-up allows analysis only to 500 °C and therefore it is possible that the required weight loss could be attained at higher temperatures. Interestingly, the precursors [Cl₃Ga{NH(SiMe₂Ph)₂}] (2) and [Cl₂Ga{NH(SiMe₂Ph)₂}]₂ (7), show total weight losses corresponding to that calculated for the formation of GaN. These results suggest that an alternative decomposition pathway (to Scheme 2) is taking place for 2 and 7 or additional decomposition routes are occurring. For example, for 7 there are two observed weight losses (44% and 26%), which do not correspond to loss of Me₂PhSiCl (calcd 59%) and HCl (calcd 13%), respectively. Furthermore, pyrolysis experiments carried out on 2 and 7 showed that they are poor precursors to GaN due to the presence of high levels of carbon contaminants. Interestingly, pyrolysis of the related base-stabilised compounds [Cl₂Ga{N(SiMe₃)₂}(L)] (L = NMe₃, quinuclidine) to ≈200 °C have been reported to result in the formation of the methyl migration products [MeGaCl₂(L)] and unidentified products.²⁸ If alkyl or aryl migration takes place this could account for the high carbon levels in the resulting material. Both [Cl₂Ga{NH(Bu^t)₂}]₂ (8) and [Cl₃Ga{NH(Bu^t)(SiMe₃)₂}] (3) may follow a different decomposition route to that shown in Scheme 2 due to the presence of the Bu^t group.

It is worth noting that TGA at atmospheric pressure only gives an indication of the potential of the precursors to form bulk GaN. Any sublimation of the precursor would register as a further mass loss. Nevertheless the TGA measurements show

**Fig. 3** TGA for the decomposition of [Cl₃Ga{NH(SiMe₃)₂}] (1).

that all of the complexes decompose by 500 °C to form a solid that is predominantly GaN but with, in some cases, significant impurities. The TGA results also indicate that a temperature ≥ 500 °C should be employed in the pyrolysis experiments in order to prepare GaN.

The precursors, [Cl₃Ga{NH(SiMe₃)₂}] (1) and [Cl₂Ga{NH(SiMe₃)₂}]₂ (6), gave mass losses of 71% and 53%, respectively, with clean decompositions (Fig. 3 and 4). The pyrolysis of these compounds was therefore investigated in more detail. Pyrolysis of 6 below 500 °C gave rise to amorphous grey powders, which were found to contain low levels of carbon (0.41–2.8%) and high levels of chlorine (≈24%, by elemental analysis). These results support the proposed formation of the intermediate compound [ClGaNH]_n (calculated %Cl = 29.5). Furthermore,

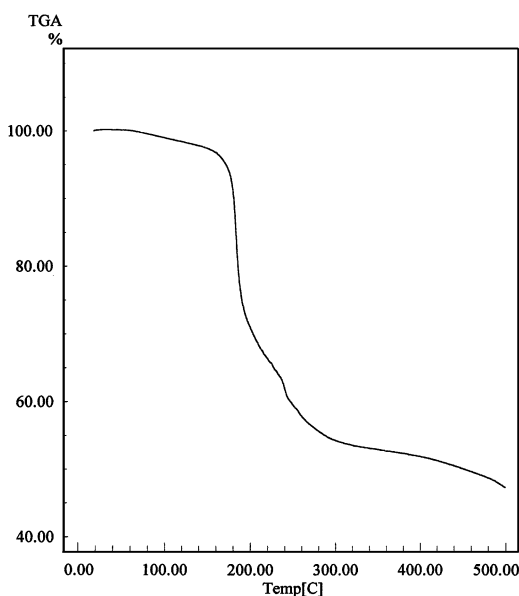


Fig. 4 TGA for the decomposition of $[\text{Cl}_2\text{Ga}\{\text{NH}(\text{SiMe}_3)_2\}_2]$ (**6**).

the ^1H NMR spectrum of the liquid by-products obtained (collected in a liquid N_2 cooled trap) when **6** was thermolysed, showed resonances assigned to $-\text{SiMe}_3$ groups.

At higher decomposition temperatures (550–650 °C) polycrystalline yellow powders were obtained which contained lower levels of chlorine ($\approx 15\%$) suggesting that incomplete decomposition has occurred. The XRD patterns of the powders obtained at 550–650 °C (Fig. 5) were similar to the mixture of cubic and hexagonal GaN reported previously from the thermal decomposition of $[\text{H}_2\text{GaNH}_2]_3$ ⁶ and $[\text{Ga}(\text{NH})_{3/2}]_n$.²⁹ Thus, the powder XRD of the pyrolysed product (650 °C) exhibited diffraction peaks that were assigned to the 111, 220 and 311 reflections of GaN possessing the zinc blende structure (indexing the reflections gave a lattice constant of 4.506(1) Å).⁶ However, diffraction peaks at 32.54 and 36.70 ° θ were also present and assigned to the 100 and 101 reflections of hexagonal (wurtzitic) GaN.

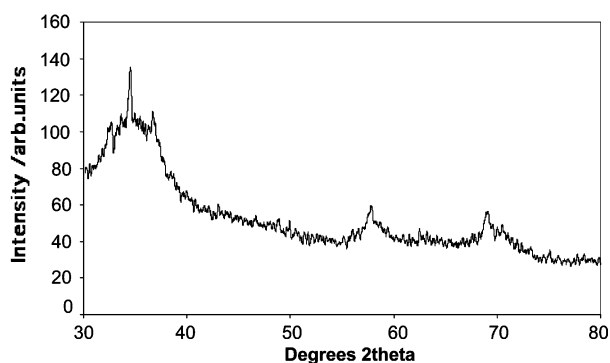


Fig. 5 X-Ray powder diffraction pattern of the yellow product obtained from the pyrolysis of $[\text{Cl}_2\text{Ga}\{\text{NH}(\text{SiMe}_3)_2\}_2]$ (**6**) at 650 °C.

Pyrolysis of **6** above 650 °C (650–850 °C) resulted in the isolation of yellow powders with even lower levels of chlorine ($< 5\%$). The powder XRD pattern indicates that hexagonal GaN has formed at these higher temperatures. The lattice constants obtained were $a_0 = 3.17(2)$ Å and $c_0 = 5.16(2)$ Å, which correspond to the values reported previously for microcrystalline bulk GaN ($a_0 = 3.18$ Å and $c_0 = 5.18$ Å).¹⁵ It should be noted that an unusually intense (002) peak was present in the powder XRD pattern, which was observed for GaN prepared from the pyrolysis of other related single-source precursors.^{6,15} This has been attributed to a preferential orientation of (00 l) in

GaN.^{6,15} On the basis of the Scherrer formula the crystallite sizes were in the range 60–100 nm. The IR spectra of the pyrolysed products obtained above 500 °C supported the formation of GaN (strong Ga–N band at 570 cm^{-1}).

The pyrolysis of compound **1** was identical to compound **6**. Furthermore, the pyrolysis of **1** and **6** was carried out under a number of different conditions including vacuum (10^{-3} Torr), under a flow of NH_3 and under N_2 . From analytical and XRD data obtained on the powders there was no apparent differences between the products isolated. Compositional analysis by EDAX shows the presence of gallium and nitrogen in the solids. In addition, significant impurities (Si, Cl by EDAX and C, H, Cl by elemental analysis) were detected and attempts to eliminate these impurities by changing conditions failed.

Conclusions

The synthesis and characterisation of the adducts $[\text{X}_3\text{M}\{\text{N}-\text{H}(\text{R})(\text{R}')\}]$ ($\text{X} = \text{Cl}$, $\text{R} = \text{R}' = \text{SiMe}_3$, SiMe_2Ph , $\text{R} = \text{Bu}^t$, $\text{R}' = \text{SiMe}_3$; $\text{X} = \text{Br}$, $\text{R} = \text{R}' = \text{SiMe}_3$, SiMe_2Ph), and dimeric complexes $[\text{X}_2\text{Ga}\{\text{NH}(\text{R})\}_2]$ ($\text{X} = \text{Cl}$, $\text{R} = \text{SiMe}_3$, SiMe_2Ph , $\text{R} = \text{Bu}^t$; $\text{X} = \text{Br}$, $\text{R} = \text{SiMe}_3$), have been described. The crystal structures of two of the complexes $[\text{Cl}_3\text{Ga}\{\text{NH}(\text{SiMe}_3)_2\}]$ and $[\text{Cl}_2\text{Ga}(\mu\text{-NH}(\text{Bu}^t))_2]$ were also reported. The pyrolysis of $[\text{Cl}_2\text{Ga}\{\text{NH}(\text{SiMe}_3)_2\}_2]$ and $[\text{Cl}_3\text{Ga}\{\text{NH}(\text{SiMe}_3)_2\}]$ has been investigated and showed that the elimination of Me_3SiCl takes place at low temperature. However, elimination of HCl requires elevated temperatures (> 650 °C) and is often incomplete resulting in chlorine contamination in the pyrolysed powders. We are currently investigating organometallic precursors, of the type $[\text{R}(\text{X})\text{Ga}\{\text{NH}(\text{SiMe}_3)_2\}_2]$, because of the potentially more facile loss of alkane (rather than HCl) and these results will be appear in a future publication.³⁰

Experimental

General procedures

All manipulations were performed under a dry, oxygen-free dinitrogen atmosphere using standard Schlenk techniques or in a Mbraun Unilab glove box. All solvents were distilled from appropriate drying agents prior to use (sodium for diethyl ether and hexanes; CaH_2 for CH_2Cl_2). All other reagents were procured commercially from Aldrich and used without further purification. Microanalytical data were obtained at University College London (UCL).

Physical measurements

NMR spectra were recorded on a Brüker AMX400 spectrometer at UCL, referenced to CD_2Cl_2 or CDCl_3 , which was dried and degassed over molecular sieves prior to use; ^1H and ^{13}C chemical shifts are reported relative to SiMe_4 (δ 0.00). FT-IR spectra were run on a Shimadzu FTIR-8200 instrument. Melting points were obtained in sealed glass capillaries under nitrogen and are uncorrected. TGA of the compounds were obtained from the Thermal Methods Laboratory at Birkbeck College. TGA samples were handled under nitrogen and the measurement made under flowing N_2 ; heating rates were 10 °C min^{-1} . Powder XRD measurements were recorded on a Siemens D5000 transmission diffractometer using germanium monochromated Cu-K α_1 radiation ($\lambda = 1.5406$ Å) as thin films.

Synthesis

Compounds **1–5** were prepared according to the method outlined below for the synthesis of $[\text{Cl}_3\text{Ga}\{\text{NH}(\text{SiMe}_3)_2\}]$ (**1**).

$[\text{Cl}_3\text{Ga}\{\text{NH}(\text{SiMe}_3)_2\}]$ 1. $\text{HN}(\text{SiMe}_3)_2$ (2.52 cm^3 , 12 mmol) was added dropwise to a solution of GaCl_3 (2.1 g, 12 mmol) in hexane (20 cm^3) at room temperature. A white precipitate

formed immediately. The mixture was stirred for 1 h at room temperature. The white solid was separated and dried under vacuum. Compound **1** was obtained as a white powder (3.62 g, 90% yield), mp 126–128 °C. Colourless X-ray quality crystals of **1** were obtained by cooling a concentrated CH₂Cl₂ solution of **1** to –20 °C overnight. Anal. Calc. for C₆H₁₉NCl₃Si₂Ga: C, 21.35; H, 5.67; N, 4.15. Found C, 21.43; H, 5.73; N, 3.41%. ¹H NMR δ/ppm (CD₂Cl₂): 0.40 (s, SiCH₃), 0.43 (s, SiCH₃), 0.56 (s, SiCH₃), 0.61 (s, SiCH₃), 2.07 (s, v br, NH). FT-IR (KBr disc, cm⁻¹): 3200 s, 2950 m, 1390 m, 1260 s, 1125 m, 1060 w, 925 m, 850 vs, 740 m, 640 w, 540 m, 500 m, 405 m.

[Cl₃Ga{NH(SiMe₂Ph)}]₂ **2**. Compound **2** was isolated as a white powder (2.14 g 93% yield). Anal. Calc. for C₁₆H₂₃NCl₃SiGa: C, 41.64; H, 5.02; N, 3.03. Found C, 41.28; H, 5.23; N, 2.04%. ¹H NMR δ/ppm (CD₂Cl₂): 0.78 (s, SiCH₃), 0.82 (s, SiCH₃), 2.41 (s, NH), 7.00–7.39 (m, SiC₆H₅). ¹³C{¹H} NMR (CD₂Cl₂): δ 1.16 (s, SiCH₃), 3.10 (s, SiCH₃), 127.9, 128.4 (s, *m*-SiC₆H₅), 129.3, 131.0 (s, *p*-SiC₆H₅), 133.7, 133.9 (s, *o*-SiC₆H₅), 134.4 (s, *ipso*-SiC₆H₅). FT-IR (KBr disc, cm⁻¹): 3115 w, 2959 w, 1427 m, 1259 vs, 1180 br, 1117 s, 1024 w, 934 m, 860 w, 800 m, 740 w, 731 w, 700 m, 594 w, 460 w.

[Cl₃Ga{NH(Bu^t)(SiMe₃)}] **3**. A white powder formed immediately (1.44 g, 79% yield), mp 126 °C. Anal. Calc. for C₇H₁₉NCl₃SiGa: C, 26.16; H, 5.96; N, 4.36. Found C, 25.17; H, 5.79; N, 4.58%. ¹H NMR δ/ppm (CDCl₃): 0.05 (s, SiCH₃), 0.42 (s, SiCH₃), 1.36 (s, NC(CH₃)₃), 1.47 (s, NC(CH₃)₃), 1.45 (s, NC(CH₃)₃), 2.56 (s, br, NH), 2.64 (s, br, NH), 3.54 (s br, NH). ¹³C{¹H} NMR (CDCl₃): δ 1.93 (s, SiCH₃), 3.25 (s, SiCH₃), 30.1 (s, NC(CH₃)₃), 31.3 (s, NC(CH₃)₃), 31.6 (s, NC(CH₃)₃), 56.8 (s, NC(CH₃)₃), 57.0 (s, NC(CH₃)₃), 57.1 (s, NC(CH₃)₃). FT-IR (Nujol, cm⁻¹): 3152 vs, 1564 m, 1408 m, 1337 m, 1261 vs, 1240 w, 1177 s, 1079 s, 1027 m, 932 w, 845 s br, 772 m, 735 s, 664 m, 627 m, 568 m, 416 w.

[Br₃Ga{NH(SiMe₂)}] **4**. Compound **4** was obtained as a white powder (0.47 g, 56% yield), mp 113–115 °C. Anal. Calc. for C₆H₁₉NBr₃Si₂Ga: C, 15.31; H 4.07; N, 2.98. Found C, 15.30; H, 3.85; N, 1.56%. IR (KBr disc) 3410 m, 3141 m, 2960 m, 2361 w, 1399 m, 1260 vs, 1062 s, 848 s, 757 w, 677 w, 580 w.

[Br₃Ga{NH(SiMe₂Ph)}] **5**. Compound **5** was isolated as a white powder (0.59 g, 77% yield), mp 108–109 °C. Anal. Calc. for C₁₆H₂₃NBr₃Si₂Ga: C, 32.30; H, 3.90; N, 2.35. Found: C, 32.08; H, 3.93; N, 1.57%. IR (Nujol, cm⁻¹): 3155 m, 3070 w, 1590 m, 1428 s, 1258 s, 1178 w, 1161 w, 1116 vs, 1015 s, 998 m, 931 m, 884 s, 830 s, 801 s, 740 m, 672 m, 635 m, 585 s, 507 s, 465 s, 457 s.

Compounds **6, 8** and **9** were prepared according to the method outlined below for the synthesis of [Cl₂Ga{NH(SiMe₃)}]₂ (**6**). Compound **7** was prepared as described previously.¹⁶

[Cl₂Ga{NH(SiMe₃)}]₂ **6**. A solution of HN(SiMe₃)₂ (0.42 cm³, 2.0 mmol) in CH₂Cl₂ (10 cm³) was added dropwise with stirring to a cooled solution (–78 °C) of GaCl₃ (0.35 g, 1.99 mmol). During the addition the solution turned from colourless to cloudy. After stirring for about 5 min a white precipitate formed in the cooled solution. The solution was allowed to warm slowly to room temperature during which time the precipitate redissolved. The mixture was stirred for 1 h at room temperature and the solvent was removed under reduced pressure. The resulting white crystalline solid was dissolved in a minimum amount of CH₂Cl₂ giving a clear solution, which was cooled to –20 °C for 24 h. Colourless plate-like crystals of **6** were obtained (0.174 g, 40% yield), mp 153 °C. Anal. Calc. for C₃H₁₀Cl₂NSiGa: C, 15.75; H, 4.40; N, 6.12; Cl, 30.99. Found: C, 14.91; H, 4.30; N, 5.69; Cl, 32.95%. ¹H NMR δ/ppm (CDCl₃): 0.40 (s, SiCH₃), 0.56 (s, SiCH₃), 2.07 (s, br, NH), 2.80 (s, br, NH), 5.28 (s, CH₂Cl₂). ¹³C NMR (CDCl₃): δ 1.3 (s,

SiCH₃), 2.8 (s, SiCH₃). IR (KBr disc, cm⁻¹): 3205 s, 2950 m, 1410 m, 1260 s, 1130 m, 1060 w br, 925 m, 850 vs, 770 w, 740 m, 705 w, 640 w, 535 m, 500 m, 405 m.

[Cl₂Ga{NH(Bu^t)}]₂ **8**. Colourless X-ray quality crystals of **8** were obtained by cooling a concentrated CH₂Cl₂ solution to –20 °C for 24 h (0.757 g, 63% yield). Anal. Calc. for C₄H₁₀NCl₂Ga: C, 22.58; H, 4.74; N, 6.58. Found C, 22.58; H, 4.80; N, 5.62%. ¹H NMR δ/ppm (CDCl₃): 1.36 (s, C(CH₃)₃), 1.44 (s, C(CH₃)₃), 1.46 (s, C(CH₃)₃), 2.56 (s, br, NH), 2.68 (s, br, NH), 3.57 (s br, NH). ¹³C{¹H} NMR (CDCl₃): δ 30.1 (s, NC(CH₃)₃), 31.3 (s, NC(CH₃)₃), 31.6 (s, NC(CH₃)₃), 56.8 (s, NC(CH₃)₃), 57.0 (s, NC(CH₃)₃), 57.3 (s, NC(CH₃)₃).

[Br₂Ga{NH(SiMe₃)}]₂ **9**. After cooling a CH₂Cl₂ solution of **9** to –20 °C overnight, a white solid had formed (0.13 g, 32% yield). Anal. Calc. for C₃H₁₀NBr₂SiGa: C, 11.34; H, 3.17; N, 4.41. Found C, 12.35; H, 3.35; N, 2.25%. ¹H NMR δ/ppm (CD₂Cl₂): 0.43 (s, Si(CH₃)₃), 0.54 (s, Si(CH₃)₃), 0.63 (s, Si(CH₃)₃), 0.73 (s, Si(CH₃)₃), 3.08 (s, br, NH). ¹³C{¹H} NMR (CD₂Cl₂): δ 0.7 (s, Si(CH₃)₃), 1.7 (s, Si(CH₃)₃), 3.8 (s, Si(CH₃)₃), 4.2 (s, Si(CH₃)₃). IR (Nujol, cm⁻¹): 3193 m, 1515 m, 1260 vs br, 1172 m, 1129 m, 1096 m, 991 w, 848 vs br, 519 m, 490 m.

Pyrolysis of [Cl₃Ga{NH(SiMe₃)}]₂ (**1**) and [Cl₂Ga{NH(SiMe₃)}]₂ (**6**)

The pyrolysis of **1** and **6** were carried out using the method outlined below. A sample of the precursor (0.30 g) was loaded into a glass or quartz ampoule (30 cm length × 9 mm diameter) in the glove box. The ampoule was then placed in a furnace, which had been pre-heated to the decomposition temperature such that the sample was at the centre of the furnace. It was necessary to pre-heat the furnace to minimise loss of the precursor due to vaporisation. The ampoule was heated for 5 min under a N₂ atmosphere and for a further 4 h under a dynamic vacuum (10⁻³ Torr). The samples were heated to 350, 430, 500, 550, 650, 750 and 850 °C. In some experiments the ampoule was attached to a liquid nitrogen cold trap (–196 °C) in order to isolate any volatile decomposition products. Any liquids isolated in the cold trap were analysed by ¹H NMR. During the heating process the white materials changed to light grey, grey, grey/yellow and finally yellow. The isolated powders were analysed by X-ray powder diffraction, EDAX, elemental analysis and FT-IR. Elemental analysis for the solid products resulting from the pyrolysis of **6** (temperature of pyrolysis, colour of product): 350 °C (grey) C, 2.84; H, 2.37; N, 9.13; Cl, 24.05%. 500 °C, (yellow/grey): C, 0.41; H, 0.56; N, 12.17; Cl, 24.27%. 650 °C (yellow): C, 0.42; H, 0.42; N, 11.87; Cl, 15.91%. 750 °C (yellow): C, 0.41; H, 0.81; N, 13.39; Cl 4.24%.

Calc. for [ClGaNH]_n C 0.00, H 0.84, N 11.65, Cl 29.50. Calc. for GaN, C 0.00, H 0.00, N 16.73, Cl 0.00%.

X-Ray crystallography

Crystals of **1** and **8** were grown from CH₂Cl₂ solutions at –20 °C.

Crystal data for 1. C₆H₁₉NSi₂Cl₃Ga, *M* = 337.5, orthorhombic, *Pbca* (no. 61), *a* = 13.160(1), *b* = 11.856(1), *c* = 19.657(2) Å, *V* = 3066.9(4) Å³, *Z* = 8, *D*_c = 1.462 g cm⁻³, μ(Cu-Kα) = 8.50 mm⁻¹, *T* = 183 K, colourless platy needles; 2090 independent measured reflections, *F*² refinement, *R*₁ = 0.054, *wR*₂ = 0.132, 1655 independent observed absorption corrected reflections [*F*_o] > 4σ(*F*_o), 2θ_{max} = 120°], 176 parameters. The structure exhibits a *ca.* 95 : 5 mirror disorder of the entire molecule about a plane that contains the N–H group. CCDC reference number 207598.

Crystal data for 8. C₈H₂₀N₂Cl₄Ga₂, *M* = 425.5, monoclinic, *P2₁/n* (no. 14), *a* = 6.462(1), *b* = 11.849(2), *c* = 10.730(2) Å, *b*

= 96.29(1)°, $V = 816.7(2) \text{ \AA}^3$, $Z = 2$ (C_i symmetry), $D_c = 1.730 \text{ g cm}^{-3}$, $\mu(\text{Cu-K}\alpha) = 9.90 \text{ mm}^{-1}$, $T = 183 \text{ K}$, colourless prisms; 1361 independent measured reflections, F^2 refinement, $R_1 = 0.035$, $wR_2 = 0.093$, 1343 independent observed absorption corrected reflections [$|F_o| > 4\sigma(|F_o|)$], $2\theta_{\text{max}} = 128^\circ$], 78 parameters.

CCDC reference number 207599.

See <http://www.rsc.org/suppdata/dt/b3/b307763m/> for crystallographic data in CIF or other electronic format.

Acknowledgements

We thank EPSRC for a studentship (J. D. M.).

References

- 1 For reviews on Group 13 nitrides see: D. A. Neumayer and J. G. Ekerdt, *Chem. Mater.*, 1996, **8**, 9; D. M. Hoffman, *Polyhedron*, 1994, **13**, 1169; S. Strite and H. Morkoç, *J. Vac. Sci. Technol., B*, 1992, **10**, 1237.
- 2 S. W. Choi, K. J. Bachmann and G. Lucovsky, *J. Mater. Res.*, 1993, **8**, 847.
- 3 R. C. Schoonmaker and C. E. Burton, *Inorg. Synth.*, 1963, **7**, 16.
- 4 W. C. Johnson, J. B. Parsons and M. C. Crew, *J. Phys. Chem.*, 1932, **36**, 2651.
- 5 T. D. Getman and G. W. Franklin, *Comments Inorg. Chem.*, 1995, **17**, 79.
- 6 J. A. Jegier, S. Mckernan, A. P. Purdy and W. L. Gladfelter, *Chem. Mater.*, 2000, **12**, 1003; J. W. Hwang, S. A. Hanson, D. Britton, J. F. Evans, K. F. Jensen and W. L. Gladfelter, *Chem. Mater.*, 1990, **2**, 342; J. W. Hwang, J. P. Campbell, J. Kozubowski, S. A. Hanson, J. F. Evans and W. L. Gladfelter, *Chem. Mater.*, 1995, **7**, 517.
- 7 D. A. Neumayer, A. H. Cowley, A. Decken, R. A. Jones, V. Lakohotia and J. G. Ekerdt, *J. Am. Chem. Soc.*, 1995, **117**, 5893.
- 8 C. J. Carmalt, A. H. Cowley, R. D. Culp and R. A. Jones, *Chem. Commun.*, 1996, 1453; A. Miehr, O. Ambacher, T. Metzger, E. Born and R. A. Fischer, *Chem. Vap. Deposition*, 1996, **2**, 51.
- 9 S. T. Barry and D. S. Richeson, *Chem. Mater.*, 1994, **6**, 2220.
- 10 A. C. Frank and R. A. Fischer, *Adv. Mater.*, 1998, **10**, 961.
- 11 J. McMurran, D. Dai, D. Balasubramanian, C. Steffek, J. Kouvetakis and J. L. Hibbard, *Inorg. Chem.*, 1998, **37**, 6638.
- 12 R. L. Wells, C. G. Pitt, A. T. McPhail, A. P. Purdy, S. Schafieezad and R. B. Hallock, *Chem. Mater.*, 1989, **1**, 4; J. F. Janik, R. A. Baldwin and R. L. Wells, *Organometallics*, 1993, **12**, 2832; R. L. Wells, S. R. Aubuchon, S. S. Kher and M. S. Lube, *Chem. Mater.*, 1995, **7**, 793; S. R. Aubuchon, A. T. McPhail, R. L. Wells, J. A. Giambra and J. R. Bowser, *Chem. Mater.*, 1994, **6**, 82; R. L. Wells and W. L. Gladfelter, *J. Cluster Sci.*, 1997, **8**, 217.
- 13 J. F. Janik, R. L. Wells and P. S. White, *Inorg. Chem.*, 1998, **37**, 3561; J. F. Janik, R. L. Wells, V. G. Young, A. L. Rheingold and I. A. Guzei, *J. Am. Chem. Soc.*, 1998, **120**, 532.
- 14 Q. M. Cheng, O. Stark, K. Merz, M. Winter and R. A. Fischer, *J. Chem. Soc., Dalton Trans.*, 2002, 2933.
- 15 Q. M. Cheng, O. Stark, F. Stowasser, A. Wohlfart and R. A. Fischer, *J. Mater. Chem.*, 2002, **12**, 2470.
- 16 C. J. Carmalt, J. D. Mileham, A. J. P. White, D. J. Williams and J. W. Steed, *Inorg. Chem.*, 2001, **40**, 6035.
- 17 A. Newport, C. J. Carmalt, I. P. Parkin and S. O'Neill, *J. Mater. Chem.*, 2002, **12**, 1906.
- 18 N. Wiberg and K. H. Schmid, *Z. Anorg. Allg. Chem.*, 1966, **345**, 93.
- 19 M. Jansen and T. Jäschke, *Z. Naturforsch., Teil B*, 2000, **55**, 763.
- 20 J. Pauls, S. Chitsaz and B. Neumuller, *Z. Anorg. Allg. Chem.*, 2001, **627**, 1723.
- 21 M. Valet and D. M. Hoffman, *Chem. Mater.*, 2001, **13**, 2135.
- 22 W. R. Nutt, J. S. Blanton, F. O. Kroh and J. D. Odom, *Inorg. Chem.*, 1989, **28**, 2224.
- 23 W. Clegg, M. Haase, U. Klingebiel, J. Neemann and G. M. Sheldrick, *J. Organomet. Chem.*, 1983, **251**, 281.
- 24 W. R. Nutt, J. A. Anderson, J. D. Odom, M. M. Williamson and B. H. Rubin, *Inorg. Chem.*, 1985, **24**, 159.
- 25 A. Y. Timoshkin, H. F. Bettinger and H. F. Schaefer III, *J. Crystal Growth*, 2001, **222**, 170.
- 26 A. Y. Timoshkin, H. F. Bettinger and H. F. Schaefer III, *Inorg. Chem.*, 2002, **41**, 738.
- 27 A. Kovács, *Inorg. Chem.*, 2002, **41**, 3067.
- 28 B. Luo, V. G. Young, Jr. and W. L. Gladfelter, *J. Organomet. Chem.*, 2002, **649**, 268.
- 29 J. F. Janik and R. L. Wells, *Chem. Mater.*, 1996, **8**, 2708.
- 30 C. J. Carmalt, J. D. Mileham and E. Sabir, unpublished results.