JOURNAL OF Materials CHEMISTRY

A study on the thermal properties and the solid state pyrolysis of the Lewis acid/base adducts [$X_3M{\cdot}N(SnMe_3)_3$] (X = Cl, Br; M = Al, Ga, In) and [$Cl_2MeM{\cdot}N(SnMe_3)_3$] (M = Al, Ga) as molecular precursors for group 13 nitride materials

Q. M. Cheng, O. Stark, F. Stowasser, A. Wohlfart and R. A. Fischer*

Lehrstuhl für Anorganische Chemie II - Organometallics & Materials Chemistry,
Ruhr-Universität Bochum, D-44780 Bochum, Germany.
E-mail: rfischer@aci.ruhr-uni-bochum.de

Received 8th April 2002, Accepted 2nd May 2002
First published as an Advance Article on the web 12th June 2002

The Lewis acid/base adducts [$X_3M{\cdot}N(SnMe_3)_3$] (**1–3**: X = Cl, Br; M = Al, Ga, In) and [$Cl_2MeM{\cdot}N(SnMe_3)_3$] (**4**: M = Al, **5**: M = Ga) were studied as precursors for group 13 nitride materials. The compounds were prepared by the 1 : 1 mole reaction of MX_3 and MCl_2Me with $N(SnMe_3)_3$ at room temperature in diethyl ether and crystallised from CH_2Cl_2 at −20 °C. As shown by thermal analysis and the analysis of the volatile by-products, the precursors of the type [$X_3M{\cdot}N(SnMe_3)_3$] decompose between 100 and 350 °C predominantly in two steps *via* dehalostannylation by partly releasing Me_3SnCl. Polycrystalline powders of AlN, GaN and InN were obtained after prolonged pyrolysis under inert conditions (argon, and *in vacuo*) above 350 °C and were contaminated with metallic tin according to the X-ray powder diffraction patterns. The pyrolysis of the organometallic precursors [$Cl_2MeM{\cdot}N(SnMe_3)_3$] (**4**, **5**) yielded tin-free nitride materials at temperatures below 350 °C due to the parallel elimination of $SnMe_4$ and Me_3SnCl, as evidenced by X-ray powder diffraction, elemental analysis, NMR and IR spectroscopy of the products.

Introduction

The group 13 nitrides MN (M = Al, Ga, In) are interesting semiconductor materials with a direct band gap from 1.4 eV (InN) to 3.4 eV (GaN) and up to 6.2 eV (AlN) and have become among the most promising materials for advanced opto-electronics and high power devices due to an unique combination of properties.[1] Group 13 nitrides are accessible by a number of chemical routes, including salt metathesis[2,3] as well as the treatment of group 13 metal sources (*e.g.* metals, oxides and organometallic group 13 sources) with a large excess of ammonia at high temperatures of 600 °C (In) to 1100 °C (Al, Ga).[4]

Only quite recently, efforts have been focused on developing alternative chemical approaches to group 13 nitrides using tailored molecular precursors, especially single molecule precursors containing performed M–N bonds.[5] The main aim is to lower the growth temperature and thus to achieve molecular control over the crystal growth and the processing of the materials. This is particularly interesting for the fabrication of nitride nanofibers[6] and nanocolloids[7] by non-aqueous sol–gel type chemistry or by pyrolysis of suitable precursors in hydrocarbon solutions below 300 °C as well as for nanoscale powders[8] and composites[9] obtained by solid state pyrolysis. The control over particle size and dispersion depends on suitable molecular precursors allowing low temperature processing. Most of this work has concentrated in the past on molecular amido/imido and azido precursors to AlN[10] and GaN[11] whereas still only very few reports exist on related single molecule precursors to InN.[12] In the case of GaN,[11] for example, cyclotrigallazane, [H_2GaNH_2]$_3$, has been used as a single source precursor for nanocrystalline GaN at 600 °C. The pyrolysis of [$Ga(NH)_{3/2}$]$_n$ at 450 °C *in vacuo* or under NH_3 can be employed to obtain nanocrystalline GaN powder samples. The decomposition of $Ga_2[NMe_2]_6$ under a stream of NH_3 at 600 °C leads to cubic GaN. The precursor $Ga[N(SiMe_3)_2]$-$(OSiMe_3)_2(py)$ (py = pyridine) was shown to decompose into (dark coloured) GaN at 210 °C in a toluene solution by splitting off the stable leaving group $(Me_3Si)_2O$. Inorganic and organometallic group 13 azido compounds have been extensively studied.[13,14] For example $(N_3)_2Ga[(CH_2)_3NMe_2]$ has been successfully used to obtain high quality epitaxial thin films by the MOCVD technique.[14]

For a number of materials (typically compound semiconductors), dehydrosilylation elimination–condensation reactions and dehalosilylation reactions have been studied as routes for synthesising ME compounds even in solution from the starting materials MX_3 and $E(SiMe_3)_3$ (X = Cl, Br, I, H; M = Ga, In; E = As, P) by formation of intermediates such as the primary Lewis acid/base adducts [$X_3M{\cdot}E(SiMe_3)_3$] and the subsequent stepwise elimination involving further intermediates such as [$X_2M\{\mu\text{-}E(SiMe_3)_2\}$]$_2$.[15–17] However, for E = N, similar reactions are not feasible under comparable conditions. This is mostly due to the strong N–Si bond and the steric congestion in $N(SiMe_3)_3$, which significantly reduces the Lewis base properties of $N(SiMe_3)_3$, as compared with $E(SiMe_3)_3$ and thus reducing the stability of the likely adduct intermediates [$X_3M{\cdot}N(SiMe_3)_3$]. In contrast to $N(SiMe_3)_3$, its tin derivative $N(SnMe_3)_3$ is a very strong Lewis base and easily forms stable adducts with numerous Lewis acids, *i.e.* with group 13 compounds $X_{3-a}R_aM$ (X = halide, R = alkyl) on which properties we and others have reported elsewhere.[18,19] The N–Sn bond of $N(SnMe_3)_3$ is significantly weaker than the N–Si bond thus leading to a more facile nitrogen transfer by the tin reagent. However, on the other hand, the trimethylstannyl group is also prone to side-reactions involving Sn–C cleavage like the corresponding trimethylsilyl group, which may be an obvious drawback.[20–22] Quite recently Carmalt *et al.* reported on some new gallium silylamido complexes and also described the reaction of $GaCl_3$ with $N(SiMe_3)$ which did not give the adduct [$Cl_3GaN(SiMe_3)_3$] but the methyl transfer product [$MeGaCl_2$]$_2$ showing exactly the problem discussed above.[22] These considerations led us to evaluate in some detail the potential of the Lewis acid/base adducts [$X_3M{\cdot}N(SnMe_3)_3$]

DOI: 10.1039/b203444c

(X = Cl, Br; M = Al, Ga, In) and [$Cl_2MeM{\cdot}N(SnMe_3)_3$] (M = Al, Ga) as single molecular precursors for the respective group 13 nitride materials.

Experimental section

General considerations

All manipulations were undertaken using standard Schlenk and glove-box techniques under inert gas atmospheres (purified N_2 or argon). Solvents (including solvent for NMR measurements) were dried under Ar by standard methods and stored over molecular sieves (4 Å, Merck; residual water <3 ppm, Karl Fischer). The precursors were synthesised form $N(SnMe_3)_3$,[23] MX_3 (purchased from Aldrich, dried and purified by sublimation) and MX_2Me[21] as described below. Infrared spectra were recorded from the powder dispersed in KBr pellets using a Perkin-Elmer 1720X Fourier Transform spectrometer and are reported in reciprocal centimeters. ^1H, ^{13}C and ^{119}Sn NMR spectra were recorded on Bruker DPX 250, DPX 200 and DRX 400 spectrometers (^1H and ^{13}C NMR were referred to internal solvent and corrected to TMS; ^{119}Sn NMR was referenced to the external standard tetramethyltin). Elemental analyses were provided by the Microanalytic Laboratory of the Ruhr University of Bochum. The thermal analysis data (TGA curves) were obtained on a Seiko TG/DTA 6300S11 thermogravimetric analyser. The X-ray powder diffraction data were collected on a Bruker AXS D8 Advance diffractometer using Cu $K\alpha_{1+2}$ radiation ($\lambda_{K\alpha_1}$ = 1.54059 Å, $\lambda_{K\alpha_2}$ = 1.544493 Å).

Synthesis of the precursors [$X_3M{\cdot}N(SnMe_3)_3$] (1: X = Cl, M = Al; 2a: X = Cl, M = Ga; 2b: X = Br, M = Ga; 3a: X = Cl, M = In; 3b: X = Br, M = In) and [$Cl_2MeM{\cdot}N(SnMe_3)_3$] (4: M = Al, 5: M = Ga)

Compounds **1–5** were prepared according to the recipe outlined below for the synthesis of [$Cl_3Ga{\cdot}N(SnMe_3)_3$] (**2a**) as a representative example: A sample of 0.246 g (1.4 mmol) of $GaCl_3$ was dissolved in 50 mL of dry diethyl ether in a Schlenk flask (150 mL) and a solution of $N(SnMe_3)_3$ (0.708 g, 1.4 mmol) in 30 ml of diethyl ether was slowly added with vigorous stirring at 25 °C. An instantaneous formation of a white precipitate was observed. After overnight stirring, the volatile components were removed in *vacuo* to yield **2a** as a white powder, 0.887 g (yield 93%).

Compounds **1–5** are moisture and air sensitive as well as thermally labile when kept in solution at room temperature for prolonged times. The compounds are soluble in CH_2Cl_2 and THF and were purified by recrystallisation from saturated solutions in CH_2Cl_2 at −20 °C. Full details on the synthesis, properties and analytical characterisation as well as on the single crystal structure determination has been published elsewhere.[19]

Pyrolysis of the precursors [$X_3M{\cdot}N(SnMe_3)_3$] (1: X = Cl, M = Al; 2a: X = Cl, M = Ga; 2b: X = Br, M = Ga; 3a: X = Cl, M = In; 3b: X = Br, M = In) and [$Cl_2MeM{\cdot}N(SnMe_3)_3$] (4: M = Al, 5: M = Ga)

The pyrolysis of **1–5** were carried out following the general method outline below. Samples of the precursors [$Cl_3Ga{\cdot}N(SnMe_3)_3$] (**2a**: 0.252 g, 0.37 mmol) and [$Br_3Ga{\cdot}N(SnMe_3)_3$] (**2b**: 0.326 g, 0.4 mmol) were transferred into quartz Schlenk tubes, which were attached to a cold trap at dry ice temperature (−78 °C). The system was kept under dynamic vacuum (10^{-3} Torr). The Schlenk tubes were heated stepwise to 180 °C (30 min), 350 °C (60 min) and finally to 650 °C for 1 h. During the heating process, the colour of the initially white materials changed to light yellow, then brown and eventually dark powders were formed. The powders were washed with CH_2Cl_2 and allowed to dry *in vacuo* (0.192 g, 61.9% yield for **2a**, 0.195 g, 58.3% yield for **2b**). About 0.144 g of $ClSnMe_3$ (65% yield) and 0.175 g (59.76% yield) of $BrSnMe_3$ were collected and isolated (fractional condensation) from the cold trap as the dominant by-product and identified by their ^1H, ^{13}C and ^{119}Sn NMR spectra. The solid residues of the pyrolysis were analysed by X-ray powder diffraction, elemental analysis and IR. Elemental analyses (%) for the solid products resulting from the decomposition: for **2a**: calc. (found): N 16.72 (12.25); C 0.00 (3.21); H 0.00 (2.06); Ga 83.28 (67.5); Ga/N = 1.11 : 1. For **2b**: calc. (found): N 16.72 (12.11); C 0.00 (3.50); H 0.00 (2.15); Ga 83.28 (65.79); Ga/N = 1.09 : 1.

Pyrolysis of [$Cl_3Al{\cdot}N(SnMe_3)_3$] (**1**, 0.160 g, 0.250 mmol) and [$Cl_2MeAl{\cdot}N(SnMe_3)_3$] (**4**, 0.195 g, 0.315 mmol), heating scheme: 200 °C (30 min), 350 °C (60 min), 650 °C (60 min) and finally at 1000 °C for 4 h. The residues were characterised by X-ray powder diffraction.

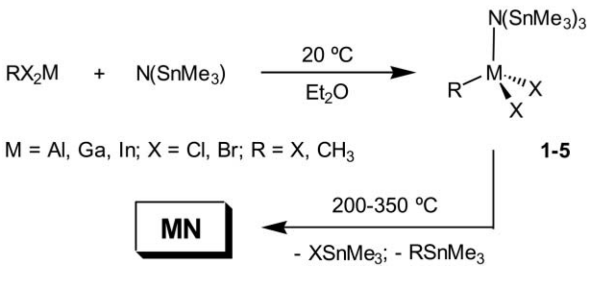
Pyrolysis of [$Cl_3In{\cdot}N(SnMe_3)_3$] (**3a**, 0.160 g, 0.220 mmol) and [$Br_3In{\cdot}N(SnMe_3)_3$] (**3b**, 0.240 g, 0.280 mmol), *in vacuo*, heating scheme: 150 °C (30 min), 300 °C (30 min) and a final step at 450 °C for 30 min under argon (1 atm). The resulting dark powders (yields not determined) were washed with CH_2Cl_2, dried *in vacuo* and analysed by X-ray powder diffraction.

Pyrolysis of [$Cl_2MeGa{\cdot}N(SnMe_3)_3$] (**5**, 0.660 g, 1.0 mmol), *in vacuo*, heating scheme: 180 °C for 30 min, then at 350 °C for 60 min. Finally the temperature was raised to 650 °C and kept constant for 2 h. The resulting dark powder was washed with CH_2Cl_2, allowed to dry *in vacuo* (yield: 0.10 g, 15%) and was characterised by X-ray powder diffraction (Fig. 2) and IR spectroscopy (Fig. 3). About 0.310 g of $ClSnMe_3$ (77.5% yield) and 0.160 g (65% yield) of $SnMe_4$ were collected and isolated (fractional condensation) from the traps as the dominant by-products and identified by their ^1H, ^{13}C and ^{119}Sn NMR spectra. Elemental analyses for the solid products resulting from the decomposition of **5**: calc. (found): N 16.72 (15.55); C 0.00 (0.61); H 0.00 (0.50); Ga 83.28 (80.5); Ga/N = 1.05 : 1.

Results and discussion

Precursor synthesis

The 1 : 1 adducts of MX_3 and MCl_2Me with $N(SnMe_3)_3$ [$X_3M{\cdot}N(SnMe_3)_3$] (**1–3**) and [$Cl_2MeM{\cdot}N(SnMe_3)_3$] (**4, 5**) are quantitatively formed at room temperature in diethyl ether solution (Scheme 1). These adducts were isolated as air and moisture sensitive colourless crystalline solids by recrystallisation from saturated dichloromethane solutions at −20 °C. At room-temperature and above the compounds are not stable, especially when kept in solution. Prolonged stirring of suspensions (longer than 15 h) at room temperature in diethyl ether during the preparation, leads to decomposition into the dimeric compounds, *e.g.* [$X_2GaN(SnMe_3)_2]_2$, as indicated by the NMR data of the reaction solution, with formation of Me_3SnCl. However, at temperatures below −20 °C the compounds are more stable and the isolated pure crystalline compounds can be stored under argon with cooling (−20 °C).



Scheme 1

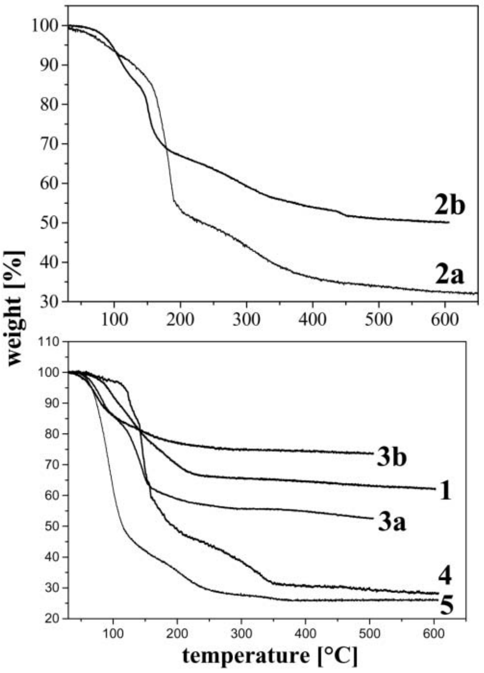


Fig. 1 *Above*: Thermogravimetric analysis data (TGA) for the decomposition of [$Cl_3Ga\cdot N(SnMe_3)_3$] (**2a**) and [$Br_3Ga\cdot N(SnMe_3)_3$] (**2b**). *Below*: Thermogravimetric analysis data (TGA) for the decomposition of [$Cl_3Al\cdot N(SnMe_3)_3$] (**1**), [$Cl_3In\cdot N(SnMe_3)_3$] (**3a**), [$Br_3In\cdot N(SnMe_3)_3$] (**3b**), [$MeCl_2Al\cdot N(SnMe_3)_3$] (**4**) and [$MeCl_2Ga\cdot N(SnMe_3)_3$] (**5**).

More details on the synthesis, analytical data and structural properties have been published elsewhere.[19]

Thermal analysis and pyrolysis

We started out with a study of the thermal behaviour of [$X_3Ga\cdot N(SnMe_3)_3$] (**2a**: X = Cl; **2b**: X = Br) by TGA (Fig. 1). The data were obtained under a stream of dry Ar and a heating rate of 5 °C min^{-1}. Three regions of weight loss up to 600 °C are evident. The first two steps occur from 50 to 350 °C with corresponding weight losses of 60 and 45%, respectively. The third stage up to 600 °C is associated with a smaller weight loss (4 and 5%) and the final weight of about 32% (**2a**) and 50% (**2b**) is still much above the theoretical value of 12.3% (**2a**) and 10.3% (**2b**) for the clean formation of GaN. This behaviour indicates an incomplete and non-selective elimination of the $XSnMe_3$. Then both precursors were decomposed under similar conditions on a preparative scale. Fig. 2 shows the XRD pattern of the resultant solid products derived from pyrolysis of **2a** giving evidence for the formation of hexagonal GaN. The obtained lattice constants are a_0 = 319.2(2) pm and c_0 = 519.5(2) pm which are a little larger than the respective values of relaxed bulk microcrystalline GaN of a_0 = 318.9 pm and c_0 = 518.5 pm. A small peak close to 40° is assigned to the (200) reflection of cubic GaN. An unusually intense (002) peak in the pattern indicates a preferential orientation of (00*l*) in GaN due to a non-isotropic crystallite size (needles or sheets) as observed in some other studies on the pyrolysis of related single source precursors to GaN.[11,24] The peaks are broadened with respect to microcrystalline GaN reference samples indicating smaller crystallite sizes or crystalline domains in the range of 10–30 nm (using the Scherrer equation) quite similar as observed in numerous studies on the pyrolysis of other precursors to group 13 nitrides.[11,24] Generally, the size of the crystalline domains depend very much on the conditions of the heat treatment of the sample (*e.g.* the annealing temperature and time). We studied these issues in some detail in the case of the controlled detonation of gallium azide precursors of the general formula [$(N_3)_3Ga(NR_3)$].[24] The particular samples discussed here, most likely consist of agglomerated crystalline primary particles together with a more or less amorphous matrix and of course do not contain free standing, isolated nanoparticles of the nitrides. A more detailed analysis of the distribution of particle sizes and shapes of the group 13 nitride powder samples reported here is thus not meaningful. The IR spectra of the solid products (Fig. 3) show a strong peak at about 580 cm^{-1}. This feature again compares nicely with other GaN samples derived from single source precursors and is thus assigned to the Ga–N stretching mode (E2).[1,24] The materials obtained from pyrolysis of **2a** (and also **2b**) however still contain significant impurities (metal Sn, C, H and even halide X), which are easily observed from the XRD patterns and the elemental analysis. We tried to optimise the conditions in order to eliminate the leaving group $XSnMe_3$ completely at lower temperatures up to a maximum of 350 °C. These attempts however failed. When the temperature was raised above 350 °C, another fraction of $XSnMe_3$ started to eliminate again and collected in the cold trap, but also the formation of metallic tin occurred simultaneously.

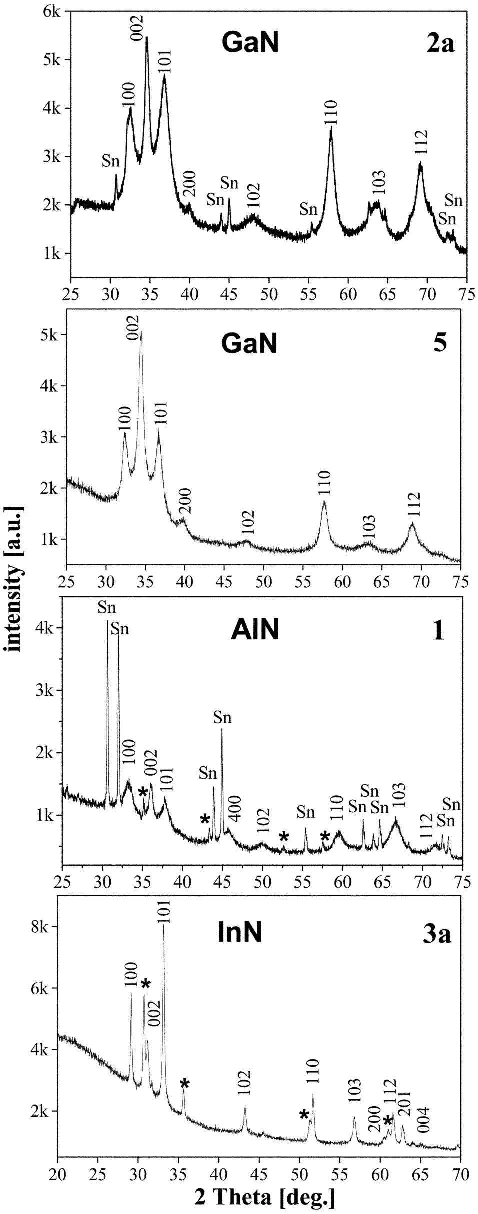


Fig. 2 X-Ray powder diffraction patterns of the solid products resulting from the thermal decomposition of [$Cl_3Ga\cdot N(SnMe_3)_3$] (**2a**), [$MeCl_2Ga\cdot N(SnMe_3)_3$] (**5**), [$Cl_3In\cdot N(SnMe_3)_3$] (**3a**) and [$Cl_3Al\cdot N(SnMe_3)_3$] (**1**) at 350 °C and an additional annealing step (1–2 h) at 650 °C. The asterisk (*) denotes oxide impurities (*e.g.* Al_2O_3 and In_2O_3).

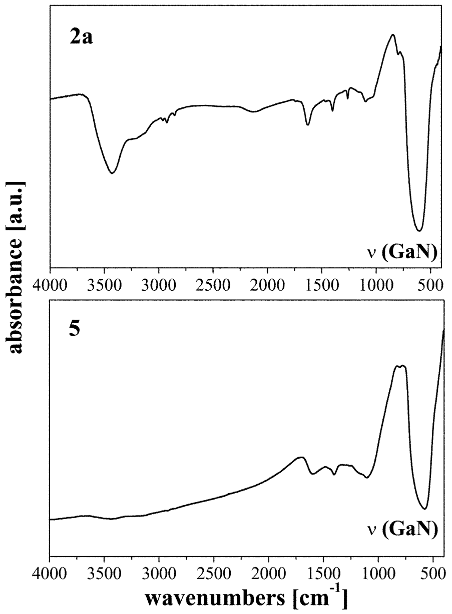


Fig. 3 IR spectra of the products resulting from the thermal decomposition of [$Cl_3Ga{\cdot}N(SnMe_3)_3$] (**2a**) at 350 °C and an additional annealing step at 650 °C and of [$MeCl_2Ga{\cdot}N(SnMe_3)_3$] (**5**) at 300 °C.

The AlN and InN precursors **1** and **3a,b** showed a quite similar behavior of incomplete and non-selective elimination of $XSnMe_3$ below 350 °C. The resulting black powders were characterized by X-ray powder diffraction giving some evidence for the formation of AlN (broadened reflections at the respective θ values for the hexagonal phases) and InN. As the temperature was raised above 350 °C, another fraction of $BrSnMe_3$ and $ClSnMe_3$ was removed from the solid, as observed for **2a** and **2b**, and collected in the cold trap. In the case of **1** parallel decomposition to give metallic tin also took place. Also, the competitive formation of oxide impurities is thermodynamically much more favourable for Al and In than for Ga. While all experiments were conducted in the same and very controlled manner, traces of moisture and oxygen (unavoidable leaking of the glass apparatus) could not be fully excluded, at least under our conditions (pyrolysis under dynamic vacuum). This caused the formation of some traces of Al_2O_3 and In_2O_3 (as denoted with an asterisk in the XRD pattrens of Fig. 2). Our observation of incomplete elimination of $XSnMe_3$ using the halide precursors **1–3** is similar to a number of related cases, for example the preparation of GaP from the solid state pyrolysis of [$Cl_3GaP(SiMe_3)_3$] using the dehalosilylation strategy.[15] Some silicon, carbon, and possibly halide is tenaciously retained in the solid products and influenced the mass balance.

To further evaluate precursors **2a** and **2b** for the growth of crystalline GaN, we conducted the pyrolysis under a series of different conditions: vacuum (10^{-3} Torr), dry Ar current (1 atm) as well as under a flow of NH_3 (1 atm) and up to temperatures of 650 °C. However, there were no particular differences between the obtained products. Therefore, complete removal of the $XSnMe_3$ group appears to be very difficult and the retention of some Sn, C, H, and X in the final products seems to be an intrinsic property of these particular precursor systems. The bromo derivatives behave less satisfactorily than the chloro precursors, which is ascribed to the thermodynamically somewhat less favourable formation of $BrSnMe_3$.

Consequently, more labile precursors and more selective decomposition reactions are needed which allow the elimination of volatile tin species below 350 °C. Since the alkyltrimethyltin elimination reaction has particularly been shown to serve as a simple, single-step, low-temperature pathway to substituted aminogallanes we looked at the possibility for the elimination of tetramethyltin.[23] In addition, a short note in a paper by Dehnicke *et al.* from 1995 on the pyrolysis of the adducts [$Me_3M{\cdot}N(SnMe_3)_3$] referred to the formation of $SnMe_4$ as the dominant by-product. Pure MN phases were however not obtained.[18] Thus we turned our interest to the *mixed* substituted methyl derivatives [$Cl_2MeM{\cdot}N(SnMe_3)_3$] **4** and **5** in order to *combine* dehalostannylation with tetramethyltin elimination.

The TGA curves of Fig. 1 for precursors **1**, **3a**, **3b**, **4** and **5** together with TGA for **2a** and **2b** show, that the monomethyl derivatives **4** and **5** indeed show much smoother decomposition behavior than their trihalide congeners. The elimination of volatile tin species is now much more effective and is almost completed below 300 °C. There is no significant further loss of weight during prolonged heat treatment. In the TGA experiments (Ar current), the accessible total mass loss of about 70–80% for **4** and **5** was closer to the theoretical values of weight losses of 87.3% (GaN) and 93.4% (AlN) than in the case of the other halide precursors.

The pyrolysis of the methyl derivative [$Cl_2MeGa{\cdot}N(SnMe_3)_3$] (**5**) was then conducted *in vacuo* on a preparative scale in a stepwise manner up to a maximum temperature of 650 °C. The GC/MS analysis of the resulting volatile by-products collected in the cold trap (liquid nitrogen) expectedly confirmed the presence of both $ClSnMe_3$ and $SnMe_4$ as the dominant products. Likely organic side-products such as CH_3Cl, C_2H_6, *etc.* were not detected by GC/MS (Scheme 1). This elimination appeared to be complete even below 300 °C, thus avoiding the decomposition of residual tin species into metallic tin at high temperature. However, under such mild conditions (200–300 °C), the solid residue did not show the characteristic XRD features of crystalline GaN. However, the IR spectrum of the product (Fig. 3) exhibits an intense peak centred at 580 cm^{-1}. This is assigned to the Ga–N lattice vibration (E2 mode) as observed for the pyrolysis of **2a** and **2b** and other related GaN materials.[24] After subsequent annealing at 650 °C for 1–2 h the resultant, now only slightly brownish coloured product was identified as the hexagonal phase of GaN by X-ray diffraction without any other detectable crystalline impurities, *e.g.* tin, Ga_2O_3, *etc.*(Fig. 2). A small reflection near 40° can be indexed to cubic GaN. The pyrolysis of [$Cl_2MeAl{\cdot}N(SnMe_3)_3$] (**4**) was also carried out in dynamic vacuum in a similar manner with a final annealing step at 1000 °C and resulted in a black solid containing cubic AlN. Impurities of tin were again not detected by XRD.

Conclusions

The potential of dehalostannylation reactions for the synthesis of group 13 nitrides using the Lewis acid/base adducts [$X_3M{\cdot}N(SnMe_3)_3$] (X = Cl, Br; M = Al, Ga, In) and the mixed substituted [$Cl_2MeM{\cdot}N(SnMe_3)_3$] (M = Al, Ga) as molecular precursors has been evaluated. As expected, most of the elimination of $XSnMe_3$ from the trihalide precursors [$X_3M{\cdot}N(SnMe_3)_3$] (**1–3**) takes place at moderate conditions below 350 °C. The chloro precursors are generally better choices than the bromo congeners. However, in both cases the pyrolysis at elevated temperatures (600 °C) is accompanied with unselective decomposition and formation of metallic tin impurities. By employing the thermally more labile mixed substituted organometallic precursor **5**, tin-free nitride samples of nanocrystalline GaN were obtained at moderate conditions (below 300 °C) because of the more facile and selective parallel elimination of $ClSnMe_3$ and $SnMe_4$. However, as seen from the mass balance, the elemental analysis and even by the unaided eye (brown products rather than white samples) chemically pure nitride materials have not, as yet, been obtained. The best results were obtained for the GaN precursor **5**. Whilst, further optimisation of the precursors and conditions is needed, the results clearly indicate that tris(trimethyltin)amine represents an interesting synthetic equivalent for ammonia for the growth of group 13 nitride materials, and possibly for metal nitride materials in general. For example, the precursor [$Cl_2MeGa\cdot N(SnMe_3)_3$] (**5**) is possibly labile enough to be useful for the growth of free-standing, surface stabilised nanoparticles of GaN as colloids by injection into suitable, thermally stable and chemically inert hydrocarbon solvents heated to 250–300 °C in the presence of suitable surfactants.[7]

Acknowledgement

Dr Qing min Cheng is grateful for a fellowship by the Alexander von Humboldt Foundation in Germany. This work was also supported by the Deutsche Forschungsgemeinschaft (DFG), grant No: Fi 502/9-2.

References

1 S. Nakamura and G. Fasol, *The Blue Laser Diode*, Springer, Berlin, 1997.

2 Y. Xie, Y. Qian, W. Wang, S. Zhang and Y. Zhang, *Science*, 1996, **272**, 1926.

3 C. H. Wallace, S. H. Kim, G. A. Ross, L. Rao, J. R. Heath, M. Nicol and R. B. Kaner, *Appl. Phys. Lett.*, 1998, **72**, 596.

4 R. C. Schoonmaker and C. E. Burton, *Inorg. Synth.*, 1963, **7**, 16; W. C. Johnsone, J. B. Parsons and M. C. Crew, *J. Phys. Chem.*, 1932, **36**, 2651; R. Juza and H. Z. Hahn, *Z. Anorg. Allg. Chem.*, 1940, **244**, 111; C. M. Balkas and R. F. Davies, *J. Am. Ceram. Soc.*, 1996, **79**, 2309; A. C. Jones, C. R. Whitehouse and J. S. Roberts, *Chem. Vap. Deposition*, 1995, **1**, 65.

5 D. A. Neumayer and J. G. Ekerdt, *Chem. Mater.*, 1996, **8**, 9; T. D. Getman and G. W. Franklin, *Comments Inorg. Chem.*, 1995, **17**, 79.

6 S. D. Dingman, N. P. Rath, P. D. Markowitz, P. C. Gibbons and W. E. Buhro, *Angew. Chem., Int. Ed.*, 2000, **39**, 1470.

7 O. I. Micic, S. P. Ahrenkiel, D. Bertram and A. J. Nozik, *Appl. Phys. Lett.*, 1999, **75**, 478; A. Manz, A. Birkner, M. Kolbe and R. A. Fischer, *Adv. Mater.*, 2000, **18**, 569.

8 A. C. Frank and R. A. Fischer, *Adv. Mater.*, 1998, **10**, 961.

9 H. Winkler, A. Birkner, V. Hagen, I. Wolf, R. Schmechel, H. von Seggern and R. A. Fischer, *Adv. Mater.*, 1999, **17**, 1444.

10 R. Riedel, S. Schaible, U. Klingebiel, M. Noltemeyer and E. Werner, *Z. Anorg. Allg. Chem.*, 1991, **603**, 119; L. V. Interrante, G. A. Sigel, M. Garbauskas, C. Hejna and G. A. Slack, *Inorg. Chem.*, 1989, **28**, 252; W. Rockensüβ and H. W. Roesky, *Adv. Mater.*, 1993, **5**, 443; S. Koyama, H. Takeda, Y. Saito, Y. Sugahara and K. Kuroda, *J. Mater. Chem.*, 1996, **6**, 1055; X. H. Chen and K. E. Gonsalves, *J. Mater. Res.*, 1997, **12**, 1274; Y. Saito, Y. Sugahara and K. Kuroda, *J. Am. Ceram. Soc.*, 2000, **83**, 2436.

11 J. W. Hwang, J. P. Campbell, J. Kozubowski, S. A. Hanson, J. F. Evans and W. L. Gladfelter, *Chem. Mater.*, 1995, **7**, 517; J. F. Janik and R. L. Wells, *Chem. Mater.*, 1996, **8**, 2708; K. E. Gonsalves, G. Carlson, S. P. Rangarajan, M. Benaissa and M. J. Yacaman, *J. Mater. Chem.*, 1996, **6**, 1451; S. T. Barry and D. S. Richardson, *Chem. Mater.*, 1994, **6**, 2220; D. Rodewald, J. Bill, U. Beck, M. Puchinger, T. Wagner, A. Greiner and F. Aldinger, *Adv. Mater.*, 1999, **11**, 1502.

12 A. P. Purdy, *Inorg. Chem.*, 1994, **33**, 282; R. A. Fischer, A. Miehr, T. Metzger, E. Born, O. Ambacher, H. Angerer and R. Dimitrov, *Chem. Mater.*, 1996, **8**, 1356; R. A. Fischer, H. Sussek, A. Miehr, H. Pritzkow and E. Herdtweck, *J. Organomet. Chem.*, 1997, **548**, 73; B. J. Bae, J. E. Park, B. Kim and J. T. Park, *J. Organomet. Chem.*, 2000, **616**, 128.

13 J. McMurran, J. Kouvetakis, D. C. Nesting, D. J. Smith and J. L. Hubbard, *J. Am. Chem. Soc.*, 1998, **120**, 5233; J. Kouvetakis, J. McMurran, C. Steffek, T. L. Groy and J. L. Hubbard, *Inorg. Chem.*, 2000, **39**, 3805.

14 A. Devi, H. Sussek, H. Pritzkow, M. Winter and R. A. Fischer, *Eur. J. Inorg. Chem.*, 1999, **12**, 2127; A. Devi, W. Rogge, A. Wohlfart, F. Hipler, H. W. Becker and R. A. Fischer, *Chem. Vap. Deposition*, 2000, **6**, 245; A. Miehr, O. Ambacher, T. Metzger, E. Born and R. A. Fischer, *Chem. Vap. Deposition*, 1996, **2**, 51.

15 J. F. Janik, R. A. Baldwin and R. L. Wells, *Organometallics*, 1996, **15**, 5385; R. L. Wells, S. R. Aubuchon, S. S. Kher and M. S. Lube, *Chem. Mater.*, 1995, **7**, 793.

16 R. L. Wells, M. F. Self, A. T. Mcphail, S. R. Aubuchon, R. C. Woudenberg and J. P. Jasinski, *Organometallics*, 1993, **12**, 2832; R. L. Wells, C. G. Pitt, A. T. Mcphail, A. P. Purdy, S. Shafieezad and R. B. Hallock, *Chem. Mater.*, 1989, **1**, 4; S. R. Aubuchon, A. T. McPhail, R. L. Wells, J. A. Giambra and J. R. Bowser, *Chem. Mater.*, 1994, **6**, 82.

17 J. F. Janik, R. L. Wells, V. G. Young, Jr., A. L. Rheingold and I. A. Guzei, *J. Am. Chem. Soc.*, 1998, **120**, 532.

18 R. Hillwig, K. Harms and K. Dehnicke, *J. Organomet. Chem.*, 1995, **501**, 327.

19 Q. M. Cheng, O. Stark, K. Merz, M. Winter and R. A. Fischer, *J. Chem. Soc., Dalton Trans.*, 2002 (DOI: 10.1039/b203489c).

20 X. Cheng, C. Slebodnick, P. A. Deck, D. R. Billodeaux and F. R. Fronczek, *Inorg. Chem.*, 2000, **39**, 4921; J. J. Eisch and B. W. Kotowicz, *Eur. J. Inorg. Chem.*, 1998, **6**, 761.

21 H. Schmidbaur and W. Findeis, *Chem. Ber.*, 1966, **9**, 2187.

22 C. J. Carmalt, J. D. Mileham, A. J. P. White, D. J. Williams and J. W. Steed, *Inorg. Chem.*, 2001, **40**, 6035.

23 W. R. Nutt, K. J. Murray, J. M. Gulick, J. D. Odom, Y. Ding and L. Lebioda, *Organometallics*, 1996, **15**, 1728.

24 A. C. Frank, F. Stowasser, O. Stark, H. T. Kwak, H. Sussek, A. Rupp, H. Pritzkow, O. Ambacher, M. Giersig and R. A. Fischer, *Adv. Mater. Opt. Electron.*, 1998, **8**, 135.