Journal of Organometallic Chemistry, 443 (1993) 137–143

JOM 23047

Organometallic precursors for the formation of gallium nitride by metal organic chemical vapour deposition. Thermal decomposition of trineopentyl gallium and of its adducts with ammonia, dimethylamine and t-butylamine

Matthew J. Almond, Carolyn E. Jenkins and David A. Rice

Department of Chemistry, University of Reading, P.O. Box 224, Whiteknights, Reading, RG6 2AD (UK)

(Received May 14, 1992)

Abstract

In the absence of air $Np_3Ga(Np = (CH_3)_3CCH_2–)$ decomposes thermally at 310–340°C to yield isobutene and neopentane as the principal gaseous products together with a film of a material of metallic appearance. Np_3Ga reacts readily with NH_3, Me_2NH and $^tBuNH_2$ to form 1:1 adducts $Np_3Ga \cdot NH_3$ (I), $Np_3Ga \cdot NMe_2H$ (II) and $Np_3Ga \cdot N^tBuH_2$ (III). Adducts I and II decompose initially at 130–140°C to give neopentane and a solid containing gallium–nitrogen; on prolonged heating at this temperature all the N-containing groups are lost by Ga–N bond rupture. For III complete dissociation occurs at the relatively low temperature of 100°C. Thus none of these adducts would appear to be suitable precursors for the formation of GaN by metal organic chemical vapour deposition (MOCVD).

1. Introduction

Metal organic chemical vapour deposition (MOCVD) is one of the methods used to grow thin layers of the wide-band-gap semiconductor gallium nitride (GaN). Commonly a gaseous mixture of Me_3Ga and NH_3 is allowed to pass over a heated substrate at 1000°C, where formation of GaN takes place [1,2]. There are two major disadvantages of this method. First, at such a high temperature structural damage to the layers being formed is always likely, and secondly, incorporation of carbon into the GaN layer may occur. Thus alternatives to Me_3Ga are being sought. An obvious alternative is Et_3Ga and it has been used in the preparation of GaAs [3]. The decomposition of Et_3Ga occurs by a β-hydrogen elimination mechanism, and so it decomposes at much lower temperatures than Me_3Ga with little incorporation of carbon into the GaAs. A disadvantage of Et_3Ga, shared by Me_3Ga, is that they are both very pyrophoric and therefore dangerous to handle. A number of alkylgallium compounds has been prepared, including $^iBu_3Ga$ [4], $^nPr_3Ga$ [5], $Vi_3Ga(Vi = CH_2{=}CH–)$ [5], Ph_3Ga [6], Np_3Ga $(Np = (CH_3)_3CCH_2–)$ [7] and $(PhMe_2CCH_2)_3Ga$ [8]. One of these, Np_3Ga, although it has received little attention, is known to be a non-pyrophoric liquid and, while it has no β-hydrogen atoms, the bulkiness of the Np groups is believed to impart reactivity to the Ga–C bonds so promoting thermolysis at relatively low temperature. It is clear that an assessment of the potential of Np_3Ga as a precursor in the formation of binary compounds by MOCVD is overdue. This statement is substantiated by the recent reports of the use of Np_3In to prepare good quality layers of InP and InSb by MOCVD [9].

Against the above background we decided to study the potential of Np_3Ga for use in MOCVD first by studying its thermal decomposition (so ascertaining whether any solid products are likely to contain carbon) and second, by characterising amine adducts of Np_3Ga. We chose to study the formation and thermal chemistry of amine adducts because in the formation of GaN from Me_3Ga and NH_3 the first step of the reaction is believed to be formation of an adduct, $Me_3Ga \cdot NH_3$, which then decomposes thermally via

---

Correspondence to: Dr. M. J. Almond.

0022-328X/93/$6.00

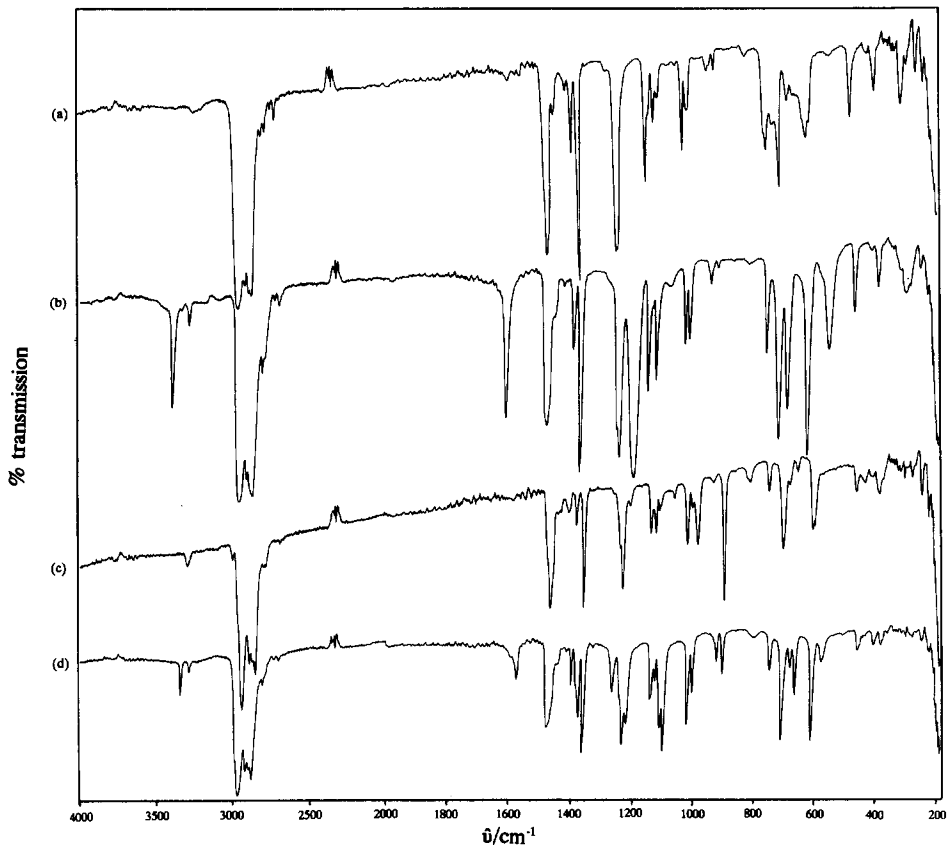

Fig. 1. IR spectra of (a) Np_3Ga, (b) $Np_3Ga \cdot NH_3$ (I), (c) $Np_3Ga \cdot NMe_2H$ (II) and (d) $Np_3Ga \cdot N^tBuH_2$ (III). All spectra were recorded as thin films on a CsI window held at 77 K since the samples were too involatile to allow gas phase spectra to be recorded and too air-sensitive to allow the preparation of conventional mulls.

loss of CH_4 [10–12*]. Moreover the chemistry of amine adducts of Np_3Ga has been very little explored. To our knowledge the only amine adduct of Np_3Ga which has been characterised to date is $Np_3Ga \cdot NMe_3$ [7]. Thermolysis studies should provide answers to the question "do the adducts decompose primarily by rupture of Ga–N bonds?" If, for the amine adducts of Np_3Ga, the answer to this question is "yes", then loss of nitrogen from any solid material produced is likely. Thus Np_3Ga would probably not be a suitable precursor to GaN. It was with these points in mind that we commenced our study of Np_3Ga.

2. Experimental section

Np_3Ga was prepared by the method described by Beachley and Pazik [7]. The Grignard reagent, NpMgCl was treated with Ga_2Cl_6 under an atmosphere of Ar in ethereal solution. The excess $(C_2H_5)_2O$ was removed at the pump and the crude Np_3Ga purified by distillation at 55°C on a vacuum line. The product was characterised, and its purity assessed, by means of its ^1H NMR spectrum in benzene-d_6 and its mass spectrum. The mass spectrum contained a very weak parent ion peak (Np_3Ga^+) but a much stronger signal due to the ion Np_2Ga^+, *i.e.* Np_3Ga behaves much as Me_3Ga in the mass spectrometer [10,13]. All ions containing a Ga atom were readily distinguished by the presence of two peaks in the intensity ratio 100:67 corresponding to the natural abundance of ^{69}Ga and ^{71}Ga. The sample was found to be at least 98% pure.

On an all-glass vacuum line, amine adducts of Np_3Ga were prepared by condensing an excess of an amine on to samples of Np_3Ga. The excess of amine was removed to leave white solid materials very sensitive to air. The amines used were NH_3, Me_2NH and $^tBuNH_2$, and care was taken to dry and de-gas them prior to use. The three adducts $Np_3Ga \cdot NH_3$ (I), $Np_3Ga \cdot NMe_2H$ (II) and $Np_3Ga \cdot N^tBuH_2$ (III) were found to have melting points of *ca.* 60, 70, and 90°C respectively.

IR spectra were recorded, by a Perkin–Elmer model 983 dispersive spectrometer, of solid films, held at 77 K

---

* Reference number with an asterisk indicates a note in the list of references.

and formed in a cryogenic cell whose design is described in detail elsewhere [10]. For some samples it was possible to record IR spectra from Nujol mull or vapour phase (in a 10 cm gas cell) samples. NMR spectra (^1H) were recorded with a Perkin–Elmer R36 220 MHz instrument and mass spectra with a VG SXP800 Spectramass quadrupole spectrometer.

3. Results

3.1. Characterisation of amine adducts of Np_3Ga

The adducts **I**, **II** and **III** were characterised by a combination of IR and ^1H NMR spectroscopy and mass spectrometry. The vapour pressures of the adducts are too low at room temperature to allow gas phase IR spectra to be recorded, so the samples were condensed as thin films on to a CsI window held at 77 K. All three adducts, whilst being held at room temperature, were deposited onto the spectroscopic window over 30 min. The spectra obtained are shown in Fig. 1, and the positions of peaks are given in Table 1 together with approximate assignments. Ready confirmation of adduct formation was obtained from these IR spectra by a comparison of the bands from the products with those from the reactants. The Np group has a very rich spectrum, as shown by the IR spectrum of Np_3Ga (Fig.

TABLE 1. A comparison of the band positions in the infrared spectra of Np_3Ga, $Np_3Ga \cdot NH_3$ (I), $Np_3Ga \cdot NMe_2H$ (II), $Np_3Ga \cdot N^tBuH_2$ (III) and $[Np_2GaNH_2]_n$

$\nu(cm^{-1})$					Approximate assignment
Np_3Ga	$Np_3Ga \cdot NH_3$	$Np_3Ga \cdot NMe_2H$	$Np_3Ga \cdot N^tBuH_2$	$[Np_2GaNH_2]_n$	
	3392 (m)	3305 (w)	3336 (wm)	3398 (w)	ν_{as}(N–H)
	3288 (w)		3281 (w)	3328 (w)	ν_s(N–H)
2943 (vs)	2941 (vs)	2941 (vs)	2944 (vs)	2952 (s)	ν_{as}(C–H)
2858 (s)	2857 (vs)	2895 (s)	2899 (s)	2861 (s)	ν_s(C–H)
			2858 (s)		ν(C–H) [^{t}Bu]
			2800 (wm)		ν(C–H) [^{t}Bu]
	1600 (ms)		1574 (wm)		δ_{as}(NH)
1467 (s)	1466 (ms)	1467 (s)	1474 (ms)	1470 (ms)	$\delta_{as}(CH_3)$ [Ga]
1441 (wm)	1441 (wm)	1441 (w)	1441 (w)		$\delta_{as}(CH_3)$ [Ga]
		1408 (w)	1398 (wm)	1399 (w)	$\delta_{as}(CH_3)$ [N]
1382 (wm)	1381 (wm)	1382 (wm)	1382 (sh)	1384 (w)	$\delta_{as}(CH_3)$ [Ga]
			1371 (m)	1360 (ms)	$\delta_{as}(CH_3)$ [N]
1359 (s)	1358 (s)	1358 (s)	1358 (s)		$\delta_{as}(CH_3)$ [Ga]
1241 (ms)	1242 (ms)	1240 (m)	1262 (m)		
1235 (ms)	1232 (s)	1229 (ms)	1228 (s)	1233 (m)	
		1205 (w)	1215 (ms)		$\rho(CH_3)$ [N]
	1183 (s)				$\delta_s(NH_3)$
1138 (m)	1138 (m)	1138 (wm)	1138 (m)	1138 (w)	$\delta_s(CH_3)$ [Ga]
1111 (wm)	1111 (m)	1120 (wm)	1123 (wm)		
			1105 (ms)	1103 (wm)	
		1060 (w)	1094 (s)	1064 (m)	ν(C–N)
1018 (m)	1017 (wm)	1018 (m)	1016 (ms)	1017 (wm)	
1003 (wm)	1003 (wm)	1003 (w)	1001 (m)	1002 (w)	
		984 (m)	924 (wm)		ν(C–N)
935 (w)	934 (w)	932 (vw)	934 (vw)	934 (w)	ν(C–C)
		896 (s)	904 (wm)	808 (ms)	$\rho(CH_3)$ [N]
747 (m)	749 (m)	749 (w)	747 (wm)	750 (w)	$\rho(CH_3)$ [Ga]
701 (m)	708 (s)	703 (ms)	707 (s)	707 (m)	$\rho(CH_3)$ [Ga]
672 (wm) [a]	681 (ms)	684 (w)	681 (wm)	633 (wm)	ν_{as}(Ga–C)
		655 (w)	664 (m)		
612 (m) [a]	613 (s)	605 (m)	609 (s)	602 (wm)	ν_s(Ga–C)
	546 (m)		578 (w)	578 (w)	$\rho(NH_3)$
464 (wm)	462 (wm)	461 (wm)	463 (w)		
			456 (sh)	454 (wm)	
		432 (w) [b]		439 (m) [d]	ν(Ga–N)
			409 (w)		δC_2N
383 (wm)	384 (w)	387 (w)	385 (w)		δCCC
	292 (wm,br) [b]		366 (w) [b]		ν(Ga–N)
295 (wm)		[c]	[c]		δCGaC

[a] ν_{as}(Ga–C) *and* ν_s(Ga–C) were observed, which implies that the GaC_3 fragment of the molecule is not planar in the solid state.

[b] See text for comment. [c] The peaks in this region were too weak to be measured, with any confidence. [d] Ring mode.

1(a)). In the spectra of the adducts all of the fundamentals of Np_3Ga were observed (and therefore readily assigned, since there was little change in any of the peak positions) alongside features arising from the amine moieties and a new, low wavenumber, vibration which was, in each case, assigned to ν(Ga–N). In the case of **I** we carried out experiments in which NH_3 was replaced by ND_3 in order to confirm which features arose from the NH_3 moiety. Bands of **I** which were found to shift upon deuteration are indicated in Table 2; the shifts reported agree approximately with the expected shift of $\nu_H/\nu_D = 1.4$.

Bands arising from Ga–C stretching vibrations in Np_3Ga and its adducts were assigned to modes in the region 600–685 cm^{-1} on the basis of a comparison of the IR spectrum of Np_3Ga with corresponding spectra of other gallium alkyls [10,14,15]. Only very small shifts are observed in the features assigned to ν_{asym}(Ga–C) and ν_{sym}(Ga–C) upon adduct formation. Whilst for the amine adducts of Me_3Ga, whose IR spectra are described elsewhere [10,11,15], the positions of the ν_{asym}(Ga–C) and ν_{sym}(Ga–C) bands were very similar for a range of adducts, the values varied significantly from the positions of stretches of uncoordinated Me_3Ga. The similarity in the values of ν_{sym}(Ga–C) and ν_{asym}(Ga–C) in the case of Np_3Ga and its amine adducts implies that the large Np group is but little perturbed upon coordination of the Ga atom.

In the IR spectrum of **II** the band at 432 cm^{-1} could readily be assigned to ν(Ga–N); in **III** the same vibrational feature was found at the lower wavenumber of 366 cm^{-1} by a process of elimination of all other low-frequency features. In the spectrum of **I** there was no obvious feature assignable to ν(Ga–N), but on closer examination it was noticed that the feature at 292 cm^{-1}, which was initially thought to correspond solely to the 295 cm^{-1} peak in Np_3Ga, was in fact very broad and possibly consisted of two or more unresolvable peaks (see Fig. 1(b)). Therefore ν(Ga–N) in this molecule was assigned to a band in this region, *i.e.* at approximately 292 cm^{-1}. The very low frequency of this stretch corresponds to the low frequency of the same vibration in $Me_3Ga \cdot NH_3$ (350 cm^{-1}) [10,11,16], while the bands observed in **II** (432 cm^{-1}) and **III** (366 cm^{-1}) resemble those found in the corresponding Me_3Ga adducts (431 and 413 cm^{-1}, respectively) [10,17].

TABLE 2. Bands in the infra-red spectrum of $Np_3Ga \cdot NH_3$ (I) which shift upon deuteration

ν (cm^{-1})		ν_H/ν_D	Approximate assignment
$Np_3Ga \cdot NH_3$	$Np_3Ga \cdot ND_3$		
3392	2529	1.34	ν_{as}(N–H)
3288	2385	1.38	ν_s(N–H)
1600	1170	1.37	$\delta_{as}(NH_3)$
1183	915	1.29	$\delta_s(NH_3)$
546	[a]		$\rho(NH_3)$

[a] Peak obscured by spectrum noise.

TABLE 3. ^1H NMR spectra of Np_3Ga and of its amine adducts

Compound	δ (ppm)
Np_3Ga	1.06(s, 27H,$-CMe_3$); 1.01 (s, 6H,$-CH_2-$)
$Np_3Ga \cdot NH_3$	1.13(s, 27H,$-CMe_3$); 0.71 (s, 6H,$-CH_2-$)
$Np_3Ga \cdot NMe_2H$	1.73(d, 6H,$-NMe_2$); 1.16(s, 27H,$-CMe_3$); 0.60 (s, 6H,$-CH_2-$)

The existence of the compounds as 1 : 1 adducts, and a confirmation of their purity, is demonstrated by their ^1H NMR spectra, recorded with solutions in benzene-d_6. In Table 3 are given the positions of the resonances observed in the spectra of **I** and **II** together with those for Np_3Ga. It is noticeable that the methyl and methylene protons in the free alkyl have resonances in the ^1H NMR spectrum that are very close in position since the electronegativity of gallium is similar to that of carbon. For the adducts, the N–H resonances were not observed, but there were quite large shifts in the positions of the methylenic proton resonances from those observed in the case of Np_3Ga; this appears to be a feature which alkyl–gallium amine adducts have in common. For example, the resonances of the Np group in the spectrum of $Np_3Ga \cdot NMe_3$ occur at $\delta = 1.25$ ppm ($-CMe_3$) and 0.74 ppm ($-CH_2-$) [7]. It may be concluded from all of these results that upon coordination of a donor molecule to Np_3Ga, there is little effect transmitted to the protons of $-CMe_3$, but the $-CH_2-$ protons are significantly shielded, as shown by the shift upfield in δ values, owing to the electron releasing nature of the amine. It is interesting that in the adduct $Np_3Ga \cdot PPh_2H$, the CH_2 and CMe_3 resonances are at similar positions [$\delta = 1.10$ ppm ($-CMe_3$) and 1.04 ppm ($-CH_2-$)] [18] to those in the free alkyl, reflecting the weaker basicity of phosphines. From a consideration of the two results presented here the degree of shielding of the CH_2 protons appears to depend upon the strength of the amine as a Lewis base, *i.e.* $NMe_2H > NH_3$.

In the mass spectra of **I**, **II**, and **III** the molecular ions were not visible which is not surprising because no peaks corresponding to the parent ions were observed in the mass spectra of a series of $Me_3Ga \cdot$ amine adducts [10,11,17]. These results indicate that the Ga–N bonds in the amine adducts are weak. The three amine adducts give rise to mass spectra resembling that of Np_3Ga, *i.e.* they show weak features at $m/e = 282/284$ (Np_3Ga^+), very strong peaks at 211/213 (Np_2Ga^+), and other fragments relating to Np_3Ga at lower m/e

TABLE 4. Retention times of the products of the thermolysis of Np_3Ga at 310°C

Retention time (min)	% area	Product [a]
1.78	1.90	methane
2.47	0.23	ethane
4.57	0.48	propene
9.59	36.83	isobutene
10.71	54.10	neopentane

[a] The products were identified by comparison with the retention times of the pure samples under the same conditions.

values, together with clusters of peaks arising from the amines. In the spectrum of **III** it was not possible to distinguish between the peaks arising from the Np fragment from those from the amine moiety. In none of the spectra were peaks of *m/e* values higher than 284 observed.

3.2. *Thermal decomposition of Np_3Ga and of its amine adducts*

3.2.1. *Np_3Ga*

This was found to be quite thermally stable in the absence of air and moisture. When it was heated to 310°C under a pressure of 500 Torr (1 Torr = 133 Pa) of Ar evolution of gas commenced. The IR spectrum of the gaseous products showed that the main components were neopentane and isobutene and this was confirmed by a gas chromatographic study (Table 4). The residue was an orange oil mixed with a grey solid. Upon prolonged heating at 340°C, further isobutene, neopentane and a trace of methane were evolved, and the residue was a film of metallic appearance, probably of impure gallium. This suggestion is supported by the observation that pyrolysis of Me_3Ga at 520°C in Ar carrier gas produces a film of Ga containing 8% of C [19].

3.2.2. *$Np_3Ga \cdot NH_3$ (I)*

When **I** was heated under 500 Torr of Ar at 130°C until evolution of gas ceased, the IR spectrum of the gaseous product was that of neopentane, and no evidence was obtained for NH_3 production. The residue, a clear liquid, became crystalline when kept overnight. It was found to be fairly involatile, although it was possible to obtain a very weak IR spectrum as a condensed film on a CsI window held at 77 K. Better quality spectra were obtained from mulls of the residue, which was found to be not so sensitive to air as **I**. Features seen in the IR spectra of **I** and of its decomposition product are listed in Table 1, along with assignments of the bands.

This product is most likely to contain a $[GaN]_n$ ring, *i.e.* $[Np_2GaNH_2]_n$ where $n = 2$ or higher. From a consideration of the steric requirements of the Np groups we suggest that *n* is probably 2 [20]. Examination of the IR spectrum of this product shows that the positions of the large number of vibrations and deformations of the Np groups are virtually unchanged from those in **I**. However, whilst the product exhibits both asymmetric and symmetric N–H stretches, $\nu_{sym}(N-H_2)$ has shifted considerably from its position in **I** and there have been significant shifts in the bands assigned to $\nu_{asym}(Ga-C)$ and $\nu_{sym}(Ga-C)$. A new feature, of medium intensity, occurring at 439 cm^{-1} is perhaps ascribable to a Ga–N ring vibration which is at a considerably higher wavenumber than that of the Ga–N stretch in **I** (292 cm^{-1}). This shift in wavenumber is consistent with the formation of a cyclic $(Ga-N)_n$ fragment [20]. From mass spectrometric studies evidence was obtained for the trimeric and dimeric nature of $[Me_2GaNH_2]_3$ [20] and $[Me_2GaNMe_2]_2$ [17] respectively, and so it was hoped that mass spectrometry would provide information on the degree of oligomerisation of the species formed in the pyrolysis of **I**. However, the spectrum of the vapour above the residue consisted of peaks arising only from Np_2Ga^+ and related fragments. Thus, it would appear that the $[Ga-N]_n$ unit in the product is more weakly bonded than those in $[Me_2GaNH_2]_3$ and $[Me_2GaNMe_2]_2$.

When a sample of **I**, under 500 Torr of Ar, was held at 140°C until evolution of gas had ceased an IR spectroscopic study showed that the gaseous products were neopentane and ammonia, and this was confirmed by mass spectrometry. The IR spectrum of a mull of the solid residue showed the presence of very strong features in the C–H stretching region and the absence of any features arising from a unit containing N–H bonds. The IR spectrum implied that the product contained Np groups. An elemental analysis of the residue gave the following results (uncertainty ±2.0%): C, 56.1; H, 10.7; N 1.9%.

When the above experiment was repeated but with $Np_3Ga \cdot ND_3$ in place of $Np_3Ga \cdot NH_3$ it was found that the initial gaseous product was NpD (as evidenced by $\nu(C-D)$ and $\delta(CH_2D)$ modes at 2181 and 1296 cm^{-1}, respectively) while at a later stage a very large amount of ND_2H together with a much smaller quantity of ND_3 was obtained [21]. These results suggest that at 140°C the decomposition pathway involves formation of neopentane from an Np group from the Ga atom and an H atom from the N atom, with subsequent loss of NH_3.

3.2.3. *$Np_3Ga \cdot NMe_2H$ (II)*

Thermolysis of **II** in the temperature range 140–160°C yielded NpH and NMe_2H as gaseous products, leaving an off-white solid together with a trace of an orange viscous liquid. The solid had identical elemental analysis and IR spectrum to that formed on prolonged thermolysis of **I**.

3.2.4. $Np_3Ga \cdot N^tBuH_2$ (III)

Thermolysis experiments demonstrated that this adduct decomposed at a lower temperature (100°C) than **I** and **II**. The IR spectrum of the gaseous product showed that it was $^tBuNH_2$. No neopentane, which was the initial product in the thermolysis reactions of I and **II**, was evolved. Thus, it would appear that the adduct dissociates at the Ga–N bond to liberate the free constituents.

4. Discussion

Np_3Ga readily forms adducts with a number of amines, although the coordinate Ga–N bond is shown (by mass spectral studies) to be quite weak. Whilst Np_3Ga can form an adduct with the bulky amine $^tBuNH_2$, this adduct dissociates to yield the free amine at *ca.* 100°C.

An insight into the mechanism of the thermal decomposition of Np_3Ga is given by consideration of thermolysis products. Traces of ethane and methane were formed, so a radical process must take place as a secondary pathway. The major products, however, were neopentane and isobutene. Whilst the formation of isobutene could be explained by the rearrangement of a t-butyl radical, whose formation from a Np group could be expected, it is unlikely that such a radical was produced, since if it were it would necessarily undergo reaction (1) to give isobutene and isobutane, and no isobutane was detected.

$$2Me_3C \rightarrow CH_2{=}CMe_2 + Me_3CH \qquad (1)$$

A rearrangement of the Np group also appears unlikely, since one of the products would be isopentene (reaction 2) which was also not observed

$$Me_3CCH_2 \rightarrow Me_2CCH_2Me \rightarrow Me_2C{=}CHMe \qquad (2)$$

Therefore, the most probable mechanism of decomposition of Np_3Ga is via a 1,5-shift of an H atom from a Me group of a $-CMe_3$ unit to the CH_2 unit of a second Np group. This would result in the formation of neopentane, isobutene, and $NpGaCH_2$, which was observed as a very intense peak in the mass spectrum of Np_3Ga. Once formed, the $NpGaCH_2$ would be expected to polymerise.

Having discussed the thermal decompositions of Np_3Ga we now consider the thermolyses of **I** and **II**, which occur at lower temperatures than that of the parent alkyl. However, as with the alkyl Np_3Ga the initial volatile decomposition product of **I** and **II** is neopentane. It appears that the initial reaction in the thermal decomposition of both **I** and **II** is the abstraction of a hydrogen from a N–H bond with formation of oligomeric products of the type $[Np_2GaNR_2]_n$ [for **I** R = H, for **II** R = Me]. Similar decomposition reactions are observed with the adducts formed by Me_3Ga and amines containing acidic hydrogen atoms [10,11,17,20]. When **I** and **II** were heated at higher temperatures than those required to initiate the initial reaction, the volatile products were neopentane and species containing nitrogen. Thus the oligomers $[Np_2GaNR_2]_n$ [R = H or Me] decompose by a different route from that taken by the trimer $[Me_2GaNH_2]_3$ [10], which on thermolysis gave methane and a polymeric material containing gallium and nitrogen. The fact that this route was not followed shows that although the oligomeric species $[Np_2GaNR_2]_n$[R = H or Me] can exist at temperatures below 140°C, the Ga–N bonds in the compounds are weak and are readily broken at elevated temperatures. This behaviour appears to be characteristic of compounds with bulky groups attached to Ga. In this context it is noteworthy that Beachley *et al.* [22], who characterised the dimer $[Np_2GaPPh_2]_2$ prepared it by the reaction of Np_2GaCl with $KPPh_2$ at a low temperature, rather than by alkane elimination from the corresponding adduct. It is also of interest to note that this dimer has a butterfly ring, perhaps as a result of the steric requirements of the bulky groups on both the Ga and P atoms. Conversely, $[Np_2InPPh_2]_3$ exists as a trimer [21], although this structure may be feasible because of the larger size of the In atom than of the Ga atom. The analysis of the residues from the thermolysis of $[Np_2GaNR_2]_n$ are consistent with the formation of a polymeric material of empirical formula $GaC_{10}H_{21}$ (Calculated: C 56.9 H 10.0. Observed: C 56.1, H 10.7%). This finding is consistent with a reaction such as (3) [R = H]:

$$[Np_2GaNH_2]_n \rightarrow NH_3 + [CHCMe_3GaNp]_m (n, m > 2) \qquad (3)$$

The explanation is supported by the results of deuteration experiments confirming that ND_2H was lost from $[Np_2GaND_2]_n$.

From the evidence presented here it may be concluded that $Np_3Ga \cdot NH_3$ and other similar amine adducts are not suitable precursors for gallium nitride production because of the ease with which the Ga–N bond is broken.

Acknowledgments

We thank SERC for provision of the mass spectrometer and University of Reading for awarding the Wilkie Calvert Research Studentship to CEJ.

References and notes

1 H. M. Manasevit and W. I. Simpson, *J. Electrochem. Soc.*, *116* (1969) 1225.
2 M. Hashimoto, H. Amano, N. Sawaki and I. Akasaki, *J. Cryst. Growth*, *68* (1984) 163.
3 T. F. Kuch and R. Potemski, *Appl. Phys. Lett.*, *47* (1985) 821.
4 K. W. Egger, *J. Chem. Soc. A*, (1971) 3603.
5 J. P. Oliver and L. G. Stevens, *J. Inorg. Nucl. Chem.*, *24* (1962) 953.
6 J. F. Malone and W. S. McDonald, *J. Chem. Soc. A*, (1970) 3362.
7 O. T. Beachley, Jr. and J. C. Pazik, *Organometallics*, *7* (1988) 1516.
8 O. T. Beachley, Jr., M. J. Noble, M. R. Churchill and C. H. Lake, *Organometallics* *11* (1992) 1051.
9 J. C. Chen, W. K. Chen, P. L. Liu, J. D. Maloney and O. T. Beachley, Jr., *Proc. SPIE-Int. Soc. Opt. Eng.*, *877* (1988) 21.
10 C. E. Jenkins, *PhD thesis*, University of Reading, 1991.
11 M. J. Almond, K. Hagen, C. E. Jenkins and D. A. Rice, *J. Organomet. Chem.*, in the press.
12 This proposed mechanism is also analogous to that for the decomposition of $Me_3Ga \cdot AsH_3$ to give GaAs; see: D. J. Schlyer and M. A. Ring, *J. Organomet. Chem.*, *114* (1976) 9.
13 F. Glockling and R. G. Strafford, *J. Chem. Soc. A*, (1971) 1761.
14 J. R. Durig and K. K. Chaterjee, *J. Raman Spectrosc.*, *11* (1981) 168.
15 A. P. Kurbakova, L. A. Leites, V. T. Alexsanyon, L. M. Golubinskaya, E. N. Zerina and V. I. Bregadze, *J. Struct. Chem. (Engl.)*, *15* (1974) 961.
16 J. R. Durig, C. B. Bradley and J. D. Odom, *Inorg. Chem.*, *21* (1982) 1466.
17 M. J. Almond, K. Hagen, C. E. Jenkins and D. A. Rice, unpublished results.
18 M. A. Banks, O. T. Beachley, Jr., J. D. Maloney and R. D. Rogers, *Polyhedron*, *9* (1990) 335.
19 W. A. Graham, A. R. Gratti and D. A. Little, *Cambridge Mass., Final Report, Contract AF19(604)-4975, Dec. 31*, 1960.
20 M. J. Almond, M. G. B. Drew, C. E. Jenkins and D. A. Rice, *J. Chem. Soc., Dalton Trans.*, (1992) 5, and references cited therein.
21 L. Abouaf-Marguin, M. E. Jacox and D. E. Milligan, *J. Mol. Spectrosc.*, *67* (1977) 1.
22 M. A. Banks, O. T. Beachley, Jr., L. A. Buttrey, M. R. Churchill and J. C. Fettinger, *Organometallics*, *10* (1991) 1901.