

# Matrix isolation of HGaX<sub>2</sub> (X = Cl or Br): IR spectroscopy and *ab initio* calculations

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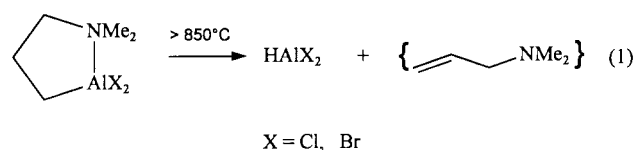
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Received 28th June 1999, Accepted 8th October 1999

High-vacuum thermolyses of the intramolecularly co-ordinated gallanes Me<sub>2</sub>N(CH<sub>2</sub>)<sub>3</sub>GaX<sub>2</sub> with X = Cl **1** or Br **2** were investigated with matrix isolation techniques. Among the products, which have been identified with IR spectroscopy, *ab initio* calculations, and known literature data, are monomeric HGaCl<sub>2</sub> and HGaBr<sub>2</sub>. The experimental vibrational frequencies of these hydrides are compared with calculated harmonic frequencies at the MP2(fc)/6-311+G(2d,p) and B3LYP/6-311+G(2d,p) level of theory. Beside monomeric HGaX<sub>2</sub>, the argon matrices of the thermolyses experiments contained CH<sub>4</sub>, HCN, H<sub>2</sub>C=CH<sub>2</sub>, H<sub>2</sub>C=NMe, [H<sub>2</sub>CCHCH<sub>2</sub>]<sup>+</sup>, H<sub>2</sub>C=CHCH<sub>3</sub>, HX, and GaX (X = Cl or Br). In the case of GaBr the difference between the known gas-phase value and the measured IR frequency in argon matrices is discussed and explained with the help of SCRF-B3LYP calculations.

## Introduction

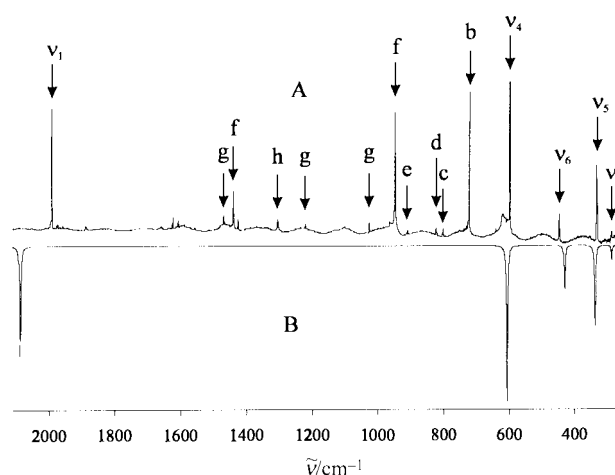
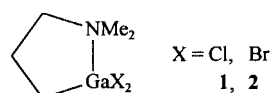
Recently, we reported on the high-vacuum thermolyses of alanes, which were intramolecularly co-ordinated with the dimethylaminopropyl ligand, eqn. (1).<sup>1</sup> The first aim of this



investigation was to get an insight into the fragmentation pattern of compounds of the type Me<sub>2</sub>N(CH<sub>2</sub>)<sub>3</sub>MX<sub>2</sub>, because they had been used as single-source precursors for metal organic chemical vapor deposition (MOCVD).<sup>2</sup> In particular, GaN, which is a promising material for new micro- and opto-electronic devices, can be deposited from the diazidogallane Me<sub>2</sub>N(CH<sub>2</sub>)<sub>3</sub>Ga(N<sub>3</sub>)<sub>2</sub>.<sup>3</sup>

We investigated the thermolysis reactions (1) by the application of matrix isolation techniques, *i.e.*, volatile products which emerged from the Al<sub>2</sub>O<sub>3</sub> pyrolysis tube were trapped in argon matrices at 15 K and identified by IR spectroscopy with the help of *ab initio* calculations. Within this investigation we identified the two monomeric hydrides HAlX<sub>2</sub> (X = Cl or Br); the chloride was already known by an early investigation of Schnöckel,<sup>4</sup> whereas the bromide was described for the first time.<sup>1</sup> Quite probably, these hydrides were formed by β-hydrogen eliminations (1), but the second product, allyl-dimethylamine, was not detected in matrices. Instead, we identified the carbon-containing molecules CH<sub>4</sub>, HCN, H<sub>2</sub>C=CH<sub>2</sub>, H<sub>2</sub>C=NMe, [H<sub>2</sub>CCH<sub>2</sub>CH<sub>2</sub>]<sup>+</sup>, and H<sub>2</sub>C=CHCH<sub>3</sub>. Furthermore, the aluminium halogens AlX, AlX<sub>2</sub>, and AlX<sub>3</sub> were found among the thermolysis products, presumably as the result of secondary reactions of HAlX<sub>2</sub>.

Besides being interested in the fragmentation of single-source precursors, we began to explore the scope of synthesizing monomeric hydrides by thermal β-hydrogen eliminations. In this publication we report on thermolysis experiments with the chloro- and bromo-gallane, **1** and **2**, respectively.



**Fig. 1** Experimental and calculated IR spectra: A, products of thermolysis of compound **2** at *ca.* 1000 °C trapped in argon at 15 K for assignments  $\nu_1$ – $\nu_6$  see Table 1; for wavenumbers of compounds a–h see Table 3: [HGaBr<sub>2</sub> ( $\nu_1$ – $\nu_6$ ), GaBr (a), HCN (b), [H<sub>2</sub>CCHCH<sub>2</sub>]<sup>+</sup> (c), Ga<sub>2</sub>O (d), H<sub>2</sub>C=CHCH<sub>3</sub> (e), H<sub>2</sub>C=CH<sub>2</sub> (f), H<sub>2</sub>C=NMe (g), CH<sub>4</sub> (h)]; B, HGaBr<sub>2</sub>, calculated at the MP2(fc)/6-311+G(2d,p) level (half band width of 2 cm<sup>-1</sup>).

## Results and discussion

The two starting gallanes **1** and **2** are volatile and moisture sensitive compounds which can be purified by sublimation in high vacuum. In accordance with the known method to prepare the chloro compound **1**,<sup>2a</sup> we synthesized analytically pure bromogallane **2** in high yields starting from Li[(CH<sub>2</sub>)<sub>3</sub>NMe<sub>2</sub>] and GaBr<sub>3</sub>.

A series of high-vacuum thermolyses of the precursors **1** and **2**, respectively, were carried out. Between ambient temperature and oven temperatures of *ca.* 700 °C the IR spectra of matrix isolated precursors were unchanged. Around 800 °C new IR bands appeared, indicating the beginning of fragmentation. At 1000 °C the typical IR absorptions of compound **2** could no longer be detected in argon matrices, however small amounts of **1** were still detectable after thermolysis. Fig. 1 shows a typical IR spectrum recorded after a thermolysis of the bromide **2** at 1000 °C. At first glance, the intense IR band at 1991.5 cm<sup>-1</sup> hints to a species with a Ga–H bond (spectrum A); this intense band lies in the well known region for gallium–

**Table 1** Experimental IR frequencies and calculated harmonic frequencies of HGaCl<sub>2</sub> and HGaBr<sub>2</sub>

			MP2/6-311+G(2d,p)				B3LYP/6-311+G(2d,p)		
			Experimental frequency <sup>a</sup> / cm <sup>-1</sup>	frequency <sup>a</sup> / cm <sup>-1</sup>	intensity/ km mol <sup>-1</sup>	obs.: calc. ratio	frequency <sup>a</sup> / cm <sup>-1</sup>	intensity/ km mol <sup>-1</sup>	obs.: calc. ratio
HGaCl <sub>2</sub> <sup>b</sup>									
A <sub>1</sub>	ν <sub>1</sub>	ν(GaH)	2015.0	2101.5	96.1	0.9588	2071.9	76.5	0.9725
	ν <sub>2</sub>	ν <sub>sym</sub> (GaCl <sub>2</sub> )	414.0	420.8	28.7	0.9838	400.5	23.8	1.0337
	ν <sub>3</sub>	δ(GaCl <sub>2</sub> )		133.7	8.9		132.3	7.5	
B <sub>1</sub>	ν <sub>4</sub>	δ(ClGaH)	607.5	605.2	122.4	1.0038	570.3	75.2	1.0652
	ν <sub>5</sub>	ν <sub>asym</sub> (GaCl <sub>2</sub> )	437.5	454.3	141.0	0.9630	428.9	132.5	1.0201
B <sub>2</sub>	ν <sub>6</sub>	γ(H)	464.0	443.2	60.1	1.0470	401.5	36.3	1.1557
HGaBr <sub>2</sub>									
A <sub>1</sub>	ν <sub>1</sub>	ν(GaH)	1991.5	2087.3	110.3	0.9541	2050.9	90.3	0.9710
	ν <sub>2</sub>	ν <sub>sym</sub> (GaBr <sub>2</sub> )	287.5	286.8	14.8	1.0024	272.5	12.8	1.0550
	ν <sub>3</sub>	δ(GaBr <sub>2</sub> )		94.0	2.8		92.2	2.2	
B <sub>1</sub>	ν <sub>4</sub>	δ(BrGaH)	597.0	605.7	158.3	0.9856	566.6	121.6	1.0537
	ν <sub>5</sub>	ν <sub>asym</sub> (GaBr <sub>2</sub> ) <sup>c</sup>	333.0	337.6	83.0	0.9864	322.3	79.8	1.0332
B <sub>2</sub>	ν <sub>6</sub>	γ(H)	445.5	430.0	43.6	1.0360	380.0	25.4	1.1724

<sup>a</sup> Listed are the wavenumbers concerning the main isotopomers. <sup>b</sup> Known frequencies of HGaCl<sub>2</sub> from ref. 6 are: 2015.3, 414.3, 437.3, 607.5, and 464.3 cm<sup>-1</sup>. Calculated frequencies of HGaCl<sub>2</sub> at the B3LYP/6-31G(d,p) level, see ref. 20. <sup>c</sup> The ν<sub>asym</sub>(GaBr<sub>2</sub>) results in two IR bands: the one at 333.0 cm<sup>-1</sup> is caused by H<sup>69</sup>Ga<sup>79</sup>Br<sup>79</sup>Br, H<sup>69</sup>Ga<sup>79</sup>Br<sup>81</sup>Br, and H<sup>69</sup>Ga<sup>81</sup>Br<sup>81</sup>Br; that at 330.0 cm<sup>-1</sup> is caused by H<sup>71</sup>Ga<sup>79</sup>Br<sup>79</sup>Br, H<sup>71</sup>Ga<sup>79</sup>Br<sup>81</sup>Br, and H<sup>71</sup>Ga<sup>81</sup>Br<sup>81</sup>Br.

**Table 2** Calculated bond lengths (Å) and angles (°) of HGaCl<sub>2</sub> and HGaBr<sub>2</sub><sup>a</sup>

	X = Cl	X = Br
Ga–H	1.550 (1.542)	1.553 (1.546)
Ga–X	2.156 (2.147)	2.300 (2.299)
X–Ga–X	115.15 (115.40)	116.20 (116.85)

<sup>a</sup> MP2(fc)/6-311+G(2d,p) and B3LYP/6-311+G(2d,p); results of the B3LYP calculations in parentheses.

hydrogen stretching vibrations of terminal GaH groups.<sup>5</sup> Beside the experimental spectrum A, Fig. 1 shows a theoretical IR spectrum of monomeric HGaBr<sub>2</sub> (C<sub>2v</sub> symmetry), calculated at the MP2(fc)/6-311+G(2d,p) level of theory. There is a good match between the calculated and the measured IR spectra depicted which applies to frequencies and intensities of the IR bands and shows that monomeric HGaBr<sub>2</sub> was formed by the thermolysis. The experiments with the chloride **1** gave similar results; *i.e.* monomeric HGaCl<sub>2</sub> was formed and unequivocally identified by comparison with literature data and *ab initio* calculations. This gallium hydride was synthesized for the first time by Schnöckel and co-workers<sup>6</sup> photochemically from GaCl with HCl in argon matrices. Within the experimental error, our measured frequencies of HGaCl<sub>2</sub> match with the published ones. Table 1 shows the experimental and calculated IR data of HGaCl<sub>2</sub> and HGaBr<sub>2</sub>; for the prediction of the harmonic frequencies we chose the MP2 and B3LYP method with the 6-311+G(2d,p) basis set.

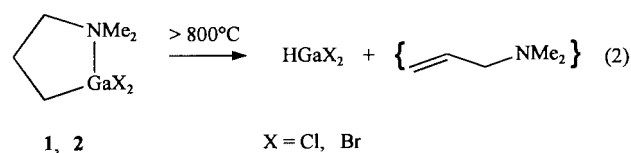
As in the case of the corresponding alanes, HAlCl<sub>2</sub> and HAlBr<sub>2</sub>, the *ab initio* calculations predict C<sub>2v</sub>-symmetrical equilibrium geometries (Table 2), therefore one expects six normal modes for the two gallium hydrides belonging to the irreducible representations A<sub>1</sub> (3), B<sub>1</sub> (2), and B<sub>2</sub> (1). Only five of the six modes could be observed; the frequencies of the XGaX-deformation vibration ν<sub>3</sub> are out of the detectable range of 240–4000 cm<sup>-1</sup>.

We found an acceptable fit of the MP2 data and the measured frequencies, which can be shown by the observed:calculated ratios of 0.959–1.047 and 0.954–1.036 for HGaCl<sub>2</sub> and HGaBr<sub>2</sub>, respectively (Table 1). The B3LYP values do not match with the experimental frequencies as well as the MP2

**Table 3** Detected species from the thermolysis of compound **2** at 1000 °C (see Fig. 1)

Wavenumbers/cm <sup>-1</sup>	Assignment
2900.5, 2855.0, 1469.5, 1221.0, 1026.5	H <sub>2</sub> C=NMe <sup>8</sup>
1440.5, 947.5	H <sub>2</sub> C=CH <sub>2</sub> <sup>9,10</sup>
1305.0	CH <sub>4</sub> <sup>9</sup>
801.0	[H <sub>2</sub> CCH <sub>2</sub> CH <sub>2</sub> ] <sup>11</sup>
909.5	H <sub>2</sub> C=CHCH <sub>3</sub> <sup>12</sup>
3305.5, 721.0	HCN <sup>13</sup>
2568.5, 2453.5, 2431.0	(HBr) <sub>x</sub> <sup>14</sup>
822.5	Ga <sub>2</sub> O <sup>15</sup>
251.5, 250.0, 248.5	GaBr

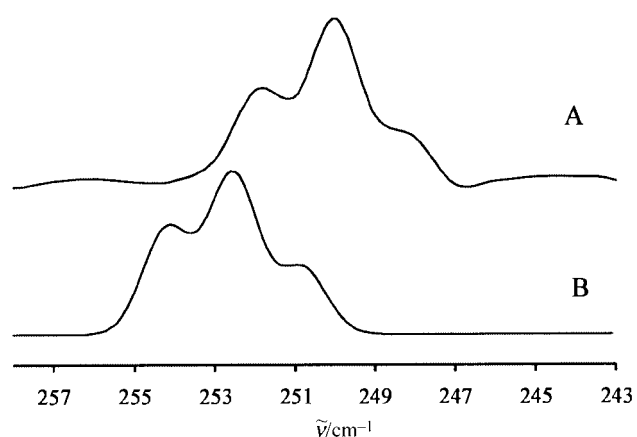
data. The observed:calculated ratios vary in the range of 0.973–1.156 (HGaCl<sub>2</sub>) and 0.971–1.172 (HGaBr<sub>2</sub>). The most problematic mode is the out-of-plane deformation mode ν<sub>6</sub> which gave observed:calculated ratios of 1.156 for HGaCl<sub>2</sub> and 1.172 for HGaBr<sub>2</sub>. The respective values of the two aluminum compounds HAlCl<sub>2</sub> and HAlBr<sub>2</sub> are 1.051 and 1.056.<sup>1</sup> Even though it is known that the B3LYP method underestimates low frequencies,<sup>7</sup> ratios of 1.156 and 1.172 are unusually high. Keeping in mind that the respective values of 1.047 and 1.036 from the MP2 calculations are quite normal (Table 1), we assume that the unusual ratios mainly result from an inadequate description of the heavy dihalogenogallanes at the B3LYP/6-311+G(2d,p) level of theory.



The first step of the thermolysis is probably a β-hydrogen elimination, eqn. (2). Since the applied temperatures are quite high, allyldimethylamine is not stable and fragments to several carbon-containing molecules. We identified the well known species CH<sub>4</sub>, HCN, H<sub>2</sub>C=CH<sub>2</sub>, H<sub>2</sub>C=NMe, [H<sub>2</sub>CCH<sub>2</sub>CH<sub>2</sub>]<sup>9</sup>, and H<sub>2</sub>C=CHCH<sub>3</sub> by comparison with literature data (Table 3). The relative amounts of these compounds are dependent on the applied thermolysis conditions, but the intensity ratios of IR

**Table 4** Calculated frequencies of the four isotopomers of GaBr

Species	Abundance (%)	MP2(fc)/6-311+G(3df)		B3LYP/6-311+G(3df)	
		frequency/ cm <sup>-1</sup>	intensity/ km mol <sup>-1</sup>	frequency/ cm <sup>-1</sup>	intensity/ km mol <sup>-1</sup>
<sup>69</sup> Ga <sup>79</sup> Br	30.5	269.4	65.6	254.2	55.9
<sup>69</sup> Ga <sup>81</sup> Br	29.9	267.9	64.9	252.7	55.3
<sup>71</sup> Ga <sup>79</sup> Br	20.0	267.4	64.7	252.3	55.1
<sup>71</sup> Ga <sup>81</sup> Br	19.6	265.8	63.9	250.8	54.4

**Fig. 2** Experimental and calculated isotopic pattern of GaBr: A, expanded region from Fig. 1; B, calculated isotopic pattern (B3LYP/6-311+G(3df), see Table 4).

bands for a given species are always preserved. The same carbon-containing molecules were found in the thermolyses experiments on the aluminium compounds mentioned before, eqn. (1).<sup>1</sup> Furthermore, we found HBr and monomeric GaBr in the argon matrices among the thermolysis products of **2** (Table 3); one feasible reaction path to these two species is the fragmentation of HGaBr<sub>2</sub>. Similar results were obtained starting with the dichlorogallane **1**. [GaCl was identified by its IR band at 342.0 cm<sup>-1</sup> (see ref. 16); we tentatively assigned the IR band at 2786.0 cm<sup>-1</sup> to HCl (see ref. 14(b)).]

It must be pointed out that the thermolyses of compounds **1** and **2** seems to be quite complex. For example, the fragmentation of the intramolecularly co-ordinated alanes, eqn. (1), yielded beside the hydrides HAlX<sub>2</sub> the three aluminium halogens AlX, AlX<sub>2</sub>, and AlX<sub>3</sub>, with the latter resulting in an intense IR band.<sup>1</sup> In the case of gallium we could only identify GaX; in particular, there were no IR absorptions of the well known GaX<sub>3</sub>.<sup>17</sup> One might suppose that if GaX<sub>3</sub> was formed in the gas phase it fragmented, quite probably to a large extent, to GaX and X<sub>2</sub>, a reaction which was used to synthesize GaX for gas-phase spectroscopy.<sup>18</sup> Hence, we attribute the main differences between the results of the thermolyses of intramolecularly co-ordinated alanes and gallanes to the higher stability of the oxidation state +I for gallium.

A comment is needed on the GaX species. While the matrix IR spectrum of GaCl is well known,<sup>16</sup> the respective data for GaBr are to our knowledge not published. We unequivocally identified GaBr in argon matrices by its split IR band at 251.5/250.0/248.5 cm<sup>-1</sup>. This splitting is due to the presence of four isotopomers. Table 4 shows calculated harmonic frequencies of GaBr, and Fig. 2 illustrates the fit between the predicted and the measured isotopic pattern. The measured frequency of 250.0 cm<sup>-1</sup> (<sup>69</sup>Ga<sup>81</sup>Br) is shifted by 4.9% to lower frequencies in comparison with the gas-phase value of 263.0 cm<sup>-1</sup>,<sup>19</sup> a similar trend is known for <sup>69</sup>Ga<sup>35</sup>Cl, 342.9 cm<sup>-1</sup> in argon matrices and 365.3 cm<sup>-1</sup> in the gas phase.<sup>20</sup> These are unusually large differences between gas-phase IR data and a respective value in a rare gas matrix. Recently, this was pointed out in a reinvestigation of the reaction of GaCl with

HCl using the B3LYP method with self consistent reaction field (SCRFF)<sup>21</sup> calculations based on the Onsager<sup>22</sup> model.<sup>20</sup> The authors calculated that the GaCl stretching frequency decreases by 6.5% on solvation. [The frequencies for GaCl are 352.2 (B3LYP/6-31G(d) level) and 329.2 cm<sup>-1</sup> (SCRFF-B3LYP/6-31G(d) level; polar sphere with ε = 2; see ref. 20).] We conducted SCRFF calculations for GaBr at the B3LYP/6-311+G(3df) level with a polar sphere with a relative permittivity equal to that of solid argon (ε = 1.5).<sup>23</sup> The SCRFF method predicts 246.2 cm<sup>-1</sup> for the GaBr stretch which is 3.1% lower than the frequency of the undisturbed molecule (<sup>69</sup>Ga<sup>79</sup>Br: 254.2 cm<sup>-1</sup>, Table 4). This shows that the GaBr frequency is even sensitive to a slightly polar environment. The calculated decrease of 3.1% should not be overestimated; it is dependent on the size of the selected cavity and, of course, on the relative permittivity, whose exact value is unknown (see Experimental section). Moreover, the calculation is based on a simple theoretical model, which can not predict the reality precisely.

After a series of thermolyses experiments the pyrolyses oven had to be cleaned. Therefore, we tempered the Al<sub>2</sub>O<sub>3</sub> tube at ca. 1000 °C in high vacuum, purged it with argon, and trapped all gases onto the CsI window at 15 K. The most intense signal in these matrix IR spectra appeared at 822.5 cm<sup>-1</sup>. Through comparison with literature data we assigned this band to ν<sub>asym</sub> (GaO) of Ga<sub>2</sub>O.<sup>15</sup> During a thermolysis experiment a part of the gallium compounds must be deposited inside the thermolysis tube. When this pyrolysis oven is exposed to air all substituents bound to gallium are probably hydrolysed leaving a gallium oxide/hydroxide layer behind, which is subsequently evaporated as Ga<sub>2</sub>O during the cleaning procedure described above. The IR band at 822.5 cm<sup>-1</sup>, which was sometimes present in matrix IR spectra of thermolysis experiments, can be suppressed by a thorough preceding cleaning procedure.

## Conclusion

Recently, we reported on the syntheses of monomeric hydrides of aluminium starting from intramolecularly co-ordinated alanes. Within this paper we have shown that this method can be transferred to gallium chemistry, *i.e.* the monomeric hydrides HGaCl<sub>2</sub> and HGaBr<sub>2</sub> were obtained thermolytically from the 3-dimethylaminopropylgallanes **1** and **2**. So far, only three monomeric gallanes of the type H<sub>a</sub>GaX<sub>3-a</sub> have been characterized, namely GaH<sub>3</sub>,<sup>24</sup> HGaCl<sub>2</sub>,<sup>6</sup> and H<sub>2</sub>GaCl;<sup>25</sup> with HGaBr<sub>2</sub> we characterized a new compound of this class. Surprisingly, the gallium hydrides HGaCl<sub>2</sub> and HGaBr<sub>2</sub> withstand the rather harsh thermolyses conditions.

This report is not the first one concerning β-hydrogen eliminations to synthesize gallium hydrides; *e.g.*, Russel<sup>26</sup> investigated intensively the fragmentation of trialkylgallanes with the infrared laser powered homogeneous pyrolysis (IR LPHP) technique. With this method GaEt<sub>3</sub> was thermolysed to give either (HGaEt<sub>2</sub>)<sub>x</sub> or (H<sub>2</sub>GaEt)<sub>x</sub> and ethane. The pure hydrides as well as their NMe<sub>3</sub> adducts were identified by FTIR and NMR spectroscopy. The gallanes are oligomeric, however monomeric species have not been detected.

Currently, we are exploring the scope of using β-hydrogen

eliminations to synthesize new monomeric hydrides of Group 13 elements.

## Experimental

### General remarks

All procedures for syntheses were carried out under dry nitrogen atmospheres with standard Schlenk techniques. Solvents were dried by standard procedures, distilled, and stored under nitrogen and molecular sieves (4 Å). The reagents  $\text{Me}_2\text{N}(\text{CH}_2)_3\text{GaCl}_2$  **1**<sup>2a</sup> and  $\text{Li}(\text{CH}_2)_3\text{NMe}_2$ <sup>27</sup> were prepared according to the literature procedures. NMR: Varian Unity 500 (ambient temperature; 499.843 MHz for <sup>1</sup>H and 125.639 MHz for <sup>13</sup>C), calibrated against residual protons of the deuteriated solvents; <sup>1</sup>H and <sup>13</sup>C chemical shifts are reported relative to TMS. Elemental analysis (C, H, N): Carlo-Erba elemental analyzer, Model 1106. MS: Finnigan MAT 95.

### Dibromo[3-(dimethylamino)propyl]gallium 2

The compound  $\text{Li}(\text{CH}_2)_3\text{NMe}_2$  (0.70 g, 7.52 mmol) was added to a freshly prepared solution of 2.20 g (7.11 mmol) of  $\text{GaBr}_3$  in 30 ml of diethyl ether at  $-78^\circ\text{C}$ . The mixture was allowed to warm to room temperature and stirred overnight. After removal of the solvent in high vacuum, sublimation ( $80\text{--}96^\circ\text{C}$ ,  $10^{-3}$  mbar) gave 1.85 g (82%) of **2** as a colorless solid, mp  $88\text{--}90^\circ\text{C}$ . <sup>1</sup>H NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  0.71 (t,  $^3J = 7.6$  Hz, 2 H,  $\text{GaCH}_2$ ), 1.06 (m, 2 H,  $\text{GaCH}_2\text{CH}_2$ ), 1.51 (t,  $^3J = 6.1$  Hz, 2 H,  $\text{NCH}_2$ ) and 1.75 (s, 6 H,  $\text{CH}_3$ ). <sup>13</sup>C-<sup>1</sup>H NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  12.72 ( $\text{GaCH}_2$ ), 21.45 ( $\text{GaCH}_2\text{CH}_2$ ), 45.99 ( $\text{CH}_3$ ) and 61.11 ( $\text{NCH}_2$ ). MS (70 eV): *m/z* (%) 315 (5) [ $\text{M}^+$ ], 287 (5) [ $\text{M}^+ - \text{C}_2\text{H}_4$ ], 236 (16) [ $\text{M}^+ - \text{Br}$ ] and 58 (100) ( $\text{C}_3\text{H}_8\text{N}$ ). Calc. for  $\text{C}_5\text{H}_{12}\text{Br}_2\text{GaN}$  (315.68): C, 19.02; H, 3.83; N, 4.44. Found: C, 18.70; H, 4.09; N, 4.39%.

### Matrix isolation

The matrix apparatus consisted of a vacuum line (Leybold Turbovac 151; Leybold Trivac D4B) and a Displex CSW 202 cryogenic closed-cycle system (APD Cryogenics Inc.) fitted with CsI windows. In a typical experiment the starting compound was kept in a small metal container in high vacuum at constant temperature ( $10^{-6}$  to  $10^{-7}$  mbar; compound **1**,  $55\text{--}65^\circ\text{C}$ ; **2**,  $80\text{--}90^\circ\text{C}$ ), while a flow of argon was conducted over the sample (Linde 6.0; flow =  $1.0$  ml  $\text{min}^{-1}$  ( $0^\circ\text{C}$ , 1.013 bar); MKS mass flow controller type 1179). Subsequently, this gaseous mixture was passed through an  $\text{Al}_2\text{O}_3$  tube (inner diameter of 1 mm; heated by tungsten wire coiled around the last 10 mm). The hot end of the pyrolysis tube was just 25 mm away from the cooled CsI window to assure that the maximum amount of volatile fragments emerging from the oven was trapped in the matrix. For the temperature determination of the pyrolysis oven a current-to-temperature relation was measured with a thermocouple (Thermocoax: NiCr/NiAl) inside the  $\text{Al}_2\text{O}_3$  tube. For the experiments with compound **2** an oven fitted with an  $\text{Al}_2\text{O}_3$  tube with two parallel, inner canals was used (outer diameter 4 mm; inner diameter 1 mm each; last 10 mm heated with a tungsten wire), with one of the inner canals equipped with a thermocouple (Thermocoax: NiCrSi/NiSi) and through the other canal the argon/compound mixture was conducted. With this set-up reliable thermolysis temperatures could be measured during the experiment without contact between the substance and the thermocouple.

The concentrations of the samples in the matrices are unknown. Therefore, several experiments under various conditions were carried out to assure that the molecules were indeed matrix isolated. The concentration of the samples decreases significantly at lower sublimation temperatures ( $40^\circ\text{C}$  for **1** and  $70^\circ\text{C}$  for **2**), but no differences in the IR spectra were observed. At higher concentrations the half band widths of IR bands

increased and new broad IR bands appeared indicating that notable parts of the molecule were no longer matrix isolated under these conditions.

The IR spectra of the matrices (15 K) were recorded on a Perkin-Elmer FTIR 1720x instrument from 240 to  $4000\text{ cm}^{-1}$  with a resolution of  $1\text{ cm}^{-1}$ .

### Ab initio calculations

The GAUSSIAN 94 package,<sup>28</sup> run on a cluster of workstations (Rechenzentrum der RWTH Aachen), was applied for all *ab initio* calculations. The total energies  $E_h$  (in Hartrees) and the zero point vibrational energy (in  $\text{kJ mol}^{-1}$ ; in parentheses) are as follows:  $\text{HGaCl}_2$ ,  $-2843.298259$  (24.88) for MP2(fc)/6-311+G(2d,p),  $-2846.028291$  (23.96) for B3LYP/6-311+G(2d,p);  $\text{HGaBr}_2$ ,  $-7068.959265$  (22.98) for MP2(fc)/6-311+G(2d,p),  $-7073.862273$  (22.04) for B3LYP/6-311+G(2d,p);  $\text{GaBr}$ ,  $-4495.872086$  (1.61) for MP2(fc)/6-311+G(3df),  $-4499.089983$  (1.52) for B3LYP/6-311+G(3df).

The SCRF calculations for  $\text{GaBr}$  were conducted at the B3LYP/6-311+G(3df) level with a polar sphere of  $\epsilon = 1.5$ <sup>23</sup> and a radius of  $3.45\text{ \AA}$ . This radius was obtained by adding  $0.50\text{ \AA}$  to the radius gained from the calculated molecular volume (keyword: volume = tight). The total energy  $E_h$  (in Hartrees) and the ZPVE (in  $\text{kJ mol}^{-1}$ ; in parentheses) for  $\text{GaBr}$  with the reaction field is  $-4499.090559$  (1.47); the  $\text{GaBr}$  distance is  $2.408\text{ \AA}$ .

### Acknowledgements

We are grateful to the Deutsche Forschungsgemeinschaft and to the Fonds der Chemischen Industrie for generous financial support and to the Rechenzentrum der RWTH Aachen for providing generous computer time. Especially, we would like to thank T. Eifert and J. Risch for their support, and P. Geisler for the construction of the thermolysis oven.

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Paper 9/05183J