Matrix isolation of $HGaX_2$ (X = Cl or Br): IR spectroscopy and *ab initio* calculations

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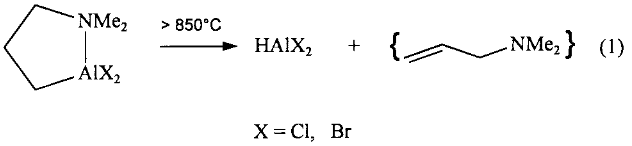
High-vacuum thermolyses of the intramolecularly co-ordinated gallanes $Me_2N(CH_2)_3GaX_2$ with X = Cl **1** or Br **2** were investigated with matrix isolation techniques. Among the products, which have been identified with IR spectroscopy, *ab initio* calculations, and known literature data, are monomeric $HGaCl_2$ and $HGaBr_2$. 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 $HGaX_2$, the argon matrices of the thermolyses experiments contained CH_4, HCN, $H_2C{=}CH_2$, $H_2C{=}NMe$, $[H_2CCHCH_2]^{\bullet}$, $H_2C{=}CHCH_3$, 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

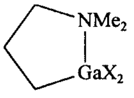
Recently, we reported on the high-vacuum thermolyses of alanes, which were intramolecularly co-ordinated with the dimethylaminopropyl ligand, eqn. (1).[1] The first aim of this



investigation was to get an insight into the fragmentation pattern of compounds of the type $Me_2N(CH_2)_3MX_2$, because they had been used as single-source precursors for metal organic chemical vapor deposition (MOCVD).[2] In particular, GaN, which is a promising material for new micro- and opto-electronic devices, can be deposited from the diazidogallane $Me_2N(CH_2)_3Ga(N_3)_2$.[3]

We investigated the thermolysis reactions (1) by the application of matrix isolation techniques, *i.e.*, volatile products which emerged from the Al_2O_3 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 $HAlX_2$ (X = Cl or Br); the chloride was already known by an early investigation of Schnöckel,[4] whereas the bromide was described for the first time.[1] Quite probably, these hydrides were formed by β-hydrogen eliminations (1), but the second product, allyldimethylamine, was not detected in matrices. Instead, we identified the carbon-containing molecules CH_4, HCN, $H_2C{=}CH_2$, $H_2C{=}NMe$, $[H_2CCH_2CH_2]^{\bullet}$, and $H_2C{=}CHCH_3$. Furthermore, the aluminium halogens AlX, AlX_2, and AlX_3 were found among the thermolysis products, presumably as the result of secondary reactions of $HAlX_2$.

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.



X = Cl, Br
1, **2**

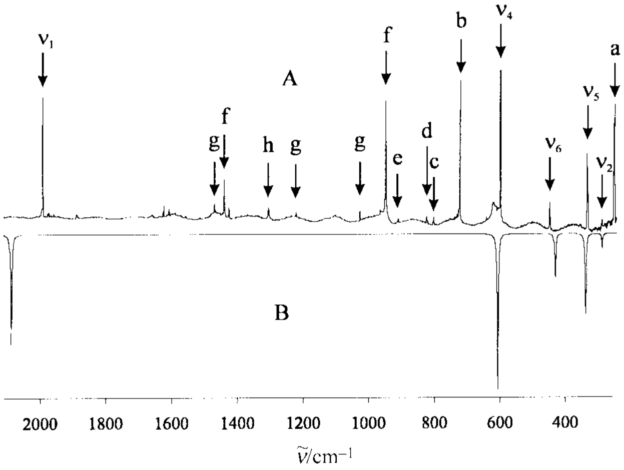


Fig. 1 Experimental and calculated IR spectra: A, products of thermolysis of compound **2** at *ca.* 1000 °C trapped in argon at 15 K for assignments ν_1–ν_6 see Table 1; for wavenumbers of compounds a–h see Table 3: $[HGaBr_2$ (ν_1–ν_6), GaBr (a), HCN (b), $[H_2CCHCH_2]^{\bullet}$ (c), Ga_2O (d), $H_2C{=}CHCH_3$ (e), $H_2C{=}CH_2$ (f), $H_2C{=}NMe$ (g), CH_4 (h)]; B, $HGaBr_2$ calculated at the MP2(fc)/6-311+G(2d,p) level (half band width of 2 cm^{-1}).

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**,[2a] we synthesized analytically pure bromogallane **2** in high yields starting from $Li[(CH_2)_3NMe_2]$ and $GaBr_3$.

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^{-1} 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 $HGaCl_2$ and $HGaBr_2$

			Experimental frequency[a]/cm^{-1}	MP2/6-311+G(2d,p)			B3LYP/6-311+G(2d,p)		
				frequency[a]/cm^{-1}	intensity/km mol^{-1}	obs. : calc. ratio	frequency[a]/cm^{-1}	intensity/km mol^{-1}	obs. : calc. ratio
		$HGaCl_2$[b]							
A_1	ν_1	ν(GaH)	2015.0	2101.5	96.1	0.9588	2071.9	76.5	0.9725
	ν_2	$\nu_{sym}(GaCl_2)$	414.0	420.8	28.7	0.9838	400.5	23.8	1.0337
	ν_3	$\delta(GaCl_2)$		133.7	8.9		132.3	7.5	
B_1	ν_4	δ(ClGaH)	607.5	605.2	122.4	1.0038	570.3	75.2	1.0652
	ν_5	$\nu_{asym}(GaCl_2)$	437.5	454.3	141.0	0.9630	428.9	132.5	1.0201
B_2	ν_6	γ(H)	464.0	443.2	60.1	1.0470	401.5	36.3	1.1557
		$HGaBr_2$							
A_1	ν_1	ν(GaH)	1991.5	2087.3	110.3	0.9541	2050.9	90.3	0.9710
	ν_2	$\nu_{sym}(GaBr_2)$	287.5	286.8	14.8	1.0024	272.5	12.8	1.0550
	ν_3	$\delta(GaBr_2)$		94.0	2.8		92.2	2.2	
B_1	ν_4	δ(BrGaH)	597.0	605.7	158.3	0.9856	566.6	121.6	1.0537
	ν_5	$\nu_{asym}(GaBr_2)$[c]	333.0	337.6	83.0	0.9864	322.3	79.8	1.0332
B_2	ν_6	γ(H)	445.5	430.0	43.6	1.0360	380.0	25.4	1.1724

[a] Listed are the wavenumbers concerning the main isotopomers. [b] Known frequencies of $HGaCl_2$ from ref. 6 are: 2015.3, 414.3, 437.3, 607.5, and 464.3 cm^{-1}. Calculated frequencies of $HGaCl_2$ at the B3LYP/6-31G(d,p) level, see ref. 20. [c] The $\nu_{asym}(GaBr_2)$ results in two IR bands: the one at 333.0 cm^{-1} is caused by $H^{69}Ga^{79}Br^{79}Br$, $H^{69}Ga^{79}Br^{81}Br$, and $H^{69}Ga^{81}Br^{81}Br$; that at 330.0 cm^{-1} is caused by $H^{71}Ga^{79}Br^{79}Br$, $H^{71}Ga^{79}Br^{81}Br$, and $H^{71}Ga^{81}Br^{81}Br$.

Table 2 Calculated bond lengths (Å) and angles (°) of $HGaCl_2$ and $HGaBr_2$[a]

	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)

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

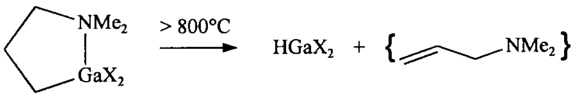
Table 3 Detected species from the thermolysis of compound **2** at 1000 °C (see Fig. 1)

Wavenumbers/cm^{-1}	Assignment
2900.5, 2855.0, 1469.5, 1221.0, 1026.5	$H_2C{=}NMe$[8]
1440.5, 947.5	$H_2C{=}CH_2$[9,10]
1305.0	CH_4[9]
801.0	$[H_2CCH_2CH_2]^{\bullet}$[11]
909.5	$H_2C{=}CHCH_3$[12]
3305.5, 721.0	HCN[13]
2568.5, 2453.5, 2431.0	$(HBr)_x$[14]
822.5	Ga_2O[15]
251.5, 250.0, 248.5	GaBr

hydrogen stretching vibrations of terminal GaH groups.[5] Beside the experimental spectrum A, Fig. 1 shows a theoretical IR spectrum of monomeric $HGaBr_2$ (C_{2v} 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 $HGaBr_2$ was formed by the thermolysis. The experiments with the chloride **1** gave similar results; *i.e.* monomeric $HGaCl_2$ 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[6] photochemically from GaCl with HCl in argon matrices. Within the experimental error, our measured frequencies of $HGaCl_2$ match with the published ones. Table 1 shows the experimental and calculated IR data of $HGaCl_2$ and $HGaBr_2$; 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, $HAlCl_2$ and $HAlBr_2$, the *ab initio* calculations predict C_{2v}-symmetrical equilibrium geometries (Table 2), therefore one expects six normal modes for the two gallium hydrides belonging to the irreducible representations A_1 (3), B_1 (2), and B_2 (1). Only five of the six modes could be observed; the frequencies of the XGaX-deformation vibration ν_3 are out of the detectable range of 240–4000 cm^{-1}.

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 $HGaCl_2$ and $HGaBr_2$, respectively (Table 1). The B3LYP values do not match with the experimental frequencies as well as the MP2 data. The observed : calculated ratios vary in the range of 0.973–1.156 ($HGaCl_2$) and 0.971–1.172 ($HGaBr_2$). The most problematic mode is the out-of-plane deformation mode ν_6 which gave observed : calculated ratios of 1.156 for $HGaCl_2$ and 1.172 for $HGaBr_2$. The respective values of the two aluminum compounds $HAlCl_2$ and $HAlBr_2$ are 1.051 and 1.056.[1] Even though it is known that the B3LYP method underestimates low frequencies,[7] 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.



(2)

1, 2 X = Cl, Br

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_4, HCN, $H_2C{=}CH_2$, $H_2C{=}NMe$, $[H_2CCH_2CH_2]^{\bullet}$, and $H_2C{=}CHCH_3$ 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

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

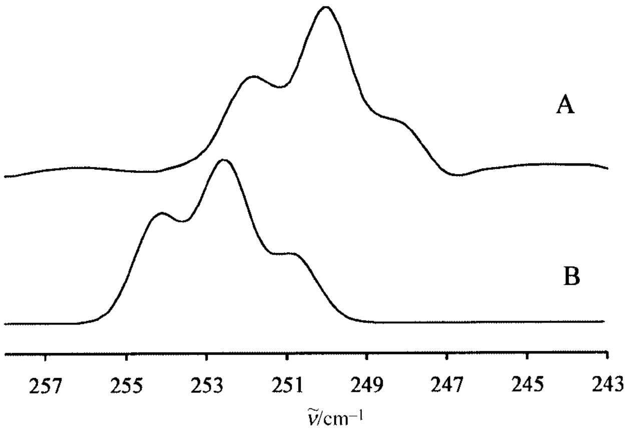


Fig. 2 Experimental and calculated isotopic pattern of GaBr: A, expanded region from Fig. 1; B, calculated isotopic pattern (B3LYP/6-311+G(3df), see Table 4).

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).[1] 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 $HGaBr_2$. Similar results were obtained starting with the dichlorogallane **1**. [GaCl was identified by its IR band at 342.0 cm^{-1} (see ref. 16); we tentatively assigned the IR band at 2786.0 cm^{-1} to HCl (see ref. 14(*b*)).]

It must be pointed out that the thermolyses of compounds **1** and **2** seams to be quite complex. For example, the fragmentation of the intramolecularly co-ordinated alanes, eqn. (1), yielded beside the hydrides $HAlX_2$ the three aluminium halogens AlX, AlX_2, and AlX_3, with the latter resulting in an intense IR band.[1] In the case of gallium we could only identify GaX; in particular, there were no IR absorptions of the well known GaX_3.[17] One might suppose that if GaX_3 was formed in the gas phase it fragmented, quite probably to a large extent, to GaX and X_2, a reaction which was used to synthesize GaX for gas-phase spectroscopy.[18] 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,[16] 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^{-1}. 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^{-1} ($^{69}Ga^{81}Br$) is shifted by 4.9% to lower frequencies in comparison with the gas-phase value of 263.0 cm^{-1};[19] a similar trend is known for $^{69}Ga^{35}Cl$, 342.9 cm^{-1} in argon matrices and 365.3 cm^{-1} in the gas phase.[20] 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 (SCRF)[21] calculations based on the Onsager[22] model.[20] 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^{-1} (SCRF-B3LYP/6-31G(d) level; polar sphere with $\varepsilon = 2$; see ref. 20).] We conducted SCRF 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 ($\varepsilon = 1.5$).[23] The SCRF method predicts 246.2 cm^{-1} for the GaBr stretch which is 3.1% lower than the frequency of the undisturbed molecule ($^{69}Ga^{79}Br$: 254.2 cm^{-1}, 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_2O_3 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^{-1}. Through comparison with literature data we assigned this band to ν_{asym} (GaO) of Ga_2O.[15] 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_2O during the cleaning procedure described above. The IR band at 822.5 cm^{-1}, 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 $HGaCl_2$ and $HGaBr_2$ were obtained thermolytically from the 3-dimethylaminopropylgallanes **1** and **2**. So far, only three monomeric gallanes of the type H_aGaX_{3-a} have been characterized, namely GaH_3,[24] $HGaCl_2$,[6] and H_2GaCl;[25] with $HGaBr_2$ we characterized a new compound of this class. Surprisingly, the gallium hydrides $HGaCl_2$ and $HGaBr_2$ withstand the rather harsh thermolyses conditions.

This report is not the first one concerning β-hydrogen eliminations to synthesize gallium hydrides; *e.g.*, Russel[26] investigated intensively the fragmentation of trialkylgallanes with the infrared laser powered homogeneous pyrolysis (IR LPHP) technique. With this method $GaEt_3$ was thermolysed to give either $(HGaEt_2)_x$ or $(H_2GaEt)_x$ and ethane. The pure hydrides as well as their NMe_3 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 $Me_2N(CH_2)_3$-$GaCl_2$ **1**[2a] and $Li(CH_2)_3NMe_2$[27] were prepared according to the literature procedures. NMR: Varian Unity 500 (ambient temperature; 499.843 MHz for ^1H and 125.639 MHz for ^{13}C), calibrated against residual protons of the deuteriated solvents; ^1H and ^{13}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 $Li(CH_2)_3NMe_2$ (0.70 g, 7.52 mmol) was added to a freshly prepared solution of 2.20 g (7.11 mmol) of $GaBr_3$ in 30 ml of diethyl ether at −78 °C. The mixture was allowed to warm to room temperature and stirred overnight. After removal of the solvent in high vacuum, sublimation (80–96 °C, 10^{-3} mbar) gave 1.85 g (82%) of **2** as a colorless solid, mp 88–90 °C. ^1H NMR (C_6D_6): δ 0.71 (t, $^3J = 7.6$ Hz, 2 H, $GaCH_2$), 1.06 (m, 2 H, $GaCH_2CH_2$), 1.51 (t, $^3J = 6.1$ Hz, 2 H, NCH_2) and 1.75 (s, 6 H, CH_3). ^{13}C-{^1H} NMR (C_6D_6): δ 12.72 ($GaCH_2$), 21.45 ($GaCH_2CH_2$), 45.99 (CH_3) and 61.11 (NCH_2). MS (70 eV): *m*/*z* (%) 315 (5) [M^+], 287 (5) [$M^+ - C_2H_4$], 236 (16) [$M^+ - Br$] and 58 (100) (C_3H_8N). Calc. for $C_5H_{12}Br_2GaN$ (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**, 55–65 °C; **2**, 80–90 °C), while a flow of argon was conducted over the sample (Linde 6.0; flow = 1.0 ml min^{-1} (0 °C, 1.013 bar); MKS mass flow controller type 1179). Subsequently, this gaseous mixture was passed through an Al_2O_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 Al_2O_3 tube. For the experiments with compound **2** an oven fitted with an Al_2O_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 °C for **1** and 70 °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 cm^{-1} with a resolution of 1 cm^{-1}.

Ab initio calculations

The GAUSSIAN 94 package,[28] 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 kJ mol^{-1}; in parentheses) are as follows: $HGaCl_2$, −2843.298259 (24.88) for MP2(fc)/6-311+G(2d,p), −2846.028291 (23.96) for B3LYP/6-311+G(2d,p); $HGaBr_2$, −7068.959265 (22.98) for MP2(fc)/6-311+G(2d,p), −7073.862273 (22.04) for B3LYP/6-311+G(2d,p); 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 GaBr were conducted at the B3LYP/6-311+G(3df) level with a polar sphere of $\varepsilon = 1.5$[23] and a radius of 3.45 Å. This radius was obtained by adding 0.50 Å to the radius gained from the calculated molecular volume (keyword: volume = tight). The total energy E_h (in Hartrees) and the ZPVE (in kJ mol^{-1}; in parentheses) for GaBr with the reaction field is −4499.090559 (1.47); the GaBr distance is 2.408 Å.

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