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Synthesis of Monomeric Me_2GaD via a β-Hydrogen Elimination at High Temperatures. A Matrix-Isolation Study

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The selectively deuterated, intramolecular coordinated gallane $Me_2NCH_2CD_2CH_2GaMe_2$ (**1D**) was synthesized and characterized by standard methods (^1H and ^{13}C NMR, mass spectrometry, CN elemental analysis). The thermolysis of **1D** has been investigated with matrix-isolation techniques in the range of ambient temperatures to 950 °C. Among the products of the thermolysis the monomeric deuteride $DGaMe_2$ has been identified by IR spectroscopy supported by ab initio calculations. Aside from this deuteride, small amounts of the known hydride $HGaMe_2$ were found. In comparison with known reported data $GaMe_3$, GaMe, $H_2C{=}NMe$, and $H_2C{=}CD(CH_2NMe_2)$ have been identified in the matrixes. The characterization of $DGaMe_2$ proves the fragmentation of the starting compound **1D** via a β-hydrogen elimination at high temperatures.

Introduction

The group 13 nitrides AlN, GaN, and InN and their ternary alloys $Al_xGa_yIn_zN$ ($x + y + z = 1$) are materials exhibiting a unique combination of properties that are useful for several advanced applications in optoelectronics and various other fields.[1] In particular, blue-light emitting diodes and lasers can be constructed; this initiated tremendous research activities worldwide during the past decade. Thin films of these nitrides usually can be grown epitaxially by chemical vapor deposition (CVD) from the trimethyl compounds MMe_3 (M = Al, Ga, In) with a large excess of ammonia. These organometallics are toxic and very air and moisture sensitive, and many efforts have been made to synthesize alternative precursors. If the element is equipped with a ligand that is capable of intramolecular coordination, then nonpyrophoric organometallics are accessible. In particular, the 3-dimethylaminopropyl ligand, $Me_2N(CH_2)_3$, was successfully applied to various precursors; for example, the compound $Me_2N(CH_2)_3GaMe_2$ (**1H**) can be used as a gallium source in metal organic chemical vapor deposition (MOCVD) processes.[2] A comparable species but with a build-in nitrogen source is the diazide $Me_2N(CH_2)_3Ga(N_3)_2$; ammonia is not necessary for the MOCVD of GaN from this single-source precursor.[3] Recently, we started to investigate the fragmentation of organometallic compounds of aluminum and gallium equipped with the 3-dimethylaminopropyl ligand using matrix-isolation techniques (Figure 1 M = Al, X = Cl, Br[4]; M = Ga, X = Cl, Br,[5] and Me (**1H**)[6]).

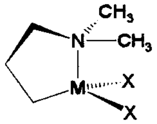

Figure 1. Intramolecularly coordinated alanes and gallanes.

We intend to trap intermediates that might be formed between the starting compound and the deposited material. In all the investigated cases monomeric hydrides HMX_2 were trapped in argon matrixes and characterized by IR spectroscopy. These findings have been interpreted as the result of β-hydrogen eliminations.

In addition to the use of matrix-isolation techniques, we investigated the fragmentation of the dimethyl gallane **1H** with mass spectrometry (Figure 1).[6] In contrast to matrix isolation, mass spectrometry is generally used as an in situ analysis in CVD processes. The major disadvantage of mass spectrometry (MS) occurs because the fragments must be ionized before detection, resulting in an excess energy deposited in the molecule causing fragmentation. On the other hand, at low-ionization energies the efficiency of the production of ions is low; therefore, the applied ionization energies are often a tradeoff between high sensitivity and low fragmentation. The mass spectrometric investigation of **1H** in the range of ambient temperature to 800 °C revealed a signal at 85 u for allyldimethylamine, but a respective signal for the expected hydride $HGaMe_2$ was below the detection limit.[6] Instead, we found a signal for the $GaMe_2^+$ ion which was interpreted as resulting from $HGaMe_2$. We did not prove *directly* the formation of the $HGaMe_2$ in the gas phase at high temperatures by mass spectrometry. However, the matrix isolation experiments showed that $HGaMe_2$ was present in the matrixes, which were obtained by trapping the thermolysis products of **1H** onto the cooled CsI window in an excess of solid argon at 15 K. This finding was interpreted as evidence for a β-hydrogen elimination of **1H** in the gas phase. Alternatively, $HGaMe_2$ could be formed via a radical reaction route; for example, $GaMe_2$, formed by homolysis from the precursor **1H**, could be saturated with a hydrogen atom to form the detected hydride $HGaMe_2$. Of course, other reaction sequences to explain the presence of $HGaMe_2$ in matrixes are feasible too.

In this article, we report matrix thermolysis experiments with gallane **1D**, which is a selectively deuterated derivative of compound **1H**.

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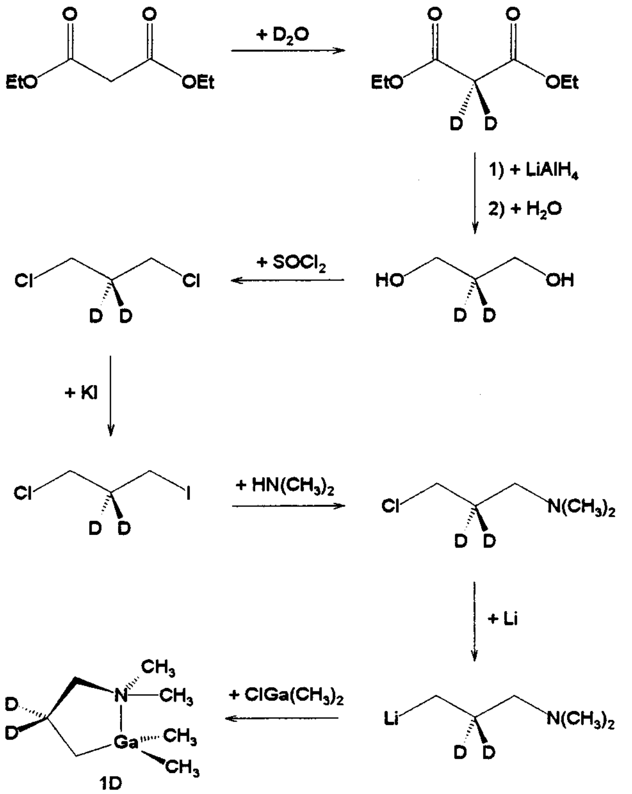
SCHEME 1



Results and Discussion

The synthesis of the starting gallane **1D** is shown in Scheme 1.

Malonic acid diethyl ester is deuterated and then reduced with $LiAlH_4$ to give the diol $(HOCH_2)_2CD_2$ after hydrolysis. Subsequent chloridizing followed by a Finkelstein reaction yields the 1,3-chloroiodopropane, from which the iodide is readily replaced by a dimethylamino group to give $ClCH_2CD_2CH_2$-NMe_2. Reduction with Li powder and reaction with chlorodimethylgallane gives the final product **1D**. The purity of the gallane **1D** was checked with standard methods (see Experimental Section for details). As expected, the deuteration results in simple NMR spectra; for example, the ^1H NMR spectrum of **1D** consists of four singlets, with half-bandwidths of the two singlets of the CH_2 groups slightly increased indicative of the proximity of deuterium atoms. Deduced from mass spectrometry the degree of deuteration of compound **1D** is better than 99(±1)%.

As in the nondeuterated species **1H**, we investigated the fragmentation of **1D** with common matrix-isolation techniques; specifically, we used argon as an inert gas and identified matrix-isolated species with IR spectroscopy. An Al_2O_3 tube heated along its last 10 mm was used for the thermolysis experiments. The hot end of the Al_2O_3 tube was only 25 mm away from the cooled matrix window (CsI at 15 K) to ensure that a maximum of volatile fragments emerging from the oven were trapped in argon matrixes. With this setup two different kinds of thermolysis series were performed: one series with high vacuum conditions, where a continuous gas flow of the precursor-argon mixture was used, and a second series, where short pulses of the precursor-argon mixture were conducted through the pyrolysis tube. Figure 2 shows a typical IR spectrum of matrix-isolated species from a pulsed nozzle thermolysis of compound **1D** at 850 °C. At this temperature the thermolysis is not completed and residual amounts of the starting gallane **1D** are eliminated electronically from the spectrum depicted in Figure 2. In addition to the experimental IR spectrum, Figure 2 shows a calculated IR spectrum of $DGaMe_2$. This spectrum is based on the published ab initio data of the hydride $HGaMe_2$ [MP2(fc)/6-311+G(2d,p)].[6] The calculated and measured vibrational frequencies of $HGaMe_2$ and $DGaMe_2$ are compiled in Table 1.

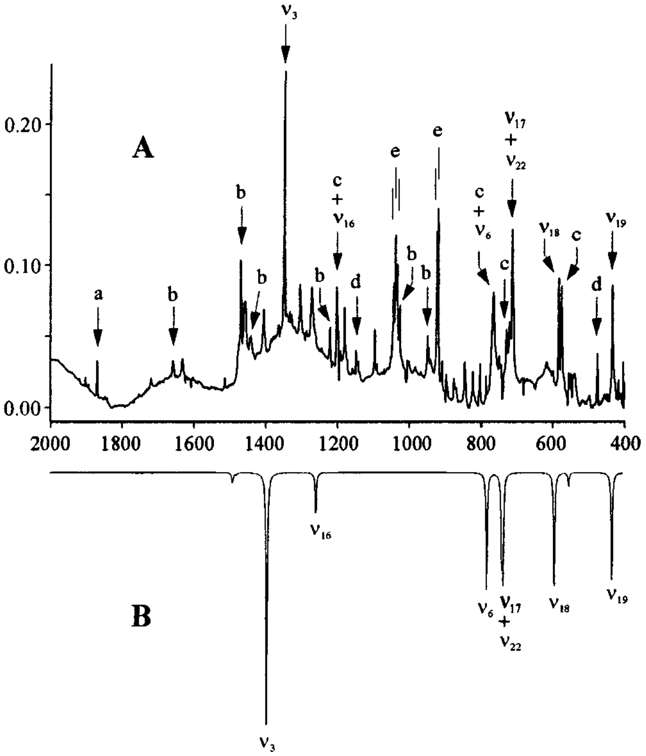


Figure 2. Experimental and calculated IR spectra: *x*-axis, 400−2000 cm^{-1}; *y*-axis, absorbance. Spectrum A, products of thermolysis of compound **1D** at ca. 850 °C trapped in argon at 15 K. $DGaMe_2$ (ν_3, ν_6, ν_{16}–ν_{19}, ν_{22}; assignment, see Table 1); a, $HGaMe_2$ (1869.3 cm^{-1}); b, $H_2C{\simeq}NMe$ (2953.4, 2900.6, 2854.8, 2849.1, 1658.7, 1469.5, 1441.3, 1220.8, 1026.4, 949.2 cm^{-1}); c, Me_3Ga (1201.0, 765,^{d} 728.8, 575.6 cm^{-1}); d, MeGa (1148.3, 476.2 cm^{-1}); e, $H_2C{\simeq}CD(CH_2NMe_2)$ (2819.8, 2779.6, 2774.0, 1043.7, 1038.4, 1033.4, 922.7, 919.8 cm^{-1}). Spectrum B, harmonic vibrational frequencies of $DGaMe_2$ calculated at the MP2(fc)/6-311+G(2d,p) level.

With respect to the ab initio calculation, $DGaMe_2$ should exhibit five intense IR bands and one medium intense IR band in the region of 400−2000 cm^{-1} and we can assign all these normal modes to experimental IR bands (Figure 2).[6] Table 1 shows that the respective modes have been assigned for the hydride $HGaMe_2$ previously. As expected, the modes of the deuteride and the hydride give similar observed/calculated frequency ratios (Table 1, values in square brackets). For example, the GaH stretching mode was detected at 1969.5 cm^{-1} resulting in an observed/calculated frequency ratio of 0.9560 at the MP2(fc)/6-311+G(2d,p) level. Based on this frequency ratio the GaD stretching mode is expected at 1332.0 cm^{-1} in good agreement with the intense measured IR band at 1347.4 cm^{-1}. The ratio of the experimental frequencies of ν(GaH):ν(GaD) = 1.39 shows that the respective modes are indeed characteristic hydrogen stretches. In addition to the frequencies, there is a good fit between the calculated and measured intensity pattern, which is illustrated in Figure 2.

Besides $HGaMe_2$ we identified $H_2C{=}NMe$,[7] $GaMe_3$,[8] and GaMe in comparison with reported data; these compounds had been identified in the thermolysis experiments of **1H** previously.[6] Methylgallium(I), a well-known molecule from mass spectrom-

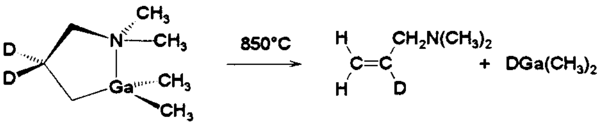
TABLE 1: Calculated Harmonic Frequencies and Experimental IR Frequencies of Me_2GaH^b and Me_2GaD^a

			MP2(fc)/6-311+G(2d,p)		experimental frequencies	
			$HGaMe_2^b$	$DGaMe_2$	$HGaMe_2^b$	$DGaMe_2$
A_1^c	ν_1	$\nu_{as}(CH_3)$	3165.9 (20.2)	3165.9 (19.9)		
	ν_2	$\nu_s(CH_3)$	3059.1 (1.9)	3059.1 (2.0)		
	ν_3	$\nu(GaH)$	1955.5 (274.6)	1393.3 (143.5)	1869.5 [0.9560]	1347.4 [0.9671]
	ν_4	$\delta_{as}(CH_3)_{scis}$	1487.9 (1.2)	1488.1 (3.0)		
	ν_5	$\delta_s(CH_3)_{umbr}$	1258.9 (2.8)	1257.8 (0.6)		
	ν_6	$\delta_{as}(CH_3)_{rock}$	779.0 (65.7)	779.0 (65.8)	768 [0.9859]^e	765 [0.9820]^{e,f}
	ν_7	$\nu_s(GaC_2)$	550.7 (8.2)	550.5 (7.9)		
	ν_8	$\delta(GaC_2)$	155.9 (4.5)	155.7 (4.5)		
A_2^c	ν_9	$\nu_{as}(CH_3)$	3138.7 (0.0)	3138.7 (0.0)		
	ν_{10}	$\delta_{as}(CH_3)$	1486.3 (0.0)	1486.3 (0.0)		
	ν_{11}	$\delta_{as}(CH_3)_{twist}$	615.8 (0.0)	615.8 (0.0)		
	ν_{12}	$\tau(CH_3)$	12.4 (0.0)	12.4 (0.0)		
B_1^c	ν_{13}	$\nu_{as}(CH_3)$	3165.7 (1.2)	3165.7 (1.2)		
	v_{14}	$\nu_s(CH_3)$	3059.0 (14.6)	3059.0 (14.7)		
	ν_{15}	$\delta_{as}(CH_3)_{scis}$	1479.2 (1.0)	1479.2 (1.2)		
	ν_{16}	$\delta_s(CH_3)_{umbr}$	1256.7 (23.6)	1256.7 (22.5)	1202.5 [0.9569]	1202.4 [0.9567]
	ν_{17}	$\delta_{as}(CH_3)_{rock}$	792.9 (119.2)	737.4 (42.5)	768 [0.9686]^e	712.9 [0.9668]
	ν_{18}	$\nu_{as}(GaC_2)$	590.5 (57.7)	590.3 (65.2)	589.5 [0.9983]^d	583.9 [0.9905]
	ν_{19}	$\delta(CGaH)$	554.5 (74.4)	429.8 (60.9)	556.0 [1.0027]	433.7 [1.0091]
B_2^c	ν_{20}	$\nu_{as}(CH_3)$	3138.8 (16.7)	3138.8 (16.7)		
	ν_{21}	$\delta_{as}(CH_3)$	1491.0 (3.4)	1490.6 (4.1)		
	ν_{22}	$\delta_{as}(CH_3)_{twist}$	747.3 (77.1)	733.5 (55.5)	729.0 [0.9755]	712.9 [0.9719]
	ν_{23}	$\gamma(H)$	397.5 (48.5)	305.1 (30.4)	415.5 [1.0453]^d	
	ν_{24}	$\tau(CH_3)$	31.2 (0.0)	31.1 (0.0)		

[a] Harmonic frequencies (cm^{-1}) and intensities in parentheses (km mol^{-1}); experimental IR frequencies (cm^{-1}) and observed/calculated frequency ratios in square brackets. [b] Values taken from ref 6. [c] The harmonic frequencies are classified assuming C_{2v} symmetry (see ref 6 for details). [d] Tentative assignment.[6] [e] Broad IR band. [f] Overlap with IR bands of $GaMe_3$.

etry,[9] was identified for the first time in matrixes by H. Himmel et al.[10] and our group[6] independently. In all thermolysis experiments of the gallane **1D** the IR band at 1969.3 cm^{-1} unequivocally indicates the presents of the hydride $HGaMe_2$. Based on the calculated intensities of the hydrogen stretching modes ν_3 of the hydride and the deuteride, the ratio of $DGaMe_2$:$HGaMe_2$ is 13.70:1.00 equivalent with 6.8% $HGaMe_2$ in the spectrum of Figure 2.[11]

The identification of the deuteride $DGaMe_2$ unequivocally proves that a β-hydrogen elimination in the gas phase takes place at high temperatures (eq 1).



(1)

The $HGaMe_2$ formed is not the product resulting directly from a β-hydrogen elimination, because, based on the degree of deuteration of the starting compound **1D** of 99(±1)%, a much lower amount is expected. How the hydride was formed is unknown.

According to eq 1 monodeuterated allyldimethylamine should be among the thermolysis products. We assign the remaining most intense IR bands of the thermolysis spectra to $H_2C{=}CD(CH_2NMe_2)$ (designation e in spectrum A). This assignment is based on the known IR data of matrix-isolated nondeuterated allyldimethylamine, which we identified in the thermolysis of the gallane **1H**.[6] Allyldimethylamine shows the strongest IR bands at 2819.5, 2780.0, 1036.5, and 923.0 cm^{-1}. Around the IR band at 1036.5 cm^{-1} two other intense absorptions at 1043.5 and 1033.0 cm^{-1} can be seen; two IR bands at 920.0 and 918.5 cm^{-1} are close by 923.0 cm^{-1}. A similar intensity pattern with comparable frequencies were found in the product matrixes of **1D** (Figure 2): two intense IR bands at 2819.8 and 2779.6 cm^{-1}, and a ‘triplet’ at 1043.7, 1038.4, and 1033.4 cm^{-1}, plus a ‘doublet’ at 922.7 and 919.8 cm^{-1}. Other less intense absorptions of the matrix IR spectra could not be assigned to $H_2C{=}CD(CH_2NMe_2)$ with certainty. However, a complete assignment of all IR bands of $H_2C{=}CD(CH_2NMe_2)$ would have been possible if an IR spectrum of pure matrix isolated $H_2C{=}CD(CH_2NMe_2)$ were available for comparison. Even without an IR spectrum for direct comparison, monodeuterated allyldimethylamine could be identified unequivocally among the thermolysis products.

Within the investigation of the thermolysis of **1H**, the dihydride H_2GaMe was identified in matrixes.[6] We speculated that this species was formed by ligand-exchange reactions in the gas phase; that is, two molecules of $HGaMe_2$ yielded H_2GaMe and $GaMe_3$. If this is true then the deuteride D_2GaMe is expected as a thermolysis product of the gallane **1D**. We could not identify the expected dideuteride, with IR bands for the GaD stretching modes in the range of 1370−1360 cm^{-1}, in any of our thermolysis experiments. Weak IR bands are present in this region, but an assignment is impossible so far. On the other hand, we have not observed the known IR bands of the dihydride, H_2GaMe, in any of our experiments.

Conclusion

Dimethylgallane can be synthesized as a bulk material from Me_3Ga and freshly prepared $Li[GaH_4]$ under solvent- and grease-free conditions.[12] The hydride is quite sensitive, and at ambient temperatures it decomposes within days to $GaMe_3$, H_2, and a polymer approximating $(MeGa)_x$ in composition. The structure of dimethylgallane in the solid state is unknown, however, as shown by Downs and Rankin et al.[12] The vapor phase of this hydride mainly consists of the dimers $Me_2Ga(\mu\text{-}H)_2GaMe_2$.

Recently, we characterized the monomeric Me_2GaH in argon matrixes by IR spectroscopy. This compound was synthesized via a high-temperature thermolysis of the intramolecularly coordinated gallane **1H**. The results of matrix-isolation experiments and mass spectrometry have been interpreted as a β-hydrogen elimination occurring in the first step of the fragmentation. In this article, we have described the synthesis and matrix-isolation thermolysis experiments of the selectively deuterated gallane **1D**. We have proven experimentally that the intramolecularly coordinated gallane **1D** mainly undergoes a β-hydrogen elimination to give the monomeric deuteride $DGaMe_2$ at high temperatures.

Experimental Section

General Remarks. Synthetic procedures were conducted under dry nitrogen or argon atmospheres with standard Schlenk techniques where appropriate. Solvents were dried by standard procedures, distilled, and stored under nitrogen or argon and molecular sieves (4 Å). *NMR*. Varian Unity 500 [ambient temperature (temp): 499.84 and 125.64 MHz for ^1H and ^{13}C, respectively], Varian Mercury 200 (ambient temp: 199.97 MHz for ^1H), and Bruker Advance DRX 400 (ambient temp: 400.13 and 100.62 MHz for ^1H and ^{13}C, respectively) calibrated against residual protons of the deuterated solvents. ^1H and ^{13}C chemical shifts are reported relative to tetramethylsilane. *Elemental analyses* (C, H, N): Carlo-Erba elemental analyzer (model 1106) and Elementar Vario EL Analysator. *MS*: Finnigan MAT 95 and Varian MAT CH5.

$ClGaMe_2$ was synthesized according to the literature.[13] We synthesized the known compounds $(EtO_2C)_2CD_2$[14] and $(HOCH_2)_2CD_2$[15] in variations of known procedures. The syntheses of the hitherto unknown compounds $(ClCH_2)_2CD_2$,[16] $ICH_2CD_2CH_2Cl$,[17] $Me_2NCH_2CD_2CH_2Cl$,[17] $LiCH_2CD_2CH_2NMe_2$,[18] and $Me_2NCH_2CD_2CH_2GaMe_2$[19] were based on known procedures.

$(EtO_2C)_2CD_2$. Malonic acid diethyl ester (300 g, 1.873 mol), a spatula-tipfull of dry K_2CO_3 and D_2O (60 g, 2.996 mol) were kept at 90 °C and stirred for 24 h. After the reaction mixture was cooled to ambient temperature, the organic layer was separated from the water layer. This procedure was repeated an additional six times to achieve a high degree of deuteration. After pentane (200 mL) was added to the combined organic layers the organic phase was dried overnight with Na_2SO_4. The Na_2SO_4 was filtered off and washed several times with small portions of pentane. The solvent was removed at ambient temperature by distillation (50 mbar) and 195 g (64%) of the pure product was yielded by distillation (78 °C, 10 mbar). ^1H NMR (499.84 MHz; $CDCl_3$): $\delta = 1.27$ (t, $J = 7.2$ Hz, 6H, CH_2CH_3), 3.33 (t, $J = 2.3$ Hz, residual protons of CD_2), 4.19 (q, $J = 7.1$ Hz, 4H, CH_2CH_3).

$(HOCH_2)_2CD_2$. To a suspension of $LiAlH_4$ (30.5 g, 804 mmol) in diethyl ether (750 mL) a solution of $(EtO_2C)_2CD_2$ (110.0 g, 678 mmol) in diethyl ether (350 mL) was added during a 2-h period from a dropping funnel so that the reaction mixture was kept under reflux. The reaction mixture was kept under reflux for an additional hour and then it was hydrolyzed during 1 h with a solution of H_2O (85.0 g, 4.718 mol) and NaOH (2.5 g, 63 mmol). The ether solution was separated by filtration and the solid residue was extracted with diethyl ether in a Soxhlet apparatus. After the combined organic layers were dried with Na_2SO_4, the solvent was removed at ambient temperature in a vacuum (6 mbar). The product (26.2 g, 49%) was yielded by a flask-to-flask distillation (60 °C, 1×10^{-3} mbar). ^1H NMR (199.97 MHz; DMSO): $\delta = 1.53$ (m, residual protons of CD_2), 3.42 (d, $J = 4.9$ Hz, $HOCH_2$, 4H), 4.30 (t, $J = 5.1$ Hz, $HOCH_2$).

$(ClCH_2)_2CD_2$. $SOCl_2$ (249.9 g, 2.101 mol) was placed in a four-neck flask equipped with a dropping funnel, gas inlet, thermometer, and reflux condenser. At 5−10 °C pyridine (6.25 g, 79.0 mmol) and subsequently ethanol (4.1 g, 89 mmol) was added. At −5−0 °C $(HOCH_2)_2CD_2$ (61.9 g, 792 mmol) was added dropwise during 1.5 h and the reaction mixture was slowly warmed to ambient temperature overnight. The reaction mixture was heated to 30 °C and N_2 was slowly bubbled through the solution. Every 45 min the temperature was increased by 5 °C; at 55−58 °C the side product allyl chloride was removed by an opening of the reaction flask for a short time. After the reaction mixture was kept for 1 h at 60 °C and an additional hour at 80 °C, it was cooled to ambient temperature and poured into a water/ice bath. The product was extracted five times with 40-mL portions of pentane, and the combined organic layers were washed with diluted $NaHCO_3$ (50 mL), cleaned with filter charcoal, and dried with Na_2SO_4. The product (62.5 g, 77%) was obtained by a flask-to-flask condensation at ambient temperature (6−30 mbar). ^1H NMR (499.84 MHz; C_6D_6): $\delta = 1.42$ (m, residual protons of CD_2), 3.05 (s, $ClCH_2$). $^{13}C\{^1H\}$ NMR (125.64 MHz; C_6D_6): $\delta = 34.12$ (p, CD_2), 41.12 (s, $ClCH_2$). MS (70 eV): m/z (%) = 114 (1) [M^+], 79 (5) [$M^+ - Cl$], 78 (100) [$M^+ - HCl$]. Anal. Calcd for $C_3D_2H_4Cl_2$ (114.999): C 31.33. Found: C 31.24.

$ICH_2CD_2CH_2Cl$. KI (63.6 g, 383 mmol) and $(ClCH_2)_2CD_2$ (67.3 g, 653 mmol) in acetone (750 mL) were heated under reflux for 12 h in the dark. All volatile compounds were removed at ambient temperature at 75 mbar; all solids were filtered off and washed with pentane. After the solvent was removed at 75 mbar at ambient temperature, 73.4 g of crude product was obtained. Through a distillation (15 cm Vigreux column, 100 mbar) unreacted starting material (55−63 °C, 28.9 g) was collected and again reacted with respective amounts of KI. This procedure was repeated until 90% of the starting compound had reacted. Through a distillation of the combined product fractions (50 cm Vigreux column, 30 mbar, 69.0−70.5 °C) 30.8 g (23%) of the pure product was obtained. ^1H NMR (499.84 MHz; C_6D_6): $\delta = 1.45$ (m, residual protons of CD_2), 2.63 (m, 2H, ICH_2CD_2), 2.95 (m, $ClCH_2CD_2$). $^{13}C\{^1H\}$ NMR (125.64 MHz; C_6D_6): $\delta = 1.97$ (s, ICH_2CD_2), 34.76 (m, $ClCH_2CD_2$), 44.37 (s, $ClCH_2CD_2$). MS (70 eV): m/z (%) = 206 (84) [M^+], 205 (4) [$M^+ - H$], 171 (1) [$M^+ - Cl$], 157 (7) [$M^+ - CH_2Cl$], 141 (5) [$M^+ - CH_2Cl$], 128 (6) [HI^+], 127 (18) [I^+]; 79 (100) [$M^+ - I$]. Anal. Calcd for $C_3H_4D_2ClI$ (206.446): C 17.45. Found: C 17.31.

$Me_2NCH_2CD_2CH_2Cl$. To a solution of $ICH_2CD_2CH_2Cl$ (66.8 g, 324 mmol) in diethyl ether (400 mL) dimethylamine (52 g, 1.15 mol) was condensed at −78 °C. After the cooling bath was removed, the reaction mixture was stirred for 24 h, cooled to ca. −20 °C, and added to a solution (ca. −20 °C) of NaOH (14 g, 0.35 mol) in H_2O (200 mL). After vigorous stirring for a short time, the organic layer was separated and the water phase extracted four times with 60-mL portions of diethyl ether. After the combined organic layers were dried with Na_2SO_4 and the solvent was distilled off (15 cm Vigreux column, 80 mbar), 31.7 g of pure product (79%) was left behind. ^1H NMR (499.84 MHz; C_6D_6): $\delta = 1.55$ (m, residual protons of CD_2), 1.93 [s, 6H, $N(CH_3)$], 2.08 (s, 2H, CD_2CH_2N), 3.27 (m, $J = 0.9$ Hz, 2H, $ClCH_2CD_2$). $^{13}C\{^1H\}$ NMR (125.64 MHz; C_6D_6): $\delta = 30.27$ (m, $ClCH_2CD_2$), 42.89 (s, CD_2CH_2N), 45.37 [s, $N(CH_3)$], 56.32 (s, $ClCH_2CD_2$). MS (70 eV): m/z (%) = 123 (6) [M^+], 122 (1) [$M^+ - H$], 58 (100) [$H_2CN(CH_3)_2^+$]. Anal. Calcd for $C_5H_{10}D_2ClN$ (123.622): C 48.58, N 11.33. Found: C 47.24, N 11.01.

$LiCH_2CD_2CH_2NMe_2$. This reaction was performed with argon as an inert gas. To a suspension of Li powder (4.3 g, 620 mmol, 0.5% Na) in diethyl ether (300 mL) $Me_2NCH_2CD_2CH_2Cl$ (30.5 g, 247 mmol) was added slowly during 1 h and subsequently refluxed for 2 h. After all volatile material had been removed at ambient temperature in a vacuum (1×10^{-3}

mbar), the residue was extracted in a Soxhlet apparatus with pentane for 24 h and crystallization at −24 °C gave the pure, colorless product (13.4 g, 57%).

$Me_2NCH_2CD_2CH_2GaMe_2$ (1D). This reaction was performed with argon as an inert gas. A solution of $ClGaMe_2$ (1.98 g, 14.6 mmol) in pentane (20 mL) was added slowly to a suspension of $LiCH_2CD_2CH_2NMe_2$ (1.40 g, 14.7 mmol) in pentane (20 mL) at O °C. After the cooling bath was removed, the reaction mixture was stirred overnight and filtered, and the solid was washed with two 5-mL portions of pentane. After removal of the solvent under vacuum two times sublimation yielded 1.70 g (62%) of the pure compound **1D** as a colorless solid. ^{1}H NMR (400.13 MHz, C_6D_6): $\delta = -0.19$ [s, 6H, $Ga(CH_3)_2$], 0.51 (s, 2H, H_2CGa), 1.69 [s, 6H, $N(CH_3)_2$], 1.80 (s, 2H, NCH_2). ^{13}C-{^{1}H} NMR (100.62 MHz, C_6D_6): $\delta = -6.12$ [s, $Ga(CH_3)_2$], 9.03 (s, $GaCH_2$), 23.61 (p, CD_2), 45.79 [s, $N(CH_3)_2$], 63.77 (s, NCH_2). MS (70 eV): m/z (%) = 172 (100) [$M^+ - CH_3$], 99 (9) [$Ga(CH_3)_2{}^+$], 86 (32) [$H_2CCDCH_2N(CH_3)_2{}^+$], 69 (17) (Ga^+), 58 (94) [$H_2CN(CH_3)_2{}^+$]. Anal. Calcd for $C_7H_{16}D_2GaN$ (187.962): C 44.73, N 7.45. Found: C 44.71, N 7.59.

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. Compound **1D** was kept in a small metal container connected to the matrix apparatus via a pulse valve (Pulse Valve Series 9, IOTA One, General Valve Corporation, opening diameter 0.8 mm). In a typical experiment **1D** was kept under an argon pressure of 2 bar (Linde 6.0) and heated to ca. 70 °C. Pulses of 500 μs at 20 Hz were passed through an Al_2O_3 tube with two parallel, inner canals (outer diameter of 4 mm; inner diameter of 1 mm each; last 10 mm heated with a tungsten wire) with one of the inner canals equipped with a thermocouple (Thermocoax: NiCrSi/NiSi). With this setup it was possible to measure reliable thermolysis temperatures without a contact between the substance and the thermocouple. Similar thermolysis experiments were performed with the same oven, but without the pulse valve, using a continuous-flow technique. (For details see ref 6.) The experiments were performed with oven temperatures in the range of ambient temperature to 950 °C. The gaseous mixtures were trapped onto the CsI window at 15 K. The IR spectra of the matrixes, cooled to 10−11 K, were recorded on a Bruker EQUINOX 55 with a KBr beam splitter in the range of 400−4000 cm^{-1} with a resolution of 1.0 cm^{-1}.

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