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Lewis Base Adduct Stabilized Organogallium Azides: Synthesis and Dynamic NMR Spectroscopic Studies of Novel Precursors to Gallium Nitride and Role of Ammonia as Reactive Carrier Gas

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The organogallium azides $(N_3)_{2-a}(R)_aGa[(CH_2)_3NMe_2]_{1-a}$ (**1a-c**: R = CH_3, ^tBu; $a = 0, 1$), $(Et)(N_3)_2Ga$ (**2a**), and $(Et)(N_3)_2Ga\cdot L$ (**2b**−**d**: L = thf, H_2N^tBu, py, NC_7H_{13}) are quantitatively synthesized by salt metathesis from the chloro species $(Cl)_{2-a}(R)_aGa[(CH_2)_3NMe_2]_{1-a}$ ($a = 0$, 1) or $EtGaCl_2$ and sodium azide. The preferential ammonolysis of Ga−N_3 bonds for $[Et_2Ga(N_3)]_3$ (**4**) and **1** and **2** is demonstrated; e.g. the dimer $Et_2Ga(\mu\text{-}NH_2)(\mu\text{-}N_3)GaEt_2$ (**3**) was obtained. The characterization of these compounds by means of elemental analysis, ^1H-, ^{13}C-, ^{14}N-, and ^{15}N-NMR, MS, and infrared $\nu(N_3)$ data is reported. The dynamics of the intramolecular Ga−N donor−acceptor bonded heterocycle and the azide group is discussed on the basis of variable-temperature NMR data. The barrier of activation of the bimolecular azide exchange process for $(N_3)_2Ga[(CH_2)_3NMe_2]$ (**1c**) amounts about 50 $kJ\cdot mol^{-1}$. The role of ammonia as reactive carrier gas for low-pressure metal organic chemical vapor deposition (MOCVD) of GaN with **1c** as precursor is discussed.

Introduction

Gallium nitride, GaN, is a very promising semiconductor with a wide, direct band gap (3.45 eV). It might serve as a key material for optoelectronic devices operating in the blue, violet, and ultraviolet regions of the optical spectrum.[1] The current deposition technology of commercial blue light emitting diodes based on hexagonal GaN relies on MOCVD of GaN from $Ga(CH_3)_3$ or $Ga(C_2H_5)_3$ and NH_3 at temperatures > 950 °C, V/III ratios > 10^3, employing rather complex fluid dynamics and process control.[2] A quite recent strategy to avoid these hazardous and pyrophoric precursors and very harsh conditions to deposit GaN from the gas phase uses organometallic gallium azides, such as $[R_2Ga(N_3)]_3$[3] and $[(\mu\text{-}Me_2N)Ga(N_3)(NMe_2)]_2$.[4] Those so-called single molecule precursors yield GaN thin films of reasonable purity at mild conditions (360−650 °C) by conventional thermal MOCVD or MBE techniques (MBE: molecular beam epitaxy). It was shown, that the azide group serves as the major nitrogen source for the GaN growth.[3,4] Compared to this promising potential for various applications in microelectronics the chemistry of (organometallic) gallium azides seems to be still rather undeveloped[4,5] since the early work of Wiberg et al. on $Ga(N_3)_3$[6] and Dehnicke et al. on $[R_2Ga(N_3)]_3$.[7] Here we present the synthesis, spectroscopic characterization, some aspects of the reactivity, and the solution dynamics of new organogallium azides, as well as a discussion of the suitability of some of the described compounds as molecular sources for GaN deposition.

Experimental Section

All manipulations were undertaken by use of standard Schlenk, high-vacuum line, and glove box techniques under inert gas atmosphere (purified argon). Solvents were dried under argon according to standard methods; *n*-pentane and toluene were stored over Na/K alloy, and diethyl ether and thf over potassium benzophenoate (residual water < 1 ppm, Karl Fischer). NaN_3 was dried at 115 °C at the HV line for several days. Infrared spectra were recorded as thin films (dry Nujol mull) or solutions between carefully dried CaF_2 plates with a Perkin-Elmer 1600 FT-IR instrument (sample preparation in the glovebox). JEOL JNM-GX 400 and Bruker DPX 400 spectrometers were used for NMR spectroscopy. ^1H- and ^{13}C-NMR spectra were referenced to internal solvent and corrected to TMS (400.13 and 100.6 MHz, respectively). ^{14}N- and ^{15}N-NMR spectra were referenced to external neat nitromethane ($\delta(CH_3NO_2) = 0.0$ ppm). All samples for NMR spectra were placed in high-vacuum sealed NMR tubes, using carefully dried deuterated solvents. X-ray powder diffraction studies on MOCVD grown GaN thin films were undertaken using on a Philips PW 3040 diffractometer including a PW 3020 $\omega-2\theta$ two-circle diffractometer equipped with the thin film package and a graphite monochromator. Cu Kα radiation was used. Sapphire substrates were epipolished and cleaned according to common procedures. Mass spectra were recorded

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(1) (a) Detchprohm, T.; Hiramatsu, K.; Sawaki, N.; Akasaki, I. *J. Cryst. Growth* **1994**, *137*, 171−174. (b) Goldenberg, B.; Zook, J. D.; Ulmer, R. J. *Appl. Phys. Lett.* **1993**, *62*, 381−383. (c) Khan, M. A.; Kuznia, J. N.; Van Hove, J. M.; Olson, D. T. *Appl. Phys. Lett.* **1991**, *58*, 526−531. (d) Nakamura, S. *Jpn. J. Appl. Phys.* **1991**, *10A*, L1705-L1707. (e) Matsuka, T. *J. Cryst. Growth* **1992**, *124*, 433−438. (f) Kesamainly, F. P. *Sov. Phys. Semicond.* **1974**, *8*, 147−152. (g) Pankove, J. I. *J. Luminesc.* **1973**, *7*, 114−118.

(2) (a) Eddy, C. R.; Moustakas, T. D. *J. Appl. Phys.* **1993**, *73*, 448−455. (b) Paisley, M. J.; Sitar, Z.; Posthill, J. B.; Davis, R. F. *J. Vac. Sci. Technol.* **1989**, *A7*, 701−706.

(3) Kouvetakis, J.; Beach, D. *Chem. Mater.* **1989**, *1*, 476−478.

(4) (a) Lakhotia, V. ; Neumayer, D. A; Cowley, A. H.; Jones, R. A.; Ekerdt, J. G. *Chem. Mater.* **1995**, *7*, 546−552. (b) Neumayer, D. A.; Cowley, A. H.; Decken, A.; Jones, R. A.; Lakhotia, V.; Ekerdt, J. G. *J. Am. Chem. Soc.* **1995**, *117*, 5893−5894.

(5) Cowley, A. H.; Gabbai, F. P.; Olbrich, F.; Corbelin, S.; Lagow, R. J. *J. Organomet. Chem.* **1995**, *487*, C5−C7.

(6) Wiberg, E.; Michaud, H. *Z. Naturforsch.* **1954**, *9b*, 502−503.

(7) Müller, J.; Dehnicke K. *J. Organomet. Chem.* **1968**, *12*, 37−47.

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with a Varian MAT 311-A instrument (EI spectra) and with a Varian MAT FS-90 instrument (CI spectra). Melting points were determined in sealed capillaries and are not corrected. Elemental analysis were provided by the Microanalytic Laboratory of the Technical University at Munich.

Synthesis of the Compounds $(N_3)_{2-a}(R)_aGa[(CH_2)_3NMe_2]_{1-a}$ (1a–c: R = CH_3, ^tBu; a = 0, 1). The compounds **1a–c** were synthesized according to the procedure for the synthesis of **1c** (R = N_3; a = 0) outlined below. A 5.0 g (22.1 mmol) amount of freshly sublimed $Cl_2Ga[(CH_2)_3NMe_2]$[8a] was dissolved in 30 mL of dry toluene and added slowly to a slurry of 5.73 g (88.2 mmol) of NaN_3 suspended in 20 mL of toluene at −78 °C with vigorous stirring. After being warmed up to room temperature, the reaction mixture was heated to 70−90 °C for 12 h to complete the reaction. After filtration, removal of the solvent and purification by short-path distillation (140 °C and 10^{-3} Torr, dynamic vacuum) the product was obtained as colorless viscous liquid (4.5 g; 85%). Selected analytical and spectroscopic data for **1a–c** are as follows.

Characterization Data for $(N_3)(CH_3)Ga[(CH_2)_3NMe_2]$ (1a): Colorless viscous liquid. ^1H NMR (C_6D_6, 25 °C; δ): −0.28 (s, 3H, $GaCH_3$); 0.47 (t, 2H, $GaCH_2$); 1.79 (m, 2H, $-CH_2-$); 2.44 (s, 6H, NCH_3); 2.52 (t, 2H, NCH_2). ^{13}C NMR (THF-d_8, 25 °C; δ): −10.6 ($GaCH_3$); 6.2 ($GaCH_2$), 23.4 ($-CH_2-$); 45.5 (NCH_3); 63.8 (NCH_2). Anal. Calcd for $C_6H_{15}N_4Ga$ (M_r = 212.93): C, 33.84; H, 7.10; N, 26.31. Found: C, 33.79; H, 7.09; N, 26.79.

Characterization Data for $(N_3)(^tBu)Ga[(CH_2)_3NMe_2]$ (1b): Pale yellow viscous liquid. ^1H NMR (C_6D_6, 25 °C; δ): 0.44 (s, broad, 2H, $GaCH_2$); 1.17 (s, 9H, CH_3); 1.26 (m, 2H, $-CH_2-$); 1.39 (m, 2H, NCH_2); 1.69 (s, broad, 3H, NCH_3); 1.92 (s, broad, 3H, NCH_3). ^{13}C NMR (C_6D_6, 25 °C; δ): −1.0 ($GaCH_2$); 19.3 ($-CH_2-$); 20.3 ($-CCH_3$); 26.7 (CCH_3); 40.9 (broad, NCH_3); 43.2 (NCH_3); 60.5 (NCH_2). Anal. Calcd for $C_9H_{21}N_4Ga$ (M_r = 255.01): C, 42.39; H, 8.30; N, 21.97. Found: C, 42.17; H, 8.02; N, 22.05.

Characterization Data for $(N_3)_2Ga[(CH_2)_3NMe_2]$ (1c): Colorless viscous liquid; mp −28(±2) °C. ^1H NMR (C_6D_6, 25 °C; δ): 0.34 (t, 2H, $GaCH_2$); 1.05 (quin, 2H, $-CH_2-$); 1.44 (t, 2H, NCH_2); 1.67 (s, 6H, NCH_3). ^{13}C NMR (C_6D_6, 25 °C; δ): 3.9 ($GaCH_2$); 21.9 ($-CH_2-$); 45.3 (NCH_3); 62.5 (NCH_2). MS (EI, 70 eV): m/z (%) 241 (10) [$(M + 2H)^+$]. Anal. Calcd for $C_5H_{12}N_7Ga$ (M_r = 239.92): C, 25.03; H, 5.04; N, 40.87. Found: C, 25.26; H, 5.11; N, 40.15.

Synthesis of the Compounds $(Et)(N_3)_2Ga$ (2a) and $(Et)(N_3)_2Ga{\cdot}L$ (2c,d: L = thf, H_2N^tBu, py, NC_7H_{13}). A 3.0 g (17.7 mmol) amount of $EtGaCl_2$ was dissolved in 30 mL of dry thf and added slowly to a slurry of 4.6 g (70.7 mmol) of NaN_3 in the same solvent at −78 °C. After being warmed up to room temperature, the reaction mixture was stirred for 12 h to complete the reaction. After filtration and removal of the solvent the analytical pure $EtGa(N_3)_2$ (**2a**) was obtained as white solid in quantitative yield (3.23 g). Traces of thf can be removed by drying in vacuo (10^{-3} Torr) at 50 °C for several hours.

To synthesize **2b–d**, a solution of the respective donor in dry toluene was added slowly to a slurry of $EtGa(N_3)_2$ (**2a**) in toluene at room temperature. After being strirred for 2 days at room temperature, the reaction mixture was filtered and the solvent removed in vacuo. **2b–d** were obtained analytically pure as pale brownish viscous liquids (>80%).

Characterization Data for $(Et)(N_3)_2Ga$ (2a): Mp 93 °C (dec). ^1H NMR (thf-d_8, 25 °C; δ): 0.46 (q, 2H, $GaCH_2$); 1.07 (t, 3H, CH_3). ^{13}C NMR (thf-d_8, 25 °C; δ): 2.6 ($GaCH_2$); 9.5 (CH_3). Anal. Calcd for $C_2H_5N_6Ga$ (M_r = 182.83): C, 13.14; H, 2.76; N, 45.97. Found: C, 13.51; H, 3.37; N, 43.61.

Characterization Data for $(Et)(N_3)_2Ga{\cdot}NC_7H_{13}$ (2b): Pale brownish viscous liquid. ^1H NMR (C_6D_6, 25 °C; δ): 0.62 (q, 2H, $GaCH_2$), 0.96 (m, 6H, CH_2), 1.14 (t, 1H, CH), 1.26 (t, 3H, CH_3), 2.41 (t, 6H, NCH_2). ^{13}C NMR (C_6D_6, 25 °C; δ): 1.1 ($GaCH_2$), 9.5 (CH_3), 19.4 (CH), 24.1 (CH_2), 46.9 (NCH_2). Anal. Calcd for $C_9H_{18}N_7Ga$ (M_r = 294.01): C, 36.77; H, 6.17; N, 33.35. Found: C, 37.27; H, 6.61; N, 33.21.

Characterization Data for $(Et)(N_3)_2Ga{\cdot}py$ (2c): Pale brownish viscous liquid; mp −24 °C. ^1H NMR (neat, 25 °C; δ): 0.65 (q, 2H, CH_2), 0.88 (t, 3H, CH_3), 7.52 (m, 2H, $-CH_2-$), 7.96 (t, 1H, CH), 8.34 (d, 2H, NCH). ^{13}C NMR (neat, 25 °C; δ): 2.3 ($GaCH_2$), 8.9 (CH_3), 126.7 (m-CH), 142.9 (p-CH), 146.8 (NCH). ^{14}N NMR (neat, 25 °C, line width in parentheses; $\delta(N_3)$): −138.8 (240 Hz), −260 (1400 Hz). Anal. Calcd for $C_7H_{10}N_7Ga$ (M_r = 261.92): C, 32.10; H, 3.85; N, 37.43. Found: C, 32.66; H, 4.15; N, 36.11.

Characterization Data for $(Et)(N_3)_2Ga{\cdot}H_2N^tBu$ (2d): Colorless needles. ^1H NMR (C_6D_6, 25 °C; δ): 0.73 (q, 2H, $GaCH_2$), 0.74 (s, 9H, CCH_3), 1.26 (t, 3H, CH_3), 3.65 (s, broad, 2H, NH_2). ^{13}C NMR (C_6D_6, 25 °C; δ): 4.6 ($GaCH_2$), 9.1 (CH_3), 29.2 (CCH_3), 52.3 (CCH_3). Anal. Calcd for $C_6H_{16}N_7Ga$ (M_r = 255.96): C, 28.66; H, 6.30; N, 38.31; Ga, 27.24. Found: C, 27.92; H, 6.75; N, 38.40; Ga, 27.34.

Synthesis of $Et_2Ga(\mu\text{-}NH_2)(\mu\text{-}N_3)GaEt_2$ (3). A mixture of dry N_2 and NH_3 (100:1) was bubbled through $[Et_2GaN_3]_3$[6] for 7 h at 40 °C using a Schlenk tube (l = 25 cm, ϕ = 25 mm). **3** was obtained as colorless crystals which were collected at the walls of the Schlenk tube in 80% yield (some loss of $[Et_2GaN_3]_3$ due to volatilization).

Characterization Data for 3. ^1H NMR (C_6D_6, 25 °C; δ): 0.35 (q, 2H, CH_2); 0.54 (s, broad, 2H, NH_2); 1.12 (t, 3H, CH_3). ^{13}C NMR (100.5 MHz, C_6D_6, 25 °C; δ): 2.5 ($GaCH_2$); 9.4 (CH_3). MS (CI, isobutene): m/z (%) 315 (11) [$(M + H)^+$]. Anal. Calcd for $C_8H_{22}N_4Ga_2$ (M_r = 313.73): C, 30.63; H, 7.07; N, 17.86; Ga, 44.45. Found: C, 31.08; H, 7.43; N, 18.11; Ga, 42.96.

MOCVD Experiments. The horizontal hot wall quartz tube reactor (l = 45 cm, ϕ = 35 mm), described in detail elsewhere,[9] was kept at 450 °C at a basic pressure of 10^{-6} Torr for 5 h after loading it with the cleaned substrates. Then the precursor reservoir was filled with 0.50 g of the precursors, e.g. $(N_3)_2Ga[(CH_2)_3NMe_2]$ (**1c**) or $[Et_2Ga(N_3)]_3$ (**4**), under inert-gas atmosphere and cooled to −30 °C. The system was evacuated again to 10^{-6} Torr for 1−2 h. During this time the substrates were heated to 100−150 °C above the deposition temperature for 30 min (to liberate any condensed precursor compounds). After this the temperature of the oven was allowed to stabilize at the desired value (350−700 °C). The temperature of the bubbler was then adjusted between 70 and 100 °C allowing the precursors to sublime through the hot zone of the reactor at pressures of 1.9×10^{-4} to 3.0×10^{-4} Torr. In the case of carrier gas experiments and flow conditions, the temperature of the bubbler was kept in the range between 80 and 110 °C at a pressure of $(1.5-1.8) \times 10^{-1}$ Torr at typical flow rates of 30−50 sccm (N_2) and 5−40 sccm (NH_3).

Results and Discussion

A. Synthesis and Properties. The first organogallium azides, e.g. $R_2Ga(N_3)$ (R = CH_3, C_2H_5),[7] already textbook examples,[10] were synthesized by the selective elimination of 1 mol of alkyl chloride from R_3Ga and ClN_3. But the azide group can usually more easily be introduced by salt metathesis with NaN_3. Some authors reported the necessity of phase-transfer catalysts (e.g.

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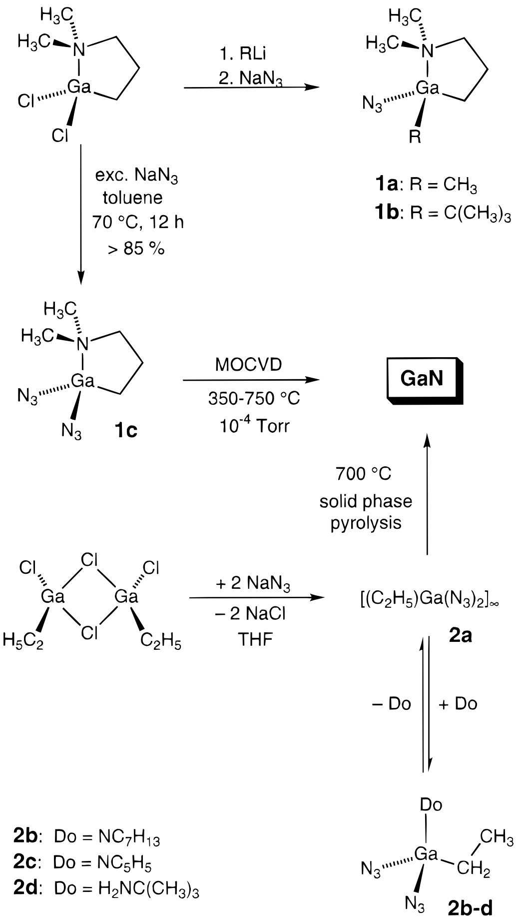
[8] (a) Schumann, H.; Hartmann, U.; Wassermann, W.; Just, O.; Dietrich, A.; Pohl, L.; Hostalek, M.; Lokai, M. *Chem. Ber.* **1991**, *124*, 1113−1119. (b) Fischer, R. A.; Priermeier, T.; Scherer, W. *J. Organomet. Chem.* **1993**, *459*, 65−71.

[9] Fischer, R. A.; Kleine, M.; Lehmann, O.; Stuke, M. *Chem. Mater.* **1995**, *7*, 1836−1843.

[10] Taylor, M. J.; Brothers, P. J. In *Chemistry of Aluminum, Gallium, Indium and Thallium*; Downs, A. J., Ed.; Chapman & Hall: London, 1993; p 191.

Scheme 1. Synthesis of the Organogallium Azides $(N_3)_{2-a}(R)_aGa[(CH_2)_3NMe_2]_{1-a}$ (1a–c: R = CH_3, ^tBu; a = 0, 1), $(Et)(N_3)_2Ga$ (2a), and $(Et)(N_3)_2Ga{\cdot}L$ (2b–d: L = thf, H_2N^tBu, py, NC_7H_{13})



dibenzo-18-crown-6) in these cases.[11] However, we found that this is not generally mandantory. The intramolecular donor stabilized gallium azides $(N_3)_{2-a}(R)_aGa[(CH_2)_3NMe_2]_{1-a}$ (**1a**–**c**: R = CH_3, ^tBu; a = 0, 1; Scheme 1) were obtained in high yields (>80%) by the treatment of the respective organogallium chloride with a suspension of excess dry sodium azide in toluene at elevated temperatures of 70–90 °C for at least 12 h. Only incomplete substitution occurs at room temperature. The new compounds are colorless to pale yellowish more or less viscous liquids which can be purified by short path distillation (ca. 100–140 °C and 10^{-3} Torr). After this procedure only trace residues of Cl (<10 ppm) were found in test samples.

1a–**c** and their "open chain" congeners $(Et)(N_3)_2Ga{\cdot}L$ (**2b**–**d**: L = thf, H_2N^tBu, py, NC_7H_{13}; Scheme 1) were characterized by thermal analysis (TGA-MS and DSC, atmospheric pressure, inert gas). *Exothermic* decomposition occurs around 300 °C (e.g. 270 °C for **1c**; see the DSC diagram of Figure 1), giving a dark residue. From this exothermic behavior it follows that these azide compounds may, in principle, detonate under certain conditions. However, **1a**–**c** and **2b**–**d** are not explosive upon heating, mechanical impact, or any other usual laboratory conditions (e.g. distillation, exposure to UV light, MOCVD experiments, contact with air and moisture). This thermal stability is somewhat special, because the empirical lower limit for the explosivity of covalent azides is about 25 weight % of azide nitrogen[12] (e.g. **1c**: N, 41 weight %). The presence of a Lewis base donor contributes to the thermal stability and apparent nonexplosivity of the compounds. This corresponds well with the behavior of $Ga(N_3)_3$ and its N-base adducts. $Ga(N_3)_3$, a white and insoluble solid, probably a coordination polymer,[6,13] detonates when heated suddenly above 300 °C or when attempts are made to sublime it at 180 °C and 10^{-5} Torr and is also sensitive to intense shock. The respective monomeric N-base adducts $Ga(N_3)_3(L)_n$ (L = NEt_3, n = 1; L = py, n = 3) do not detonate upon heating or mechanical impact.[13] The recently reported related compound $[2,6\text{-}(Me_2NCH_2)_2C_6H_3]Ga(N_3)_2$, exhibiting a *penta*coordinated Ga center, is even more stable and does not decompose up to 600 °C.[5]

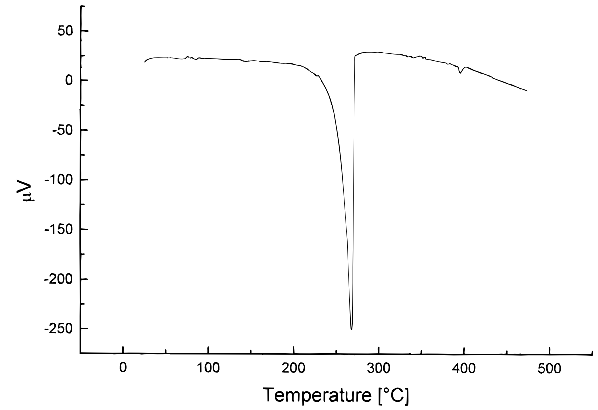


Figure 1. Differential scanning calorimetry (DSC) diagram of $(N_3)_2Ga[(CH_2)_3NMe_2]$ (**1c**).

As compared with **1a**–**d**, the synthesis of $EtGa(N_3)_2$ (**2a**) is slightly different because of its poor solubility in other solvents than thf. Adding a toluene solution of $EtGaCl_2$ to a toluene suspension of sodium azide at −78 °C gives a insoluble bulky gel. In thf as solvent, however, the reaction is completed within a few hours at room temperature. After filtration, removal of the solvent and drying in high vacuo **2a** is obtained as white solid, which is insoluble in toluene and other noncoordinating hydrocarbon solvents (hexane, dichloromethane), indicating its polymeric nature. **2a** *explodes* when heated rapidly above 281 °C (>10 °C/s), but interestingly it melts with very slow decomposition (N_2 liberation) at 93 °C. Lewis base adduct stabilized derivatives of **2a**, namely $EtGa(N_3)_2(L)$ (**2b**–**d**), were synthesized by adding the respective nitrogen donor compound (L = H_2H^tBu, py, NC_7H_{13}) to a toluene suspension of **2a** at −78 °C and stirring the reaction mixture for some time. **2b**–**d** are obtained as pale brownish viscous liquids which are soluble in all polar solvents, toluene, and benzene. Interesting aspects of the reactivity of **1** and **2** with ammonia and the synthesis and properties of compound $Et_2Ga(\mu\text{-}NH_2)(\mu\text{-}N_3)GaEt_2$ (**3**) from $[Et_2Ga(N_3)]_3$ (**4**) (Scheme 3) are discussed in section C.

B. Spectroscopic Characterization. $\nu(N_3)$ IR Spectroscopy. The IR spectra of **1**–**3** exhibit the

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(11) Neumayer, D. A.; Cowley, A. H.; Decken, A.; Jones, R. A.; Lakhotia, V.; Ekerdt, J. G. *J. Am. Chem. Soc.* **1995**, *117*, 5893–5894.

(12) Tornieporth-Oetting, I. C.; Klapötke, T. M. *Angew. Chem.* **1995**, *107*, 559–568 and references cited therein.

(13) Fischer, R. A.; Miehr, A.; Herdtweck, E.; Mattner, M. R.; Ambacher, O.; Metzger, T.; Born, E.; Weinkauf, S. Manuscript in preparation. The compound $(N_3)_3Ga(NC_5H_5)_3$ and related derivatives were characterized by single-crystal X-ray diffraction and serve also as a single molecule sources of GaN.

Table 1. Infrared Data (cm^{-1}) for the Compounds 1−4 ($R = [(CH_2)_3NMe_2]$)

compd	no.	solvent	$\nu(N_3)_{asym}$	$\nu(N_3)_{sym}$
$(N_3)Ga(CH_3)(R)$	**1a**	benzene	2082 vs	1291 w
$(N_3)Ga(^tBu)(R)$	**1b**	toluene	2082 vs	1290 w
$(N_3)_2Ga(R)$	**1c**	toluene	2111 vs	1342 m
			2091 vs	1291 m
		neat	2110 vs	1345 s
			2090 vs	1291 s
		acetonitrile	2115 vs	1347 m
			2093 vs	1297 m
		thf	2111 vs	1345 w
			2090 vs	1296 w
		toluene/py	2102 vs	1345 m
			2085 vs	1295 m
$(Et)Ga(N_3)_2$	**2a**	Nujol	2111 s, br	1377 s
			2000 m, br	1272 s
		thf	2118 m	1344 m
			2083 vs	1294 m
$(Et)Ga(N_3)_2(NC_7H_{13})$	**2b**	toluene	2109 s	1343 w
			2088 vs	1290 w
$(Et)Ga(N_3)_2(py)$	**2c**	benzene	2108 vs	1342 s
			2089 vs	1291 s
		thf	2109 vs	1343 m
			2089 vs	1294 m
		acetonitrile	2112 vs	1345 m
			2092 vs	1295 m
$(Et)Ga(N_3)_2(H_2N^tBu)$	**2d**	toluene	2102 vs	1342 w
			2090 vs	1288 w
$[Et_2GaN_3]_3$	**4**	neat	2108 vs	1241 m
$(\mu-NH_2)(\mu-N_3)[Et_2Ga]_2$	**3**	toluene	2082 vs	1243 w

Table 2. Chemical Shifts and Line Widths (Hz) of 1c (Saturated Solution in Toluene-d_8)

(a) ^{14}N NMR

T (K)	$\delta(N_a)$ ($\Delta\nu_{1/2}$)	$\delta(N_b)$ ($\Delta\nu_{1/2}$)	$\delta(N_c)$ ($\Delta\nu_{1/2}$)	$\delta(N_{a+c})$ ($\Delta\nu_{1/2}$)	$\delta(NMe_2)$ ($\Delta\nu_{1/2}$)
217		−131 (1200)	−215 (1200)		
233		−137 (650)	−222 (800)		
250		−139 (320)	−225 (700)		
258		−138 (250)	−226 (720)		
266		−139 (200)	−230 (1000)		
274	−340 (1700)	−138 (150)	−240 (1300)		
282	−330 (1600)	−138 (120)	−255 (1400)		
290		−139 (100)			
298		−139 (90)		−270 (800)	
305		−139 (80)		−270 (770)	
312		−139 (60)		−270 (700)	351 (800)
320		−139 (55)		−270 (570)	351 (700)

(b) ^{15}N NMR

T (K)	$\delta(N_a)$ ($\Delta\nu_{1/2}$)	$\delta(N_b)$ ($\Delta\nu_{1/2}$)	$\delta(N_c)$ ($\Delta\nu_{1/2}$)	$\delta(NMe_2)$ ($\Delta\nu_{1/2}$)
200	−324 (14)	−144 (2.6)	−229 (14)	−356 (7)
213	−324 (40)	−144 (2.4)	−229 (32)	−356 (8)
225	−324 (120)	−144 (2.2)	−229 (120)	−356 (10)
233	−324 (250)	−144 (2.5)	−228 (120)	−356 (17)
266		−144 (2.0)		−356 (8)
298		−144 (2.0)		−356 (9)
327		−139 (2.5)		−351 (8)

expected absorptions of the asymmetric and symmetric modes of covalently bonded *terminal* azide groups.[14] The $\nu(N_3)$ spectra of $(N_3)(R)Ga[(CH_2)_3NMe_2]$ (**1a,b**) are almost identical, which is understandable because of the similarity of the chemical environment of the azide groups in these two compounds. The IR spectrum of the bis(azide) $(N_3)_2Ga[(CH_2)_3NMe_2]$ (**1c**) shows two asymmetric and two symmetric stretching modes for the N_3 units each of about the same intensity, which compares to the respective spectra of $[2,6\text{-}(Me_2NCH_2)_2C_6H_3]Ga(N_3)_2$ (**5**), the only other monomeric gallium compound with a $Ga(N_3)_2$ structural element exhibiting two *terminal* azide groups (Table 1).[5] Compared with **1c**, the azide modes of **5** are somewhat stronger coupled in this pentacoordinated compound, as is indicated by the larger frequency splitting of the vibrational modes (**5**, $\Delta\nu_{asym}(N_3) = 70$ cm^{-1}; **1c**, $\Delta\nu_{asym}(N_3) = 20$ cm^{-1}). The type of the donor ligand and the solvent have a minor effect on the position of the absorption bands (see Table 1; **1c** and **2b,c**). To explain the slightly different position and splitting of the bands for **2a** in thf solution, it seems reasonable to assume that **2a** is higher coordinated in solution; probably a species such as $(N_3)_2(Et)Ga\cdot(thf)_2$ may be present ($\Delta\nu_{asym}(N_3) = 36$ cm^{-1}).

Mass Spectroscopy. The EI as well as the CI spectra of **1c** are complex and exhibit a signal for the molecular ion $[(M + 2H)^+]$ with 10% relative intensity. The fragmentation of **1c** involves a successive loss of N_2 and apparently N and the cleavage of the 3-(dimethylamino)propyl group ($m/z = 86$). Interestingly, $[GaN^+]$ ($m/z = 83$) and $[GaNH^+]$ ($m/z = 84$) species were detected by high-resolution measurements. The EI spectra of the dimeric compound **3** exhibit the molecular ion $[(M + H)^+]$ in 11% relative intensity (correct isotope pattern for a Ga_2 unit). Loss of N_2 and a successive cleavage of the ethyl groups are observed. The Ga_2N_2 core remains without further fragmentation.

^{14}N- and ^{15}N-NMR Spectroscopy. Despite rather broad line widths ^{14}N NMR spectroscopy has proved to be of great value in the study of covalent azides.[15] To gain spin-coupling information ^{15}N-enriched azides had been measured by ^{15}N NMR spectroscopy,[16] providing evidence for a chemical exchange of the azide groups between $[Me_2Ga(N_3)]_3$ molecules. To study the solution dynamics of $(N_3)_2Ga[(CH_2)_3NMe_2]$ (**1c**) with respect to related bimolecular azide exchange processes, ^{14}N and ^{15}N variable-temperature NMR spectra were recorded (saturated solutions in toluene-d_8). The ^{14}N chemical shifts at different temperatures are compiled in Table 2. The signal of N_b (Scheme 2) shows a decrease of the line width with increasing temperature, which is attributed to a reduction of the correlation time. This explanation is based on the assumption of a dominating quadrupolar relaxation mechanism. Rigid (nonexchanging) $Ga-N_a-N_b-N_c$ groups should show a similar behavior for the N_a and N_c signals, the only difference being a much broader peak for N_a due to the adjacent quadrupolar Ga nucleus. Instead a more complicated situation is revealed. The line width of N_c passes a minimum (700 Hz at 250 K), and the resonance strongly shifts with the temperature. A resonance signal for N_a is only detectable in the temperature range from 274 to 282 K. At 290 K none of the two signals, N_a or N_c, is observed. Above this point the signals coalescence. This behavior indicates fluxionality of the azide ligand and can be explained by an *inter*molecular exchange model (Scheme 2a). The chemical environments of N_a and N_c interchange during the transfer of the azid group from

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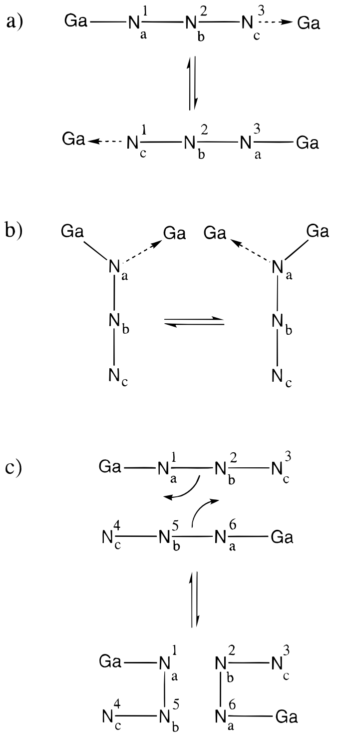
[14] (a) Dehnicke, K.; Wilson, I. L. *J. C. S. Dalton,* **1973**, 1428−1432. (b) Dehnicke, K.; Krüger, N. *Z. Anorg. Allg. Chem.* **1978**, *444*, 71−76. (c) Dehnicke, K.; Röder, N. *J. Organomet. Chem.* **1975**, *86*, 335−345.

[15] (a) Beck, W; Becker, W.; Chew, K. F.; Derbyshire, W.; Logan, N.; Revitt, D. M.; Sowerby, D. B. *J. Chem. Soc., Dalton Trans.* **1972**, 245−247. (b) Geissler, P.; Klapötke, T. M.; Kroth, H.-J. *Spectrochim. Acta Part A* **1995**, *51A*, 1075−1078.

[16] (a) Müller, J. *Z. Naturforsch.* **1978**, *33b*, 993−996. (b) Müller, J. *Ibid.* **1979**, *34b*, 531−535.

Scheme 2. Possible Mechanisms for the Chemical Azide Exchange of 1c in Solution



one Ga center to another. The nucleus N^1 in the former position **a** (directly Ga-bound) becomes the nucleus furthest away from the Ga center to which the azide group is now attached (position **c**). Nucleus N^3 switches from position **c** to **a**. Only nitrogen N^2 stays at position **b** all the time. This leads to a chemical exchange induced line broadening of the resonances N$_a$ and N$_c$. These two signals merge above 290 K. The rate constant of the exchange process at the coalescence temperature can be estimated from the relation $k_{coal} = 2.22\Delta\nu$.[17] The necessary frequency difference of ^{14}N$_a$ and ^{14}N$_c$ can be determined only very roughly because of quadrupolar and chemical exchange broadening. To circumvent this problem ^{15}N NMR spectra of **1c** were recorded. The results are shown in Table 2. The values for ^{15}N$_a$ and ^{15}N$_c$ (−324 and −229 ppm, respectively) lead to a calculated ^{14}N frequency difference of $\Delta\nu = 2750$ Hz. A value of (290 ± 8) K is estimated for the T_{coal}. A rate constant of $k_{290} = 6100$ s^{-1} and an activation barrier of $\Delta G^{\ddagger} = (50.0 \pm 0.5)$ kJ mol^{-1} were calculated from these data. Variable concentration ^{14}N NMR measurements (concentration range from 0.5 to 2.0 mol L^{-1}) show a decrease of the T_{coal} of roughly 10 K on doubling the concentration of **1c**. This behavior is in accordance with an *inter*molecular exchange model, which postulates a simultaneous splitting and forming of Ga−N bonds.

Two alternative mechanisms for the observed exchange of the azide groups may be worth being discussed. Mechanism B (Scheme 2b) involves only μ-N$_a$ bridging units rather than linear bridging groups (μ-N$_a$,μ-N$_c$), which however are postulated by mechanism A (Scheme 2a). Mechanism B cannot explain the observed temperature dependence of the $^{14/15}$N spectra of **1c**. None of the nitrogen nuclei are changing their positions relative to the Ga center during the exchange, as the spectra indicate. Therefore mechanism A is more likely. Of course it cannot be ruled out that parallel to the proposed exchange mechanism A (Scheme 2a) other mechanisms are taking place to some extent (for example Scheme 2c). At least, they are not observed by NMR.

The ^{15}N chemical shift of the NMe$_2$ group does not show a significant variation within the temperature region from 200 to 298 K (Table 2). At 327 K a small upfield shift is observed. The absolute value of this chemical shift does not contain much information about the Ga−N metallacycles, as the resonance of dimethylpropylamine (−352 ppm) is very close to the value measured for **1c**. The intramolecular Lewis base adduct shows however a dynamic behavior, which was analyzed by ^{1}H and ^{13}C NMR as discussed below.

Dynamics of the Intramolecular Base Adduct. The *N*-methyl groups of **1a,b** are diastereotopic if the Ga center is chiral and the adduct ring is closed. Higher temperatures favor the opening of the ring and consecutively the exchange of both *N*-methyl groups (in other words, the inversion at the nitrogen atom). This effect leads to coalescence of the ^{1}H and ^{13}C resonances for the N−CH$_3$ groups and therefore nicely allows the study of the adduct dynamics by variable-temperature NMR.

First, we were interested in the comparison of the influence of the azide group (pseudohalide) with a halide ligand, e.g. Cl, in our compounds. The following parameters were found for (N$_3$)(Me)Ga[(CH$_2$)$_3$NMe$_2$] (**1a**) and (Cl)(Me)Ga[(CH$_2$)$_3$NMe$_2$] (**6a**)[8b] in THF-d_8. THF was chosen as a coordinating solvent for these measurements to suppress any bimolecular effect (involving bridging azide groups) by the solvent basicity. The activation energy $\Delta G^{\ddagger}(183\text{ K}) = 35.7 \pm 0.2$ kJ mol^{-1} of **1a**, resulting from the equation $\Delta G^{\ddagger}_{coal} = T_{coal}[45.67 + 4.58 \log(T_{coal}/(\Delta\nu)]$ [17] with $T_{coal} = 183 \pm 1$ K and $\Delta\nu(\text{NMe}_2) = 240$ Hz, ^{13}C NMR, is significantly lower than $\Delta G^{\ddagger}(248\text{ K}) = 49.0 \pm 0.2$ kJ mol^{-1} of **6a** [$T_{coal} = 248 \pm 1$ K and $\delta\nu(\text{NMe}_2) = 248$ Hz, ^{13}C NMR], showing that the overall effect of the azide substituent as a donor is more significant than that of the Cl ligand in these compounds. The intermolecular azide exchange described in the paragraph before can be coupled with this N−CH$_3$ interconversion. To gain insight into this complex matter, (N$_3$)(^{t}Bu)Ga[(CH$_2$)$_3$NMe$_2$] (**1b**) was selected to study the concentration dependence of the N−CH$_3$ interconversion in various solvents. Compound **1b** dissolved into toluene-d_8 did not show any azide exchange similar to **1c**. Very sharp signals for all N atoms of **1b** were observed by ^{14}N NMR at various concentrations (0.1 to 2 mol L^{-1}) at different temperatures (280−350 K). Again, the N−CH$_3$ interconversion showed a concentration dependence. The coalescence temperature drops when the concentration of **1b** is raised ($T_{coal} = 332$ K, $c = 0.1$ mol L^{-1}; $T_{coal} = 314$ K, $c = 0.75$ mol L^{-1}). Using THF-d_8 as solvent however, no concentration dependence of the N−CH$_3$ interconversion of **1b** is observed at all and the coalescence temperature is much lower: 273 °C ($\Delta G^{\ddagger}(273\text{ K}) = 51.8 \pm 0.5$ kJ mol^{-1}).

These studies clearly show that there is some residual Lewis acidity at the gallium center in the compounds **1a**−**c**. To understand the dynamic properties of the

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(17) Günther, H. In *NMR-Spektroskopie,* 2nd ed.; Thieme: Stuttgart, Germany, 1983; pp 227−231.

Table 3. ^{14}N Chemical Shifts (T = 310 K) and Line Widths (Hz) of Selected Covalent Gallium Azides for Comparison with NaN$_3$

compd	$\delta(N_a)$ ($\Delta\nu_{1/2}$)	$\delta(N_b)$ ($\Delta\nu_{1/2}$)	$\delta(N_c)$ ($\Delta\nu_{1/2}$)	$\delta(N_{a+c})$ ($\Delta\nu_{1/2}$)	solvent
Na(N$_3$)		−128 (22)		−277 (55)	D$_2$O
[(Me)$_2$Ga(N$_3$)]$_3$[a]	−326 (2)	−142 (2)	−227 (2)		toluene-d_8
(N$_3$)(Me)Ga[(CH$_2$)$_3$NMe$_2$] (**1a**)	−325 (500)	−138 (50)	−235 (1200)		thf-d_8
(N$_3$)(^{t}Bu)Ga[(CH$_2$)$_3$NMe$_2$] (**1b**)	−325 (550)	−138 (50)	−232 (1200)		thf-d_8
	−320 (350)	−136 (60)	−233 (70)		toluene-d_8
(N$_3$)$_2$Ga[(CH$_2$)$_3$NMe$_2$] (**1c**)		−139 (80)		−270 (770)	toluene-d_8
		−139 (25)		−226 (720)	thf-d_8
(N$_3$)$_2$Ga(Et)(py) (**2c**)		−139 (240)		−260(1400)	neat

[a] ^{15}N NMR data for a ^{15}N enriched sample (95%); see ref 16b.

NMR spectra it is necessary to postulate the importance of liner bridging azide groups (Scheme 2a). The observation that the monoazides **1a,b** do not show an azide exchange similar to the bis(azide) **1c** is somewhat surprising. The strong concentration dependence of the azide exchange of **1c** may indicate a possible explanation. It could be that a certain degree of association may be necessary to drive the exchange, which is more easily achieved when two azide groups are present per gallium atom. In this respect, the solid-state structures of **1a**−**c** would be interesing to know. However, suitable single crystals could not be grown from these rather low melting compounds, so far.

C. MOCVD Experiments and Reactivity with Ammonia. Deposition of GaN from 1c. We have deposited crystalline hexagonal GaN films from **1a**−**c** and the known compound [Et$_2$Ga(N$_3$)]$_3$ (**4**) on various substrates using a horizontal hot walled tube reactor in vacuo at 10^{-4} Torr or with carrier gases (N$_2$, NH$_3$, H$_2$) at 10^{-1} Torr between 350 and 750 °C. The best results in terms of crystallinity and optical properties, which are communicated in more detail elsewhere,[18] were obtained using precursor **1c** at substrate temperatures of 650−700 °C and 2.0×10^{-4} Torr on sapphire(0001) in the *absence* of carrier gases, particularly without additional NH$_3$. For the discussion given here, it is important to note that the substrate temperature is crucial for the *crystallographic* and *optoelectronic* properties of the grown GaN material only. The new precursors **1a**−**c** as well as the known compound **4** decompose completely around 300 °C (see Figure 1). In these cases, without a special treatment of the substrates used (prenucleation), homogeneous, very smooth films of poorly oriented, almost amorphous GaN were obtained, which already exhibited the correct band gap.[18]

The analysis of the condensable fractions of the exhaust gases and in situ mass spectroscopy of the gas phase during the MOCVD process showed that the alkyl substituent is cleaved from the Ga center predominantly as unsaturated amines, H$_2$C=CHCH$_2$NMe$_2$ and isomers of this. The nitrogen atom of the chelate ring of **1a**−**c** is thus unlikey to be the (major) N-source for GaN growth. Precursor **1c** represents the first liquid and volatile azide type GaN precursor which exhibits *two* azide groups as nitrogen source per gallium atom and decomposes completely at very low temperatures. In contrast to this, the related compound [2,6-(Me$_2$NCH$_2$)$_2$C$_6$H$_3$]Ga(N$_3$)$_2$ (**5**) with a pentacoordinated Ga center was reported to be exceptionally thermally stable and gave no GaN depositions under similar conditions.[5] Thus, **1c** appears to be a very good compromise between a high azide nitrogen content and the way of stabilizing the monomeric structure of an organometallic single molecule precursor for GaN.

Role of Ammonia as Reactive Carrier Gas. Jensen et al. have pointed out that it is not possible to grow high-quality GaN from organogallium azide precursors such as [Et$_2$GaN$_3$]$_3$ (**4**) alone. GaN films with good crystallinity could only be grown from **4** by using NH$_3$ as an additional carrier gas at substrate temperatures above 650 °C.[19] From (macroscopic) kinetic data (growth rates, etc.) it was deduced that the Ga−N bonds preformed in the precursor **4** were not broken during the deposition of GaN. Furthermore it was argued that the improved crystallinity of the GaN films grown from **4** in the presence of ammonia may be due to a then enhanced surface mobility of oligomeric small [GaN]$_x$ units.[19]

We also have grown GaN films from **4** with and without ammonia under similar conditions. From thermal gas effusion experiments of GaN films grown from **4** *without* NH$_3$ it is clear that hydrocarbon fragments (CH$_n$, n = 1−4) are still incorporated in the films grown at temperatures up to 500 °C (maxima of hydrocarbon desorption at 380, 500, and 580 °C). A postdeposition treatment of the thin layers with ammonia at 650 °C as well as deposition in the presence of ammonia leads to a significant decrease in hydrocarbon desorption. However, those samples exhibit a high NH$_x$ content, which desorbs at 700 °C. (The maximum oxygen desorption is found at about 400 °C, and goes along with the maximum desorption of the hydrocarbon species.)[20] From these measurements, and comprehensive studies on a variety of MOCVD-deposited group III nitrides[20] from classic precursors, it is clear that ammonia has complex effects on the quality of the GaN films grown from trimeric single sources such as **4**.

To improve the understanding of the role of ammonia on a molecular level we started to study systematically the reactivity of the organogallium azides **1**, **2**, and especially **4** with ammonia. Pure liquid **4** reacts with excess ammonia (diluted in N$_2$; 1:100) to give a new crystalline compound Et$_2$Ga(μ-NH$_2$)(μ-N$_3$)GaEt$_2$ (**3**). The analytical properties agree with a structure depicted in Scheme 3.

This compound is analogous to the aluminum amide intermediates described by Interrante et al. during the pyrolytic decomposition of alkylaluminum and ammonia

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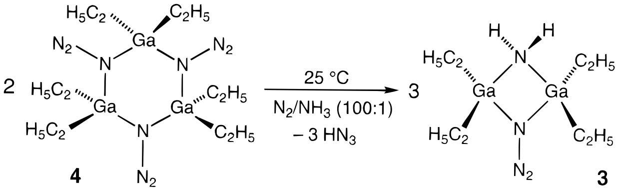
(18) Miehr, A.; Ambacher, O.; Metzger, T.; Born, E.; Fischer, R. A. *Chem. Vap. Deposition*, in press.

(19) Ho, K.-L.; Jensen, K. F.; Hwang, J.-W.; Gladfelter, W. L.; Evans, J. F. *J. Cryst. Growth* **1991**, *107*, 376−380.

(20) Miehr, A. Dissertation, Technische Universität München, 1996.

Scheme 3. Synthesis of $Et_2Ga(\mu\text{-}NH_2)(\mu\text{-}N_3)GaEt_2$ (3)



to AlN.[21] Therefore the described dimer **3** is thought to represent one of the first steps to form GaN from $[Et_2GaN_3]_3$ (**4**) and ammonia. From this finding, it follows that similar deoligomerization steps of **4** introducing NH_2 bridging units may also be involved during MOCVD growth of GaN from **4** and NH_3. Some Ga−(μ-N_3)−Ga bond splitting, not detected by the kinetic investigations, could occure at least to some extent. It may be that the nucleation of GaN growth from **4** benefits from this partial ammonolysis and deoligomerization, and by this the degree of crystallographic orientation and quality of the GaN layers is increased.

Interestingly, the effect of ammonia on our monomeric GaN precursor **1c** is rather different. From the analysis of the rocking curves of the 002 reflection of the GaN films grown from **1c** on sapphire, it is deduced that the crystallographic orientation of the films grown from **1c** with ammonia is poorer than those grown without ammonia.[18] Probably, ammonia leads to some *oligomerization* of the monomeric **1c** under growth conditions, which represents the opposite effect compared to **4**. Investigating the reactivity of **1c** with ammonia we found that **1c** as well as the other bis(azides) **2a**−**c** react spontaneously with ammonia even at low temperatures in solution (−78 °C), giving white solids that are insoluble in all common solvents and do not exhibit azide absorptions in the IR spectra (Nujol mull). By treating **2a** with a less reactive amine ($^tBuNH_2$), we could isolate the respective base adduct **2d** as colorless needles. Upon melting and heating of this primary alkylamine adduct of **2a** in vacuo, HN_3 is liberated.

These findings show that it is necessary to study in detail the chemistry of ammonia with organogallium azides in order to obtain optimized single source precursors based on azide derivatives for low-temperature growth of perfectly oriented GaN.

Conclusions

We have shown that the conception of intramolecularly base adduct stabilization, which was introduced by Schumann et al. for alternative group III precursors for GaAs MOCVD,[8a] can be further extended toward a new type of nitrogen-rich GaN single source precursors. MOCVD experiments gave good results in terms of crystallinity and physical properties. The stabilizing effect of the chelating ligand allows the use of compounds with a high azide nitrogen to gallium ratio without increasing the inherent explosion danger of the azides. The handling of these novel precursors to obtain good quality GaN is much easier than that of the binary system $GaEt_3/NH_3$. Taking together all the results on the reactivity and dynamic properties of the organogallium azides reported in this study, it is rather likely that in the first step of the reaction of those azides with amines, especially with ammonia, a base adduct is formed. Ammonolysis under formation of some mixed bridged gallium amido−azide species similar to $Et_2Ga(\mu\text{-}NH_2)(\mu\text{-}N_3)GaEt_2$ (**3**) may occur in due course. Because of the preferential reaction of the azide group with ammonia there is reason to conclude that under such conditions the azide group is probably not playing the dominant role as N-source for GaN growth as previously has been suggested.

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[21] (a) Sauls, F. C.; Czekaj, C. L.; Interrante, L. V. *Inorg. Chem.* **1990**, *29*, 4688−4692. (b) Hurley, W. J.; Interrante, L. V.; Marchetti, P. S.; Maciel, G. E. *Chem. Mater.* **1995**, *7*, 1361−1368.