Intramolecular, Metallacyclic Organoaluminium, -gallium and -indium Addition Compounds
Crystal Structure of 1-Galla-5-azabicyclo[3.3.3]undecane

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Intramolecularly base-stabilized four-coordinated metallacyclic organoaluminium, -gallium, and -indium compounds $C_5H_{10}Al(CH_2)_3NMe_2$ (4), $C_4H_8Ga(CH_2)_3NMe_2$ (5), $C_5H_{10}Ga(CH_2)_3NMe_2$ (6), $C_5H_{10}GaCH_2CH(Me)CH_2NMe_2$ (7), $C_4H_8Ga(CH_2)_4NMe_2$ (8), $C_5H_{10}Ga(CH_2)_4NMe_2$ (9), $EtAl[(CH_2)_3]_2NMe$ (10), $MeGa[(CH_2)_3]_2NMe$ (11), $EtGa[(CH_2)_3]_2NMe$ (12), $MeIn[(CH_2)_3]_2NMe$ (13), and $MeIn(CH_2)_3N(Me)CH_2CH_2N(Me)(CH_2)_2CH_2$ (14) have been synthesized by the reaction of [3-(dimethylamino)propyl]aluminium dichloride (1), [3-(dimethylamino)propyl]gallium dichloride (2), [3-(dimethylamino)-2-methylpropyl]gallium dichloride (3), or [4-(dimethylamino)butyl]gallium dichloride with the respective bis-Grignard reagents or by the reaction of the organometal dichlorides $RMCl_2$ with bis[3-(chloromagnesio)propyl]methylamine or with *N,N'*-bis[3-(chloromagnesio)propyl]-*N,N'*-dimethylethylenediamine. Aluminium or gallium trichloride reacts with tris[3-(chloromagnesio)-propyl]amine to give $Al[(CH_2)_3]_3N$ (15) and $Ga[(CH_2)_3]_3N$ (16). The ^1H-, ^{13}C-NMR and mass spectra of the new compounds as well as the X-ray crystal structure of 16 are discussed. 4, 6, and 12 have been tested successfully as MOVPE precursors.

Group III/V semiconductors are of great interest in the optoelectronic industry because of their utility in digital high speed devices[1]. The production of such semiconducting layers can be achieved by vapor phase epitaxy (MOVPE) by using organometallic compounds as source materials[2-5]. In general, a group III trialkyl compound, like trimethylgallium or triethylindium, is treated with a group V hydride, like PH_3 or AsH_3, at 600–700°C to give the respective III/V product as illustrated in the following equation for the case of GaAs.

$$(CH_3)_3Ga + AsH_3 \longrightarrow GaAs + 3\ CH_4$$

However, owing to their limited chemical and thermal stability, the commonly used group III precursors cause difficulties during the epitaxial process. Very often formation of alkoxy impurities due to traces of oxygen is observed, and even spontanous decomposition of the source material may occur. In addition, some compounds like solid trimethylindium require heating of the bubbler and the gas lines in order to overcome evaporation problems.

By the application of intermolecular adducts like solid $Me_3Ga \cdot NMe_3$ or $Me_3In \cdot PEt_3$ as source materials such side reactions can be reduced drastically; but even these precursors of significantly enhanced thermal stability cause evaporation problems[6,7]. The use of the concept of intramolecular coordination, however, has been expected to yield monomeric volatile compounds which are liquids at room temperature or very low melting solids.

Recently, we have reported on the synthesis and characterization of some novel intramolecularly base-stabilized gallium and indium compounds with the bidentate 3-(dimethylamino)propyl and 4-(dimethylamino)butyl ligands as well as on initial results in MOVPE[8-10]. In this paper we report on our detailed studies on metallacyclic compounds of aluminium, gallium and indium.

Synthesis and Properties

[3-(Dimethylamino)propyl]lithium or [3-(dimethylamino)-2-methylpropyl]lithium, obtained from 3-(dimethylamino)propyl chloride or 3-(dimethylamino)-2-methylpropyl chloride and lithium powder, react with equimolar amounts of aluminium trichloride or gallium trichloride in ether at −78°C to room temperature to yield the new monoorganometal dichlorides [3-(dimethylamino)propyl]aluminium di-

$$MCl_3 + LiCH_2CH_2CH_2NMe_2 \xrightarrow[-LiCl]{Et_2O} Cl_2MCH_2CH_2CH_2NMe_2$$

1: M = Al

2: M = Ga

$$GaCl_3 + LiCH_2CH(CH_3)CH_2NMe_2 \xrightarrow[-LiCl]{Et_2O} Cl_2GaCH_2CH(CH_3)CH_2NMe_2$$

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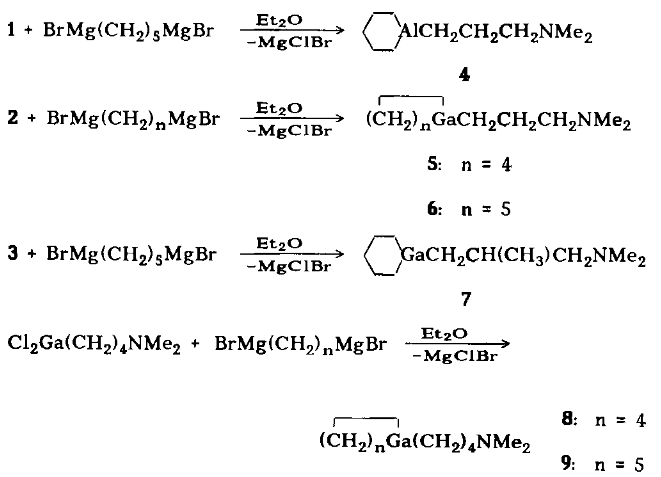
chloride (**1**), [3-(dimethylamino)propyl]gallium dichloride (**2**), and [3-(dimethylamino)-2-methylpropyl]gallium dichloride (**3**) as colorless viscous oils.

The further reaction of **1**, **2**, or **3** with the bis-Grignard reagent of 1,4-dibromobutane or 1,5-dibromopentane affords the metallacycles **4**–**7** in high yields as colorless almost air-stable liquids. The reaction of [4-(dimethylamino)-butyl]gallium dichloride, prepared by hydrogallation of 4-(dimethylamino)-1-butene with dichlorogallane[9], with 1,4-bis(bromomagnesio)butane or 1,5-bis(bromomagnesio)pentane results in the formation of 1-[4-(dimethylamino)butyl]-1-gallacyclopentane (**8**) or 1-[4-(dimethylamino)butyl]-1-gallacyclohexane (**9**).


4

5: n = 4

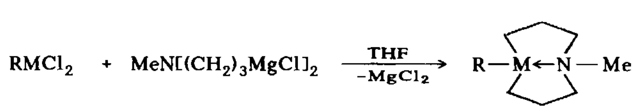
6: n = 5

7

8: n = 4

9: n = 5

The treatment of ethylaluminium or ethylgallium dichloride as well as of methylgallium or methylindium dichloride with bis[3-(chloromagnesio)propyl]methylamine in 1:1 molar ratio in THF gives the corresponding 1-metalla-5-aza-cyclooctanes **10**–**13**. In contrast to the ethyl compounds **10** and **12**, which are liquids at room temperature, the methyl compounds **11** and **13** are low-melting solids.

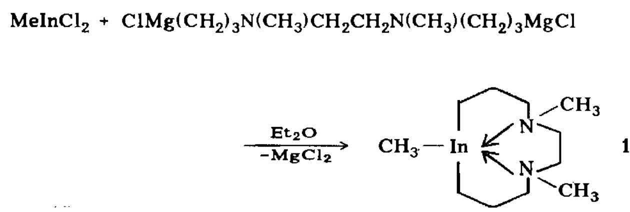

10: R = Et M = Al

11: R = Me M = Ga

12: R = Et M = Ga

13: R = Me M = In

The reaction between methylindium dichloride and *N,N'*-bis[3-(chloromagnesio)propyl]-*N,N'*-dimethylethylenediamine in ether gives **14** as a colorless liquid.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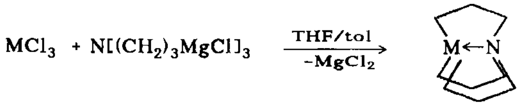
The bicyclic compounds **15** and **16** are prepared from the corresponding metal trichlorides and tris[3-(chloromagnesio)propyl]amine in THF/toluene. In order to avoid side reactions or polymerization, both compounds are added simultaneously over a period of three hours to toluene at elevated temperature. Under these conditions the reaction proceeds smoothly to give **15** and **16** in high yields as low-melting solids. Needle-shaped crystals of **16** are obtained after repeated sublimation.


15: M = Al

16: M = Ga

All substances described above are either liquids or low-melting solids and show a high solubility in common non-polar solvents like hydrocarbons and ethers. Water or protic solvents like methanol cause their slow decomposition.

Both, the ^{1}H- and ^{13}C-NMR spectra of the new compounds show the expected signals. In the mass spectra no fragments with a mass higher than that of the respective molecular ion are observed which agrees well with the proposed monomeric molecular unit.

Molecular Structure

The molecular structure of **16**, which crystallizes in the rhombohedral space group *R*3*c*, has been determined by X-ray diffraction[11] (data in Tables 1–3). Figure 1 shows an ORTEP[12] plot with the atom numbering scheme and Figure 2 an ORTEP[13] drawing of **16** in the unit cell.

16 consists of discrete monomeric units. The gallium atom is surrounded trigonal-monopyramidally by three methylene groups and the amine nitrogen. It is very remarkable that the gallium atom lies in the center of the plane formed by the three methylene groups because so far, in comparable triorganogallium–amine complexes which are even free of steric strain, gallium has been found to be coordinated in a

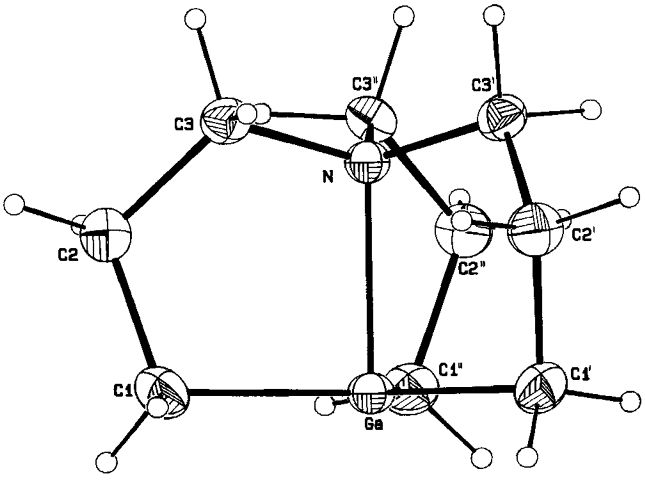


Figure 1. Molecular structure of **16** with atomic numbering scheme

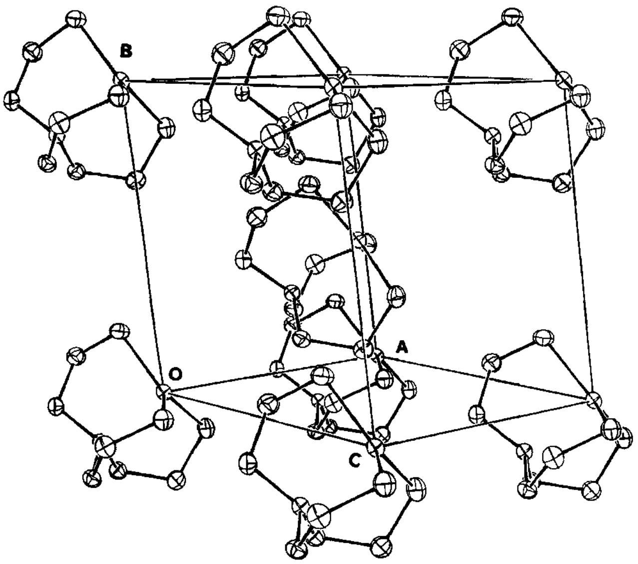


Figure 2. ORTEP drawing of **16** in the unit cell

distorted tetrahedral fashion[14-16]. The electron deficiency of the metal is balanced by the intramolecular coordinative bonding of the nitrogen atom situated at the apex of the pyramid. Due to the ring strain, the Ga–N distance in **16** (209.5 pm) is somewhat longer than the sum of the covalent radii of Ga and N (195 pm)[17], but shorter than in pure donor-acceptor complexes like $Me_3Ga \cdot NMe_3$ [220(3) pm][14] or $Me_3Ga \cdot$[urotropine] [214(2) pm][15]. The distance between the gallium atom and the nitrogen atom of the neighboring molecule is 409 pm, thus an intermolecular donor-acceptor interaction can be ruled out. In spite of this large distance which should allow a nucleophilic attack from the sterically unprotected side of the pyramid, the molecule is rather stable against moisture and air.

Table 1. Crystal and data collection parameters of **16**[a]

Formula $C_9H_{18}GaN$; molecular mass 209.97 g/mol; cell parameters a = 787.7(1) pm, α = 95.099(5)°; cell volume V = 482.6(1) 10^{-30} m^3; Z = 2; calculated density 1.44 g/cm^3; linear absorption coefficient 26.96 cm^{-1}; F(000) 220; crystal system rhombohedral (hexagonal setting); space group R3c; crystal size 0.65 x 0.22 x 0.14 mm^3; Enraf-Nonius CAD 4 four circle diffractometer; radiation MoK_α, λ= 71.069 pm; monochromator graphite crystal; experimental temperature 139(5) K; 2Θ range $1° < 2\Theta < 64°$; hkl boundaries $-11 \rightarrow 11$, $-11 \rightarrow 11$, $-11 \rightarrow 11$; scan technique $\Theta/2\Theta$; scan time variabel, max. 60 s; scan angle $(1.30 + 0.20 \tan\Theta)°$; aperture 2.00 mm; total number of measured reflections 7079, unique reflections 1121, R_{int}= 0.018, observed reflections with $F_o > 4\sigma(F_o)$ 1121; corrections for Lorentz-, polarisation, absorption, and anomalous dispersion effects; max. shift/error (Δ/σ) 0.011; residual electron density max. 0.61, min. -0.58 $e\text{Å}^{-3}$; number of refined parameters 57; $R = \Sigma \, ||F_o| - |F_c|| \, / \, \Sigma \, |F_o| = 0.027$; $R_w = [\Sigma \, w(|F_o| - |F_o|)^2 \, / \, \Sigma \, w \, F_o^2]^{1/2} = 0.024$; $w = 1/[\sigma^2(F_o) + 0.000206 \cdot F_o^2]$

[a] Further details of the crystal structure investigation are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, W-7514 Eggenstein-Leopoldshafen 2, Germany, on quoting the depository number CSD-53203, the names of the authors, and the journal citation.

Table 2. Fractional atomic coordinates and equivalent isotropic thermal parameters [Å^2] of **16** with estimated standard deviations in parentheses. $B_{eq} = 8/3 \cdot \pi^2 \sum_i \sum_j U_{ij} \, a_i^* \, a_j^* \, a_i \, a_j$

Atoms	**x/a**	**y/b**	**z/c**	$\mathbf{B_{eq}}$
Ga	0.5000	0.5000	0.5000	1.38
C1	0.6845(2)	0.4620(2)	0.3462(2)	1.95
C2	0.5859(2)	0.3847(2)	0.1756(2)	2.00
C3	0.4388(2)	0.2535(2)	0.2051(2)	1.65
N	0.3307(2)	0.3307(2)	0.3307(2)	1.32

Table 3. Selected bond distances [pm] and angles and torsion angles [°] of **16** with estimated standard deviations in parentheses

Atoms	**Distances**	**Atoms**	**Distances**
Ga-C1	199.8(2)	C1-C2	153.9(2)
C2-C3	153.0(2)	C3-N	148.6(2)
Ga-N	209.5(2)		
Atoms	**Angles**	**Atoms**	**Angles**
C1-Ga-C1	120.0	C1-C2-C3	100.4(1)
C1-Ga-N	89.2(1)	C2-C3-N	109.8(1)
C3-N-Ga	105.2(1)	C3-N-C3	113.3(2)
Ga-C1-C2	103.7(1)		
Ga-C1-C2-C3	- 41.6(1)	C3-N-Ga-C1	8.3(1)
C1-C2-C3-N	52.2(2)	N-Ga-C1-C2	17.7(1)
C2-C3-N-Ga	- 33.2(1)		

MOVPE Results

Recently it has been established that group III organometallic compounds, which are coordinatively saturated by nitrogen like the compounds discussed in this paper, are promising new precursors for the production of III/V semiconductors by low-pressure as well as by atmosphere *m*etal *o*rganic *v*apor *p*hase *e*pitaxy[10,18-22]. It has been demonstrated that they can be applied together with conventional group V compounds like AsH_3 or PH_3 as well as with new organic group V sources like phenylarsane, *tert*-butylarsane, or *tert*-butylphosphane[23,24].

Due to their non-pyrophoricity and resistance against air and moisture, the liquid or low-melting group III precursors can be easily handled, thus making MOVPE safer.

[*cyclo*-$C_5H_{10}Al$]$(CH_2)_3N(CH_3)_2$ (**4**) and [*cyclo*-$C_5H_{10}Ga$]-$(CH_2)_3N(CH_3)_2$ (**6**) have been demonstrated[22,23] to be inherently free of oxygen-(alkoxy-)containing impurities. They both exhibit a reactivity suitable for large area growth, a chemical stability which provides a long-term stability of the evaporation rate without undesired side-(pre-)reactions or adduct formation with group V sources in the gas phase and a run-to-run reproducibility of epitaxy. No intrinsic nitrogen uptake, no or less intrinsic carbon uptake, and no oxygen incorporation in epilayers occur.

Both **4** and **6** allow the growth of AlGaAs layers, the luminescence properties of which are comparable with the best quoted in the literature. With *tert*-butylarsane (American Cyanamide) as group V precursor, 77-K mobilities of 15000 cm^2/Vs at carrier concentrations of 2×10^{15} cm^{-3} have been measured in AlGaAs layers grown under low-pressure conditions (10–20 hPa) at 700°C growth temperature.

With highly purified **6** and with AsH_3 (Phönix Plus) as group V source 77-K Hall mobilities of more than 50000 cm^2/Vs at a carrier concentration of 8×10^{14} cm^{-3} have been observed for GaAs grown under routine conditions at 600°C growth temperature with low-pressure MOVPE (10–20 hPa).

In GaAs grown from **12** and AsH_3 at 20 hPa and 600°C growth temperature a 300-K mobility of 7200 cm^2/Vs and a 77-K mobility of 48000 cm^2/Vs at carrier concentrations in the low 10^{15}-cm^{-3} range have been measured.

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Experimental

All reactions were carried out in dry, oxygen-free argon by using Schlenk tubes. The solvents used were dried and freed of oxygen with $LiAlH_4$ or Na/benzophenone and were distilled prior to use. – Elemental analyses: Perkin-Elmer 240 C CHN Analyzer, determination of Ga and In with a Perkin-Elmer 2380 Atomic Absorption Spectrophotometer. – MS: Varian MAT 311 A. – NMR: Bruker WH 270 at 270 MHz (^{1}H) and 67.93 MHz (^{13}C).

The starting materials were prepared according to literature procedures. The monoorganometal dichlorides were obtained either from ethyl chloride and aluminium turnings ($EtAlCl_2$[25]), by alkylation of gallium trichloride with tetraethyl- or tetramethylsilane ($EtGaCl_2$[26], $MeGaCl_2$[27]), or by a redistribution reaction of dimethylindium chloride and indium trichloride ($MeInCl_2$[28]). Dichlorogallane[29] was prepared from gallium trichloride and trimethylsilane. [4-(Dimethylamino)butyl]gallium dichloride[9] was prepared by hydrogallation of 4-(dimethylamino)-1-butene[30]. The lithium reagents[31,32] used were synthesized from the corresponding chlorides and lithium powder, and the bis-Grignard reagents[33–36] were obtained by the reaction of the corresponding dichlorides with magnesium turnings.

[3-(Dimethylamino)propyl]aluminium Dichloride (**1**): 200 g (1.65 mol) of 3-(dimethylamino)propyl chloride was slowly added at room temp. to a stirred suspension of 80.2 g (3.3 mol) of magnesium turnings in 1200 ml of diethyl ether. After the addition, the reaction mixture was then refluxed for 2 h. 240 g (1.8 mol) of aluminium trichloride dissolved in diethyl ether was added at 0°C and the resulting suspension refluxed with vigorous stirring for 2 h. After cooling to room temp., the reaction mixture was filtered and the ether evaporated in vacuo. Subsequent distillation of the residue gave **1** as a colorless liquid; yield 205.3 g (68%), b. p. 200°C/0.2 hPa. – ^{1}H NMR (C_6D_6, 20°C): δ = 0.54 (t, 2H, CH_2Al), 1.50 (quint, 2H, CH_2CH_2N), 1.99 (t, 2H, CH_2N), 2.01 [s, 6H, $(CH_3)_2N$].

[3-(Dimethylamino)propyl]gallium Dichloride (**2**): A suspension of 6.8 g (72.7 mmol) of [3-(dimethylamino)propyl]lithium in 400 ml of diethyl ether was slowly added to a stirred solution of 12.8 g (72.7 mmol) of gallium trichloride in 500 ml of ether at −78°C. After the addition, the reaction mixture was stirred at room temp. for 12 h. The main part of the ether was removed in vacuo, and the remaining suspension was filtered over a frit to remove the lithium chloride. The resulting clear solution was evaporated at room temp.; **2** remains as a viscous, colorless liquid. The crude product was not further purified and subsequently transformed into compound **4**; yield 11.7 g (71%). – ^{1}H NMR (C_6D_6, 20°C): δ = 0.47 (t, 2H, CH_2Ga), 1.59 (t, 2H, CH_2N), 1.75–2.15 (m, 2H, CH_2CH_2N), 1.98 [s, 6H, $(CH_3)_2N$]. – ^{13}C-NMR (C_6D_6, 20°C): δ = 8.8 (s, CH_2Ga), 22.0 (s, CH_2CH_2N), 45.1 [s, $(CH_3)_2N$], 61.4 (s, CH_2N).

$C_5H_{12}Cl_2GaN$ (226.8)	Calcd.	C 26.48 H 5.33 N 6.17
	Found	C 26.33 H 5.28 N 6.34

[3-(Dimethylamino)-2-methylpropyl]gallium Dichloride (**3**): A solution of 3.4 g (32.1 mmol) of [3-(dimethylamino)-2-methylpropyl]lithium in 350 ml of ether was added to a stirred solution of 5.6 g (32.1 mmol) of gallium trichloride in 250 ml ether at −78°C. After the addition, the reaction mixture was stirred at room temp. for 12 h and decanted from lithium chloride. After removal of the solvent in vacuo, **3** was obtained as a colorless oil. The crude product was not further purified and subsequently used to synthesize compound **5**; yield 5.5 g (70%). – ^{1}H NMR (C_6D_6, 20°C): δ = 0.02 (d, 2H, CH_2Ga), 0.87 (d, 3H, CH_3CH), 1.39–1.68 (m, 1H, $CH_3C\mathit{H}$), 1.81–2.18 (m, 2H, CH_2N), 2.02 [s, 6H, $(CH_3)_2N$]. – ^{13}C NMR (C_6D_6, 20°C): δ = 18.7 (s, CH_2Ga), 22.4 (s, $\mathit{C}H_3CH$), 29.4 (s, $CH_3\mathit{C}H$), 46.7 [s, $(CH_3)_2N$], 69.0 (s, CH_2N).

$C_6H_{14}Cl_2GaN$ (240.8)	Calcd.	C 29.93 H 5.86 N 5.82
	Found	C 30.02 H 5.93 N 6.04

1-[3-(Dimethylamino)propyl]-1-aluminacyclohexane (**4**): 27.8 g (0.10 mol) of 1,5-dibromopentane was slowly added at room temp. to a stirred suspension of 9.72 g (0.40 mol) of magnesium turnings in 100 ml of diethyl ether. After the addition, the reaction mixture was refluxed for 2 h and filtered after cooling to room temp. The resulting clear Grignard solution and a solution of 16.1 g (90 mmol) of [3-(dimethylamino)propyl]aluminium dichloride in 100 ml of diethyl ether were added simultaneously to 100 ml of ether at room temp. with vigorous stirring. After the addition was completed, the reaction mixture was stirred for further 60 min, the ether removed in vacuo, and the residue distilled to give **4** as a colorless liquid; yield 7.9 g (49%), b. p. 98°C/0.6 hPa. – MS (EI, 70 eV): *m/z* (%) = 183 (61) [M^+], 140 (85) [$M^+ - C_3H_6$], 127 (35) [$M^+ - C_4H_7$], 113 (100) [$M^+ - C_5H_{10}$], 99 (27) [$M^+ - C_6H_{12}$], 85 (15) [$M^+ - C_7H_{14}$], 71 (20) [$M^+ - C_8H_{16}$], 58 (62) [$C_3H_8N^+$]. – ^{1}H NMR (C_6D_6, 20°C): δ = 0.28 (t, 2H, CH_2Al), 0.40 (m, 4H, $C\mathit{H}_2CH_2CH_2CH_2C\mathit{H}_2Al$), 1.68–1.80 (m, 4H, $CH_2C\mathit{H}_2CH_2C\mathit{H}_2CH_2Al$), 1.88 to 2.02 (m, 2H, $C\mathit{H}_2CH_2N$), 2.14 [s, 6H, $(CH_3)_2N$], 2.18 (t, 2H, CH_2N), 2.42–2.58 (m, 2H, $CH_2CH_2C\mathit{H}_2CH_2CH_2Al$). – ^{13}C NMR ($C_6D_6$, 20°C) δ = 2.2 (s, CH_2Al), 9.3 (s, $\mathit{C}H_2CH_2CH_2CH_2\mathit{C}H_2Al$), 21.5 (s, $CH_2CH_2CH_2\mathit{C}H_2CH_2Al$), 28.3 (s, $\mathit{C}H_2CH_2N$), 33.5 (s, $CH_2CH_2\mathit{C}H_2CH_2CH_2Al$), 44.4 [s, $(CH_3)_2N$], 63.6 (s, CH_2N).

$C_{10}H_{22}AlN$ (183.3)	Calcd.	C 65.54 H 12.10
	Found	C 65.41 H 12.09

1-[3-(Dimethylamino)propyl]-1-gallacyclopentane (**5**): In analogy to the synthesis of **4**, the reaction of 33.0 g (145 mmol) of **2**, dissolved in 150 ml of diethyl ether, with a solution of the bis-Grignard reagent, prepared from 18.4 g (145 mmol) of 1,4-dibromobutane and 14.1 g (580 mmol) of magnesium turnings in ether, yielded **5** as a colorless liquid; yield 17.5 g (57%), b. p. 81°C/0.01 hPa. – MS (EI, 70 eV): *m/z* (%) = 211/213* (18) [M^+], 182 (10) [$M^+ - C_2H_6$], 155/157* (39) [$M^+ - C_4H_8$], 86 (66) [$C_5H_{12}N^+$], 69/71* (23) [Ga^+], 58 (100) [$C_3H_8N^+$]; *isotope pattern clearly visible. – ^{1}H NMR (C_6D_6, 20°C): δ = 0.55 (m, 2H, $\overline{\mathrm{CH_2CH_2CH_2C}\mathit{H}_2\mathrm{Ga}}$), 0.70 (m, 2H, $\overline{\mathrm{C}\mathit{H}_2\mathrm{CH_2CH_2CH_2Ga}}$), 0.92 (t, 2H, CH_2Ga), 1.75 (m, 2H, $\mathrm{C}\mathit{H}_2\mathrm{CH_2N}$), 1.87 [s, 6H, $(CH_3)_2N$], 1.95 (t, 2H, CH_2N), 2.15 (m, 2H, $\overline{\mathrm{CH_2CH_2C}\mathit{H}_2\mathrm{CH_2Ga}}$), 2.25 (m, 2H, $\overline{\mathrm{CH_2C}\mathit{H}_2\mathrm{CH_2CH_2Ga}}$). – ^{13}C NMR ($C_6D_6$, 20°C): δ = 7.1 (s, CH_2Ga), 10.3 (s, $\overline{\mathrm{CH_2CH_2CH_2}\mathit{C}\mathrm{H_2Ga}}$), 25.0 (s, $\mathit{C}\mathrm{H_2CH_2N}$), 31.1 (s, $\overline{\mathrm{CH_2}\mathit{C}\mathrm{H_2CH_2CH_2Ga}}$), 46.8 [s, $(CH_3)_2N$], 64.6 (s, CH_2N).

$C_9H_{20}GaN$ (212.0) Calcd. C 50.99 H 9.51 Ga 32.88 N 6.60
Found C 50.98 H 9.38 Ga 32.62 N 6.69

1-[3-(Dimethylamino)propyl]-1-gallacyclohexane (**6**): In analogy to the synthesis of **4**, the reaction of 14.1 g (60 mmol) of **2**, dissolved in 150 ml of diethyl ether, with a solution of the bis-Grignard reagent, prepared from 17.3 g (60 mmol) of 1,5-dibromopentane and 5.8 g (240 mmol) of magnesium turnings in ether, yielded **6** as a colorless liquid; yield 8.4 g (60%), b. p. 67°C/0.1 hPa. – MS (EI, 70 eV): *m/z* (%) = 225 (34) [M^+], 182 (51) [$M^+ - C_3H_7$], 155 (38) [$M^+ - C_5H_{10}$], 86 (52) [$C_5H_{12}N^+$], 69 (33) [Ga^+], 58 (100) [$C_3H_8N^+$]. – ^{1}H NMR (C_6D_6, 20°C): δ = 0.72 (t, 2H, CH_2Ga), 0.82–0.98 (m, 4H, $\overline{\mathrm{C}\mathit{H}_2\mathrm{CH_2CH_2CH_2C}\mathit{H}_2\mathrm{Ga}}$), 1.68–1.88 (m, 4H, $\overline{\mathrm{CH_2C}\mathit{H}_2\mathrm{CH_2C}\mathit{H}_2\mathrm{CH_2Ga}}$), 1.95–2.20 (m, 2H, $\mathrm{C}\mathit{H}_2\mathrm{CH_2N}$ and quint, 2H, $\overline{\mathrm{CH_2CH_2C}\mathit{H}_2\mathrm{CH_2CH_2Ga}}$), 2.02 [s, 6H, $(CH_3)_2N$], 2.58–2.72 (m, 2H, CH_2N). – ^{13}C NMR (C_6D_6, 20°C): δ = 6.5 (s, CH_2Ga), 12.8 (s, $\overline{\mathrm{CH_2CH_2CH_2CH_2}\mathit{C}\mathrm{H_2Ga}}$), 25.4 (s, $\mathit{C}\mathrm{H_2CH_2N}$), 28.9 (s, $\overline{\mathrm{CH_2}\mathit{C}\mathrm{H_2CH_2}\mathit{C}\mathrm{H_2CH_2Ga}}$), 32.8 (s, $\overline{\mathrm{CH_2CH_2}\mathit{C}\mathrm{H_2CH_2CH_2Ga}}$), 45.0 [s, $(CH_3)_2N$], 65.2 (s, CH_2N).

$C_{10}H_{22}GaN$ (226.0) Calcd. C 53.14 H 9.81 N 6.19
Found C 53.25 H 9.82 N 6.64

1-[3-(Dimethylamino)-2-methylpropyl]-1-gallacyclohexane (**7**): In analogy to the synthesis of **4**, the reaction of 5.5 g (22.7 mmol) of **3** with 18.5 ml of a bis-Grignard solution of 1,5-dibromopentane in diethyl ether (1.23 mol/l) yielded **7** as a colorless liquid; yield 2.9 g (52%), m. p. –2°C, b. p. 115°C/0.01 hPa. – ^{1}H NMR (C_6D_6, 20°C): δ = 0.39 (m, 2H, CH_2Ga), 0.60 (m, 4H, $\overline{\mathrm{C}\mathit{H}_2\mathrm{CH_2CH_2CH_2}\text{-}\mathrm{C}\mathit{H}_2\mathrm{Ga}}$], 0.88 (d, 3H, $\mathrm{C}\mathit{H}_3\mathrm{CH}$), 1.31 (tq, 1H, $\mathrm{CH_3C}\mathit{H}$), 1.45–1.78 (m, 6H, $\overline{\mathrm{CH_2C}\mathit{H}_2\mathrm{C}\mathit{H}_2\mathrm{C}\mathit{H}_2\mathrm{CH_2Ga}}$), 1.93 and 2.08* [s, 6H, $(CH_3)_2N$], 2.29 (m, 2H, CH_2N). – ^{13}C NMR (C_6D_6, 20°C): δ = 13.5 and 14.1 [s, $\overline{\mathit{C}\mathrm{H_2CH_2CH_2CH_2}\mathit{C}\mathrm{H_2Ga}}$], 18.6 (s, CH_2Ga), 23.1 (s, $\mathit{C}\mathrm{H_3CH}$), 29.6 and 30.0 (s, $\overline{\mathrm{CH_2}\mathit{C}\mathrm{H_2CH_2}\mathit{C}\mathrm{H_2CH_2Ga}}$), 31.6 (s, $\mathit{C}\mathrm{HCH_3}$), 33.6 (s, $\overline{\mathrm{CH_2CH_2}\mathit{C}\mathrm{H_2CH_2CH_2Ga}}$], 45.3 and 48.3* [s, $(CH_3)_2N$], 71.2 (s, CH_2N); *temperature-dependent, one broad signal at the coalescence temperature of 50°C.

$C_{11}H_{24}GaN$ (240.0) Calcd. C 55.04 H 10.07 N 5.83
Found C 54.94 H 10.06 N 6.03

1-[4-(Dimethylamino)butyl]-1-gallacyclopentane (**8**): In analogy to the synthesis of **5**, the reaction of 17.4 g (72.2 mmol) of [4-(dimethylamino)butyl]gallium dichloride, dissolved in 400 ml of diethyl ether, with 67.5 ml of the bis-Grignard solution of 1,4-dibromobutane in ether (1.07 mol/l) at –78°C gave **8** as a colorless liquid; yield 9.4 g (58%), b. p. 140°C/0.01 hPa. – ^{1}H NMR (C_6D_6, 20°C): δ = 0.24–0.55 (m, 10H, CH_2Ga, $\overline{\mathrm{C}\mathit{H}_2\mathrm{CH_2CH_2C}\mathit{H}_2\mathrm{Ga}}$, $\overline{\mathrm{CH_2C}\mathit{H}_2\mathrm{C}\mathit{H}_2\mathrm{CH_2Ga}}$), 1.24–1.77 (m, 4H, $\mathrm{C}\mathit{H}_2\mathrm{CH_2Ga}$, $\mathrm{C}\mathit{H}_2\mathrm{CH_2N}$), 1.86 [s, 6H, $(CH_3)_2N$], 2.20 (t, 2H, CH_2N). – ^{13}C NMR (C_6D_6, 20°C): δ = 9.7 (s, CH_2Ga), 12.1 (s, $\overline{\mathrm{CH_2CH_2CH_2}\mathit{C}\mathrm{H_2Ga}}$], 27.0 and 27.6 (s, $\mathit{C}\mathrm{H_2}\mathit{C}\mathrm{H_2CH_2Ga}$), 34.5 (s, $\overline{\mathrm{CH_2}\mathit{C}\mathrm{H_2}\mathit{C}\mathrm{H_2CH_2Ga}}$), 46.2 [s, $(CH_3)_2N$], 62.6 (s, CH_2N).

$C_{10}H_{22}GaN$ (226.0) Calcd. C 53.14 H 9.81 N 6.19
Found C 52.85 H 9.66 N 6.80

1-[4-(Dimethylamino)butyl]-1-gallacyclohexane (**9**): In analogy to the synthesis of **4**, the reaction of 3.8 g (15.8 mmol) of [4-(dimethylamino)butyl]gallium dichloride, dissolved in 200 ml of diethyl ether, with 12.9 ml of the bis-Grignard solution of 1,5-dibromopentane in ether (1.23 mol/l) gave **9** as a colorless liquid; yield 2.5 g (67%), b. p. 138°C/0.01 hPa. – ^{1}H NMR (C_6D_6, 20°C): δ = 0.49 (t, 2H, CH_2Ga), 0.61 (t, 4H, $\overline{\mathrm{C}\mathit{H}_2\mathrm{CH_2CH_2CH_2C}\mathit{H}_2\mathrm{Ga}}$), 0.39–0.69 (m, 4H, $\overline{\mathrm{CH_2C}\mathit{H}_2\mathrm{CH_2C}\mathit{H}_2\mathrm{CH_2Ga}}$), 1.09–1.30 (m, 4H, $\mathrm{C}\mathit{H}_2\mathrm{CH_2Ga}$, $\mathrm{C}\mathit{H}_2\mathrm{CH_2N}$), 1.85 [s, 6H, $(CH_3)_2N$], 1.99–2.26 (m, 4H, CH_2N, $\overline{\mathrm{CH_2CH_2C}\mathit{H}_2\mathrm{CH_2CH_2Ga}}$). – ^{13}C NMR ($C_6D_6$, 20°C): δ = 9.7 (s, CH_2Ga), 11.7 (s, $\overline{\mathrm{CH_2CH_2CH_2CH_2}\mathit{C}\mathrm{H_2Ga}}$), 26.7 and 27.3 (s, $\mathit{C}\mathrm{H_2}\mathit{C}\mathrm{H_2CH_2Ga}$), 29.8 (s, $\overline{\mathrm{CH_2}\mathit{C}\mathrm{H_2CH_2}\mathit{C}\mathrm{H_2CH_2Ga}}$), 33.9 (s, $\overline{\mathrm{CH_2CH_2}\mathit{C}\mathrm{H_2CH_2CH_2Ga}}$), 46.3 [s, $(CH_3)_2N$], 62.6 (s, CH_2N).

$C_{11}H_{24}GaN$ (240.0) Calcd. C 55.04 H 10.07 Ga 29.04 N 5.83
Found C 54.94 H 10.06 Ga 30.22 N 6.03

1-Ethyl-5-methyl-1-alumina-5-azacyclooctane (**10**): In analogy to the synthesis of **4**, the reaction of 63.5 g (0.50 mol) of ethylaluminium dichloride dissolved in 80 ml of THF with a solution of the bis-Grignard reagent prepared from 92.1 g (0.50 mol) of bis(3-chloropropyl)methylamine and 24.3 g (1.0 mol) of magnesium turnings in 200 ml of THF yielded **10** as a colorless liquid; yield 51.0 g (60%), b. p. 71°C/0.6 hPa. – MS (EI, 70 eV): *m/z* (%) = 169 (6) [M^+], 140 (100) [$M^+ - C_2H_5$], 112 (18) [$M^+ - C_4H_9$], 84 (13) [$M^+ - C_4H_9 - C_2H_4$], 70 (9) [$M^+ - C_4H_9 - C_3H_6$]. – ^{1}H NMR (C_6D_6, 20°C): δ = 0.25–0.52 [m, 6H, $\mathrm{C}\mathit{H}_2\mathrm{Al(C}\mathit{H}_2\mathrm{)_2}$], 1.55 (t, 3H, $\mathrm{C}\mathit{H}_3\mathrm{CH_2Al}$), 1.68–1.95 [m, 4H, $\mathrm{(C}\mathit{H}_2\mathrm{CH_2)_2N}$], 2.18 (s, 3H, CH_3N), 2.28–2.48 [m, 4H, $(CH_2)_2N$].

$C_9H_{20}AlN$ (169.2) Calcd. C 63.85 H 11.92
Found C 63.57 H 11.85

1,5-Dimethyl-1-galla-5-azacyclooctane (**11**): A solution of 10.0 g (54 mmol) of bis(3-chloropropyl)methylamine in 40 ml of THF was added to a stirred suspension of 2.9 g (119 mmol) of magnesium turnings in 100 ml of boiling THF. After refluxing the suspension for 2 h, the concentration of the Grignard reagent was determined by the Gilman method[37]. 100 ml of this bis-Grignard solution (0.36 mol/l) was slowly added to 5.4 g (35.0 mmol) of methylgallium dichloride in 20 ml of THF. After stirring the reaction mixture at room temp. for 24 h, the solvent was removed in vacuo. The residue was dissolved in pentane and the solution decanted from magnesium chloride. After removal of the solvent, the residue was sublimed in vacuo to give **11** as a colorless, low-melting solid; yield 3.9 g (56%), m. p. 34°C, b. p. 83°C/12 hPa. – MS (EI, 70 eV): *m/z* (%) = 197/199* (2) [M^+], 182/184* (100) [$M^+ - CH_3$], 154/156* (6) [$M^+ - CH_3 - C_2H_4$], 84 (41) [$C_5H_{10}N^+$], 69/71* (38) [Ga^+], 57 (12) [$C_3H_7N^+$], 42 (26) [$C_2H_4N^+$]; *isotope pattern clearly visible. – ^{1}H NMR (C_6D_6, 20°C): δ = –0.21 (s, 3H, CH_3Ga), 0.50 [t, 4H, $(CH_2)_2Ga$], 1.60–1.90 [m, 4H, $\mathrm{(C}\mathit{H}_2\mathrm{CH_2)_2N}$], 1.93–2.32 [m, 4H, $(CH_2)_2N$], 2.09 (s, 3H, CH_3N). – ^{13}C NMR (C_6D_6, 20°C): δ = –7.7 (s, CH_3Ga), 10.4 [s, $(CH_2)_2Ga$], 25.5 [s, $\mathrm{(}\mathit{C}\mathrm{H_2CH_2)_2N}$], 44.5 (s, CH_3N), 60.5 [s, $(CH_2)_2N$].

$C_8H_{18}GaN$ (198.0) Calcd. C 48.54 H 9.17 Ga 35.22 N 7.08
Found C 47.98 H 8.93 Ga 34.98 N 7.37

1-Ethyl-5-methyl-1-galla-5-azacyclooctane (**12**): In analogy to the synthesis of **10**, the reaction of 44.2 g (260 mmol) of ethylgallium dichloride dissolved in 80 ml of THF with a solution of the bis-Grignard reagent prepared from 47.9 g (260 mmol) of bis(3-chloropropyl)methylamine and 12.8 g (530 mmol) of magnesium turnings in 200 ml of THF yielded **12** as a colorless liquid; yield 41.7 g (76%), b. p. 64°C/1 hPa. – MS (EI, 70 eV): *m/z* (%) = 182 (100) [$M^+ - C_2H_5$], 110 (8) [$C_3H_5Ga^+$], 84 (37) [$C_5H_{10}N^+$], 69 (26) [Ga^+]. – ^{1}H NMR (C_6D_6, 20°C): δ = 0.58–0.88 [m, 6H, $\mathrm{C}\mathit{H}_2\mathrm{Ga(C}\mathit{H}_2\mathrm{)_2}$], 1.60 (t, 3H, $\mathrm{C}\mathit{H}_3\mathrm{CH_2}$), 1.78–2.18 [m, 4H,

(CH_2CH$_2$)$_2$N], 2.15 (s, 3H, CH_3N), 2.22–2.33 [m, 4H, $(CH_2)_2N$]. – ^{13}C NMR (C_6D_6, 20°C): δ = 2.7 (s, CH_3CH_2Ga), 7.3 [s, $(CH_2)_2Ga$), 10.3 (s, CH_3CH_2), 24.0 [s, $(CH_2CH_2)_2N$], 43.3 (s, CH_3N), 59.7 [s, $(CH_2)_2N$].

$C_9H_{20}GaN$ (212.0) Calcd. C 50.97 H 9.51
Found C 50.94 H 9.51

1,5-Dimethyl-1-inda-5-azacyclooctane (**13**): In analogy to the synthesis of **11**, the reaction of 5.5 g (27.2 mmol) of methylindium dichloride dissolved in 100 ml of ether with the Grignard reagent prepared from 5.0 g (27.2 mmol) of bis(3-chloropropyl)methylamine and 1.3 g (54.4 mmol) of magnesium turnings in 100 ml of ether gave **13** as a colorless liquid; yield 3.4 g (51%), b.p. 38°C/0.05 hPa. – MS (EI, 70 eV): m/z (%) = 244 (13) [M^+ + H], 243 (4) [M^+], 228 (84) [$M^+ - CH_3$], 115 (100) [In^+], 84 (24) [$C_5H_{11}N^+$], 57 (6) [$C_3H_7N^+$], 42 (13) [$C_2H_4N^+$]. – ^1H NMR (C_6D_6, 20°C): δ = −0.26 (s, 3H, CH_3In), 0.53 [t, 4H, $(CH_2)_2In$], 1.80 [tt, 4H, (CH_2CH$_2$)$_2$N], 1.96 (s, 3H, CH_3N), 2.05 [t, 4H, $(CH_2)_2N$]. – ^{13}C NMR (C_6D_6, 20°C): δ = −8.5 (s, CH_3In), 11.8 [s, $(CH_2)_2In$], 26.8 [s, (CH_2CH$_2$)$_2$N], 44.5 (s, CH_3N), 60.5 [s, $(CH_2)_2N$].

$C_8H_{18}InN$ (243.1) Calcd. C 39.53 H 7.46 In 47.24 N 5.76
Found C 39.46 H 7.50 In 46.96 N 5.99

1,5,8-Trimethyl-1-inda-5,8-diazacycloundecane (**14**): In analogy to the synthesis of **11**, the reaction of 5.0 g (25.0 mmol) of methylindium dichloride, dissolved in ether, with the Grignard reagent prepared from 6.0 g (25.0 mmol) of *N,N'*-bis(3-chloropropyl)-*N,N'*-dimethylethylenediamine and 1.22 g (50.0 mmol) of magnesium in ether yielded **14** as a colorless liquid; yield 3.5 g (47%), b.p. 114°C/1 hPa. – ^1H NMR (C_6D_6, 20°C): δ = −0.27 (s, 3H, CH_3In), 0.54 [t, 4H, $(CH_2)_2In$], 1.78 [tt, 4H, (CH_2CH$_2$)$_2$N], 1.87 [s, 6H, $(CH_3N)_2$], 1.99 [t, 4H, $(CH_2)_2N$], 2.34 (s, 4H, NCH_2CH_2N). – ^{13}C NMR (C_6D_6, 20°C): δ = −8.4 (s, CH_3In), 12.0 [s, $(CH_2)_2In$], 25.3 [s, (CH_2CH$_2$)$_2$N], 41.9 [s, $(CH_3N)_2$], 55.7 (s, NCH_2CH_2N), 62.0 [s, $(CH_2)_2N$].

$C_{11}H_{25}InN_2$ (300.15) Calcd. C 44.02 H 8.40 In 38.25 N 9.33
Found C 43.88 H 8.29 In 37.64 N 9.75

1-Alumina-5-azabicyclo[3.3.3]undecane (**15**): A solution of 64.1 g (260 mmol) of tris(3-chloropropyl)amine in 240 ml of THF was added to a stirred suspension of 20.4 g (840 mmol) of magnesium turnings in 500 ml of boiling THF. The mixture was refluxed for 2 h. Subsequently, this Grignard reagent and a solution of 33.3 g (250 mmol) of aluminium trichloride in 300 ml of THF were simultaneously added dropwise into 800 ml of toluene at 60°C over a period of 3 h. After the addition, the mixture was refluxed for 2 h, ca. 700 ml of the solvent removed by distillation, and the remaining suspension filtered over a frit to remove the magnesium chloride. The resulting clear solution was evaporated to dryness and the residue sublimed in vacuo at 20°C to yield **15** as colorless crystals; yield 14.8 g (36%), b.p. 80°C/0.4 hPa. – ^1H NMR (C_6D_6, 20°C): δ = 0.35 [t, 6H, $(CH_2)_3Al$], 1.88 [quint, 6H, (CH_2CH$_2$)$_3$N], 2.30 [t, 6H, $(CH_2)_3N$].

1-Galla-5-azabicyclo[3.3.3]undecane (**16**): In analogy to the synthesis of **15**, the reaction of the Grignard reagent prepared from 6.4 g (25.9 mmol) of tris(3-chloropropyl)amine and 2.1 g (84.4 mmol) of magnesium turnings in 50 ml of THF with 4.5 g (25.8 mmol) of gallium trichloride in 70 ml of THF yielded **16** as colorless needles; yield 1.2 g (22%), m.p. 54°C. – MS (EI, 70 eV): m/z (%) = 209/211* (100) [M^+], 180/182* (32) [$M^+ - C_2H_5$], 166/168* (68) [$M^+ - C_3H_7$], 153/155* (76) [$M^+ - C_3H_6N$], 140 (34) [$C_9H_{18}N^+$], 84 (52) [$C_5H_{10}N^+$], 69/71* (76) [Ga^+], 42 (20) [$C_2H_4N^+$]; *isotope pattern clearly visible. – ^1H NMR (C_6D_6, 20°C): δ = 0.59 [t, 6H, $(CH_2)_3Ga$], 1.76 [tt, 6H, (CH_2CH$_2$)$_3$N], 2.14 [t, 6H, $(CH_2)_3N$]. – ^{13}C NMR (C_6D_6, 20°C): δ = 9.8 [s, $(CH_2)_3Ga$], 26.5 [s, (CH_2CH$_2$)$_3$N], 57.0 [s, $(CH_2)_3N$].

$C_9H_{18}GaN$ (210.0) Calcd. C 51.48 H 8.64 Ga 33.21 N 6.67
Found C 51.05 H 8.62 Ga 32.73 N 7.27

X-ray Structure Determination of **16**: A colorless, needle-shaped crystal (3.20 × 0.22 × 0.14 mm) was shortened for the X-ray experiment to (0.65 × 0.22 × 0.14 mm). The crystals slowly decompose when exposed to air at room temperature. Data collection and calculations were carried out with an Enraf-Nonius CAD-4 automatic diffractometer, controlled by a μ-VAX II. – The diffraction pattern revealed a rhombohedral lattice. The cell parameters were obtained from a least-squares fit of the 2Θ values of 48 reflections in the range of $33° < 2\Theta < 59°$. Reflections were scanned with variable scan time, depending on intensities, with 2/3 of the time used for scanning the peak and 1/6 measuring each the left and the right background. The intensities of three reflections were checked every 1.5 h to determine crystal decomposition. The total loss of intensity during the time of data collection was 12.8%. Respective corrections were applied to the uncorrected data. Every 150 measurements the crystal orientation was checked by scanning three reflections distributed in reciprocal space. A new orientation matrix was automatically calculated from a list of 25 reflections in case the angular change was greater than 0.1°. The intensity data were corrected for Lorentz, polarization, and absorption (Ψ-scan method[38], max./min. transmission coefficients 0.97/0.76) effects. Symmetry-related reflections were averaged. The correct space group *R*3*c* was deduced from intensity statistics and confirmed by successful refinement. Initial coordinates for the Ga position were interpolated from a Patterson synthesis and showed the gallium atom to lie on the threefold axis. The coordinates for the remaining carbon and nitrogen atoms were determined from the subsequent Fourier summation and revealed the nitrogen to lie on the threefold axis as well. After anisotropic refinement of the non-hydrogen atoms, all hydrogen atoms were located from the difference Fourier map and refined isotropically. Full-matrix least-squares refinement of the positional and thermal parameters minimized the quantity $\Sigma w_i(|F_o| - s|F_c|)^2$ in which the individual weight factor, w_i, is equal to $1/[\sigma^2(F_o) + k(F_o)^2]$ and s is the scale factor. The scattering factors utilized for all structure factor calculations were taken from Cromer and Mann[39] for the non-hydrogen atoms and from Stewart et al.[40] for the hydrogen atoms with corrections included for anomalous dispersion effects. Data reduction and heavy-atom location were performed by using the SDP software package[41]. All other calculations were undertaken with SHELX 76[42].

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1: 131904-27-3 / **2**: 126957-14-0 / **3**: 131904-28-4 / **4**: 124690-62-6 / **5**: 125283-48-9 / **6**: 125283-49-0 / 7: 131904-29-5 / **8**: 131904-30-8 / **9**: 131904-31-9 / **10**: 131904-32-0 / **11**: 115796-82-2 / **12**: 124719-46-6 / **13**: 131904-33-1 / **14**: 131904-34-2 / **15**: 126894-76-6 / **16**: 115796-83-3 / $Cl(CH_2)_3NMe_2$: 109-54-6 / $Li(CH_2)_3NMe_2$: 56633-21-7 / $AlCl_3$: 7446-70-0 / $GaCl_3$: 13450-90-3 / $LiCH_2CH(CH_3)CH_2NMe_2$: 131904-35-3 / $Cl_2Ga(CH_2)_4NMe_2$: 128276-74-4 / $EtGaCl_2$: 6917-79-9 / $MeN[(CH_2)_3Cl]_2$: 2159-66-2 / $Cl(CH_2)_3N(CH_3)CH_2CH_2N(CH_3)(CH_2)_3Cl$: 80191-97-5 / $N[(CH_2)_3Cl]_3$: 79189-90-5 / $Br(CH_2)_5Br$: 111-24-0 / $Br(CH_2)_4Br$: 110-52-1 / $EtAlCl_2$: 563-43-9 / $MeGaCl_2$: 6917-74-4 / $MeInCl_2$: 20533-24-8

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