

Intramolecularly Stabilized Organoaluminium, -gallium and -indium Derivatives

Crystal Structures of *o*-[(Dimethylamino)methyl]phenyl}dimethylgallium and *o*-[(Diethylamino)methyl]phenyl}dimethylindium

Herbert Schumann^{*a}, Uwe Hartmann^a, Wilfried Wassermann^a, Andreas Dietrich^a, Frank H. Görlitz^a, Ludwig Pohl^b, and Martin Hostalek^b

Institut für Anorganische und Analytische Chemie der Technischen Universität Berlin^a,
Straße des 17. Juni 135, D-1000 Berlin 12

E. Merck^b,
Frankfurter Straße 250, D-6100 Darmstadt 1

Received April 2, 1990

Key Words: Organoaluminium compounds / Organogallium compounds / Organoindium compounds / Intramolecular base stabilization

Intramolecularly stabilized four-coordinated organoaluminium, -gallium, and -indium compounds $R_2MC_6H_4CH_2NR'_2$ (2) (1–7), $Me_2MCH_2C_6H_4NMe_2$ (2) (8, 9), $Me_2MCH_2C_6H_4CH_2NMe_2$ (2) (10, 11), and $Me_2GaC_6H_4NMe_2$ (12) have been synthesized from *o*-[(dialkylamino)methyl]phenyllithium, [*o*-(di-

methylamino)phenyl]methylolithium, *o*-[(dimethylamino)methyl]phenyl}methylolithium and *o*-(dimethylamino)phenyl}methylolithium, respectively. The ¹H-, ¹³C-NMR, and mass spectra of the new compounds and the X-ray crystal structures of 2 and 7 are reported and discussed.

In recent years an increasing interest in the synthesis of new organoaluminium, -gallium, and -indium compounds is observed because of their potential use as precursors for the production of InP and GaAs semiconductor layers^{1–3} substituting the currently used compounds trimethylaluminium (TMA), trimethylgallium (TMG), trimethylindium (TMI), or triethylindium (TEI). In general, these coordinatively unsaturated organometallic compounds are extremely pyrophoric, and thus it is difficult to avoid alkoxy contamination. Therefore, their use is limited and substitutes are needed which allow safer handling. The formation of adducts of TMG, TMI, or TEI with amines greatly enhances the chemical stability. Yet those intermolecularly coordinated, base-stabilized adducts are solids at room temperature, and their vapor pressure is decreased significantly^{4,5a)} in comparison to trimethylaluminium^{5b)}, -gallium^{5c)}, and -indium^{5d)}.

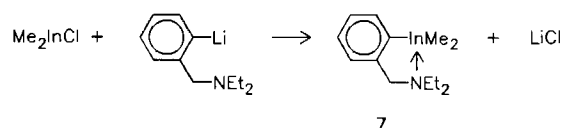
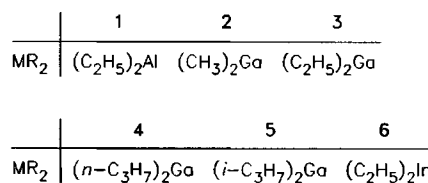
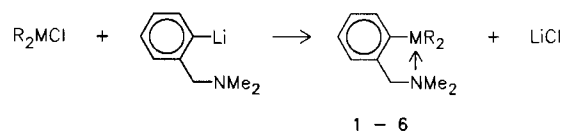
Recently, we have synthesized a series of intramolecularly stabilized organogallium and -indium compounds containing the 3-(dimethylamino)propyl, 3-(diethylamino)propyl or 4-(dimethylamino)butyl ligand⁶⁾. Some of them have been tested as new metal sources in metal organic vapor phase epitaxy (MOVPE)^{7,8,9a,b)}.

This intramolecular stabilization has also been well-documented for the *o*-[(dimethylamino)methyl]phenyl ligand. A variety of such compounds with main group as well as transition metals like tin¹⁰⁾, gold¹¹⁾, cobalt¹²⁾, chromium¹³⁾, and lutetium¹⁴⁾ have been investigated. Structural information of such compounds has been obtained by temperature-dependent NMR studies¹⁵⁾ and X-ray structure analyses^{16,17)}. Furthermore, these ligands are believed to be good leaving groups in epitaxy.

In this paper we report on the synthesis and characterization of new organoaluminium, -gallium, and -indium compounds using the potentially bidentate *o*-[(dialkylamino)methyl]phenyl, [*o*-(dimethylamino)phenyl]methyl, *o*-[(dimethylamino)methyl]phenyl}methyl and *o*-(dimethylamino)phenyl}methyl ligands.

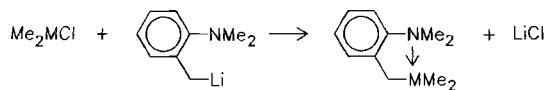
Synthesis and Properties

The reactions of *o*-[(dimethylamino)methyl]phenyllithium with diethylaluminium chloride, dimethyl-, diethyl-, di-*n*-propyl-, diisopropylgallium chloride as well as diethylindium chloride and the reaction of the newly prepared *o*-[(diethylamino)methyl]phenyllithium with dimethylindium chloride, all carried out at room temperature in pentane,



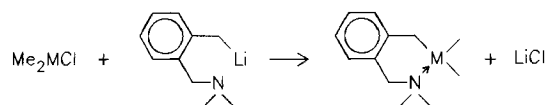
give the triorganometal compounds **1**–**7** as colorless liquids or low-melting solids in high yield.

The use of [*o*-(dimethylamino)phenyl]methyl lithium and of {*o*-[(dimethylamino)methyl]phenyl}methyl lithium results in the formation of the corresponding intramolecularly stabilized derivatives of gallium and indium. This stabilization can be achieved with the [*o*-(dimethylamino)phenyl]methyl ligand via a five-membered ring (**8**, **9**) and with the {*o*-[(dimethylamino)methyl]phenyl}methyl ligand via a six-membered ring (**10**, **11**).



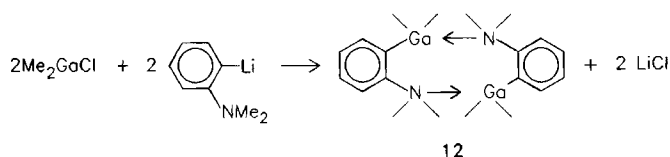
8: M = Ga

9: M = In



10: M = Ga

11: M = In



A compound containing a four-membered ring could not be obtained. The reaction of dimethylgallium chloride with *o*-(dimethylamino)phenyllithium results in the formation of a dimer **12** with intermolecular formation of an eight-membered ring system, which has been proved by cryoscopic mass determination in benzene solution.

All compounds are almost stable in air and show only slow decomposition in contact with moisture, except the dimeric **12**. They are all readily soluble in organic solvents, like ether, hydrocarbons, and aromatic solvents. Vapor pressure measurements of **2** carried out by the entrainment method¹⁸⁾ give the results shown in Table 1. Additional values can be calculated by the Nernst equation $p = \exp(27.4 - 9702.3/T)$ hPa. A comparison of the vapor pressure of **2** with the values obtained for intramolecularly stabilized [3-(dimethylamino)propyl]dimethylgallium⁶⁾ shows them to be significantly smaller. They are similar to the vapor pressure of $\text{Me}_3\text{Ga} \cdot \text{NMe}_3$ ⁴⁾. This vapor pressure is high enough only at elevated temperatures or for low-pressure MOVPE. Therefore, the use of **2** is limited to quantum well structures^{19a)}.

The ¹H- and ¹³C-NMR spectra of all compounds show the expected pattern and shifts with the exception of **5**, where two sets of doublets are observed at room temperature for the isopropyl groups. Broadening of the signals occurs at elevated temperatures indicating the splitting of the internal coordination which results in the free rotation of the *o*-[(dimethylamino)methyl]phenyl and the two isopropyl ligands. The coalescence temperature in **5** is significantly higher (above 80°C) in comparison to that of [3-

(dimethylamino)propyl]dimethylgallium⁶⁾ (56°C) because of a more sterically hindered rotation.

Table 1. Vapor pressures [Pa] of **2** in comparison to other GaAs precursors

Temperature [°C]	Me ₂ GaC ₆ H ₄ CH ₂ NMe ₂ (2)	Me ₂ Ga[CH ₂] ₃ NMe ₂	Me ₃ Ga · NMe ₃
20	0.32	40	2.4
50	6.9	230	12.1
75	61.9	1050	37.8
100	390	—	—

The mass spectra of **1**–**11** show no peaks higher than the expected molecular mass which is in agreement with the proposed monomeric structure and is proved cryoscopically in benzene for **2** and by X-ray investigations for **2** and **7**. The most dominant feature in the mass spectra is the loss of CH₃, C₂H₅, or C₃H₇, respectively. In the case of the higher homologs, β-hydride elimination is observed besides the σ-alkyl fragmentation. Furthermore, the stable tropylium cation (C₇H₇⁺ *m/z* = 91) and the Schiff base fragment (Me₂N⁺CH₂ *m/z* = 58) are observed.

Molecular Structure

The molecular structures of **2** and **7** have been determined by X-ray diffraction. Details are given in Tables 2 and 3, the atomic coordinates are listed in Tables 4 and 5, and selected bond lengths, angles and torsion angles are compiled in Tables 6 and 7. Figures 1 and 2 show ORTEP²⁰⁾ plots of **2** and **7**.

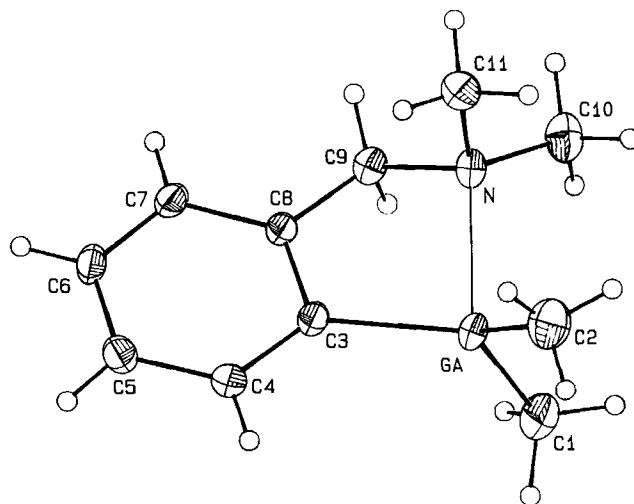
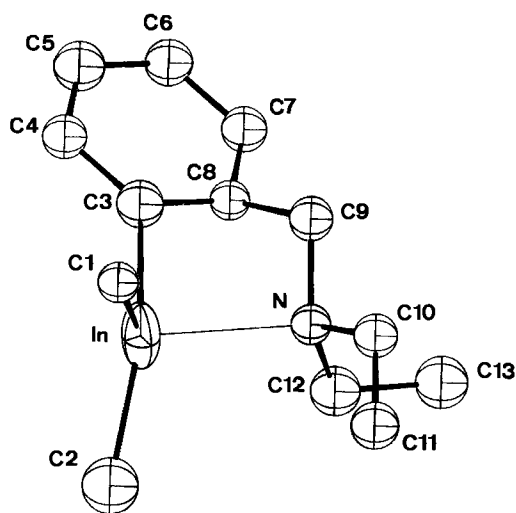


Figure 1. Molecular structure of **2** with atomic numbering scheme

The X-ray structure shows **2** as a discrete monomer with the gallium atom in a distorted tetrahedral environment bonded to the three carbon atoms and the nitrogen of the dimethylamino group (Figure 1). The GaC₃ moiety is close to planarity with the gallium atom pulled out of the C1,C2,C3 plane by 28.4(5) pm. This tetrahedral distortion

Figure 2. Molecular structure of **7** with atomic numbering schemeTable 2. Crystal and data collection parameters of **2**^{a)}

Formula $C_{11}H_{18}GaN$; molecular mass 233.99 g/mol; cell parameters $a = 2881.5(4)$, $c = 737.0(1)$ pm; cell volume $V = 5299.5 \cdot 10^6$ pm³; $Z = 18$; calculated density 1.32 g/cm³; linear absorption coefficient 22.14 cm⁻¹; $F(000)$ 2196; crystal system rhombohedral (hexagonal setting); space group $R\bar{3}$; crystal size 0.13 × 0.31 × 0.40 mm³; Enraf-Nonius CAD-4 four-circle diffractometer; radiation Mo- K_{α} , $\lambda = 71.071$ pm; monochromator graphite crystal; experimental temperature 140(5) K; 2θ range, $1^\circ < 2\theta < 52^\circ$; hkl boundaries $-35 \rightarrow 35$, $-35 \rightarrow 35$, $0 \rightarrow 9$; scan technique $\Theta - 2\Theta$; scan time variable, max. 65 s; scan angle $(0.65 + 0.34 \tan \Theta)^\circ$; aperture 2.20 mm; total number of measured reflections 7496, unique reflections 2282, $R_{int} = 0.018$, observed reflections with $F_o \geq 4\sigma(F_o)$ 1951; corrections for Lorentz-, polarisation, absorption, and anomalous dispersion effects; max. shift/error (Δ/σ) 0.001; residual electron density max. 0.27, min. -0.25 eÅ⁻³; number of refined parameters 190; $R = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|} = 0.022$; $R_w = \frac{[\sum w(|F_o| - |F_c|)^2]}{[\sum w F_o^2]}^{1/2} = 0.030$; $w = 1/[\sigma^2(F_o) + 0.00011 \cdot F_o^2]$

^{a)} Further details of the crystal structure investigations are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-7514 Eggenstein-Leopoldshafen 2, on quoting the depository number CSD-54701, the names of the authors, and the journal citation.

showing nearly "normal" angles C1–Ga–N (104.7°) and C2–Ga–N (105.1°), and also a significantly different angle C3–Ga–N (84.4°), is caused by the transannular Ga–N–interaction, which also affects the geometry around the phenyl ring: the angle C8–C3–Ga is smaller (110.7°) than the expected 120° angle of the sp²-hybridized carbon C3. The intramolecular N–Ga interaction bends C9 out of the phenyl plane by 12 pm, resulting in a torsion angle Ga–C3–C8–C9 of 5.4°. The Ga–N distance [213.3(2) pm] is in agreement with the corresponding values observed in C₉H₁₈NGa [209.5(2) pm]²¹⁾, (CH₃)₃Ga(N₄C₆H₁₂) [213.9(17) pm]²²⁾, (CH₃)₃GaN(CH₃)₃ [220(3) pm]²³⁾, but is longer than the sum of the covalent radii for Ga and N [195 pm]²⁴⁾. Ga–C3 [199.1(2) pm] is slightly longer than the other two Ga–C distances [197.7(3) and 197.8(3) pm].

The geometry of **7** (Figure 2) is influenced in the same manner as in **2** now by the intramolecular N–In bond. The

Table 3. Crystal and data collection parameters of **7**^{a)}

Formula C₁₃H₂₂InN; molecular mass 307.15 g/mol; cell parameters $a = 941.4(2)$, $b = 1013.7(3)$, $c = 2242.6(3)$ pm, $\beta = 100.89(2)^\circ$; cell volume $V = 2100.9 \cdot 10^6$ pm³; $Z = 6$; calculated density 1.456 g/cm³; linear absorption coefficient 15.24 cm⁻¹; $F(000)$ 936; crystal system monoclinic; space group $P2_1$; crystal size 0.32 × 0.22 × 0.44 mm³; Enraf-Nonius CAD-4 four-circle diffractometer; radiation Mo- K_{α} , $\lambda = 71.071$ pm; monochromator graphite crystal; experimental temperature 140(5) K; 2θ range, $2^\circ < 2\theta < 45^\circ$; hkl boundaries $0 \rightarrow 11$, $0 \rightarrow 12$, $-26 \rightarrow 26$; scan technique $\Theta - 2\Theta$; scan time variable, max. 60 s; scan angle $(0.65 + 0.34 \tan \Theta)^\circ$; aperture 2.00 mm; total number of measured reflections 4184, unique reflections 3006, $R_{int} = 0.0252$, observed reflections with $F_o \geq 3\sigma(F_o)$ 1952; corrections for Lorentz-, polarisation, absorption (Ψ -scan) and anomalous dispersion effects; residual electron density max. 1.84, min. -1.63 eÅ⁻³; number of refined parameters 157; $R = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|} = 0.0675$; $R_w = \frac{[\sum w(|F_o| - |F_c|)^2]}{[\sum w F_o^2]}^{1/2} = 0.0828$; $w = 2.2924/[\sigma^2(F_o) + 0.000741 \cdot F_o^2]$

^{a)} See Table 2.

Table 4. Fractional atomic coordinates and equivalent isotropic thermal parameters [\AA^2] of **2** with estimated standard deviations in parentheses. $B_{eq} = 8\pi^2/3 \sum_i \sum_j U_{ij} a_i^* a_j^* a_i a_j$

Atoms	x/a	y/b	z/c	B _{eq}
Ga	0.19258(1)	0.26808(1)	0.20575(3)	1.48
N	0.1971(1)	0.2238(1)	-0.0189(2)	1.55
C1	0.2555(1)	0.2840(1)	0.3571(4)	2.50
C2	0.1884(1)	0.3286(1)	0.0968(4)	2.80
C3	0.1259(1)	0.2001(1)	0.2657(3)	1.34
C4	0.0830(1)	0.1885(1)	0.3824(3)	1.54
C5	0.0396(1)	0.1368(1)	0.4004(3)	1.66
C6	0.0379(1)	0.0954(1)	0.3000(3)	1.53
C7	0.0796(1)	0.1052(1)	0.1835(3)	1.45
C8	0.1233(1)	0.1571(1)	0.1684(3)	1.27
C9	0.1715(1)	0.1683(1)	0.0544(3)	1.61
C10	0.2520(1)	0.2413(1)	-0.0829(4)	2.46
C11	0.1649(1)	0.2260(1)	-0.1725(3)	2.06

Table 5. Fractional atomic coordinates and equivalent isotropic thermal parameters [\AA^2] of **7** with estimated standard deviations in parentheses. $B_{eq} = 8\pi^2/3 \sum_i \sum_j U_{ij} a_i^* a_j^* a_i a_j$

Atoms	x/a	y/b	z/c	B _{eq}
In	-0.2094(2)	-0.2479(8)	-0.9016(1)	5.23
C1	-0.3165(20)	-0.0599(17)	-0.9147(13)	2.50
C2	-0.3363(24)	-0.4235(20)	-0.9172(20)	6.81
C3	0.0197(9)	-0.2137(13)	-0.9059(5)	3.34
C4	0.0842(9)	-0.1713(13)	-0.9537(5)	3.00
C5	0.2345(9)	-0.1711(13)	-0.9472(5)	3.92
C6	0.3203(9)	-0.2133(13)	-0.8929(5)	3.40
C7	0.2559(9)	-0.2557(13)	-0.8452(5)	3.18
C8	0.1056(9)	-0.2559(13)	-0.8516(5)	2.42
C9	0.0379(17)	-0.2025(18)	-0.8002(9)	2.95
N	-0.0983(14)	-0.2738(15)	-0.7976(6)	2.48
C10	-0.1747(17)	-0.2043(19)	-0.7565(9)	2.91
C11	-0.3288(17)	-0.2330(25)	-0.7544(9)	3.46
C12	-0.0692(22)	-0.4163(18)	-0.7823(10)	3.83
C13	0.0180(22)	-0.4452(22)	-0.7179(10)	4.26

In atom resides 24.4(1) pm above the plane formed by the carbon atoms C1, C2 and C3. The angle C3–In–N is only 78.9°, and the angle C8–C3–In (108.9°) differs also significantly from the expected sp² angle of 120°. The increase in

Table 6. Selected bond distances [pm] and angles and torsion angles [°] of **2** with estimated standard deviations in parentheses

Atoms	Distances	Atoms	Distances
Ga-N	213.3(2)	N-C10	147.7(3)
Ga-C1	197.8(3)	N-C11	148.6(3)
Ga-C2	197.7(3)	C3-C8	140.0(3)
Ga-C3	199.1(2)	C8-C9	151.4(3)
N-C9	148.8(3)		

Atoms	Angles	Atoms	Angles
C1-Ga-N	104.7(1)	C11-N-C9	109.8(2)
C2-Ga-N	105.1(1)	C11-N-C10	109.1(2)
C2-Ga-C1	118.5(1)	C4-C3-Ga	132.3(2)
C3-Ga-N	84.4(1)	C8-C3-Ga	110.7(2)
C3-Ga-C1	115.2(1)	C3-C8-Ga	41.5(1)
C3-Ga-C2	120.3(1)	C9-C8-C3	117.3(2)
C9-N-Ga	102.4(1)	C9-C8-C7	120.8(2)
C10-N-Ga	114.8(1)	N-C9-Ga	46.9(1)
C10-N-C9	110.7(2)	C8-C9-N	109.8(2)
C11-N-Ga	109.8(1)		

C4-C3-C8-C9	175.0(2)	Ga-C3-C8-C9	5.4(2)
C3-C8-C9-N	-33.3(2)	Ga-C3-C8-C7	-178.4(1)
C1-Ga-C3-C8	-88.7(1)	C8-C9-N-C10	163.1(2)
C2-Ga-C3-C8	119.2(1)	C8-C9-N-C11	-76.3(2)

Table 7. Selected bond distances [pm] and angles and torsion angles [°] of **7** with estimated standard deviations in parentheses

Atoms	Distances	Atoms	Distances
In-N	238.0(10)	N-C10	146.0(20)
In-C1	215.0(20)	N-C12	150.0(20)
In-C2	214.0(20)	C10-C11	149.0(20)
In-C3	220.5(8)	C12-C13	155.0(20)
N-C9	148.0(20)		

Atoms	Angles	Atoms	Angles
C1-In-N	109.8(9)	C12-N-In	111.0(10)
C2-In-N	101.0(10)	C10-N-C12	114.0(20)
C1-In-C2	118.9(7)	C4-C3-In	130.8(3)
C3-In-N	78.9(4)	C8-C3-In	108.9(3)
C1-In-C3	107.0(7)	C3-C8-C9	107.3(8)
C2-In-C3	130.2(9)	C8-C9-N	110.0(10)
C9-N-In	98.0(10)	N-C10-C11	122.0(20)
C9-N-C10	109.0(10)	N-C12-C13	116.0(20)
C9-N-C12	111.0(10)		

C4-C3-C8-C9	139.7(13)	In-C3-C8-C9	-46.1(12)
C3-C8-C9-N	71.6(15)	In-C3-C8-C7	174.2(10)
C1-In-C3-C8	121.7(11)	C8-C9-N-C10	-168.8(12)
C2-In-C3-C8	-81.3(16)	C8-C9-N-C12	64.5(15)

radii when going from Ga in **2** to In in **7** results in a larger bend of C9 out of the phenyl ring plane by 94 pm with a torsion angle In-C3-C8-C9 of 46.1° compared to only 4.6° for Ga-C3-C8-C9 in **2**. The In-N distance [238(1) pm] is slightly longer than the sum of the covalent radii (219 pm)¹⁶, but significantly shorter than the sum of the van der Waals radii (345 pm)²⁴. Comparatively short In-N distances are found in C₂H₅InI₂(Me₂NCH₂CH₂NMe₂) [233(1) and 244(1) pm]²⁵ in contrast to the smaller In-N distances in CH₃In[CH₃NC(CH₃)₂N]₂ [213.8(5) pm]²⁶, [(CH₃)₂In]₂-C₂(NCH₃)₄ [218.2(5) pm]²⁷, CH₃In{[CH₃(CH₂)₂NCH₃]-In(CH₃)₂}₂ (218.7(13) pm)²⁶, methyl(tetraphenylporphinato)-

indium(III) [220(1) pm]²⁸, CH₃InCl₂(t-C₄H₉NH₂) [221(1) pm]²⁹, and (CH₃)₂InN(CH₃)₂ [222(1) pm]³⁰. Recently we have found even longer In-N distances of 260.3(3) and 260.7(3) pm in CH₃{2,6-[(C₂H₅)₂NCH₂]₂C₆H₃}InCl, another intramolecularly coordinated compound of this type¹⁶.

Financial support by the *Fonds der Chemischen Industrie*, the *Bundesminister für Forschung und Technologie* (Contract No. 415-7291-NT-2717 E3), and the *Bundesminister für Bildung und Wissenschaft* (Graduiertenkolleg "Synthese und Strukturaufklärung niedermolekularer Verbindungen") is gratefully acknowledged. We thank Prof. Dr. J. Pickardt for supplying helpful software to us.

Experimental

All reactions were carried out in dry, oxygen-free argon using Schlenk tubes. The solvents used were dried and freed of oxygen with LiAlH₄ or Na/benzophenone and were distilled prior to use. — Elemental analyses: Perkin-Elmer 240C CHN Analyzer, determination of Ga and In with a Perkin-Elmer 2380 Atomic Absorption Spectrophotometer. — Molecular masses: cryoscopically in benzene. — MS: Varian MAT 311 A. — NMR: Bruker WH 270 at 270 MHz (¹H) or at 67.93 MHz (¹³C).

The starting materials were prepared according to literature procedures. The triorganometal compounds were obtained either by alkylation of the metal trichlorides with triorganoaluminium compounds³¹ (Me₃Ga, Et₃Ga) or by Grignard reactions (nPr₃Ga, iPr₃Ga³², Et₃In³³). The corresponding diorganometal chlorides were prepared by redistribution reactions of the triorganometal compounds with the metal trichlorides^{34,35}. Dimethylindium chloride was obtained from indium trichloride and methyl lithium³⁶. The lithium reagents used were synthesized as described in the literature^{12,13,37,38,39} by metallation of the corresponding amines with *n*-butyllithium.

o-[(Dimethylamino)methyl]phenyl}diethylaluminium (**1**): A solution of 23.2 g (190.0 mmol) of diethylaluminium chloride in 150 ml of pentane was added to a stirred suspension of 27.2 g (190.0 mmol) of *o*-[(dimethylamino)methyl]phenyllithium¹² in 150 ml of pentane at 0°C. After stirring at room temp. for 12 h, the solution was decanted from lithium chloride. The clear solution was distilled under reduced pressure. **1** was obtained as a colorless liquid; yield 27.2 g (65%), b. p. 79°C/0.1 hPa. — MS (EI, 70 eV): *m/z* (%) = 190 (100) [M⁺ - C₂H₅], 162 (55) [M⁺ - C₂H₅, - C₂H₄], 146 (6) [162 - CH₄], 135 (38) [C₆H₅CH₂N⁺(CH₃)₂], 134 (24) [C₆H₄CH₂N⁺(CH₃)₂], 91 (36) [C₇H₇⁺], 58 (67) [Me₂N⁺CH₂]. — ¹H-NMR (C₆D₆; 20°C): δ = 0.40 [m, 4H, (CH₃CH₂)₂Al], 1.60 [t, 6H, (CH₃CH₂)₂Al], 2.02 [s, 6H, (CH₃)₂N], 3.39 [s, 2H, CH₂N], 7.10–8.18 (m, 4H, aromatic H).

C₁₃H₂₂AlN (219.3) Calcd. C 71.20 H 10.11
Found C 70.93 H 10.13

o-[(Dimethylamino)methyl]phenyl}dimethylgallium (**2**): A solution of 4.0 g (30.0 mmol) of dimethylgallium chloride in 50 ml of pentane was added to a stirred suspension of 4.3 g (30.0 mmol) of *o*-[(dimethylamino)methyl]phenyllithium¹² in 50 ml of pentane at 0°C. After stirring at room temp. for 12 h, the solution was decanted from lithium chloride, the solvent removed in vacuo, and the residue sublimed at 0.01 hPa/40°C bath temperature. **2** was obtained as colorless crystals; yield 4.9 g (70%), m. p. 34°C, b. p. 208°C; vapor pressure *p* = exp(27.4 - 9702.3/*T*) [hPa]. — MS (EI, 70 eV): *m/z* (%) = 218/220* (100) [M⁺ - CH₃], 175/177* (22) [MeGa⁺C₇H₇], 135 (6) [C₆H₅CH₂N⁺Me₂], 134 (6) [C₆H₄CH₂N⁺Me₂], 99/101* (2) [Me₂Ga⁺], 91 (6) [C₇H₇⁺], 77 (1) [C₆H₅⁺], 69/71* (34) [Ga⁺], 58 (6) [Me₂N⁺CH₂], 44 (4) [C₂H₆N⁺]; *isotope pattern clearly visi-

ble. — $^1\text{H-NMR}$ (C_6D_6 ; 20°C): $\delta = -0.08$ [s, 6H, $(\text{CH}_3)_2\text{Ga}$], 1.95 [s, 6H, $(\text{CH}_3)_2\text{N}$], 3.30 (s, 2H, CH_2N), 6.85–7.87 (m, 4H, aromatic H). — $^{13}\text{C-NMR}$ (C_6D_6 , 20°C): $\delta = -7.7$ [s, $(\text{CH}_3)_2\text{Ga}$], 45.4 [s, $(\text{CH}_3)_2\text{N}$], 67.2 (s, CH_2N), 124.3, 126.7, 127.1, 136.0 (s, aromatic C), 142.9 (s, C– CH_2), 154.7 (s, C–Ga).

$\text{C}_{11}\text{H}_{18}\text{GaN}$ (234.0) Calcd. C 56.46 H 7.75 Ga 29.80 N 5.99
Found C 56.39 H 7.86 Ga 29.70 N 6.48
Mol. mass 226.4 (by cryoscopy in benzene)

$\{o\text{-}[(\text{Dimethylamino})\text{methyl}]\text{phenyl}\}\text{diethylgallium}$ (3): A solution of 3.1 g (19.0 mmol) of diethylgallium chloride in 20 ml of pentane was added to a stirred suspension of 2.8 g (20.0 mmol) of $o\text{-}[(\text{dimethylamino})\text{methyl}]\text{phenyllithium}^{12}$ in 20 ml of pentane at 0°C . After stirring at room temp. for 12 h, the solution was decanted from lithium chloride, the solvent removed in vacuo, and the residue distilled under reduced pressure. **3** was obtained as a colorless liquid; yield 3.1 g (62%), b. p. $92^\circ\text{C}/0.01$ hPa. — MS (EI, 70 eV): m/z (%) = 232/234* (58) [$\text{M}^+ - \text{C}_2\text{H}_5$], 204/206* (21) [$\text{M}^+ - \text{C}_2\text{H}_5$, $-\text{C}_2\text{H}_4$], 161/163* (6) [$\text{HGa}^+ - \text{C}_7\text{H}_7$], 135 (32) [$\text{C}_6\text{H}_5\text{CH}_2\text{N}^+ \text{Me}_2$], 134 (29) [$\text{C}_6\text{H}_4\text{CH}_2\text{N}^+ \text{Me}_2$], 91 (47) [C_7H_7^+], 77 (5) [C_6H_5^+], 69/71* (44) [Ga^+], 58 (100) [$\text{Me}_2\text{N}^+ \text{CH}_2$], 44 (29) [$\text{C}_2\text{H}_6\text{N}^+$]; *isotope pattern clearly visible. — $^1\text{H-NMR}$ (C_6D_6 ; 20°C): $\delta = 0.64$ [m, 4H, $(\text{CH}_3\text{CH}_2)_2\text{Ga}$], 1.43 [t, 6H, $(\text{CH}_3\text{CH}_2)_2\text{Ga}$], 1.97 [s, 6H, $(\text{CH}_3)_2\text{N}$], 3.29 (s, 2H, CH_2N), 6.88–7.92 (m, 4H, aromatic H). — $^{13}\text{C-NMR}$ (C_6D_6 , 20°C): $\delta = 2.5$ [s, $(\text{CH}_3\text{CH}_2)_2\text{Ga}$], 11.1 [s, $(\text{CH}_3\text{CH}_2)_2\text{Ga}$], 45.6 [s, $(\text{CH}_3)_2\text{N}$], 67.6 (s, CH_2N), 124.3, 126.7, 126.9, 136.6 (s, aromatic C), 143.2 (s, C– CH_2), 153.4 (s, C–Ga).

$\text{C}_{13}\text{H}_{22}\text{GaN}$ (262.05) Calcd. C 59.59 H 8.46 Ga 26.61 N 5.35
Found C 60.67 H 8.48 Ga 26.88 N 6.54

$\{o\text{-}[(\text{Dimethylamino})\text{methyl}]\text{phenyl}\}\text{di-}n\text{-propylgallium}$ (4): In analogy to the synthesis of **3**, the reaction of 2.9 g (15.0 mmol) of di-*n*-propylgallium chloride with 2.2 g (16.0 mmol) of $o\text{-}[(\text{dimethylamino})\text{methyl}]\text{phenyllithium}^{12}$ yielded **4** as a colorless liquid; 2.5 g (58%), b. p. $97^\circ\text{C}/0.01$ hPa. — MS (EI, 70 eV): m/z (%) = 246/248* (100) [$\text{M}^+ - \text{C}_3\text{H}_7$], 204/206* (48) [$\text{M}^+ - \text{C}_3\text{H}_7$, $-\text{C}_3\text{H}_6$], 161/163* (12) [$\text{HGa}^+ - \text{C}_7\text{H}_7$], 135 (19) [$\text{C}_6\text{H}_5\text{CH}_2\text{N}^+ \text{Me}_2$], 134 (27) [$\text{C}_6\text{H}_4\text{CH}_2\text{N}^+ \text{Me}_2$], 91 (30) [C_7H_7^+], 69/71* (45) [Ga^+], 58 (52) [$\text{Me}_2\text{N}^+ \text{CH}_2$], 44 (27) [$\text{C}_2\text{H}_6\text{N}^+$]; *isotope pattern clearly visible. — $^1\text{H-NMR}$ (C_6D_6 ; 20°C): $\delta = 0.68$ [t, 4H, $(\text{CH}_3\text{CH}_2\text{CH}_2)_2\text{Ga}$], 1.27 [t, 6H, $(\text{CH}_3\text{CH}_2\text{CH}_2)_2\text{Ga}$], 1.81 [m, 4H, $(\text{CH}_3\text{CH}_2\text{CH}_2)_2\text{Ga}$], 1.96 [s, 6H, $(\text{CH}_3)_2\text{N}$], 3.28 (s, 2H, CH_2N), 6.98–7.88 (m, 4H, aromatic H). — $^{13}\text{C-NMR}$ (C_6D_6 , 20°C): $\delta = 14.7$ [s, $(\text{CH}_3\text{CH}_2\text{CH}_2)_2\text{Ga}$], 20.4 [s, $(\text{CH}_3\text{CH}_2\text{CH}_2)_2\text{Ga}$], 20.9 [s, $(\text{CH}_3\text{CH}_2\text{CH}_2)_2\text{Ga}$], 45.7 [s, $(\text{CH}_3)_2\text{N}$], 67.7 (s, CH_2N), 124.2, 126.6, 127.0, 136.4 (s, aromatic C), 143.0 (s, C– CH_2), 154.2 (s, C–Ga).

$\text{C}_{15}\text{H}_{26}\text{GaN}$ (290.1) Calcd. C 62.10 H 9.03 N 4.83
Found C 62.43 H 8.73 N 5.41

$\{o\text{-}[(\text{Dimethylamino})\text{methyl}]\text{phenyl}\}\text{diisopropylgallium}$ (5): In analogy to the synthesis of **3**, the reaction of 3.1 g (16.2 mmol) of diisopropylgallium chloride with 2.4 g (17.0 mmol) of $o\text{-}[(\text{dimethylamino})\text{methyl}]\text{phenyllithium}^{12}$ yielded **5** as a colorless liquid; 2.6 g (56%), b. p. $92^\circ\text{C}/0.01$ hPa. — MS (EI, 70 eV): m/z (%) = 246/248* (47) [$\text{M}^+ - \text{C}_3\text{H}_7$], 204/206* (15) [$\text{M}^+ - \text{C}_3\text{H}_7$, $-\text{C}_3\text{H}_6$], 135 (74) [$\text{C}_6\text{H}_5\text{CH}_2\text{N}^+ \text{Me}_2$], 134 (65) [$\text{C}_6\text{H}_4\text{CH}_2\text{N}^+ \text{Me}_2$], 91 (77) [C_7H_7^+], 69/71* (18) [Ga^+], 65 (29) [C_3H_5^+], 58 (100) [$\text{Me}_2\text{N}^+ \text{CH}_2$], 44(38) [$\text{C}_2\text{H}_6\text{N}^+$]; *isotope pattern clearly visible. — $^1\text{H-NMR}$ (C_6D_6 ; 20°C): $\delta = 1.06$ [sept, 2H, $[(\text{H}_3\text{C})_2\text{CH}]_2$], 1.46 [d, 6H, $(\text{H}_3\text{C})_2\text{CH}$], 1.52 [d, 6H, $(\text{H}_3\text{C})_2\text{CH}$], 2.03 [s, 6H, $(\text{CH}_3)_2\text{N}$], 3.29 (s, 2H, CH_2N), 6.88–7.80 (m, 4H, aromatic H). — $^{13}\text{C-NMR}$ (C_6D_6 , 20°C): $\delta = 13.7$ [s, $[(\text{H}_3\text{C})_2\text{CH}]_2$], 22.2 and 22.3 [s, $[(\text{H}_3\text{C})_2\text{CH}]_2$], 46.2 [s, $(\text{CH}_3)_2\text{N}$], 68.1 (s, CH_2N), 124.3, 126.7, 126.9, 136.9 (s, aromatic C), 143.2 (s, C– CH_2), 153.0 (s, C–Ga).

$\text{C}_{15}\text{H}_{26}\text{GaN}$ (290.1) Calcd. C 62.10 H 9.03 N 4.83
Found C 63.53 H 8.90 N 5.57

$\{o\text{-}[(\text{Dimethylamino})\text{methyl}]\text{phenyl}\}\text{diethylindium}$ (6): In analogy to the synthesis of **3**, the reaction of 4.2 g (20.0 mmol) of diethylindium chloride with 2.8 g (20.0 mmol) of $o\text{-}[(\text{dimethylamino})\text{methyl}]\text{phenyllithium}^{12}$ yielded **6** as a colorless liquid; 3.5 g (57%), b. p. $115^\circ\text{C}/0.1$ hPa. — $^1\text{H-NMR}$ (C_6D_6 ; 20°C): $\delta = 0.76$ [q, 4H, $(\text{CH}_3\text{CH}_2)_2\text{In}$], 1.52 [t, 6H, $(\text{CH}_3\text{CH}_2)_2\text{In}$], 1.94 [s, 6H, $(\text{CH}_3)_2\text{N}$], 3.21 (s, 2H, CH_2N), 7.00–7.22 (m, 4H, aromatic H). — $^{13}\text{C-NMR}$ (C_6D_6 , 20°C): $\delta = 5.2$ [s, $(\text{CH}_3\text{CH}_2)_2\text{In}$], 13.6 [s, $(\text{CH}_3\text{CH}_2)_2\text{In}$], 45.6 [s, $(\text{CH}_3)_2\text{N}$], 68.5 (s, CH_2N), 125.7 (s, C-5), 126.5 (s, C-4), 126.8 (s, C-3), 139.0 (s, C-6), 144.7 (s, C– CH_2), 159.4 (s, C–In).

$\text{C}_{13}\text{H}_{22}\text{InN}$ (307.15) Calcd. C 50.84 H 7.22 In 37.38 N 4.56
Found C 51.01 H 7.25 In 37.12 N 4.33

$\{o\text{-}[(\text{Diethylamino})\text{methyl}]\text{phenyl}\}\text{dimethylindium}$ (7): In analogy to the synthesis of **2**, the reaction of 4.6 g (25.5 mmol) of dimethylindium chloride with 4.3 g (25.5 mmol) of $o\text{-}[(\text{diethyl-amino})\text{methyl}]\text{phenyllithium}^{39}$ yielded **7** as a colorless low-melting solid; 5.3 g (68%), m. p. $30\text{--}31^\circ\text{C}$, b. p. $104^\circ\text{C}/0.2$ hPa. — MS (EI, 70 eV): m/z (%) = 292 (12) [$\text{M}^+ - \text{CH}_3$], 163 (7) [$\text{C}_6\text{H}_4\text{CH}_2\text{N}^+ \text{HEt}_2$], 162 (4) [$\text{C}_6\text{H}_4\text{CH}_2\text{N}^+ \text{Et}_2$], 148 (32) [$\text{C}_6\text{H}_4\text{CH}_2\text{N}^+ \text{MeEt}$], 145 (2) [Me_2In^+], 115 (9) [In^+], 91 (100) [C_7H_7^+], 86 (7) [$\text{Et}_2\text{N}^+ \text{CH}_2$], 65 (9) [C_3H_5^+], 58 (3) [$\text{C}_3\text{H}_8\text{N}^+$], 56 (4) [$\text{C}_3\text{H}_6\text{N}^+$]. — $^1\text{H-NMR}$ (C_6D_6 ; 20°C): $\delta = -0.06$ [s, 6H, $(\text{CH}_3)_2\text{In}$], 0.53 [t, 6H, $(\text{CH}_3\text{CH}_2)_2\text{N}$], 2.29 [q, 4H, $(\text{CH}_3\text{CH}_2)_2\text{N}$], 3.24 (s, 2H, CH_2N), 6.86–7.78 (m, 4H, aromatic H). — $^{13}\text{C-NMR}$ (C_6D_6 , 20°C): $\delta = -8.2$ [s, $(\text{CH}_3)_2\text{In}$], 8.5 [s, $(\text{CH}_3\text{CH}_2)_2\text{N}$], 44.2 [s, $(\text{CH}_3\text{CH}_2)_2\text{N}$], 61.4 (s, CH_2N), 125.4, 126.6, 126.9, 138.4 (s, aromatic C), 144.3 (s, C– CH_2), 159.9 (s, C–In).

$\text{C}_{13}\text{H}_{22}\text{InN}$ (307.15) Calcd. C 50.84 H 7.22 In 37.38 N 4.56
Found C 51.08 H 7.26 In 37.22 N 4.42

$\{o\text{-}[(\text{Dimethylamino})\text{phenyl}]\text{methyl}\}\text{dimethylgallium}$ (8): A solution of 1.5 g (10.7 mmol) of dimethylgallium chloride in 20 ml of hexane was added to a stirred yellow suspension of 1.6 g (11.3 mmol) of $o\text{-}[(\text{dimethylamino})\text{phenyl}]\text{methyl}^{13}$ in 20 ml of hexane at room temp. The color of the reaction mixture turned slowly into white. After stirring for further 24 h, the reaction mixture was refluxed for 2 h. Subsequently, it was decanted from lithium chloride, the solvent removed and the residue distilled under reduced pressure. **8** was obtained as a colorless liquid; yield 1.6 g (65%), m. p. $\approx 11^\circ\text{C}$, b. p. $\approx 80^\circ\text{C}/0.01$ hPa. — MS (EI, 70 eV): m/z (%) = 218/220* (100) [$\text{M}^+ - \text{CH}_3$], 203/205* (29) [$\text{M}^+ - 2 \times \text{CH}_3$], 188/190* (6) [$\text{M}^+ - 3 \times \text{CH}_3$], 134 (32) [$\text{CH}_2\text{C}_6\text{H}_4\text{N}^+ \text{Me}_2$], 99/101* (62) [Me_2Ga^+], 91 (1) [C_7H_7^+], 77 (6) [C_6H_5^+], 69/71* (26) [Ga^+]; *isotope pattern clearly visible. — $^1\text{H-NMR}$ (C_6D_6 ; 20°C): $\delta = -0.14$ [s, 6H, $(\text{CH}_3)_2\text{Ga}$], 1.81 [s, 2H, CH_2Ga], 2.23 [s, 6H, $(\text{CH}_3)_2\text{N}$], 6.68–7.49 (m, 4H, aromatic H). — $^{13}\text{C-NMR}$ (C_6D_6 , 20°C): $\delta = -7.4$ [s, $(\text{CH}_3)_2\text{Ga}$], 16.4 (s, CH_2Ga), 46.6 [s, $(\text{CH}_3)_2\text{N}$], 118.4, 125.0, 126.7, 132.5 (s, aromatic C), 143.2 [s, C– $\text{N}(\text{CH}_3)_2$], 150.1 (s, C– CH_2).

$\text{C}_{11}\text{H}_{18}\text{GaN}$ (234.0) Calcd. C 56.46 H 7.75 Ga 29.80 N 5.99
Found C 56.39 H 7.86 Ga 29.70 N 6.48

$\{o\text{-}[(\text{Dimethylamino})\text{phenyl}]\text{methyl}\}\text{dimethylindium}$ (9): In analogy to the synthesis of **8**, the reaction of 3.3 g (18.3 mmol) of dimethylindium chloride with 2.6 g (18.3 mmol) of $o\text{-}[(\text{dimethylamino})\text{phenyl}]\text{methyl}^{13}$ yielded **9** as a colorless liquid; 3.6 g (71%), m. p. 47°C , b. p. $94^\circ\text{C}/0.04$ hPa. — MS (EI, 70 eV): m/z (%) = 264 (37) [$\text{M}^+ - \text{CH}_3$], 145 (6) [Me_2In^+], 135 (27) [$\text{CH}_2\text{C}_6\text{H}_5\text{N}^+ \text{Me}_2$], 134 (100) [$\text{CH}_2\text{C}_6\text{H}_4\text{N}^+ \text{Me}_2$], 130 (2) [MeIn^+], 115 (30) [In^+], 91 (18) [C_7H_7^+], 77 (6) [C_6H_5^+], 65 (11) [C_3H_5^+]; — $^1\text{H-NMR}$ (C_6D_6 ; 20°C): $\delta = -0.42$ [s, 6H, $(\text{CH}_3)_2\text{In}$], 1.76 (s, 2H, CH_2In), 2.28 [s, 6H, $(\text{CH}_3)_2\text{N}$], 6.76–7.44 (m, 4H, aromatic H). — $^{13}\text{C-NMR}$ (C_6D_6 , 20°C): $\delta = -4.6$ [s, $(\text{CH}_3)_2\text{In}$], 18.3 (s, CH_2In),

45.3 [s, (CH₃)₂N], 118.3, 123.7, 125.1, 131.2 (s, aromatic C), 143.8 (s, C-CH₂), 149.8 [s, C-N(CH₃)₂].

C₁₁H₁₈InN (279.1) Calcd. C 47.34 H 6.50 In 41.14 N 5.02
Found C 47.26 H 6.41 In 40.98 N 4.80

<{o-[(Dimethylamino)methyl]phenyl}methyl>dimethylgallium (10): In analogy to the synthesis of 2, the reaction of 1.3 g (9.6 mmol) of dimethylgallium chloride with 1.7 g (11.0 mmol) of {o-[(dimethylamino)methyl]phenyl}methyl lithium³⁸⁾ yielded 10 as colorless crystals; 1.1 g (45%), m. p. ≈ 35°C, b. p. 105°C/0.01 hPa. — MS (EI, 70 eV): *m/z* (%) = 247/249* (6) [M⁺], 232/234* (100) [M⁺ - CH₃], 189/191* (18) [M⁺ - CH₃, - CH₃NCH₂], 135 (6) [C₆H₅CH₂N⁺Me₂], 105 (24) [C₈H₉⁺], 99/101* (17) [Me₂Ga⁺], 77 (6) [C₆H₅⁺]; *isotope pattern clearly visible. — ¹H-NMR (C₆D₆, 20°C): δ = -0.36 [s, 6H, (CH₃)₂Ga], 1.79 [s, 6H, (CH₃)₂N], 1.88 (s, 2H, CH₂Ga), 3.08 (s, 2H, CH₂N), 6.75–7.24 (m, 4H, aromatic H). — ¹³C-NMR (C₆D₆, 20°C): δ = -7.2 [s, (CH₃)₂Ga], 21.4 (s, CH₂Ga), 47.3 [s, (CH₃)₂N], 64.8 (s, CH₂N), 122.2, 128.6, 129.3, 130.2 (s, aromatic C), 131.0 (s, C-CH₂N), 147.8 (s, C-CH₂Ga).

C₁₂H₂₀GaN (248.0) Calcd. C 58.11 H 8.13 Ga 28.11 N 5.65
Found C 58.12 H 8.14 Ga 29.27 N 6.12

<{o-[(Dimethylamino)methyl]phenyl}methyl>dimethylindium (11): In analogy to the synthesis of 3, the reaction of 2.4 g (13.3 mmol) of dimethylindium chloride with 2.1 g (13.3 mmol) of {o-[(dimethylamino)methyl]phenyl}methyl lithium³⁸⁾ yielded 11 as a colorless liquid; 2.1 g (54%), b. p. 78–79°C/0.03 hPa. — MS (EI, 70 eV): *m/z* (%) = 293 (3) [M⁺], 278 (46) [M⁺ - CH₃], 263 (12) [M⁺ - 2 × CH₃], 219 (14) [M⁺ - 2 × CH₃, - Me₂N], 149 (24) [C₇H₇CH₂N⁺Me₂], 148 (30) [C₇H₇CH₂N⁺Me₂], 145 (11) [Me₂In⁺], 130 (4) [MeIn⁺], 119 (11) [C₇H₇CH₂N⁺], 115 (100) [In⁺], 105 (49) [C₇H₇CH₂⁺], 104 (33) [C₆H₄CH₂⁺], 91 (21) [C₇H₇⁺], 77 (26) [C₆H₅⁺], 65 (10) [C₅H₅⁺], 58 (59) [Me₂N⁺CH₂]; — ¹H-NMR (C₆D₆, 20°C): δ = -0.37 [s, 6H, (CH₃)₂In], 1.67 [s, 6H, (CH₃)₂N], 1.90 (s, 2H, CH₂In), 2.96 (s, 2H, CH₂N), 6.71–7.16 (m, 4H, aromatic H). — ¹³C-NMR (C₆D₆, 20°C): δ = -8.6 [s, (CH₃)₂In], 21.6 (s, CH₂In), 46.9 [s, (CH₃)₂N], 64.8 (s, CH₂N), 121.3 (s, C-4), 127.6 (s, C-6), 129.30 (s, C-5), 130.9 (s, C-3), 149.2 (s, C-CH₂N), 130.0 (s, C-CH₂In).

C₁₂H₂₀InN (293.12) Calcd. C 49.17 H 6.88 In 39.17 N 4.78
Found C 49.05 H 6.92 In 39.02 N 4.66

[o-(Dimethylamino)phenyl]dimethylgallium (12): A solution of 2.3 g (17.0 mmol) of dimethylgallium chloride in 50 ml of pentane was added to a stirred solution of 2.4 g (19.0 mmol) of o-(dimethylamino)phenyllithium³⁷⁾ in 50 ml of pentane at room temp. Subsequently, the reaction mixture was refluxed for 2 h and then decanted from lithium chloride. 12 crystallized from a concentrated pentane solution at -30°C; yield 3.2 g (86%), m. p. 68°C. — ¹H-NMR (C₆D₆, 20°C): δ = 0.29 [s, 6H, (CH₃)₂Ga], 2.69 [s, 6H, (CH₃)₂N], 6.35–7.95 (m, 4H, aromatic H). — ¹³C-NMR (C₆D₆, 20°C): δ = -4.7 [s, (CH₃)₂Ga], 60.9 [s, (CH₃)₂N], 115.8, 126.8, 128.8, 136.6 (s, aromatic C), 127.7 (s, C-N), 128.9 (s, C-Ga).

C₁₀H₁₆GaN (220.0) Calcd. C 54.60 H 7.33 N 6.37
Found C 52.78 H 6.92 N 7.01

Mol. mass Calcd. 219.97 (monomer), 439.94 (dimer)
Found 398.6 (by cryoscopy in benzene)

X-ray Structure Determination of 2 and 7: Data collections were carried out with an Enraf-Nonius CAD-4 automatic diffractometer, controlled by a μ-VAX II computer and fitted with a low-temperature equipment (Tables 2 and 3). The diffraction experiment for 2 initially revealed a cell with rhombohedral symmetry which then was transformed into an obverse hexagonal lattice. The cell parameters were obtained from the angles of 25 reflections in the range

of 33° ≤ 2Θ ≤ 49°. 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 hours to determine crystal decomposition. The total loss of intensity during the entire period of data collection was 0.3%. No decay correction was applied. The crystal orientation was checked every 150 intensity measurements by scanning three reflections distributed in reciprocal space. A new orientation matrix was automatically calculated from a list of 25 recentered reflections in case the angular change was greater than 0.09°. The raw data were corrected for Lorentz polarization, and absorption (Ψ-scan method, min./max. transmission 77.5 and 99.9%)⁴⁰⁾ effects. Considering the normalized structure factor statistic and the present extinctions, the possible space groups were limited to R $\bar{3}$ and R $\bar{3}m$ (No. 148 and 166 of the International Tables of X-ray Crystallography)⁴¹⁾. Refinement in space group R $\bar{3}$ was successful. The position of the gallium atom was determined from a three-dimensional Patterson synthesis. The calculated difference Fourier map revealed all missing carbon and nitrogen atoms. The hydrogen positions were refined isotropically. Several least-squares cycles minimized the quantity Σw(|F_o| - |F_c|)². Atomic scattering factors and anomalous dispersion terms for gallium, nitrogen, and carbon were taken from ref.^{42,43)}. Scattering factors for hydrogen were taken from ref.⁴⁴⁾. Data reduction was performed using the SDP software package⁴⁵⁾. All other calculations were undertaken with SHELX 76⁴⁶⁾.

Cell parameters for 7 were obtained from 25 reflections in the 2Θ-range 20.6° ≤ 2Θ ≤ 24.5°. Intensity checks were carried out every 2 h of X-ray exposure time (decay 1.5%, no decay correction). Orientation was checked as for 2 every 200 reflections. Correction of raw data was performed as for 2 (min. and max. transmission coefficients 0.75 and 0.99). The compound 7 crystallizes either in the space group P2₁ or P2₁/m. The coordinates of three heavy-atom positions were located by an automatic search routine using the program SHELX 86⁴⁷⁾. Attempts to refine the structure in P2₁/m gave for some atoms positions on a mirror plane. In the case of the phenyl rings these positions are prohibited by the planarity of the aromatic system. Therefore, P2₁ is the only possible space group. The pseudosymmetry caused problems in refinement. The phenyl carbons were put on calculated positions. Indium atoms were refined anisotropically, all non-hydrogen atoms (except the metal atoms) were refined isotropically (Table 5). Scattering factors and anomalous dispersion terms for In, C, and N were taken from ref.^{42,43)}. All further details are listed in Table 3.

CAS Registry Numbers

1: 127793-25-3 / 2: 127793-26-4 / 3: 127793-27-5 / 4: 127793-28-6 / 5: 127793-29-7 / 6: 127793-30-0 / 7: 127793-31-1 / 8: 127793-32-2 / 9: 127793-33-3 / 10: 127793-34-4 / 11: 127793-35-5 / 12: 127793-36-6 / Me₂GaCl: 6917-81-3 / Et₂GaCl: 30914-08-0 / Pr₂GaCl: 55681-97-5 / iPr₂GaCl: 127793-24-2 / Et₂InCl: 14774-82-4 / Me₂InCl: 14629-99-3 / Et₂AlCl: 96-10-6 / 2-LiC₆H₄CH₂NMe₂: 60528-57-6 / 2-LiC₆H₄CH₂NEt₂: 127793-37-7 / 2-LiCH₂C₆H₄NMe₂: 64308-58-3 / 2-LiCH₂C₆H₄CH₂NMe₂: 60528-54-3 / 2-LiC₆H₄NMe₂: 22608-37-3

¹⁾ A. H. Cowley, R. A. Jones, *Angew. Chem.* **101** (1989) 1235; *Angew. Chem. Int. Ed. Engl.* **28** (1989) 1208.

²⁾ J. P. Mullin, S. J. C. Irvine, R. H. Moss, P. N. Robson, D. R. Wright (Eds.), Proc. 2nd Intern. Conf. Metalorg. Vapor Phase Epitaxy, Sheffield 1984; *J. Cryst. Growth* **68** (1984) 1.

³⁾ G. B. Springfield (Ed.), Proc. 3rd Intern. Conf. Metalorg. Vapor Phase Epitaxy, Universal City, CA, 1986; *J. Cryst. Growth* **77** (1986) 1.

- ⁴⁾ E. Wiberg, T. Johannsen, O. Stecher, *Z. Anorg. Allg. Chem.* **251** (1943) 114.
- ⁵⁾ ^{5a)} G. E. Coates, R. A. Whitcombe, *J. Chem. Soc.* **1956**, 3351. — ^{5b)} A. W. Laubengayer, W. F. Gilliam, *J. Am. Chem. Soc.* **63** (1941) 477. — ^{5c)} L. H. Long, J. F. Sackman, *Trans. Faraday Soc.* **54** (1958) 1797. — ^{5d)} L. M. Dennis, R. W. Work, E. G. Rochow, *J. Am. Chem. Soc.* **56** (1934) 1047.
- ⁶⁾ H. Schumann, U. Hartmann, W. Wassermann, *Polyhedron* **9** (1990) 353.
- ⁷⁾ A. Molassioti, M. Moser, A. Stapor, F. Scholz, M. Hostalek, L. Pohl, *Appl. Phys. Lett.* **54** (1989) 857.
- ⁸⁾ M. Hostalek, L. Pohl, A. Brauers, P. Balk, V. Freese, H. Hardtdegen, R. Hövel, G. K. Regel, A. Molassioti, M. Moser, F. Scholz, *Thin Solid Films* **174** (1989) 1.
- ⁹⁾ ^{9a)} V. Freese, G. K. Regel, H. Hardtdegen, A. Brauers, P. Balk, M. Hostalek, M. Lokai, L. Pohl, *J. Cryst. Growth* **1990**, in press.. — ^{9b)} V. Freese, G. K. Regel, H. Hardtdegen, A. Brauers, P. Balk, M. Hostalek, M. Lokai, L. Pohl, A. Miklis, K. Werner, *J. Electron. Mater.* **19** (1990) 305.
- ¹⁰⁾ G. van Koten, J. T. B. H. Jastrzebski, J. G. Noltes, A. L. Spek, J. C. Schoone, *J. Organomet. Chem.* **148** (1978) 233.
- ¹¹⁾ G. van Koten, C. A. Schaap, J. T. B. H. Jastrzebski, J. G. Noltes, *J. Organomet. Chem.* **186** (1980) 427.
- ¹²⁾ A. C. Cope, R. N. Gourley, *J. Organomet. Chem.* **8** (1967) 527.
- ¹³⁾ L. E. Manzer, *J. Organomet. Chem.* **135** (1977) C6.
- ¹⁴⁾ A. L. Wayda, *Organometallics* **2** (1983) 565.
- ¹⁵⁾ J. T. B. H. Jastrzebski, G. van Koten, D. G. Tuck, H. A. Meinenma, J. G. Noltes, *Organometallics* **1** (1982) 1492.
- ¹⁶⁾ M. Khan, R. C. Steevensz, D. G. Tuck, J. G. Noltes, P. W. R. Corfield, *Inorg. Chem.* **19** (1980) 3407.
- ¹⁷⁾ H. Schumann, W. Wassermann, A. Dietrich, *J. Organomet. Chem.* **365** (1989) 11.
- ¹⁸⁾ R. Brdička, *Grundlagen der Physikalischen Chemie*, 15. Aufl., VEB. Deutscher Verlag der Wissenschaften, Berlin 1982.
- ¹⁹⁾ ^{19a)} W. Stolz, J. Lorberth, E. Göbel, Materiallabor der Phillips-Universität Marburg, private communication. — ^{19b)} Compound **2** and **10** have been prepared recently: J. M. Ferry, D. J. Cole-Hamilton, J. B. Mullin, *Chemtronics* **4** (1989) 141. **2** and **10** have already been prepared by us and are protected. **2**: E. Merck G.m.b.H. (D. Erdmann, M. E. van Ghemen, L. Pohl, H. Schumann, U. Hartmann, W. Wassermann, M. Heyen, H. Jürgensen, Erf.), Deutsche Offenlegungsschrift DE 3 631 469 (1986/88); **10**: Merck G.m.b.H. (M. Hostalek, L. Pohl, D. Erdmann, H. Schumann, U. Hartmann, W. Wassermann, M. Heyen, H. Jürgensen, Erf.), Deutsche Anmeldung 3913 165 (1989).
- ²⁰⁾ C. K. Johnson, ORTEP II, Report ORNL-5138, Oak Ridge National Laboratory, Tennessee, USA 1976.
- ²¹⁾ H. Schumann, U. Hartmann, A. Dietrich, J. Pickardt, *Angew. Chem.* **100** (1988) 1119; *Angew. Chem. Int. Ed. Engl.* **27** (1988) 1077.
- ²²⁾ H. Krause, K. Sille, H.-D. Hausen, J. Weidlein, *J. Organomet. Chem.* **235** (1982) 253.
- ²³⁾ L. M. Golubinskaya, A. V. Golubinskii, V. S. Mastryukov, L. V. Vilkov, V. I. Bregadze, *J. Organomet. Chem.* **117** (1976) C4.
- ²⁴⁾ A. Bondi, *J. Phys. Chem.* **68** (1964) 441.
- ²⁵⁾ M. A. Khan, C. Peppe, D. G. Tuck, *J. Organomet. Chem.* **280** (1985) 17.
- ²⁶⁾ A. M. Arif, D. C. Bradley, H. Dawes, D. M. Frigo, M. B. Hursthouse, B. Hussain, *J. Chem. Soc., Dalton Trans.* **1987**, 2159.
- ²⁷⁾ F. Gerstner, W. Schwarz, H.-D. Hausen, J. Weidlein, *J. Organomet. Chem.* **175** (1979) 33.
- ²⁸⁾ C. Lecomte, J. Protas, *Acta Crystallogr., Sect. B*, **36** (1980) 2769.
- ²⁹⁾ M. Veith, O. Recktenwald, *J. Organomet. Chem.* **264** (1984) 19.
- ³⁰⁾ K. Mertz, W. Schwarz, B. Eberwein, J. Weidlein, H. Hess, H.-D. Hausen, *Z. Anorg. Allg. Chem.* **429** (1977) 99.
- ³¹⁾ D. F. Gaines, J. Borlin, E. P. Fody, *Inorg. Synth.* **15** (1974) 203.
- ³²⁾ J. P. Oliver, L. G. Stevens, *J. Inorg. Nucl. Chem.* **24** (1962) 953.
- ³³⁾ F. Runge, W. Zimmermann, I. Pfeiffer, *Z. Anorg. Allg. Chem.* **267** (1951) 39.
- ³⁴⁾ J. J. Eisch, *J. Am. Chem. Soc.* **84** (1962) 3830.
- ³⁵⁾ J. J. Eisch, R. B. King, *Organometallic Synth.* **2** (1981) 150.
- ³⁶⁾ H. C. Clark, A. C. Pickard, *J. Organomet. Chem.* **8** (1967) 427.
- ³⁷⁾ H. Gilman, I. Banner, *J. Am. Chem. Soc.* **62** (1940) 344.
- ³⁸⁾ F. N. Jones, M. F. Zinn, L. R. Hauser, *J. Org. Chem.* **28** (1963) 663.
- ³⁹⁾ V. M. Micovic, M. L. Mihailovic, *J. Org. Chem.* **18** (1953) 1190.
- ⁴⁰⁾ A. C. T. North, D. C. Phillips, F. S. Mathews, *Acta Crystallogr., Sect. A*, **24** (1968) 351.
- ⁴¹⁾ *International Tables for X-ray Crystallography*, vol. I, Kynoch Press (present distributor Kluwer Academic Publishers, Dordrecht) 1974.
- ⁴²⁾ D. T. Cromer, J. B. Mann, *Acta Crystallogr., Sect. A*, **24** (1968) 321.
- ⁴³⁾ D. T. Cromer, D. Liberman, *J. Chem. Phys.* **53** (1970) 1891.
- ⁴⁴⁾ R. F. Stewart, E. R. Davidson, W. T. Simpson, *J. Chem. Phys.* **42** (1965) 3175.
- ⁴⁵⁾ B. A. Frenz, *Enraf-Nonius, SDP — Plus Structure Determination Package*, Version 3.0, Enraf-Nonius, Delft 1985.
- ⁴⁶⁾ G. M. Sheldrick, SHELX 76, Program for Crystal Structure Determination, University of Cambridge, England, 1976.
- ⁴⁷⁾ G. M. Sheldrick, SHELX 86, Program for Crystal Structure Solution, Universität Göttingen, 1986.

[120/90]