Synthesis and Characterization of Organogallium and Organoindium Compounds with Tridentate 2,6-Bis[(dialkylamino)methyl]phenyl Ligands

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The intramolecularly stabilized five-coordinated organogallium and organoindium compounds $\{2,6\text{-}[(CH_3)_2NCH_2]_2C_6H_3\}GaMe_2$ (**1**), $\{2,6\text{-}[(CH_3)_2NCH_2]_2C_6H_3\}InR_2$ (**2-4**), and $\{2,6\text{-}[(C_2H_5)_2NCH_2]_2C_6H_3\}InEt_2$ (**5**) have been synthesized from {2,6-bis[(dimethylamino)methyl]phenyl}lithium or from {2,6-bis[(diethylamino)methyl]phenyl}lithium and the corresponding diorganogallium or diorganoindium chloride. The ^{1}H-, ^{13}C-NMR and mass spectra of the new compounds are reported and discussed.

The concept of intramolecular base stabilization of trialkylaluminium, -gallium, and -indium compounds has created a series of new precursors for the production of semiconducting layers of GaAs or InP by *m*etal *o*rganic *v*apor *p*hase *e*pitaxy (MOVPE)[1]. Recent investigations have established their ability to act as GaAs or InP precursors, which can be applied together with conventional (AsH_3, PH_3) as well as with new organic group V sources like $(C_6H_5)AsH_2$, $t\text{-}C_4H_9AsH_2$, or $t\text{-}C_4H_9PH_2$[2], thus allowing the replacement of the commonly used highly pyrophoric precursors trimethylgallium and -indium[3,4], which makes MOVPE safer. Epitaxial InP layers grown by use of [3-(dimethylamino)propyl]dimethylindium as a source material[5] show electron mobilities of μ_{77K} = 49900 cm^{2}V^{-1}s^{-1} and carrier concentrations of n = 3.3 × 10^{14} cm^{-3}. More recent investigations employing [3-(dimethylamino)propyl]diethylgallium or 1-[3-(dimethylamino)propyl]-1-gallacyclohexane confirm these encouraging results[6,7].

In these new compounds organic ligands containing a terminal functional group with Lewis basicity like (dimethylamino)propyl[8] are used, which enable an intramolecular coordination of the nitrogen lone pair into empty metal orbitals, resulting in the formation of five- or six-membered metallacycles[9].

In our continuous effort to enhance the stability of such group III compounds toward water and oxygen, we have previously prepared {2,6-bis[(diethylamino)methyl]phenyl}methylindium chloride[10]. In this molecule with pentacoordinate indium, as demonstrated by an X-ray structure analysis, nucleophilic attack of water or oxygen at the metal center is significantly impeded due to the steric demand of the bulky ligand.

We now report on the synthesis and properties of some new triorganogallium and -indium compounds containing tridentate 2,6-bis[(dialkylamino)methyl]phenyl ligands. All compounds have been characterized by elemental analyses, ^{1}H-NMR, ^{13}C-NMR, and mass spectra.

Synthesis and Properties

The reactions of {2,6-bis[(dimethylamino)methyl]phenyl}lithium with dimethylgallium chloride, dimethyl-, diethyl-, and di-*n*-propylindium chloride, all carried out at room temperature in pentane, result in the formation of the triorganometal compounds **1**–**4**, which are isolated in high yields as colorless liquids or low-melting solids after distillation or sublimation.

M = Ga, R = Me **1**

M = In, R = Me **2**, Et **3**, n-Pr **4**

Diethylindium chloride reacts with {2,6-bis[(diethylamino)methyl]phenyl}lithium under the same conditions to yield {2,6-bis[(diethylamino)methyl]phenyl}diethylindium (**5**).

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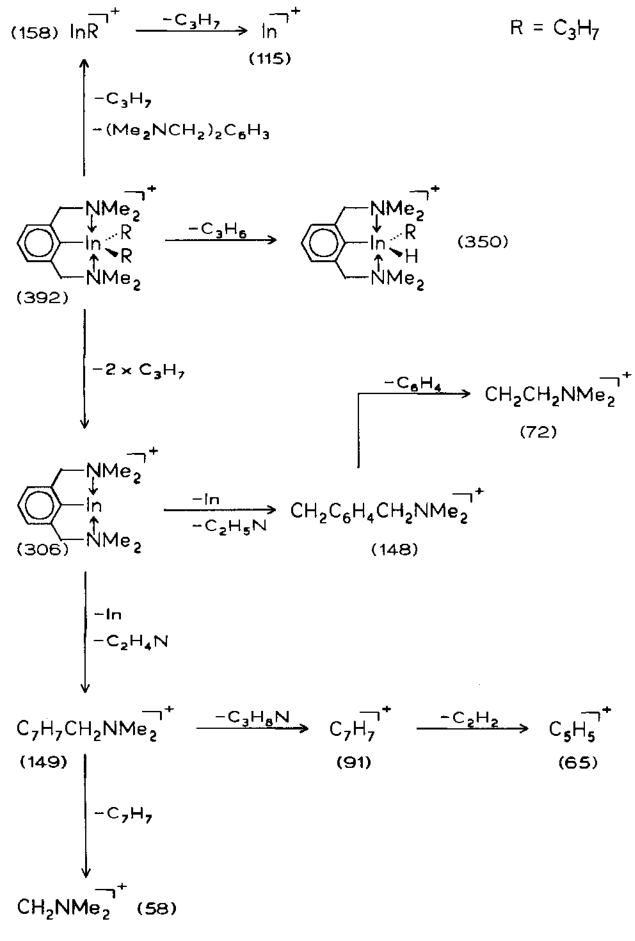
The new compounds are readily soluble in aliphatic or aromatic hydrocarbons and ethers. A decomposition of these compounds has not been observed at room temperature, neither upon storage in substance nor in solution. They show no sign of decomposition or impairment by water or oxygen even after prolonged exposure to air.

The ^{1}H- and ^{13}C-NMR spectra of all compounds recorded in benzene show the expected chemical shifts and coupling patterns. However, due to a spin of 7/2 for gallium or 9/2 for indium nuclei the signals for carbon atoms bound directly to the metal center appear as broad signals with low intensity. This is observed especially in the case of the quaternary carbon atom of the phenyl ring for which the signal-enhancing nuclear Overhauser effect does not apply because of the lack of hydrogen atoms attached to it.

The low melting points of **1**–**5** are a consequence of the stabilization of these molecules by intramolecular coordination resulting in monomeric molecules in the solid state. This is supported by their mass spectra, which show no peaks higher than that for the molecular ion of the respective compound. The characteristic fragmentation pattern of the 2,6-bis[(dimethylamino)methyl]phenyl ligand is the dominant feature in these spectra as is illustrated in Scheme 1 for compound **4**.

Scheme 1. Fragmentation of {2,6-bis[(dimethylamino)methyl]phenyl}di-*n*-propylindium



The most interesting fragment with an intensity of 41% of thc base peak (In^+, 115) is the ion with $m/z = 149$ originating in the decay of the 2,6-bis[(dimethylamino)methyl]phenyl ligand. In this ion the very stable tropylium cation $C_7H_7^+$ is already preformed by the rearrangement of the parent ion and appears as a peak with the mass of 91 after the loss of the Schiff's base fragment $C_3H_8N^+$ ($m/z = 58$). The ion $C_7H_7^+$ is characteristic of the fragmentation of alkyl-substituted phenyl ligands. It is also observed in the mass spectra of analogous organogallium and -indium compounds with mono(dialkylamino)methyl-substituted phenyl ligands[11]. Loss of acetylene results in the formation of the cyclic $C_5H_5^+$ cation with a mass of 65[12].

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Experimental

All reactions were carried out in dry, oxygen-free argon using Schlenk tubes. The solvents used were dried and freed from oxygen with $LiAlH_4$ or Na/benzophenone and distilled prior to use. — Elemental analyses: Perkin Elmer 240C 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 (^1H) or at 67.93 MHz (^{13}C).

The *starting materials* were prepared according to literature procedures. The triorganometal compounds were obtained either by alkylation of the metal trichlorides with trimethylaluminium (Me_3Ga)[13] or by Grignard reactions (Et_3In, *n*-Pr_3In)[14]. The corresponding diorganometal chlorides were prepared by redistribution reactions of the triorganometal compounds with the metal trichlorides[15,16]. Dimethylindium chloride was obtained by reaction of indium trichloride with methyllithium[17]. The lithium reagents used were synthesized from the corresponding 2,6-bis[(dialkylamino)methyl]phenyl bromides and *n*-butyllithium[10,18,19,20].

{2,6-Bis[(dimethylamino)methyl]phenyl}dimethylgallium (**1**): The lithium reagent prepared from 0.82 g (3.0 mmol) of 2,6-$[(CH_3)_2NCH_2]_2C_6H_3Br$ and 1.9 ml of *n*-butyllithium (3.0 mmol, 1.6 mol/l in hexane) was added to a stirred solution of 0.4 g (3.0 mmol) of dimethylgallium chloride in 10 ml of hexane. After stirring at room temp. for 12 h, the reaction mixture was filtered, the solvent evaporated in vacuo and the residue sublimed at 25°C onto a 15°C cold finger to yield **1** as colorless crystals; yield 0.70 g (80%), m.p. 34°C. — MS (EI, 70 eV): m/z (%) = 275/277* (100) [$M^+ - CH_3$], 232/234* (37) [$M^+ - CH_2NMe_2$], 189/191* (62) [$M^+ - Me_2NCH_2 - MeNCH_2$], 146 (12) [$MeC_6H_3CH_2N^+Me_2$], 105 (24) [$C_8H_9^+$], 69/71* (50) [$Ga^+$], 58 (25) [$Me_2N^+CH_2$], 42 (8) [$C_2H_4N^+$]; *isotope pattern clearly visible. — ^1H NMR (C_6D_6; 20°C): $\delta = -0.70$ [s, 6H, $(CH_3)_2Ga$], 2.08 [s, 6H, $(CH_3)_2N$], 3.32 (s, 4H, CH_2N), 6.90–7.38 (m, 3H, aromatic H). — ^{13}C NMR (C_6D_6, 20°C): $\delta = -8.3$ [s, $(CH_3)_2Ga$], 45.5 [s, $(CH_3)_2N$], 66.1 (s, CH_2N), 123.0 (s, C-3,5), 124.0 (s, C-4), 144.9 (s, C-2,6), C-1 not detected.

$C_{14}H_{25}GaN_2$ (291.1) Calcd. C 57.77 H 8.66 Ga 23.90 N 9.62
Found C 56.80 H 8.48 Ga 23.36 N 10.14

{2,6-Bis[(dimethylamino)methyl]phenyl}dimethylindium (**2**): By analogy with the synthesis of **1**, the reaction of the lithium reagent prepared from 2.71 g (10.0 mmol) of 2,6-$[(CH_3)_2NCH_2]_2C_6H_3Br$ in 40 ml of hexane and 6.3 ml of *n*-butyllithium (10.0 mmol, 1.6 mol/*l* in hexane) with 1.8 g (10.0 mmol) of dimethylindium chloride in 20 ml of hexane yielded **2** as colorless crystals upon cooling the concentrated hexane solution to −30°C; yield 2.3 g (68%), m.p. 53°C. — MS (EI, 70 eV): m/z (%) = 264 (39) [$M^+ - Me_2N - C_2H_4$], 145 (7) [Me_2In^+], 135 (22) [$C_6H_5CH_2N^+Me_2$], 134 (100) [$C_6H_4CH_2N^+Me_2$], 130 (2) [$MeIn^+$], 115 (33) [In^+], 91 (17) [$C_7H_7^+$], 77 (7) [$C_6H_5^+$], 65 (10) [$C_5H_5^+$], 56 (2) [$C_3H_6N^+$], 44 (5) [Me_2N^+]. — ^1H NMR (C_6D_6; 20°C): $\delta = -0.09$ [s, 6H, $(CH_3)_2In$], 2.01 [s, 12H, $(CH_3)_2N$], 3.20 (s, 4H, CH_2N), 6.82–7.29 (m, 3H, aromatic H). — ^{13}C NMR (C_6D_6, 20°C): $\delta = -10.4$ [s, $(CH_3)_2In$], 45.5 [s, $(CH_3)_2N$], 66.7 (s, CH_2N), 124.3 (s, C-3,5), 126.9 (s, C-4), 145.5 (s, C-2,6), 158.9 (s, C-1).

$C_{14}H_{25}InN_2$ (336.2) Calcd. C 50.02 H 7.50 In 34.15 N 8.33
Found C 49.94 H 7.49 In 33.98 N 8.16

{2,6-Bis[(dimethylamino)methyl]phenyl}diethylindium (**3**): By analogy with the synthesis of **1**, the reaction of the lithium reagent prepared from 2.50 g (9.2 mmol) of 2,6-$[(CH_3)_2NCH_2]_2C_6H_3Br$ in 40 ml of hexane and 5.8 ml of *n*-butyllithium (9.2 mmol, 1.6 mol/*l* in hexane) with 1.92 g (10.0 mmol) of diethylindium chloride in 20 ml of hexane yielded **3** as colorless crystals upon cooling the concentrated hexane solution to −30°C; yield 1.9 g (57%), m.p. 41°C. — MS (EI, 70 eV): m/z (%) = 336 (16) [$M^+ - C_2H_4$], 335 (100) [$M^+ - C_2H_5$], 264 (3) [$M^+ - 2 \times C_2H_4 - Me_2N$], 263 (21) [$M^+ - C_2H_5 - C_2H_4 - Me_2N$], 191 (5) [$M^+ - In(C_2H_5)_2$], 144 (4) [$C_2H_5In^+$], 115 (93) [$In^+$], 105 (8) [$C_7H_7N^+$], 58 (10) [$C_3H_8N^+$], 43 (4) [$C_3H_7^+$]. — ^1H NMR (C_6D_6; 20°C): $\delta = 0.79$ [t, 6H, $(CH_3CH_2)_2In$], 1.61 [q, 4H, $(CH_3CH_2)_2In$], 2.02 [s, 12H, $(CH_3)_2N$], 3.20 (s, 4H, CH_2N), 6.93–7.16 (m, 3H, aromatic H). — ^{13}C NMR (C_6D_6, 20°C): $\delta = 3.7$ [s, $(CH_3CH_2)_2In$], 13.7 [s, $(CH_3CH_2)_2In$], 45.6 [s, $(CH_3)_2N$], 67.1 (s, CH_2N), 124.4 (s, C-3,5), 126.8 (s, C-4), 145.8 (s, C-2,6), 158.6 (s, C-1).

$C_{16}H_{29}InN_2$ (364.2) Calcd. C 52.76 H 8.03 In 31.52 N 7.69
Found C 52.92 H 7.83 In 31.22 N 7.48

{2,6-Bis[(dimethylamino)methyl]phenyl}di-n-propylindium (**4**): By analogy with the synthesis of **1**, the reaction of the lithium reagent prepared from 2.2 g (8.1 mmol) of $2,6\text{-}[(CH_3)_2NCH_2]_2C_6H_3Br$ in 40 ml of hexane and 5.1 ml of *n*-butyllithium (8.1 mmol, 1.6 mol/*l* in hexane) with 1.90 g (8.1 mmol) of di-*n*-propylindium chloride in 20 ml of hexane yielded **4** as a colorless liquid after distillation under reduced pressure; yield: 2.1 g (66%), b.p. 125°C/0.03 mbar. – MS (EI, 70 eV): *m/z* (%) = 350 (7) $[M^+ - C_3H_6]$, 349 (26) $[M^+ - C_3H_7]$, 306 (2) $[M^+ - 2\,C_3H_7]$, 158 (3) $[C_3H_7In^+]$, 149 (41) $[C_7H_7CH_2N^+Me_2]$, 148 (22) $[CH_2C_6H_4CH_2N^+Me_2]$, 115 (85) $[In^+]$, 105 (47) $[C_7H_7N^+]$, 91 (33) $[C_7H_7^+]$, 86 (17) $[Me_2N^+(CH_2)_3]$, 84 (7) $[Me_2N^+CHCHCH_2]$, 65 (13) $[C_5H_5^+]$, 58 (46) $[C_3H_8N^+]$, 56 (11) $[C_3H_6N^+]$. – ^1H NMR (C_6D_6, 20°C): δ = 0.75 [t, 4H, $(CH_3CH_2C\mathit{H}_2)_2In$], 1.22 [t, 6H, $(C\mathit{H}_3CH_2CH_2)_2In$], 1.86 [m, 4H, $(CH_3C\mathit{H}_2CH_2)_2In$], 2.10 [s, 12H, $(CH_3)_2N$], 3.28 (s, 4H, CH_2N), 7.02–7.15 (m, 3H, aromatic H). – ^{13}C NMR (C_6D_6, 20°C): δ = 16.1 [s, $(CH_3CH_2\mathit{C}H_2)_2In$], 21.4 [s, $(\mathit{C}H_3CH_2CH_2)_2In$], 23.0 [s, $(CH_3\mathit{C}H_2CH_2)_2In$], 45.8 [s, $(CH_3)_2N$], 67.2 (s, CH_2N), 124.5 (s, C-3,5), 126.7 (s, C-4), 145.7 (s, C-2,6), 158.9 (s, C-1).

$C_{18}H_{33}InN_2$ (392.3) Calcd. C 55.11 H 8.48 In 29.27 N 7.14
Found C 55.17 H 8.15 In 29.85 N 6.99

{2,6-Bis[(diethylamino)methyl]phenyl}diethylindium (**5**): By analogy with the synthesis of **1**, the reaction of the lithium reagent prepared from 2.40 g (7.3 mmol) of $2,6\text{-}[(C_2H_5)_2NCH_2]_2C_6H_3Br$ in 40 ml of hexane and 4.6 ml of *n*-butyllithium (7.3 mmol, 1.6 mol/*l* in hexane) with 1.50 g (7.3 mmol) of diethylindium chloride in 20 ml of hexane yielded **5** as a colorless liquid after distillation under reduced pressure; yield 1.6 g (52%), b.p. 115°C/0.04 mbar. – ^1H NMR (C_6D_6, 20°C): δ = 0.47 [t, 6H, $(C\mathit{H}_3CH_2)_2In$], 0.60 [q, 4H, $(CH_3C\mathit{H}_2)_2In$], 1.32 [t, 12H, $(C\mathit{H}_3CH_2)_2N$], 2.24 [q, 8H, $(CH_3C\mathit{H}_2)_2N$], 3.13 (s, 4H, CH_2N), 6.59–7.26 (m, 3H, aromatic H). – ^{13}C NMR (C_6D_6, 20°C): δ = 5.1 [s, $(CH_3CH_2)_2In$], 8.7 [s, $(\mathit{C}H_3CH_2)_2N$], 12.2 [s, $(\mathit{C}H_3CH_2)_2In$], 44.1 [s, $(CH_3CH_2)_2N$], 60.6 (s, CH_2N), 124.6 (s, C-3,5), 127.4 (s, C-4), 146.0 (s, C-2,6), 159.8 (s, C-1).

$C_{20}H_{37}InN_2$ (420.35) Calcd. C 57.15 H 8.87 In 27.32 N 6.66
Found C 57.03 H 8.62 In 26.89 N 6.35

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1: 133495-11-1 / **2**: 102499-78-5 / **3**: 133495-12-2 / **4**: 133495-13-3 / **5**: 133495-14-4 / Me_2GaCl: 6917-81-3 / Me_2InCl: 14629-99-3 / Et_2InCl: 14774-82-4 / Pr_2InCl: 101185-56-2 / $2,6\text{-}(Me_2NCH_2)_2C_6H_3Br$: 66479-06-9 / $2,6\text{-}(Et_2NCH_2)_2C_6H_3Br$: 131508-05-9

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[1] H. Schumann, U. Hartmann, A. Dietrich, J. Pickardt, *Angew. Chem.* **100** (1988) 1119; *Angew. Chem. Int. Ed. Engl.* **27** (1988) 1077.

[2] L. Pohl, M. Hostalek, H. Schumann, U. Hartmann, W. Wassermann, A. Brauers, G. K. Regel, R. Hövel, P. Balk, F. Scholz, *Proc. 5th International Conference on Metalorganic Vapor Phase Epitaxy*, Aachen 1990.

[3] M. J. Ludowise, *J. Appl. Phys.* **58** (1985) 31.

[4] M. R. Leys, *Chemtronics* **2** (1987) 155.

[5] A. Molassioti, M. Moser, A. Stapor, F. Scholz, M. Hostalek, L. Pohl, *Appl. Phys. Lett.* **54** (1987) 857.

[6] H. Schumann, U. Hartmann, W. Wassermann, O. Just, A. Dietrich, L. Pohl, M. Hostalek, M. Lokai, *Chem. Ber.* **124** (1991) 1113.

[7] M. Hostalek, L. Pohl, A. Brauers, P. Balk, V. Frese, H. Hardtdegen, R. Hövel, G. K. Regel, A. Molassioti, M. Moser, F. Scholz, H. Schumann, U. Hartmann, W. Wassermann, *Mat. Res. Soc. Symp. Proc.* **145** (1989) 205.

[8] K.-H. Thiele, E. Langguth, G. E. Müller, *Z. Anorg. Allg. Chem.* **462** (1980) 152.

[9] H. Schumann, U. Hartmann, W. Wassermann, *Polyhedron* **9** (1990) 353.

[10] H. Schumann, W. Wassermann, A. Dietrich, *J. Organomet. Chem.* **365** (1989) 11.

[11] H. Schumann, U. Hartmann, W. Wassermann, A. Dietrich, F. H. Görlitz, L. Pohl, M. Hostalek, *Chem. Ber.* **123** (1990) 2093.

[12] J. Müller, *Angew. Chem.* **84** (1972) 725; *Angew. Chem. Int. Ed. Engl.* **11** (1972) 653.

[13] D. F. Gaines, J. Borlin, E. P. Fody, *Inorg. Synth.* **15** (1974) 203.

[14] F. Runge, W. Zimmermann, H. Pfeiffer, I. Pfeiffer, *Z. Anorg. Allg. Chem.* **267** (1951) 39.

[15] J. J. Eisch, *J. Am. Chem. Soc.* **84** (1962) 3830.

[16] J. J. Eisch, R. B. King, *Organomet. Synth.* **2** (1981) 150.

[17] H. C. Clark, A. C. Pickard, *J. Organomet. Chem.* **8** (1967) 427.

[18] F. Vögtle, *Chem. Ber.* **102** (1969) 1784.

[19] G. van Koten, J. T. B. H. Jastrzebski, J. G. Noltes, A. L. Spek, J. C. Schoone, *J. Organomet. Chem.* **148** (1978) 233.

[20] E. Wehman, J. T. B. H. Jastrzebski, J.-M. Ernsting, D. M. Grove, G. van Koten, *J. Organomet. Chem.* **353** (1988) 145.

[44/91]