Organometallics **1996,** *15,* 4559−4564

Synthesis, Structure, and Properties of Gallium Compounds with the Heterodifunctional [2-(*N*,*N*-Dimethylamino)ethyl]cyclopentadienyl Ligand[1]

Peter Jutzi,* Michael Bangel, Beate Neumann, and Hans-Georg Stammler

Fakultät für Chemie, Universität Bielefeld, Universitätsstrasse 25,
D-33615 Bielefeld, Germany

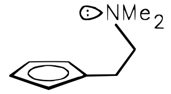
Received June 19, 1996⊗

Several new gallium compounds containing the [2-(*N*,*N*-dimethylamino)ethyl]cyclopentadienyl ligand (Cp^N) are described. Reaction of the respective element halide with Cp^NK **1** leads to the compounds **2**−**6** of the type [2-($Me_2NCH_2CH_2$)C_5H_4]GaX_2 [**2**: X = Cl; **3**: X = Br; **4**: X = I; **5**: X = CH_3; **6**: X = H]. Each compund was characterized by ^1H and ^{13}C NMR spectroscopy, mass spectrometry, and elemental analysis; the molecular structures of **2**−**5** were determined by X-ray crystallography. In the solid state and presumably also in solution all compounds feature a monomeric structure with an intramolecularly coordinated dimethylamino group. The resulting coordinative and electronic saturation of the metal center leads to a drastically decreased reactivity against moisture and air. The observed dynamic behavior in solution is based on fast haptotropic shifts in a "windscreen-wiper" type process. Sufficient volatility and well-behaved fragmentation makes **6** a suitable precursor for the deposition of gallium in the MOCVD process.

Introduction

In recent years, we have reported about many compounds of s-, p-, d-, and f-block elements containing the 1-[2-(*N*,*N*-dimethylamino)ethyl]-2,3,4,5-tetramethylcyclopentadienyl ligand (Cp^).[2−13] If required, an intramolecular coordination of the amino group to the respective metal center is observed. In the case of the group 13 elements Al, Ga, and In, such intramolecular coordination leads to monomeric molecules, which show drastically decreased reactivity against moisture and air in comparison with the parent pentamethylcyclopentadienyl (Cp*) compounds. Although the volatility of these complexes is rather low, some of them nevertheless are candidates for the growth of thin films in the MOMBE (metal organic molecular beam epitaxy) process. To gain compounds with increased volatility, which are potential precursors for MOCVD (metal organic chemical vapor deposition) processes, we now have changed to the [2-(*N*,*N*-dimethylamino)ethyl]cyclopentadienyl ligand (Cp^N) **I**,[14] the ring nonmethylated analogon of Cp^.

Chart 1



I

This ligand, too, has already found application in the chemistry of s-, p-, d-, and f-block elements. We and others have shown that, under appropriate conditions, the nitrogen atom in **I** coordinates intramolecularly to a metal center.[4,6−9,14a,15−21] In this paper, we report in detail[4,21] on the preparation and characterization of compounds of the general formula [2-($Me_2NCH_2CH_2$)-C_5H_4]GaX_2 (X = Cl; Br, I; Me; H) and their structure both in solution and in the solid state. Special emphasis is put on the coordination mode of the ligand. In comparison with compounds derived from the parent cyclopentadienyl unit (Cp), we observed significant changes in stability, reactivity, and structure. First deposition experiments in a hot-wall MOCVD reactor are described.

⊗ Abstract published in *Advance ACS Abstracts,* September 15, 1996.

(1) Presented in part at the 49th Southwest Regional Meeting of the American Chemical Society, Austin, TX, Oct 1993 and at the 1st Journal of Organometallic Chemistry Conference on Applied Organometallic Chemistry, Munich, Germany, Nov 1993.

(2) Jutzi, P.; Dahlhaus, J.; Kristen, M. O. *J. Organomet. Chem.* **1993**, *450*, C1.

(3) Jutzi, P.; Kristen, M. O.; Dahlhaus, J.; Neumann, B.; Stammler, H. G. *Organometallics* **1993**, *12*, 2980.

(4) Jutzi, P.; Dahlhaus, J.; Bangel, M. *J. Organomet. Chem.* **1993**, *460*, C13.

(5) Jutzi, P.; Kristen, M. O.; Neumann, B.; Stammler, H. G. *Organometallics* **1994**, *13*, 3854.

(6) Jutzi, P.; Dahlhaus, J. *Phosphorus, Sulfur, Silicon* **1994**, *87*, 73.

(7) Dahlhaus, J.; Bangel, M.; Jutzi, P. *J. Organomet. Chem.* **1994**, *474*, 55.

(8) Jutzi, P.; Dahlhaus, J. *Coord. Chem. Rev.* **1994**, *137*, 179.

(9) Jutzi, P.; Kleimeier, J.; Redeker, T.; Stammler, H. G.; Neumann, B. *J. Organomet. Chem.* **1995**, *498*, 85.

(10) Jutzi, P.; Redeker, T.; Neumann, B.; Stammler, H. G. *J. Organomet. Chem.* **1995**, *498*, 127.

(11) Jutzi, P.; Schmidt, H.; Neumann, B.; Stammler, H. G. *J. Organomet. Chem.* **1995**, *499*, 7.

(12) (a) Stammler, H. G.; Jutzi, P.; Neumann, B.; Kristen, M. O.; Hölscher H. *Acta Crystallogr.* **1995**, *C51*, 2494; (b) Stammler, H. G.; Jutzi, P.; Neumann, B.; Kristen, M. O. *Acta Crystallogr.* **1995**, *C51*, 2496.

(13) Jutzi, P.; Dahlhaus, J.; Neumann, B.; Stammler, H. G. *Organometallics* **1996**, *15*, 747.

(14) (a) Wang, T.-F.; Lee, T.-Y.; Chou, J.-W.; Ong, C.-W. *J. Organomet. Chem.* **1992**, *423*, 31. (b) Rees, W. S., Jr.; Dippel, K. A. *Org. Prep. Proced. Int.* **1992**, *24*, 527.

(15) Wang, T.-F.; Wen, Y.-S. *J. Organomet. Chem.* **1992**, *439*, 155.

(16) Herrmann, W. A.; Anwander, R.; Munck, F. C.; Scherer, W. *Chem. Ber.* **1993**, *126*, 331.

(17) Anwander, R.; Herrmann, W. A.; Scherer, W.; Munck, F. C. *J. Organomet. Chem.* **1993**, *462*, 163.

(18) Rees, W. S., Jr.; Lay, U. W.; Dippel, K. A. *J. Organomet. Chem.* **1994**, *483*, 27.

(19) Flores, J. C.; Chien, J. C. W.; Rausch, M. D. *Organometallics* **1994**, *13*, 4140.

(20) Jutzi, P.; Kleimeier, J. *J. Organomet. Chem.* **1995**, *486*, 287.

(21) Jutzi, P.; Bangel, M. *J. Organomet. Chem.* **1994**, *480*, C18.

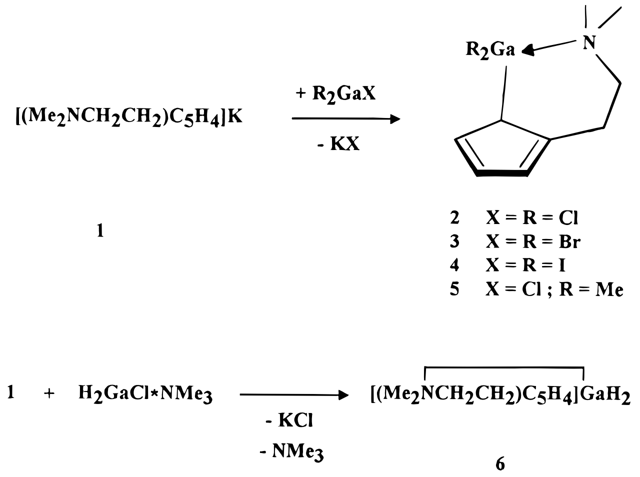
S0276-7333(96)00497-9 CCC: $12.00

Table 1. Crystallographic Data of Compounds 2−5

	2	3	4	5
empirical formula	$C_9H_{14}Cl_2GaN$	$C_9H_{14}Br_2GaN$	$C_9H_{14}GaI_2N$	$C_{11}H_{20}GaN$
cryst size, mm^3	1.00 × 0.60 × 0.50	0.60 × 0.60 × 0.50	0.30 × 0.15 × 0.10	0.80 × 0.30 × 0.05
fw	276.83	365.75	459.73	236.00
cryst syst	orthorhombic	monoclinic	orthorhombic	monoclinic
space group	$P2_12_12_1$	$P2_1/n$	$P2_12_12_1$	$P2_1/n$
lattice parameter				
a, Å	$a = 8.733(6)$	$a = 7.330(2)$	$a = 7.3560(10)$	$a = 7.411(2)$
b, Å	$b = 9.738(7)$	$b = 14.743(5)$	$b = 11.711(2)$	$b = 14.352(4)$
c, Å	$c = 13.381(8)$	$c = 11.047(3)$	$c = 14.610(2)$	$c = 11.204(3)$
α, deg	α = 90	α = 90	α = 90	α = 90
β, deg	$\beta = 90$	$\beta = 91.10(3)$	$\beta = 90$	$\beta = 90.21(2)$
γ, deg	$\gamma = 90$	$\gamma = 90$	$\gamma = 90$	$\gamma = 90$
V, Å^3	1137.9(13)	1193.6(6)	1258.6(3)	1191.7(6)
Z	4	4	4	4
d_{calc} g/cm^3	1.616	2.035	2.426	1.315
diffractometer	Siemens $P2_1$	Siemens $P2_1$	Siemens $P2_1$	Siemens $P2_1$
$F(000)$	560	704	848	496
μ (Mo Kα), mm^{-1}	2.843	8.958	7.053	2.269
temp. °C	−100	−100	−100	−100
$2\Theta_{max}$, deg	60	55	55	55
no. data collected	1902	2928	3347	2970
no. of parameters refined	120	120	120	122
no. obsd data [$F > 4\sigma(F)$]	1714	1965	2560	1722
residuals: R_F, wR_F2 for observed data	0.0597, 0.1465	0.0781, 0.2151	0.0336, 0.0704	0.0620, 0.1369
lagest peak in final diff map e/Å^3	1.2	1.5	0.5	0.8
abs corr	none	semiempirical from ψ-scans	semiempirical from ψ-scans	none

[a] X-ray structure determination. A single crystal was coated with a layer of hydrocarbon oil, attached to a glass fiber and cooled to 173 K for data collection. Crystallographic programs used for structure solution and refinement were from SHELXTL PLUS and SHELXL-93. The structures were solved by using direct methods and were refined by using full-matrix least squares on F^2 of all unique reflections with anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were included at the calculated positions with U(H) = $1.2U_{eq}$ for CH and CH_2 groups, U(H) = $1.5U_{eq}$ for CH_3 groups.

Scheme 1



Results and Discussion

Synthesis. The reaction of potassium [[2-(*N*,*N*-dimethylamino)ethyl]cyclopentadienide] **1** (Cp^{N}K) with 1 equiv of gallium trihalide GaX_3 led to the formation of the complexes **2**−**4** of type [η^1:η^1-$C_5H_4(CH_2CH_2NMe_2)$]-GaX_2 (**2**: X = Cl, **3**: X = Br, **4**: X = I) (Scheme 1). In these reactions the order of addition of the reagents is of crucial importance. It is essential to add Cp^{N}K to the respective gallium trihalide and not vice versa; otherwise **2**−**4** can be isolated only in low yields (out of a mixture of products). Compounds **2**−**4** were isolated as colorless (**2**, **3**) or pale yellow (**4**) crystals, which are moderately air-stable.

Treatment of **1** with a stoichiometric amount of $Me_2GaCl{\cdot}OEt_2$ led to [η^1:η^1-$C_5H_4(CH_2CH_2NMe_2)$]$GaMe_2$ **5** (Scheme 1). Complex **5** was obtained as colorless and moisture-sensitive crystals, which are unexpectedly stable against air and readily soluble in common organic solvents.

A pronounced thermal stability was observed for compounds **2**−**5**; treatment at 100 °C in toluene solution for 2 weeks did not lead to any decomposition.

The reaction of **1** with a stoichiometric amount of $H_2GaCl{\cdot}NMe_3$ led to [η^1:η^1-$C_5H_4(CH_2CH_2NMe_2)$]GaH_2 **6**. When $H_2GaCl{\cdot}NMe_3$ was added to **1**, spontaneous gas evolution was observed, which arose from the substitution of trimethylamine in the coordination sphere of the gallium center by the amino unit of **1**. Subsequent elimination of potassium chloride led to **6**, which was isolated as a colorless solid by vacuum sublimation. The gallane **6** is very moisture- and also rather air-sensitive, but stable at room temperature under inert gas atmosphere for prolonged periods of time.

Solid-State Structures of 2−**5.** To get information about the ground state geometries of the compounds described above, single-crystal X-ray structure investigations have been performed with compounds **2**−**5**. Crystallographic data are presented in Table 1, and atomic coordinates are given in the Supporting Information. The molecular structures of **2**−**5** all are very similar. As examples, the structures of the dichloro compound **2** and of the dimethyl compound **5** are shown in Figures 1 and 2, respectively, along with the relevant atom numbering schemes.

General findings in the molecular structures of **2**−**5** are as follows: The compounds consist of monomeric molecules with no abnormally short intermolecular contacts. The cyclopentadienyl ligand is η^1-bonded from the allylic position to the gallium center. Within the planar C_5-perimeter, bond length (Table 2) and bond angles (Table 3) are characteristic of σ-bonded Cp units. The side chain is bonded to a vinylic carbon atom of the Cp ring in α-position to the allylic carbon atom. A coordination number of four at gallium is realized by an intramolecular interaction with the nitrogen atom in the side chain. The Ga−N distances are slightly

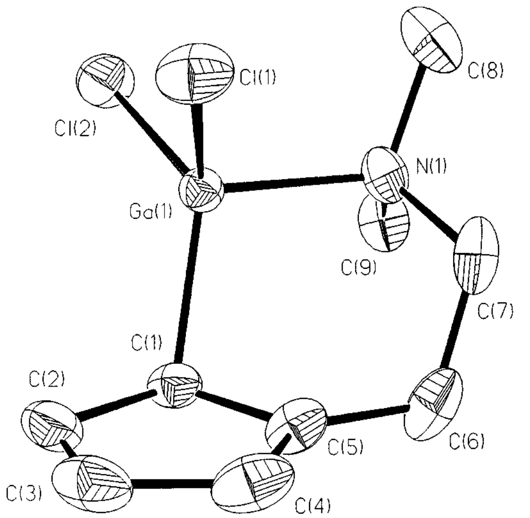


Figure 1. Molecular structure of **2**, with thermal ellipsoids at the 50% probability level.

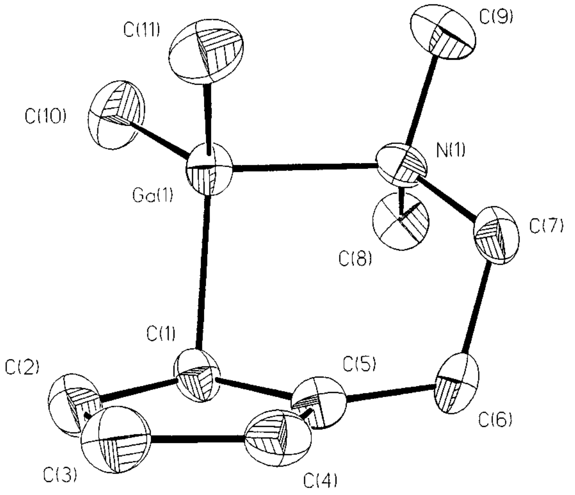


Figure 2. Molecular structure of **5**, with thermal ellipsoids at the 50% probability level.

Table 2. Selected Bond Lengths (Å) for $[2\text{-}(Me_2NCH_2CH_2)C_5H_4]GaCl_2$ 2, $[2\text{-}(Me_2NCH_2CH_2)C_5H_4]GaBr_2$ 3, $[2\text{-}(Me_2NCH_2CH_2)C_5H_4]GaI_2$ 4, and $[2\text{-}(Me_2NCH_2CH_2)C_5H_4]GaMe_2$ 5

	2	3	4	5
Ga−C(1)	1.989(6)	2.003(11)	2.013(7)	2.081(6)
Ga−N	2.028(5)	2.034(8)	2.062(5)	2.125(5)
C(1)−C(2)	1.469(8)	1.453(13)	1.419(10)	1.448(8)
C(2)−C(3)	1.350(10)	1.33(2)	1.358(11)	1.359(9)
C(3)−C(4)	1.434(10)	1.45(2)	1.449(12)	1.420(9)
C(4)−C(5)	1.372(8)	1.34(2)	1.341(10)	1.367(8)
C(1)−C(5)	1.487(8)	1.48(2)	1.467(10)	1.453(8)
C(5)−C(6)	1.481(9)	1.506(13)	1.492(10)	1.483(8)
C(6)−C(7)	1.536(11)	1.52(2)	1.547(9)	1.531(8)
C(7)−N	1.487(9)	1.495(14)	1.485(8)	1.493(7)
C(8)−N	1.484(8)	1.478(13)	1.483(9)	1.483(7)
C(9)−N	1.467(7)	1.497(14)	1.499(8)	1.476(7)
Ga−Hal(1)	2.166(2)	2.314(2)	2.5465(9)	
Ga−Hal(2)	2.178(2)	2.321(2)	2.5277(9)	
Ga−C(10)				1.970(7)
Ga−C(11)				1.972(6)

Table 3. Selected Bond Angles (deg) for $[2\text{-}(Me_2NCH_2CH_2)C_5H_4]GaCl_2$ 2, $[2\text{-}(Me_2NCH_2CH_2)C_5H_4]GaBr_2$ 3, $[2\text{-}(Me_2NCH_2CH_2)C_5H_4]GaI_2$ 4, and $[2\text{-}(Me_2NCH_2CH_2)C_5H_4]GaMe_2$ 5

	2	3	4	5
Ga−N−C(7)	107.6(4)	108.0(6)	107.7(4)	110.1(3)
Ga−N−C(8)	111.9(4)	109.0(6)	109.2(4)	110.3(4)
Ga−N−C(9)	109.5(4)	111.5(7)	111.3(4)	109.5(4)
C(7)−N−C(8)	108.4(5)	110.2(8)	112.1(5)	110.1(4)
C(7)−N−C(9)	110.7(6)	109.3(8)	109.0(5)	108.8(5)
C(8)−N−C(9)	108.6(5)	108.8(9)	107.7(6)	108.0(5)
C(1)−Ga−N	102.5(2)	102.8(4)	100.4(3)	96.5(2)
C(1)−Ga−Hal(1)	116.1(2)	115.5(3)	116.9(2)	
C(1)−Ga−Hal(2)	119.9(2)	117.5(3)	115.8(2)	
Hal(1)−Ga−Hal(2)	109.17(7)	109.72(7)	110.26(3)	
Hal(1)−Ga−N	104.4(2)	105.1(2)	105.7(2)	
Hal(2)−Ga−N	102.4(2)	104.7(2)	106.2(2)	
C(1)−Ga−C(10)				112.1(3)
C(1)−Ga−C(11)				114.9(2)
C(10)−Ga−C(11)				120.1(3)
C(10)−Ga−N				104.9(3)
C(11)−Ga−N				104.4(2)

longer than the sum of covalent radii (1.95 Å),[22a] but significantly shorter than the sum of van der Waals radii (3.45 Å).[22b] The compounds possess a bicyclic structure which is formed by the fusion of a cyclopentadienyl unit and a six-membered GaC_4N ring. The geometries at gallium and nitrogen are only roughly tetrahedral, with considerable deviations from the ideal angle at both centers (see Table 3). The Ga−C(1) and the Ga−N distances both depend on the electronic properties of the residual substituents at the gallium center. In the dihalogen derivatives **2**−**4** these bonds are significantly shorter than in the dimethyl species **5**; these results are consistent with different Lewis acidities at the gallium atom. The Ga−C(1) distance in **5** (2.081(6) Å) is similar to those reported for $[\eta^1{:}\eta^1\text{-}C_5H_4(CH_2CH_2P^tBu_2)]GaMe_2$ (2.103(5) Å)[23] and for $[\eta^1\text{-}C_5H_5]_3Ga$ (average 2.05(2) Å),[24] respectively. The Ga−N distance of **5** (2.125(5) Å) is comparable to that observed for the intramolecular coordination compounds $Ga(CH_2CH_2CH_2)_3N$ (2.095(2) Å)[25] and $[2\text{-}(Me_2NCH_2)C_6H_4]GaMe_2$ (2.133(2) Å),[26] and for the Lewis base adducts of trimethylgallane with urotropine, $(C_6H_{12}N_4)\cdot GaMe_3$ (2.139(17) Å)[27] and benzoquinoline, $(C_{13}N_9N)\cdot GaMe_3$ (2.152(3) Å).[28]

Structures of 2−6 in Solution. Information about the structure and the dynamic behavior of **2**−**6** in solution has been gained from cryoscopic molecular mass determinations and from ^1H and ^{13}C NMR data. Molecular mass determinations inform about the degree of association in the respective solvent; NMR investigations inform about the especially interesting bonding within the Cp unit and about the coordination of the nitrogen atom to a gallium center. Cryoscopic molecular mass determinations have been performed with **5** and prove the monomeric structure of this compound in benzene solution. The species **2**−**4** and **6** could not be investigated due to low solubility (**2**−**4**) or pronounced air-sensitivity (**6**).

---

(22) (a) Emsley, J. *The Elements*; Oxford University Press: Oxford, 1991. (b) Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441.

(23) Cowley, A. H.; King, C. S.; Decken, A. *Organometallics* **1995**, *14*, 20.

(24) Beachley, O. T., Jr.; Getman, T. D.; Kirss, R. U.; Hallock, R. B.; Hunter, W. E.; Atwood, J. L. *Organometallics* **1985**, *4*, 751.

(25) Schumann, H.; Hartmann, U.; Dietrich, A.; Pickard, T., *Angew. Chem.* **1988**, *100*, 1119; *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1077.

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

(27) Krause, H.; Sille, K.; Hausen, H.-D.; Weidlein, J. *J.Organomet. Chem.* **1982**, *235*, 253.

(28) Sun, H.-S.; Wang, X.-M.; You, X.-Z.; Huang, X.-Y. *Polyhedron* **1995**, *14*, 2159.

Table 4. Correlation of ^{1}H NMR Chemical Shifts (δ, in $CDCl_3$) of the $CH_2N(CH_3)_2$ Protons in [(Dimethylamino)ethyl]cyclopentadienyl Compounds with the Coordination Behavior

compound		CH_2NMe_2	NCH_3	coordination
$C_5H_5(CH_2CH_2NMe_2)$		2.42−2.57 (m)	2.24 (s)	−
$[C_5H_4(CH_2CH_2NMe_2)]SiMe_3$	[ref 7]	2.41−2.57 (m)	2.24 (s)	−
$[C_5H_4(CH_2CH_2NMe_2)]SnMe_3$	[ref 7]	2.57−2.63 (m)	2.25 (s)	−
$[C_5H_4(CH_2CH_2NMe_2)]AlMe_2$	[ref 8]	2.86−2.90 (m)	2.52 (s)	+
$[C_5H_4(CH_2CH_2NMe_2)]AlEt_2$	[ref 8]	2.88−2.92 (m)	2.53 (s)	+
$[C_5H_4(CH_2CH_2NMe_2)]AlH_2$	[ref 8]	2.89−2.94 (m)	2.57 (s)	+
$[C_5H_4(CH_2CH_2NMe_2)]AlCl_2$	[ref 8]	2.90−2.95 (m)	2.75 (s)	+
$[C_5H_4(CH_2CH_2NMe_2)]AlBr_2$	[ref 8]	2.91−2.99 (m)	2.80 (s)	+
$[C_5H_4(CH_2CH_2NMe_2)]InMe_2$	[ref 8]	2.82 (t)	2.34 (s)	+
$[C_5H_4(CH_2CH_2NMe_2)]GaCl_2$	**2**	2.88 (s)[a]	2.73 (s)	+
$[C_5H_4(CH_2CH_2NMe_2)]GaBr_2$	**3**	2.88−2.91 (m)	2.75 (s)	+
$[C_5H_4(CH_2CH_2NMe_2)]GaI_2$	**4**	2.91−2.95 (m)	2.78 (s)	+
$[C_5H_4(CH_2CH_2NMe_2)]GaMe_2$	**5**	2.79 (t)	2.42 (s)	+
$[C_5H_4(CH_2CH_2NMe_2)]GaH_2$	**6**	2.85 (t)	2.54 (s)	+

[a] Only one singlet is observed for the four CH_2CH_2 protons in $CDCl_3$. In C_6D_6 these protons give rise to two triplets (see Experimental Section).

As already experienced with other [(dimethylamino)ethyl]cyclopentadienyl compounds,[6−9,20] the coordination behavior of the amino group can be checked by ^{1}H NMR spectroscopy. Coordination to a metal center leads to a significant downfield shift for the protons of the methyl and methylene groups bonded directly to the nitrogen atoms; $\Delta\delta$ values of up to 0.6 ppm are observed in the chemistry of s- and p-block elements.[8] From the ^{1}H NMR data collected in Table 4 it is evident that in compounds **2**−**6** the amino group is coordinated to the gallium center. In combination with the molecular mass determination mentioned above, an intramolecular coordination can be assumed for most of the compounds investigated.

In the ^{1}H NMR spectrum of **6**, the gallium-bonded hydrogen atoms give rise to a broad singlet with the right intensity at $\delta = 3.85$ ppm ($w_{1/2} = 41$ Hz), which is due to the quadrupolar nature of gallium (^{69}Ga: 60%, ^{71}Ga: 40%, $I = {}^3/_2$). In the IR spectrum of **6**, the presence of the GaH_2 moiety is documented by the two stretching modes at 1890 cm^{-1} and at 1836 cm^{-1}. These data are simlar to those reported for $[2\text{-}(Me_2NCH_2)C_6H_4]GaH_2$.[29]

Not unexpectedly, the low symmetry in the solid-state structures of the above compounds is not reflected in the solution NMR data. In the ^{1}H and ^{13}C NMR spectra of **2**−**6**, averaged signals are observed for the cyclopentadienyl unit; the signal pattern does not change with temperature. These observations can be explained as follows: Fast haptotropic rearrangements of the gallium fragment lead to averaged ^{1}H and ^{13}C NMR signals even at low temperatures.[30] The chain length of the coordinated (dimethylamino)ethyl substituent is not flexible enough to allow all carbon positions of the Cp ring to participate in the rearrangement process. The dynamic behavior thus is determined by the rearrangements described in Scheme 2 and resembles a "windscreen wiper" process.

Strucure B has not been observed in the NMR spectra of **2**−**6**. In the ^{13}C NMR spectra of **2**−**6** no resonance for a quaternary ring carbon atom in the alylic region (at about 50 ppm), which is expected for C_5 in structure B, has been observed. Presumably the ring strain of the five-membered GaC_3N ring makes structure B energetically unfavorable in comparison with the structures A and A′. Thus the dynamic process observed by NMR is restricted to the A $\rightleftharpoons$ A′ rearrangement. On the basis of Scheme 2, the signal pattern and the chemical shift values observed in the ^{1}H and ^{13}C NMR spectra of the above compounds can be assigned as follows: The protons H_A possess both allylic and vinylic character and resonate as typical for an averaged situation at about 5 ppm, while the protons H_B remain vinylic in character and thus resonate at lower field (about 6.5 ppm). In the ^{13}C NMR spectra of **2**−**6**, three resonances are observed for the five ring carbon atoms. In Figure 3, the cyclopentadienyl part of the ^{13}C NMR spectrum (JMODXH) of **6**, which assigned carbon resonances, is shown for clarity.

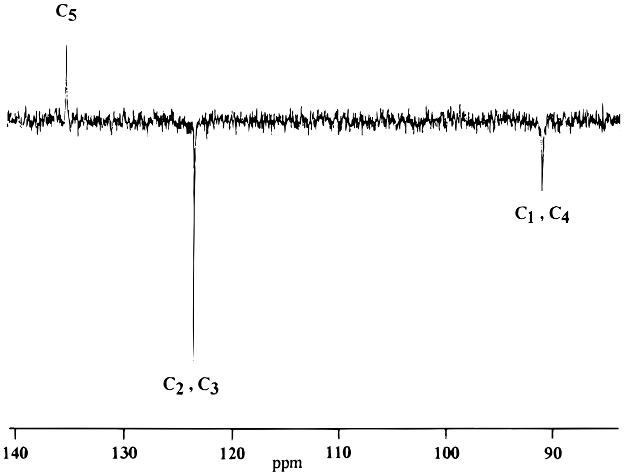
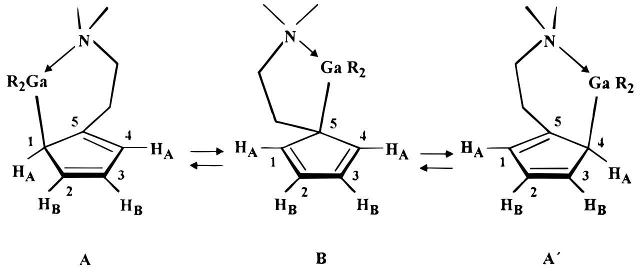


Figure 3. Cp part of the ^{13}C NMR spectrum of **6** ($CDCl_3$, JMODXH).

Scheme 2. Rearrangement Processes in Compunds 2−6



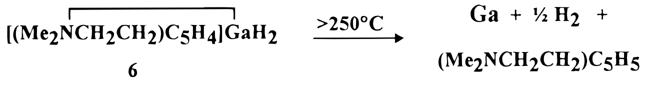
In the structures A and A′ (see Scheme 2) the ring carbon atoms C_1 and C_4 possess both allylic and vinylic

---

(29) Isom, H. S.; Cowley, A. H.; Decken, A.; Sissingh, F.; Corbelin, S.; Lagow, R. J. *Organometallics* **1995**, *14*, 2400.

(30) For dynamic processes in cp element compounds see: Jutzi, P. *Chem. Rev.* **1986**, *86*, 983, and references cited within.

Scheme 3



$$[(Me_2NCH_2CH_2)C_5H_4]GaH_2 \xrightarrow{>250°C} Ga + \tfrac{1}{2}H_2 + (Me_2NCH_2CH_2)C_5H_5$$

6

character and resonate as typical for an averaged situation at 91.2 ppm. For the ring carbon atoms C_2 and C_3, which remain vinylic in character at any time, a single signal is observed at 123.7 ppm. The quaternary vinylic ring carbon atom (C_5) gives rise to a signal at 135.6 ppm. Both the signal pattern and the chemical shift values are very similar for the compounds **2**−**6** (see Experimental Section).

Mass Spectroscopic Data of 2−6. From the CI mass spectra of **2**−**6** it is evident that the compounds exist as monomeric molecules in the gas phase. No peaks higher than the $[M^+ + H]$ ion peaks have been observed. The isotopic distribution observed for **2**−**6** is in good agreement with the theoretically calculated values. The α fragmentation product $[CH_2NMe_2^+]$ (*m*/*z* 58) is the base peak in the mass spectra of **2**−**6**.

MOCVD Investigations of 6. Due to our interest in using cyclopentadienyl compounds as substrates in MOCVD processes,[31] we have carried out hot wall MOCVD experiments, using **6** as a source for the deposition of gallium. Formation of shiny Ga films is observed at reactor temperatures above 250 °C; lower temperatures did not result in deposition of Ga. To examine the fragmentation reactions occurring during CVD, we analyzed the volatile byproducts, which were trapped in a liquid nitrogen cold trap, by ^1H NMR spectroscopy. As a high precursor conversion facilitates byproduct distribution analysis, the reactor temperature was raised until the amount of unreacted precursor that passed through the reactor decreased to an undetectable quantity (400 °C). The reaction product which was formed almost exclusively was identified as [2-(*N*,*N*-dimethylamino)ethyl]cyclopentadiene (Cp^NH);[14] one can assume that molecular hydrogen has been formed as a product, too. The overall decomposition process is outlined in Scheme 3.

Although the qualities of the obtained Ga films are not yet investigated, the well-behaved fragmentation of **6** should provide a route to films without carbon impurities. Furthermore, the fragmentation product Cp^NH can be reused for the synthesis of the precursor. The observed clean fragmentation process supports our concept to use cyclopentadienyl systems as leaving groups in MOCVD experiments.[31]

Conclusion

In the compounds described above an *intramolecular* coordination of the amino unit of the [2-(*N*,*N*-dimethylamino)ethyl]cyclopentadienyl ligand to the gallium center is observed. The resulting coordinative and electronic saturation of the metal center in **2**−**6** leads to a drastically decreased reactivity against moisture and air in comparison with the parent compounds $(C_5H_5)GaR_2$ (R = Me, Et, C_5H_5).[24,32−36] With the exception of **6**, the complexes are stable at 100 °C in toluene solution for several days, while for example $(C_5H_5)_3Ga$ decomposes at temperatures as low as 45 °C.[24] In the gas phase, in the solid state, and presumably also in solution compounds **2**−**6** exist as monomeric molecules. In contrast, the solid state structure of $(C_5H_5)GaMe_2$ consists of polymer chains of dimethylgallium groups bridged by cyclopentadienyl rings.[34] For the structures and properties of the dihalogen derivatives **2**−**4** no comparable data concerning the parent compounds $(C_5H_5)GaX_2$ (X = F, Cl, Br, J) are available. Only the synthesis of $(C_5H_5)GaCl_2$[24] is briefly mentioned in the literature, but no details about yields, properties or structures are given. To the best of our knowledge, compound **6** is the only cyclopentadienylgallane known so far. The MOCVD experiments performed up to now show the suitability of **6** for the growth of thin gallium films.

Experimental Section

General Comments. All experiments were performed under an atmosphere of dry argon by using standard Schlenk techniques. Solvents were dried by refluxing over $LiAlH_4$ (ether, *n*-hexane), or sodium (toluene) and distilled before use. ^1H (300.1 MHz), and $^{13}C\{^1H\}$ (75.5 MHz) NMR spectra were recorded on a Bruker AM 300 spectrometer. Chemical shifts for ^1H and $^{13}C\{^1H\}$ spectra were recorded in ppm downfield from TMS and referenced to internal deuteriochloroform, toluene-d_8 or deuteriobenzene. Mass spectra were recorded on a VG AutoSpec instrument (CI, CH_4); only characteristic fragments and isotopes of the highest abundance are listed. The IR spectrum of **6** was obtained from solution in Et_2O using a Bruker FTIR IFS 66 spectrophotometer. Melting points were measured on a Büchi 510 melting point apparatus (sealed cappilaries) and are uncorrected. Elemental microanalyses were performed by Analytisches Labor der Fakultät für Chemie, Universität Bielefeld, and by Mikroanalytisches Laboratorium Beller, Göttingen.

Materials. Potassium [[2-(*N*,*N*-dimethylamino)ethyl]cyclopentadienide] **1** (Cp^NK) was prepared according to the literature method.[16] The gallium trihalides were prepared from the elements, purified by sublimation, and stored in a glove box. Chlorodimethylgallium diethyl ether complex was synthesized by a published method.[37] Monochlorogallane−trimethylamine adduct was prepared in analogy to the synthesis of monochloroalane−trimethylamine adduct by treating the gallane−trimethylamine adduct with $HgCl_2$ in a 2:1 stoichiometry.[38]

Dichloro[η^1:η^1-2-(*N*,*N*-dimethylamino)ethylcyclopentadienyl]gallium (2). A suspension of 2.65 g (15.1 mmol) of Cp^NK (**1**) in toluene (30 mL) was added to a solution of 2.66 g (15.1 mmol) of $GaCl_3$ in toluene (30 mL) at −50 °C. The reaction mixture was allowed to warm to room temperature and stirred for 12 h. After additional refluxing for 2 h the resulting mixture was filtered at 80 °C. Slow cooling of the solution to room temperature afforded colorless crystals of (**2**) (2.62 g, 63%), suitable for an X-ray structure determination. Mp: 147 °C. ^1H NMR ($CDCl_3$): $\delta = 2.73$ (s, 6 H, NCH_3), 2.88 (s, 4 H, $CH_2CH_2NMe_2$), 5.17−5.19 (m, 2 H, ring-H_A), 6.61−6.63 (m, 2 H, ring-H_B). ^1H NMR (C_6D_6): $\delta = 1.80$ (s, 6 H, NCH_3), 1.83 (t, $J = 6.0$ Hz, 2 H, CH_2), 2.05 (t, $J = 6.0$ Hz, 2 H, CH_2NMe_2), 5.01 (s, 2 H, ring-H_A), 6.72 (s, 2 H, ring-H_B). ^{13}C

---

[31] (a) Dahlhaus, J.; Jutzi, P.; Frenck, H.-J.; Kulisch, W. *Adv. Mater.* **1993**, *5* ,377. (b) Dahlhaus, J.; doctoral thesis, Universität Bielefeld, 1993.

[32] Stadelhofer, J.; Weidlein, J.; Haaland, A. *J. Organomet. Chem.* **1975**, *84*, C1.

[33] Stadelhofer, J.; Weidlein, J.; Fischer, P.; Haaland, A. *J. Organomet. Chem.* **1976**, *116*, 55.

[34] Mertz, K.; Zettler, F.; Hausen, H. D.; Weidlein, J. *J. Organomet. Chem.* **1976**, *122*, 159.

[35] Beachley, O. T., Jr.; Royster, T. L., Jr.; Arhar, J. R. *J. Organomet. Chem.* **1992**, *434*, 11.

[36] Beachley, O. T., Jr.; Rosenblum, D. B.; Churchill, M. R.; Lake, C. H.; Krajkowski, L. M. *Organometallics* **1995**, *14*, 4402.

[37] Coates, G. E.; Graham, J. *J. Chem. Soc.* **1963**, 233.

[38] Ruff, J. U. *J. Am. Chem. Soc.* **1961**, *83*, 1798.

NMR ($CDCl_3$): $\delta = 26.3$ (CH_2), 45.4 (NCH_3), 61.6 (CH_2NMe_2), 91.2 (ring-$C_{1,4}$), 129.1 (ring-$C_{2,3}$), 135.7 (ring-C_5). MS [m/z (relative intensity %)]: 278 (3) [$M^+ + H$], 277 (2) [M^+], 242 (11) [$M^+ - {}^{35}Cl$], 240 (10) [$M^+ - {}^{37}Cl$], 136 (20) [$C_5H_4CH_2CH_2NMe_2^+$], 58 (100) [$Me_2NCH_2^+$]. Anal. Calcd for $C_9H_{14}Cl_2GaN$ (276.83): C, 39.05; H, 5.10; N, 5.06. Found: C, 39.19; H, 5.29; N, 5.20.

Dibromo[[η^1:η^1-2-(N,N-dimethylamino)ethyl]cyclopentadienyl]gallium (3). A suspension of 2.26 g (12.9 mmol) of Cp^NK (**1**) in toluene (30 mL) was added to a solution of 3.99 g (12.9 mmol) of $GaBr_3$ in toluene (50 mL) at −50 °C. The reaction mixture was allowed to warm to room temperature and was refluxed for 2 h. The resulting mixture was filtered at 80 °C and cooled very slow to room temperature. Colorless crystals of **3** (2.78 g, 59%) formed, which were suitable for X-ray crystallographic studies. Mp: 174 °C dec. ^1H NMR ($CDCl_3$): $\delta = 2.75$ (s, 6 H, NCH_3), 2.88−2.91 (m, 4 H, $CH_2CH_2NMe_2$), 5.21 (s, 2 H, ring-H_A), 6.60−6.62 (m, 2 H, ring-H_B). ^{13}C NMR ($CDCl_3$): $\delta = 26.3$ (CH_2), 45.7 (NCH_3), 61.3 (CH_2NMe_2), 92.9 (ring-$C_{1,4}$), 129.1 (ring-$C_{2,3}$), 135.1 (ring-C_5). MS [m/z (relative intensity %)]: 366 (15) [$M^+ + H$], 365 (24) [M^+], 287 (12) [$M^+ + H - {}^{79}Br$], 286 (64) [$M^+ - {}^{79}Br$], 285 (8) [$M^+ + H - {}^{81}Br$], 284 (45) [$M^+ - {}^{81}Br$], 136 (12) [$C_5H_4CH_2CH_2NMe_2^+$], 58 (100) [$Me_2NCH_2^+$]. Anal. Calcd for $C_9H_{14}Br_2GaN$ (365.75): C, 29.55; H, 3.85; N, 3.82. Found: C, 29.62; H, 3.83; N, 3.86.

Diiodo[[η^1:η^1-2-(N,N-dimethylamino)ethyl]cyclopentadienyl]gallium (4). A suspension of 2.84 g (16.2 mmol) of Cp^NK (**1**) in toluene (40 mL) was added to a solution of 7.30 g (16.2 mmol) of GaI_3 in toluene (120 mL) at −50 °C. The reaction mixture was allowed to warm to room temperature and stirred for 12 h. After additional refluxing for 2 h, the resulting mixture was filtered at 80 °C, concentrated, and cooled. Compound **4** was isolated as pale yellow crystals (3.65 g, 49%), suitable for an X-ray structure determination. Mp: 140 °C. ^1H NMR ($CDCl_3$): $\delta = 2.78$ (s, 6 H, NCH_3), 2.85−2.89 (m, 2 H, CH_2), 2.91−2.95 (m, 2 H, CH_2NMe_2), 5.27 (s, 2 H, ring-H_A), 6.55−6.57 (m, 2 H, ring-H_B). ^{13}C NMR ($CDCl_3$): $\delta = 26.2$ (CH_2), 46.1 (NCH_3), 60.5 (CH_2NMe_2), 94.2 (ring-$C_{1,4}$), 129.1 (ring-$C_{2,3}$), 134.4 (ring-C_5). MS [m/z (relative intensity %)]: 459 (3) [M^+], 332 (44) [$M^+ - I$], 136 (8) [$C_5H_4CH_2CH_2NMe_2^+$], 58 (100) [$Me_2NCH_2^+$]. Anal. Calcd for $C_9H_{14}GaI_2N$ (459.73): C, 23.51; H, 3.06; N, 3.04. Found: C, 22.81; H, 3.25; N, 2.74.

Dimethyl[[η^1:η^1-2-(N,N-dimethylamino)ethyl]cyclopentadienyl]gallium (5). A solution of 2.87 g (13.7 mmol) of $Me_2GaCl{\cdot}OEt_2$ in n-hexane (30 mL) was added to a suspension of 2.40 g (13.7 mmol) of Cp^NK (**1**) in n-hexane (30 mL) at −50 °C. The reaction mixture was allowed to warm to room temperature, stirred for 12 h, and filtered. The resulting colorless solution was concentrated and cooled. Storage at −35 °C afforded colorless crystals of **5** (1.75 g, 54%), suitable for an X-ray structure determination. Mp: 82 °C. ^1H NMR ($CDCl_3$): $\delta = -0.80$ (s, 6 H, Ga-CH_3), 2.42 (s, 6 H, NCH_3), 2.62 (t, J = 6.0 Hz, 2 H, CH_2), 2.79 (t, J = 6.0 Hz, 2 H, CH_2NMe_2), 5.21−5.23 (m, 2 H, ring-H_A), 6.33−6.35 (m, 2 H, ring-H_B). ^{13}C NMR ($CDCl_3$): $\delta = -11.0$ (Ga-CH_3), 26.8 (CH_2), 45.4 (NCH_3), 62.1 (CH_2NMe_2), 92.2 (ring-$C_{1,4}$), 122.8 (ring-$C_{2,3}$), 133.6 (ring-C_5). MS [m/z (relative intensity %)]: 236 (4) [$M^+ + H$], 136 (22) [$C_5H_4CH_2CH_2NMe_2^+$], 99 (18) [$M^+ - C_5H_4CH_2CH_2NMe_2$], 58 (100) [$Me_2NCH_2^+$]. Anal. Calcd for $C_{11}H_{20}GaN$ (236.00): C, 55.98; H, 8.54; N, 5.93. Found: C, 56.23; H, 8.98; N, 5.88. Molecular weight determination (cryoscopic in benzene): $M = 230$.

[[η^1:η^1-2-(N,N-dimethylamino)ethyl]cyclopentadienyl]gallane (6). A solution of 2.41 g (14.5 mmol) of $H_2GaCl{\cdot}NMe_3$ in Et_2O (30 mL) was added to a suspension of 2.54 g (14.5 mmol) of Cp^NK (**1**) in Et_2O (30 mL) at −50 °C. After stirring for 12 h, at this temperature the reaction mixture was filtered and the solvent removed in vacuo. The colorless, oily residue was purified by vacuum sublimation (50 °C/0.03 mbar). Compound **6** (1.48 g, 48%) was isolated as a colorless solid. ^1H NMR ($CDCl_3$): $\delta = 2.54$ (s, 6 H, NCH_3), 2.73 (t, $J = 5.8$ Hz, 2 H, CH_2), 2.85 (t, $J = 5.8$ Hz, 2 H, CH_2NMe_2), 3.85 (br, s, $w_{1/2} = 41$ Hz, 2 H, Ga-H), 5.23−5.25 (m, 2 H, ring-H_A), 6.49−6.51 (m, 2 H, ring-H_B). ^1H NMR (toluene-d_8, −40 °C); $\delta = 1.60$ (s, 6 H, NCH_3), 1.74 (t, J = 5.8 Hz, 2 H, CH_2), 2.32 (t, J = 5.8 Hz, 2 H, CH_2NMe_2), 4.35 (br s, 2 H, Ga-H), 5.32 (s, 2 H, ring-H_A), 6.89−6.91 (m, 2 H, ring-H_B). ^{13}C NMR ($CDCl_3$): $\delta = 26.7$ (CH_2), 46.5 (NCH_3), 63.0 (CH_2NMe_2), 91.2 (ring-$C_{1,4}$), 123.7 (ring-$C_{2,3}$), 135.6 (ring-C_5). MS [m/z (relative intensity %)]: 208 (15) [$M^+ + H$], 206 (22) [$M^+ - H$], 136 (8) [$C_5H_4CH_2CH_2NMe_2^+$], 58 (100) [$Me_2NCH_2^+$]. Anal. Calcd for $C_9H_{16}GaN$ (207.96): C, 51.98; H, 7.75; N, 6.74. Found: C, 51.81; H, 7.74; N, 6.74. IR: $\nu_{Ga-H} = 1836, 1890\ cm^{-1}$.

Hot Wall CVD of 6. The experiments were carried out using an externally thermostated quartz reactor[31b] (15 mm internal diameter and 355 mm length) which was evacuated to a base pressure of 10^{-3} mbar. The precursor **6** (200 mg) was sublimed into the reaction zone. The reactor was heated independently of the precursor evaporator by a separate furnace. Deposition was accomplished onto quartz glass. No carrier gas was used during the depositions. Deposition was continued until all of the precursor had evaporated (2 h).

Acknowledgment. The financial support of the "Deutsche Forschungsgemeinschaft" (Forschergruppe Nanometerschichtsysteme) and of the "Fonds der Chemischen Industrie" as well as a gift of gallium from the Chemetall GmbH, Frankfurt/Main, Germany, is gratefully acknowledged.

Supporting Information Available: Tables of anisotropic displacement coefficients, hydrogen coordinates, and isotropic displacement coefficients for **2**−**5** (24 pages). Ordering information is given on any current masthead page.

OM960497E