Synthesis, Structure, and Significance for MOCVD of Intramolecularly Base-Stabilized Monomeric Cyclopentadienylaluminum and -gallium Dihydrides[#]

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The (*N*,*N*-dialkylaminoethyl)cyclopentadienyl group 13 element dichlorides **3** and **4** of the type $[(R_2NCH_2CH_2)C_5H_4]MCl_2$ {M = Al, R = Me (**3**); M = Ga, R = *i*-Pr (**4**)} were prepared via salt elimination reactions of $[(R_2NCH_2CH_2)C_5H_4]K$ {R = Me (**1**), *i*-Pr (**2**)} with the respective group 13 element trichlorides. The reaction of **3** with $LiAlH_4$ afforded the cyclopentadienylaluminum dihydride $[(Me_2NCH_2CH_2)C_5H_4]AlH_2$ (**5**) in nearly quantitative yield. Treatment of the organogallium dichlorides $[(R_2NCH_2CH_2)C_5H_4]GaCl_2$ {R = *i*-Pr (**4**), Me (**6**)} with $LiAlH_4$ led via transmetalation to the organoaluminum dihydrides $[(R_2NCH_2CH_2)C_5H_4]AlH_2$ {R = Me (**5**), *i*-Pr (**7**)} in good yields. The reaction of **6** with $LiGaH_4$ resulted in the formation of the organogallium dihydride $[(Me_2NCH_2CH_2)C_5H_4]GaH_2$ (**8**). The novel compounds **3**−**5**, **7**, and **8** were characterized by elemental analysis, NMR spectroscopy, mass spectrometry, and X-ray crystallography. In the solid state and also in solution, all compounds feature a monomeric structure with an intramolecularly coordinated dialkylamino group. The coordinative and electronic saturation of the metal center in these compounds leads to a drastically decreased reactivity toward moisture and air in comparison to nondonor-stabilized Cp−group 13 element compounds. The dynamic behavior observed in solution is based on fast haptotropic shifts in a “windshield-wiper” type process. Sufficient volatility makes the organodihydrido compounds **5** and **8** suitable precursors for the deposition of aluminum and gallium, respectively, in the MOCVD process. Ex-situ characterization with sputter auger electron spectroscopy (SAES) provides information about the chemical composition of the aluminum and gallium layers. Irradiation of **5** and **8** in solution is followed by decomposition into the respective metal and into the hydrogen-functionalized ligand $[C_5H_5(CH_2CH_2NMe_2)]$.

Introduction

During the last years we have shown that 2-(*N*,*N*-dialkylamino)ethylcyclopentadienyl ligands are able to stabilize electronically and sterically unsaturated group 13 metal centers.[1−5] The stabilization takes place via an intramolecular coordination of the *N*,*N*-dialkylamino group. This phenomenon results in (i) monomolecular structures in the solid state, in the gas-phase, and in solution and (ii) decreased reactivity toward moisture and air in comparison with the parent cyclopentadienyl and with pentamethylcyclopentadienyl (Cp*) compounds.[6−34] Recently, we described the preparation and characterization of compounds of the general formula $[2\text{-}(Me_2NCH_2CH_2)C_5H_4]GaX_2$ (X = Cl, Br, I, Me).[1−3] We also reported on a low-yield synthesis of the organo-

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[#] Dedicated to Professor H. Schmidbaur on the occasion of his 65th birthday.

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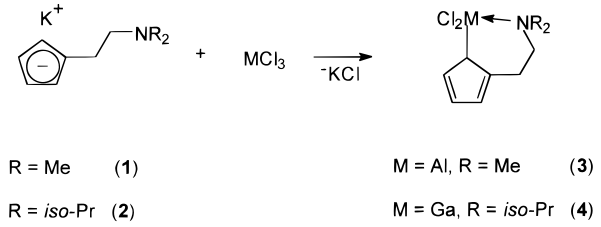
Scheme 1. Synthesis of 3 and 4 via Salt Elimination



gallium dihydride $[(Me_2NCH_2CH_2)C_5H_4]GaH_2$ (**8**).[1] In this paper, we present in an extension of our recent work the synthesis and characterization of further dichloro and dihydrido aluminum and gallium compounds with different dialkylamino groups in the side chain of the cyclopentadienyl ligand. In this context, we present a novel high-yield synthesis of **8**. We also report preliminary MOCVD experiments with the dihydrido compounds **5** and **8** and on the first results in photochemical decomposition processes.

Results and Discussion

Synthesis. The salt elimination reactions of potassium (*N*,*N*-dimethylamino)ethylcyclopentadienide **1** with 1 equiv of freshly sublimed $AlCl_3$ and of potassium (*N*,*N*-diisopropylamino)ethylcyclopentadienide **2** with 1 equiv of freshly sublimed $GaCl_3$ in toluene led to the formation of the complexes **3** and **4** of the type $[\eta^1:\eta^1\text{-}C_5H_4(CH_2CH_2NR_2)]MCl_2$ {M = Al, R = Me (**3**); M = Ga, R = *i*-Pr (**4**)}, respectively (Scheme 1). The order of addition of the reagents is of crucial importance. It is essential to add the potassium cyclopentadienide to the respective group 13 element trihalide and not vice versa; otherwise **3** and **4** can be isolated only in low yields (out of a mixture of products). Compounds **3** and **4** were obtained as pale yellow (**3**) or colorless (**4**) crystals, which are moderately air-stable.

Treatment of the aluminum compound **3** with 2 equiv of $LiAlH_4$ in Et_2O led in nearly quantitative yield to $[\eta^1:\eta^1\text{-}C_5H_4(CH_2CH_2NMe_2)]AlH_2$ (**5**), the first known cyclopentadienyl dihydridoalane (Scheme 2, eq 1). Reaction of the dichlorogallium compounds **4** and **6**[1] with 2 equiv of $LiAlH_4$ in Et_2O led via transmetalation to the dihydrido alanes **7** and **5** (Scheme 2, eq 2). Treatment of the cyclopentadienyldichlorogallane **6**[1] with an excess of $LiGaH_4$ in Et_2O gave in nearly quantitative yield the cyclopentadienyldihydridogallane $[\eta^1:\eta^1\text{-}C_5H_4(CH_2CH_2NMe_2)]GaH_2$ (**8**) (Scheme 2, eq 3). As reported previously, gallane **8** can also be prepared via salt elimination reaction of **1** with 1 equiv $H_2GaCl{\cdot}NMe_3$.[1]

The compounds **5, 7**, and **8** were obtained as colorless moisture- and rather air-sensitive crystals, which are stable at room temperature under an inert gas atmosphere for a long period of time. In the CI mass spectra of **3**−**5**, **7**, and **8**, no peak higher than the $(M + H)$ peak is observed. We conclude that **3**−**5**, **7**, and **8** are monomeric in the gas phase. The dihydrido compounds **5** and **8** sublime readily at 60 °C (0.01 mbar) and 50 °C (0.03 mbar), respectively. The compounds **3**, **4**, and **7** did not sublime due to low vapor pressures. Satisfactory elemental analyses were obtained for all compounds except for **3** and **5**, where too low carbon contents were found.[35] EI−HRMS data could not be obtained, as compounds **3**−**8** need a soft ionization method.

Several attempts have been made to synthesize the *N*,*N*-diisopropyl-substituted gallane $[(i\text{-}Pr_2NCH_2CH_2)C_5H_4]GaH_2$ by reaction of **4** with $LiGaH_4$. Instead of the desired compound, we isolated the hydrogen-substituted ligand $(i\text{-}Pr_2NCH_2CH_2)C_5H_5$ in nearly quantitative yield. This unexpected result may be the consequence of the sterically demanding situation caused by the diisopropyl-subsituted amino group. Transmetalation reactions similar to those shown in Scheme 2 have been observed previously by Cowley et al. for the reactions of intramoleculary base-stabilized aryl group 13 element dihalides with $LiElH_4$ (El = Al, Ga, In).[36−39]

Solid-State Structures. Single-crystal X-ray structure investigations have been performed with compounds **3**−**5**, **7**, and **8**. Crystallographic data are presented in Table 1, and atomic coordinates are given in the Supporting Information. The structural patterns are all very similar. As examples, the molecular structures of the dihydrido compounds **7** and **8** are shown in the Figures 1 and 2.

General findings in the structures of **3**−**5**, **7**, and **8** are as follows: The compounds consist of monomeric molecules with no abnormally short intermolecular contacts. The cyclopentadienyl ligands are η^1-bonded from the allylic position to the metal center; within the planar C_5-perimeter, bond lengths (Table 2) and bond angles (Table 3) are characteristic of σ-bonded Cp units with alternating C−C distances, e.g., in compound **3** [for numbering pattern see Scheme 3]: long bonds {C(1)−C(2) 1.462(4) Å, C(3)−C(4) 1.433(4) Å, C(1)−C(5) 1.463(4) Å} and short bonds {C(2)−C(3) 1.371(4) Å, C(4)−C(5) 1.374(4) Å}. The side chains are bonded to vinylic carbon atoms of the Cp ring in α-position to the allylic carbon atoms. A coordination number of 4 at the group 13 element centers is achieved by an intramolecular interaction with the nitrogen atom in the side chain. The arrangements of the substituents at the group 13 atoms and at the nitrogen atoms are only roughly tetrahedral, with considerable deviations from the ideal angle at both centers (see Table 3). The M−C(Cp) and the M−N distances both depend on the electronic properties of the

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Scheme 2. Synthesis of 5, 7, and 8 via Hydride Transfer of Transmetalation

$$[(Me_2NCH_2CH_2)C_5H_4]AlCl_2 \;+\; 2\,LiAlH_4 \longrightarrow [(Me_2NCH_2CH_2)C_5H_4]AlH_2 \qquad \text{eq. 1}$$

3 **5**

$$[(R_2NCH_2CH_2)C_5H_4]GaCl_2 \;+\; 2\,LiAlH_4 \longrightarrow [(R_2NCH_2CH_2)C_5H_4]AlH_2 \qquad \text{eq. 2}$$

R = Me (**6**) R = Me (**5**)
R = *iso*-Pr (**4**) R = *iso*-Pr (**7**)

$$[(Me_2NCH_2CH_2)C_5H_4]GaCl_2 \;+\; 2\,LiGaH_4 \longrightarrow [(Me_2NCH_2CH_2)C_5H_4]GaH_2 \qquad \text{eq. 3}$$

6 **8**

Table 1. Crystallographic Data of Compounds 3–5, 7, and 8[a]

	3	4	5	7	8[b]
empirical formula	$C_9H_{14}AlCl_2N$	$C_{13}H_{22}Cl_2GaN$	$C_9H_{16}AlN$	$C_{13}H_{24}AlN$	$C_9H_{16}GaN$
cryst size, mm	1.0 × 0.6 × 0.15	0.3 × 0.2 × 0.05	0.2 × 0.2 × 0.3	0.3 × 0.2 × 0.2	0.5 × 0.4 × 0.2
fw	234.09	332.94	165.21	221.31	207.95
cryst syst.	monoclinic	orthorhombic	monoclinic	monoclinic	monoclinic
space group	$P2_1/n$	*Pbca*	$P2_1/n$	$P2_1/c$	$P2_1/c$
a, Å	7.265(2)	14.050(1)	10.800(12)	11.491(3)	8.517(3)
b, Å	14.279(4)	13.446(2)	13.346(9)	10.307(2)	10.282(2)
c, Å	10.940(3)	16.141(4)	14.063(7)	11.592(2)	11.479(3)
β, deg	90.29(2)	90	92.68(7)	98.74(2)	101.77(2)
V, Å^3	1134.9(5)	3049.3(9)	2025(3)	1357.0(5)	984.1(5)
Z	4	8	8	4	4
d_{calc} g/cm^3	1.370	1.450	1.084	1.083	1.404
diffractometer	Siemens P2(1)	Siemens P2(1)	Siemens P2(1)	Siemens P2(1)	Siemens P2(1)
$F(000)$	488	1376	720	488	432
μ(Mo Kα), mm^{-1}	0.605	2.135	0.143	0.122	2.737
temp, K	163(2)	173(2)	173(2)	173(2)	173(2)
$2\theta_{max}$, deg	60.0	60.0	60.0	60.0	60.0
no. data collected	2759	4437	7459	2501	3029
no. of params refined	120	158	233	148	108
no. obs data [$F > 4\sigma(F)$]	2038	1931	2718	1340	2031
residuals: R_F, wR_{F^2} for obsd data	0.0472, 0.1231	0.0737, 0.1157	0.083, 0.1724	0.0631, 0.1287	0.0495, 0.1063
largest peak in final diff map, e/Å^3	0.50	0.72	0.41	0.22	0.50

[a] **X-ray Structure Determination**. A single crystal was coated with a layer of hydrocarbon oil, attached to a glass fiber, and cooled 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. [b] H(1) and H(2) were refined isotropically.

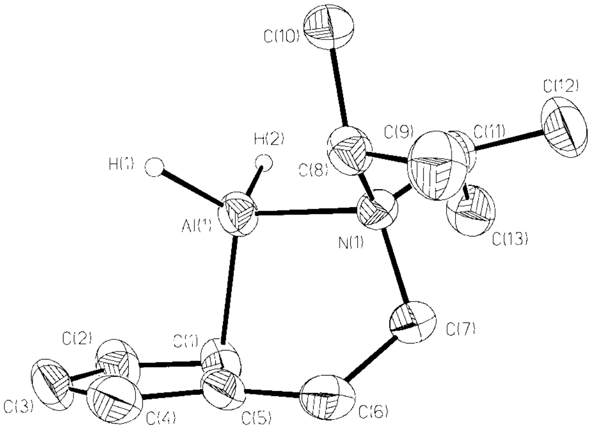

Figure 1. Molecular structure of **7**, with thermal ellipsoids at the 50% probability level.

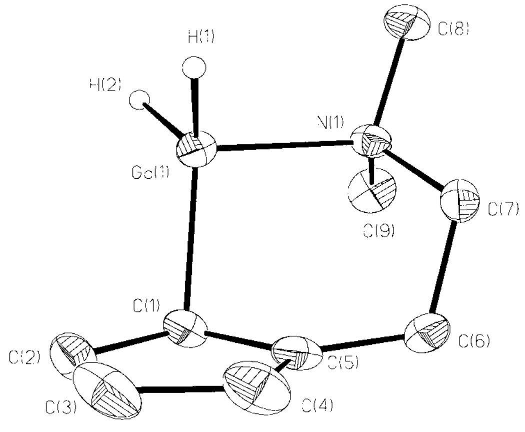

Figure 2. Molecular structure of **8**, with thermal ellipsoids at the 50% probability level.

other substituents of the group 13 elements; in the dichloro derivatives **3** and **4**, these bonds are significantly shorter than in the dihydrido species **5**, **7,** and **8**, as expected from the different Lewis acidities of the group 13 element fragments. A comparison of the structure of **3** and of its ring permethylated analogue $[\eta^{2/3}{:}\eta^1\text{-}C_5Me_4(CH_2CH_2NMe_2)]AlCl_2$[4] shows that the Al–Cl and Al–N distances are in good agreement, while the Cp–metal bonds in these compounds are quite different: in **3** the Cp ligand is η^1-bonded to the aluminum center, while in the latter the Cp ligand is bonded to the metal center in an asymmetrical $\eta^{2/3}$ fashion.[4] This finding is in accord with earlier observations. Shapiro et al. have discussed the different hapticities found in aluminum cyclopentadienyl compounds.[40] Concerning the group 13 element–nitrogen

Table 2. Selected Bond Lengths (Å) for $[2\text{-}(Me_2NCH_2CH_2)C_5H_4]AlCl_2$, 3, $[2\text{-}(i\text{-}Pr_2NCH_2CH_2)C_5H_4]GaCl_2$, 4, $[2\text{-}(Me_2NCH_2CH_2)C_5H_4]AlH_2$, 5, $[2\text{-}(i\text{-}Pr_2NCH_2CH_2)C_5H_4]AlH_2$, 7, and $[2\text{-}(Me_2NCH_2CH_2)C_5H_4]GaH_2$, 8; for Numbering Pattern See Scheme 3

	3	**4**	**5**	**7**	**8**
El(1)−C(1)	1.995(3)	1.989(6)	2.062(4)	2.036(4)	2.052(4)
El(1)−N(1)	1.987(2)	2.092(5)	2.014(3)	2.085(3)	2.097(3)
C(1)−C(2)	1.462(4)	1.473(9)	1.442(5)	1.440(6)	1.454(5)
C(2)−C(3)	1.371(4)	1.357(10)	1.375(5)	1.369(6)	1.354(6)
C(3)−C(4)	1.433(4)	1.418(12)	1.405(5)	1.414(6)	1.433(6)
C(4)−C(5)	1.374(4)	1.331(11)	1.375(5)	1.384(6)	1.366(5)
C(1)−C(5)	1.463(4)	1.453(9)	1.452(5)	1.438(6)	1.472(5)
C(5)−C(6)	1.509(4)	1.504(9)	1.496(5)	1.491(6)	1.503(5)
C(6)−C(7)	1.528(4)	1.530(9)	1.530(5)	1.511(5)	1.530(5)
N(1)−C(7)	1.507(4)	1.499(8)	1.494(4)	1.504(5)	1.498(4)
N(1)−C(8)	1.492(4)	1.542(8)	1.494(5)	1.528(5)	1.487(4)
N(1)−C(9)	1.490(3)		1.488(4)		1.481(5)
N(1)−C(11)		1.527(7)		1.521(5)	
El(1)−H(1)				1.48(3)	1.55(5)
El(1)−H(2)				1.49(4)	1.58(5)
El(1)−Cl(1)	2.1333(12)	2.193(2)			
El(1)−Cl(2)	2.1343(12)	2.184(2)			

bond, a comparison of the structures of **4**−**8** shows the following: The Ga−N distance in **4** (2.092(5) Å) is longer than that in **6** (2.028(5) Å).[1] It is evident that the sterically demanding diisopropylamino group in **4** prevents a stronger Ga←N interaction. A comparable result is obtained on regarding the Al←N distances in **5** (2.014(3) Å) and **7** (2.085(3) Å). The Ga−N distance in **8** (2.097(3) Å) is in good agreement with that in $[o\text{-}(Me_2NCH_2)C_6H_4]GaH_2$ (2.087(7) Å).[37] The comparison of the Al−H bond lengths in **7** with those of other alanes does not show any remarkable differences.[37−39,41,42] A comparison with **5** is not possible due to the fact that the positions of the hydrogen atoms in **5** could not be determined. The gallium−hydrogen bond lengths in **8** determinated by X-ray analysis are 1.55(5) and 1.58(5) Å, respectively, and in good agreement with terminal Ga−H bonds in gallane−amine adducts, e.g., $H_3Ga{\cdot}NMe_3$ (1.497(2) Å).[43]

Solution Behavior of 3−5, 7, and 8. The compounds **3**−**5**, **7**, and **8** have been investigated by ^1H and ^{13}C NMR spectroscopy (see Table 4). As described elsewhere,[1−5] significant downfield shifts for the hydrogen atoms of the aminomethyl and of the methylene group in comparison to those in the parent hydrogen-substituted compound indicate the intramolecular coordination of the amino group. The corresponding NMR data (δ and $\Delta\delta$ values) are listed in Table 4. According to these data, a direct connection between the $\Delta\delta$ value and the electronic effect of the corresponding substituent R at the group 13 element center is shown: the downfield shift is more pronounced in the case of R = Cl than in the case of R = H.

Analogous to known compounds of the same type, averaged signals are observed for the cyclopentadienyl unit in the ^1H and ^{13}C NMR spectra. Therefore, the same dynamic "windshield-wiper" process as explained in detail elsewhere describes the rearrangement processes of **3**−**5**, **7**, and **8** in solution.[1−5]

NMR experiments show that the dihydrido compounds **5** and **8** are stable for many weeks in solution and do not undergo any ligand redistribution. Cowley et al. investigated the behavior of $[o\text{-}(Me_2NCH_2)C_6H_4]GaH_2$ in solution and observed that this compound undergoes a ligand redistribution reaction to the diaryl species $[o\text{-}(Me_2NCH_2)C_6H_4]_2GaH$.[37,38]

Further experiments designed to obtain additional information about the monomeric nature of **5**, **7**, and **8** in solution have been performed: We investigated the degree of association of **8** by molecular mass determination and found that this compound is monomeric in benzene. Thus, an association by intermolecular coordination of the amino group or by bridging hydrogen atoms can be excluded. Molecular mass determinations could not be performed with the aluminum compounds **5** and **7** because of their low solubility. Therefore, these compounds and also **8** have been further investigated by IR spectroscopic studies. In diethyl ether solution, we did not observe any absorption due to bridging El−H−El units, which should be found in the region of 1620 cm^{-1}.[37] Symmetric (**5**, 1844 cm^{-1}; **8**, 1890 cm^{-1}) and asymmetric (**5**, 1822 cm^{-1}; **8**, 1836 cm^{-1}) stretching frequencies of terminal El−H units were detected; for **7** only one very broad signal (1890 cm^{-1}) without further splitting was observed due to overlapping bands. These findings support the monomeric nature of **5**, **7**, and **8** in solution. In contrast, Cowley et al. reported on the dimeric, intramolecularly base-stabilized aminoaryl alane $[(2\text{-}Me_2NCH_2C_6H_4)AlH_2]_2$;[37] this compound contains terminal and bridging Al−H bonds (coordination number of 5 at the aluminum center). For the stretching frequency of the bridging Al−H−Al units, an absorption at 1622 cm^{-1} was found.[37]

A comparison of the symmetric Al−H stretching frequencies of **5** and **7** shows the influence of the steric requirements of the dialkylamino group on the strength of the Al−H bond. The sterically demanding *N*,*N*-diisopropylamino group is less strongly bound to the metal center; the consequence is a stronger Al−H bond in **7** than in **5**. The Ga−H stretching frequencies found for **8** are in the expected range for terminal Ga−H bonds.[37,44,45]

The weakness of the group 13 element C(Cp) bond in the dihydrido species **5** and **8** has been demonstrated by irradiation experiments in a quartz NMR tube. A highly reflective metallic film of elementary gallium was obtained by irradiation of a solution of **8** in deuterated benzene with a Hg lamp. Simultaneously, the evolution of a colorless gas (presumably H_2) and the formation of the hydrogen-functionalized ligand $[C_5H_5(CH_2CH_2NMe_2)]$ (Scheme 4) were observed. These findings are in accord with those of Cowley et al. for the compound Mes^*GaH_2.[44,46] The irradiation of **5** under the same conditions results in the slow formation of aluminum as a gray powder and of the hydrogen functionalized

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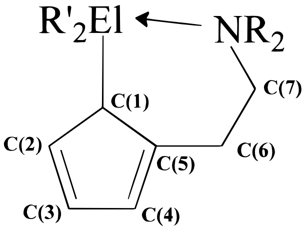
Table 3. Selected Bond Angles (deg) for [2-($Me_2NCH_2CH_2$)C_5H_4]$AlCl_2$, 3, [2-(*i*-$Pr_2NCH_2CH_2$)C_5H_4]$GaCl_2$, 4, [2-($Me_2NCH_2CH_2$)C_5H_4]AlH_2, 5, [2-(*i*-$Pr_2NCH_2CH_2$)C_5H_4]AlH_2, 7, and [2-($Me_2NCH_2CH_2$)C_5H_4]GaH_2, 8; for Numbering Pattern See Scheme 3

	3	4	5	7	8
C(1)−El(1)−N(1)	102.9(1)	100.6(2)	99.24(14)	100.4(2)	97.19(14)
N(1)−El(1)−X(1)	105.24(8)	110.4(1)		106.0(1)	103.0(2)
N(1)−El(1)−X(2)	106.00(8)	108.2(2)		114.0(1)	99.0(2)
C(9)−N(1)−C(7)	109.7(2)		108.9(3)		110.7(3)
C(11)−N(1)−C(7)		111.6(5)		110.1(3)	
C(8)−N(1)−C(7)	108.4(2)	109.1(5)	110.5(3)	110.6(3)	108.3(3)
C(8)−N(1)−El(1)	111.7(2)	108.4(4)	111.3(2)	103.5(2)	109.2(2)
C(1)-El(1)−X(1)	118.93(9)	111.2(2)		112.0(1)	118.0(2)
C(1)-El(1)−X(2)	112.39(9)	121.5(2)		114.0(1)	117.0(2)
X(1)-El(1)−X(2)	110.06(5)	104.68(7)		118.0(2)	117.0(3)
C(9)−N(1)−El(1)	109.8(2)		107.5(2)		110.1(2)
C(11)−N(1)−El(1)		106.3(3)		109.8(2)	
C(7)−N(1)−El(1)	109.6(2)	106.3(4)	110.5(2)	107.9(2)	109.8(2)
C(5)−C(1)−El(1)	95.6(2)	96.3(4)	90.9(2)	91.3(2)	98.0(2)

Table 4. Correlation of ^1H NMR Chemical Shifts (δ, in $CDCl_3$) of the $CH_2N(CHR_2)_2$ Protons and $\Delta\delta$ ^1H NMR Chemical Shifts (in $CDCl_3$) in (*N*,*N*-Dialkylaminoethyl)cyclopentadienyl Compounds

	^1H NMR chemical shifts		^1H NMR chemical shifts	
compound	δ $CH_2N(CHR_2)_2$	δ $CH_2N(CHR_2)_2$	$\Delta\delta$ $CH_2N(CHR_2)_2$	$\Delta\delta$ $CH_2N(CHR_2)_2$
$C_5H_5(CH_2CH_2NMe_2)$[46]	2.42−2.57 (m)	2.24 (s)	0	0
$C_5H_5(CH_2CH_2N$-*i*-$Pr_2)$[47]	2.54−2.61 (m)	2.97−3.07 (m)	0	0
$[C_5H_5(CH_2CH_2NMe_2)]AlCl_2$, **3**	2.91−2.97 (m)	2.75 (s)	0.45	0.51
$[C_5H_5(CH_2CH_2NMe_2)]AlH_2$, **5**	2.92 (t)	2.57 (s)	0.43	0.33
$[C_5H_5(CH_2CH_2NMe_2)]GaCl_2$[1]	2.88 (s)	2.73 (s)	0,39	0.49
$[C_5H_5(CH_2CH_2NMe_2)]GaH_2$, **8**	2.85 (t)	2.54 (s)	0.36	0.30
$[C_5H_5(CH_2CH_2N$-*i*-$Pr_2)]GaCl_2$, **4**	3.21 (t)	3.79 (sep)	0.64	0.77
$[C_5H_5(CH_2CH_2N$-*i*-$Pr_2)]AlH_2$, **7**	3.16 (t)	3.60 (sep)	0.59	0.58

Scheme 3. Numbering Pattern



Scheme 4. Decomposition of 5 and 8 by MOCVD and Irradiation

$$[(Me_2NCH_2CH_2)C_5H_4]\mathbf{El}H_2 \xrightarrow[h * \nu]{\Delta \text{ or}} \mathbf{El} + (Me_2NCH_2CH_2)C_5H_5 + 1/2\ H_2$$

El = Al (**5**)
El = Ga (**8**)

ligand. Similarly, the evolution of a colorless gas (presumably H_2) was observed.

MOCVD Experiments. Compounds of the type [($Me_2NCH_2CH_2$)C_5R_4]MR'_2, with M = Al, Ga, R= H, Me and R′ = H, *i*-Bu, have a sufficient volatility and a well-understood fragmentation behavior in thermolysis experiments. Therefore, they are useful precursors for the deposition of Al and Ga, respectively, in the MOCVD process.[1−4,47] We carried out MOCVD experiments using **5** and **8** as precursor molecules in a hot-wall reactor and observed the formation of highly reflective metal films. The films of aluminum were deposited at substrate temperatures between 580 and 620 °C. The depositions were carried out at a reduced pressure of 1×10^{-3} mbar; the precursor source was operated at 60 °C. In the case of gallium deposition, the films were obtained at substrate temperatures between 240 and 260 °C at a reduced pressure of 1×10^{-3} mbar, while operating the precursor source at 50 °C. In these experiments, quartz glass substrates were used without carrier gas. ^1H NMR spectroscopy of the volatile byproducts showed that almost exclusively (2-*N*,*N*-dimethylamino)ethylcyclopentadiene was formed during the pyrolysis. The decomposition process is outlined in Scheme 4. The deposited films have been investigated by sputter auger electron spectroscopy (SAES). The surfaces of the aluminum and of the gallium layers are contaminated with several impurities, mostly carbon (29% in the aluminum layers; 28% in gallium layers) and oxygen (10% in the aluminum and in gallium films) due to surface-adsorbed carbon dioxide and oxygen. The analysis of the inner layers of the aluminum films showed that the carbon content is very close to the detection limit of the measurement (<2−4%), while the content of oxygen remained unchanged at 10%. This constant oxygen content is a result of the contamination probably from residual gases in the reactor and from leaks in the MOCVD apparatus. Similar obervations concerning the characterization of thin aluminum films have been made by Scherer and Kruck.[47]

Experimental Section

General Procedures. All manipulations were performed under a dry, oxygen-free argon atmosphere using standard Schlenk techniques or an MB 150B-G-I Vacuum Atmospheres drybox. Solvents were dried by refluxing over $LiAlH_4$ (ether) or Na/K (toluene) and distilled before use. The reagents [($Me_2NCH_2CH_2$)C_5H_4]K (**1**),[48] [(*i*-$Pr_2NCH_2CH_2$)C_5H_4]K (**2**),[49] [($Me_2NCH_2CH_2$)C_5H_4]$GaCl_2$ (**6**),[1] and $LiGaH_4$[50] were prepared

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according to literature methods. Elemental microanalyses were performed by Analytisches Labor der Fakultät für Chemie, Universität Bielefeld, Bielefeld, Germany, and by Mikroanalytisches Laboratorium Beller, Göttingen, Germany.

Physical Measurements. ^{1}H (500.1 MHz), ^{13}C {^{1}H} (125.8 MHz), and ^{27}Al {^{1}H} (130.3 MHz) NMR spectra were recorded on a Bruker Avance DRX 500 spectrometer. Chemical shifts for ^{1}H and ^{13}C {^{1}H} spectra were recorded in ppm downfield from TMS and referenced with internal deuteriochloroform, toluene-d_8, or deuteriobenzene. ^{27}Al {^{1}H} spectra were recorded in ppm and referenced with external $[Al(H_2O)_6]^{3+}$. 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 spectra were 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 capillaries) and are uncorrected.

Dichloro[η^1:η^1-2-(N,N-dimethylamino)ethylcyclopentadienyl]aluminum (3). A suspension of 5.35 g (30.5 mmol) of $[(Me_2NCH_2CH_2)C_5H_4]K$ (**1**) in toluene (40 mL) was added to a solution of 4.07 g (30.5 mmol) of freshly sublimed $AlCl_3$ in toluene (40 mL) at −50 °C. The reaction temperature was maintained at −50 °C for 1 h, and afterward the reaction mixture was allowed to warm slowly to ambient temperature. After being stirred for an additional 3 days the suspension was filtered, and the volume of the colorless filtrate was reduced by evacuation by half. Cooling of the resulting solution to −70 °C for 3 weeks afforded a 60% yield (4.28 g) of pale yellow crystalline **3** (mp 113−115 °C, dec), suitable for an X-ray structure determination.

^{1}H NMR ($CDCl_3$): $\delta = 2.75$ (s, 6 H, NCH_3), 2.91−2.97 (m, 4 H, CH_2CH_2NMe$_2$), 5.36 (s*, 2 H, ring-H_A), 6.63 (s*, 2 H, ring-H_B). ^{1}H NMR (C_6D_6): $\delta = 1.77$ (s, 6 H, NCH_3), 1.87 (t, $^3J_{H-H} =$ 5.9 Hz, 2 H, CH_2), 2.17 (t, $^3J_{H-H} = 5.9$ Hz, 2 H, CH_2NMe$_2$), 5.28 (s*, 2 H, ring-H_A), 6.85 (s*, 2 H, ring-H_B). ^{13}C NMR ($CDCl_3$): $\delta = 26.3$ (CH$_2$), 45.7 (NCH$_3$), 62.6 (CH$_2$NMe$_2$), 94.2 (ring-$C_{1,4}$), 126.3 (ring-$C_{2,3}$), 131.0 (ring-C_5). ^{27}Al NMR ($CDCl_3$): $\delta = 116.7$ ($\nu_{1/2} \approx 500$ Hz). MS [m/z (rel int %)]: 234 (9) [$M^+ + H$], 233 (5) [M^+], 198 (8) [$M^+ - {}^{35}Cl$], 136 (19) [$C_5H_4CH_2CH_2NMe_2^+$], 58 (100) [$Me_2NCH_2^+$]. Anal. Calcd for $C_9H_{14}AlCl_2N$ (234.10): C, 46.18; H, 6.03; N, 5.98. Found: C, 43.37; H, 6.24; N, 5.70.

Dichloro[η^1:η^1-2-(N,N-diisopropylamino)ethylcyclopentadienyl]gallium (4). A suspension of 2.31 g (10.0 mmol) of $[(i\text{-}Pr_2NCH_2CH_2)C_5H_4]K$ (**2**) in toluene (30 mL) was added to a solution of 1.76 g (10.0 mmol) of $GaCl_3$ in toluene (20 mL) at −50 °C. The reaction temperature was maintained at −50 °C for 1 h, and afterward the suspension was allowed to warm slowly to ambient temperature. After being stirred for an additional 12 h the reaction mixture was filtered, and the volume of the colorless filtrate was reduced by evacuation by ~50%. Cooling of the resulting solution to −70 °C for 3 days afforded a 42% yield (1.38 g) of colorless crystalline **4** (mp 53−55 °C, dec), suitable for an X-ray structure determination.

^{1}H NMR ($CDCl_3$): $\delta = 1.48$ (d, $^3J_{H-H} = 6.8$ Hz, 6 H, CHCH_3), 1.50 (d, $^3J_{H-H} = 6.8$ Hz, 6 H, CHCH_3), 2.92 (t, $^3J_{H-H} = 5.8$ Hz, 2 H, CH_2), 3.21 (t, $^3J_{H-H} = 5.8$ Hz, 2 H, CH_2N), 3.79 (sep, $^3J_{H-H}$ = 6.8 Hz, 2 H, CHCH$_3$), 5.18 (s*, 2 H, ring-H_A), 6.64 (s*, 2 H, ring-H_B). ^{1}H NMR (C_6D_6): $\delta = 0.77$ (d, $^3J_{H-H} = 6.8$ Hz, 6 H, CHCH_3), 0.97 (d, $^3J_{H-H} = 6.8$ Hz, 6 H, CHCH_3), 2.32 (m, 2 H, CH_2), 2.41 (m, 2 H, CH_2N), 3.31 (sep, $^3J_{H-H} = 6.8$ Hz, 2 H, CHCH$_3$), 5.14 (s*, 2 H, ring-H_A), 6.86 (s*, 2 H, ring-H_B). ^{13}C NMR ($CDCl_3$): $\delta = 20.9$, 21.0 (CHCH$_3$), 26.6 (CH$_2$), 51.4 (CH$_2$N), 55.5 (CHCH$_3$), 92.0 (ring-$C_{1,4}$), 129.5 (ring-$C_{2,3}$), 135.0 (ring-C_5). ^{13}C NMR (C_6D_6): $\delta = 20.4$, 20.6 (CHCH$_3$), 26.6 (CH$_2$), 51.3 (CH$_2$N), 55.1 (CHCH$_3$), 92.0 (ring-$C_{1,4}$), 129.8 (ring-$C_{2,3}$), 135.2 (ring-C_5). MS [m/z (rel int %)]: 331 (1) [M^+], 296 (3) [$M^+ - {}^{35}Cl$], 294 (3) [$M^+ - {}^{37}Cl$], 192 (3) [$C_5H_4(CH_2CH_2N\text{-}i\text{-}Pr_2)^+$], 114 (100) [$i\text{-}Pr_2NCH_2^+$]. Anal. Calcd for $C_{13}H_{22}Cl_2GaN$ (332.95): C, 46.89; H, 6.66; N, 4.20. Found: C, 46.76; H, 6.75; N, 4.18.

Dihydrido[η^1:η^1-2-(N,N-dimethylamino)ethylcyclopentadienyl]aluminum (5). Method A. A solution of 702 mg (3.00 mmol) of $[(Me_2NCH_2CH_2)C_5H_4]AlCl_2$ (**3**) in Et_2O (20 mL) was added slowly to a suspension of 228 mg (6.00 mmol) of $LiAlH_4$ in Et_2O (10 mL) at −60 °C. The reaction temperature was maintained at −60 °C for 1 h, and afterward the reaction mixture was allowed to warm slowly to ambient temperature. After being stirred for an additional 2 days the mixture was filtered, and the volume of the colorless filtrate was reduced by evacuation by ~50%. Cooling of the resulting colorless solution to −70 °C for 3 days afforded a 92% yield (456 mg) of colorless crystalline **5**, suitable for an X-ray structure determination.

Method B. A solution of 1.38 g (5.00 mmol) of $[(Me_2NCH_2CH_2)C_5H_4]GaCl_2$ in Et_2O (40 mL) was added slowly to a suspension of 38.0 mg (10.0 mmol) of $LiAlH_4$ in Et_2O (20 mL) at −60 °C. The reaction temperature was maintained at −60 °C for 1 h. After warming up slowly to ambient temperature, the reaction mixture was stirred for additional 2 days. Filtration and evaporation of the volatiles in vacuo afforded >90% yield of colorless solid **5**.

^{1}H NMR ($CDCl_3$): $\delta = 2.57$ (s, 6 H, NCH_3), 2.81 (t, $^3J_{H-H} =$ 5.4 Hz, 2 H, CH_2), 2.92 (t, $^3J_{H-H} = 5.4$ Hz, 2 H, CH_2NMe$_2$), 3.10−4.20 (br s, 2H, Al-H), 5.46 (t*, 2 H, ring-H_A), 6.54 (t*, 2 H, ring-H_B). ^{13}C NMR ($CDCl_3$): $\delta = 26.3$ (CH$_2$), 45.1 (NCH$_3$), 63.1 (CH$_2$NMe$_2$), 95.5 (ring-$C_{1,4}$), 121.1 (ring-$C_{2,3}$), 128.6 (ring-C_5). ^{27}Al NMR ($CDCl_3$): $\delta = 142.7$ ($\nu_{1/2} \approx 1400$ Hz). MS [m/z (rel int %)]: 165 (25) [M^+], 164 (100) [$M^+ - H$], 58 (95) [$Me_2NCH_2^+$]. Anal. Calcd for $C_9H_{16}AlN$ (165.21): C, 65.43; H, 9.76; N, 8.48. Found: C, 63.78; H, 9.68; N, 8.13. IR: $\nu_{Al-H} =$ 1844, 1822, 1758 cm^{-1}.

Dihydrido[η^1:η^1-2-(N,N-diisopropylamino)ethylcyclopentadienyl]aluminum (7). A solution of 1.23 g (3.69 mmol) of $[(i\text{-}Pr_2NCH_2CH_2)C_5H_4]GaCl_2$ (**4**) in Et_2O (20 mL) was added to a suspension of 28.0 mg (7.39 mmol) of $LiAlH_4$ in Et_2O (10 mL) at −60 °C. The reaction temperature was maintained at −60 °C for 1 h, and afterward the suspension was allowed to warm slowly to ambient temperature. After being stirred for an additional 12 h, the reaction mixture was filtered and the volume of the colorless filtrate was reduced by evacuation by ~50%. Cooling of the resulting colorless solution to −70 °C for 3 days afforded a 61% yield (500 mg) of colorless crystalline **7** (mp 94−96 °C, dec), suitable for an X-ray structure determination. ^{1}H NMR ($CDCl_3$): $\delta = 1.30$ (d, $^3J_{H-H} = 6.6$ Hz, 6 H, CHCH_3), 1.38 (d, $^3J_{H-H} = 6.8$ Hz, 6 H, CHCH_3), 2.99 (t, $^3J_{H-H}$ = 6.2 Hz, 2 H, CH_2), 3.16 (t, $^3J_{H-H} = 6.2$ Hz, 2 H, CH_2N), 3.60 (sep, $^3J_{H-H} = 6.6$ Hz, 2 H, CHCH$_3$), 5.49 (s*, 2 H, ring-H_A), 6.56 (s*, 2 H, ring-H_B). ^{1}H NMR (C_6D_6): $\delta = 0.77$ (d, $^3J_{H-H} =$ 6.5 Hz, 12 H, CHCH_3), 2.41 (t, $^3J_{H-H} = 6.1$ Hz, 2 H, CH_2), 2.63 (t, $^3J_{H-H} = 6.2$ Hz, 2 H, CH_2N), 3.17 (sep, $^3J_{H-H} = 6.5$ Hz, 2 H, NCHCH$_3$), 5.65 (s*, 2 H, ring-H_A), 6.97 (s*, 2 H, ring-H_B). ^{13}C NMR ($CDCl_3$): $\delta = 19.8$ (CHCH$_3$), 25.9 (CH$_2$), 46.5 (CH$_2$N), 52.6 (CHCH$_3$), 95.9 (ring-$C_{1,4}$), 121.6 (ring-$C_{2,3}$), 126.4 (ring-C_5). ^{13}C NMR (C_6D_6): $\delta = 19.4$ (CHCH$_3$), 26.5 (CH$_2$), 46.8 (CH$_2$N), 52.6 (CHCH$_3$), 96.1 (ring-$C_{1,4}$), 122.1 (ring-$C_{2,3}$), 126.2 (ring-C_5). ^{27}Al NMR ($CDCl_3$): $\delta = 122.2$ ($\nu_{1/2} \approx 2000$ Hz). ^{27}Al NMR (C_6D_6): $\delta = 121.9$ ($\nu_{1/2} \approx 2700$ Hz). MS [m/z (rel int %)]: 221 (21) [M^+], 220 (100) [$M^+ - H$], 114 (100) [$i\text{-}Pr_2NCH_2^+$]. IR: $\nu_{Al-H} = 1890$ cm^{-1}; $C_{13}H_{24}AlN$ (221.32).

Dihydrido[η^1:η^1-2-(N,N-dimethylamino)ethylcyclopentadienyl]gallium (8). A solution of 1.11 g (4.00 mmol) of $[(Me_2NCH_2CH_2)C_5H_4]GaCl_2$ (**6**) in Et_2O (40 mL) was added slowly to a suspension of 646 mg (8.00 mmol) of $LiGaH_4$ in Et_2O (30 mL) at −50 °C. The reaction temperature was maintained at −50 °C for 12 h, and afterward the solution was allowed to warm slowly to 0 °C. At nearly 0 °C, a spontaneous gas evolution (H_2) accompanied by the precipitation of a gray solid (Ga) was observed. The reaction mixture was im-

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(49) Jutzi, P.; Redeker, T.; Neumann, B.; Stammler, H.-G. *Organometallics* **1996**, *15*, 4153.

mediately filtered, and the volume was reduced by evaporation by ~50%. Cooling of the resulting colorless solution to −70 °C for 3 days afforded >90% yields of colorless crystalline **8** (mp 90 °C, dec), suitable for an X-ray structure determination.

^{1}H NMR (CDCl$_3$): $\delta = 2.54$ (s, 6 H, NCH_3), 2.73 (t, $^3J_{H-H} = 5.8$ Hz, 2 H, CH_2), 2.85 (t, $^3J_{H-H} = 5.8$ 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). ^{1}H NMR (C$_6$D$_6$): $\delta = 1.68$ (s, 6 H, NCH_3), 1.87 (t, $^3J_{H-H} = 6.0$ Hz, 2 H, CH_2), 2.36 (t, $^3J_{H-H} = 6.0$ Hz, 2 H, CH_2NMe$_2$), ~4.40 (v br s, ~2 H, Ga-H), 5.33 (s*, 2 H, ring-H_A), 6.88 (t*, 2 H, ring-H_B). ^{1}H NMR (toluene-d_8, −40 °C): $\delta = 1.60$ (s, 6 H, NCH_3), 1.74 (t, $^3J_{H-H} = 5.8$ Hz, 2 H, CH_2), 2.32 (t, $^3J_{H-H} = 5.8$ 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$_2$NMe$_2$), 91.2 (ring-$C_{1,4}$), 123.7 (ring-$C_{2,3}$), 135.6 (ring-C_5). MS [m/z (rel int %)]: 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}. Molecular weight determination: calcd for $C_9H_{16}GaN$ 208.0, found 215.7.

Photochemical Experiments. All experiments were carried out with a Hg-lamp from Heraeus, Original Hanau TQ 150 (150 W, irradiation maxima at 254 and 366 nm) in a quartz NMR tube.

MOCVD Experiments. The experiments were carried out in an externally thermostated quartz-hot-wall MOCVD reactor (15 mm diameter and 355 mm in length), which was evacuated to a base pressure of 10^{-3} mbar. The precursors **5** and **8** were sublimed into the reaction zone. The reactor was heated independently of the precursor evaporator by a separate furnace. Deposition was accomplished on quartz glass. No carrier gas was used during the depositions. To examine the fragmentation reactions occurring during CVD, volatile byproducts were collected in a liquid nitrogen-cooled trap and were characterized by ^{1}H and ^{13}C NMR spectroscopy.

Molecular Weight Determinations. The degree of association in solution was investigated by a technique that has been described by Signer,[51] Zoellner,[52] and Burger and Beraro.[53] This method involves the principle of isothermal distillation of two solutions solely in vapor phase contact. The distillation proceeds until the apparent concentrations of the solutions are equal.

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Supporting Information Available: Fully labeled ORTEP drawings and tables of atomic coordinates, displacement parameters, bond lengths, bond angles, and hydrogen coordinates for **3**−**5**, **7**, and **8**. This material is available free of charge via the Internet at http://pubs.acs.org.

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