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Synthesis and Properties of Group 13 Element Compounds (Al, Ga, In) with the Polydentate 1-[2-(Dimethylamino)ethyl]-2,3,4,5-tetramethylcyclopentadienyl Ligand. X-ray Crystal Structures of $(C_5Me_4CH_2CH_2NMe_2)MX_2$ (MX_2 = $AlMe_2$, $AlCl_2$, $InCl_2$)[1]

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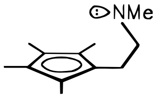
Several new group 13 element compounds containing the 1-[2-(dimethylamino)ethyl]-2,3,4,5-tetramethylcyclopentadienyl ligand (Cp∧) are described. Reaction of the respective element halide with Cp^Li leads to the compounds **2**−**8** of the type $(C_5Me_4CH_2CH_2NMe_2)$-MX_2 [**2**, M = Al, X = CH_3; **3**, M = Al, X = C_2H_5; **4**, M = Al, X = Cl; **5**, M = Al, X = Br; **6**, M = Al, X = I; **7**, M = Ga, X = Cl; **8**, M = In, X = Cl]. All compounds feature monomeric structures with intramolecularly coordinated dimethylamino groups. The dynamic behavior in solution is based on fast haptotropic shifts in a "windscreen-wiper" type process. In the reaction of **5** with $H_3Al{\cdot}NMe_3$, the compound $(C_5Me_4CH_2CH_2NMe_2)Al(H)Br$ (**9**) is formed. The known correlation of the ^{27}Al NMR shift with the coordination number at aluminum can be extended to cyclopentadienyl compounds. The structures of **2**, **4**, and **8** were established by X-ray crystallography.

Introduction

Tetramethylcyclopentadienyl systems[1] with a pendant ligand are currently explored with great success in the chemistry of many metals.[2−9] They combine the advantages of a peralkylated cyclopentadienyl system with the properties of a further functionality. If the modified side chain possesses a substituent with donor function (i.e. Lewis basicity), these bi(poly)dentate ligands do not just act as "spectator" ligands but are capable of showing an additional coordinative bonding. Mostly, an *intramolecular* coordination is obtained, which results in interesting effects on both structure and reactivity. As part of our continuing interest in functionalized cyclopentadienyl systems with novel substitution patterns,[10] we have introduced the 1-[2-(dimethylamino)ethyl]-2,3,4,5-tetramethylcyclopentadienyl ligand (Cp∧)[10a] (**I**), which offers both a hard and a soft donor function (following Pearson's[11] concept of hard and soft acids and bases). We have shown with some typical examples in the chemistry of s-, p-, d-, and f-block elements[12,13] that, under appropriate conditions, the nitrogen atom can coordinate intramolecularly to a metal center (in addition to the cyclopentadienyl system).



I

Very recently, we reported preliminary results on the synthesis and structure of new complexes of group 13 elements containing ligand **I**.[14] In comparison with compounds derived from the parent pentamethylcyclopentadienyl unit (Cp*), we observed significant changes

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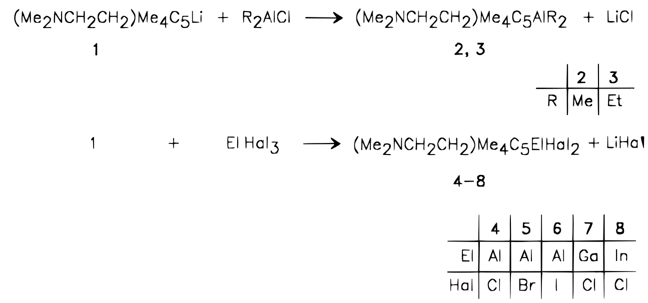
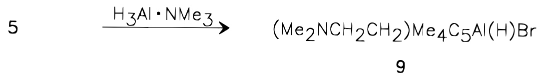
Scheme 1



Scheme 2



in stability, reactivity, and structure. These effects are due to an intramolecular base stabilization of the central atoms. In this paper, we report in detail on the preparation and characterization of compounds of the general formula ($C_5Me_4CH_2CH_2NMe_2$)MX_2 (M = Al, Ga, In; X = Me, Et, Cl, Br, I) and on their structure both in solution and in the solid-state. Special emphasis is put on the coordination mode of the ligand.

Results and Discussion

Synthesis. The reaction of lithiated [2-(dimethylamino)ethyl]tetramethylcyclopentadiene (**1**, Cp^Li) with stoichiometric amounts of the corresponding dialkylaluminum chloride leads to the formation of the dialkyl($\eta^1{:}\eta^1$-1-[2-(dimethylamino)ethyl]-2,3,4,5-tetramethylcyclopentadienyl)aluminum compounds **2** (R = Me) and **3** (R = Et), respectively (Scheme 1). These compounds are obtained as colorless and moisture-sensitive crystals, which are unexpectedly stable against air and readily soluble in common organic solvents.

Reaction of **1** with 1 equiv of an aluminum trihalide AlX_3 yields the complexes **4**–**6** of type ($\eta^{2/3}{:}\eta^1$-C_5Me_4-$CH_2CH_2NMe_2$)AlX_2 (**4**, X = Cl; **5**, X = Br; **6**, X = I) (Scheme 1). In these reactions the order of addition of the reagents is of crucial importance. It is essential to add Cp∧Li to the respective aluminum trihalide and *not* vice versa; otherwise **4**–**6** can be isolated only in low yields (out of a mixture of products). The compounds **4**–**6** are colorless and moderately air-stable solids.

Treatment of **1** with the metal chlorides MCl_3 (M = Ga, In) leads to the dichloro($\eta^1{:}\eta^1$-1-[2-(dimethylamino)ethyl]-2,3,4,5-tetramethylcyclopentadienyl)metal complexes **7** (M = Ga) and **8** (M = In), respectively (Scheme 1). These compounds are obtained as colorless (**7**) or yellow (**8**) moderately air-stable solids. Again, the order of addition is of crucial importance.

In the reaction of **5** with the alane adduct $H_3Al{\cdot}NMe_3$, one bromo ligand in **5** is substituted by a hydrido ligand. The resulting halogeno(hydrido)aluminum compound **9** is formed in almost quantitative yield as a colorless, rather air-sensitive solid (Scheme 2). Compound **9** is characterized by spectroscopic and analytical data only (vide infra). Low solubility prevents a molecular mass determination. Although an excess of alane is used, only monosubstitution takes place.

Crystal Structure Data for 2, 4, and 8. To get information on the coordination mode of the ((dimethylamino)ethyl)tetramethylcyclopentadienyl ligand in the solid-state structure of the compounds described above, X-ray crystal structure investigations have been performed with representative examples. In the following, we describe the results of diffraction studies of the compounds **2**, **4**, and **8**. The molecular structures together with selected bond lengths and bond angles are depicted in Figures 1–3. Crystallographic data are presented in Table 1, and atomic coordinates are given in Tables 2–4.

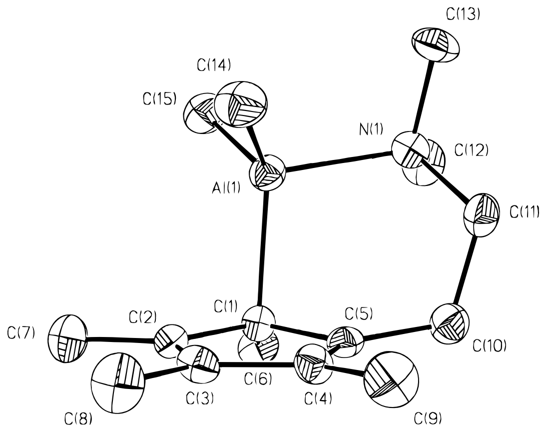


Figure 1. Molecular structure of **2** in the solid, with thermal ellipsoids at the 50% probability level: Selected distances (Å) and angles (deg): Al–C(1) 2.091(4), Al–N 2.067(4), C(1)–C(2) 1.452(6), C(2)–C(3) 1.370(6), C(3)–C(4) 1.426(6), C(4)–C(5) 1.393(6), C(1)–C(5) 1.459(6); C(1)–Al–C(14) 118.6(2), C(1)–Al–N 101.7(1), C(6)–C(1)–Al 112.7(3), Al–N–C(11) 111.4(2), C(14)–Al–C(15) 113.8(2). Nonbonded distances: Al–C(2) 2.672(4), Al–C(5) 2.575(4).

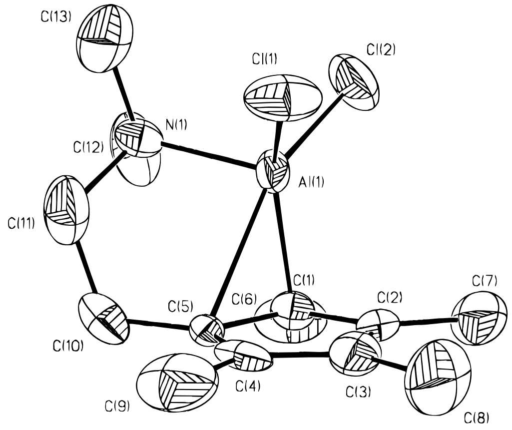


Figure 2. Molecular structure of **4** in the solid state, with thermal ellipsoids at the 50% probability level. Selected distances (Å) and angles (deg): Al–Cl(1) 2.124(4), Al–C(1) 2.063(11), Al–C(2) 2.509(11), Al–C(5) 2.317(10), Al–N 2.005(10), C(1)–C(2) 1.395(16), C(2)–C(3) 1.322(17), C(3)–C(4) 1.404(17), C(4)–C(5) 1.351(16), C(1)–C(5) 1.487(14); C(1)–Al–Cl(1) 131.4(4), C(1)–Al–N 104.7(4), C(6)–C(1)–Al 117.6(8), Al–N–C(11) 106.3(7), Cl(1)–Al–Cl(2) 105.8(2). Nonbonded distances: Al–C(2) 2.509(11).

Compound **2** consists of monomeric units, in which the Cp ligand is η^1-bonded from the allylic position to the aluminum center. A coordination number of 4 at aluminum is realized by an intramolecular interaction of the nitrogen atom in the side chain. Within the planar C_5-perimeter, bond lengths and bond angles are characteristic for a σ-bonded Cp unit. The carbon atoms from the Cp ring substituents (4 methyl groups, 1 (dimethylamino)ethyl group) deviate slightly from the ring plane in probable response to small nonbonded interactions (methyl groups) and to ring-strain effects (coordinated (dimethylamino)ethyl group). The side

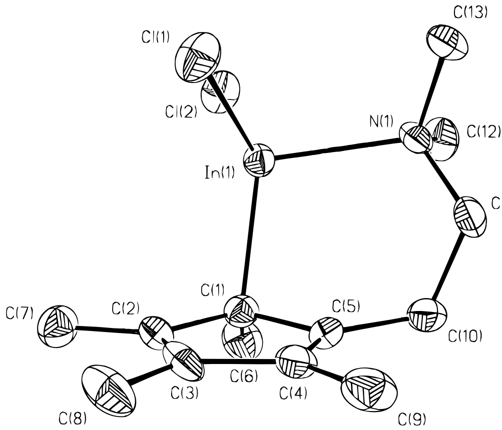


Figure 3. Molecular structure of **8** in the solid state, with thermal ellipsoids at the 50% probability level: Selected distances (Å) and angles (deg): In−C(1) 2.176(5), In−N 2.265(5), C(1)−C(2) 1.467(8), C(2)−C(3) 1.350(8), C(3)−C(4) 1.450(9), C(4)−C(5) 1.363(8), C(1)−C(5) 1.481(8); C(1)−In−Cl(1) 120.6(2), C(1)−In−N 104.8(2), C(6)−C(1)−In 110.6(4), In−N−C(11) 110.1(3), Cl(1)−In−Cl(2) 106.6(1). Nonbonded distances: In−C(2) 2.915(5), In−C(5) 2.715(5).

chain is bonded to a vinylic carbon atom of the Cp ring in α position to the allylic carbon atom. The Al−C(Cp)distance is in the range of Al−C(terminal) and Al−C(bridging) distances and typical for Cp aluminum compounds.[16] The Al−N distance is comparable to those of related alane−amine adducts (e.g. $Me_3Al-N(CH_2CH_2)_3N-AlMe_3$: 2.10(6) Å [17]). The gross structural feature of **2** resembles that of the compound (σ-Me_5C_5)$AlMe_2\cdot$THF.[18]

For compound **3**, which is not discussed here, comparable structural parameters have been found by an X-ray diffraction analysis.[13]

The structural analysis of **4** shows a deviation from the gross structural pattern found for **2**. Compound **4** crystallizes in the form of monomeric units with the (dimethylamino)ethyl group intramolecurlarly coordinated to the aluminum center and with an asymmetrically η^2-bonded Cp ligand. As a consequence of the Cp bonding mode, the C−C bond lengths within the Cp unit differ from those expected for a classical cyclopentadiene structure.[19] The Al−N distance is significantly shorter than that in **2** and approaches the distance found in $Cl_3Al-NMe_3$ (Al−N: 1.96 Å].[20] The η^2-coordination and the short Al−N distance compensate the enhanced electron deficiency at aluminum caused by the presence of two chloro ligands.

A monomeric structure similar to the structure of the dimethylaluminum compound **2** is found for the dichloroindium compound **8**. The Cp ligand is η^1 bonded to the indium centre, and the (dimethylamino)ethyl group coordinates intramolecurlarly. The In−C(Cp) and the In−N distances are in the range expected for bonding distances in base-stabilized dihalogenoorganoindium compounds.[21] The In−N bond is markedly shorter than those in adducts of the type $Me_3In\cdot NR_2H$ (2.36−2.50 Å).[22]

Structures of 2−9 in Solution. Information about the structure and the dynamic behavior of **2**−**9** in solution has been gained from cryoscopic molecular mass determinations and from ^{1}H, ^{13}C, and ^{27}Al 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 in the case of ^{27}Al NMR also about the coordination number at the respective aluminum atom.

Cryoscopic molecular mass determinations in benzene solution have been performed with **2**−**4**, **7**, and **8**; they prove the monomeric structure of these compounds. The species **5**, **6**, and **9** could not be investigated due to low solubility (**5**, **6**) or pronounced air-sensivity (**9**).

As already experienced with other ((dimethylamino)ethyl)tetramethylcyclopentadienyl compounds,[13,23] 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 atom; $\Delta\delta$ values up to 0.6 ppm are observed in the chemistry of s- and p-block elements.[13] From the ^{1}H NMR data collected in Table 5 it is evident that in the compounds **2**−**8** the amino group is coordinated to the corresponding central atom. In combination with the above mentioned molecular mass determinations, an intramolecular coordination can be assumed for most of the compounds investigated.

Not unexpectedly, the low symmetry in the solid-state structures **2**−**8** is not reflected in the solution NMR data. In the ^{1}H and ^{13}C NMR spectra of **2**−**8** (see Experimental Section), two singlets in a 1:1 ratio are observed for the four methyl Cp groups; the signal pattern does not change with temperature. The ring carbon atom give rise to only three resonances in the vinylic/allylic region. This observation can be explained as follows: Fast haptotropic rearrangements of the group 13 fragments lead to avaraged ^{1}H and ^{13}C NMR signals even at low temperature. The chain length of the coordinated (dimethylamino)ethyl substitutent is not flexible enough to allow all carbon positions of the Cp ring to participate in the rearrangement processes. The dynamic behavior thus is determined by the rearrangements described in Scheme 3 and resembles a “windscreen-wiper” process. As a consequence, two carbon atoms of the Cp ring always remain vinylic in character, whereas the other three carbon atoms are partly allylic (one-third) and partly vinylic (two-thirds). In the case of fast rearrangements, three resonances for the ring carbon atoms and two resonances for the methyl substituents are expected.

In the ^{1}H and ^{13}C NMR spectra of the hydrido-containing bromoalane **9**, the presence of four methyl group resonances is noticeable (see Experimental Section). The nonequivalence of the methyl groups is caused by the apparent low symmetry at the aluminum center.

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Table 1. Crystallographic Data for Compounds 2, 4, and 8[a]

	2	4	8
empirical formula	$C_{15}H_{28}AlN$	$C_{13}H_{22}AlCl_2N$	$C_{13}H_{22}Cl_2InN$
cryst size, mm^3	0.2 × 0.25 × 0.4	0.3 × 0.5 × 0.6	0.3 × 0.4 × 0.5
fw	249.4	290.2	378.0
cryst syst	monoclinic	orthorhombic	orthorhombic
space group	$P2_1/n$	$P2_12_12_1$	$Pbca$
lattice params			
a, Å	9.858(5)	8.143(2)	14.727(2)
b, Å	13.847(7)	10.201(3)	12.882(2)
c, Å	11.479(4)	18.211(4)	16.558(3)
α, deg			
β, deg	94.17 (4)		
γ, deg			
V, Å^3	1562.7(13)	1512.7(7)	3141.5(9)
Z	4	4	8
d_{calc}, g/cm^3	1.060	1.274	1.599
diffractometer	Siemens $P2_1$	Siemens $P2_1$	Siemens $P2_1$
F(000)	552	616	1520
μ(Mo Kα), mm^{-1}	0.108	0.467	1.807
temp, °C	−97	−100	−107
$2\theta_{max}$, deg	50	60	60
no. of data collected	3050	2547	5088
no. of obsd data [$F > 4\,\sigma(F)$]	1484	1212	3073 [$F > 5\,\sigma(F)$]
no. of params refined	154	154	154
residuals: R, R_w	0.066, 0.046	0.094, 0.068	0.050, 0.048
largest peak in final diff map, e/Å^3	0.30	1.05	1.04
abs corr	no	semiempirical (ψ-scan)	semiempirical (ψ-scan)

[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. The structures were solved by using direct methods and were refined by using full-matrix least squares with anisotropic thermal parameters for all non-hydrogen atoms. All the hydrogen atoms were fixed at the calculated positions with an isotropic U-value of 0.08 Å^2.

Table 2. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Coefficients (Å^2 × 10^3) of 2

	x	y	z	U(eq)[a]
Al(1)	561(1)	2026(1)	2919(1)	26(1)
N(1)	−466(3)	3314(2)	3088(3)	25(1)
C(1)	1517(4)	1855(3)	4592(3)	21(1)
C(2)	2633(4)	1262(3)	4241(3)	23(1)
C(3)	3681(4)	1851(3)	3968(3)	24(2)
C(4)	3315(4)	2830(3)	4168(3)	25(2)
C(5)	2024(4)	2845(3)	4586(3)	23(1)
C(6)	540(4)	1497(3)	5483(3)	33(2)
C(7)	2606(4)	168(3)	4216(4)	37(2)
C(8)	4988(4)	1544(3)	3458(3)	40(2)
C(9)	4154(4)	3699(3)	3873(4)	39(2)
C(10)	1199(4)	3732(3)	4778(3)	31(2)
C(11)	451(4)	4079(3)	3641(3)	32(2)
C(12)	−1697(4)	3205(3)	3763(3)	41(2)
C(13)	−962(4)	3641(3)	1885(3)	38(2)
C(14)	1703(4)	2223(3)	1594(3)	40(2)
C(15)	−913(4)	1063(3)	2603(4)	41(2)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table 3. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Coefficients (Å^2 × 10^3) of 4

	x	y	z	U(eq)[a]
Al(1)	3207(4)	9638(3)	5876(2)	39(1)
Cl(1)	602(3)	9531(4)	5865(2)	58(1)
Cl(2)	3967(5)	9460(4)	4740(2)	74(1)
N(1)	3862(11)	7876(9)	6266(5)	37(3)
C(1)	4791(13)	10939(11)	6376(6)	33(4)
C(2)	3806(16)	11994(10)	6167(6)	39(4)
C(3)	2541(14)	12095(12)	6619(7)	43(4)
C(4)	2611(13)	11088(12)	7144(5)	38(4)
C(5)	3977(14)	10363(11)	7031(5)	34(4)
C(6)	6615(13)	10819(12)	6198(7)	74(5)
C(7)	4228(20)	12915(12)	5538(6)	84(6)
C(8)	1095(15)	13067(12)	6575(7)	79(6)
C(9)	1295(15)	10876(13)	7715(6)	80(6)
C(10)	4509(18)	9181(12)	7425(6)	72(6)
C(11)	3649(18)	7943(12)	7088(6)	69(6)
C(12)	5538(15)	7562(14)	6114(7)	77(6)
C(13)	2785(16)	6814(11)	6011(8)	72(6)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

^{27}Al NMR spectroscopy is an important tool for the determination of solution structures of aluminum compounds. Benn and co-workers[24] showed that there is a correlation between the coordination number at the aluminum atom and the ^{27}Al NMR chemical shift in organoaluminum compounds of the type R_2AlY: The lower the coordination number, the higher is the chemical shift value. Our investigations show that this correlation can be extended to cyclopentadienylaluminum compounds. Table 6 lists several pentamethylcyclopentadienyl and ((dimethylamino)ethyl)tetramethylcyclopentadienyl compounds and their ^{27}Al shift values together with the coordination number as determined by X-ray diffraction analysis.

For the compounds **5**, **6**, and **9** with unknown solid-state structures, a coordination number between 5 and 6 at aluminum can be extrapolated. It is assumed that the coordination is the same in the solid-state and in solution. With this assumption and with the knowledge of the degree of association in solution, the hapticity of the Cp−Al bond (η^1, $\eta^{2/3}$, or η^5) in Cp aluminum compounds can be predicted.

Due to the low solubility of **9**, a cryoscopic molecular mass determination could not be performed. Thus, the

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Table 4. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Coefficients (Å^2 × 10^3) of 8

	x	y	z	U(eq)[a]
In(1)	2040(1)	989(1)	238(1)	23(1)
Cl(1)	1166(1)	−518(1)	60(1)	39(1)
Cl(2)	3461(1)	676(1)	−404(1)	39(1)
N(1)	1385(3)	2154(4)	−605(3)	25(1)
C(1)	2085(4)	1766(4)	1404(3)	25(2)
C(2)	1858(4)	953(5)	1991(3)	27(2)
C(3)	958(4)	984(5)	2142(3)	30(2)
C(4)	559(4)	1841(5)	1698(3)	27(2)
C(5)	1223(4)	2333(4)	1272(3)	25(2)
C(6)	2975(5)	2386(5)	1496(4)	41(2)
C(7)	2559(4)	230(5)	2340(4)	36(2)
C(8)	426(5)	259(5)	2664(3)	40(2)
C(9)	−444(4)	2091(6)	1697(4)	39(2)
C(10)	1091(4)	3191(5)	672(3)	31(2)
C(11)	726(4)	2821(5)	−149(3)	30(2)
C(12)	2110(5)	2817(5)	−966(4)	36(2)
C(13)	884(5)	1630(5)	−1277(3)	36(2)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

degree of association and hence the hapticity of the Cp ligand in **9** are unknown.

Experimental Section

General Comments. All experiments were performed under a dry argon atmosphere using standard Schlenk techniques. Solvents were dried by refluxing over $LiAlH_4$ (ether, pentane), potassium benzophenone ketyl (THF), or sodium (toluene) and distilled before use. ^1H (300.1 MHz), $^{13}C\{^1H\}$ (75.5 MHz), and $^{27}Al\{^1H\}$ (78.2 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 with internal deuteriochloroform, toluene-d_8, or deuteriobenzene. $^{27}Al\{^1H\}$ chemical shifts were recorded in ppm and referenced with external $[Al(H_2O)_6]^{3+}$. Mass spectra were recorded on a Varian MAT CH_5 (70 eV EI, 300 μA) and on a VG AutoSpec (70 eV EI, 200 μA); only characteristic fragments and isotopes of the highest abundance are listed. Melting points were taken on a Büchi 510 melting point apparatus (sealed capillaries) and are uncorrected. Elemental microanalyses were performed by Analytisches Labor der Fakultät für Chemie, Universität Bielefeld, and by Mikroanalytisches Laboratorium Beller, Göttingen, Germany.

Materials. [2-(dimethylamino)ethyl]tetramethylcyclopentadiene (**1**) (Cp∧H) was prepared according to our previous reported procedure.[10a] The aluminum trihalides and indium trichloride were used as purchased; gallium trichloride was freshly sublimed prior to use. Alane−trimethylamine adduct was synthesized by a published method.[25]

Dimethyl(η^1:η^1-1-[2-(dimethylamino)ethyl]-2,3,4,5-tetramethylcyclopentadienyl)aluminum (2). To a solution of 1.94 g (10.0 mmol) of Cp∧H (**1**) in Et_2O (50 mL) stirred at room temperature was added dropwise 6.25 mL of *n*-butyllithium (1.6 M in hexane, 10.0 mmol). After the solution was stirred overnight, 10.0 mL of dimethylaluminum chloride (1.0 M in hexane, 10.0 mmol) was added to the resulting suspension. Stirring was continued for 1 h, and then the solution was filtered from the lithium chloride, concentrated, and cooled. Colorless crystals of **2** (1.90 g, 76%) were formed, which were suited for X-ray cystallographic studies. Mp: 94 °C (dec).

^1H NMR (C_6D_6): $\delta = -0.97$ (s, 6 H, Al−CH_3), 1.59, 1.89 (2 s, 2 × 6 H, CH_3), 1.91 (t, $J = 6.1$ Hz, 2 H, CH_2), 2.19 (s, 6 H, NCH_3), 2.31 (t, $J = 6.1$ Hz, 2 H, CH_2NMe$_2$). ^1H NMR ($CDCl_3$): $\delta = -1.30$ (s, 6 H, Al−CH_3), 1.82, 1.90 (2 s, 2 × 6 H, CH_3), 2.38 (s, 6 H, NCH_3), 2.70 (s, 4 H, CH_2). ^{13}C NMR ($CDCl_3$): $\delta = -13.1$ (br, Al−CH_3), 11.0, 11.8 (CH$_3$), 22.2 (CH$_2$), 46.2 (NCH$_3$), 62.1 (CH$_2$NMe$_2$), 100.9, 118.6, 127.3 (ring-C). ^{27}Al NMR ($CDCl_3$): $\delta = 155.2$ ($\nu_{1/2} \approx 2000$ Hz). MS [*m/z* (relative intensity %)]: 193 (8) $[C_5Me_4H(CH_2CH_2NMe_2)^+]$, 58 (100) $[Me_2NCH_2^+]$. Anal. Calcd for $C_{15}H_{28}AlN$ (249.37): C, 72.25; H, 11.32; N, 5.62. Found: C, 72.28; H, 11.50; N, 5.70. Molecular weight determination (cryoscopic in benzene): M = 255.

Diethyl(η^1:η^1-1-[2-(dimethylamino)ethyl]-2,3,4,5-tetramethylcyclopentadienyl)aluminum (3). To a solution of 1.94 g (10.0 mmol) of Cp∧H (**1**) in THF (20 mL) stirred at −30 °C was added dropwise 6.25 mL of *n*-butyllithium (1.6 M in hexane, 10.0 mmol). After the mixture was stirred for 30 min at this temperature, 1.24 mL (1.21 g, 10.0 mmol) of diethylaluminum chloride was added to the yellow solution. The reaction mixture was allowed to warm to room temperature and stirred overnight, and then the solvents were removed in vacuo. The residue was extracted with pentane, and the extracts were filtered. The solution was kept at −30 °C overnight, allowing the formation of colorless needles. The crystals (suitable for X-ray determination) were separated and dried under vacuum. Yield: 1.93 g (70%). Mp: 80−82 °C.

^1H NMR (C_6D_6): $\delta = -0.33$ (dq, $^2J = 14.1$ Hz, $^3J = 8.1$ Hz, 2 H, Al−CH_AH$_B$−CH$_3$), -0.24 (dq, $^2J = 14.1$ Hz, $^3J = 8.1$ Hz, 2 H, Al−CH$_A$$H_B$−CH$_3$), 1.23 (t, $^3J = 8.1$ Hz, 6 H, Al−CH_2−CH_3), 1.61, 1.87 (2 s, 2 × 6 H, CH_3), 1.90 (t, $^3J = 6.1$ Hz, 2 H, CH_2), 2.23 (s, 6 H, NCH_3), 2.27 (t, $^3J = 6.1$ Hz, 2 H, CH_2NMe$_2$). ^1H NMR ($CDCl_3$): $\delta = -0.51$ (q, $^3J = 8.0$ Hz, 4 H, Al−CH_2−CH$_3$), 0.87 (t, $^3J = 8.0$ Hz, 6 H, Al−CH$_2$−CH_3), 1.81, 1.95 (2 s, 2 × 6 H, CH_3), 2.37 (s, 6 H, NCH_3), 2.64−2.71 (m, 4 H, CH_2). ^{13}C NMR (C_6D_6): $\delta = -1.2$ (br, $\nu_{1/2} \approx 100$ Hz, Al−CH$_2$−CH$_3$), 10.4, 12.0, 12.4 (CH$_3$, Al−CH$_2$−CH$_3$), 22.6 (CH$_2$), 45.8 (NCH$_3$), 62.2 (CH$_2$NMe$_2$), 100.0, 120.5, 128.9 (ring-C). ^{27}Al NMR (C_6D_6): $\delta = 152.9$ ($\nu_{1/2} \approx 2300$ Hz). MS [*m/z* (relative intensity %)]: 277 (1) [M$^+$], 248 (40) [M$^+$ − C_2H_5], 193 (10) $[C_5Me_4H(CH_2CH_2NMe_2)^+]$, 58 (100) $[Me_2NCH_2^+]$. Anal. Calcd for $C_{17}H_{32}AlN$ (277.43): C, 73.60; H, 11.63; N, 5.05. Found: C, 72.57; H, 11.75; N, 5.34. Molecular weight determination (cryoscopic in benzene): M = 290.

Dichloro($\eta^{2/3}$:η^1-1-[2-(dimethylamino)ethyl]-2,3,4,5-tetramethylcyclopentadienyl)aluminum (4). A suspension of 15.4 mmol of Cp∧Li in diethyl ether (40 mL)/hexane (9 mL) was added to a solution of 2.05 g (15.4 mmol) of $AlCl_3$ in Et_2O (30 mL) at -60 °C. The reaction mixture was allowed to warm to room temperature and stirred for 12 h. After evaporation of the solvents, toluene was added and the mixture filtered. The resulting solution was concentrated and cooled. Compound **4** could then be isolated as colorless crystals (2.90 g, 65%). Mp: 116 °C. Crystals suitable for an X-ray structure determination were grown from a toluene solution at -35 °C.

^1H NMR (C_6D_6): $\delta = 1.84$, 1.88 (2 s, 2 × 6 H, CH_3), 1.86−1.91 (m, 2 H, CH_2), 2.11−2.16 (m, 2 H, CH_2NMe$_2$), 2.13 (s, 6 H, NCH_3). ^1H NMR ($CDCl_3$): $\delta = 1.91$, 1.97 (2 s, 2 × 6 H, CH_3), 2.59 (s, 6 H, NCH_3), 2.79 (s, 4 H, CH_2). ^1H NMR (toluol-d_8, −50 °C): $\delta = 1.74$ (m, 2 H, CH_2), 1.81, 1.87 (2 s, 2 × 6 H, CH_3), 2.09 (m, 2 H, CH_2NMe$_2$), 2.20 (s, 6 H, NCH_3). ^{13}C NMR ($CDCl_3$): $\delta = 11.2$, 11.8 (CH$_3$), 21.6 (CH$_2$), 47.4 (NCH$_3$), 61.4 (CH$_2$NMe$_2$), 104.6, 114.8, 128.1 (ring-C). ^{27}Al NMR (C_6D_6): $\delta = 65.4$ ($\nu_{1/2} \approx 300$ Hz). ^{27}Al NMR ($CDCl_3$): $\delta = 55.7$ ($\nu_{1/2} \approx 300$ Hz). MS [*m/z* (relative intensity %)]: 289 (2) [M$^+$], 193 (5) $[C_5Me_4H(CH_2CH_2NMe_2)^+]$, 58 (100) $[Me_2NCH_2^+]$. Anal. Calcd for $C_{13}H_{22}AlCl_2N$ (290.21): C, 53.80; H, 7.64; N, 4.83. Found: C, 52.18; H, 7.50; N, 4.60. Molecular weight determination (cryoscopic in benzene): M = 320.

Dibromo($\eta^{2/3}$:η^1-1-[2-(dimethylamino)ethyl]-2,3,4,5-tetramethylcyclopentadienyl)aluminum (5). Compound **5** is prepared according to the procedure described above for **4** except that $AlBr_3$ was used instead of $AlCl_3$. The scale of the reaction was 18.9 mmol. **5** was obtained as colorless microcrystals (5.14 g, 72%). Mp: 146 °C.

^1H NMR (C_6D_6): $\delta = 1.79$, 1.88 (2 s, 2 × 6 H, CH_3), 1.84−1.90 (m, 2 H, CH_2), 2.07−2.13 (m, 2 H, CH_2NMe$_2$), 2.12 (s, 6 H, NCH_3). ^1H NMR ($CDCl_3$): $\delta = 1.86$, 1.94 (2 s, 2 × 6 H, CH_3), 2.66 (s, 6 H, NCH_3), 2.76−2.84 (m, 4 H, CH_2). ^1H NMR (toluol-d_8, −50 °C): $\delta = 1.66$, 1.80 (2 s, 2 × 6 H, CH_3), 1.71 (br, s, 2 H, CH_2), 1.98−2.02 (m, 2 H, CH_2NMe$_2$), 2.09 (s, 6 H, NCH_3). ^{13}C NMR ($CDCl_3$): $\delta = 11.4$, 12.1 (CH$_3$), 21.6 (CH$_2$),

Table 5. Correlation of ^{1}H NMR Chemical Shifts (δ, ppm, in $CDCl_3$) of the $CH_2N(CH_3)_2$ Protons in ((Dimethylamino)ethyl)tetramethylcyclopentadienyl Compounds with the Coordination Behavior

compound (ref)	(CH_2NMe_2)	(NMe_2)	coord
$C_5Me_4H(CH_2CH_2NMe_2)$[a] (10a)	2.42−2.57 (m)	2.26−2.27 (m)	−
$C_5Me_4(CH_2CH_2NMe_2)SiMe_3$ (12c)	2.42 (s)	2.15−2.26	−
$C_5Me_4(CH_2CH_2NMe_2)SnMe_3$ (12a)	2.32−2.37 (m)	2.21 (s)	−
$[C_5Me_4(CH_2CH_2NMe_2)_2]Fe$ (12a)	2.43−2.49 (m)	2.17 (s)	−
2	2.70 (s)	2.38 (s)	+
3	2.64−2.71	2.37 (s)	+
4	2.79	2.59 (s)	+
5	2.76−2.84 (m)	2.66 (s)	+
6	2.88 (s)	2.74 (s)	+
7	2.75 (s)	2.65 (s)	+
8	2.68−2.77 (m)	2.59 (s)	+
9[a]	2.29−2.34 (m)	2.07 (s), 2.27 (s)	−

[a] In C_6D_6.

Scheme 3. Rearrangement Processes in Compounds 2−8

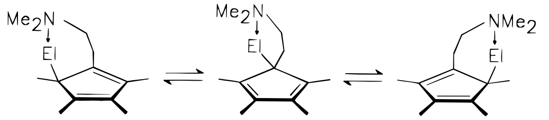

Table 6. ^{27}Al NMR Chemical Shifts (δ, ppm, in $CDCl_3$) and Coordination Numbers at Al in Cyclopentadienylaluminum Compounds

compound	^{27}Al	coord no. (solid state)
$Me_5C_5AlMe_2{\cdot}THF$	150.6 (26)	4
2	155.2	4
3	152.9	4
4	55.7	5−6
5	69.2	
6	79.2	
9	62.0	
$[Me_5C_5AlMeCl]_2$	8.5 (27)	6
$[Me_5C_5AlCl_2]_2$	−52.8 (28)	8

47.6 (N*C*H$_3$), 61.4 (*C*H$_2$NMe$_2$), 104.6, 116.6, 130.2 (ring-*C*). ^{27}Al NMR ($CDCl_3$): $\delta = 69.2$ ($\nu_{1/2} \approx 390$ Hz). MS [*m/z* (relative intensity %)]: 193 (11) $[C_5Me_4H(CH_2CH_2NMe_2)^+]$, 133 (10) $[C_{10}H_{13}^+]$, 80 (34) $[HBr^+]$, 79 (13) $[Br^+]$, 58 (100) $[Me_2NCH_2^+]$. MS (CI; CH_4) [*m/z* (relative intensity %)]: 379 (19) $[M^+]$, 300 (17) $[M^+ - {}^{79}Br]$, 298 (18) $[M^+ - {}^{81}Br]$, 193 (20) $[C_5Me_4H(CH_2CH_2NMe_2)^+]$, 192 (20) $[C_5Me_4(CH_2CH_2NMe_2)^+]$, 58 (100) $[Me_2NCH_2^+]$. Anal. Calcd for $C_{13}H_{22}AlBr_2N$ (379.11): C, 41.19; H, 5.85; N, 3.69. Found: C, 41.30; H, 5.87; N, 3.53.

Diiodo($\eta^{2/3}$:η^1-1-[2-(dimethylamino)ethyl]-2,3,4,5-tetramethylcyclopentadienyl)aluminum (6). The procedure of the reaction was as detailed above except that AlI_3 was used (scale: 27.6 mmol). Compound **6** was isolated as a microcrystalline solid (4.94 g, 38%). Mp: 208-212 °C (dec).

^{1}H NMR (C_6D_6): $\delta = 1.74$, 1.90 (2 s, 2 × 6 H, C*H*$_3$), 1.86-1.91 (m, 2 H, C*H*$_2$), 2.03−2.09 (m, 2 H, C*H*$_2$NMe$_2$), 2.08 (s, 6 H, NC*H*$_3$). ^{1}H NMR ($CDCl_3$): $\delta = 1.81$, 1.90 (2 s, 2 × 6 H, C*H*$_3$), 2.73−2.77 (m, 2 H, C*H*$_2$), 2.74 (s, 6 H, NC*H*$_3$), 2.88 (t, 2 H, *J* = 5.9 Hz, C*H*$_2$NMe$_2$). ^{13}C NMR ($CDCl_3$): $\delta = 11.7$, 12.5 (*C*H$_3$), 21.6 (*C*H$_2$), 47.9 (N*C*H$_3$), 61.5 (*C*H$_2$NMe$_2$), 104.0, 119.1, 132.9 (ring-*C*). ^{27}Al NMR ($CDCl_3$): $\delta = 79.2$ ($\nu_{1/2} \approx 600$ Hz). MS [*m/z* (relative intensity %)]: 133 (8) $[C_{10}H_{13}^+]$, 128 (83) $[HI^+]$, 127 (56) $[I^+]$, 58 (100) $[Me_2NCH_2^+]$. Anal. Calcd for $C_{13}H_{22}AlI_2N$ (473.11): C, 33.00; H, 4.69; N, 2.96. Found: C, 32.65; H, 4.79; N, 2.79.

Dichloro(η^1:η^1-1-[2-(dimethylamino)ethyl]-2,3,4,5-tetramethylcyclopentadienyl)gallium (7). A suspension of 15.3 mmol of Cp∧Li in diethyl ether (30 mL) / hexane (9 mL) was added to a solution of 2.69 g (15.3 mmol) of $GaCl_3$ in Et_2O (20 mL) at -60 °C. The reaction mixture was allowed to warm to room temperature, stirred for 12 h, and then worked up as described for **4**. Compound **7** was obtained as colorless crystals (3.21 g, 63%). Mp: 105 °C.

^{1}H NMR ($CDCl_3$): $\delta = 1.68$, 1.91 (2 s, 2 × 6 H, C*H*$_3$), 2.65 (s, 6 H, NC*H*$_3$), 2.69, 2.75 (2 dt, 2 × 2 H, C*H*$_2$). ^{1}H NMR (C_6D_6): $\delta = 1.65$, 1.89 (2 s, 2 × 6 H, C*H*$_3$), 1.85−1.89 (m, 2 H, C*H*$_2$), 2.04 (s, 6 H, NC*H*$_3$), 2.05−2.09 (m, 2 H, C*H*$_2$NMe$_2$). ^{13}C NMR ($CDCl_3$): $\delta = 11.2$, 12.5 (*C*H$_3$), 21.7 (*C*H$_2$), 46.5 (N*C*H$_3$), 62.0 (*C*H$_2$NMe$_2$), 99.6, 127.8, 135.4 (ring-*C*). MS [*m/z* (relative intensity %)]: 331 (7) $[M^+]$, 193 (4) $[C_5Me_4H(CH_2CH_2NMe_2)^+]$, 133 (4) $[C_{10}H_{13}^+]$, 58 (100) $[Me_2NCH_2^+]$. Anal. Calcd for $C_{13}H_{22}Cl_2GaN$ (332.95): C, 46.90; H, 6.66; N, 4.21. Found: C, 46.49; H, 6.79; N, 4.06.

Dichloro(η^1:η^1-1-[2-(dimethylamino)ethyl]-2,3,4,5-tetramethylcyclopentadienyl)indium (8). A suspension of 10.3 mmol of Cp∧Li in diethyl ether (50 mL) was added to a suspension of 2.27 g (10.3 mmol) of $InCl_3$ in Et_2O (30 mL) at −70 °C. The reaction mixture was allowed to warm to room temperature, stirred for 12 h, and filtered. The resulting solution was concentrated and cooled to −35 °C, allowing the formation of yellow crystals. The crystals were suited for X-ray crystallographic studies. Yield: 2.12 g (55%). Mp: 119 °C.

^{1}H NMR ($CDCl_3$): $\delta = 1.82$, 1.96 (2 s, 2 × 6 H, C*H*$_3$), 2.59 (s, 6 H, NC*H*$_3$), 2.68−2.77 (m, 4 H, C*H*$_2$). ^{1}H NMR (C_6D_6): $\delta = 1.71$, 1.86 (2 s, 2 × 6 H, C*H*$_3$), 1.84−1.88 (m, 2 H, C*H*$_2$), 1.97 (s, 6 H, NC*H*$_3$), 2.03−2.07 (m, 2 H, C*H*$_2$NMe$_2$). ^{13}C NMR ($CDCl_3$): $\delta = 11.2$, 12.5 (*C*H$_3$), 22.5 (*C*H$_2$), 46.3 (N*C*H$_3$), 61.4 (*C*H$_2$NMe$_2$), 106.0, 132.7 (ring-*C*). MS [*m/z* (relative intensity %)]: 193 (9) $[C_5Me_4H(CH_2CH_2NMe_2)^+]$, 133 (10) $[C_{10}H_{13}^+]$, 58 (100) $[Me_2NCH_2^+]$. Anal. Calcd for $C_{13}H_{22}Cl_2InN$ (378.05): C, 41.30; H, 5.87; N, 3.70. Found: C, 40.96; H, 5.98; N, 3.65.

Bromo(1-[2-(dimethylamino)ethyl]-2,3,4,5-tetramethylcyclopentadienyl)alane (9). Compound **5** (1.65 g, 4.35 mmol) and $H_3Al{\cdot}NMe_3$ (0.28 g, 3.14 mmol) were stirred in toluene (40 mL) at room temperature for 24 h. After filtration of the mixture, the resulting clear and colorless solution was concentrated. Crystallization at −70 °C afforded 1.22 g (93%) of **9** as a microcrystalline solid. Mp: 157 °C.

^{1}H NMR (C_6D_6): $\delta = 1.63$, 1.82, 1.89, 1.91 (4 s, 4 × 3 H, C*H*$_3$), 2.01−2.11 (m, 2 H, C*H*$_2$), 2.07, 2.27 (2 s, 2 × 3 H, NC*H*$_3$), 2.29−2.34 (m, 2 H, C*H*$_2$NMe$_2$), 4.15 (very broad, s, 1 H, Al*H*). ^{13}C NMR (C_6D_6): $\delta = 11.0$, 11.1, 11.7, 12.1 (*C*H$_3$), 21.6 (*C*H$_2$), 44.0, 45.4 (N*C*H$_3$), 60.9 (*C*H$_2$NMe$_2$), 113.7, 124.5, 124.9 (ring-*C*). ^{27}Al NMR (C_6D_6): $\delta = 62.0$ ($\nu_{1/2} \approx 2200$ Hz). MS [*m/z* (relative intensity %)]: 193 (9) $[C_5Me_4H(CH_2CH_2NMe_2)^+]$, 133 (7) $[C_{10}H_{13}^+]$, 58 (100) $[Me_2NCH_2^+]$. Anal. Calcd for $C_{13}H_{23}AlBrN$ (300.22): C, 52.01; H, 7.72; N, 4.67. Found: C, 50.97; H, 7.31; N, 4.44.

Although this compound was spectroscopically pure, satisfactory microanalyses could not be obtained.

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Supporting Information Available: Tables of crystallographic data collection parameters, anisotropic displacement coefficients, and hydrogen coordinates and isotropic displacement coefficients for **2**, **4**, and **8** (15 pages). Ordering information is given on any current masthead page.

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