

HALIDES OF *o*-SUBSTITUTED ARYL-ALUMINUM COMPOUNDS WITH COORDINATION NUMBERS FOUR AND FIVE

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ABSTRACT

The THF adduct of dichloro(2,4,6-triisopropylphenyl)aluminum (**1**) was prepared. Dehalogenation of **1** with Na/K alloy gave a tricyclic compound with a dioxonia-dialuminata central unit (**2**). The reaction of 2,6-bis{[(dimethylamino)methyl]phenyl}lithium with AlX_3 ($\text{X} = \text{Cl, Br, I}$), EtAlCl_2 or Et_2AlCl (in 1:1 ratio) yielded compounds **B** and **3 - 6** containing penta-coordinated aluminum atoms. From 2-[(dimethylamino)methyl]phenyllithium and AlCl_3 , AlBr_3 , EtAlCl_2 or Et_2AlCl (1:1) the tetracoordinated Al-species **7, 8, C** and **D** were obtained while with the same reactants in 2:1 ratio the pentacoordinated species **9, 10** and **E** are formed. The reaction of 3 equivalents of 2-[(dimethylamino)methyl]phenyllithium with AlCl_3 gave **11** (coordination number five, fluxional behaviour in solution). From 8-(dimethylamino)naphthyllithium, AlCl_3 , AlBr_3 and EtAlCl_2 the tetracoordinated species **12 - 14** were synthesized. By treating the dibromo species **6** and **C** with lithiated 2,6-dimethyl-N-(trimethylsilyl)aniline the correspondingly substituted monobromo species **15** and **16** were obtained. The compounds are characterized by NMR (^1H , ^{13}C and ^{29}Si) and mass spectrometry, most of them also by ^{27}Al NMR and elemental analyses. X-ray structure analyses are provided for **2, 4, 6, 7, 11** and **16**.

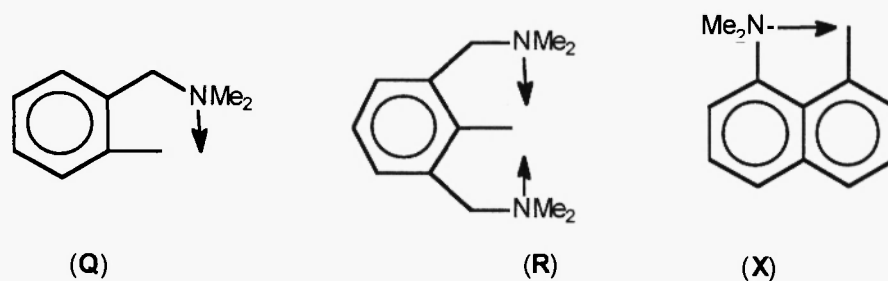
INTRODUCTION

It is generally known that the coordination of metal atoms can be governed as well by the steric requirement of the substituents as by inter- and specially intramolecular donor stabilization. Aryl substituted aluminum atoms did not find much interest in the past, compared to their alkyl substituted analogs. Research activity, however, did increase considerably within the last years. Stimulated by the isolation of the first monomeric aluminum dihalide with coordination number three, $\text{Mes}^*\text{AlBr}_2$ ($\text{Mes}^* = 2,4,6\text{-}t\text{-Bu}_3\text{C}_6\text{H}_2$)¹ and our own results about supermesityl substituted halides of gallium and indium²⁻⁴, we wanted to extend our research to halides of aluminum stabilized either by inter- or by intramolecular coordination. The aim was primarily to compare the influence of different substituents on NMR and structural data. With *o*-substituted aromatic groups, $\text{Mes}^*\text{AlCl}_2$ ⁶ with the coordination number three as well as $\text{MesAlCl}_2\cdot\text{THF}$ ⁵ ($\text{Mes} = \text{mesityl}$), $\text{Mes}^*\text{AlCl}_2\cdot\text{THF}$ ⁶, and $\text{TripAlBr}_2\cdot\text{OEt}_2$ ¹ ($\text{Trip} = 2,4,6\text{-triisopropylphenyl}$) with the coordination number four are already known. Furthermore arylaluminumhalides stabilized by intramolecular coordination with the coordination numbers four and five should be included. The 2-[(dimethylaminomethyl)phenyl]-, (**Q**), the 2,6-bis[(dimethylaminomethyl)phenyl]-, (**R**), and the 8-[(dimethylaminomethyl)naphthyl]-ligand, (**X**), were applied.

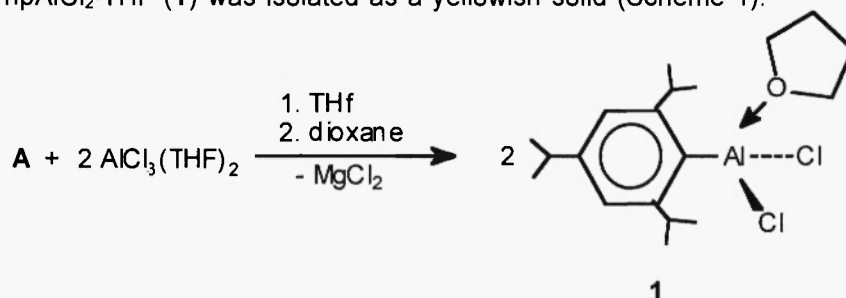
So far the following halides of aluminum with the ligands (**Q** and **R**) have been described: QAlCl_2 ⁷, QAlBr_2 ^{8,9}, $\text{QAl}(\text{Me})\text{Cl}$ ⁷, $\text{QAl}(t\text{-Bu})\text{Cl}$ ⁹, $\text{QAl}(\text{CSiMe}_3)_3\text{Cl}$ ⁷ and RAlCl_2 ⁸⁻¹⁰. Ligand (**X**) was not used before.

RESULTS AND DISCUSSION

Bis(2,4,6-triisopropylphenyl)magnesium · 2 THF (**A**)¹¹ was prepared by a Grignard reaction from the corresponding bromide in THF followed by a Schlenk-dismutation with dioxane.

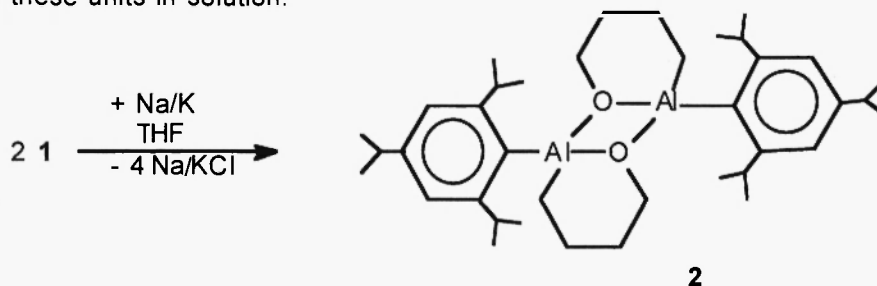


By the reaction of $\text{Trip}_2\text{Mg} \cdot 2 \text{ THF}$ (**A**) with $\text{AlCl}_3(\text{THF})$ and by the addition of dioxane and THF, $\text{TripAlCl}_2 \cdot \text{THF}$ (**1**) was isolated as a yellowish solid (Scheme 1).



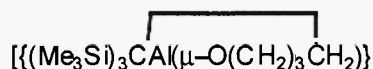
Scheme 1

Upon the reaction of **1** with Na/K alloy in THF, 2,8-bis(2,4,6-triisopropylphenyl)-1,7-dioxonia-2,8-dialuminatatricyclo[6,4,0,0^{2,7}]dodecane, **2** was obtained (Scheme 2). Compound **2** is apparently formed by the reaction of a species containing subvalent aluminum with THF (Scheme 2). Due to the conformations of the bridging C₄-units in solution, there are two conformers of **2** as shown by the splittings of the ¹H- and ¹³C-NMR signals of these units in solution.



Scheme 2

Recrystallization of **2** from hexane yielded crystals and an X-ray structure analysis was performed. The molecule possesses an inversion centre (see. Figure 1) leading to an exactly planar Al_2O_2 ring and trans Al–O–C₄ rings. This is in contrast to the other compound exhibiting a tricyclic



structure where the Al–O–C₄ ring is not planar (mean deviation 0.13 Å) and where the Al–O–C₄ rings are in cis configuration¹².

By the reaction of 2,6-bis[(dimethylaminomethyl)phenyl]lithium with AlX_3 (X = Cl, Br, I), EtAlCl_2 or Et_2AlCl the compounds **B**⁹ and **3** - **6** containing pentacoordinate Al atoms (Scheme 3) were obtained.

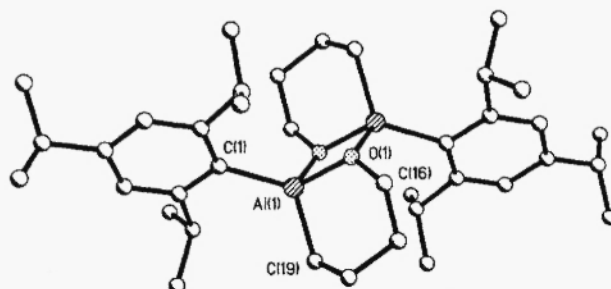
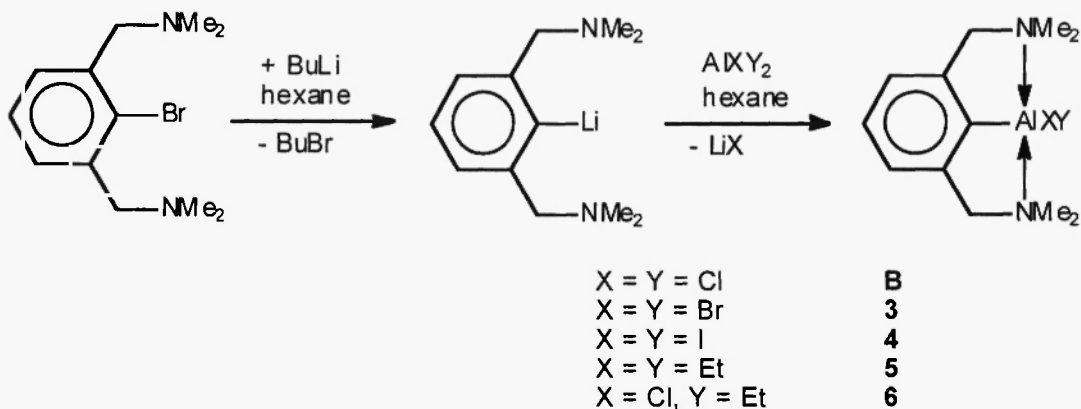


Figure 1. Crystal structure of **2**, selected bond lengths [Å] and angles [°]: Al(1)-O(1) 1.854(2), Al(1)-O(1)#1 1.836(2), Al(1)-C(19) 1.959(2), Al(1)-C(1) 1.992(2), O(1)#1-Al(1)-O(1) 80.9(1), O(1)#1-Al(1)-C(19) 114.0(1), O(1)-Al(1)-C(19) 100.0(1), O(1)#1-Al(1)-C(1) 112.7(1), O(1)-Al(1)-C(1) 121.5(1), C(19)-Al(1)-C(1) 120.9(1), C(16)-O(1)-Al(1)#1 127.3(1), C(16)-O(1)-Al(1) 122.6(1), Al(1)#1-O(1)-Al(1) 99.1(1), symmetry transformations used to generate equivalent atoms: #1 - x+1, -y+2, -z.



Scheme 3

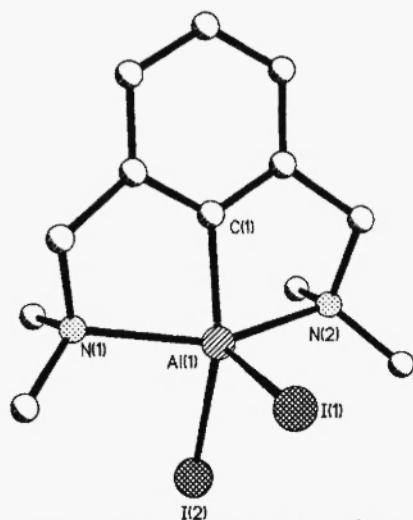


Figure 2. Crystal structure of **4**, selected bond lengths [Å] and angles [°]: I(1)-Al(1) 2.544(1), I(2)-Al(1) 2.559(1), Al(1)-C(1) 1.927(4), Al(1)-N(2) 2.180(4), Al(1)-N(1) 2.197(4), C(1)-Al(1)-N(2) 80.0(2), C(1)-Al(1)-N(1) 80.0(2), N(2)-Al(1)-N(1) 150.2(2), C(1)-Al(1)-I(1) 106.4(1), N(2)-Al(1)-I(1) 102.0(1), N(1)-Al(1)-I(1) 104.7(1), C(1)-Al(1)-I(2) 149.7(1), N(2)-Al(1)-I(2) 93.4(1), N(1)-Al(1)-I(2) 92.8(1), I(1)-Al(1)-I(2) 103.9(1).

Recrystallization from hexane and benzene resp. gave single crystals of **4** and **6** and X-ray structure analyses were performed (Figures 2 and 3). In both structures the aluminum atom is coordinated in a distorted trigonal-bipyramidal fashion with the nitrogen atoms occupying the axial positions. The (AlN) distance is 0.1 Å shorter in **4** compared to **6**. The (AlC) distances are nearly the same in both compounds. In **B**⁹ the (AlC) bond is in identical range (1.911(7)) as observed in **4** and **6** (1.927(4) and 1.936(3)), while r(AlN) (2.261(5) Å) corresponds to that in **6** (2.282(2) Å).

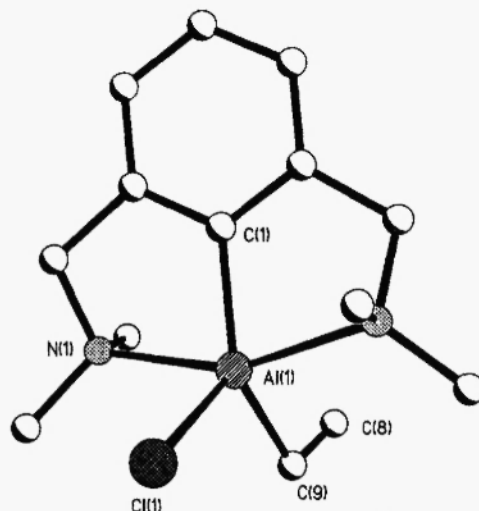


Figure 3. Crystal structure of **6**, selected bond lengths [Å] and angles [°]: Al(1)-C(1) 1.936(3), Al(1)-C(9) 1.942(6), Al(1)-N(1) 2.282(2), Al(1)-Cl(1) 2.290(3), C(1)-Al(1)-C(9) 136.9(2), C(1)-Al(1)-N(1) 78.6(1), C(9)-Al(1)-N(1) 98.1(2), N(1)#1-Al(1)-N(1) 157.2(1), C(1)-Al(1)-Cl(1) 117.0(1), N(1)-Al(1)-Cl(1) 96.3(1), symmetry transformation used to generate the equivalent atoms: #1 - x,y,-z+1/2.

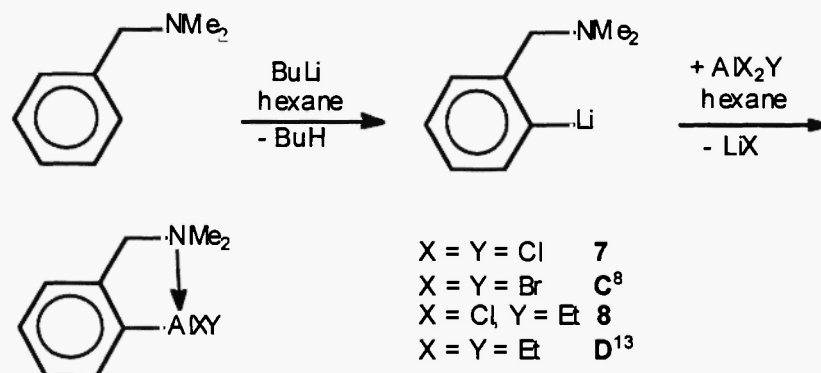
In the monomeric organyl aluminum halides, $\text{Mes}^*\text{AlBr}_2$ ¹, $\text{Mes}^*\text{AlCl}_2$ ⁶ and Mes^*AlClH ⁶, which were characterized by X-ray structure analyses r(AlC) is observed at 1.94 – 1.95 Å, r(AlBr) = 2.28 Å and r(AlCl) = 2.12 – 2.19 Å. Therefore r(AlC) apparently is more controlled by structural influences in the solid state than by the hybridization at the Al atom or possible π -interactions in the sp^2 -case.

Table 1 exhibits a correlation of the chemical shifts $\delta^{27}\text{Al}$ and $\delta^{13}\text{C}$ (of the ipso carbon atom). The influence of the halogeno and the ethyl substituents on $\delta^{27}\text{Al}$ is documented by the highfield shift of **B** and **3** (slightly) and **4** (strongly) compared to other shifts reported for pentacoordinated Al^{13} . On the other hand the signals for **5** and **6** appear at low field. The same trend can be seen in the tables 2 and 3 (for tetracoordinated species).

Table 1. Selected NMR-Data of **3** - **6** (in C_6D_6)

Compound	X	Y	$\delta^{27}\text{Al}$ [ppm]	$\delta^{13}\text{C}$ [ppm]
B	Cl	Cl	99	C(1) 142.9
3	Br	Br	98	C(1) 143.3
4	I	I	74	C(1) 144.0
5	Et	Et	163	C(1) 151.2
6	Cl	Et	120	C(1) 146.9

Compounds with tetracoordinated aluminum atoms were prepared from AlX_3 (X = Cl, Br) and EtAlCl_2 respectively according to Scheme 4:



Scheme 4

Single crystals of **7** were grown from hexane and data provided by the X-ray structure analysis make it possible to compare them with the results reported for $\mathbf{7} \cdot \text{H}_2\text{N}^i\text{Pr}^7$ and for **C**.⁸ In the tetrahedrally coordinated derivatives $r(\text{AlN}) = 1.994(2) \text{ \AA}$ (for **7**) and $2.003(5) \text{ \AA}$ (for **C**). In $\mathbf{7} \cdot \text{H}_2\text{N}^i\text{Pr}$ (pentacoordinated) $r(\text{AlNMe}_2) = 2.171(1) \text{ \AA}$ and $r(\text{AlNH}_2^i\text{Pr}) = 2.070(1) \text{ \AA}$. The (AlC) distances are $1.945(2) \text{ \AA}$ (for **7**), $1.987(1) \text{ \AA}$ (for $\mathbf{7} \cdot \text{H}_2\text{N}^i\text{Pr}$) and $1.967(6) \text{ \AA}$ (for **C**). The distances between Al and the halogens (mean values) are $r(\text{AlCl}) = 2.127 \text{ \AA}$ (for **7**), 2.196 \AA (for $\mathbf{7} \cdot \text{H}_2\text{N}^i\text{Pr}$) and $r(\text{AlBr}) = 2.313 \text{ \AA}$ (for **C**). Thus, pentacoordination (compared to tetracoordination) leads to an elongation of about 0.18 \AA in the (AlN) distance and 0.07 \AA for $r(\text{AlCl})$ as to be expected. The crystal structure of **7** is depicted in Figure 4.

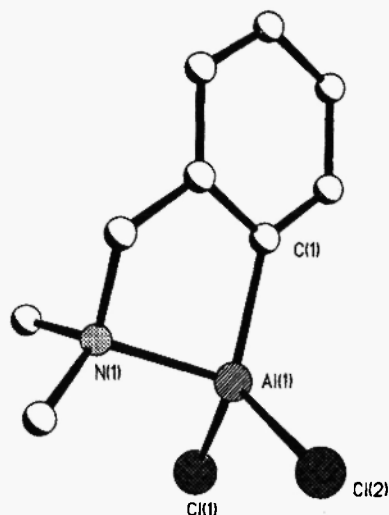


Figure 4. Crystal structure of **7**, selected bond lengths [\AA] and angles [$^\circ$]: Al-C(1) 1.945(2), Al-N 1.994(2), Al-Cl(1) 2.121(1), Al-Cl(2) 2.133(1), C(1)-Al-N 88.4(1), C(1)-Al-Cl(1) 123.7(1), N-Al-Cl(1) 105.2(1), C(1)-Al-Cl(2) 116.7(1), N-Al-Cl(2) 105.1(1), Cl(1)-Al-Cl(2) 111.9(1).

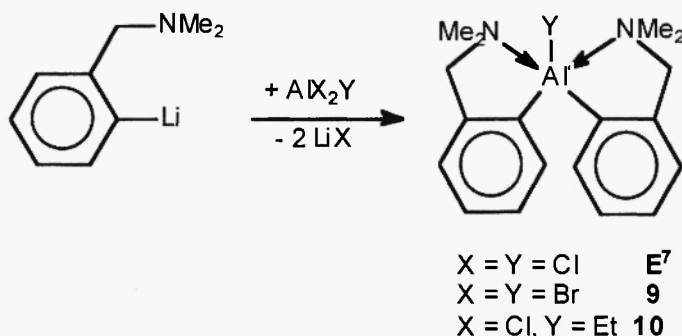
Table 2. Selected NMR-Data of **7**, **8**, **C⁷** and **D¹³** (in C_6D_6)

Compound	X	Y	$\delta^{27}\text{Al}$ [ppm]	$\delta^{13}\text{C}$ [ppm]
7	Cl	Cl	128	C(1) 142.5
C	Br	Br	129	C(1) 142.0
8	Cl	Et	156	C(1) 146.3
D	Et	Et	174	C(1) 151.7

We have also prepared diethyl-2-[(dimethylaminomethyl)phenyl]aluminum (**D**).¹⁴ The new determined $\delta^{13}\text{C}$ (for **D**) and $\delta^{27}\text{Al}$ (for **C** and **D**) NMR data are included together with those of **7** and **8** in Table 2.

Like in the pentacoordinated species (Table 1) the alkyl substituted moieties appear at lower field, however, the difference in the shift values is less pronounced: $\Delta\delta^{27}\text{Al} = 64$ ppm between **B** and **5**, and 46 ppm between **7** and **D** (Table 2). It should be noted that the chemical shift is almost the same for the dichloro- and dibromo moiety (like in Table 1). On the other hand the influence of the substituents (halogeno/alkyl) is more pronounced than that of the coordination number (5/4). For the ^{27}Al NMR chemical shift range as a function of the coordination number in aluminum compounds compare¹⁵. The only monomeric aryldihalogenoaluminum compound (sp^2) for which a ^{27}Al signal was detected is $\text{Mes}^*\text{AlCl}_2$ $\delta^{27}\text{Al} = 130$ ppm (in C_6D_6 , 80°C)⁶. The signal of the corresponding THF adduct⁶ (sp^3) is at $\delta^{27}\text{Al} = 108$ ppm.

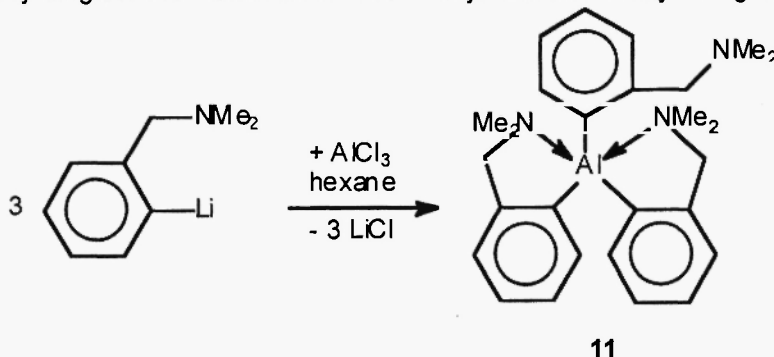
The reaction of 2-[(dimethylaminomethyl)phenyl]lithium with AlBr_3 in a molar ratio of 2:1 gave **9** (Scheme 5). Compound **9** and the corresponding Cl derivative **E**⁷ are also formed as by-products in the synthesis of **7** and **C**⁸. In the reaction with EtAlCl_2 , **10** was obtained. The dynamic behaviour observed at elevated temperatures was examined extensively on the basis of a detailed NMR study for **E**⁷.



Scheme 5

The difference between chemical shifts $\delta^{27}\text{Al}$ between **E** ($\delta^{27}\text{Al} = 148$)⁶ and **10** ($\delta^{27}\text{Al} = 126$) is only 22 ppm in this case, due to the exchange of only one substituent.

Finally **11** was prepared in the reaction of three molar equivalents of 2-[(dimethylaminomethyl)phenyl]lithium with AlCl_3 (Scheme 6). The X-ray structure analysis (single crystals from hexane) shows, that in the solid state only two of the three amino groups are coordinated to the aluminum atom, thus giving pentacoordination (Figure 5). The aluminum atom is distorted trigonal bipyramidally coordinated with the nitrogen atoms in the axial positions. The Al–N distances (2.273(2) and 2.310(2) Å) are similar to those in **6** (2.282(2) Å), while the Al–C bonds (2.009(2) – 2.018(2) Å) are slightly elongated compared to **4** and **6** (1.927(4) (**4**) and 1.936(3) (**6**)). In solution there exists a fluctuating structure as only singlets are observed for the methyl and the methylene groups.



Scheme 6

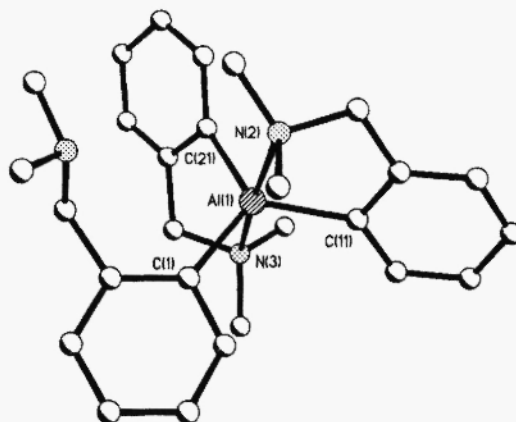
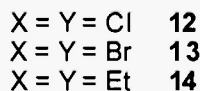
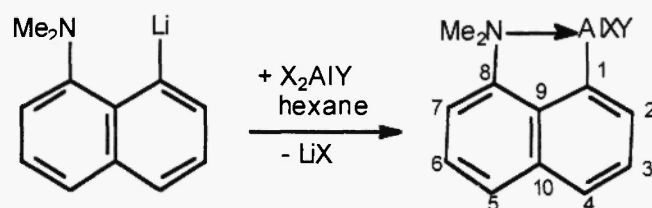


Figure 5. Crystal structure of **11**, selected bond lengths [Å] and angles [°]: Al(1)-C(11) 2.009(2), Al(1)-C(21) 2.014(2), Al(1)-C(1) 2.018(2), Al(1)-N(2) 2.273(2), Al(1)-N(3) 2.310(2), C(11)-Al(1)-C(21) 127.2(1), C(11)-Al(1)-C(1) 114.8(1), C(21)-Al(1)-C(1) 117.6(1), C(11)-Al(1)-N(2) 80.0(1), C(21)-Al(1)-N(2) 99.3(1), C(1)-Al(1)-N(2) 97.2(1), C(11)-Al(1)-N(3) 95.7(1), C(21)-Al(1)-N(3) 78.4(1), C(1)-Al(1)-N(3) 90.1(1), N(2)-Al(1)-N(3) 172.5(1).

Upon the reactions of 8-[(dimethylamino)naphthyl]lithium with AlCl_3 , AlBr_3 and Et_2AlCl according to Scheme 7, compounds **12** - **14** were prepared.



Scheme 7

The $\delta^{27}\text{Al}$ - and $\delta^{13}\text{C}$ -NMR data (for C₁) confirm the tetracoordination at the aluminum atom.

Table 3. Selected NMR-Data of **12** - **14** (in C_6D_6)

Compound	X	Y	$\delta^{27}\text{Al}$ [ppm]	$\delta^{13}\text{C}$ [ppm]
12	Cl	Cl	128	C(1) 137.4
13	Br	Br	131	C(1) 138.6
14	Et	Et	174	C(1) 148.6

By reacting 2,6-dimethyl-N-(trimethylsilyl)aniline with **3** and **C** we prepared **15** (pentacoordinated) and **16** (tetracoordinated) (colorless solids) (Scheme 8). An X-ray structure analysis was performed of **16** (single crystals from hexane). The asymmetric unit contains two nearly identical molecules. Figure 6 presents one of them.

All bond lengths in **16** are comparable to the other tetracoordinated species **7** and **C**: $r(\text{AlBr}) = 2.328(2)$, $2.329(2)$ Å (**16**) and $2.313(2)$ Å (**C**), $r(\text{AlC}) = 1.945(5)$, $1.939(5)$ Å (**16**), $1.945(2)$ (**7**) and $1.967(6)$ (**C**), $r(\text{AlNMe}_2) = 2.010(4)$, $2.019(4)$ (**16**), $1.994(2)$ (**7**) and $2.003(5)$ (**C**). The covalent bond to the bulky amine (Al(1)-N(1)) is about 0.2 Å shorter than (AlN) bond distances by the coordinating ligand.

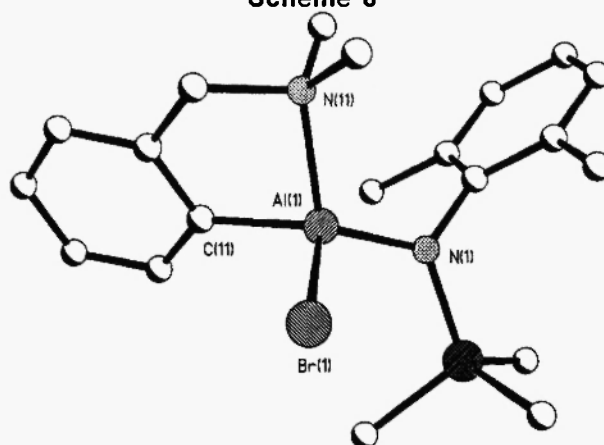
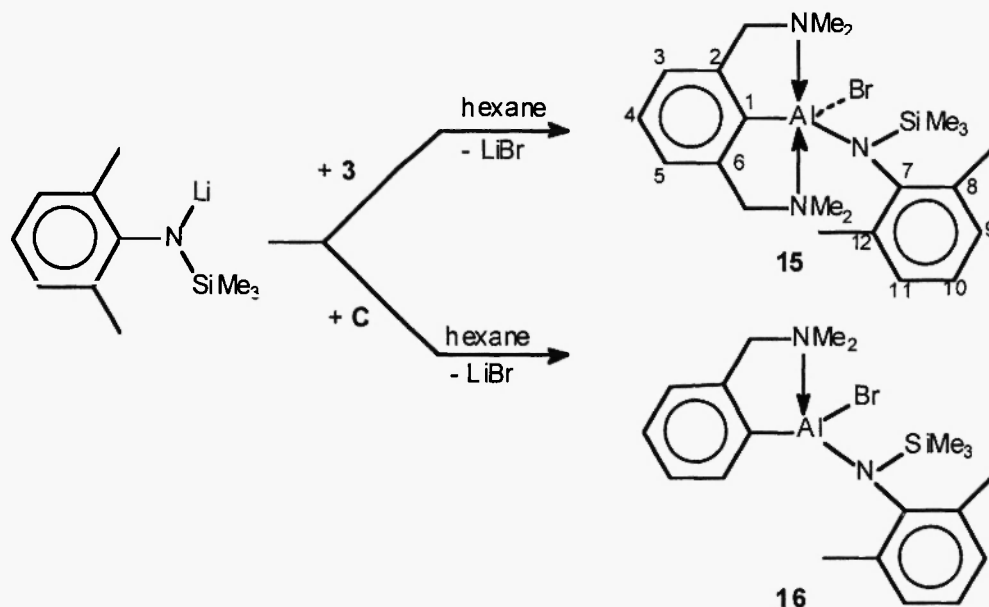


Figure 6. Crystal structure of **16**, selected bond lengths [Å] and angles [°]: Al(1)-N(1) 1.802(4), Al(1)-C(11) 1.945(5), Al(1)-N(11) 2.010(4), Al(1)-Br(1) 2.328(2), Al(2)-N(2) 1.805(4), Al(2)-C(41) 1.939(5), Al(2)-N(41) 2.019(4), Al(2)-Br(2) 2.329(2), N(1)-Al(1)-C(11) 128.1(2), N(1)-Al(1)-N(11) 116.7(2), C(11)-Al(1)-N(11) 87.8(2), N(1)-Al(1)-Br(1) 110.1(1), C(11)-Al(1)-Br(1) 107.7(1), N(11)-Al(1)-Br(1) 102.0(1), N(2)-Al(2)-C(41) 127.3(2), N(2)-Al(2)-N(41) 117.1(2), C(41)-Al(2)-N(41) 87.4(2), N(2)-Al(2)-Br(2) 110.4(1), C(41)-Al(2)-Br(2) 108.4(1), N(41)-Al(2)-Br(2) 102.0(1).

EXPERIMENTAL

All reactions and manipulations were performed in an inert atmosphere of dry nitrogen in dry solvents saturated with nitrogen. Solutions of the aluminum alkyls in hexane or toluene were added to the reaction mixtures with a special syringe (Merck AG) through a rubber diaphragm. Most high vacuum distillations or sublimations were performed using a rotating three-bulb system. In these cases, boiling point (bp) and sublimation point (sublp) temperatures are those of the air bath. Melting points (mp) were determined in sealed capillaries. Elemental analyses were performed in the analytical laboratory of the institute of inorganic chemistry and by Mikroanalytisches Labor Beller, Göttingen, Germany. Due to the formation of Al_4C_3 there are deviations of some analytical results. NMR spectra were recorded on Bruker AM-250 or MSL-400 instruments. Heteroatom spectra were recorded in

the proton-decoupled mode. Assignments of ^{13}C signals were made by distortionless enhancement of polarization transfer (DEPT, 100,60 MHz), HH-Cosy and CH-correlations. Solvents and standards used were as follows: ^1H , ^{13}C , ^{29}Si $\text{C}_6\text{D}_6/\text{TMS}$ or CDCl_3/TMS (internal); ^{27}Al : $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$ (external). Mass spectra were obtained in a Varian CH5 instrument (electron impact (EI) 70 eV and field ionization (FI)) and a Finnigan MAT 8230 (EI, 70 eV) spectrometer.

Starting materials were prepared according to the following references: bromo-2,4,6-tert-butylbenzene¹⁴; bromo-2,4,6-triisopropylbenzene¹⁶; 2,4,6-triisopropylphenyllithium¹⁷; aluminumtrichloride · 2 THF^{18,19}; 1-bromo-2,6-(dimethylaminomethyl)benzene¹⁹; di(2,4,6-triisopropylphenyl)magnesium · 2 THF¹¹; trimesitylaluminum⁵; 2,6-bis(dimethylaminomethyl)-1-lithiobenzene²¹; 2-(dimethylaminomethyl)-1-lithiobenzene²²; 8-(dimethylamino)-1-lithionaphthalene²³; 2,6-dimethyl-N-(trimethylsilyl)aniline^{24,25}. All other starting materials are commercial.

Bis(2,4,6-triisopropylphenyl)magnesium · 2 tetrahydrofuran: Was prepared according to⁵. NMR (in C_6D_6): δ (^1H) + δ (^{13}C) CCH_2 (THF): 1.21 (m, 4H) + 25.42; CHCH_3 (p): 1.38 (d, $^3J_{\text{HH}} = 6.9$ Hz, 6H) + 25.19; CHCH_3 (o): 1.42 (d, $^3J_{\text{HH}} = 6.8$ Hz, 12H) + 26.36; CH_2 (p): 2.85 (sept., $^3J_{\text{HH}} = 6.8$ Hz, 1H) + 35.09; CHMe_2 (o): 2.97 (sept., $^3J_{\text{HH}} = 6.9$ Hz, 2H) + 35.40; OCH_2 (THF): 3.51 (m, 4H) + 69.58; C_1 : 164.63, $\text{C}_{2,6}$: 158.18; $\text{C}_{3,5}\text{H}$: 7.15 (s, 2H) + 118.84; C_4 : 146.48.

Dichloro(2,4,6-triisopropylphenyl)aluminum-tetrahydrofuran (1): To 56 g (0.2 mol) $\text{AlCl}_3 \cdot 2$ THF, dissolved in 500 ml THF, 58 g (0.1 mol) **A** were added in small portions. After stirring 18 h at 23°C, 62 ml dioxane were added dropwise and the stirring continued for 4 more h. After decantation from MgCl_2 the solution was concentrated to 100 ml. The precipitated crystals were separated using a pressure filtration funnel and recrystallized from THF. The yield was 36 g (47%). The colorless crystals melted at 55°C. NMR (in CDCl_3): δ (^1H) + δ (^{13}C) CCH_2 (THF): 1.22 (m, 4H) + 24.61; CHCH_3 (p): 1.28 (d, $^3J_{\text{HH}} = 6.9$ Hz, 6H) + 25.49; CHCH_3 (o): 1.38 (d, $^3J_{\text{HH}} = 6.7$ Hz, 12H) + 26.01; CHMe_2 (p): 2.86 (sept., $^3J_{\text{HH}} = 6.9$ Hz, 1H) + 35.17; OCH_2 (THF): 3.71 (m, 4H) + 70.75; CHMe_2 (o): 3.73 (sept., $^3J_{\text{HH}} = 6.7$ Hz, 2H) + 36.29; $\text{C}_{2,6}$: 158.62; $\text{C}_{3,5}\text{H}$: 7.18 (s, 2H) + 121.22; C_4 : 150.40. $\text{C}_{15}\text{H}_{23}\text{AlCl}_2$ (OC_4H_8) (373.34). Anal. Calcd: C, 61.13; H, 8.40; Al, 7.22. Found: C, 60.93; H, 8.21; Al, 7.43.

2,8-Bis(2,4,6-triisopropylphenyl)-1,7-dioxonia-tricyclo[6,4,9,0^{2,7}]dodecane (2): To a suspension prepared from 0.2 mol Na/K alloy (1.7 g Na/5.2 g K) in 200 ml THF containing 6 g benzene, 35 g (0.094 mol) 2,4,6- $\text{Pr}_3\text{C}_6\text{H}_2\text{AlCl}_2 \cdot \text{THF}$, dissolved in 50 ml, were added dropwise with stirring. The solution turned from blue to black color. Stirring was continued for 16 hrs at 20°C and for 16 more hrs under reflux. Solids were filtered off on a pressure funnel and the solvent evaporated from the filtrate. Distillation in high vacuum in a 3-bulb tube gave a yield of 5.2 g (18%) of **2** (highly viscous); bp 215°C/0.001 mbar (air bath temp.). Colorless crystals from hexane, mp 136°C. NMR (in CDCl_3). Signals labeled with * are partly covered by the signals of the ^iPr groups and are not completely resolved: δ (^1H) + δ (^{13}C) for isomer 1: AlCH_2 : 0.63 (t, $^3J_{\text{HH}} = 7$ Hz, 2H) + 11.8; OCH_2 : 3.9 - 4.2 (m, 2H) + 68.0; CH_2 : 1.23 (m*, 2H) + 23.8; CH_2 : 1.63 - 1.72 (m, 2H) + 32.8; C_1 : 139.7; $\text{C}_{2,6}$: 157.2; $\text{C}_{3,5}\text{H}$: 7.18 (s, 2H) + 120.4; C_4 : 149.9. Isomer 2: AlCH_2 : 0.53 (t, $^3J_{\text{HH}} = 7$ Hz, 2H) + 9.3; OCH_2 : 3.9 - 4.2 (m, 2H) + 67.0; CH_2 : 1.96 - 2.09 (m, 2H) + 23.9; CH_2 : 1.45 (m*, 2H) + 33.5; C_1 : 140.7; $\text{C}_{2,6}$: 157.0, $\text{C}_{3,5}\text{H}$: 7.00 (s, 2H) + 119.8; C_4 : 149.4. It was not possible to make assignments of the ^iPr groups to the individual isomers: 3 x CHMe_2 : 2.8 und 2.83 (m, 4H); 3.2 (m, 2H) + 38.0 + 34.9 + 38.0. 6 x CHCH_3 : 1.04 (d, $^3J_{\text{HH}} = 6.6$ Hz, 6H) + 24.3; 1.23 (d, $^3J_{\text{HH}} = 6.9$ Hz, 6H) + 24.4; 1.27 (d, $^3J_{\text{HH}} = 6.8$ Hz, 6H) + 24.3; 1.28 (d, $^3J_{\text{HH}} = 6.83$ Hz, 6H) + 26.2; 1.37 (d, $^3J_{\text{HH}} = 6.75$, 6H) + 26.2; 1.46 (d, $^3J_{\text{HH}} = 6.6$ Hz, 6H) + 25.4. MS (EI): m/z (%) 604(100). ($\text{C}_{19}\text{H}_{31}\text{AlO}$)₂ (604.84). Anal. Calcd: Al, 8.99. Found: Al, 8.97.

2,6-Bis[(dimethylamino)methyl]phenylaluminum compounds (3 - 6, B)

General preparation procedure: To a solution of 10 g (0.037 mol) 1-bromo-2,6-bis(dimethylaminomethyl)benzene in 175 ml hexane, a solution of butyllithium (23% in hexane, 25 ml) is added dropwise with stirring and stirring is continued for 1 more h. To this solution, 0.037 mol of the aluminum halide dissolved in 175 ml hexane are added dropwise and the

reaction mixture is stirred at 20°C for 20 h and under reflux 4 h. After removal of solids by pressure filtration, the solvent was distilled off and the remainder fractionated in vacuum.

Dibromo-2,6-bis[(dimethylamino)methyl]phenyl-*N,N'*-aluminum (3): The reaction of 2,6-bis[(dimethylamino)methyl]phenyllithium with AlBr_3 was slightly exothermic. Yield: 8.78 g (62.8%). The colorless, viscous distillation product crystallizes within a few days. bp: 125°C/0.001 mbar (air bath temp.). NMR (in C_6D_6): δ (^1H) + δ (^{13}C) NCH_3 : 2.21 (s, 12H) + 47.39; CH_2N : 3.12 (s, 4H) + 65.14; C_1 : 143.3 (br); $\text{C}_{2,6}$: 145.08; $\text{C}_{3,5}\text{H}$: 6.76 (d, $^3\text{J}_{\text{HH}} = 7.3$ Hz, 2H) + 123.35; C_4H : 7.21 (t, $^3\text{J}_{\text{HH}} = 7$ Hz, 1H) + 129.91. ^{27}Al -NMR: δ 98 ($h_{1/2} = 4500$ Hz). $\text{C}_{12}\text{H}_{19}\text{AlBr}_2\text{N}_2$ (378.08). MS (EI): m/z % 378(17) [M^+], 58(100). HRMS: Found: 377.971028. Calcd: 377.97099. Anal. Calcd: N, 7.40; Al, 7.38. Found: N, 7.27; Al, 7.38.

Diiodo-2,6-bis[(dimethylamino)methyl]phenyl-*N,N'*-aluminum (4): From the reaction of 2,6-bis[(dimethylaminomethyl)phenyl]lithium with AlI_3 a yield of 4.9 g (28%) of **4**, bp 149°C/0.001 mbar (air bath temp.) was obtained. Single crystals resulted from the recrystallization from hexane. mp 86°C. NMR (in C_6D_6): δ (^1H) + δ (^{13}C) NCH_3 : 2.22 (s, 12H) + 47.60; CH_2N : 3.10 (s, 4H) + 64.15; C_1 : 144 (br), $\text{C}_{2,6}$: 145.66; $\text{C}_{3,5}\text{H}$: 6.76 (d, $^3\text{J}_{\text{HH}} = 7.3$ Hz, 2H) + 123.49; C_4H : 7.15 (not resolved $\sim\text{C}_6\text{D}_6$ (H), 1H) + 129.96. ^{27}Al -NMR: δ 74 ($h_{1/2} = 5480$ Hz). $\text{C}_{12}\text{H}_{19}\text{AlI}_2\text{N}_2$ (472.07). MS (EI): m/z % 472(4) [M^+], 345(100) [$\text{M}^+ - \text{I}$]. MS (FI): m/z % 472(100). Anal. Calcd.: N, 5.93; I, 53.76. Found: N, 5.88; I, 53.37.

Diethyl-2,6-bis[(dimethylamino)methyl]phenylaluminum (5): The exothermic reaction of 2,6-bis[(dimethylaminomethyl)phenyl]lithium was performed at 0°C. **5** is a colorless liquid. bp 89°C/0.001 mbar (air bath temp.). Yield: 3.3 g (32%). NMR (in C_6D_6): δ (^1H) + δ (^{13}C) AlCH_2 : 0.16 (q, $^3\text{J}_{\text{HH}} = 8.1$ Hz, 4H) + (-0.67 br); AlCH_2CH_3 : 1.28 (t, $^3\text{J}_{\text{HH}} = 8.1$, 6H) + 10.83; NCH_3 : 2.09 (s, 12H) + 46.11; CH_2N : 3.29 (s, 2H) + 67.29; C_1 : 151.2 (br); $\text{C}_{2,6}$: 146.65; $\text{C}_{3,5}\text{H}$: 6.85 (d, $^3\text{J}_{\text{HH}} = 7.4$ Hz, 2H) + 123.25; C_4H : 7.2 (t, $^3\text{J}_{\text{HH}} = 7.4$ Hz, 1H) + 127.62. ^{27}Al -NMR: δ 163 ($h_{1/2} = 5400$ Hz). $\text{C}_{16}\text{H}_{29}\text{AlN}_2$ (276.40). MS (EI): m/z % 275(3) [$\text{M}^+ - \text{H}$], 247(100) [$\text{M}^+ - \text{C}_2\text{H}_5$]. Anal. Calcd: C, 69.52; H, 10.57; N, 10.13. Found: C, 69.33; H, 10.35; N, 9.91.

Chloro(ethyl)-2,6-bis[(dimethylamino)methyl]phenylaluminum (6): From EtAlCl_2 and 2,6-bis[(dimethylamino)methyl]phenyllithium **6** was obtained upon distillation as a highly viscous colorless melt; bp 93°C/0.001 mbar. The viscous distillate crystallizes within a week. Yield: 8.25 g (79%). mp 60°C. NMR (in C_6D_6): δ (^1H) + δ (^{13}C) AlCH_2 : 0.30 (q, $^3\text{J}_{\text{HH}} = 8.1$ Hz, 2H) + 0.34 (br); AlCH_2CH_3 : 1.26 (t, $^3\text{J}_{\text{HH}} = 8.1$ Hz, 3H) + 10.24; NCH_3 : 2.14 (s, 12H) + 46.46; CH_2N : 3.17 (d, $^2\text{J}_{\text{HH}} = 14.1$ Hz, 2H) + 66.32; CH_2N : 3.28 (d, $^2\text{J}_{\text{HH}} = 13.9$ Hz, 2H); C_1 : 146.01 (br); $\text{C}_{2,6}$: 145.24; $\text{C}_{3,5}\text{H}$: 6.82 (d, $^3\text{J}_{\text{HH}} = 7.4$ Hz, 2H) + 123.23; C_4H : 7.18 (t, $^3\text{J}_{\text{HH}} = 7.4$ Hz, 1H) + 128.33. ^{27}Al -NMR: δ 121 ($h_{1/2} = 6860$ Hz).

$\text{C}_{14}\text{H}_{24}\text{AlClN}_2$ (282.79). MS (EI): m/z % 253(60) [$\text{M}^+ - \text{C}_2\text{H}_5$], 58(100) [$\text{C}_3\text{H}_8\text{N}^+$]. MS (FI): m/z (%) 282(24) [M^+], 192(100) [$\text{C}_{12}\text{H}_{20}\text{N}_2^+$]. Anal. Calcd: N, 9.60. Found: 10.26.

Dichloro-2,6-bis[(dimethylamino)methyl]phenylaluminum (B)⁹: The synthesis is described in a short form by⁹, but we prepared B also from 2,6-bis[(dimethylaminomethyl)phenyl]lithium and AlCl_3 in hexane. bp 95°C/0.01 mbar (air bath temp.). NMR (in C_6D_6): δ (^1H) + δ (^{13}C) NCH_3 : 2.21 (s, 12H) + 47.07; CH_2N : 3.16 (s, 4H) + 65.62; C_1 : 142.9 (br); $\text{C}_{2,6}$: 145.25; $\text{C}_{3,5}\text{H}$: 6.79 (d, $^3\text{J}_{\text{HH}} = 7.2$ Hz, 2H) + 123.23; C_4H : 7.20 (t, $^3\text{J}_{\text{HH}} = 7.3$ Hz, 1H) + 129.87. ^{27}Al -NMR: δ 99 ($h_{1/2} = 6330$ Hz). $\text{C}_{12}\text{H}_{19}\text{AlCl}_2\text{N}_2$ (289.18). MS (EI): m/z % 288(26) [M^+], 245(100) [$\text{M}^+ - \text{C}_2\text{H}_5\text{N}$]. MS (FI): m/z (%) 288(100). Anal. Calcd: N, 9.68; Al, 9.33. Found: 9.44; Al, 9.76.

Dichloro-2-(dimethylaminomethyl)phenyl-*N,1*-aluminum (7): The reaction product of 2-[(dimethylaminomethyl)phenyl]lithium with AlCl_3 is a colorless solid, bp 120°C/0.001 mbar (air bath temp.). After recrystallization from hexane the mp was 91°C; the yield 7.3 g (32%). **E**⁷ is obtained as a by-product (4.63 g, 14% yield). NMR (in C_6D_6): δ (^1H) + δ (^{13}C) NCH_3 : 1.86 (s, 6H) + 45.64, NCH_2 : 3.03 (s, 2H) + 65.32; C_1 : 142.5 (br); C_2 : 142.57; C_3H : 6.69 (d, $^3\text{J}_{\text{HH}} = 7.3$ Hz, 1H) + 124.92; $\text{C}_{4,6}\text{H}$: 7.11 (m, 2H) + 127.40, 129.50; C_6H : 7.63 (d, $^3\text{J}_{\text{HH}} = 6.4$ Hz, 1H) + 136.57. ^{27}Al -NMR: δ 127 ($h_{1/2} = 2540$ Hz).

$\text{C}_9\text{H}_{12}\text{AlCl}_2\text{N}$ (232.08). MS (EI): m/z % 231(10) [M^+], 58(100). MS (FI): m/z (%) 231(100). HRMS: Calcd: 231.016224. Found: 231.016223. Anal. Calcd: N, 6.04; Cl, 30.55. Found: N, 5.93; Cl, 29.23.

Dibromo-2-[(dimethylamino)methyl]phenyl-*N,1*-aluminum (C): Synthesis, spectroscopic data and an x-ray structure analysis of **C** were completely described. Our own results are fully in agreement with the results by⁸.

Chloro-(ethyl)-2-[(dimethylamino)methyl]phenylaluminum (8): Was prepared from 2-[(dimethylamino)methyl]phenyllithium and EtAlCl₂; bp 98°C/0.001 mbar (air bath temp.), colorless solid, mp 64°C. Yield: 15.8 g (70%). NMR (in C₆D₆): δ (¹H) + δ (¹³C) AlCH₂: 0.26 (q, ³J_{HH} = 8.15 Hz, 2H) + -0.18 (br); AlCH₂CH₃: 1.32 (t, ³J_{HH} = 8.2 Hz, 3H) + 8.95; NCH₃: 1.71 (s, 3H) + 44.25; NCH₃: 2.07 (s, 3H) + 45.73; CH₂N: 2.89 (d, ²J_{HH} = 14.2 Hz, 1H) + 65.55; C₁: 146.3 (br); C₂: 143.58; C₃H: 6.81 (m, 1H) + 124.45; C_{4,5}H: 7.16 (m, 2H) + (127.28, 128.43); C₆H: 7.72 (m, 1H) + 136.96. ²⁷Al-NMR: δ 156 (h_{1/2} = 3960 Hz). C₁₁H₁₇AlClN (225.69). MS (EI): *m/z* % 196(92) [M⁺-C₂H₅], 58(100). MS (FI): *m/z* (%) 225(6) [M⁺], 135(100).

Bis{2-[(dimethylamino)methyl]phenyl}aluminum compounds 9, 10 and E

General preparation procedure: To a slurry of 0.1 mol of the aluminum halide in 300 ml of hexane, a solution of 28 g (0.2 mol) of 2-[(dimethylamino)methyl]phenyllithium (23% in hexane) is added dropwise with stirring and the stirring is continued for 20 h at ambient temp. and 6 more h under reflux. In due course solids are removed by pressure filtration, the solvent distilled off and the remainder distilled in high vacuum (3-bulb apparatus).

Bromo-bis{2-[(dimethylamino)methyl]phenyl}aluminum (9): The light yellow substance prepared from 2-[(dimethylamino)methyl]phenyllithium and AlBr₃ was sublimed at 130°C/0.001 mbar (air bath temp.). Yield 9.0 g (24%). NMR (in CDCl₃): δ (¹H) + δ (¹³C) NCH₃: 2.64 (s, 12H) + 46.7; CH₂N: 3.72 (br, 2H) und 4.27 (br, 2H) + 66.44; C₁: 147.3 (br); C₂: 146.62; C_{3,5}H: 7.06 - 7.23 (m, 6H) + (125.78, 125.79, 127.5), C₆H: 7.77 (d, 2H) + 137.68. C₁₈H₂₄AlBrN₂ (375.28). MS (EI): *m/z* % 374(3) [M⁺], 58(100). MS (FI): *m/z* (%) 374(18), 295(100) [M⁺-Br]. Anal. Calcd: Br, 21.29; Found: Br, 21.85.

Ethyl-bis{2-(8(dimethylamino)methyl]phenyl}aluminum (10): Was prepared from 2-[(dimethylamino)methyl]phenyllithium and 100 ml of a solution of EtAlCl₂ in hexane (1.0 molar); the reaction mixture was filtered hot. After 14 h yellow crystals of **10** were collected and dried in vacuum. bp 125°C/0.001 mbar (air bath temp.); mp 73°C. Yield: 22.4 g (69%). NMR (in C₆D₆): δ (¹H) + δ (¹³C) AlCH₂: 0.15 (q, ³J_{HH} = 8 Hz, 2H) + (-1.1 br); AlCH₂CH₃: 1.32 (t, ³J_{HH} = 8.1 Hz, 3H) + 10.97; NCH₃: 2.11 (s, 12H) + 46.22; CH₂N: 3.26 (s, 4H) + 67.48; C₁: 151.8 (br); C₂: 147.32; C₃H: 6.98 - 7.02 (m, 2H) + 125.74; C_{4,5}H: 7.22 - 7.25 (m, 4H) + (125.86, 126.71); C₆H: 7.82 - 7.85 (m, 2H) + 138.78. ²⁷Al-NMR: δ 126 (h_{1/2} = 4920 Hz). C₂₀H₂₉AlN₂ (324.44). MS (EI): *m/z* % 295(100) [M⁺-C₂H₅]. MS (FI): *m/z* (%) 324(100) [M⁺]. Anal. Calcd: N, 8.63; Al, 8.05. Found: N, 8.27; Al, 8.05.

Chloro-bis{2-[(dimethylamino)methyl]phenyl}aluminum (E): Our data are in full agreement with those published by⁷.

Tris{2-[(dimethylamino)methyl]phenyl}aluminum (11): A solution of 25 g (0.17 mol) 2-[(dimethylamino)methyl]phenyllithium in 300 ml of hexane was reacted with 7.8 g (0.058 mol) AlCl₃ with stirring. After 24 h reflux, LiCl was filtered off, the hexane evaporated and the honeylike residue distilled at 185°C/0.001 mbar. Recrystallization from hexane delivered colorless crystals, mp 85°C. Yield: 8.9 g (35%). From the forerun (bp 165 - 170°C/0.001 mbar) and from the mother liquor about 10 g of **E** were obtained. NMR (**11**) (in C₆D₆): δ (¹H) + δ (¹³C) NCH₃: 2.04 (s, 6H) + 46.01; CH₂N: 3.55 (s, 2H) + 67.30; C₁: 151.8 (br); C₂: 147.38; C₃H und C_{4,5}H: 7.18 - 7.31 (m, 3H) + (125.71, 126.60, 126.83); C₆H: 7.91 (d, ³J_{HH} = 6.76 Hz, 1H) + 138.76. Remark: In the NMR spectra in solution all ligands appear equivalent. The x-ray structure analysis, however, shows one of the ligands bonded only via the C₁ atom, the two others additionally coordinating via their N atoms.

C₂₇H₃₆AlN₃ (429.57). MS (EI): *m/z* % 295(100) [M⁺-C₉H₁₂N]. Anal. Calcd: N, 9.78; Al, 6.28; Found: N, 9.59; Al, 6.08.

8-(Dimethylamino)naphthylaluminum compounds 12 - 14

General preparation procedure: To a stirred solution of 17.3 g (0.1 mol) N,N-dimethyl-1-naphthylamine in 100 ml hexane, 42 ml BuLi (23% in hexane) were added dropwise. After 24 h under reflux, this solution was added during 2 h to a slurry of 0.1 mol of the aluminum halide in 500 ml hexane. The reaction mixture was refluxed for 6 h, solids removed by hot pressure filtration, the solvent distilled off and the residue fractionated in high vacuum.

Dichloro-[8-(dimethylamino)naphthyl-1]-aluminum (12): The reaction between 8-(dimethylamino)naphthyllithium and AlCl_3 gave a yield of 7.5 g (28%) of **12**, a colorless liquid, bp $128^\circ\text{C}/0.001$ mbar (air bath temp.). 6.1 g 1-(dimethylamino)naphthylalene we recovered. NMR (in C_6D_6): δ (^1H) + δ (^{13}C) NCH_3 : 2.32 (s, 6H) + 49.58; C_1 : 137.4 (br); C_8 : 148.12; $\text{C}_{9/10}$: 133.17 + 136.01; 6 x ArH: 6.57 (dd, $^3\text{J}_{\text{HH}} = 7.6$ Hz, $^5\text{J}_{\text{HH}} = 0.9$ Hz, 1H) + 115.21; 7.04 (dd, $^3\text{J}_{\text{HH}} = 8.2$ Hz, $^5\text{J}_{\text{HH}} = 7.6$ Hz, 1H) + 125.19; 7.30 (dd, $^3\text{J}_{\text{HH}} = 8.3$ Hz, $^5\text{J}_{\text{HH}} = 6.5$ Hz, 1H) + 128.15; 7.45 (dd, $^3\text{J}_{\text{HH}} = 8.3$ Hz, $^5\text{J}_{\text{HH}} = 0.9$ Hz, 1H) + 128.28; 7.55 (dd, $^3\text{J}_{\text{HH}} = 8.3$ Hz, $^5\text{J}_{\text{HH}} = 0.9$ Hz, 1H) + 128.34; 7.81 (dd, $^3\text{J}_{\text{HH}} = 6.4$ Hz, $^5\text{J}_{\text{HH}} = 1.0$ Hz, 1H) + 135.42. ^{27}Al -NMR: δ 129 ($h_{1/2} = 3650$ Hz). $\text{C}_{12}\text{H}_{12}\text{AlCl}_2\text{N}$ (268.18). MS (FI): m/z (%) 267(100) [M^+]. Anal. Calcd: C, 53.75; H, 4.51; N, 5.22; Found: C, 53.66; H, 4.89; N, 4.92.

Dibromo-[8-(dimethylamino)naphthyl-1]aluminum (13): The analogous reaction with AlBr_3 delivered **13** (5.7 g, 10% yield) as colorless crystals; mp 132°C . NMR (in C_6D_6): δ (^1H) + δ (^{13}C) NCH_3 : 2.32 (s, 6H) + 50.52. C_1 : 138.6 (br); C_8 : 147.86; $\text{C}_{9/10}$: 133.2, 135.54; 6 x ArH: 6.50 (dd, $^3\text{J}_{\text{HH}} = 7.6$ Hz, $^5\text{J}_{\text{HH}} = 0.8$ Hz, 1H) + 115.39; 6.99 (dd, $^3\text{J}_{\text{HH}} = 8.2$ Hz, $^5\text{J}_{\text{HH}} = 7.9$ Hz, 1H) + 125.41; 7.29 (dd, $^3\text{J}_{\text{HH}} = 8.2$ Hz, $^5\text{J}_{\text{HH}} = 6.5$ Hz, 1H) + 128.28; 7.43 (dd, $^3\text{J}_{\text{HH}} = 8.3$ Hz, $^5\text{J}_{\text{HH}} = 0.7$ Hz, 1H) + 128.36; 7.52 (dd, $^3\text{J}_{\text{HH}} = 8.2$ Hz, $^5\text{J}_{\text{HH}} = 1.0$ Hz, 1H) + 128.38; 7.81 (dd, $^3\text{J}_{\text{HH}} = 6.5$ Hz, $^5\text{J}_{\text{HH}} = 1.0$ Hz, 1H) + 135.08. ^{27}Al -NMR: δ 131 ($h_{1/2} = 3125$ Hz). $\text{C}_{12}\text{H}_{12}\text{AlBr}_2\text{N}$ (357.02). MS (FI): m/z (%) 357(60) [M^+], 171(100) [$\text{C}_{12}\text{H}_{13}\text{N}^+$]. Anal. Calcd: C, 40.37; H, 3.39; N, 3.92; Br, 44.74. Found: C, 39.56; H, 3.64; N, 3.55; Br, 43.88.

Diethyl-[8-(dimethylamino)naphthyl-1]aluminum (14): Was obtained as a colorless liquid, bp $105^\circ\text{C}/0.001$ mbar, from 8-(dimethylamino)naphthyllithium and 150 ml of a 1 molar Et_2AlCl solution in hexane. Yield: 8.4 g (33%). NMR (in C_6D_6): δ (^1H) + δ (^{13}C) AlCH_2 : 0.24 (q, $^3\text{J}_{\text{HH}} = 8.21$ Hz, 2H) + 0.20 (br); AlCH_3 : 0.29 (q, $^3\text{J}_{\text{HH}} = 8.0$ Hz, 2H) + 0.68 (br); AlCH_2CH_3 : 1.36 (t, $^3\text{J}_{\text{HH}} = 8.0$ Hz, 6H) + 9.96, NCH_3 : 2.25 (s, 6H) + 48.5; C_1 : 148.67 (br); C_8 : 151.23; $\text{C}_{9/10}$: 133.7, 137.53. 6 x ArH: 6.70 (dd, $^3\text{J}_{\text{HH}} = 7.5$ Hz, $^5\text{J}_{\text{HH}} = 1.0$ Hz, 1H) + 114.33; 7.13 (dd, $^3\text{J}_{\text{HH}} = 8.1$ Hz, $^5\text{J}_{\text{HH}} = 7.5$ Hz, 1H) + 124.66; 7.47 (dd, $^3\text{J}_{\text{HH}} = 8.2$ Hz, $^5\text{J}_{\text{HH}} = 6.3$ Hz, 1H) + 126.01; 7.55 (dd, $^3\text{J}_{\text{HH}} = 8.2$ Hz, $^5\text{J}_{\text{HH}} = 0.8$ Hz, 1H) + 127.85; 8.03 (dd, $^3\text{J}_{\text{HH}} = 6.3$ Hz, $^5\text{J}_{\text{HH}} = 1.3$ Hz, 1H) + 134.94. ^{27}Al -NMR: δ 173 ($h_{1/2} = 4750$ Hz).

$\text{C}_{16}\text{H}_{22}\text{AlN}$ (255.34). MS (EI): m/z % 254(6) [$\text{M}^+ - \text{H}$], 183(100) [$\text{M}^+ - \text{C}_5\text{H}_{12}$]. MS (FI): m/z (%) 255(100) [M^+]. Anal. Calcd: C, 75.26; H, 8.68; N, 5.49. Found: C, 75.57; H, 9.11; N, 5.15.

Bromo-{2,6-bis[(dimethylamino)methyl]phenyl}-[N,N-(2,6-dimethylphenyl)(trimethylsilyl)amino]-aluminum (15): At 0°C 0.035 mol BuLi were added to the stirred solution of 6.76 g (0.035 mol) (2,6-dimethylphenyl)(trimethylsilyl)amine in 100 ml hexane. This reagent was added dropwise to a solution of 13.2 g (0.035 mol) of **3** in 500 ml of hexane. Stirring was continued for 3 d at ambient temperature, LiBr removed by pressure filtration, hexane distilled off and the residue fractionated in the 3-bulb apparatus. Bp $165^\circ\text{C}/0.001$ mbar (air bath temp.); mp 89°C . Yield: 3.1 g (18%). NMR (in C_6D_6): δ (^1H) + δ (^{13}C) $\text{Si}(\text{CH}_3)_3$: 0.34 (s, 9H) + 3.89; NCH_3 : 2.07 (s, 12H) + 45.82 (br), ArCH_3 : 2.24 (s, 6H) + 21.25; 2 x CH_2N : 3.26 (d, $^2\text{J}_{\text{HH}} = 13.3$ Hz, 2H) + 66.50 (br), 3.45 (d, $^2\text{J}_{\text{HH}} = 13.2$ Hz, 2H) + 66.50 (br); ArH: 6.75 - 7.2 (m); C_1 : 145.32 (br); C_2 : 145.68; C_3 : 122.22; C_4 : 129.22; C_7 : 148.35; $\text{C}_{8/12}$: 136.80; $\text{C}_{9/11}$: 128.65; C_{10} : 122.98. ^{29}Si -NMR: δ 2.96.

$\text{C}_{23}\text{H}_{37}\text{AlBrN}_3\text{Si}$ (490.54). MS (FI): m/z (%) 489(70) [M^+], 192(100) [$\text{C}_{11}\text{H}_{18}\text{NSi}^+$]. Anal. Calcd: C, 56.32; H, 7.60; N, 8.57; Si, 5.73. Found: C, 55.96; H, 7.96; N, 8.58; Si, 5.57.

Bromo-{2-[(dimethylamino)methyl]phenyl}-[N,N-(2,6-dimethylphenyl)(trimethylsilyl)amino]aluminum (16): Analogously to **15**, the reaction starting from 4.8 g (0.025 mol) 2,6-dimethylphenyl-trimethylsilylamin, 0.025 mol. BuLi and 8.25 g (0.025 mol) **C** gave **16** as a colorless solid: bp $148^\circ\text{C}/0.001$ mbar. Recrystallization from toluene gave single crystals (mp 124°C) in 2.5 g (23%) yield. NMR (in C_6D_6): δ (^1H) + δ (^{13}C) SiCH_3 : 0.41 (s, 9H) + 3.00; NCH_3 : 1.34 (s, 3H) + 44.05; NCH_3 : 2.09 (s, 3H) + 46.45; CH_2N : 2.45 (d, $^2\text{J}_{\text{HH}} = 13.9$ Hz, 1H) + 66.32; CH_2N : 3.74 (d, $^2\text{J}_{\text{HH}} = 13.9$ Hz, 1H) + 66.32; ArCH_3 : 2.27 (s, 3H) + 20.95; ArCH_3 : 2.40 (s, 3H) + 20.96; C_1 : 145.9 (br); C_2 : 142.55; C_3H : 7.75 (d^X, $^3\text{J}_{\text{HH}} = 6.9$ Hz, 1H) + 124.57; C_4H : 7.14 (d^X, $^3\text{J}_{\text{HH}} = 7.1$ Hz, 1H) + 127.62; C_5H : 7.12 (d^X, $^3\text{J}_{\text{HH}} = 7.1$ Hz, 1H) + 128.51; C_6H : 6.70 (d, $^3\text{J}_{\text{HH}} = 6.9$ Hz, 1H) + 136.55; (X these signals are not fully resolved, due to multiple coupling).

Table 4. Crystal data for the structures **2**, **4**, **6**, **7**, **11** and **16**

Structure	2	4	6 · C₆H₆
Empirical formula	C ₃₈ H ₆₂ Al ₂ O ₂	C ₁₂ H ₁₉ AlI ₂ N ₂	C ₂₀ H ₃₀ AlClN ₂
Formula weight	604.84	472.07	360.89
Crystal system	monoclinic	monoclinic	monoclinic
Space group	P2 ₁ /n	P2 ₁ /c	C2/c
a [Å]	9.047(2)	12.807(3)	8.284(2)
b [Å]	9.270(2)	8.024(2)	17.128(3)
c [Å]	21.862(4)	16.083(3)	14.381(3)
α [°]	90	90	90
β [°]	95.78(3)	100.19(3)	98.43(3)
γ [°]	90	90	90
V [Å ³]	1824.1(7)	1626.7(6)	2018.4(7)
Z	2	4	4
D _x [Mg/m ³]	1.101	1.928	1.188
μ [mm ⁻¹]	0.109	3.904	0.237
F(000)	664	896	776
Crystal size [mm]	0.5 x 0.4 x 0.3	0.4 x 0.3 x 0.2	0.8 x 0.6 x 0.3
2θ range	8 > 2θ > 55	8 > 2θ > 50	7 > 2θ > 50
Reflections collected	6594	3580	3543
Independent Reflections	4197	2853	1774
Reflections with I > 2σ(I)	2979	2499	1464
R _{int}	0.0474	0.0322	0.0605
Data used	4197	2847	1771
Parameters	196	158	127
GOOF	1.019	1.072	1.052
R1 ^a	0.0546	0.0282	0.0541
wR2 ^b	0.1379	0.0756	0.1510
Max. [eÅ ⁻³]	0.741	0.690	0.548
Min. [eÅ ⁻³]	-0.345	-0.960	-0.451

Structure	7	11	16
Empirical formula	C ₉ H ₁₂ AlCl ₂ N	C ₂₇ H ₃₆ AlN ₃	C ₂₀ H ₃₀ AlBrSiN ₂
Formula weight	232.08	429.57	433.44
Crystal system	monoclinic	triclinic	monoclinic
Space group	P2 ₁ /c	P 1	P2 ₁ /c
a [Å]	9.342(2)	9.260(1)	13.953(3)
b [Å]	13.094(4)	9.385(1)	35.685(7)
c [Å]	10.282(2)	14.250(1)	8.797(2)
α [°]	90	94.87(1)	90
β [°]	116.30(1)	97.79(1)	90.28(3)
γ [°]	90	97.90(1)	90
V [Å ³]	1127.5(5)	1208.5(2)	4380(2)
Z	4	2	8
D _x [Mg/m ³]	1.367	1.180	1.315
μ [mm ⁻¹]	0.609	0.103	1.977
F(000)	480	464	1808
Crystal size [mm]	0.8 x 0.6 x 0.5	0.6 x 0.5 x 0.4	0.6 x 0.6 x 0.5
2θ range	5 > 2θ > 45	8 > 2θ > 45	8 > 2θ > 45
Reflections collected	2781	3292	5997
Independent Reflections	1465	3198	5742
Reflections with I > 2σ(I)	1349	2755	4153
R _{int}	0.0132	0.0332	0.0272
Data used	1465	3198	5738
Parameters	120	286	465
GOOF	1.077	1.057	1.031
R1 ^a	0.0237	0.0378	0.0443
wR2 ^b	0.0614	0.0896	0.1027
Max. [eÅ ⁻³]	0.310	0.255	0.520
Min. [eÅ ⁻³]	-0.183	-0.191	-0.425

$$R1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|} \text{ for all reflections with } I > 2\sigma(I)$$

$$wR2 = \sqrt{\frac{\sum (F_o^c - F_c^c)^2}{\sum F_o^4}} \text{ for all data}$$

C₇: 147.97; C₈: 136.2; C₉H: 6.89 (d^X, ³J_{HH} = 7.4 Hz, 1H) + 128.59; C₁₀H: 6.80 (t, ³J_{HH} = 7.5 Hz, 1H) + 129.90; C₁₁H: 6.97 (d^X, ³J_{HH} = 7.4 Hz, 1H) + 128.65; C₁₂: 136.81. ⁴⁷Al-NMR: δ 125 (h_{1/2} = 7000 Hz). ²⁹Si-NMR: δ 2.98 (¹J_{SiC} = 28.15 Hz). C₂₀H₃₀AlBrN₂Si (433.44). MS (EI): *m/z* % 434(6) [M⁺], 58(100). MS (FI): *m/z* (%) 434(100). Anal. Calcd: N, 6.46. Found: N, 6.44.

X-Ray Crystal Structure Analyses of 2, 4, 6, 7, 11 and 16²⁶

A summary of the crystallographic data is presented in Table 4. Data were collected for **6** on a Stoe-Siemens-AED 2 diffractometer, for **7** and **11** on a Stoe-Siemens-Huber-diffractometer and for **2**, **4** and **16** on a Stoe-Siemens AED diffractometer using Mo-K_α radiation (λ = 0.71073 Å). All X-ray measurements were performed at -120°C. For the structures of **4** and **16** semiempirical absorption corrections via Ψ scans were employed. The structures were solved by direct methods using SHELXS-90²⁷. The structures were refined against F² using SHELXL-93²⁸. All non hydrogen atoms were refined anisotropically. The hydrogen atoms were positioned ideally and refined with the riding model. The U(H) values were obtained by using 1.2 or 1.5 (for CH₃) as multiplication factors for the U_{eq}-values of the respective carbon atoms. The molecule of structure **6** is positioned on a 2-fold axis just as the solvent benzene, therefore the chlorine atom and the ethyl group are disordered. An attempted refinement in the space group C_c did not lead to better results. For the refinement in C2/c we applied Similarity Restraints²⁸ and the Rigid Bond Restraint²⁹⁻³¹ for the U_i values of the atoms concerned.

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