Syntheses and Structures of Intramolecularly Stabilized Organoaluminium Compounds☆

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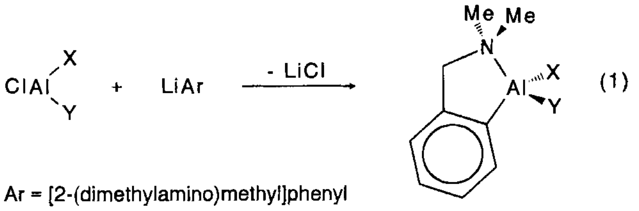
The reaction of LiAr (Ar = 2-[(dimethylamino)methyl]phenyl) with $AlCl_3$, $MeAlCl_2$, and Me_2AlCl in a 1:1 ratio yields the corresponding organoaluminium compounds $ArAlCl_2$, ArAl(Cl)Me, and $ArAlMe_2$ (**1**–**3**). The alanes Ar_2AlCl and Ar_2AlMe (**4** and **5**) were synthesized from $AlCl_3$ and $MeAlCl_2$ with two equivalents of LiAr. The products ArAl(Cl)R [R = *t*Bu, $C(SiMe_3)_3$] **6** and **7** are formed by the reaction of LiR with **1**. The Lewis acid **1** adds the bases iPrNH$_2$ and THF to yield the adducts **1** · iPrNH$_2$ and **1** · THF. The structures of the products were deduced from the ^{1}H-, ^{13}C-, and ^{27}Al-NMR spectra and were confirmed by X-ray structural determinations of **5** and **1** · iPrNH$_2$.

The 2-[(dimethylamino)methyl]phenyl ligand (Ar) is a widely used chelating ligand in organometallic chemistry. The lithium compound LiAr, first published in 1963[1], is the common starting material for the preparation of new complexes. To date, many examples in transition and main-group chemistry have been known, and the intramolecular donor ability of the ligand is well-documented[2]. Surprisingly, little is known about {2-[(dimethylamino)methyl]phenyl}alanes, and to our knowledge $ArAlEt_2$ is the only published example[3]. In this paper we report on the syntheses and structures of four- and five-coordinated aluminium compounds containing one or two 2-[(dimethylamino)methyl]phenyl ligands.

Results and Discussion

The reaction of LiAr with $AlCl_3$, $MeAlCl_2$, and Me_2AlCl[4] in ether gives the compounds **1**–**3** in good yields. These solids are soluble in organic solvents like toluene, hexane, and ether and are volatile in high vacuo between 45 and 80°C.

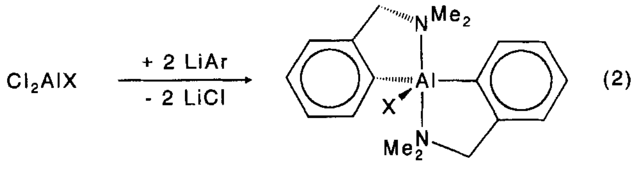


Ar = [2-(dimethylamino)methyl]phenyl

	1	2	3
X	Cl	Me	Me
Y	Cl	Cl	Me

The compounds **1**, **3** (C_s point group) and the unsymmetrically substituted alane **2** (C_1 point group) show the expected signal pattern in the ^{1}H- and ^{13}C-NMR spectra. The ^{27}Al-NMR shifts δ = 127, 155, and 176 for **1**, **2**, and **3**, respectively, are in the typical range of δ = 125–180 for tetracoordinated aluminium with the given type of substituents[5]. Unfortunately, ^{27}Al-NMR data are not available for the known $ArAlEt_2$[3], but the recorded shift of δ = 180 for [3-(dimethylamino)propyl]diethylaluminium $Me_2N[CH_2]_3$-$AlEt_2$, which was proven by cryoscopic measurement to be monomeric in solution[5], matches with the value of the dimethyl compound **3**. The mass spectra of **1**–**3** show no peaks higher than the expected molecular mass, which is in accord with the proposed structures. The heavier homologue of **3**, the known gallium compound $ArGaMe_2$, exhibits a distorted tetrahedral coordination of the metal center in the solid state[3].

The reaction of two equivalents of LiAr with $AlCl_3$ and $MeAlCl_2$ readily gives the organometallic substances **4** and **5** as crystalline solids in high yields (78 and 62%).



	4	5
X	Cl	Me

The structure of the methyl compound **5** was determined by X-ray structural analysis. It crystallizes in the space group *Pbca* with no unusual intermolecular contacts. Compound **5** exhibits a distorted trigonal-bipyramidal geometry with the two nitrogen donor atoms in the axial positions and three carbon atoms in the equatorial plane (Figure 1). The pyramidal axis deviates only slightly from linearity (N1–Al–N2 = 173°), and the three C–Al–C angles sum up to 360°, thus defining an equatorial AlC_3 plane. A deviation from ideal trigonal-bipyramidal geometry arises from the angle 101° between the least-squares plane defined by

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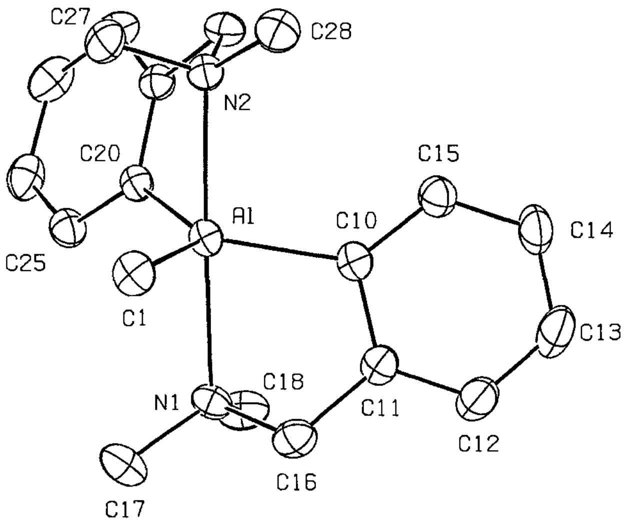


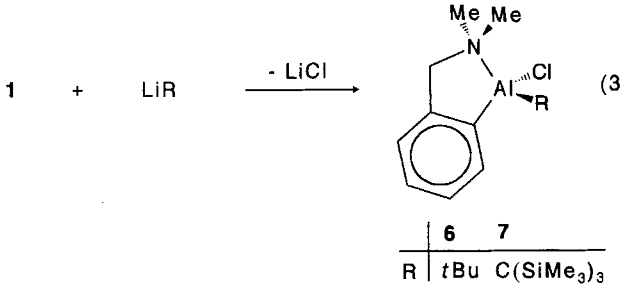
Figure 1. Molecular structure of **5** (thermal ellipsoids at 30% probability). – Selected bond lengths [pm], angles, and dihedral angles [°]: Al–N1 229.0(2), Al–N2 224.5(2), Al–C1 197.8(3), Al–C10 201.8(2), C10–C11 141.6(3), C11–C16 150.6(3), C16–N1 148.9(3), Al–C20 200.7(2), C20–C21 139.8(3), C21–C26 152.3(3), C26–N2 148.4(2); N1–Al–N2 173.00(7), N1–Al–C1 92.8(1), N1–Al–C10 79.58(7), Al–N1–C16 99.4(1), N2–Al–C1 94.0(1), N2–Al–C20 78.88(7), Al–N2–C26 101.5(2), C1–Al–C10 116.6(1), C1–Al–C20 122.4(1), C10–Al–C20 120.97(8), C17–N1–C18 108.6(2), C27–N2–C28 107.0(1), C1–Al–N1–C17 39.9(2), C1–Al–N1–C18 167.8(2), C1–Al–N2–C27 –45.9(2), C1–Al–N2–C28 78.0(2), Al–C10–C11–C16 1.7(3), Al–C20–C21–C26 –2.2(3)

N1, Al, N2, and C1[6] and the equatorial plane. The three Al–C bond lengths of 198, 202, and 201 pm for Al–C1, Al–C10, and Al–C20, respectively, are comparable to those found for $Me_3N \cdot AlMe_3$ (199 pm, GED)[7] and $(AlPh_3)_2$ (196 pm)[8]. The most interesting bond lengths in **5** are the Al–N distances of 229 and 224 pm. Nitrogen donor bond lengths are known to cover quite a large range, depending on the coordination number and the substitution pattern. The difference between the values found in $(HMe_2N)_2AlCl_3$ (206 pm)[9] and $(Me_3N)_2AlH_3$ (218 pm)[10] reflects the different acceptor strengths of $AlCl_3$ and AlH_3[11]. The hypothetical molecule $(Me_3N)_2AlMe_3$, useful for comparison with **5**, is not available, since the weak Lewis acidity of $AlMe_3$ allows only one molecule of NMe_3 to be coordinated. The long Al–N bond lengths of **5** may be partly ascribed to the small acceptor ability of the central atom.

Compound **5** consists of two five-membered rings with the aluminium atom in a spiro position. Both rings are in an envelope conformation with the "flap" atoms N1 and N2 displaced out of the respective plane by 83 and 81 pm. Two fused five-membered rings like these give rise to several possible isomers, depending on the "bending directions" of the nitrogen tips. In compound **5** N1 is bent towards the space between the two aromatic rings and N2 is bent towards the opposite direction, what could be called an "*endo*/*exo*" isomer (C_1 point group). As a result of the different "bending directions" the two methyl substituents at N2 and the methyl group bound to aluminium are staggered, and the methyl substituents at N1 and the corresponding aromatic ring are also arranged in a staggered way. The well-characterized gallium[2h] and indium[2e] compounds Ar_2MCl both exhibit a trigonal-bipyramidal coordination of the metal centers. The main difference with respect to **5** is that the nitrogen atoms are bent towards the same directions giving an "*endo*/*endo*" isomer which is very close to C_2 point group symmetry.

The ^{27}Al-NMR shifts of **4** and **5** (δ = 96, 118) are distinctly different from those of **2** and **3** (δ = 155, 176) and illustrate the five- and fourfold coordination. Compound **5** gives an unexpected simple signal pattern in the ^{1}H-NMR spectrum at 24°C; three singlets at δ = –0.59, 2.10, and 3.53 for AlMe, NMe_2, and CH_2 and one set of multiplets at δ = 6.94–7.76 for the ABCD spin system in the aromatic range. A similar result is obtained for the chloro compound **4** at 70°C. The ^{1}H-NMR spectra are much more complex at –80°C. Compound **4** shows four singlets for the NMe_2 groups, four doublets for the CH_2 groups, and two partly overlapping signal sets for two ABCD spin systems in the aromatic region. Compound **5** exhibits a comparable spectrum under the same conditions. Apparently, the geometry for **4** and **5** in solution resembles the structure of the methyl compound **5** in the solid state. The simple signal pattern at higher temperature can be explained by assuming two dynamic processes. One is a coupled envelope inversion converting an "*endo*/*exo*" isomer into the corresponding "*exo*/*endo*" species giving an C_2-symmetrical molecule on time average. The other one is the interchange of two chelating ligands, i.e. a fast interconversion of two C_2-symmetrical enantiomers with the result of a C_{2v} symmetry. Between the high-temperature C_{2v} and the low-temperature C_1 case several coalescences of signals can be seen. The two dynamic processes, envelope inversion and ligand exchange, more or less overlap. There is a relatively large gap from 30 to –20°C where the alane **4** appears as a C_2-symmetrical molecule (two ^{1}H-NMR signals for CH_2 and two for NMe_2). Compound **5**, on the other hand, shows two singlets at –40°C and already four singlets at –45°C for the CH_2 protons, whereas the NMe_2 unit is represented by a broad signal at those temperatures.

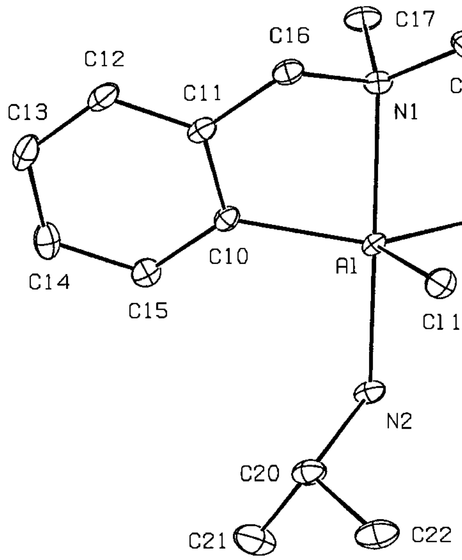
According to Eq. (3) one of the two chlorine atoms of the alane **1** can be selectively replaced by organic ligands to give the crystalline alanes ArAl(Cl)R **6** and **7**. The NMR spectra of these products resemble those of **2**. The ^{27}Al-NMR shifts (δ = 145, 141) indicate a fourfold coordination.



(3)

The Lewis acid **1** adds the bases *i*PrNH$_2$ and THF to yield the adducts **1**·*i*PrNH$_2$ and **1**·THF. The trigonal-bipyramidal coordination of the metal center was proven by the single-crystal X-ray determination of the **1**·*i*PrNH$_2$ (Figure 2).

Figure 2. Molecular structure of **1**·THF (thermal ellipsoids at 30% probability). – Selected bond lengths [pm], angles, and dihedral angles [°]: Al–N1 217.1(1), Al–N2 207.0(1), Al–Cl1 218.06(4), Al–Cl2 221.09(4), Al–C10 198.7(1), C10–C11 140.7(2), C11–C16 151.5(2), C16–N1 148.9(2); N1–Al–N2 175.50(5), Cl1–Al–Cl2 115.19(2), Cl1–Al–C10 116.18(4), Cl2–Al–C10 128.10(4), Al–N1–C16 101.71(7), N1–Al–C10 81.95(4), Al–N2–C20 122.70(8), C17–N1–C18 107.5(1), Cl1–Al–N1–C18 39.6(1), Cl2–Al–N2–C20 176.7(2), Al–C10–C11–C16 0.2(2)



The N donor atoms occupy the axial sites (N1–Al–N2 = 176°), and the aluminium atom is in a trigonal-planar environment formed by two chloro ligands and the C10 atom. The angle between the equatorial plane and the least-squares plane defined by N1, Al, N2, and C10[12] is 90°. The five-membered ring adopts an envelope conformation; the N1 atom is situated 77 pm outside the plane Al–C10–C11–C16. Two hydrogen bridges between the N2 atom and the chlorine substituent Cl2 of an adjacent molecule (H···Cl2′ = 266 pm, N2–H···Cl2′ = 170°) result in a pairwise arrangement of molecules close to crystallographic inversion centers. The remaining intermolecular contacts are not unusual and of the van der Waals type. The Al–Cl bond lengths (Al–Cl1 = 218, Al–Cl2 = 221 pm) are comparable to those of (HMe$_2$N)$_2$AlCl$_3$ (218 pm), whereas the two Al–N bond lengths (Al–N1 = 217, Al–N2 = 207 pm) turn out to be longer than those of (HMe$_2$N)$_2$AlCl$_3$ (206 pm)[9].

A C_s symmetry of **1**·*i*PrNH$_2$ and **1**·THF in solution is derived from the ^{1}H- and ^{13}C-NMR spectra. This can be explained by a trigonal-bipyramidal geometry with two donor atoms in the axial positions and a fast envelope inversion. The adduct formation causes an upfield shift in the ^{27}Al-NMR spectra from δ = 127 for the dichloroalane **1** to δ = 78 and 85 for **1**·*i*PrNH$_2$ and **1**·THF. In contrast to the amine adduct the crystalline **1**·THF loses the base completely in high vacuo at ambient temperature.

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Experimental

All manipulations were carried out under dry nitrogen in Schlenk glassware. Solvents were dried by standard procedures, distilled and stored under nitrogen and molecular sieves (4 Å). – Me$_2$AlCl (1.0 M in hexane), MeAlCl$_2$ (1.0 M in hexane), LiMe (1.6 M in Et$_2$O), Li*t*Bu (1.7 M in pentane) were purchased from Aldrich, and AlCl$_3$ (>99%, Fluka) was sublimed prior to use. Li[C$_6$H$_4$(CH$_2$NMe$_2$)][1] and HC(SiMe$_3$)$_3$[13] were synthesized as described in the literature. – NMR: Varian Unity 500 at 499.843 (^{1}H, standard: TMS intern), 130.195 (^{27}Al, standard: [Al(acac)$_3$] in C$_6$D$_6$ extern), 125.639 MHz (^{13}C{^{1}H}, APT, standard: TMS intern). As a result of the electric quadrupole moment of the ^{27}Al nucleus the ^{13}C-NMR signals of the carbon atoms bound to aluminium could not be detected. Assignments of the signals in the aromatic region (^{1}H and ^{13}C NMR) for **4** and **5** were deduced from ^{1}H/^{1}H and ^{1}H/^{13}C COSY experiments. – Elemental analyses (C, H, N): Carlo-Erba elemental analyzer, Modell 1106. – MS: Finnigan MAT 95.

Dichloro{2-[(dimethylamino)methyl]phenyl}aluminium (**1**): Li[C$_6$H$_4$(CH$_2$NMe$_2$)] (0.84 g, 6.0 mmol) was added to a solution of AlCl$_3$ (0.79 g, 5.9 mmol) in Et$_2$O (30 ml) at −78°C. The dry-ice bath was removed, and the reaction mixture was stirred for 30 min. The solution was filtrated, and the solid residue was washed with two 10-ml portions of Et$_2$O. After removal of the solvent in high vacuo, sublimation (80°C, 0.001 mbar) gave pure **1** (1.20 g, 87%), m.p. 99–100°C. – ^{1}H NMR: δ = 1.81 (s, 6H, CH$_3$), 2.97 (s, 2H, CH$_2$), 6.64 (m, 1H, 3-H), 7.10 (m, 2H, 4,5-H), 7.64 (m, 1H, 6-H). – ^{13}C NMR: δ = 45.22 (CH$_3$), 65.42 (CH$_2$), 124.56 (CH), 129.28 (2 CH), 137.02 (C-6), 142.60 (C-2). – ^{27}Al NMR ([D$_8$]toluene): δ = 127 ($h_{1/2}$ = 1480 Hz). – MS (70 eV), *m/z* (%): 231 (16) [M$^+$], 140 (88) [M$^+$ – C$_7$H$_7$], 135 (59) [C$_9$H$_{13}$N$^+$], 134 (75) [C$_9$H$_{12}$N$^+$], 91 (76) [C$_7$H$_7^+$], 58 (100) [Me$_2$NCH$_2^+$]. – C$_9$H$_{12}$AlCl$_2$N (232.1): calcd. C 46.58, H 5.21, N 6.04; found C 46.20, H 5.36, N 6.03.

Chloro{2-[(dimethylamino)methyl]phenyl}methylaluminium (**2**): A 1.0 M solution of MeAlCl$_2$ in hexane (6.6 ml) was added to a suspension of Li[C$_6$H$_4$(CH$_2$NMe$_2$)] (0.93 g, 6.6 mmol) in Et$_2$O (40 ml) at −78°C. The dry-ice bath was removed, and the reaction mixture was stirred for 45 min. The solution was filtrated, and the solid was washed with two 5-ml portions of Et$_2$O. After removal of the solvent in high vacuo, sublimation (60°C, 0.001 mbar) gave a crude product (1.15 g). Subsequent crystallization from 10 ml hexane/10 ml Et$_2$O at −20°C afforded pure **2** (0.72 g, 52%), m.p. 75–77°C. – ^{1}H NMR: δ = −0.30 (s, 3H, AlCH$_3$), 1.56 (s, 3H, NCH$_3$), 1.95 (s, 3H, NCH$_3$), 2.77 (d, J = 14.0 Hz, 1H, CH$_2$), 3.43 (d, J = 14.0 Hz, 1H, CH$_2$), 6.75 (m, 1H, 3-H), 7.17 (m, 2H, 4,5-H), 7.75 (m, 1H, 6-H). – ^{13}C NMR: δ = 44.23 (NCH$_3$), 45.33 (NCH$_3$), 66.28 (CH$_2$), 124.22 (CH), 127.43 (CH), 128.32 (CH), 137.02 (C-6), 143.34 (C-2). – ^{27}Al NMR ([D$_8$]toluene): δ = 155 ($h_{1/2}$ = 2600 Hz). – MS (70 eV), *m/z* (%): 196 (100) [M$^+$ – CH$_3$], 153 (18) [C$_7$H$_7$AlCl$^+$], 91 (17) [C$_7$H$_7^+$], 58 (4) [Me$_2$NCH$_2^+$]. – C$_{10}$H$_{15}$AlClN (211.7): calcd. C 56.74, H 7.14, N 6.62; found C 56.72, H 7.58, N 6.74.

{2-[(Dimethylamino)methyl]phenyl}dimethylaluminium (**3**): A 1.0 M solution of Me$_2$AlCl in hexane (6.0 ml) was added to a suspension of Li[C$_6$H$_4$(CH$_2$NMe$_2$)] (0.83 g, 5.9 mmol) in Et$_2$O (40 ml) at −78°C. The dry-ice bath was removed, the reaction mixture was stirred for 30 min, and all volatile materials were removed at room temp. in high vacuo. The crude product was dissolved in hexane (40 ml), the solution was filtrated, and the undissolved residue was

washed with two 10-ml portions of hexane. After the solvent had been removed in high vacuo sublimation (45°C, 0.001 mbar) gave pure **3** (0.81 g, 72%), m.p. 70–71°C. – ^{1}H NMR: δ = −0.42 (s, 6H, $AlCH_3$), 1.73 (s, 6H, NCH_3), 3.12 (s, 2H, CH_2), 6.85 (m, 1H, 3-H), 7.23 (m, 2H, 4,5-H), 7.87 (m, 1H, 6-H). – ^{13}C NMR: δ = 45.07 (NCH_3), 67.18 (CH_2), 123.97 (CH), 127.19 (CH), 127.31 (CH), 137.32 (C-6), 143.71 (C-2). – ^{27}Al NMR ([D$_8$]toluene): δ = 176 ($h_{1/2}$ = 1960 Hz). – MS (70 eV), *m/z* (%): 176 (100) [$M^+ - CH_3$], 135 (66) [$C_9H_{13}N^+$], 134 (44) [$C_9H_{12}N^+$], 91 (40) [$C_7H_7^+$], 58 (74) [$Me_2NCH_2^+$]. – $C_{11}H_{18}AlN$ (191.25): calcd. C 69.08, H 9.49, N 7.32; found C 68.00, H 9.53, N 7.31.

Chlorobis{2-[(dimethylamino)methyl]phenyl}aluminium (**4**): Li[$C_6H_4(CH_2NMe_2)$] (3.20 g, 22.7 mmol) was added to a solution of $AlCl_3$ (1.50 g, 11.2 mmol) in Et_2O (60 ml) at −78°C. After the dry-ice bath had been removed and the reaction mixture been stirred overnight, all volatile components were distilled off at room temp. in high vacuo. The crude product was dissolved in toluene (80 ml), the solution was filtrated, and the undissolved residue was washed with two 10-ml portions of toluene. After removal of the solvent in high vacuo, pure **4** (2.91 g, 78%) was collected by sublimation (120°C, 0.001 mbar), m.p. 159–161°C. – ^{1}H NMR ([D$_8$]toluene, 70°C): δ = 2.31 (s, 12H, NCH_3), 3.66 (br. s, 4H, CH_2), 6.91 (m, 2H, 3-H), 7.14 (m, 4H, 4,5-H), 7.69 (m, 2H, 6-H). – ^{1}H NMR ([D$_8$]toluene, 24°C): δ = 2.15 (br. s, 6H, NCH_3), 2.34 (br. s, 6H, NCH_3), 3.30 (br. s, 2H, CH_2), 3.89 (br. s, 2H, CH_2), 6.91 (m, 2H, 3-H), 7.17 (m, 4H, 4,5-H), 7.68 (m, 2H, 6-H). – ^{1}H NMR ([D$_8$]toluene, −80°C): δ = 1.62 (s, 3H, NCH_3), 1.99 (s, 3H, NCH_3), 2.24 (s, 3H, NCH_3), 2.24 (d, $J \cong$ 13 Hz, 1H, CH_2), 2.44 (d, overlap with 2.45, 1H, CH_2), 2.45 (s, 3H, NCH_3), 4.08 (d, J = 13.4 Hz, 1H, CH_2), 4.56 (d, J = 13.4 Hz, 1H, CH_2), 6.89 (d, J = 7.3 Hz, 1H, 3-H), 6.93 (d, $J \cong$ 7 Hz, 1H, 3-H), 7.24 (m, 4H, 4,5-H), 7.63 (d, J = 6.7 Hz, 1H, 6-H), 7.69 (d, J = 6.7 Hz, 1H, 6-H). – ^{1}H NMR ([D$_8$]toluene): $T_{\text{coal.}}$ = 59 and −20°C (CH_2); 31 and −31°C (NCH_3). – ^{13}C NMR ([D$_8$]toluene, 24°C): δ = 45.0 (br., CH_3), 47.0 (br., CH_3), 66.48 (CH_2), 125.95 (C-3), 126.02 (C-4 or C-5), 127.51 (C-5 or C-4), 138.20 (C-6), 147.22 (C-2), 148.7 (br., C-1). – ^{27}Al NMR ([D$_8$]toluene): δ = 95 (24°C, $h_{1/2}$ = 4200 Hz); 96 (70°C, $h_{1/2}$ = 2100 Hz). – MS (70 eV), *m/z* (%): 330 (<1) [M^+], 315 (<1) [$M^+ - CH_3$], 196 (<1) ($M^+ - C_9H_{12}N$), 135 (60) [$C_9H_{13}N^+$], 134 (40) [$C_9H_{12}N^+$], 91 (49) [$C_7H_7^+$], 58 (100) [$Me_2NCH_2^+$]. – $C_{18}H_{24}AlClN_2$ (330.8): calcd. C 65.35, H 7.31, N 8.47; found C 64.30, H 7.64, N 8.33.

Bis{2-[(dimethylamino)methyl]phenyl}methylaluminium (**5**): A 1.0 M solution of $MeAlCl_2$ in hexane (5.8 ml) was added to a suspension of Li[$C_6H_4(CH_2NMe_2)$] (1.64 g, 11.6 mmol) in Et_2O (60 ml) at −78°C. The dry-ice bath was removed, and the reaction mixture was stirred for 2.5 h. After the solution had been filtrated and the solid residue been washed with two 5.0-ml portions of Et_2O, all volatile materials were removed at room temp. in high vacuo. The residue was dissolved in Et_2O (10 ml), and from crystallization at −20°C the crude product (1.48 g) was obtained. A second crystallization from hexane (40 ml) gave pure **5** (1.12 g, 62%), m.p. 118–119°C. – ^{1}H NMR ([D$_8$]toluene, 24°C): δ = −0.59 (s, 3H, $AlCH_3$), 2.10 (s, 12H, NCH_3), 3.53 (s, 4H, CH_2), 6.94 (m, 2H, 3-H), 7.18 (m, 4H, 4,5-H), 7.76 (m, 2H, 6-H). – ^{1}H NMR ([D$_8$]toluene, −80°C): δ = −0.48 (s, 3H, $AlCH_3$), 1.66 (s, 3H, NCH_3), 1.72 (s, 3H, NCH_3), 2.13 (s, 6H, NCH_3), 2.28 (d, J = 13.2 Hz, 1H, CH_2), 2.47 (d, J = 13.2 Hz, 1H, CH_2), 4.04 (d, J = 13.2 Hz, 1H, CH_2), 4.26 (d, J = 13.2 Hz, 1H, CH_2), 6.95 (d, J = 6.4 Hz, 1H, 3-H), 7.01 (d, $J \cong$ 6 Hz, 1H, 3-H), 7.30 (m, 4H, 4,5-H), 7.71 (d, J = 6.4 Hz, 1H, 6-H), 7.83 (d, J = 6.1 Hz, 1H, 6-H). – ^{1}H NMR ([D$_8$]toluene): $T_{\text{coal.}}$ = −37°C (CH_2); −47°C (NCH_3). – ^{13}C NMR ([D$_8$]toluene, 24°C): δ = 45.75 (NCH_3), 67.23 (CH_2), 125.69 (C-3), 125.76 (C-4 or C-5), 126.59 (C-5 or C-4), 138.58 (C-6), 147.33 (C-2). – ^{27}Al NMR ([D$_8$]toluene): δ = 118 ($h_{1/2}$ = 3400 Hz). – MS (70 eV), *m/z* (%): 295 (46) [$M^+ - CH_3$], 135 (85) [$C_9H_{13}N^+$], 134 (54) [$C_9H_{12}N^+$], 91 (66) [$C_7H_7^+$], 58 (100) [$Me_2NCH_2^+$]. – $C_{19}H_{27}AlN_2$ (310.4): calcd. C 73.52, H 8.77, N 9.02; found C 73.81, H 9.10, N 9.05.

tert-Butylchloro{2-[(dimethylamino)methyl]phenyl}aluminium (**6**): A 1.7 M solution of Li*t*Bu in pentane (3.2 ml, 5.4 mmol) was added to a solution of **1** (1.26 g, 5.4 mmol) in Et_2O (40 ml) at −78°C. The dry-ice bath was removed, and the solution was stirred for 3 h. Subsequently, all volatile components were distilled off in high vacuo at room temp. The crude product was dissolved in hexane (40 ml), the solution separated by filtration, and the solid was washed with two 5-ml portions of hexane. The volume was then reduced to 20 ml, and crystallization at −20°C gave pure **6** (1.03 g, 75%), m.p. 62–63°C. – ^{1}H NMR: δ = 1.23 (s, 9H, *t*Bu), 1.68 (s, 3H, NCH_3), 2.01 (s, 3H, NCH_3), 2.78 (d, J = 14.0 Hz, 1H, CH_2), 3.47 (d, J = 14.0 Hz, 1H, CH_2), 6.77 (m, 1H, 3-H), 7.17 (m, 2H, 4,5-H), 7.79 (m, 1H, 6-H). – ^{13}C NMR: δ = 29.59 [$C(CH_3)_3$], 44.59 (NCH_3), 46.33 (NCH_3), 67.13 (CH_2), 124.48 (CH), 127.57 (CH), 128.55 (CH), 137.62 (C-6), 143.60 (C-2). – ^{27}Al NMR: δ = 145 ($h_{1/2}$ = 3100 Hz). – MS (70 eV), *m/z* (%): 253 (<1) [M^+], 238 (<1) [$M^+ - CH_3$], 196 (100) [$M^+ - C_4H_9$], 153 (24) [$C_7H_7AlCl^+$], 135 (94) [$C_9H_{13}N^+$], 134 (60) [$C_9H_{12}N^+$], 91 (93) [$C_7H_7^+$], 58 (60) [$Me_2NCH_2^+$]. – $C_{13}H_{21}AlClN$ (253.75): calcd. C 61.53, H 8.34, N 5.52; found C 61.89, H 8.72, N 5.54.

{2-[(Dimethylamino)methyl]phenyl}[tris(trimethylsilyl)methyl]aluminium (**7**): According to a known procedure a 1.6 M solution of LiMe in Et_2O (3.1 ml, 5.0 mmol) was added to a solution of $HC(SiMe_3)_3$ (1.08 g, 4.6 mmol) in THF (15 ml) and heated under reflux for 19 h. This red solution was then added to **1** (0.99 g, 4.3 mmol) in THF (10 ml) at −78°C, and the dry-ice bath was removed. After stirring for 3 h all volatile components were distilled off at room temp. in high vacuo. The crude material was extracted with warm hexane (70 ml), the solution was separated by filtration, and the solid residue was washed with two 10-ml portions of hexane. The volume of the solution was reduced to 40 ml, and crystallization at −20°C gave pure **7** (0.91 g, 50%), m.p. 165–167°C. – ^{1}H NMR: δ = 0.46 [s, 27H, $Si(CH_3)_3$], 1.98 (s, 3H, NCH_3), 2.20 (s, 3H, NCH_3), 2.74 (d, J = 13.7 Hz, 1H, CH_2), 3.89 (d, J = 13.7 Hz, 1H, CH_2), 6.75 (m, 1H, 3-H), 7.17 (m, 2H, 4,5-H), 8.11 (m, 1H, 6-H). – ^{13}C NMR: δ = 6.84 [$Si(CH_3)_3$], 47.20 (NCH_3), 48.21 (NCH_3), 67.92 (CH_2), 124.64 (CH), 127.51 (CH), 128.31 (CH), 137.70 (C-6), 143.25 (C-2). – ^{27}Al NMR ([D$_8$]toluene): δ = 141 ($h_{1/2}$ = 4050 Hz). – MS (70 eV), *m/z* (%): 427 (<1) [M^+], 412 (6) [$M^+ - CH_3$], 217 (37) [$C_9H_{25}Si_2^+$], 196 (56) [$M^+ - C(SiMe_3)_3$], 153 (4) [$C_7H_7AlCl^+$], 135 (75) [$C_9H_{13}N^+$], 134 (49) [$C_9H_{12}N^+$], 91 (67) [$C_7H_7^+$], 58 (100) [$Me_2NCH_2^+$]. – $C_{19}H_{39}AlClNSi_3$ (428.2): calcd. C 53.29, H 9.18, N 3.27; found C 53.48, H 9.43, N 3.07.

Dichloro{2-[(dimethylamino)methyl]phenyl}(isopropylamine)-aluminium (**1** · *i*$PrNH_2$): A solution of **1** (0.45 g, 1.9 mmol) and *i*$PrNH_2$ (0.5 ml, 5.8 mmol) in Et_2O (30 ml) was stirred for 10 min at room temp. and subsequently evaporated to dryness, which left the crude product (0.50 g). Crystallization from Et_2O (30 ml) at −20°C gave the pure title compound (0.30 g, 53%), m.p. 133–135°C. – ^{1}H NMR: δ = 0.70 [d, J = 6.4 Hz, 6H, $CH(CH_3)_2$], 2.24 (s, 6H, NCH_3), 2.62 (br. s, 2H, NH_2), 3.30 [sept, J = 6.4 Hz, 1H, $CH(CH_3)_2$], 3.40 (s, 2H, CH_2), 6.86 (m, 1H, 3-H), 7.31 (m, 2H, 4,5-H), 7.31 (m, 1H, 6-H). – ^{13}C NMR: δ = 24.00 [$CH(CH_3)_2$], 44.00 [$CH(CH_3)_2$], 45.87 (NCH_3), 64.58 (CH_2), 125.59 (CH), 126.50 (CH), 128.43 (CH), 137.01 (C-6), 146.21 (C-2). – ^{27}Al NMR: δ = 78 ($h_{1/2}$ = 1550 Hz). – MS (70 eV), *m/z* (%): 231

(2) $[\mathrm{M}^+ - i\mathrm{PrNH_2}]$, 140 (15) $[\mathrm{M}^+ - \mathrm{C_7H_7} - i\mathrm{PrNH_2}]$, 135 (29) $[\mathrm{C_9H_{13}N^+}]$, 134 (24) $[\mathrm{C_9H_{12}N^+}]$, 91 (32) $[\mathrm{C_7H_7^+}]$, 58 (58) $[\mathrm{Me_2NCH_2^+}]$, 44 (100) $[\mathrm{NMe_2^+}]$. – $\mathrm{C_{12}H_{21}AlCl_2N_2}$ (291.2): calcd. C 49.50, H 7.27, N 9.62; found C 49.01, H 7.49, N 9.65.

Dichloro{2-[(dimethylamino)methyl]phenyl}(tetrahydrofuran)aluminium (**1**·THF): **1** (0.43 g, 1.9 mmol) in THF (5 ml) was stirred for 5 min, and excess THF was removed in vacuo, which gave the crude product (0.56 g). Crystallization from hexane (30 ml) afforded pure product (0.34 g, 60%), m.p. 61–62°C. – ^{1}H NMR: δ = 1.24 [m, 4H, $\mathrm{O(CH_2C}H_2)_2$], 2.16 (s, 6H, $\mathrm{NCH_3}$), 3.32 (s, 2H, $\mathrm{CH_2}$), 3.89 [m, 4H, $\mathrm{O(C}H_2\mathrm{CH_2)_2}$], 6.85 (br. s, 1H, 3-H), 7.23 (m, 2H, 4,5-H), 7.59 (br. s, 1H, 6-H). – ^{13}C NMR: δ = 25.07 $[\mathrm{O(CH_2}C\mathrm{H_2)_2}]$, 45.83 ($\mathrm{NCH_3}$), 64.85 ($\mathrm{CH_2}$), 70.66 $[\mathrm{O(}C\mathrm{H_2CH_2)_2}]$, 125.34 (CH), 126.82 (CH), 128.57 (CH), 137.58 (C-6), 145.85 (C-2). – ^{27}Al NMR: δ = 85 ($h_{1/2}$ = 1950 Hz). – $\mathrm{C_{13}H_{20}AlCl_2NO}$ (304.2): calcd. C 51.33, H 6.63, N 4.60; found C 50.10, H 6.56, N 4.66.

X-Ray Structural Analysis of **5**: $\mathrm{C_{19}H_{27}AlN_2}$, M = 310.42 g mol^{-1}, orthorhombic space group *Pbca* (no. 61), a = 13.458(2), b = 9.572(1), c = 28.482(5) Å, U = 3669.1(9) Å^3, Z = 8, $d_{\mathrm{calcd.}}$ = 1.124 g cm^{-3}, $\mu(\mathrm{Cu}\text{-}K_\alpha)$ = 9.15 cm^{-1}, $F(000)$ = 1344. Enraf-Nonius CAD4, Cu-K_α radiation (1.5418 Å), graphite monochromator, 3247 reflections ($-h + k - l$) at 243 K with $5 \le \Theta \le 70°$, crystal size 0.4 × 0.3 × 0.3 mm^3. No absorption correction. Structure solution with direct methods[14]. Refinement[15] of the positional parameters of all atoms, with isotropic thermal parameters for hydrogen and anisotropic displacement parameters for the other atoms, converged at R = 0.044, R_w = 0.051 for 308 parameters and 2236 independent observations with $I > 1.0\sigma(I)$. The secondary extinction coefficient was refined to $1.05 \cdot 10^{-6}$. A final difference Fourier synthesis showed only fluctuation of less than 0.27 eÅ^{-3}[16].

X-Ray Structural Analysis of **1**·iPrNH$_2$: $\mathrm{C_{12}H_{21}AlCl_2N_2}$, M = 291.20 g mol^{-1}, monoclinic space group $P2_1/c$ (no. 14), a = 9.347(3), b = 18.516(5), c = 9.875(3) Å, β = 117.90(2)°, U = 1510.4(8) Å^3, Z = 4, $d_{\mathrm{calcd.}}$ = 1.281 g cm^{-3}, $\mu(\mathrm{Cu}\text{-}K_\alpha)$ = 43.60 cm^{-1}, $F(000)$ = 616. Enraf-Nonius CAD4, Cu-K_α radiation (1.5418 Å), graphite monochromator, 3655 reflections ($\pm h - k + l$ and, for $k \le 3$, the quadrant $\pm h + k + l$) at 203 K with $5 \le \Theta \le 70°$, crystal size 0.6 × 0.4 × 0.4 mm^3. No absorption correction. Structure solution with direct methods[17]. Refinement[15] with isotropic thermal parameters for hydrogen and anisotropic displacement parameters for the other atoms converged at R = 0.038, R_w = 0.051 for 234 parameters and 2695 independent observations with $I > 2.0\sigma(I)$. The displacement parameters for five hydrogen atoms refined to very small negative values and were fixed to B_{iso} = 0.1 Å^2. The secondary extinction coefficient refined to $0.71 \cdot 10^{-5}$. A final difference Fourier synthesis showed only fluctuations of less than 0.35 eÅ^{-3}[16].

☆ Dedicated to Professor *Peter Paetzold* on the occasion of his 60th birthday.

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