Syntheses of Chiral, Intramolecularly Coordinated Aluminum Bromides

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Three aluminum compounds Ar^*AlBr_2 (**1**), $Ar^*AlBr\textit{t}Bu$ (**2**), and $Ar^*{}_2AlBr$ (**3**), incorporating the chiral ligand Ar^* = 2-[1-(*S*)-$Me_2NCH(Me)]C_6H_4$, have been synthesized by salt metathesis reactions and have been characterized by multinuclear NMR (^1H, ^{13}C, and ^{27}Al), mass spectrometry, and elemental analysis. The molecular structure of compound **3** has been determined by a single-crystal X-ray analysis (space group $P2_12_12_1$). Alane **2** exists as a temperature-independent equilibrium mixture of two diastereomers in solution (ratio 45:55); results of NOE experiments on **2** are discussed. Only one isomer was found for compound **3** in solution and its dynamic behavior has been investigated by variable-temperature NMR methods; a ΔH of 56.6(4) kJ mol^{-1} and a ΔS of –0.79(1) J K^{-1}mol^{-1} were deduced from band-shape analysis of the ^1H-NMR signals of the *N*-bound methyl groups.

Introduction

The first organometallic compound with an intramolecular donor group was described by Bähr and Müller in 1955.[1] The authors synthesized the two intramolecularly coordinated alanes $[EtO(CH_2)_4]AlEt_2$ and $[Et_2N(CH_2)_3]AlEt_2$, which contain five- and six-membered rings, respectively. According to cryoscopic measurements, these air- and moisture-sensitive substances are monomeric in benzene solution.[1] Since this investigation, many more intramolecularly coordinated organometallic compounds of the Group 13 elements have been synthesized.[2] One of the driving forces behind these investigations is the need for volatile, non-pyrophoric precursors for chemical vapor deposition (CVD). Recently, it has been shown that Group 13 nitrides, which are promising materials for new microelectronic and optoelectronic devices,[3] can be grown by CVD of intramolecularly coordinated Group 13 azides.[4]

When we started our investigations of aluminum compounds, intramolecularly coordinated with the commonly used 2-[(dimethylamino)methyl]phenyl ligand, the diethyl derivative $[2\text{-}(Me_2NCH_2)C_6H_4]AlEt_2$[5] was the only known example. We investigated the tetracoordinated alanes $[2\text{-}(Me_2NCH_2)C_6H_4]AlRR'$ [R/R′ = Me/Me, Cl/Cl, Cl/Me, Cl/*t*Bu, and Cl/$C(SiMe_3)_3$] and the pentacoordinated alanes $[2\text{-}(Me_2NCH_2)C_6H_4]_2AlCl$, $[2\text{-}(Me_2NCH_2)C_6H_4]_2AlMe$, and $[2\text{-}(Me_2NCH_2)C_6H_4]AlCl_2(L)$ (L = $H_2N\textit{i}Pr$, thf).[6] In the same year, Cowley et al. published the structures of the bromide $[2\text{-}(Me_2NCH_2)C_6H_4]AlBr_2$ and the hydride $[2\text{-}(Me_2NCH_2)C_6H_4]AlH_2$, which is a dimer in the solid state.[7]

A trigonal-bipyramidal complex with two bidentate ligands and one monodentate ligand with an idealized C_2-symmetry exists as Λ and Δ enantiomers (Figure 1). In the case of the alanes $[2\text{-}(Me_2NCH_2)C_6H_4]_2AlCl$ and $[2\text{-}(Me_2NCH_2)C_6H_4]_2AlMe$, we found a rapid equilibration between the Δ and Λ isomers with respect to the ^1H-NMR time scale.[6] In order to ascertain whether a cleavage of the Al−N donor bonds is involved in this process, we synthesized some novel aluminum compounds intramolecularly coordinated through a chiral, one-armed phenyl ligand, namely 2-[1-(*S*)-(dimethylamino)ethyl]phenyl. The main advantage of this chiral ligand is illustrated by Figure 2. If we assume a fast envelope inversion of the five-membered ring in compound **A**, this species exhibits C_s point-group symmetry, i.e. the two *N*-bound methyl groups are equivalent and thus give rise to one resonance in the ^1H- and ^{13}C-NMR spectra. Similar spectra are obtained for compound **A** when the N donor atom is not coordinated to the acceptor M. Compound **B**, which incorporates the chiral phenyl ligand, shows no symmetry (C_1 point group) and therefore two resonances for the NMe_2 group are to be expected. However, if the N donor atom is not coordinated to the acceptor M, pyramidal inversion at the N atom renders the attached methyl groups equivalent on the NMR time scale, thus resulting in only one resonance. Consequently, the chiral, one-armed phenyl ligand is an ideal substituent for probing whether the amino group is coordinated to the acceptor M. This chiral ligand has previously been used in main group chemistry for similar purposes.[8]

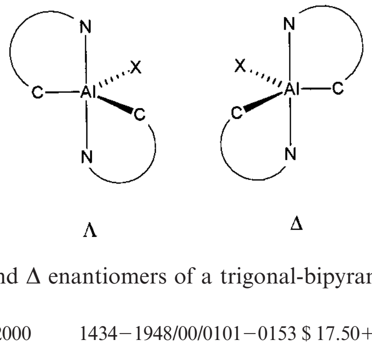

Figure 1. Λ and Δ enantiomers of a trigonal-bipyramidal complex

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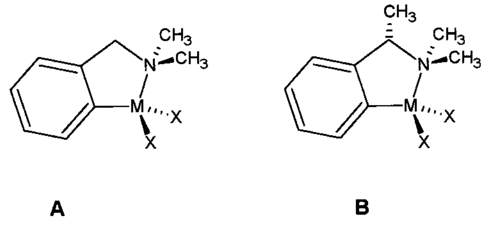
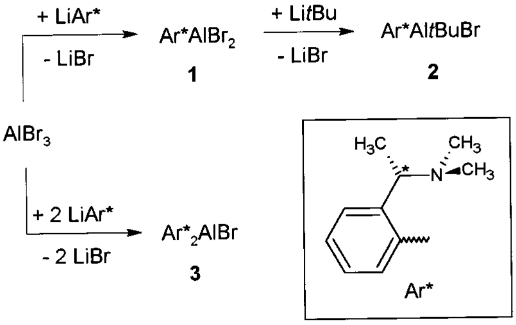


Figure 2. Complexes incorporating the achiral (**A**) and the chiral (**B**), one-armed phenyl ligand

In this paper, we report on the syntheses and properties of three chiral, intramolecularly coordinated alanes.

Results and Discussion

The intramolecularly coordinated alanes **1**, **2**, and **3**, which are accessible in high yields by salt metathesis reactions (Scheme 1), have been characterized by multinuclear NMR, mass spectrometry, and elemental analyses.



Scheme 1. Syntheses of compounds **1**, **2**, and **3**

It is known that the chemical shifts of ^{27}Al nuclei are very sensitive to the number of coordinated ligands.[9] Thus, the tetracoordination of the Al atom in compound **1** can be deduced from the ^{27}Al-NMR shift of $\delta = 129$; a similar value of $\delta = 127$ has been found for the dichloride [2-(Me_2NCH_2)C_6H_4]$AlCl_2$ incorporating the achiral, one-armed phenyl ligand.[6][10] The ^{1}H- and ^{13}C-NMR spectra of **1** each show one set of signals, in accordance with a C_1-symmetrical species having an intramolecularly coordinated dimethylamino group.

Five-membered rings, such as that in **1**, usually exist in an envelope conformation with the nitrogen atom displaced out of the AlC_3 plane. In the case of **1**, this could result in two diastereomers depending on the bending direction of the nitrogen atom. We were interested in assessing whether an envelope conformation could be "frozen" and therefore we examined compound **1** by variable-temperature ^{1}H-NMR spectroscopy. Between +80 and −80°C, the NMR spectra show only one set of signals for the chiral chelating ligand; coalescence was not observed. This means that either the inversion of the five-membered ring is fast at −80°C with respect to the NMR time scale, or that this inversion is slow but one isomer is very much favored over the other. In order to distinguish between these two alternatives, we investigated the structure of **1** by ab initio methods. Figure 3 shows the optimized geometries of the two diastereomers at the HF/6-31G(d) level of theory.[11]

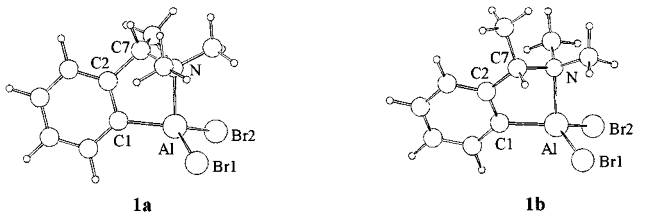
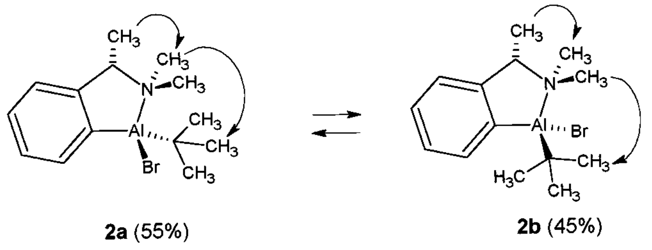


Figure 3. Calculated structures of compound **1** [HF/6-31G(d) level]; selected bond lengths [pm], angles and torsion angles [°] for **1a** (**1b**): Al−N 205.9 (205.2), Al−Br1 228.6 (229.2), Al−Br2 229.2 (228.3), Al−C1 195.6 (195.4); N−Al−C1 86.7 (86.8), N−Al−Br1 107.7 (106.2), N−Al−Br2 108.1 (107.8), C1−Al−Br1 119.6 (116.2), C1−Al−Br2 118.4 (121.6), Br1−Al−Br2 111.9 (113.0); Al−C1−C2−C7 5.8 (−3.3), C1−C2−C7−N −30.2 (−32.8)

In isomer **1a**, the H atom bound to the chiral carbon center is staggered with respect to the Me_2N group, whereas in **1b** the methyl group of the chiral carbon atom occupies this position. The difference between the calculated Gibbs free energies of **1a** and **1b** at −80°C is only 1.1 kJ/mol, which corresponds to an equilibrium mixture of **1a**/**1b** in the ratio 2:1.[12][13] Of course, too much importance should not be attached to the absolute magnitude of the ΔG value; the calculation merely shows that the two isomers **1a** and **1b** are very similar in energy. This means that the envelope inversion in **1** is not frozen at −80°C in solution, otherwise two sets of signals would be seen in the ^{1}H-NMR spectrum.

One bromide ligand in compound **1** can readily be substituted by a *tert*-butyl group to form the alane **2** in 84% isolated yield (Scheme 1). The tetracoordination of the Al atom in **2** is evident from the ^{27}Al-NMR shift of $\delta = 149$; a similar value has been found for [2-(Me_2NCH_2)C_6H_4]-$AlCltBu$ ($\delta = 145$).[6] Compound **2** consists of the two isomers **2a** and **2b** (Scheme 2), as revealed by two complete sets of signals in the ^{1}H- and ^{13}C-NMR spectra.



Scheme 2. Equilibrium between the two isomers **2a** and **2b**; arrows correspond to intense signals in the NOE experiment (see text for details)

Within experimental error, the ratio of 55:45 found for **2a**/**2b** at ambient temperature does not change over the temperature range from −80 to +80°C, which means that the transformation between **2a** and **2b** is thermally neutral ($\Delta H \approx 0$ kJ/mol). That the two species do indeed exist in equilibrium was proven by NMR methods. We did not observe coalescence of any of the signals in the ^{1}H-NMR spectra of compounds **2a**/**2b** over the temperature range from +80 to −80°C, but an NOE experiment clearly showed that an exchange between the two isomers occurs. If one nitrogen-bound methyl group of a particular isomer, e.g. **2a**, is irradiated, there is a magnetization transfer to the two nitrogen-bound methyl groups of **2b**. This can be rationalized by assuming a cleavage of the Al−N bond, followed by a 180° rotation about the Al−C bond and re-formation of the Al−N bond. Furthermore, when the N atom is not coordinated to the Al center, a rotation about the N−C* bond, N inversion, and re-formation of the Al−N bond result in an exchange of the two *N*-bound methyl groups of one particular isomer. Because of the dynamic behavior, the signals detected in the NOE experiment are caused by magnetization transfer and NOE. However, an unambiguous assignment of the two sets of signals to the respective isomer is possible; e.g. for both isomers there is an intense NOE from the methyl group bound to the chiral carbon to one nitrogen-bound methyl group, but the *tert*-butyl ligand shows an intense NOE to this NMe group in isomer **2a** and to the other NMe group in isomer **2b** (see arrows in Scheme 2).

In order to study the dynamic behavior of compound **2** in detail, we conducted 2D EXSY experiments, which we envisaged as possibly being an appropriate NMR technique.[14] Unfortunately, however, the intensities of the cross-peaks were too low for the desired evaluation (see Experimental Section).

The alane **3** was obtained in 72% yield as a pure substance (Scheme 2), which was found to crystallize in the space group $P2_12_12_1$ (Figure 4).

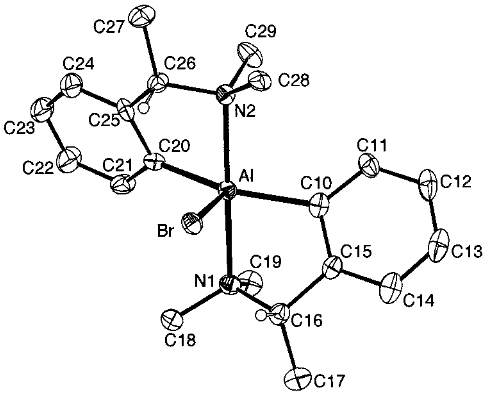


Figure 4. Molecular structure of **3** (PLATON,[20] thermal ellipsoids drawn at a 30% probability level); selected bond lengths [pm], angles and torsion angles [°]: Al−N1 217.9(7), Al−N2 216.8(7), Al−Br 239.6(2), Al−C10 202.6(8), C10−C15 140(1), C15−C16 154(1), C16−N1 150(1), C16−C17 154(1), Al−C20 199.2(8), C20−C25 142(1), C25−C26 152(1), C26−N2 150.0(9), C26−C27 1.52(1); N1−Al−N2 177.0(3), N1−Al−Br 91.7(2), N1−Al−C10 79.7(3), Al−N1−C16 103.8(5), N2−Al−Br 91.2(2), N2−Al−C20 80.0(3), Al−N2−C26 102.7(4), Br−Al−C10 105.3(2), Br−Al−C20 107.5(2), C10−Al−C20 147.2(3), C18−N1−C19 108.5(6), C28−N2−C29 108.5(6); Br−Al−N1−C18 55.5(5), Br−Al−N1−C19 177.7(4), Br−Al−N2−C28 52.9(5), Br−Al−N2−C29 175.6(5), Al−C10−C15−C16 10.8(8), Al−C20−C25−C26 5.5(8)

The aluminum atom in **3** is distorted trigonal-bipyramidally coordinated, with N1 and N2 in axial positions and C10, C20, and Br in the equatorial plane. The N1−Al−N2 axis is almost linear [N1−Al−N2 = 177.0(3)°] and the sum of the three angles in the equatorial plane is 360°. The deviation from ideal trigonal-bipyramidal geometry is manifested in an angle of 100.3(2)° between the least-squares plane comprising N1, Al, N2, and Br and the equatorial plane. Similar angles have been found in $[2\text{-}(Me_2NCH_2)\text{-}C_6H_4]_2AlMe$ (101°)[6] and $[2\text{-}(Me_2NCH_2)C_6H_4]_2Al(N_3)$ (101°)[4a] incorporating the achiral one-armed phenyl ligand. Clearly, these deviations from ideal trigonal-bypyramidal geometry can be attributed to the steric requirements of the two chelating ligands. Al−N donor bond lengths are known to vary over a wide range. The Al−N bond lengths of 217.9(7) pm for Al−N1 and 216.8(7) pm for Al−N2 in compound **3** are comparable with those found in five-fold coordinated alanes having similar chelating ligands and one electronegative substituent, e.g. 216.8(5) and 220.9(4) pm in $[2\text{-}(Me_2NCH_2)C_6H_4]_2Al(N_3)$, 218.9(2) and 221.0(2) pm in $[Me_2N(CH_2)_3]_2AlCl$, and 216.7(2) and 219.9(2) pm in $[Me_2N(CH_2)_3]_2Al(N_3)$.[4a]

As mentioned in the introduction, a trigonal-bipyramidal complex with two bidentate ligands and one monodentate ligand with an idealized C_2 symmetry exists as Λ and Δ enantiomers (Scheme 1). In the case of compound **3**, each of the chelating ligands incorporates an (*S*)-configured carbon atom, hence the Λ and Δ forms constitute a pair of diastereomers. Furthermore, five-membered rings such as those in **3** exist in envelope conformations with the nitrogen atoms being the "flap" atoms; e.g. N1 and N2 in **3** are displaced out of the respective AlC_3 planes by 79 and 81 pm. Because compound **3** contains two fused five-membered rings, three isomers for each of the Λ and Δ diastereomers are possible, depending on the "bending directions" of the nitrogen "tips". In the case of compound **3**, we found the Δ isomer with both N atoms bent in the same direction, giving an idealized C_2-symmetrical molecule.

The alane **3** shows a resonance at δ = 95 in its ^{27}Al-NMR spectrum, which is in the typical range for five-fold coordinated aluminum;[9] a similar chemical shift has been found for $[2\text{-}(Me_2NCH_2)C_6H_4]_2AlCl$ (δ = 96).[6] The ^{27}Al resonance is unchanged over the temperature range from −40 to +80°C, which means that, time-averaged, the aluminum remains pentacoordinated. However, at high temperatures, the ^{1}H-NMR spectra show only one set of signals for the two chelating ligands with only *one* singlet for the four *N*-bound methyl groups. With decreasing temperature, the resonance of the NMe_2 groups get broader and finally resolves into *two* sharp singlets at −80°C. These findings are in accord with a C_2-symmetrical compound and we assume that the geometry of the molecule in solution corresponds to that found in the crystalline state. The coalescence of the NMe_2 signals indicates that the two methyl groups of each amino group undergo rapid positional interchange with respect to the NMR time scale. This can be rationalized if one assumes that the NMe_2 group is detached from the Al atom, undergoes a subsequent 180° rotation about the C*−N bond, then N inversion, and finally a re-formation of the N−Al donor bond. From band-shape analyses of the ^{1}H-NMR signals of the NMe_2 groups, we deduced a ΔH of

56.6(4) kJ mol^{-1} and a ΔS of $-0.79(1)$ J K^{-1} mol^{-1} for this dynamic process.[15]

As mentioned in the introduction, the chiral one-armed phenyl ligand has previously been used in main group chemistry, in particular for the Group 13 elements indium[8d] and thallium[8c] by van Koten et al. They investigated $Ar^{*}InMe_2$, Ar^{*}_2InCl, $Ar^{*}TlCl_2$, and Ar^{*}_2TlCl {Ar* = 2-[1-(*S*)-$Me_2NCH(Me)]C_6H_4$} and found that in all cases the N atom is coordinated to the In or Tl atom at low temperatures in solution; for all species, a process involving cleavage and re-formation of the nitrogen−element donor bond was found by NMR methods. As in the case of the alane **3**, for the pentacoordinated species Ar^{*}_2InCl and Ar^{*}_2TlCl only one diastereomer was detected by NMR spectroscopy at low temperatures.

Experimental Section

General Remarks: All procedures were carried out under a dry nitrogen atmosphere using standard Schlenk techniques. Solvents were dried by standard procedures, distilled, and stored under nitrogen over molecular sieves (4 Å). $AlBr_3$ (> 98%, Aldrich) was sublimed prior to use; 2-[(*S*)-1-(dimethylamino)ethyl]phenyllithium was synthesized as described in the literature.[16] *t*BuLi (1.7 M in pentane) was purchased from Aldrich. − NMR: Varian Unity 500 (ambient temp.; 499.843, 130.195, and 125.639 MHz for ^{1}H, ^{27}Al, and ^{13}C, respectively); spectra were calibrated against residual protons of the deuterated solvents. ^{1}H- and ^{13}C-NMR chemical shifts are reported relative to TMS and ^{27}Al-NMR shifts relative to the external standard $[Al(acac)_3]$ in C_6D_6. As a result of the electric quadrupole moment of the ^{27}Al nucleus, the carbon atoms bound to aluminum could not be detected in the ^{13}C-NMR measurements. The assignments of the ^{1}H- and ^{13}C-NMR signals were made either with the aid of $^{1}H/^{13}C$-HMQC and NOE experiments or according to the literature.[6] The 2D EXSY ^{1}H-NMR experiments on compound **2** were performed with a Bruker DRX 500 instrument (5 mm ^{1}H probe head) over the temperature range 20−45°C. The NOESYTP pulse program, with mixing times between 0.4 and 1.2 s, was used. − Elemental analyses (C, H, N): Carlo Erba elemental analyzer, Model 1106. − MS: Finnigan MAT 95.

Band-shape analyses of nine ^{1}H-NMR spectra (−20 to +80°C) of compound **3** were performed with the program *DNMR − Sim (Version 1.0)*.[15a] The ΔH and ΔS values were calculated using the equation $\ln(k/T) = -\Delta H/RT + \Delta S/R + \ln(k_B/h)$.[15b] The standard error limits quoted for ΔH and ΔS are based on the linear regression.

Dibromo{2-[(*S*)-1-(dimethylamino)ethyl]phenyl}aluminum (1): 3.65 g (23.5 mmol) of 2-[(*S*)-1-(dimethylamino)ethyl]phenyllithium was added to a solution of 6.28 g (23.5 mmol) of $AlBr_3$ in 150 mL of toluene at −78°C. After 30 min, the cooling bath was removed and the reaction mixture was stirred at ambient temperature for 16 h. The mixture was then filtered and the solvent was removed under high vacuum. Sublimation (100°C; ca. 10^{-3} mbar) yielded 6.30 g (80%) of compound **1**. − ^{1}H NMR: δ = 0.94 (d, *J* = 6.9 Hz, 3 H, $CHCH_3$), 1.84 (s, 3 H, NCH_3), 2.05 (s, 3 H, NCH_3), 3.48 (q, *J* = 6.9 Hz, 1 H, $CHCH_3$), 6.76 (m, 1 H, 3-H), 7.08/7.14 (2 m, 2 H, 4-,5-H), 7.60 (m, 1 H, 6-H). − ^{13}C NMR: δ = 14.48 (s, $CHCH_3$), 39.19 (s, NCH_3), 45.33 (s, NCH_3), 67.71 (s, $CHCH_3$), 124.17/127.80/129.72 (3 s, 3 C, C-3/4/5), 136.32 (s, C-6), 148.31 (s, C-2). − ^{27}Al NMR: δ = 129 ($h_{1/2}$ = 1800 Hz). − HRMS: *m/z*: calcd. for $[M^{+}]$ 334.9288; found 334.9289. − MS: *m/z* (%) = 335 (13) $[M^{+}]$, 320 (21) $[M^{+} - CH_3]$, 230 (100) $[M^{+} - C_8H_9]$, 134 (48) $[C_9H_{12}N^{+}]$, 105 (20) $[C_8H_9^{+}]$, 72 (58) $[C_4H_{10}N^{+}]$. − $C_{10}H_{14}AlBr_2N$ (335.02): calcd. C 35.85, H 4.21, N 4.18; found C 35.13, H 4.20, N 4.04.

Bromo(*tert*-butyl){2-[(*S*)-1-(dimethylamino)ethyl]phenyl}aluminum (2): A 1.7 M solution of *t*BuLi in pentane (8.1 mL, 13.8 mmol) was slowly added to a solution of 4.61 g (13.8 mmol) of **1** in 100 mL of toluene at −78°C. After 15 min, the cooling bath was removed and the reaction mixture was stirred at ambient temperature for 16 h. The mixture was then filtered and the solvent was removed under high vacuum. Sublimation (115°C, ca. 10^{-3} mbar) yielded 3.61 g (84%) of a 55:45 mixture of two isomers (**2a** and **2b**). − ^{1}H NMR: Isomer **2a** (55%): δ = 0.77 (d, *J* = 6.8 Hz, 3 H, $CHCH_3$), 1.22 (s, 9 H, C_4H_9), 1.53 [s, 3 H, $N(CH_3)_2$], 2.19 [s, 3 H, $N(CH_3)_2$], 3.96 (q, *J* = 6.8 Hz, 1 H, $CHCH_3$), 6.76 (m, 1 H, 3-H), 7.10 (m, 2 H, 4-,5-H), 7.65 (m, 1 H, 6-H); isomer **2b** (45%): δ = 1.04 (d, *J* = 6.8 Hz, 3 H, $CHCH_3$), 1.16 (s, 9 H, C_4H_9), 1.88 [s, 3 H, $N(CH_3)_2$], 1.96 [s, 3 H, $N(CH_3)_2$], 3.31 (q, *J* = 6.8 Hz, 1 H, $CHCH_3$), 6.74 (m, 1 H, 3-H), 7.10 (m, 2 H, 4-,5-H), 7.68 (m, 1 H, 6-H). − ^{13}C NMR: Isomer **2a** (55%): δ = 8.62 (s, 1 C, $CHCH_3$), 29.97 (s, 3 C, C_4H_9), 36.33 [s, 1 C, $N(CH_3)_2$], 43.92 [s, 1 C, $N(CH_3)_2$], 65.50 (s, 1 C, $CHCH_3$), 123.69 (s, 1 C, C-3), 127.18/128.71 (2 s, 2 C, C-4/5), 136.59 (s, 1 C, C-6), 147.94 (s, 1 C, C-2); isomer **2b** (45%): δ = 16.26 (s, 1 C, $CHCH_3$), 29.58 (s, 3 C, C_4H_9), 41.12 [s, 1 C, $N(CH_3)_2$], 44.90 [s, 1 C, $N(CH_3)_2$], 70.20 (s, 1 C, $CHCH_3$), 123.69 (s, 1 C, C-3), 127.32/128.71 (2 s, 2 C, C-4/5), 137.26 (s, 1 C, C-6), 149.53 (s, 1 C, C-2). − ^{27}Al NMR: δ = 149 ($h_{1/2}$ = 4400 Hz). − MS: *m/z* (%) = 311 (0.3) $[M^{+}]$, 254 (100) $[M^{+} - C_4H_9]$, 211 (29) $[C_8H_9AlBr^{+}]$, 134 (81) $[C_9H_{12}N^{+}]$, 105 (15) $[C_8H_9^{+}]$, 72 (19) $[C_4H_{10}N^{+}]$. − $C_{14}H_{23}AlBrN$ (312.23): calcd. C 53.86, H 7.43, N 4.49; found C 52.72, H 7.48, N 4.37.

Bromobis{2-[(*S*)-1-(dimethylamino)ethyl]phenyl}aluminum (3): 2.18 g (14.0 mmol) of 2-[(*S*)-1-(dimethylamino)ethyl]phenyllithium was added to 1.87 g (7.0 mmol) of $AlBr_3$ in 40 mL of toluene at −78°C. After 10 min, the cooling bath was removed and the mixture was stirred for 64 h. All volatile components were then removed under high vacuum and the residue was extracted with 120 mL of hexane in a soxhlet apparatus. Removal of the hexane under high vacuum afforded 2.05 g (72%) of compound **3**. Single crystals of compound **3** were obtained from the hexane solution in the soxhlet apparatus. − ^{1}H NMR (60°C): δ = 1.12 (d, *J* = 6.4 Hz, 6 H, $CHCH_3$), 2.35 [br. s, 12 H, $N(CH_3)_2$], 4.70 (br. s, 2 H, $CHCH_3$), 7.02 (m, 2 H, 3-H), 7.20 (m, 4 H, 4-,5-H), 7.80 (m, 2 H, 6−H); (−60°C): δ = 0.82 (d, *J* = 6.7 Hz, 6 H, $CHCH_3$), 1.91 [s, 6 H, $N(CH_3)(CH_3)$], 2.45 [s, 6 H, $N(CH_3)(CH_3)$], 4.81 (q, 2 H, $CHCH_3$), 7.02 (m, 2 H, 3-H), 7.26 (m, 4 H, 4-,5-H), 7.79 (m, 2 H, 6-H); $T_{coal.}$: 22°C [$\Delta\nu$ = 270 Hz, $N(CH_3)_2$]. − ^{13}C NMR: δ = 9.19 (br. s, 2 C, $CHCH_3$), 37.12 [br. s, 2 C, $N(CH_3)_2$], 43.43 [br. s, 2 C, $N(CH_3)_2$], 63.27 (s, 1 C, $CHCH_3$), 124.77/125.73/127.76 (3 s, 6 C, C-3/4/5), 147.34 (br. s, 2 C, C-6), 151.81 (s, 2 C, C-2). − ^{27}Al NMR: δ = 95 ($h_{1/2}$ = 5500 Hz). − MS: *m/z* (%) = 387 (19) $[M^{+} - CH_3]$, 323 (15) $[M^{+} - Br]$, 254 (30) $[M^{+} - C_{10}H_{14}N]$, 134 (100) $[C_9H_{12}N^{+}]$, 105 (27) $[C_8H_9^{+}]$, 72 (64) $[C_4H_{10}N^{+}]$. − $C_{20}H_{28}AlBrN_2$ (403.34): calcd. C 59.56, H 7.00, N 6.95; found C 59.20, H 7.09, N 7.00.

Ab initio Calculations: The GAUSSIAN-94 package,[11] run on a cluster of workstations (Rechenzentrum der RWTH Aachen), was employed for all ab initio calculations. The vibrational analyses of compounds **1a** and **1b** were performed at the HF/6-31G(d) level. The total energies E_h [HF/6-31G(d) in Hartrees] and the ZPVE (in kJ mol^{-1}; in parentheses) are as follows: **1a**: −5823.185119 (634.14); **1b**: −5823.184664 (634.27).

Single Crystal X-ray Structure Determination of 3: $C_{20}H_{28}AlBrN_2$, Enraf−Nonius CAD4 diffractometer; Mo-K_α radiation, λ =

0.71073 Å, graphite monochromator; data collection by ω scans at 243 K; colorless crystal, $0.20 \times 0.28 \times 0.36$ mm, orthorhombic space group $P2_12_12_1$ (No. 19); $a = 9.452(2)$, $b = 10.937(3)$, $c = 19.225(4)$ Å, $U = 1987(2)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.35$ g/cm^3, μ(Mo-K_α) = 20.95 cm^{-1}; 3924 reflections were collected in the scan range $2 < \theta < 25°$. After Lorentz and polarization corrections, an empirical absorption correction on the basis of azimuthal scans[17] (min. trans. 0.765, max. trans. 1.000) was applied prior to averaging symmetry related intensity data. 2752 independent observations with $I > \sigma(I)$ were used in the structure solution by direct methods;[18] refinement with the SDP program system[19] for 217 variables; all non-hydrogen atoms were refined with anisotropic displacement parameters; hydrogen atoms were included as a riding model [C−H = 98 pm, $U_{iso}(H) = 1.3\ U_{iso}(C)$]. $R = 0.069$, $R_w = 0.057$, $w^{-1} = \sigma^2(F_o)$, GoF = 1.134. Max. residual electron density: 0.786 eÅ^{-3}.

Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-127942. Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. [Fax: (internat.) +44 (0)1223/336033; E-mail: deposit@ccdc.cam.ac.uk].

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