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Azaaluminatranes Exhibiting Unusual Coordination Geometries for Aluminum

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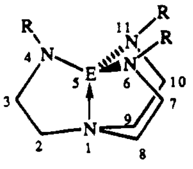
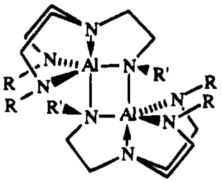
The new monomeric azaaluminatrane $Al(\textit{tert}\text{-}BuMe_2SiNCH_2CH_2)_3N$, **6**, was prepared by the reaction of $[Al(NMe_2)_3]_2$, **7**, and $(\textit{tert}\text{-}BuMe_2SiNHCH_2CH_2)_3N$, **11**, and was characterized by ^1H, ^{13}C, ^{27}Al, and ^{29}Si NMR, and IR spectroscopies and mass spectrometry. Its analogue $Al(Me_3SiNCH_2CH_2)_3N$, **3**, was structurally characterized and shown to contain a trigonal monopyramidal aluminum center. The dimeric azaaluminatrane $[Al(Me_3SiNCH_2CH_2)_2(HNCH_2CH_2)N]_2$, **5**, possesses an unusual cis configuration of the central four-membered ring, and the aluminum atoms display a distorted trigonal bipyramidal coordination sphere. Crystal data: **3**, $a = 13.503(5)$ Å, $b = 10.621(4)$ Å, $c = 17.840(6)$ Å, $\beta = 93.29(3)°$, $V = 2554(2)$ Å^3, $Z = 4$, space group $P2_1/c$, $R = 5.2\%$; **5**, $a = 12.134(3)$ Å, $b = 17.049(4)$ Å, $c = 18.297(5)$ Å, $\beta = 100.02(2)°$, $V = 3726(2)$ Å^3, $Z = 4$, space group $P2_1/n$, $R = 4.6\%$. ^{27}Al NMR chemical shifts for a series of Al—N compounds with aluminum coordination numbers ranging from three to six show increased shielding with increasing coordination number.

Introduction

The chemistry of compounds containing Al—N bonds has flourished over the past several years, mainly due to current interest in developing optimum AlN precursors.[1–5] Recently we reported the preparation and characterization of group 13 azatranes[6] such as **1–4**. These compounds exhibit monomeric or dimeric behavior, depending on the nature of the central atom and on the bulkiness of the pseudoequatorial substituents, rendering the central atom in the monomers or dimers four- or five-coordinate, respectively. Compound **2** was shown by ^1H VT NMR spectroscopy to undergo an interesting dynamic process in solution, consisting of a concerted interconversion of the Δ and Λ enantiomers. Azaaluminatrane **4** was also shown to be able to take part in a novel and complex transmetalation reaction.[6] Because of the volatility of these azatranes, they are attractive to evaluate as MOCVD precursors for nitride films.





	E	R	R'
1	B	Me	–
2	B	SiMe₃	–
3	Al	SiMe₃	–
6	Al	SiMe₂-*tert*-Bu	–
4	Al	Me	Me
5	Al	SiMe₃	H

Here we report on the group 13 azatranes **5**, which is dimeric, and **6**, which is monomeric. The configuration of the substituents at the central four-membered Al_2N_2 ring in **5** is cis as shown by X-ray crystallography. Compound **5** constitutes the first example of a pentacoordinate aluminum surrounded exclusively by nitrogen ligands. Monomeric **3** and **6** containing four-coordinate aluminums are rare examples of the trigonal monopyramidal (TMP) coordination environment for aluminum and the main-group elements in general. A comparison of the ^{27}Al NMR chemical shifts among compounds in which the central aluminum is coordinated only by nitrogens is shown to clearly reveal an upfield trend with increasing coordination number of the aluminum. As will also be shown, azaaluminatranes **3** and **6**, despite the very bulky ligands at the equatorial nitrogens, are freely fluxional in solution even down to −95 °C in contrast to the boron analogue **2**.

Experimental Section

All reactions were carried out under argon with the strict exclusion of moisture using Schlenk or drybox techniques.[7] Solvents were dried over and distilled from Na/benzophenone under nitrogen. Deuterated benzene and toluene were dried over and distilled from CaH_2 under an argon atmosphere.

$[Al(NMe_2)_3]_2$, **7**, $Al(N\text{-}i\text{-}Pr_2)_3$, and $Al[N(SiMe_3)_2]_3$ were prepared using published procedures.[8–10] $AlCl_3$, $LiN\text{-}i\text{-}Pr_2$, $LiN(SiMe_3)_2$, Me_3SiCl, and $t\text{-}BuMe_2SiCl$ were purchased from Aldrich and were used as received.

NMR spectra were recorded at 25 °C, unless otherwise stated, on a Varian VXR 300 with deuterated solvents as an internal lock using sealed 5-mm NMR tubes. ^1H (299.949-MHz) and ^{13}C (75.429-MHz) spectra were internally referenced to the corresponding Me_4Si signals. ^{27}Al (78.157-MHz) spectra were measured at 70 °C to decrease the line width of the signals and were referenced to the external standard

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0.2 M $Al(ClO_4)_3$/0.1 M $HClO_4$ in D_2O. The chemical shifts were corrected for the difference in chemical shift between D_2O and the lock solvent used. The background signal, which was found as a broad peak at ~61 ppm ($\Delta\nu_{1/2}$ = 4100 Hz at 30 °C), did not interfere with our spectra owing to its low intensity when concentrated sample solutions were used. ^{29}Si (59.591 MHz) spectra were referenced to a 30% by volume solution of Me_4Si in benzene-d_6 as an external standard. Pulses of 90° and a relaxation delay of 25 s were used for acquisition of the ^{29}Si spectra.

Mass spectra were recorded on a Finnigan 4000 low-resolution (70 eV, EI; NH_3, CI) instrument and a Kratos MS-50 high-resolution instrument. The masses are reported for the most abundant isotope present. IR spectra (4000-400 cm^{-1}) were taken on IBM IR-98 and DigiLab FTS-7 FTIR spectrometers using Nujol mulls between KBr disks or as KBr pellets. Spectra were calibrated with a 0.05-mm polystyrene film. Intensities are noted as very strong (vs), strong (s), medium (m), weak (w), and very weak (vw). Elemental analyses were carried out by Desert Analytics, Knoxville, TN. Melting points (uncorrected) were measured in sealed capillaries.

Tris(diisopropylamino)aluminum,[1b,8a,9] 8a. Because very few spectral data appear in the earlier reports on Al(N-*i*-$Pr_2)_3$ and Al[N$(SiMe_3)_2]_3$, we record them here for the sake of completeness. Mp: 60−61 °C (lit.[8a] 58−59 °C). ^{1}H NMR (benzene-d_6): δ 1.25 (d, 6 H, CH_3, $^{3}J_{CH}$ = 6.5 Hz, $^{1}J_{CH}$ = 124.0 Hz, ^{13}C satellites), 3.41 (sept., 1 H, CH, $^{3}J_{CH}$ = 6.5 Hz, $^{1}J_{CH}$ = 131.5 Hz, ^{13}C satellites). ^{13}C NMR (benzene-d_6): δ 25.6 (CH_3), 46.2 (CH). ^{27}Al NMR (benzene-d_6, 70 °C): δ 143 ± 1 ($\Delta\nu_{1/2}$ = 3600 Hz). LRMS (EI): *m/z* (ion, relative intensity) 327 (M^+, 2), 312 (M − CH_3+, 1), 226 (M − NH-*i*-Pr_2^+, 28), 211 (45), 183 (20), 169 (9), 142 (10), 128 (29), 127 (19), 126 (40), 112 (9), 100 (N-*i*-Pr_2^+, 10), 98 (6), 86 (34), 84 (19), 70 (11), 58 (10), 57 (29), 44 (100). CIMS (positive ion detection): *m/z* (ion, relative intensity) 327 (M^+, 0.2), 226 (M − HN-*i*-Pr_2^+, 13), 211 (13), 183 (6), 139 (6), 124 (3), 100 (N-*i*-Pr_2^+, 100).

Tris[bis(trimethylsilyl)amino]aluminum,[9,10] 8b. Mp: 187−190 °C (lit.[10a] 188 °C). ^{1}H NMR (toluene-d_8): δ 0.33 (s, 54 H, CH_3, $^{1}J_{CH}$ = 117.9 Hz, ^{13}C satellites, $^{2}J_{SiCH}$ = 6.4 Hz, ^{29}Si satellites) (lit.[10a,b] δ 0.25 in CCl_4). ^{13}C NMR (toluene-d_8): δ 6.03 (q sept., $^{1}J_{CH}$ = 118.0 Hz, $^{3}J_{CH}$ = 1.8 Hz, $^{1}J_{SiC}$ = 55.6 Hz, ^{29}Si satellites). ^{27}Al NMR (toluene-d_8, 70 °C): δ 136 ± 1 ($\Delta\nu_{1/2}$ = 8200 Hz). ^{29}Si NMR (toluene-d_8): δ 0.34. HRMS (EI): calcd for $C_{18}H_{54}N_3Si_6Al$ (M^+), *m/z* 507.27488; found, 507.27614; calcd for $C_{17}H_{51}N_3Si_6Al$ (M − CH_3^+), *m/z* 492.25140; found, 492.25108. LRMS (EI): *m/z* (ion, relative intensity) 507 (M^+, 1), 492 (M − CH_3^+, 8), 404 (3), 347 (M − N$(SiMe_3)_2^+$, 10), 331 (14), 291 (4), 275 (23), 259 (5), 202 (75), 186 (6), 146 (25), 130 (43), 73 ($SiMe_3^+$, 100).

Tris(trimethylsilyl)tren,[11] 9. Method A. The reaction of lithiated tetraamine tren $N(CH_2CH_2NH_2)_3$, **10**, with Me_3SiCl as described earlier in a paper from our laboratory[11a] was used, improving the reported yield of 54% to 75%. Here we also report complete spectroscopic data for **9**. Bp: 110 °C at 5 × 10^{-3} Torr. ^{1}H NMR (benzene-d_6): δ 0.13 (s, 9 H, $Si(CH_3)_3$, $^{1}J_{CH}$ = 117.9 Hz, ^{13}C satellites, $^{2}J_{SiH}$ = 6.6 Hz, ^{29}Si satellites), 0.80 (bt, 1 H, NH, $^{3}J_{HNCH}$ = 7 Hz), 2.36 (t, 2 H, $N(CH_2)_3$, $^{3}J_{HH}$ = 6.2 Hz), 2.76 (td, 2 H, $SiNCH_2$, $^{3}J_{HCCH}$ = 6.3 Hz, $^{3}J_{HNCH}$ = 7.4 Hz). ^{13}C NMR (benzene-d_6): δ 0.3 (q bm, $Si(CH_3)_3$, $^{1}J_{CH}$ = 117.8 Hz, $^{1}J_{SiC}$ = 56.4 Hz, ^{29}Si satellites), 40.2 (tq, $SiNCH_2$, $^{1}J_{CH}$ = 132.6 Hz, $^{2}J_{CNH}$ = $^{2}J_{CCH}$ = 2.3 Hz), 58.9 (tm, $N(CH_2)_3$, $^{1}J_{CH}$ = 130.8 Hz). ^{29}Si NMR (benzene-d_6): δ 2.55; LRMS (EI): *m/z* (ion, relative intensity) 363 (M + H^+, 64), 347 (M − CH_3^+, 32), 260 (M − $CH_2NHSiMe_3^+$, 42), 229 (9), 171 (100), 157 (24), 116 ($CH_2CH_2NHSiMe_3^+$, 36), 102 ($CH_2NHSiMe_3^+$, 31), 73 ($SiMe_3^+$, 78). IR (neat between KBr disks, 4000−400 cm^{-1}): ν 3384 m (ν(NH)), 2955 vs ($\nu_{as}(CH_3)$), 2898 s ($\nu_s(CH_3)$), 2841 s ($\nu_{as}(CH_2)$), 2806 s ($\nu_s(CH_2)$), 2734 w, 1449 m, 1398 vs ($\delta_{as}(CH_3)$), 1248 vs ($\delta_s(CH_3)$), 1125 vs, 1110 vs (ν(NC)), 1050 s, 990 w, 932 vs, 874 sh ($\varrho_{as}(CH_3)$), 836 vs ($\varrho_{as}(CH_3)$), 744 s ($\varrho_s(CH_3)$), 679 s (ν(SiC)), 613 m.

Method B. Me_3SiCl (13 mL, 0.10 mol) was added dropwise to a solution of tren **10** (4.9 g, 0.033 mol) and Et_3N (16 mL) in 350 mL of Et_2O at 0 °C. After being stirred over night at room temperature, the solution was filtered, the solvent was removed, and vacuum distillation afforded 5.67 g (46.8%) of **9**.

Tris(trimethylsilyl)azaaluminatrane,[12] 3. Compound **3** prepared according to our procedure[6] was purified by sublimation at 70−80 °C at 1 × 10^{-2} Torr. Single crystals suitable for X-ray diffraction experiments were grown from a pentane solution stored in a refrigerator for several weeks. The characterization of **3** by NMR techniques was reported previously.[6] IR (KBr pellet, 4000−400 cm^{-1}): ν 2953 m ($\nu_{as}(CH_3)$), 2888 m, 2834 m, 1465 w, 1449 w, 1400 w, 1359 w, 1340 w, 1331 w, 1265 m, 1246 vs ($\delta_s(CH_3)$), 1143 w, 1087 s (ν(CN)), 1066 m, 1049 m, 1031 m, 969 vs, 832 vs ($\varrho_{as}(CH_3)$), 744 s ($\varrho_s(CH_3)$), 726 w, 669 m, 663 w, 641 vw, 621 vw, 579 m, 576 m, 533 m. LRMS (EI): *m/z* (ion, relative intensity) 386 (M^+, 51), 371 (M − CH_3^+, 71), 358 (M − $CH_2CH_2^+$, 5), 284 (M − CH_2NSiMe_3-H^+, 100), 256 (9), 242 (5), 227 (5), 215 (7), 188 (6), 185 (7), 183 (8), 178 (10), 171 (19), 157 (7), 116 (11), 102 (11), 73 ($SiMe_3^+$, 68), 59 (14). CIMS (positive ion detection): *m/z* (ion, relative intensity) 387 (M + H^+, 100), 363 (18), 291 (18), 200 (5), 116 (21), 107 (46), 90 (70).

Tris(*tert*-butyldimethylsilyl)tren, 11. Method A. Tren **10** (4.82 g, 33.0 mmol) in 150 mL of THF was lithiated with 48 mL of a 2.1 M solution of *n*-BuLi at −60 °C and then stirred overnight at room temperature. This suspension was quenched with a solution of *t*-$BuMe_2SiCl$ (14.91 g, 98.94 mmol) in 150 mL of THF at −40 °C and then stirred overnight at room temperature. THF was removed under vacuum, and 250 mL of pentane was added. The precipitate of LiCl was filtered off, pentane was removed under vacuum, and the product was vacuum distilled giving 7.30 g (45.3%) of **11**. Bp: 170 °C at 0.1 Torr. ^{1}H NMR (benzene-d_6): δ 0.03 (s, 6 H, $Si(CH_3)_2$, $^{1}J_{CH}$ = 118.0 Hz, ^{13}C satellites, $^{2}J_{SiH}$ = 6.2 Hz, ^{29}Si satellites), 0.73 (t, 1 H, NH, $^{3}J_{HNCH}$ = 7.2 Hz), 0.93 (s, 9 H, $C(CH_3)_3$, $^{1}J_{CH}$ = 124.5 Hz, ^{13}C satellites, $^{3}J_{SiH}$ = 5.6 Hz, ^{29}Si satellites), 2.31 (t, 2 H, $N(CH_2)_3$, $^{3}J_{HH}$ = 6.2 Hz, $^{1}J_{CH}$ = 132.3 Hz, ^{13}C satellites), 2.75 (dt, 2 H, $SiNCH_2$, $^{3}J_{HCCH}$ = 6.2 Hz, $^{3}J_{HNCH}$ = 7.3 Hz, $^{1}J_{CH}$ = 131.8 Hz, ^{13}C satellites). ^{13}C NMR (benzene-d_6): δ −4.7 (qqd, $Si(CH_3)_2$, $^{1}J_{CH}$ = 118.0 Hz, $^{3}J_{CSiCH}$ = $^{3}J_{CSiNH}$ = 1.8 Hz, $^{1}J_{SiC}$ = 55.3 Hz, ^{29}Si satellites), 18.7 (s, *C*$(CH_3)_3$, $^{1}J_{CC}$ = 31.2 Hz, ^{13}C satellites, $^{1}J_{SiC}$ = 60.7 Hz, ^{29}Si satellites), 26.8 (q sept., C(*C*$H_3)_3$, $^{1}J_{CH}$ = 124.6 Hz, $^{3}J_{CH}$ = 5.6 Hz, $^{1}J_{CC}$ = 31.2 Hz, ^{13}C satellites), 41.0 (ttd, $SiNCH_2$, $^{1}J_{CH}$ = 133.1 Hz, $^{2}J_{CCH}$ = $^{2}J_{CNH}$ = 2.5 Hz, $^{1}J_{CC}$ = 39.2 Hz, ^{13}C satellites), 59.4 (tm, $N(CH_2)_3$, $^{1}J_{CH}$ = 132.3 Hz, $^{1}J_{CC}$ = 38.7 Hz, ^{13}C satellites). ^{29}Si NMR (benzene-d_6): δ 7.50; LRMS (EI): *m/z* (ion, relative intensity) 489 (M + H^+, 0.05), 473 (M − CH_3^+, 0.3), 431 (M − *t*-Bu^+, 0.1), 344 (11), 226 (5), 213 (35), 199 (11), 187 (38), 158 (34), 144 (29), 129 (6), 115 ($SiMe_2$-*t*-Bu^+, 7), 100 (13), 88 (10), 73 ($SiMe_3^+$, 100), 59 (18), 58 ($SiMe_2^+$, 7), 57 (*t*-Bu^+, 11), 44 (10), 43 (10). CIMS (positive ion detection): *m/z* (ion, relative intensity) 489 (M + H^+, 100), 375 (10), 344 (12), 332 (8), 299 (11), 261 (4). IR (neat between KBr disks, 4000−400 cm^{-1}): ν 3691 s (ν(NH)), 2954 vs ($\nu_{as}(CH_3)$), 2930 vs, 2885 s ($\nu_s(CH_3)$), 2856 vs, 1470 vs, 1464 vs, 1449 sh, 1401 vs, 1389 s, 1360 m, 1279 w, 1253 vs ($\delta_s(CH_3)$), 1209 w, 1127 vs, 1114 vs, 1048 s, 1005 s, 988 vw, 936 s, 906 sh, 853 sh, 830 vs, 808 s, 770 vs, 724 sh, 678 w, 658 s, 570 w. Anal. Calcd for $C_{24}H_{60}N_4Si_3$: C, 58.95; H, 12.37; N, 11.46. Found: C, 59.41; H, 12.80; N, 11.41.

Method B. This method is analogous to that used to silylate $(H_2NCH_2)_3CR$.[13] A solution of *t*-$BuMe_2SiCl$ (10.5 g, 69.8 mmol) in 100 mL of Et_2O was added dropwise to an ice-cooled solution of tren **10** (3.3 g, 2.3 mmol) and Et_3N (10 mL, 72 mmol) in 250 mL of Et_2O while stirring. The white suspension was then stirred at room temperature overnight after which solid Et_3NHCl was filtered off and

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all volatiles were removed under vacuum. Further workup and characterization was identical to that in Method A, yielding 4.45 g (40.3%) of **11**.

Tris(*tert*-butyldimethylsilyl)azaaluminatrane,[14] **6.** A solution of **7** (0.93 g, 5.8 mmol) in 80 mL of toluene was added dropwise to a stirred solution of tetraamine **11** (2.86 g, 5.84 mmol) in 100 mL of toluene over a period of 15 min. The reaction mixture was heated at 100 °C with stirring for 24 h. After cooling to room temperature, a small amount of a fine (probably polymeric) precipitate was filtered off. The volume of the filtrate was reduced under vacuum to a third, and the resulting precipitate was collected and washed with 2 × 1.5 mL of toluene giving 1.55 g (52%) of **6** as a white solid, which was further purified for characterizational purposes by sublimation at 130 °C at 2×10^{-3} Torr. Mp: 163−164 °C. ^{1}H NMR (toluene-d_8) δ 0.18 (s, 6 H, $SiCH_3$, $^{1}J_{CH} = 116.4$ Hz, ^{13}C satellites, $^{2}J_{SiH} = 6.1$ Hz, ^{29}Si satellites), 1.01 (s, 9 H, $C(CH_3)_3$, $^{1}J_{CH} = 124.3$ Hz, ^{13}C satellites, $^{3}J_{SiH} = 5.4$ Hz, ^{29}Si satellites), 2.12 (t, 2 H, $N(CH_2)_3$, $^{3}J_{HH} = 5.3$ Hz, $^{1}J_{CH} = 138.4$ Hz, ^{13}C satellites), 2.85 (t, 2 H, $SiNCH_2$, $^{3}J_{HH} = 5.3$ Hz, $^{1}J_{CH} = 135.0$ Hz, ^{13}C satellites). ^{13}C NMR (toluene-d_8): δ −2.9 (qm, $SiCH_3$, $^{1}J_{CH} = 117.3$ Hz, $^{1}J_{SiC} = 54.8$ Hz, ^{29}Si satellites), 20.6 (s, $\mathit{C}(CH_3)_3$, $^{1}J_{SiC} = 59.3$ Hz, ^{29}Si satellites, $^{1}J_{CC} = 31.0$ Hz, ^{13}C satellites), 27.7 (q sept., $C(\mathit{C}H_3)_3$, $^{1}J_{CH} = 124.3$ Hz, $^{3}J_{CH} = 5.7$ Hz, $^{1}J_{CC} = 31.0$ Hz, ^{13}C satellites), 42.6 (tt, $SiNCH_2$, $^{1}J_{CH} = 135.2$ Hz, $^{2}J_{CH} = 1.8$ Hz), 58.8 (tm, $N(CH_2)_3$, $^{1}J_{CH} = 136.4$ Hz). ^{27}Al NMR (toluene-d_8, 80 °C): δ 131 ± 1 ($\Delta\nu_{1/2} = 3030$ Hz). ^{29}Si NMR (toluene-d_8): δ 3.91. HRMS (EI): calcd for $C_{24}H_{57}N_4Si_3Al$ (M^+), *m/z* 512.37064; found, 512.37033. LRMS (EI): *m/z* (ion, relative intensity) 512 (M^+, 7), 497 ($M - CH_3^+$, 3), 455 ($M - t\text{-}Bu^+$, 100), 397 ($M - SiMe_2\text{-}t\text{-}Bu^+$, 1), 368 (3), 344(1), 341 (1), 325 (5), 298 (1), 283 (3), 199 (5), 178 (5), 169 (3), 158 (3), 144 (3), 73 ($SiMe_3^+$, 61), 59 (10), 57 ($t\text{-}Bu^+$, 25). CIMS (positive ion detection): *m/z* 513 ($M + H^+$, 100), 489 (18), 455 ($M - t\text{-}Bu^+$, 18). CIMS (negative ion detection): *m/z* 529 ($M + NH_3^-$, 17), 511 ($M - H^-$, 82), 487 (100). IR (KBr pellet, 4000−400 cm^{-1}): ν 2955 vs, 2930 vs, 2895 s, 2887 s, 2857 vs, 2817 s, 1472 s, 1465 s, 1404 m, 1400 m, 1388 w, 1361 w, 1251 s ($\delta_s(CH_3)$), 1127 m, 1112 m, 1080 w, 1060 w, 1048 m, 1006 w, 968 s, 937 m, 828 vs, 768 s, 668 w, 660 w, 599 w, 570 w, 527 w. Anal. Calcd for $C_{24}H_{57}N_4Si_3Al$: C, 56.19; H, 11.20; N, 10.92. Found: C, 55.65; H, 11.38; N, 10.57.

***cis*-Bis(trimethylsilyl)azaaluminatrane Dimer,**[15] **5.** Compound **5** was prepared during attempts to grow single crystals of **3** from a pentane solution at −20 °C (see Discussion for details). Clear plates of **5** were washed with pentane and dried in vacuum for 45 min. Mp: 160−165 °C dec. ^{1}H NMR (benzene-d_6): δ 0.253, 0.255 (s, 18 H, $Si(CH_3)_3$ groups, $^{1}J_{CH} = 117.9$ Hz, ^{13}C satellites, $^{2}J_{SiCH} = 6.2$ Hz, ^{29}Si satellites), 2.05 (ddd, 1 H, $J = 5.0$, 12.4, 12.4 Hz), 2.20 (ddd, 1 H, $J = 1.5$, 4.2, 12.2 Hz), 2.28−2.44 (m, 3 H), 2.46−2.56 (m, 1 H), 2.56−2.66 (m, 1 H), 2.70−2.97 (m, 4 H), 3.23−3.35 (m, 1 H). ^{13}C NMR (benzene-d_6): δ 1.9, 2.0 (s, $Si(CH_3)_3$ groups, $^{1}J_{SiC} = 55$ Hz, ^{29}Si satellites), 42.0, 43.8, 44.1 (s, $RN\mathit{C}H_2$ groups), 57.8, 62.6, 62.9 (s, $N(\mathit{C}H_2)_3$). ^{27}Al NMR (benzene-d_6): δ 86 ($\Delta\nu_{1/2} = 1930$ Hz 25 °C, 1080 Hz at 70 °C). ^{29}Si NMR (benzene-d_6): δ −1.30, −2.94. HRMS (EI): calcd for $C_{24}H_{62}N_8Si_4Al_2$(M^+), *m/z* 628.38052; found, 628.37925. LRMS (EI): *m/z* (ion, relative intensity) 628 (M^+, 2), 613 ($M - CH_3^+$, 1), 573 (1), 513 ($M - CH_2CH_2NSiMe_3^+$, 4), 511 (2), 471 (1), 411 (1), 398 (5), 315 (4), 313 (2), 260 (1), 188 (21), 171 (25), 159 (11), 157 (12), 147 (10), 143 (6), 117 (11), 116 (93), 115 (19), 102 (25), 100 (17), 99 (99), 87 (16), 85 (10), 75 (28), 74 (12), 73 ($SiMe_3^+$, 100), 70 (15), 59 (16), 58 (14), 56 (17), 45 (17), 44 (81), 43 (16), 42 (12). CIMS (positive ion detection): *m/z* (ion, relative intensity) 629 ($M + H^+$, 100), 363 (13), 291 (36), 219 (7). CIMS (negative ion detection): *m/z* (ion, relative intensity) 627 ($M - H^-$, 100). IR (KBr pellet, 4000−400 cm^{-1}): ν 3277 w (ν(NH)), 3267 w (ν(NH)), 2946 vs, 2891 vs, 2856 vs, 2829 s, 2799 m, 1477 w, 1461 m, 1451 vw, 1437 vw, 1396 w, 1370 w, 1353 m, 1332 m, 1300 m, 1257 sh, 1242 vs, 1209 m, 1153 m, 1116 s, 1074 vs, 1055 w, 1039 s, 1009 s, 969 vs, 952 vs, 925 w, 900 s, 845 vs, 833 vs, 799 s, 744 vs, 668 s, 643 s, 585 s, 549 vs, 508 vs, 481 s. Anal. Calcd for $C_{24}H_{62}N_8Si_4Al_2$: C, 45.82; H, 9.93; N, 17.81. Found: C, 45.73; H, 9.48; N, 17.62.

Table 1. Crystallographic Data for **3** and **5**

	3	**5**
formula	$AlC_{15}H_{39}N_4Si_3$	$Al_2C_{24}H_{62}N_8Si_4$
fw	386.74	629.11
α (Å)	13.503 (5)	12.134 (3)
b (Å)	10.621 (4)	17.049 (4)
c (Å)	17.840 (6)	18.297 (5)
β (deg)	93.29 (3)	100.02 (2)
V (Å^3)	2554 (2)	3726 (2)
Z	4	4
space group	$P2_1/c$ (No. 14)	$P2_1/n$ (No. 14)
T (°C)	−20 ± 1	−50 ± 1
λ (Å)	0.71069	1.54178
d_{calcd} (g cm^{-3})	1.006	1.122
μ (cm^{-1})	2.18	21.36
transm coeff	1.00	0.54/0.95
R (%)	5.2	4.6
R_w (%)	5.8	4.3

Single-Crystal X-ray Diffraction Studies of 3 and 5. Colorless crystals of **3** and **5** were mounted in 0.5-mm glass capillaries in a nitrogen-filled glovebox and flame-sealed. The diffraction intensity data for **3** and **5** were collected on Rigaku AFC6R and Siemens P4RA instruments, respectively, both equipped with low-temperature devices. Crystal data, experimental conditions for data collection, solution and structure refinement are listed in Table 1. The intensity of three standard reflections remained constant within the errors of measurement throughout data collection for **3** while a decay correction was applied for **5**. Lorentz and polarization corrections were applied. Azimuthal scans of several reflections indicated no need for an absorption correction for **3** while a semiempirical absorption correction based on a series of ψ-scans was applied in the case of **5**. The structures of **3** and **5** were solved by direct methods and refined by a full-matrix least-squares method, using TEXSAN (VAX)[16] and SHELXTL PLUS (VMS),[17] respectively. All non-hydrogen atoms were refined with anisotropic thermal parameters. All hydrogens in **3** were placed and refined. For **5**, the C−H hydrogen atoms were fixed with distances of 0.96 Å. The N−H hydrogen atoms were allowed to refine isotropically with free positional parameters. Neutral atom scattering factors were taken from ref 18.

Results and Discussion

Syntheses. The synthesis of silylated tetraamines **9** and **11**, which have attracted considerable attention recently,[19] was accomplished here by the reaction of a silylchloride with a lithium salt of the tetraamine tren (reaction 1) or by the direct reaction of tren with a silylchloride in the presence of a base (reaction 2), the former method giving a somewhat higher yield. Silylations of tripodal triamines by the latter method were reported recently.[13a]

$$RR'_2SiCl + (LiHNCH_2CH_2)_3N \xrightarrow[-LiCl]{} (RR'_2SiHNCH_2CH_2)_3N \quad (1)$$

9: R = R′ = Me
11: R = *t*-Bu; R′ = Me

$$t\text{-}BuMe_2SiCl + \underset{\mathbf{10}}{(H_2NCH_2CH_2)_3N} \xrightarrow[-Et_3NHCl]{Et_3N} \underset{\mathbf{11}}{(t\text{-}BuMe_2SiHNCH_2CH)_3N} \quad (2)$$

The monomeric azaaluminatrane **6** was synthesized by the transamination reaction of **7** with the tetraamine **11** according

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(14) 4,6,11-Tris(*tert*-butyldimethylsilyl)-1,4,6,11-tetraaza-5-aluminatricyclo-[3.3.3.0^{1,5}]undecane.

(15) 4,6-Bis(trimethylsilyl)-1,4,6,11-tetraaza-5-aluminatricyclo[3.3.3.0^{1,5}]-undecane.

(16) *TEXSAN-TEXRAY Structure Analysis Package*; Molecular Structure Corporation: Woodlands, TX, 1985.

(17) *SHELXTL PLUS*; Siemens Analytical X-ray Instruments, Inc.: Madison, WI.

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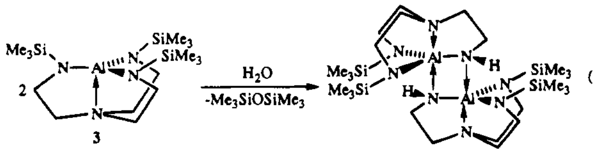
to reaction 3 in 52% yield. Compound **6** can be purified by

$$\tfrac{1}{2}[\mathrm{Al(NMe_2)_3}]_2 + \underset{\mathbf{11}}{(t\text{-}\mathrm{BuMe_2SiNHCH_2CH_2)_3N}} \xrightarrow{\text{toluene}} 3\,\mathrm{Me_2NH} + \mathbf{6} \quad (3)$$

crystallization from toluene. The ^{1}H, ^{13}C, ^{27}Al, and ^{29}Si NMR data are similar for **3**[6] and **6** and they are consistent with a 3-fold symmetry of these molecules. The monomeric aluminaazatranes **3** and **6** are moisture-sensitive solids that are easily sublimed at reduced pressure. It is worthy of note that tetraamine **11** in the presence of the monomeric amide $Al[N(SiMe_3)_2]_3$, gave no aluminaazatrane **6** even after several hours of reflux. ^{1}H NMR spectroscopy revealed only the starting compounds in the reaction solution. For the sake of argument, let us assume that a proton transfer from the NH groups of the tetraamines **9** and **11** to the nitrogen of the NR_2 groups of amides $(i\text{-}Pr_2N)_3Al$ and $[(Me_3Si)_2N]_3Al$ is a more important step in the transamination than a nucleophilic attack of the lone electron pair of the tetraamine NHR groups on the aluminum center. This assumption gains credibility from the observed higher reactivity of the silylated tetraamines in the transamination of $[Al(NMe_2)_3]_2$ compared with alkylated tetraamines such as $(MeHNCH_2CH_2)_3N$ and $(i\text{-}PrHNCH_2CH_2)_3N$. Moreover, the reactivity of metal amides with protic reagents has been correlated with their pK_a values.[9] Thus in silylated tetraamines, the basicity of the NHR nitrogens is diminished by π-bonding to silicon with consequent enhancement of the acidity of the NHR protons. In contrast, the opposite electronic situation occurs in alkylated tetraamines. The inertness of $Al[N(SiMe_3)_2]_3$ can thus be attributed to the diminished basicity of the nitrogen lone electron pairs owing to π-bonding to silicons and also to a steric shielding of the aluminum center by the bulky $SiMe_3$ groups. Similarly, the monomeric amide $Al(N\text{-}i\text{-}Pr_2)_3$ failed to react with $(Me_3SiNHCH_2CH_2)_3N$. In this case, steric blocking could be the major reason for its inertness.

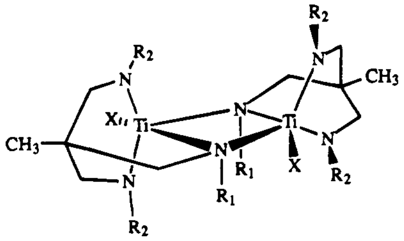
Formation of the dimeric azaaluminatrane **5** by a desilylation of **3** (summarized in reaction 4) is a novel example of the



(4)

influence of the bulkiness of the equatorial nitrogen substituents on the degree of oligomerization. Thus relaxing the steric congestion in **3** by removal of one of the three $SiMe_3$ groups leads to dimerization and, as was confirmed by the X-ray diffraction study of **5** (vide infra), an unusual cis configuration at the central four-membered ring. The presence of the trans isomer in the mother liquor was ruled out by ^{13}C NMR spectroscopy. Moreover, heating a benzene-d_6 solution of **5** in a sealed NMR tube to 130 °C for 48 h caused no observable transformation of the cis isomer to its trans counterpart.

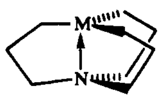
The true nature of the desilylation process (reaction 4) remains unclear so far. One possibility is that adventious water caused a partial hydrolysis of **3**. Militating against this option are our consistent efforts to maintain anhydrous conditions throughout the reaction and workup and also our inability to repeat the preparation by a controlled hydrolysis of **3** with 0.5 equiv of water by several methods including the addition of the H_2O to a pentane solution of **3** at −78 °C, slow diffusion of water vapors from ice at −20 °C, and slow release of water of crystallization from $CuSO_4{\cdot}5H_2O$. In all cases, we observed (by ^{1}H NMR spectroscopy) a mixture of the parent amine **9** as a product of complete hydrolysis and unreacted **3**. Also the amount of dimer was larger than what would be expected if only adventious water was present. Recently, a very similar observation was published[13b] for related compounds **12a,b** containing a tripodal ligand. In that case, the explanation for



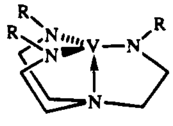
	R_1	R_2	X
12a	H	$SiMe_3$	Cl
12b	H	$SiMe_3$	Br
12c	Me	Me	Cl
12d	Me	Me	Br

the formation of a desilylated dimer involved a reaction with the solvent protons (THF) and the hydrolytic pathway was excluded.

Structural Considerations. The molecular structure of the monomeric azaaluminatrane **3** shown in Figure 1 features a central aluminum atom in a TMP coordination environment. This represents the first example of this geometry for aluminum and it is rare for the main-group elements in general. Similar compounds reported so far are the 4,6,11-tricarbametallatranes **13a** and **13b**, of which only the gallium derivative has been



	M
13a	Al
13b	Ga



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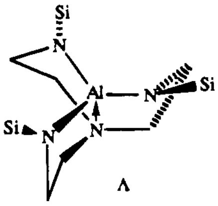
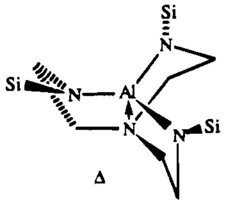
R = $SiMe_2$-*tert*-Bu

structurally characterized.[20] For the transition metals, the first TMP complex verified by X-ray crystallography was reported for nickel in $Ni(Ph_2PCH_2CH_2)_3N$.[21] TMP structures were also found for Cu, Ag, Co, and Pd complexes with tripodal ligands.[22] Recently, the molecular structure of the V(III) azatrane **14** with a TMP vanadium center was reported.[19c]

Compound **3** exists in a propeller-like conformation, possessing a pseudo-3-fold symmetry with a pseudo-C_3 axis through the Al and apical N atoms. This conformation implies the presence of Λ and Δ enantiomers in the solid state. Two





triangular units, AlN(2)N(3)N(4) and N(1)C(1)C(3)C(5) in

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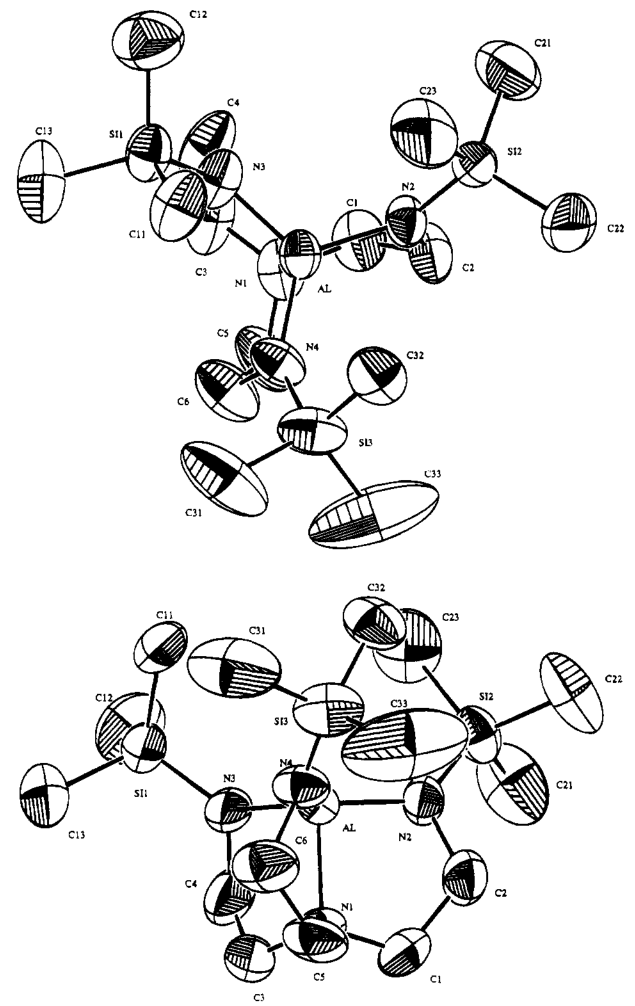


Figure 1. ORTEP drawings of monomeric $\overline{Al(Me_3SiNCH_2CH_2)_3N}$ (**3**): (a) top view; (b) side view. Ellipsoids are drawn at the 50% probability level.

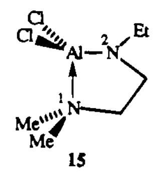
Figure 1, are nearly eclipsed with an average torsional angle of only 3.3(6)°. The three five-membered rings are in an envelope conformation with the "flap" atoms C(2), C(4), and C(6) displaced out of the plane of the envelope by 0.59 Å. The equatorial nitrogens are planar, the average of the sum of angles around them being 359.5(5)°. The planarity of these nitrogens can be attributed to engagement of nitrogen electron lone pairs in π-bonding with the adjacent silicon. The lack of inversion at the equatorial nitrogens thus connects the movement of each of the bulky $SiMe_3$ groups with the conformational inversion of the five-membered ring to which it is attached. This structural feature supports our suggestion of a concerted mechanism for racemization of the Δ and Λ conformations for the closely related boron derivative **2** from an analysis of its variable-temperature ^1H NMR spectra.[6] Unfortunately, similar experiments for **3** (and also **6** which has even bulkier substituents) revealed that these molecules are freely fluxional down to −95 °C on the NMR time scale. This prevented us from evaluating the activation entropy $\Delta S^\ddagger$ for the barriers to racemization, for which a negative value would substantiate the concerted mechanism. The less restricted fluxionality of **3** and **6** can be attributed to the substantially larger size of the aluminum atom in comparison with the smaller boron (tetrahedral covalent radii: 1.230 and 0.853 Å, respectively[23a]). Hence, longer Al—N bonds (Table 2) in comparison with B—N bonds render the azaaluminatrane cage less sterically compact and relax the strain which was found in **2**.[6]

Table 2. Selected Bond Distances (Å) and Angles (deg) for **3**[a]

Al—N(1)	1.983(6)	Si(1)—N(3)	1.697(6)
Al—N(2)	1.805(5)	Si(2)—N(2)	1.684(5)
Al—N(3)	1.812(6)	Si(3)—N(4)	1.690(6)
Al—N(4)	1.810(6)		
N(2)—Al—N(3)	119.6(3)	N(1)—Al—N(2)	92.3(3)
N(2)—Al—N(4)	120.2(3)	N(1)—Al—N(3)	92.3(3)
N(3)—Al—N(4)	119.9(3)	N(1)—Al—N(4)	91.8(3)
C(3)—N(1)—C(5)	114.9(7)	Si(2)—N(2)—Al	135.1(4)
C(1)—N(1)—C(5)	114.3(6)	Si(2)—N(2)—C(2)	118.9(5)
C(1)—N(1)—C(3)	112.5(6)	Al—N(2)—C(2)	105.9(4)
Si(1)—N(3)—Al	134.4(3)	Si(3)—N(4)—Al	133.7(3)
Si(1)—N(3)—C(4)	119.4(5)	Si(3)—N(4)—C(6)	120.2(5)
Al—N(3)—C(4)	105.4(4)	Al—N(4)—C(6)	105.6(5)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

The coordination geometry of the aluminum center in **3** very closely approaches the ideal TMP geometry. The angles between nitrogens in the basal triangular face are the same (within 2σ) and their average is 119.9(3)° (Table 2). The aluminum is drawn slightly below the plane of the basal nitrogens (0.07 Å) resulting in an N(basal)—Al—N(apical) average angle of 92.1(3)°. A similar angle of 91.3(1)° was found in the related compound **15**.[24a] The axial Al—N bond distance in **3** is 1.983(6) Å which is slightly longer than the sum of tetrahedral covalent radii of 1.949 Å.[23a] Nevertheless, the axial Al—N distance is comparable to the Al—N(1) bond length of 1.963(2) Å in **15**.[24a] Moreover the values of the Al—N distances found in compounds in which both Al and N are four-coordinate span a remarkably wide range, 1.83–2.13 Å,[1,2,4,8b,24–34] with typical values usually falling in the 1.91–1.97 Å range.[4] Bond distances in the basal AlN_3 triangle are the same (within



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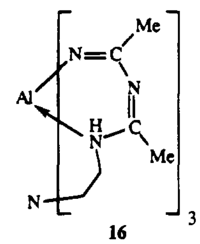

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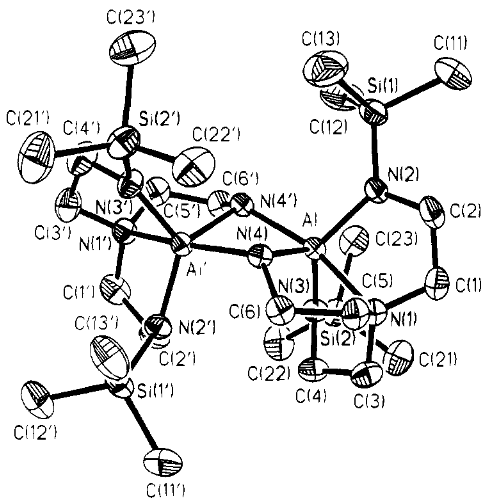


Figure 2. Thermal ellipsoid plot of $[\mathrm{Al(Me_3SiNCH_2CH_2)_2(HNCH_2CH_2)N}]_2$ (**5**). Ellipsoids are drawn at the 50% probability level.

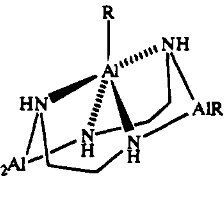
2σ), and their average is 1.809(6) Å. This is an example of a rather rare bonding situation in Al—N compounds, in which four-coordinate Al is bonded to three-coordinate N.[8b,24a,34,35] The change in the hybridization of N from sp^3 to sp^2 must largely account for the shortening of the Al—N bonds because π-bonding between Al and N is apparently inhibited by competitive π-bonding from N to Si and also by large twist angles (60–70°) between the basal $\mathrm{AlN_3}$ plane and the Al—N(basal)—Si planes. Comparable values were found for the terminal Al—N distances in $[\mathrm{Al(NMe_2)_3}]_2$ (1.802(2) Å[8b]) and in the adamantane-like cage $\mathrm{Al_4Cl_4(NMe_2)_4(NMe)_2}$ (1.79(3) Å[34]). The Al—N(2) bond length found in **15** is even shorter (1.770(2) Å[24a]). The triptych structure of **3** can be contrasted with that of **16**,[36] in which the aluminum atom does not interact with the apical nitrogen and instead satisfies its coordination needs by bonding to solvent moieties that have become incorporated into the chelating ligand by reaction. The present example **3** emphasizes the importance of the bulky $\mathrm{SiMe_3}$ groups for stabilizing the transannular bond and tetracoordination of the aluminum center, and it also points to the presently unexplored potential for the aluminum center to increase its coordination number via the sterically crowded but vacant axial coordination site.

The molecular structures of **3** and **5** offer a rare opportunity to compare structural parameters in two closely related molecules with the aluminum atoms in two different coordination environments. The molecular structure of **5** is depicted in Figure 2 and selected bond distances and angles are collected in Table 3. The heptacyclic dimer consists of two azaaluminatrane units connected in an unexpected cis fashion. The replacement of one $\mathrm{SiMe_3}$ group in **3** by hydrogen decreases the steric hindrance sufficiently to allow association of two units into a dimer. The bridging NH groups together with two aluminums form a puckered central four-membered ring in which the Al—N(4)—N(4′) and Al′—N(4)—N(4′) planes are separated by 149°. The aluminum atoms are in a distorted trigonal bipyramidal coordination sphere. This structure is to our knowledge the first example of five-coordinate aluminum ligated solely by nitrogens. Comparable examples of distorted TBP geometries are found in **17**,[28a] **18**,[37] **19**,[38] and **20**.[39]

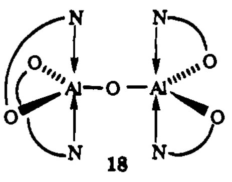
Table 3. Selected Bond Distances (Å) and Angles (deg) for **5**[a]

Al—N(1)	2.161(2)	Al′—N(1—)	2.174(2)
Al—N(2)	1.858(2)	Al′—N(2′)	1.859(2)
Al—N(3)	1.858(2)	Al′—N(3′)	1.853(2)
Al—N(4)	2.004(2)	Al′—N(4′)	2.014(2)
Al—N(4′)	1.968(2)	Al′—N(4)	1.967(2)
Si(1)—N(2)	1.712(2)	Si(1′)-N(2′)	1.705(2)
Si(2)—N(3)	1.705(2)	Si(2′)—N(3′)	1.720(2)
N(1)—Al—N(2)	86.2(1)	N(1′)—Al′—N(2′)	82.6(1)
N(1)—Al—N(3)	82.5(1)	N(1′)—Al′—N(3′)	86.6(1)
N(1)—Al—N(4)	81.6(1)	N(1′)—Al′—N(4′)	81.3(1)
N(1)—Al—N(4′)	160.5(1)	N(1′)—Al′—N(4)	159.8(1)
N(4)—Al—N(4′)	80.3(1)	N(4′)—Al′—N(4)	80.1(1)
Al—N(4)—Al′	95.3(1)	Al′—N(4′)—Al	94.9(1)
N(2)—Al—N(3)	125.4(1)	N(2′)—Al′—N(3′)	124.4(1)
N(2)—Al—N(4)	111.3(1)	N(3′)—Al′—N(4′)	111.1(1)
N(3)—Al—N(4)	119.4(1)	N(2′)—Al′—N(4′)	120.7(1)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.



	R
17a	Me
17b	Et



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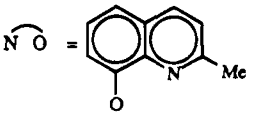

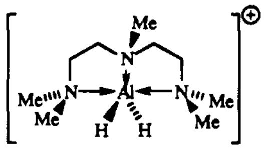

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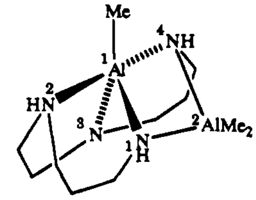

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The central $\mathrm{Al_2N_2}$ array of **5** forms a puckered rectangle with a pseudo-2-fold axis through its center. The hydrogen atoms of the NH groups were not located in the difference map, but the nitrogen atoms in the central ring are clearly pyramidal with angle sums of 335.7(2) and 336.8(2)°. This contrasts to a planar central ring in **12a**.[13b] The Al—N bonds connecting the two azaaluminatrane units (Al—N(4′) and Al′—N(4)) are shorter by approximately 2% (1.967(2) Å) than the Al—N(bridging) distances within the units (2.014(2) and 2.004(2) Å). This suggests strong bonding between the two units, which agrees

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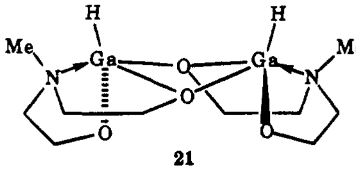
with the rigidity of the dimer as observed by ^{1}H and ^{13}C NMR spectroscopies. A similar bonding pattern was reported for **12a–d**.[13b]

The coordination environment of the nonbridging equatorial nitrogens is nearly planar, with the sum of angles around them ranging from 356.6(2) to 360.0(2)°. This planarity probably reflects Si—N and Al—N π-bonding effects.

The Al—NSiMe$_3$ distances in **5** are the same (within 3σ), and their average length is 1.857(2) Å, which is longer by ~3% than the corresponding bond lengths in **3**. This lengthening can be ascribed to the increase of the aluminum coordination number from four to five. A comparable bond distance (Al(1)—N(3)) of 1.826(2) Å was found in **20**.[39] The transannular bonds (Al—N(1), Al—N(1′)) in the two units of **5** are slightly but significantly different (2.161(2) and 2.174(2) Å). This difference, which may be caused by packing forces, demonstrates a certain amount of flexibility of these bonds. The Al—N distances fall in the range for the analogous bond distances in other compounds containing a five-coordinate TBP aluminum and a four-coordinate axial nitrogen. The upper limit of the range is 2.18(1) Å for AlH$_3$·2NMe$_3$[40] and other examples include **17a** (2.058(2), 2.073(2) Å[30a]), **18** (2.054(5)–2.110(5) Å[37]), **19** (2.158(7) Å[38]), and **20** (2.055(2), 2.135(2) Å[39]). In the related tetrameric aluminatrane [Al(OCH$_2$CH$_2$)$_3$N]$_4$,[41] the axial Al—N distance in the TBP units is 2.069(5) Å.[42] Comparison of the transannular Al—N(1) bond distance in **3** with the corresponding distances in **5** shows an approximately 10% lengthening upon increasing the TMP coordination sphere of aluminum to TBP. This considerably larger increase of the axial bond distances in **5** compared with the smaller increase of the pseudoequatorial bonds demonstrates the substantial trans influence of an apical ligand along the TBP axis compared with its cis influence.

At this time, we have no convincing rationale for the unusual preferential formation of the cis diastereomer of **5** over the trans. The reasons offered for the exclusive cis arrangement of **12**[13b] suggest that a puckered central ring in the cis isomer can more easily accommodate the strain caused by the chelating tripodal ligand compared with a planar array implied for the trans configuration. However, we have no reason to believe that a trans arrangement of substituents necessitates a planar ring. Moreover, a planar ring can bear cis substituents as has been shown for [R$_2$Al—NHBp]$_2$ (R = Me, *i*-Bu, Bp = 2-aminobiphenyl)[29c] by X-ray crystallography. An additional example of an unusual cis configuration is the dimeric gallium derivative **21**.[43]



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Infrared Spectra. The assignment of the Al—N stretching frequency in the IR spectra of **3**, **5**, and **6** is not a trivial task owing to strong mixing of the normal modes of the azatrane framework as was shown for analogous silatranes.[44] The presence of two stretching coordinates, Al—N$_{ax}$ and Al—N$_{eq}$ in **3**, and even more coordinates in **5**, together with coupling of the Al—N$_{eq}$ and Si—N stretches (which are of a similar energy[45a]), complicate the spectral assignment. Furthermore, the values for Al—N stretching modes were observed in a rather broad region, namely, 392 cm^{-1} in Al[N(SiMe$_3$)$_2$]$_3$,[10a] 460 cm^{-1} in (Me$_3$N)$_2$·AlH$_3$,[45b] 533 cm^{-1} in Me$_3$N·AlH$_3$,[45b] 565 cm^{-1} in Me$_3$N·AlCl$_3$,[45a] 582 cm^{-1} in (Me$_3$Si)$_3$N·AlCl$_3$,[45a] 460–587 cm^{-1} in the six-membered ring compounds (R$_2$AlNR$_2$′)$_3$,[25a,30] 652, 688 cm^{-1} in the tetrahedral Al(NH$_2$)$_4^-$, and 726, 742 cm^{-1} in octahedral [Al(NH$_3$)$_4$Cl$_2$]$^+$.[3] In the IR spectra of **3** and **6**, there are several bands in the region 700–500 cm^{-1} of which some may have predominant contributions from the Al—N vibrations.

Several characteristic bands of the SiMe$_3$ group were tentatively assigned by comparison with literature data.[46] The presence of NH groups in **5** was confirmed by two weak bands at 3277 and 3267 cm^{-1} for the ν(NH) mode.

NMR Spectra. The assignment of signals in the ^{1}H NMR spectra of silylated tetraamines **9** and **11** was facilitated by the presence of a three-bond coupling (~7 Hz) between the NH protons and the adjacent CH$_2$ protons. This coupling is not seen in the spectra of alkylated tren derivatives such as Me$_3$-tren[47] and *i*-Pr$_3$tren.[48] Silicon bonding to an NH group engages the lone electron pair on N in the π-bonding, thus changing the hybridization of N from sp^3 to sp^2, which increases the s-character in the H—N—CH$_2$ bonds and results in an observable scalar coupling. The formation of transannulated azatrane frameworks **3** and **6** is accompanied by a small downfield shift of the SiNCH$_2$ signals and by an upfield shift of the N(CH$_2$)$_3$ signals with respect to the free amines. In all monomeric group 13 azatranes,[6] we found the N(CH$_2$)$_3$ protons at higher field relative to the SiNCH$_2$ protons. This accords with our observations in azasilatranes,[11a,49] azastannatranes,[50] and transition metal azametallatranes.[51] As in the ^{1}H NMR spectra of **9** and **11**, silylation of the NH groups caused the appearance of a two-bond coupling H—N(Si)—CH$_2$ (~2.5 Hz) in the proton-coupled ^{13}C NMR spectra. This made an assignment of the ^{13}C signals straightforward, revealing an upfield position of the SiNCH$_2$ carbon signals relative to the N(CH$_2$)$_3$ carbons. This order is retained upon the formation of azatranes.[6,11,52] In monomeric azatranes **1**, **2**, **3**, and **6**, the RNCH$_2$ carbons appear at a lower field than in the parent tetraamines, with boron causing a larger downfield shift, in agreement with its higher electronegativity. A different situation is encountered for the N(CH$_2$)$_3$ signals, for which boron causes a downfield shift while aluminum shifts them upfield.

The magnitude of the one-bond C—H coupling constant in methylene groups is a useful indicator of the formation of a transannulated cage structure. While in the free tetraamines **9** and **11** the $^{1}J_{CH}$ coupling in the SiNCH$_2$ methylenes is higher than for N(CH$_2$)$_3$, in azatranes **3** and **6** these magnitudes are reversed. This reflects a change in the character of the nitrogens adjacent to the methylene groups in question. The apical

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Table 4. ^{27}Al NMR Chemical Shifts of Aluminum Coordinated Solely by Nitrogens

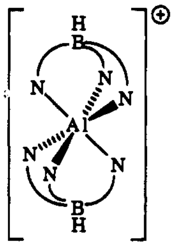
compound	CN[a]	δ^{27} Al (ppm)	$\Delta\nu_{1/2}$ (Hz)	refs
22	6 (O_h)	6.2[b]	12 at 25 °C	55a
23	6 (O_h)[c]	25−34[d]	625−2460[e]	55b,c
24	6 (O_h)	40.5[f]	sharp[g]	28b
4	5 (TBP)	83[f]	560 at 70 °C	6
5	5 (TBP)	86[f]	1080 at 70 °C	this work
7	4 (Tet)	107[f]	840[e]	8b
3	4 (TMP)	133 ± 1[f]	1860 at 70 °C	6
6	4 (TMP)	131 ± 1[h]	3030 at 80 °C	this work
8a	3 (TPl)	143 ± 1[f]	3600 at 70 °C	this work
8b	3 (TPl)	136 ± 1[h]	8200 at 70 °C	this work

[a] Coordination number; geometry of the aluminum center given in parentheses. Key: O_h = octahedral, TBP = trigonal bipyramidal, Tet = tetrahedral, TMP = trigonal monpyramidal, and TPl = trigonal planar. [b] Dichloromethane-d_2 solution. [c] Trigonally distorted. [d] Chloroform-d_1 solution. [e] Temperature not given. [f] Benzene-d_6 solution. [g] Value of $\Delta\nu_{1/2}$ not given; room temperature. [h] Toluene-d_8 solution.

nitrogen acquires a formal positive charge upon the formation of the Al—N transannular bond. This positive charge increases the electronegativity of N which in turn attracts more *p*-character into the N—C bonds and leaves more s-character in the C—H bonds, thus raising the value of the C—H coupling constant. Relative to the apical nitrogen, the nitrogens in the $SiNCH_2$ groups of **3** and **6**, have more amidic character because of the lone-pair electron density on them. This partial negative character, by the same mechanism as explained above, causes a lower value of $^1J_{CH}$ in the $SiNCH_2$ groups. However, compared with the magnitudes of the $^1J_{CH}$ values in the parent tren derivatives **9** and **11**, $^1J_{CH}$ in the $N(CH_2)_3$ and the $SiNCH_2$ groups are larger in **3** and **6**, thus manifesting transannular bonding involving an electronegative metal center. The magnitudes of the C—H coupling constants in **3** and **6** fall in the region observed for azaboratranes,[6] azasilatranes,[11b] and silatranes.[52]

A dimeric structure for **5** in solution was confirmed by its ^{1}H, ^{13}C, and ^{29}Si NMR spectra. It is not possible to decide on the basis of symmetry arguments and the number and splittings of the signals whether the azaaluminatrane **5** possesses a cis or a trans configuration in solution because both diastereomers would give the same number of signals. The ^{1}H NMR spectrum of **5** closely resembles that of **4**[6] in that the 12 diastereotopic methylene proton signals show an array of partially overlapped multiplets. The NH proton signals could not be located, however, probably due to overlap with the CH_2 multiplets. Two inequivalent $SiMe_3$ groups display separate signals in the ^{1}H, ^{13}C, and ^{29}Si NMR spectra. A pattern of six singlets similar to that displayed by **4**[6] was observed for the six inequivalent CH_2 carbons. The presence of only one set of signals in the NMR spectra, the absence of any evidence for a dynamic process at elevated temperatures, and the invariance of the spectra to prolonged heating assured us that the diastereomer observed in the solution was the same as that found by the X-ray experiment in the solid state.

^{27}Al NMR chemical shifts are well-known[53] to reflect the coordination number of the aluminum atom, and characteristic regions have been established for different coordination numbers for Al—O and Al—C compounds.[54a] Much less attention has been given to the ^{27}Al NMR spectroscopy of Al—N compounds, in spite of considerable activity in this area. Table 4 lists data for a series of compounds in which the aluminum center is coordinated solely by nitrogen ligands. This table reveals that there is only a handful of such Al—N compounds for which both ^{27}Al chemical shifts and molecular structures are known. Two examples of an octahedral geometry are **22**,[55a] **23**,[55b,c] and **24**,[28b] and their chemical shifts are in the high-field region. From the similar values of 83 and 86 ppm for **4**[6] and **5**, respectively, both dimers can be deduced to possess five-coordinate aluminums. The tetrahedrally coordinated aluminum in $[Al(NMe_2)_3]_2$, (**7**)[8b] was reported to display its signal at 107 ppm. The monomeric azaaluminatranes **3** and **6** with the four-coordinate trigonal monopyramidal aluminum atoms (which show very similar shifts of 133[6] and 130 ppm, respectively) are found in an intermediate region between tetrahedral **7** and the trigonal planar monomeric amides $(i\text{-}Pr_2N)_3Al$ (**8a**)[1b,9] and $[(Me_3Si)_2N]_3Al$ (**8b**),[9,10] for which we observed chemical shifts at 144 and 135 ppm, respectively. This trend of chemical shifts from high to low field reflects changes of the aluminum coordination geometry on going from tetrahedral to trigonal monopyramidal to trigonal planar environments.



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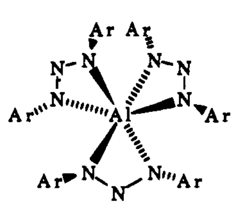
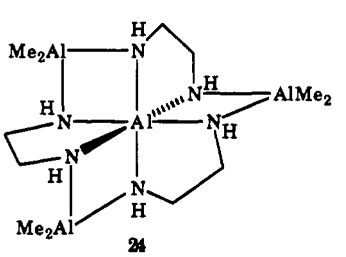


	Ar
23a	Ph
23b	2-MePh
23c	4-MePh
23d	4-MeOPh
23e	4-FPh
23f	4-ClPh
23g	4-BrPh
23h	C_6F_5

= tris(3,5-dimethyl-1-pyrazolyl)hydridoborate



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The overall sequence of chemical shifts in this complete series of Al—N compounds follows a general trend among the main-group elements wherein higher shielding is observed for higher coordination numbers and higher local symmetries.[54b] The low-field chemical shifts of the monomeric amides **8a**, **8b** contrast the value of 3.2 ppm found for $Al(OAr)_3$, (Ar = 2,6-*t*-Bu_2-4-MeC_6H_2) which possesses a trigonal planar AlO_3 array.[56] This high shielding was attributed to a p—p π-bonding between Al and O. A similar type of bonding is precluded in **8b**[10] owing to a large dihedral angle between the empty p_z orbital on Al and the lone electron pair in the p_z orbital of N, and also by competitive π-bonding of nitrogen to silicon.

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Conclusions. Compounds **3** and **5** demonstrate that the degree of oligomerization of azaaluminatranes depends strongly on the size of the substituents on the equatorial nitrogens. The monomeric compounds **3** and **6** are rare examples of trigonal monopyramidal coordination geometry as was confirmed by the X-ray diffraction analysis of **3**. This geometry is apparently imposed on aluminum by the steric influence of the tripodal tetradentate chelating ligands **9** or **11**. Dimeric **5** is the first example of a five-coordinate aluminum center coordinated exclusively by nitrogens. The X-ray diffraction study of **5** showed an unusual cis configuration of the substituents on the central Al_2N_2 ring. ^{27}Al NMR data were gathered on a series of Al—N compounds with the coordination numbers of the aluminum by nitrogen ranging from three to six. The observed trend in their chemical shifts clearly indicates increased shielding on going from a trigonal planar to trigonal monopyramidal to tetrahedral to trigonal bipyramidal to octahedral geometry.

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Supplementary Material Available: Tables of crystallographic data, positional and thermal parameters, bond lengths, and bond angles (17 pages). Ordering information is given on any current masthead page.