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Substitution Reactions of Aluminum Organoamide Complexes $[Al(\mu\text{-}NR_2)_nCl_{3-n}]_2$ (R = Et, ^{i}Pr; $n \leq 3$) with LiNR′R″ (R′ = R″ = ^{i}Pr, Et; R′ = H, R″ = ^{i}Pr): Crystal Structure of $[Al(\mu\text{-}NEt_2)(N^iPr_2)X]_2$ (X = Cl, H) and $AlCl_3(N^iPrH_2)_2\{Al(NH_3)(NH_2)[Al(N^iPrH)(N^iPr)Cl]_2\}_2$

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As part of our ongoing study of different substituents of Al_2N_2 ring systems, the synthesis, structural characterization, and spectroscopic studies on several amido derivatives of four-coordinated aluminum are described. The compounds $Al_2(NEt_2)_2(N^iPr_2)_2Cl_2$, **1**, $Al_2((N^iPr_2)_4Cl_2$, **2**, $Al((N^iPr_2)_3$, **3**, $Al(NEt_2)_3$, **4**, $\{Al(N^iPrH)_3\}_3$, **5**, $Al_2(NEt_2)_2(N^iPr_2)_2H_2$, **6**, and $AlCl_3(N^iPrH_2)_2\{Al(NH_3)(NH_2)[Al(N^iPrH)(N^iPr)Cl]_2\}_2$, **7**, were synthesized by substitution reactions and characterized by mass spectra, IR spectra, elemental analysis, and ^{1}H, ^{13}C, and ^{27}Al NMR data. The structures of three compounds, *viz.*, **1**, **6**, and **7**, have been determined by single-crystal X-ray diffraction analysis. Crystal data with Mo Kα (**1** and **7**, $\lambda = 0.710\,73$ Å) or Cu Kα (**6**, $\lambda = 1.541\,78$ Å) radiation: (**1**) $Al_2N_4C_{20}H_{48}Cl_2$, $a = 7.747(2)$ Å, $b = 9.648(2)$ Å, $c = 10.110(3)$ Å, $\alpha = 102.91(2)°$, $\beta = 83.54(2)°$, $\gamma = 110.19(2)°$, triclinic, space group $P\bar{1}$, $Z = 1$, $R = 0.053$ for 1789 ($I > 3\sigma(I)$) reflections; (**6**) $Al_2N_4C_{20}H_{50}$, $a = 15.088(2)$ Å, $b = 14.506(3)$ Å, $c = 12.439(3)$ Å, orthorhombic, space group *Cmca* (No. 64), $Z = 4$, $R = 0.045$ for 701 ($I > 3\sigma(I)$) reflections; (**7**) $Al_7N_{14}C_{30}H_{86}Cl_7$, $a = 29.914(9)$ Å, $b = 10.197(3)$ Å, $c = 20.525(5)$ Å, $\beta = 90.99(4)°$, monoclinic, space group $C2/c$, $Z = 4$, $R = 0.042$ for 2472 ($I > 2\sigma(I)$) reflections.

Introduction

Recently compounds with group 13 and 15 bonds were shown to be potential precursors for semiconductor systems.[1−12] Noteworthy are the organoaluminum compounds, which are precursors for aluminum nitride. Most amido or imido derivatives of aluminum tends to form oligomers with strong metal−nitrogen σ bonds. In complexes involving imido ligands, especially (imino)aluminum monomers, the lone pairs on nitrogen may not be involved in σ-bonding and may in principle contribute to the partial π-bonds between aluminum and nitrogen centers. Power and co-workers have reported the Al−N bond in compounds possessing a possible weak π-interaction.[13] Low valency, unsaturated coordination, and fascinating bonding are noticeably emphasized in Al−N chemistry recently.[14] Our previous studies focused mainly on the reactivity of Al−N and Mg−C bonds.[15−18] Herein we report the synthesis, characterization, and crystal structures of $Al_2(NR_2)_2(NR'_2)_2X_2$ (R = Et, ^{i}Pr; R′ = ^{i}Pr, X = Cl, H) and a novel adduct $AlCl_3(N^iPrH_2)_2\{Al(NH_3)(NH_2)[Al(N^iPrH)(N^iPr)Cl]_2\}_2$. The adduct contains unusually short Al−N bonds indicating a possible π-interaction or strong ionic attraction in the Al−N moieties.

Experimental Section

Apparatus and Materials. All manipulations were carried out in a N_2-flushed glovebag, drybox, or vacuum system. Solvents were distilled and degassed prior to use. Lithium amides were synthesized by following a reported procedure.[14] Single-crystal X-ray diffraction data were obtained using an Enraf Nonius CAD-4 diffractometer. All ^{1}H, ^{13}C, and ^{27}Al NMR spectra were measured on a Varian VXR-300 spectrometer. Chemical shifts are referenced relative to either TMS (^{1}H) or benzene-d_6 (^{1}H, δ 7.15; ^{13}C{^{1}H}, δ 128.00), while ^{27}Al NMR spectra were referenced relative to $Al(H_2O)_6^{3+}$. Mass spectral data were obtained on a VG-7025 GC/MS/MS spectrometer. IR spectra were recorded as Nujol mulls between KBr disks on a BIO-RAD FT-IR spectrometer. Elemental analyses (C, H, N) were performed at the Analytische Laboratorien, Lindlar, Germany. Deviations in the results of the elemental analyses from calculated values are attributed to the extremely air sensitive and hygroscopic nature of these compounds.

Synthesis of $Al_2(NR_2)_2(NR'_2)_2Cl_2$ (R = Et, R′ = ^{i}Pr, 1; R = R′ = ^{i}Pr, 2). Bis((μ-dialkylamido)dichloroaluminum), $Al_2(NR_2)_2Cl_4$[15] (R =

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Et, **a**; R = $^{\mathrm{i}}$Pr, **b**; 3.0 mmol; 1.02 g, **a**; 1.20 g, **b**), was added slowly to an ether solution (100 cm^3) of $\mathrm{LiNR''_2}$ (R″ = Et, 0.48 g, 6.0 mmol; R″ = $^{\mathrm{i}}$Pr, 0.65 g, 6.0 mmol) under nitrogen at −30 °C. The reaction mixture was brought back to room temperature slowly, and after 1 h the solution was centrifuged to remove LiCl powder. Crude products of compound **1** and **2** were obtained after the removal of ether. Transparent colorless crystals of $\mathrm{Al_2(NR_2)_2(NR'_2)_2Cl_2}$ were obtained by vacuum sublimation (compound **1**) and recrystallization of the crude product from toluene (compound **2**). Analytical data for **1** and **2** follows. Compound $\mathrm{Al_2(NEt_2)_2(N^iPr_2)_2Cl_2}$ (**1**): Mp 96−97 °C; yield 75%; IR (Nujol mull) 2980 (s), 2960 (s), 2910 (s), 2860 (s), 2810 (m), 1460 (m), 1370 (m), 1185 (br), 1055 (br), 690 (br) cm^{-1}. Anal. Found: C, 51.3; H, 10.3; N, 11.8. Calcd: C, 51.2; H, 10.3; N, 11.9. Analysis by mass spectroscopy gave the fragments expressed as *m*/*z* (EI: 70 eV, relative intensity (%) and assignment in parentheses): 468 (9.3, $[\mathrm{M}]^+$), 453 (17.5, $[\mathrm{M - CH_3}]^+$), 433 (9.1, $[\mathrm{M - Cl}]^+$), 390 (13.3, $[\mathrm{M - (C_3H_7 + Cl)}]^+$), 368 (74.4, $[\mathrm{M - N(C_3H_7)_2}]^+$), 334 (19.5, $[\mathrm{MH - (Cl + N(C_3H_7)_2)}]^+$), 269 (19.5, $[\mathrm{MH - 2(N(C_3H_7)_2)}]^+$), 233 (26.4 $[\mathrm{M - (Cl + 2N(C_3H_7)_2)}]^+$), 219 (100, $[\mathrm{M/2 - CH_3}]^+$), 303 (9.3, $[\mathrm{M + Cl - N(C_3H_7)_2}]^+$). ^{1}H NMR ($\mathrm{C_6D_6}$): δ 1.09 (t, 12H, $\mathrm{CH_3}$ of $\mathrm{NEt_2}$, $^3J_{\mathrm{H-H}} = 6.6$ Hz), 1.27 (d, 24H, $\mathrm{CH_3}$ of $\mathrm{N^iPr_2}$, $^3J_{\mathrm{H-H}} = 6.6$ Hz), 2.94, 2.97, 3.37, 3.41 (quart, 8H, $\mathrm{CH_2}$ of $\mathrm{NEt_2}$, $^3J_{\mathrm{H-H}} = 6.6$ Hz), 3.26 (sep, 4H, CH of $\mathrm{N^iPr_2}$, $^3J_{\mathrm{H-H}} = 6.6$ Hz). ^{13}C NMR ($\mathrm{C_6D_6}$): δ 12.40 ($\mathrm{CH_3}$ of $\mathrm{NEt_2}$), 25.50 ($\mathrm{CH_3}$ of $\mathrm{N^iPr_2}$), 40.23 ($\mathrm{CH_2}$ of $\mathrm{NEt_2}$), 46.69 (CH of $\mathrm{N^iPr_2}$). ^{27}Al NMR ($\mathrm{C_6D_6}$): δ 89 ppm (br). Compound $\mathrm{Al_2(N^iPr_2)_4Cl_2}$ (**2**): Mp (dec) 77 °C; yield 40%; IR (in KBr pellets) 2965 (s), 2945 (s), 2890 (s), 1335 (m), 1230 (m), 1132 (w), 1063 (m), 817 (br), 641 (br) cm^{-1}. Anal. Found: C, 57.2; H, 11.0; N, 9.73; Cl, 11.9. Calcd: C, 54.8; H, 10.7; N, 10.6; Cl, 13.5. Analysis by mass spectroscopy gave the fragments expressed as *m*/*z* (EI: 70 eV, relative intensity (%) and assignment in parentheses): 524 (5.2, $[\mathrm{M}]^+$), 509 (18.2, $[\mathrm{M - CH_3}]^+$), 489 (13.3, $[\mathrm{M - Cl}]^+$), 446 (12.1, $[\mathrm{M - (C_3H_7 + Cl)}]^+$), 424 (8.7, $[\mathrm{M - N(C_3H_7)_2}]^+$), 390 (12.7, $[\mathrm{MH - (Cl + N(C_3H_7)_2)}]^+$), 226 (32.6, $[\mathrm{Al(N(C_3H_7)_2 - H}]^+$), 183 (32.6, $[\mathrm{AlN(C_3H_7)_2) - (C_3H_7 + H)}]^+$), 126 (72.2, $[\mathrm{AlNC_3H_7 - H}]^+$), 100 (100, $[\mathrm{N(C_3H_7)_2}]^+$). ^{1}H NMR ($\mathrm{C_6D_6}$): δ 1.25 (d, 36H, $\mathrm{CH_3}$ of $\mathrm{N^iPr_2}$, $^3J_{\mathrm{H-H}} = 6.6$ Hz), 3.40 (sep, 4H, CH of $\mathrm{N^iPr_2}$, $^3J_{\mathrm{H-H}} = 6.6$ Hz). ^{13}C NMR ($\mathrm{C_6D_6}$): δ 23.71 ($\mathrm{CH_3}$ of $\mathrm{N^iPr_2}$), 45.31 (CH of $\mathrm{N^iPr_2}$). ^{27}Al NMR ($\mathrm{C_6D_6}$): δ 112 ppm (br).

Synthesis of $\mathbf{Al(NR'R'')_3}$ (R′ = R″ = $^{\mathrm{i}}$Pr, 3; R′ = R″ = Et, 4; R′ = $^{\mathrm{i}}$Pr, R″ = H, 5). Bis((*μ*-dialkylamido)dichloroaluminum), $\mathrm{Al_2(NR_2)_2Cl_4}$[15] (R = Et, **a**; $^{\mathrm{i}}$Pr, **b**) (4.0 mmol; 1.36 g, **a**; 1.60 g, **b**), was added dropwise to an ether solution (100 cm^3) of lithium diisopropylamide (1.71 g, 16 mmol) or lithium diethylamide (1.26 g; 16 mmol) under nitrogen at −30 °C. The reactions took place when the temperature was raised to room temperature. After 2.5 h the solution was centrifuged to remove the white precipitate. The crude product was recrystallized and characterized to be $\mathrm{Al(NR'R'')_3}$ (R′ = R″ = $^{\mathrm{i}}$Pr, **3**; R′ = R″ = Et, **4**; R′ = $^{\mathrm{i}}$Pr, R″ = H, **5**).

The compounds $\mathrm{Al(NR'R'')_3}$ (**3**−**5**) were also obtained from the reaction of $\mathrm{Al_2Cl_6}$ with $\mathrm{LiNR'R''}$ (R′ = R″ = $^{\mathrm{i}}$Pr for **3**; R′ = R″ = Et for **4**, R′ = $^{\mathrm{i}}$Pr, R″ = H for **5**) in a molar ratio of 1:6. Analytical data for **3**−**5** follows. Compound $\mathrm{Al(N^iPr_2)_3}$ (**3**): Solid; mp 58−59 °C; yield, 80%. **3** was purified by sublimation at 50 °C, 10^{-3} Torr. IR (KBr pellets): 2998 (s), 2976 (s), 2895 (s), 1441 (m), 1410 (m), 1111 (m), 1102 (w), 995 (m), 911 (br), 643 (br) cm^{-1}. Anal. Found: C, 58.5; H, 11.7; N, 11.1. Calcd: C, 66.0; H, 12.9; N, 12.8. Analysis by mass spectroscopy gave the fragments expressed as *m*/*z* (EI: 70 eV, relative intensity (%) and assignment in parentheses): 328 (2.2, $[\mathrm{M + H}]^+$), 313 (4.5, $[\mathrm{M + H - CH_3}]^+$), 298 (5.2, $[\mathrm{M + H - 2Me}]^+$), 283 (5.1, $[\mathrm{M + H - 3Me}]^+$), 226 (12.8, $[\mathrm{M - H - N(C_3H_7)_2}]^+$), 211 (32.6, $[\mathrm{AlN(C_3H_7)_2 - H - Me}]^+$), 183 (10.6, $[\mathrm{AlN(C_3H_7)_2) - (C_3H_7 + H)}]^+$), 126 (32.6, $[\mathrm{AlNC_3H_7 - H}]^+$), 100 (72.2, $[\mathrm{N(C_3H_7)_2}]^+$), 58 (100, $[\mathrm{HNC_3H_7}]^+$). ^{1}H NMR ($\mathrm{C_6D_6}$): δ 1.27 (d, 36H, $\mathrm{CH_3}$ of $\mathrm{N^iPr_2}$, $^3J_{\mathrm{H-H}} = 6.6$ Hz), 3.41 (sep, 4H, CH of $\mathrm{N^iPr_2}$, $^3J_{\mathrm{H-H}} = 6.6$ Hz). ^{13}C NMR ($\mathrm{C_6D_6}$): δ 25.66 ($\mathrm{CH_3}$ of $\mathrm{N^iPr_2}$), 46.24 (CH of $\mathrm{N^iPr_2}$) and ^{27}Al NMR ($\mathrm{C_6D_6}$): δ 162 ppm (br). Compound $\mathrm{Al(NEt_2)_3}$ (**4**): Solid; mp 68−70 °C; yield, 60%; IR (Nujol mull) 2994 (s), 2980 (s), 2891 (m), 1456 (w), 1412 (m), 1370 (m), 1080 (m), 1035 (m), 990 (br), 960 (m) cm^{-1}. Anal. Found: C, 58.9; H, 12.2; N, 17.1. Calcd: C, 59.2; H, 12.4; N, 17.3. Analysis by mass spectroscopy gave the fragments expressed as *m*/*z* (EI: 70 eV, relative intensity (%) and assignment in parentheses): 487 (18.7, $[\mathrm{2M + H}]^+$), 413 (5.5, $[\mathrm{Al_2(NEt_2)_5 - H}]^+$), 398 (12.3, $[\mathrm{Al_2(NEt_2)_5 - Me - H}]^+$, 384 (15.6, $[\mathrm{Al_2(NEt_2)_5 - 2Me - H}]^+$), 340 (17.2, $[\mathrm{Al_2(NEt_2)_4 - 2H}]^+$), 313 (13.8, $[\mathrm{Al(NEt_2)_4 - 2H}]^+$), 272 (72.3, $[\mathrm{EtAl(NEt_2)_3}]^+$), 242 (92.3, $[\mathrm{M - H}]^+$) 171 (33.0, $[\mathrm{Al(NEt_2)_2}]^+$), 100 (100, $[\mathrm{HAl(NEt_2)}]^+$). ^{1}H NMR ($\mathrm{C_6D_6}$): δ 1.24 (t, 15H, $\mathrm{CH_3}$ of $\mathrm{NEt_2}$, $^3J_{\mathrm{H-H}} = 6.6$ Hz), 3.14 (quart, 8H, $\mathrm{CH_2}$ of $\mathrm{NEt_2}$, $^3J_{\mathrm{H-H}} = 6.6$ Hz). ^{13}C NMR ($\mathrm{C_6D_6}$): δ 12.38 ($\mathrm{CH_3}$ of $\mathrm{NEt_2}$), 39.75 ($\mathrm{CH_2}$ of $\mathrm{NEt_2}$). ^{27}Al NMR ($\mathrm{C_6D_6}$): δ 157 ppm (br). Compound $\mathrm{\{Al(N^iPrH)_3\}_3}$ (**5**): Mp (dec) 189 °C; yield, 45%; IR (Nujol mull) 3340 (w), 3290 (w), 2950 (m), 2920 (s), 2850 (w), 1460 (m), 1370 (w), 1295 (w), 1190 (s), 1105 (w), 1065 (m), 1050 (m), 1010 (w), 925 (m), 840 (m), 760 (br), 690 (br), 650 (w) cm^{-1}. Analysis by mass spectroscopy gave the fragments expressed as *m*/*z* (EI: 30 eV, relative intensity (%) and assignment in parentheses): 603 (55.3, $[\mathrm{3Al(N^iPrH)_3}]^+$), 601 (100, $[\mathrm{3Al(N^iPrH)_3 - 2H}]^+$), 559 (5.5, $[\mathrm{3Al(N^iPrH)_3 - {}^iPr - H}]^+$), 549 (52.2, $[\mathrm{2Al(N^iPrH)_3 + H_2Al(N^iPrH_2)}]^+$), 384 (5.2, $[\mathrm{2Al(N^iPrH)_3 - Me - H}]^+$), 143 (7.7, $[\mathrm{Al(N^iPrH)_2}]^+$), 71 (4.3, $[\mathrm{HAl^iPr}]^+$), 57 (6.4, $[\mathrm{{}^iPrN}]^+$), 44 (23.2, $[\mathrm{HC_3H_7}]^+$), 43 (24.7, $[\mathrm{C_3H_7}]^+$). ^{1}H NMR ($\mathrm{C_7D_8}$): δ 0.19 (br, NH of $\mathrm{N^iPrH}$), 1.23 (d, $\mathrm{CH_3}$ of $\mathrm{{}^tN^iPrH}$, $^3J_{\mathrm{H-H}} = 6.3$ Hz), 1.38 (d, $\mathrm{CH_3}$ of $\mathrm{{}^bN^iPrH}$, $^3J_{\mathrm{H-H}} = 6.3$ Hz), 3.40, 3.41 (sep, CH of $\mathrm{N^iPrH}$, $^3J_{\mathrm{H-H}} = 6.3$ Hz). ^{13}C NMR ($\mathrm{C_7D_8}$): δ 29.59 ($\mathrm{CH_3}$ of $\mathrm{{}^tN^iPrH}$), 29.74 ($\mathrm{CH_3}$ of $\mathrm{{}^bN^iPrH}$), 44.84 (CH of $\mathrm{{}^tN^iPrH}$), 46.83 (CH of $\mathrm{{}^bN^iPrH}$). ^{27}Al NMR ($\mathrm{C_6D_6}$): δ 111 ppm (br).

Reaction of $\mathbf{Al_2(NEt_2)_2(N^iPr_2)_2Cl_2}$ (1) with $\mathbf{LiN^iPrH}$. Bis((*μ*-dialkylamido)chloro(diisopropylamido)aluminum), $\mathrm{Al_2(NEt_2)_2(N^iPr_2)_2Cl_2}$ (1.87 g, 4.0 mmol), was added slowly to an ether solution (100 cm^3) of lithium isopropylamide (2.60g; 24.0 mmol) under nitrogen at −30 °C. The reaction took place when the reaction mixture was warmed to room temperature. The solution was centrifuged to remove the white precipitate. The products $\mathrm{Al_2(NEt_2)_2(N^iPr_2)_2H_2}$ (**6**) and $\mathrm{\{Al(N^iPrH)_3\}_3}$ (**5**) were obtained by gradient vacuum sublimation (10^{-3} Torr) at 115 and 185 °C, respectively. Analytical data for $\mathrm{Al_2(NEt_2)_2(N^iPr_2)_2H_2}$ (**6**): Mp (dec) 145 °C; yield 10%; IR (Nujol mull) 2980 (s), 2960 (s), 2910 (s), 2860 (s), 1725 (m), 1460 (m), 1370 (m), 1185 (br), 1055 (br), 690 (br) cm^{-1}. Anal. Found: C, 59.0; H, 12.3, N, 12.7. Calcd: C, 59.2; H, 12.6; N, 14.0. Analysis by mass spectroscopy gave the fragments expressed as *m*/*z* (EI: 70 eV, relative intensity (%) and assignment in parentheses): 401 (8.7, $[\mathrm{M + H}]^+$), 385 (17.2, $[\mathrm{M - CH_3}]^+$), 384 (8.3, $[\mathrm{M - H - Me}]^+$), 357 (5.2, $[\mathrm{M - C_3H_7}]^+$), 300 (5.2, $[\mathrm{M - N(C_3H_7)_2}]^+$, 258 (12.7, $[\mathrm{MH - (C_3H_7 + N(C_3H_7)_2)}]^+$), 201 (12.7, $[\mathrm{M/2 + H}]^+$), 100 (100, $[\mathrm{N(C_3H_7)_2)}]^+$), 58 (57.2, $[\mathrm{HNC_3H_7}]^+$), 43 (72.3, $[\mathrm{C_3H_7}]^+$). ^{1}H NMR ($\mathrm{C_7D_8}$): δ −0.20 (br, 2H, Al−H), 1.08 (t, 12H, $\mathrm{CH_3}$ of $\mathrm{NEt_2}$, $^3J_{\mathrm{H-H}} = 6.6$ Hz), 1.24 (d, 24H, $\mathrm{CH_3}$ of $\mathrm{N^iPr_2}$, $^3J_{\mathrm{H-H}} = 6.6$ Hz), 2.97, 3.00, 3.34, 3.37 (q, 8H, $\mathrm{CH_2}$ of $\mathrm{NEt_2}$, $^3J_{\mathrm{H-H}} = 6.6$ Hz), 3.24 (sep, 4H, CH of $\mathrm{N^iPr_2}$, $^3J_{\mathrm{H-H}} = 6.6$ Hz). ^{13}C NMR ($\mathrm{C_7D_8}$): δ 12.40 ($\mathrm{CH_3}$ of $\mathrm{NEt_2}$), 25.53 ($\mathrm{CH_3}$ of $\mathrm{N^iPr_2}$), 40.30 ($\mathrm{CH_2}$ of $\mathrm{NEt_2}$), 46.77 (CH of $\mathrm{N^iPr_2}$). ^{27}Al NMR ($\mathrm{C_7D_8}$): δ 108 ppm (br).

Synthesis of $\mathbf{AlCl_3(N^iPrH_2)_2\{Al(NH_3)(NH_2)[Al(N^iPrH)(N^iPr)Cl]_2\}_2}$ (7). $\mathrm{Al_2Cl_6}$ (2.67 g; 10.0 mmol) was added slowly to a solution containing an ether solution (100 cm^3) of lithium isopropylamide (2.14 g; 60.0 mmol) with excess isopropylamine (20.0 mmol) under nitrogen at −30 °C. The reaction took place when the temperature returned to room temperature. The crude product was obtained after removal of solvent and LiCl precipitate. The product $\mathrm{AlCl_3(N^iPrH_2)_2\{[Al(NH_3)(NH_2)[Al(N^iPrH)(N^iPr)Cl]_2\}_2}$ (**7**) was obtained from recrystallization from a hexane/toluene mixture (1:1).

The compound $\mathrm{AlCl_3(N^iPrH_2)_2\{Al(NH_3)(NH_2)[Al(N^iPrH)(N^iPr)Cl]_2\}_2}$ (**7**) (solid) was purified by sublimation at 55 °C, 10^{-3} Torr: Mp 73−75 °C; yield, 38%; IR (Nujol mull) 3361 (w), 3295 (w), 3205 (w), 2980 (s), 2958 (s), 2950 (s), 2870 (s), 1460 (m), 1370 (m), 1172 (br), 1151 (br), 893 (m), 651 (br) cm^{-1}. Anal. Found: C, 38.3; H, 6.7; N, 15.0. Calcd: C, 33.3; H, 8.2; N, 18.1. Analysis by mass spectroscopy gave the fragments expressed as *m*/*z* (EI: 70 eV, relative intensity (%) and assignment in parentheses): 568 (17.2, $[\mathrm{AlCl_2(N^iPrH_2) + Al(NH_3)(NH_2)[Al(N^iPrH)(N^iPr)Cl]_2 - 2H}]^+$), 509 (47.2, $[\mathrm{AlCl_2 + Al(NH_3)(NH_2)[Al(N^iPrH)(N^iPr)Cl]_2 - 2H}]^+$), 435 (5.2, $[\mathrm{AlCl_3(N^iPrH_2)_2 + Al(N^iPr_2)(N^iPrH)}]^+$), 413 (2.1, $[\mathrm{Al(NH_3)(NH_2)[Al(N^iPrH)(N^iPr)Cl_2 - 2H}]^+$), 378 (7.2, $[\mathrm{AlCl_3(N^iPrH_2)_2 + Al(N^iPr_2)}]^+$), 224 (8.6, $[\mathrm{Al(N^iPrH)(N^iPr)Cl + AlCl - Me}]^+$), 69 (5.4, $[\mathrm{Al^iPr - H}]^+$), 58 (21.8, $[\mathrm{N^iPrH}]^+$), 44 (61.8, $[\mathrm{H^iPr}]^+$), 43 (100, $[\mathrm{{}^iPr}]^+$). ^{1}H NMR ($\mathrm{C_6D_6}$): δ 0.87 (br, 10H, $\mathrm{Al(NH_2)(NH_3)}$), 0.95 (d, 12H, $\mathrm{CH_3}$ of $\mathrm{N^iPrH_2}$, $^3J_{\mathrm{H-H}} = 6.6$ Hz), 1.23 (d, 24H, $\mathrm{CH_3}$ of $\mathrm{N^iPr}$, $^3J_{\mathrm{H-H}} = 6.6$ Hz), 1.26 (br, 4H, NH of $\mathrm{N^iPrH_2}$), 1.31 (br, 24H, $\mathrm{CH_3}$ of $\mathrm{N^iPrH}$), 2.80 (br, 2H, CH of $\mathrm{N^iPrH_2}$,

Table 1. Crystallographic Data Refinement Details for Compounds **1**, **6**, and **7**

	compound		
	1	**6**	**7**
formula	$C_{20}H_{48}Al_2N_4Cl_2$	$C_{24}H_{50}Al_2N_4$	$C_{30}H_{88}Al_7N_{14}Cl_7$
fw	469.49	400.51	1082.15
a, Å	7.747(2)	15.088(2)	29.914(9)
b, Å	9.648(2)	14.506(3)	10.197(3)
c, Å	10.110(3)	12.439(3)	20.525(5)
α, deg	102.91(2)		
β, deg	83.54(2)		90.99(4)
γ, deg	110.19(2)		
cryst system	triclinic	orthorhombic	monoclinic
space group	*P*1	*Cmca* (No. 64)	*C*2/*c*
2θ range, deg	16.66−28.06	60.9−78.3	15.50−20.00
cryst size, mm	0.25 × 0.30 × 0.50	0.16 × 0.45 × 0.45	0.25 × 0.50 × 0.55
V, Å^3	691(1)	2722(1)	6260(3)
Z	1	4	4
D_{calc}, Mg M^{-3}	1.129	0.977	1.148
μ, mm^{-1}	0.31	1.02 (Cu Kα)	0.45
λ, Å	0.710 70	1.541 78	0.710 70
no. of rflns measd	2449	1162	4068
no. of unique rflns	2423		4068
no. of rflns $I_0 > 2.0\sigma(I_0)$	1789	697 ($I_0 > 3.0\sigma$)	2472
transm factors (min; max)	0.942; 0.997		0.883; 1.000
R_F	0.062	0.051	0.047
R_w	0.053	0.042	0.043
GoF	4.47	3.61	1.76
max Δ/σ	0.015	0.01	0.023

$^3J_{H-H}$ = 6.6 Hz), 3.23 (sep, 4H, CH of N^{i}Pf, $^3J_{H-H}$ = 6.6 Hz), 3.38 (sep, 4H, CH of N^{i}PrH, $^3J_{H-H}$ = 6.6 Hz), 3.89 (br, 4H, NH of N^{i}PrH, $^3J_{H-H}$ = 6.6 Hz). ^{13}C NMR (C_6D_6): δ 23.70 (CH_3 of N^{i}PrH$_2$), 25.66 (CH_3 of N^{i}PrH), 25.90 (CH_3 of N^{i}Pr), 46.01 (CH of N^{i}PrH$_2$), 46.29 (CH of N^{i}PrH), 65 45 (CH of N^{i}Pr). ^{27}Al NMR (C_6D_6): δ 112 ppm (br).

X-ray Structure Analysis. Single crystals for X-ray measurements were sealed in glass capillaries. Intensity data were collected using the $\theta-2\theta$ scan mode and corrected for absorption and decay. All structures were solved by direct methods and refined with full-matrix least squares on *F*. In the final cycle all non-hydrogen atoms were fixed at idealized positions. Scattering factors for neutral atoms and anomalous scattering coefficients for non-hydrogen atoms were taken from the literature.[19] All calculations were carried out with either a Micro VAX 3600 computer using the NRCVAX program package[20a] (for **6**) or a SGI R4000 computer using the teXsan program package[20b] (for **1** and **7**). Data collection and crystal parameters are summarized in Table 1, and selected bond distances and angles of **1**, **6**, and **7** are listed in Table 2. The final positional parameters of the refined atoms are presented in Table 3.

Results and Discussion

The compound $\{Al(NR'R'')_3\}_n$ can be synthesized either by the reaction of aluminum hydride with amine or by treatment of aluminum chloride with amine and lithium amide.[2,29] The latter reaction can be controlled by stoichiometry. For the main group metals, substitution reaction via lithium amide is a common method to generate Al/NR$_2$/halide ternary compounds. In order to study the selectivity in substitution and stabilization of the $Al_2(NR_2)_nCl_{6-n}$ complexes, we have used different stoichiometric ratios of aluminum complexes and lithium amide to form the new $Al_2(NR_2)_nCl_{6-n}$ complexes. The X-ray structural determinations of the complexes are described in the following section.

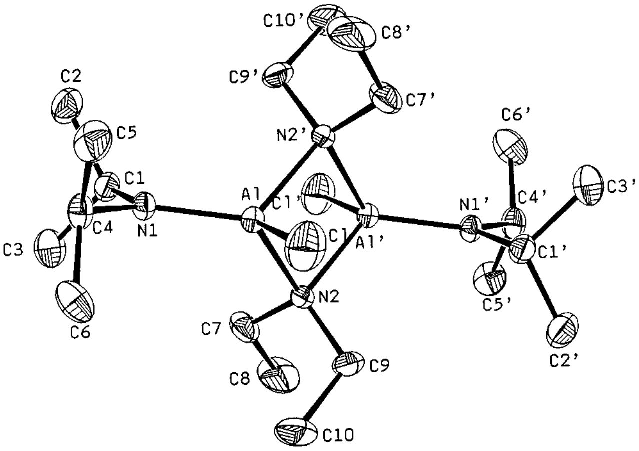

Figure 1. ORTEP view of the compound $Al_2(\mu\text{-}NEt_2)_2(N^iPr_2)_2Cl_2$ (**1**).

Table 2. Selected Bond Distances (Å) and Angles (deg) for Compounds **1**, **6**, and **7**

	Compound **1**		
Al−N(1)	1.791(4)	N(2)−C(7)	1.50(1)
Al−N(2)	1.967(4)	C(1)−C(2)	1.53(1)
Al−Cl	2.127(2)	C(7)−C(8)	1.52(1)
N(1)−C(4)	1.46(1)		
Al−N(2)−Al′	91.4(2)	Al−N(1)−C(4)	124.9(3)
N(2)−Al−N(2′)	88.6(2)	C(1)−N(1)−C(4)	113.1(3)
Cl−Al−N(2)	105.8(1)	Al−N(2)−C(7)	112.6(3)
Cl−Al−N(1)	115.2(1)	C(2)−C(1)−C(3)	109.1(4)
Al−N(1)−C(1)	122.0(3)	N(2)−C(7)−C(8)	115.0(4)
	Compound **6**		
Al(1)−N(1)	1.792(5)	N(2)−C(5)	1.49(1)
Al(1)−N(2)	1.962(3)	C(1)−C(2)	1.51(1)
Al(1)−H(14)	1.67	C(5)−C(6)	1.51(1)
N(1)−C(1)	1.47(1)		
Al(1)−N(2)−Al(1′)	92.0(2)	Al(1)−N(1)−C(3)	122.4(4)
N(2)−Al(1)−N(2′)	88.0(2)	C(1)−N(1)−C(3)	112.3(5)
N(2)−Al(1)−H(14)	107.5	Al(1)−N(2)−C(5)	115.6(2)
N(1)−Al(1)−H(14)	114.4	C(2)−C(1)−C(2′)	109.6(6)
Al(1)−N(1)−C(1)	125.3(4)	N(2)−C(5)−C(6)	115.6(2)
	Compound **7**		
Al(1)−N(1)	1.926(4)	Al(3)−N(7)	1.874(6)
Al(1)−N(2)	1.926(4)	Al(1)−Cl(1)	2.124(2)
Al(1)−N(3)	1.784(4)	N(1)−C(1)	1.50(1)
Al(2)−N(4)	1.788(5)	N(3)−C(7)	1.51(1)
Al(3)−N(3)	1.718(4)	Al(4)−Cl(4)	2.169(2)
Al(3)−N(4)	1.735(4)	Al(4)−N(5)	2.037(4)
Al(3)−N(6)	1.880(6)	N(5)−C(13)	1.51(1)
Al(1)−N(1)−Al(2)	86.9(2)	Al(2)−N(4)−Al(3)	122.9(2)
N(1)−Al(1)−N(2)	84.3(2)	Al(1)−N(3)−C(7)	123.8(3)
Cl(1)−Al(1)−N(1)	113.1(1)	Al(3)−N(3)−C(7)	113.5(3)
Cl(1)−Al(1)−N(3)	123.1(2)	N(6)−Al(3)−N(7)	106.8(3)
Al(1)−N(1)−C(1)	123.3(3)	N(7)−Al(3)−N(3)	110.4(3)
Al(2)−N(1)−C(1)	122.1(3)	N(7)−Al(3)−N(4)	110.1(3)
Al(1)−N(3)−Al(3)	122.7(2)	C(2)−C(1)−C(3)	111.0(5)
N(3)−Al(3)−N(4)	109.0(2)		

Description of Structures. Compound Al(NEt$_2$)(N^{i}Pr$_2$)Cl uses diethylamide as a bridging group to form dimer **1**, and the dimer sits on an inversion center as shown in Figure 1. The four atoms Al, N(2), Al′, and N(2′) form a coplanar four-membered ring with equal Al−N distances of 1.967(4) Å, and the internal angles of the Al_2N_2 ring are all near 90°. In the terminal amide the Al, N(1), C(1), and C(4) atoms lie on a plane as a result from the sp^2 hybridization of the N(1) atom. However, the Al−N(1) bond distance is quite short (1.791(4) Å) reaching the lowest values found in the literature (1.79−

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(20) (a) Gabe, E. J.; Le Page, Y.; White, P. S.; Lee, F. L. *Acta Crystallogr.* **1987**, *A43*, S294. (b) teXsan: Crystal Structure Analysis Package; Molecular Structure Corp.: College Station, TX, 1985, 1992.

Table 3. Atomic Parameters *x*, *y*, *z* and B_{eq} Values, Where Esd's Refer to the Last Digit Printed

	x	*y*	*z*	B_{eq}
Compound **1**				
Al	0.0926(2)	0.1008(2)	0.1135(1)	2.43(7)
C(1)	0.3787(2)	0.1307(2)	0.1017(2)	6.2(1)
N(1)	0.01448(2)	0.2055(4)	0.2632(3)	2.5(2)
N(2)	−0.0335(5)	−0.1179(4)	0.0652(3)	2.8(2)
C(1)	−0.1763(7)	0.2018(5)	0.2843(5)	3.1(2)
C(2)	−0.1981(7)	0.3543(6)	0.2903(5)	4.9(3)
C(3)	−0.2744(7)	0.1395(6)	0.4084(5)	4.9(3)
C(4)	0.1328(6)	0.3057(5)	0.3748(5)	3.3(3)
C(5)	0.2829(7)	0.4372(6)	0.3304(5)	4.8(3)
C(6)	0.2138(8)	0.2222(7)	0.4474(5)	5.2(3)
C(7)	−0.2012(8)	−0.1712(6)	0.1547(5)	4.4(3)
C(8)	−0.3141(9)	−0.3370(6)	0.1141(6)	7.2(4)
C(9)	0.0898(8)	−0.2092(6)	0.0586(5)	4.6(3)
C(10)	0.151(1)	−0.2140(7)	0.1951(6)	7.0(4)
Compound **6**				
Al(1)	1.0000	0.0902(1)	0.4575(1)	4.87(5)
N(1)	1.0000	0.1302(3)	0.3212(4)	4.9(1)
N(2)	0.9693(3)	0.0000	0.5000	5.1(1)
C(1)	1.0000	0.0709(5)	0.2254(5)	6.4(2)
C(2)	0.9182(4)	0.0802(4)	0.1563(4)	9.9(2)
C(3)	1.0000	0.2281(5)	0.2936(6)	7.2(2)
C(4)	0.9183(4)	0.2774(4)	0.3359(4)	11.2(2)
C(5)	0.8530(3)	−0.0362(3)	0.4109(4)	7.4(2)
C(6)	0.7893(3)	−0.1124(4)	0.4417(4)	10.9(2)
Compound **7**				
Al(1)	0.40561(5)	0.1164(2)	0.07064(7)	3.25(7)
Al(2)	0.35275(6)	0.0849(2)	0.17133(8)	3.95(8)
Al(3)	0.31763(5)	−0.0287(2)	0.04034(8)	3.94(8)
Al(4)	$^1/_2$	0.3494(2)	$^1/_4$	3.5(1)
Cl(1)	0.46783(5)	0.1950(2)	0.04125(8)	5.18(8)
Cl(2)	0.34654(6)	0.1250(2)	0.27266(8)	7.1(1)
Cl(3)	$^1/_2$	0.1331(2)	$^1/_4$	4.3(1)
Cl(4)	0.44918(5)	0.4529(1)	0.19362(7)	5.1(1)
N(1)	0.3718(1)	0.2357(4)	0.1234(2)	3.1(2)
N(2)	0.4100(1)	0.0137(4)	0.1493(2)	3.7(2)
N(3)	0.3674(1)	0.0371(4)	0.0157(2)	3.8(2)
N(4)	0.3116(1)	0.0005(4)	0.1230(2)	4.4(2)
N(5)	0.5405(1)	0.3419(4)	0.0128(2)	4.4(2)
N(6)	0.2697(2)	0.0463(7)	−0.0068(3)	10.1(4)
N(7)	0.3160(2)	−0.2093(6)	0.0237(3)	10.6(4)
C(1)	0.3394(2)	0.3331(5)	0.0956(2)	3.9(3)
C(2)	0.0721(2)	0.4078(6)	0.1485(3)	6.8(4)
C(3)	0.3622(2)	0.4258(6)	0.0489(3)	6.1(3)
C(4)	0.4187(2)	−0.1301(5)	0.1492(3)	4.8(3)
C(5)	0.4631(2)	−0.1621(6)	0.1199(3)	7.6(4)
C(6)	0.4157(3)	−0.1852(5)	0.2176(3)	8.5(4)
C(7)	0.3756(2)	0.0205(5)	−0.0563(3)	5.1(3)
C(8)	0.4166(2)	−0.0595(7)	−0.0694(3)	7.7(4)
C(9)	0.3768(3)	0.1497(7)	−0.0905(3)	8.3(5)
C(10)	0.2687(2)	−0.0515(7)	0.1486(3)	7.6(4)
C(11)	0.2396(2)	0.0552(9)	0.1747(4)	11.6(6)
C(12)	0.2768(3)	−0.1582(8)	0.1993(4)	12.4(6)
C(13)	0.5585(2)	0.4672(6)	0.1422(3)	5.5(3)
C(14)	0.5406(3)	0.4845(7)	0.0739(3)	8.8(4)
C(15)	0.6081(2)	0.4675(7)	0.1455(4)	9.6(5)

1.85 Å).[21] This possibly indicates more s-character in the Al−N(1) bonding. The Al−Cl(1) bond distance of 2.127(2) Å is in the same range as found in other organoaluminum chloride compounds.[22−25]

A molecular plot of compound $Al(NEt_2)(N^iPr_2)H$ (**6**), a dimer with a center of inversion, is shown in Figure 2. The selected bond lengths and bond angles are shown in Table 2. Both compound **6** and compound **1** possess an identical framework. The Al_2N_2 four-membered ring skeleton is nearly square planar. The distance of 1.792(4) Å between Al(1) and terminal N(1) atom is the same as that in **1**.[13] Although the Al−H distance may not be reliable in the X-ray analysis, the observed Al(1)−H(14) distance of 1.67 Å falls between that in a trialkylaluminum (1.75(3) Å)[26] and that in a lithium organotrihydroaluminate (1.61(2) Å).[27] The H−Al−N angles involving H(14) (108, 114°) are consistent with distorted tetrahedral geometry around the aluminum atom.

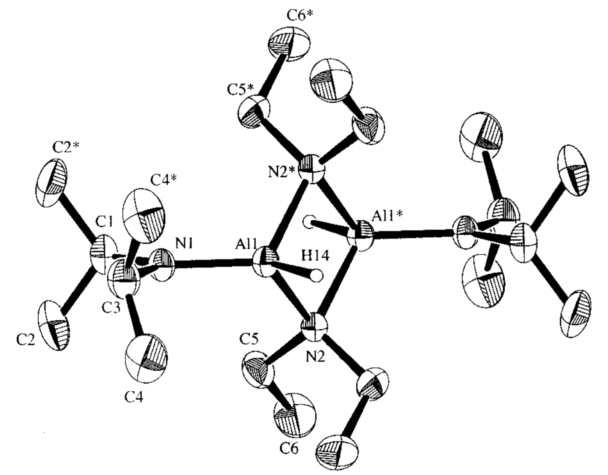

Figure 2. ORTEP drawing of the compound $Al_2(\mu\text{-}NEt_2)_2(N^iPr_2)_2H_2$ (**6**).

Compound **7** is composed of two parts of $\{Al(NH_3)(NH_2)[Al(N^iPrH)(N^iPr)Cl]_2\}_2$ (**X**) with one part of $AlCl_3(N^iPrH_2)_2$ (**Y**). The exact molecular symmetry of **7** is C_2 with the 2-fold axis passing through Al(4) and Cl(3). Coordinated to the seven aluminum atoms are ammonia, amide, imide, and free amine as shown in Figure 3. The selected bond lengths and bond angles are given in Table 2. The **X** part contains a plane formed from atoms Al(1), N(3), N(4), and Al(2) and a cyclobutane-like Al_2N_2 ring made of Al(1), Al(2), N(1), and N(2) atoms. In the three-coordinate N(3) moiety, the Al(1), N(3), C(7), and Al(3) atoms lie on a plane caused by the sp^2 hybridization of N(3) atom, and so is the N(4) atom. The short distances of Al−N involving N(3) (1.784(4), 1.718(4) Å) and N(4) (1.735(4) and 1.788(5) Å) could be caused by ionic resonance effects.[14] The **Y** molecule is an amine adduct of electronically neutral $AlCl_3$. Hence, the **X** molecule is also neutral. The nitrogen ligands coordinated to Al(3) have to be neutral amine and amido anion in order to balance the charge on **X**. After careful examination of the final difference electron density map, the N(7) is assigned as belonging to the amine ligand and N(6) is assigned as belonging to the amido ligand.

Stoichiometric Reaction of Compound $Al_2(NR_2)_2Cl_4$ (R = Et, a; R = ^{i}Pr, b) with LiN^iPr_2. The reactions of $Al_2(NR_2)_2Cl_4$ (R = Et, **a**; R = ^{i}Pr, **b**) and lithium diisopropylamide, LiN^iPr_2, in 1:2 stoichiometric ratio produced **1** and **2** as shown in eq 1. The ^1H NMR spectrum of **1** displayed a chemical shift at $\delta = 1.09$ (t, 6H), 2.98 (q, 4H), and 3.28 (q, 4H) due to the methyl and methylene protons in the ethyl groups and at $\delta = 1.27$ (d, 12H) and 3.38 (sep, 4H) due to the methyl and methine protons in the isopropyl groups. The ^{13}C NMR spectrum showed a chemical shift at $\delta = 12.40$ and 40.23 for the methyl and methylene groups of the ethyl and at $\delta = 25.50$ and 46.69

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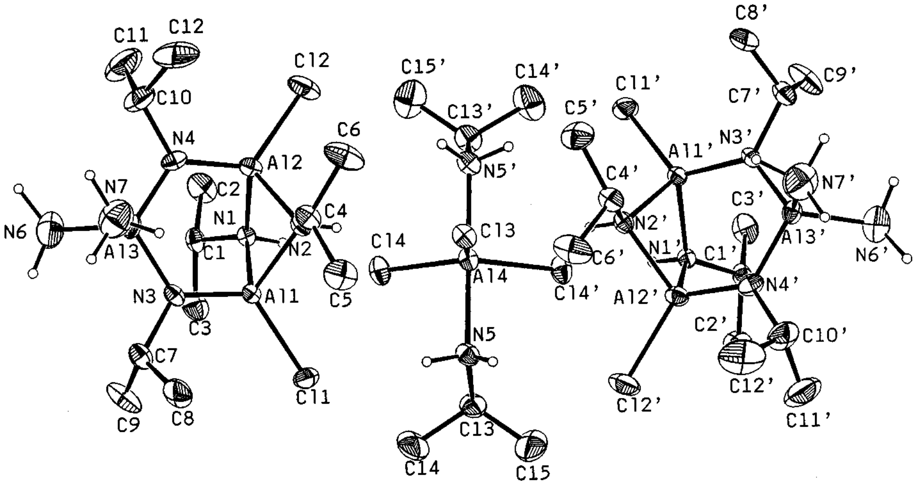

Figure 3. ORTEP drawing of the compound $\mathrm{AlCl_3(^iPrNH_2)_2\{Al(NH_3)(NH_2)[Al(N^iPrH)(N^iPr)Cl_2\}_2}$ (**7**).

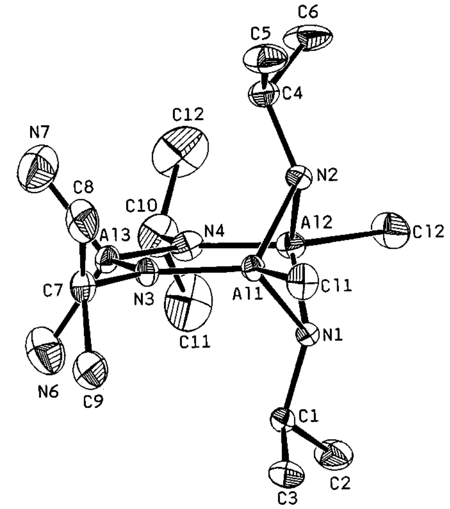

Figure 4. ORTEP drawing of the compound $\mathrm{\{Al(NH_3)(NH_2)[Al(N^iPrH)(N^iPr)Cl]_2\}_2}$ (**X**).

$$\underset{\mathbf{a},\,\mathbf{b}}{\mathrm{Al_2(NR_2)_2Cl_4}} + 2\mathrm{LiN^iPr_2} \rightarrow \mathrm{Al_2(NR_2)_2(N^iPr_2)_2Cl_2} + 2\mathrm{LiCl} \quad (1)$$

R = Et, **1**
R = ^{i}Pr, **2**

assigned to methyl groups the and methine carbon of the isopropyl group. The ^{27}Al NMR spectrum showed a chemical shift at $\delta = 89$ ppm which was assigned to a four-coordinated environment of the organoaluminum compound.[28] Mass spectral data showed the base-ion peak at $m/z = 468$ which was assigned to the molecular ion. The above spectral data are in good agreement with the crystal structure obtained from X-ray diffraction techniques. After several days, the ^{1}H NMR spectrum of **1** gradually appeared to have the additional peaks $\delta = 0.95$ (d) and 2.81 (sep), which were assigned to the methyl protons and methine protons of the *cis* form of $\mathrm{Al_2(\mu\text{-}NEt_2)_2(N^iPr_2)_2Cl_2}$. In the characterization of **2**, the ^{1}H NMR spectrum displayed chemical shifts at $\delta = 1.25$ (d) due to methyl groups of the isopropyl and at $\delta = 3.40$ (sep) which was assigned to the methine groups. Mass spectral data contain the base-ion peak at $m/z = 489$ was assigned to the dimer ion less one chloride group. Compound **2** was isolated by sublimation at 75 °C after solvent removal. It is reasonable to suggest two species, *cis* and *trans*, to exist in the solutions of compounds **1** and **2**. On variation of the molar ratio of compound **b** to $\mathrm{LiN^iPr_2}$ from 1:2 to 1:4, product **3** was obtained as shown in eq 2, while compound **1** did not react further with lithium diisopropylamide.

$$\underset{\mathbf{b}}{\mathrm{Al_2(N^iPr_2)_2Cl_4}} \xrightarrow[-\,2\mathrm{LiCl}]{2\,\mathrm{LiN^iPr_2}} \underset{\mathbf{2}}{\mathrm{Al_2(N^iPr_2)_4Cl_2}} \xrightarrow[-\,2\mathrm{LiCl}]{2\mathrm{LiN^iPr_2}} \underset{\mathbf{3}}{2\mathrm{Al(N^iPr_2)_3}} \quad (2)$$

The ^{1}H NMR spectrum of **3** displayed a chemical shift at $\delta = 1.27$ (d) due to methyl groups of isopropyl, and the septet at $\delta = 3.41$ was assigned to the methine groups of isopropyl. Mass spectral data contained the base-ion peak at $m/z = 328$ assigned to the monomeric species plus one hydrogen group. The X-ray diffraction data[35] for compound **3** showed identical parameters with the published report.[13]

Substitution Reactions of $\mathbf{Al_2(NR_2)_{2\mathit{n}}Cl_{6-2\mathit{n}}}$ (R = Et, ^{i}Pr; *n* = 1−3) with Excess LiNR′R″. Some intermediates were difficult to purify when different chemical stoichiometries were used. For instance, we were able to isolate the compounds **2** and **3** using $\mathrm{Al_2(N^iPr_2)_2Cl_4}$ and $\mathrm{LiN^iPr_2}$ in 1:2 and 1:4 stoichiometric ratios while we could not isolate the rest of the intermediates when the stoichiometry was 1:1, 1:3, 1:5, etc. They may form aluminum complexes with more amido substituents. So we used excess lithium amide to isolate the products. Compounds **4** and **5** were synthesized by the reactions of **a**, **b**, **1**, and **2** with excess lithium amide LiNR′R″ as shown in eqs 3 and 4. However, one additional compound **6**, $\mathrm{Al_2(NEt_2)_2(N^iPr_2)_2H_2}$, was isolated during the synthesis of **5**. We presume that compounds **5** and **6** were obtained through the substitution

$$\mathrm{Al_2(NR_2)_2Cl_4} + 6\,\mathrm{LiNR'R''} \xrightarrow{-4\mathrm{LiCl}} \mathrm{\{Al(NR'R'')_3\}_\mathit{n}} + 2\mathrm{LiNR_2} \quad (3)$$

R = Et, **a**
R = ^{i}Pr, **b**
R′ = R″ = Et, **4**
R′ = ^{i}Pr, R″ = H, **5**

$$\mathrm{Al_2(NR_2)_2(NR^*{}_2)_2Cl_2} \xrightarrow[-2\mathrm{LiCl}]{6\mathrm{LiNR'R''}} \mathrm{\{Al(NR'R'')_3\}_\mathit{n}} + 2\mathrm{LiNR_2} + 2\mathrm{LiNR^*{}_2} \quad (4)$$

R = Et, R* = ^{i}Pr
R = R* = ^{i}Pr
R′ = R″ = Et, **4**
R′ = ^{i}Pr, R″ = H, **5**

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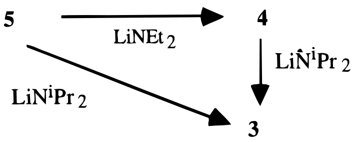
reaction of compound **1**, $Al_2(NEt_2)_2(N^iPr_2)_2Cl_2$, by lithium hydride and lithium isopropylamide, respectively. The lithium hydride may be a side product in the synthesis of lithium isopropylamide. Compounds **3**−**5** can be synthesized by other routes. Reaction of Al_2Cl_6 with LiNR′R″ in 1:6 stoichiometric ratio yields all three compounds. This result is similar to that found by Ruff *et al.*[29−32] Also, compounds **4** and **5** could also be synthesized by substitution reaction of **3** and **4** with lithium amide LiNR′R″, respectively (eq 5). The ^1H NMR spectrum of **4** displayed a chemical shift at $\delta = 1.24$ (t) due to the methyl groups of the ethyl, and the quartet at $\delta = 3.14$ was assigned to the methylenyl groups. Mass spectral data contained the base-ion peak at $m/z = 487$ assigned to the dimeric ion plus one hydrogen group.



(5)

The FT-IR spectrum of the complex **5** showed a broad peak in the 3340 cm^{-1} region which was assigned to the N−H stretching vibrations. The ^1H NMR spectrum of **5** displayed a chemical shift at $\delta = 0.19$ (br) due to NH of isopropylamide; the doublet peaks at $\delta = 1.23$ and 1.38 were assigned to the terminal and bridged methyl groups of isopropylamide, respectively. Mass spectral data contained the base-ion peak at $m/z = 603$ assigned to be a trimeric ion. Hence it is suggested that **5** exists as a trimer.

Formation of $AlCl_3(N^iPrH_2)_2\{[Al(NH_3)(NH_2)[Al(N^iPrH)(N^iPrH)(N^iPr)Cl]_2\}_2$ (7). Reaction of aluminum trichloride with lithium isopropylamide yielded a single product, $Al(N^iPrH)_3$, **5**. However, similar reactions of aluminum trichloride with lithium isopropylamide in the presence of isopropylamine have generated compound **7**. In an attempt to rationalize the formation of **7**, we propose the possible involvement of an unidentified species $LiNH_2$. A logical retrosynthesis scheme is shown in eqs 6−9.

$$\underset{\mathbf{7}}{AlCl_3(N^iPrH_2)_2\{Al(NH_3)(NH_2)[AlCl(N^iPrH)(N^iPr)]_2\}_2} \leftarrow 2\underset{\mathbf{X}}{\{Al(NH_3)(NH_2)[AlCl(N^iPrH)(N^iPr)]_2\}} + \underset{\mathbf{Y}}{AlCl_3(N^iPrH_2)_2} \qquad (6)$$

$$\underset{\mathbf{8}}{Al_2(N^iPrH)_4Cl_2} \xleftarrow[-\,4LiCl]{4\,LiN^iPrH} Al_2C_6 \qquad (7)$$

$$\underset{\mathbf{9}}{Al_2(N^iPrH)_2(NH_2)_4} \xleftarrow[-\,2LiCl]{2\,LiN^iPrH} Al_2(NH_2)_4Cl_2 \xleftarrow[-\,4LiCl]{4LiNH_2} Al_2Cl_6 \qquad (8)$$

$$\underset{\mathbf{X}}{\{Al(NH_3)(NH_2)[AlCl(N^iPrH)(N^iPr)]_2\}} \xleftarrow{-N^iPrH_2} \underset{\mathbf{8}}{Al_2(N^iPrH)_4Cl_2} + {}^1/_2\underset{\mathbf{9}}{Al_2(N^iPrH)_2(NH_2)_4} \qquad (9)$$

The compound **7** contains two different moieties with a general composition of $\mathbf{X_2Y}$. The **X** part possess the π interaction delocalized in the Al_3N_2 planar framework, which may be hypothetically built from $Al_2(N^iPrH)_4Cl_2$ (**8**) and $Al(N^iPrH)(NH_2)_2$ (**9**). Moreover, the synthesis of compounds **8** and **9** could be rationalized by the above substitution reactions. The clarification of the mechanistic details would require extensive work. However, it seems worthy of further investigation.

The FT-IR spectrum of the compound **7** showed three broaden peaks in the region 3205−3361 cm^{-1} which were attributed to the stretching vibrations of the N−H groups. The ^1H NMR spectrum of **7** displayed chemical shift at $\delta = 0.89$ (br) and 3.87 (br) due to NH of $Al(NH_3)(NH_2)$ and N^iPrH, respectively. The chemical shifts of various protons of $Al(NH_2)(NH_3)$ are comparable to those of the corresponding values in the $\{^tBu_2AlNH_2\}_3$ derivative.[33] The chemical shifts at $\delta = 0.95$ (d), 1.23 (d), and 1.31 (br) with integral ratio 1:2:2 are due to methyl groups of isopropyl of $AlCl_3(N^iPrH_2)$, isopropylimido, and isopropylamido, respectively. The ^{13}C NMR spectrum showed chemical shifts at $\delta = 23.70$, 25.66, and 25.90 assigned to the methine carbon of isopropyl of imido, amido, and amine, respectively. The peaks at $\delta = 65.45$, 46.29, 46.01 were assigned to methyl carbon of isopropyl of imido, amido, and amine. The ^{27}Al NMR spectrum showed a chemical shift at $\delta = 112$ ppm assigned to a four-coordinated environment of organoaluminum complex.[28] These spectral data support the structure as determined by X-ray diffraction technique.

Acknowledgment. We thank the National Science Council of the Republic of China for financial support.

Supporting Information Available: Text describing X-ray procedures and tables of crystal data, complete bond distances and bond angles, final fractional coordinates, and thermal parameters (21 pages). Ordering information is given on any current masthead page.

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