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Thermolysis of Halo- and Alkylaluminum Silylamido Complexes and the Al_4N_4 Cubane Core Structure of $[i\text{-}BuAlNSiPh_3]_4$

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Introduction

There are presently no known examples of alkylaluminum silylimides (compounds of the general formula $[RAlNSiR'_3]_x$), although it should be possible to prepare these by thermal decomposition of dialkylaluminum silylamido dimers $[R_2AlN(H)SiR'_3]_2$,[1] analogous to the pyrolysis of alkylamido compounds $[R_2AlN(H)R']_x$.[2] Due to presumably weak Al–N π interactions,[3] all known alkylaluminum imides are oligomeric (i.e., $x > 1$ in $[RAlNR']_x$). Most of the alkylaluminum imides that have been structurally characterized have an Al_4N_4 cubane core structure,[2d] with Al_3N_3 ring[4] and Al_7N_7 cage[5] structures also known. The influence of a silyl group bound to nitrogen on the electron density at nitrogen may affect the bridging ability of nitrogen and therefore the structure of an alkylaluminum silylimide.[6] Additionally, little is known about the reactivity of alkylaluminum imido cages. In particular, substitution of groups attached to the Al_4N_4 core is of interest in preparing cubes containing other heteroatoms, such as alkoxoaluminum silylimides, $[ROAlNSiR'_3]_x$. Thermolysis of such molecules may yield solid-state materials such as SiAlONs.[7] Previous attempts to prepare $[ROAlNSiR'_3]_4$ by alcoholytic cleavage of R–Al bonds in $[RAlNSiR'_3]_4$ have been unsuccessful, leading either to no reaction or to decomposition,[8] presumably due to preferential cleavage of Al–N bonds.[9] We describe herein preparation of compounds of the type $[RAlNSiR'_3]_4$ by thermolysis of $[R_2AlN(H)SiR'_3]_2$. Further, $[ClAlNSiPh_3]_4$ (a possible source of $[ROAlNSiPh_3]_4$ by chloride substitution reactions) is prepared by thermolysis of $[(Cl)(Me)AlN(H)SiPh_3]_2$.

Experimental Section

Reagents, Solvents, and General Procedures. Unless otherwise stated, all operations were conducted under an atmosphere of high-purity nitrogen using standard Schlenk techniques. The following were obtained from commercial sources and used without further purification: Et_3SiCl (Silar); $t\text{-}Bu_2HSiCl$ (Petrarch); NH_3 (Linde Specialty Gases anhydrous grade); Me_3Al (Ethyl Corp.); Me_2AlCl, MeLi, $(Me_3Si)_2NH$, and $AlCl_3$ (Aldrich). Benzene (Fisher) was distilled from potassium, and toluene (Fisher) was distilled from sodium. Pentane (American Scientific), hexane (American Scientific), tetrahydrofuran (Aldrich), and diethyl ether (Fisher) were distilled from sodium/potassium alloy.

Analytical Procedures. Elemental analyses were performed by the University Instrumentation Center at the University of New Hampshire and by Pascher Microanalytical Laboratories, Remagen, Germany. Infrared spectra were measured from mineral oil (Nujol) mulls between KBr plates on a Perkin-Elmer 283B spectrometer and were referenced to the 1028-cm^{-1} band of a 0.05-mm polystyrene film. Absorptions are described below as follows: strong (s), medium (m), weak (w), shoulder (sh), and broad (br). Proton and carbon FTNMR spectra were recorded on a Bruker AM-360 spectrometer (360 and 90 MHz, respectively) and were referenced internally to tetramethylsilane. Mass spectra were obtained at the University Instrumentation Center at the University of New Hampshire (Hewlett-Packard 5890).

Preparation of $[Cl_2AlN(H)SiMe_3]_2$.[10] Freshly sublimed aluminum trichloride (8.52 g, 6.39×10^{-2} mol) was cooled to −78 °C, and cold (−78 °C) diethyl ether (20 mL) was added with stirring. Upon warming of the mixture to room temperature, a colorless, slightly cloudy solution was obtained. Toluene (20 mL) was added, and excess ether was removed under reduced pressure. To this solution, hexamethyldisilazane (13.5 mL, 10.3 g, 6.39×10^{-2} mol) was slowly added. The solution was then refluxed for 1 h. All volatile material was removed from the reaction mixture under reduced pressure to yield white sticky crystals which were purified by low-temperature recrystallization from toluene at −40 °C yielding 2.37 g of colorless crystals. Concentrating the supernatant under reduced pressure and cooling to −78 °C gave an additional 1.75 g of product for a total of 4.12 g (11.1×10^{-3} mol, 35%). Mp: 165–167 °C. Anal. Calcd for $C_6H_{20}Al_2Cl_4N_2Si_2$: C, 19.36; H, 5.42; N, 7.53. Found: C, 19.51; H, 5.60; N, 7.11. IR (Nujol, 400–4000 cm^{-1}): 420 (m), 505 (m), 580 (s), 590 (s), 632 (w), 692 (w), 750 (s), 840 (s), 875 (s), 1120 (s), 1255 (s), 3200 (s) cm^{-1}. ^1H NMR (C_6D_6, 25 °C): δ 0.07, 0.12 (s, 18H, cis and trans isomer, $Si(CH_3)_3$), 1.18, 1.35 (br s, 4H, cis and trans isomer, N–*H*). MS (CI, CH_5^+): 372 amu.

Preparation of $[Me(Cl)AlN(H)SiPh_3]_2$. Dimethylaluminum chloride (4.6 mL of a 1.00 M solution in hexane, 4.6×10^{-3} mol) was added to triphenylsilylamine[11] (1.26 g, 4.6×10^{-3} mol) in hexane (50 mL) giving a white precipitate. The suspension was stirred and refluxed until evolution of gas ceased (5.25 h). The white solid was recrystallized from toluene (6 mL) to yield colorless prisms (2.00 g, 62%, mp 155–157 °C). Anal. Calcd for $C_{38}H_{38}Al_2Cl_2N_2Si_2$: C, 64.85; H, 5.44; N, 3.98. Found: C, 64.50; H, 5.25; N, 3.88. IR (Nujol, 400–4000 cm^{-1}): 435 (m), 530 (w), 575 (s), 630 (w), 680 (m), 715 (s), 748 (s), 790 (s), 835 (w), 990 (s), 1110 (s), 1240 (s), 1760 (w, br), 1835 (w, br), 1885 (w, br), 1960 (w, br). ^1H NMR (C_6D_6, 25 °C): δ −0.93 (s, 3 H, Al–CH_3), 2.69 (s, 1 H, N–*H*), 7.11 (m, C_6H_5), 7.75 (m, C_6H_5). MS (CI, CH_5^+): 688 amu (M − CH_3).

Preparation of $[MeAlNSiMe_3]_4$ (1). To a stirred solution of $[Cl_2AlN(H)SiMe_3]_2$ (1.9 g, 5.1×10^{-3} mol) dissolved in ether (50 mL) at −25 °C was added a 1.4 M solution of methyllithium (14.5 mL, 2.04×10^{-2} mol) dropwise by syringe. Rapid gas evolution and the formation of a white precipitate were observed. After 20 min the ether was removed under reduced pressure. The white residue was heated to 40 °C at 10^{-2} Torr for 10 h and then sublimed twice at 145 °C and 10^{-2} Torr onto a water-cooled cold finger, giving 0.51 g of white crystalline product (43%, mp 242 °C). Anal. Calcd for $C_{16}H_{48}Al_4N_4Si_4$: C, 37.18; H, 9.36; N, 10.84. Found: C, 36.89; H, 9.01; N, 10.50. IR (Nujol, 400–4000 cm^{-1}): 573 (m), 609 (w), 666 (s), 685 (s), 759 (s), 834 (vs), 916 (vs), 975 (sh), 1037 (w), 1196 (s), 1250 (s), 1262 (s), 1299 (w), 1401 (w). ^1H NMR

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(1) Choquette, D. M.; Timm, M. J.; Hobbs, J. L.; Rahim, M. M.; Ahmed, K. J.; Planalp, R. P. *Organometallics* **1992**, *11*, 529.

(2) (a) Wiberg, E. In *FIAT Review of German Science 1939-1946*; Bähr, G., Ed.; Dieterische Verlagsbuchhandlung: Wiesbaden, BRD, 1948; Inorganic Chemistry, Part II. (b) Mole, T.; Jeffery, E. A. *Organoaluminum Chemistry*; Elsevier: New York, 1972. (c) Lappert, M.; Power, P.; Sanger, A.; Srivastava, R. *Metal and Metalloid Amides*; Ellis Horwood: Chichester, U.K., 1980. (d) Jones, J. I.; McDonald, W. S. *Proc. Chem. Soc., London* **1962**, 366. (e) Laubengayer, A. W.; Smith, J. D.; Ehrlich, G. G. *J. Am. Chem. Soc.* **1961**, *83*, 542. (f) Amirkhalili, S.; Hitchcock, P. B.; Smith, J. D. *J. Chem. Soc., Dalton Trans.* **1979**, 1206. (g) Al-Wassail, A. A.; Hitchcock, P. B.; Sarisaban, S.; Smith, J. D.; Wilson, C. L. *J. Chem. Soc., Dalton Trans.* **1985**, 1929. (h) Beachley, O. T.; Victoriano, L. *Organometallics* **1988**, *7*, 63. (i) Hitchcock, P. B.; Jasim, H. A.; Lappert, M. F.; Williams, H. D. *Polyhedron* **1990**, *9*, 245. (j) Schauer, S. J.; Pennington, W. T.; Robinson, G. H. *Organometallics* **1992**, *11*, 3287.

(3) Petrie, M. A.; Olmstead, M. M.; Power, P. P. *J. Am. Chem. Soc.* **1991**, *113*, 8704.

(4) Waggoner, K. M.; Hope, H.; Power, P. P. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1699.

(5) Hitchcock, P. B.; McLaughlin, G. M.; Smith, J. D.; Thomas, K. M. *J. Chem. Soc., Chem. Commun.* **1973**, 934.

(6) (a) Bartlett, R. A.; Power, P. P. *J. Am. Chem. Soc.* **1987**, *109*, 6509. (b) Janes, N.; Oldfield, E. *J. Am. Chem. Soc.* **1986**, *108*, 5743 and references therein.

(7) Jack, K. H. *Endeavour* **1987**, *11*, 80.

(8) Timm, M. J. M.S. Thesis, University of New Hampshire, 1990.

(9) Reaction of $[EtAlNEt]_4$ with HCl is observed to give $[(Et)(Cl)AlN(H)Et]_2$, a product of Al–N bond cleavage: Gilbert, J. K.; Smith, J. D. *J. Chem. Soc. A* **1968**, 233.

(10) (a) Preparation modified from: Schmidbaur, H. *Angew. Chem.* **1961**, *73*, 257. (b) Becke-Goering, M.; Krill, H. *Chem. Ber.* **1961**, *94*, 1059.

(11) Kraus, C. A.; Rosen, R. *J. Am. Chem. Soc.* **1925**, *47*, 2739.

0020-1669/93/1332-2600$04.00/0

(C_6D_6, 25 °C): δ −0.25 (s, 12 H, Al–C*H*$_3$), 0.13 (s, 36 H, Si–CH$_3$). $^{13}C\{^1H\}$ NMR (C_6D_6, 25 °C): δ −10.3 (br s, Al–*C*H$_3$), 3.5 (s, Si–*C*H$_3$). MS (EI, 70 eV): 502 amu (M − CH$_3$).

Preparation of [MeAlNSiEt$_3$]$_4$ (2). The compound [$Me_2AlN(H)SiEt_3]_2$[1] (3.07 g, 8.21 × 10^{-3} mol) was heated at 240 °C for 4 h in a heavy-walled glass bottle. The white solid melted within 5 min, producing a colorless liquid. The pressure increased, peaking at 3.4 atm prior to cooling to give a white solid. Gases formed were found to be methane by gas-phase infrared spectroscopy. The solid was dissolved in hexane (15 mL), and the solution was concentrated to ca. 10 mL under reduced pressure. Crystallization at −78 °C yielded 1.34 g of white prisms (44%, 2.00 × 10^{-3} mol, mp 229–232 °C). Anal. Calcd for $C_{28}H_{72}N_4Al_4Si_4$: C, 49.08; H, 10.59; N, 8.18. Found: C, 48.67; H, 10.57; N, 7.57. IR (Nujol, 400–4000 cm^{-1}): 570 (m), 680 (m), 745 (s), 790 (w), 897 (s), 960 (w), 1020 (s), 1198 (m), 1240 (m), 1257 (w), 1400 (w). ^1H NMR (C_6D_6, 25 °C): δ 1.04 (t, 9H, –CH$_2$C*H*$_3$), 0.73 (q, 6H, –C*H*$_2$CH$_3$), −0.11 (s, 3H, Al–C*H*$_3$). $^{13}C\{^1H\}$ NMR (C_6D_6, 25 °C): δ 9.18 (s, –CH$_2$*C*H$_3$), 8.34 (s, –*C*H$_2$CH$_3$), −7.13 (br s, Al–*C*H$_3$). MS (EI, 70 eV): 669 amu (M − CH$_3$).

Preparation of [MeAlNSiPh$_3$]$_4$ (3). A sample of [$Me_2AlN(H)SiPh_3]_2$[1] (0.45 g, 6.8 × 10^{-4} mol) was heated in the solid state from 170 to 185 °C at 10^{-2} Torr for 2 days. The solid was dissolved in toluene (5 mL) and hexane (ca. 4 mL) was added causing colorless needles (0.26 g, 62%) to form over 12 h. The compound does not melt below 400 °C. Anal. Calcd for $C_{76}H_{72}Al_4N_4Si_4 \cdot C_7H_8$: C, 73.64; H, 5.96; N, 4.14. Found: C, 73.88; H, 6.13; N, 4.15. IR (Nujol, 400–4000 cm^{-1}): 525 (s), 586 (s), 595 (m, sh), 717 (s), 744 (m), 803 (w), 888 (s), 998 (w), 1029 (w), 1039 (w), 1107 (s), 1198 (w), 1260 (w), 1305 (w), 1428 (s), 1589 (w), 1778 (w, br), 1829 (w, br), 1896 (w, br), 1962 (w, br), 3046 (w), 3070 (w) cm^{-1}. ^1H NMR (C_6D_6, 25 °C): δ −0.55 (s, 12H, Al–C*H*$_3$); 7.03–7.65 (m, Ph–*H*). $^{13}C\{^1H\}$ NMR (C_6D_6, 25 °C): δ −4.24 (br s, Al–CH$_3$), 128.20, 129.62, 135.58, 136.94 (s, –*C*$_6$H$_5$).

Preparation of [*i*-BuAlNSiPh$_3$]$_4$ (4). The compound [*i*-$Bu_2AlN(H)SiPh_3]_2$[1] (0.51 g, 6.1 × 10^{-4} mol) was heated in the solid state at 130 °C and 10^{-2} Torr for 12 days. The solid was dissolved in hexane and let to stand at 20 °C for 12 h, affording colorless prisms (0.044 g, 3.1 × 10^{-5} mol, 10%). Mp: 360 °C dec. Anal. Calcd for $C_{88}H_{96}Al_4N_4Si_4$: C, 73.91; H, 6.77; N, 3.92. Found: C, 73.90; H, 6.79; N, 3.69. IR (Nujol, 400–4000 cm^{-1}): 517 (s), 708 (s), 746 (m), 806 (w, br), 997 (w), 1026 (m), 1058 (m, br), 1113 (s), 1428 (m), 1590 (w), 1779 (w, br), 1830 (w, br), 1897 (w, br), 1960 (w, br), 3048 (w), 3067 (w) cm^{-1}. ^1H NMR (C_6D_6, 25 °C): δ 0.52 (d, 24H, –CH(C*H*$_3$)$_2$), 0.83 (d, 8H, Al–C*H*$_2$), 1.43 (nonet, 4H, –C(*H*)(CH$_3$)$_2$, 7.02 (t, 24H, Ph 3,5-*H*), 7.15 (t, 12H, Ph 4-*H*), 7.75 (d, 24H, Ph 2,6-*H*). $^{13}C\{^1H\}$ NMR (C_6D_6, 25 °C): 24.92 (s, Al–CH$_2$–*C*H), 26.39 (br s, Al–*C*H$_2$), 28.02 (s, –CH(*C*H$_3$)$_2$), 128.09, 129.46, 137.76, 138.36 (s, *C*$_6$H$_5$).

Preparation of [*i*-BuAlNSi-*t*-Bu$_2$H]$_4$ (5). The compound [*i*-Bu$_2$AlN(H)Si-*t*-Bu$_2$H]$_2$[1] (0.45 g, 7.5 × 10^{-4} mol) was heated in a heavy-walled glass bottle at 145 °C for 2 days. The pressure increased, reaching 3.9 atm before cooling. Recrystallization of the white solid from hexane yielded colorless microcrystals (0.036 g, 3.7 × 10^{-5} mol, 10%). Mp: 309–310 °C. Anal. Calcd for $C_{48}H_{112}Al_4N_4Si_4$: C, 59.70; H, 11.69; N, 5.80. Found: C, 59.81; H, 11.70; N, 5.50. IR (Nujol, 400–4000 cm^{-1}): 567 (m), 582 (m), 630 (s), 663 (s), 821 (s), 842 (s), 909 (w), 1005 (w), 1095 (w), 1364 (m), 2118 (s) cm^{-1}. ^1H NMR (C_6D_6, 25 °C): δ 0.85 (d, 8H, Al–C*H*$_2$), 1.28 (d, 24H, Al–CH$_2$CH(C*H*$_3$)$_2$), 1.33 (s, 72H, Si–C(C*H*$_3$)$_3$), 2.20 (nonet, 4H, Al–CH$_2$C*H*), 4.55 (s, 4H, Si–*H*). $^{13}C\{^1H\}$ NMR (C_6D_6, 25 °C): δ 20.57 (s, Al–CH$_2$CH(*C*H$_3$)$_2$), 25.45 (s, Si–C(*C*H$_3$)$_3$), 28.06 (s, Al–CH$_2$*C*H), 30.73 (br s, Al–*C*H$_2$), 34.91 (s, Si–*C*(CH$_3$)$_3$). MS (CI, CH$_5^+$): 967 amu (M$^+$).

Preparation of [ClAlNSiPh$_3$]$_4$ (6). The compound [Me(Cl)AlN(H)SiPh$_3$]$_2$ (0.97 g, 1.4 × 10^{-3} mol) was heated in the solid state at 130 °C and 10^{-3} Torr for 36 days. Recrystallization from toluene (20 mL) at 0 °C provided colorless prisms (0.32 g, 2.4 × 10^{-4} mol, 34%). The compound does not melt below 400 °C. Anal. Calcd for $C_{72}H_{60}Al_4Cl_4N_4Si_4$: C, 64.37; H, 4.50; N, 4.17. Found: C, 64.01; H, 4.51; N, 4.02. IR (Nujol, 400–4000 cm^{-1}): 500 (m), 528 (m), 580 (m), 690 (s), 710 (s), 735 (s), 775 (s), 790 (s), 992 (m), 1108 (s), 1125 (s), 1200 (m), 1430 (s), 1585 (w), 1770 (w, br), 1820 (w, br), 1890 (w, br). ^1H NMR (C_6D_6, 25 °C): δ 7.05 (m, C$_6$*H*$_5$), 7.73 (m, C$_6$*H*$_5$).

X-ray Crystallography of 4. A crystal of **4** was coated with hydrocarbon oil to retard decomposition, attached to a glass fiber with silicone grease, and mounted in the cold stream of a Syntex P2$_1$ diffractometer equipped with a locally modified LT-1 low-temperature device. Three standard reflections monitored during the course of data collection showed no appreciable decay. All computing was carried out with SHELXTL PLUS[12] programs. Atomic scattering factors and anomalous dispersion corrections were from common sources.[13] The structure was solved by direct methods. The data were corrected for absorption empirically using F_o and F_c differences using the program XABS.[14] Full-matrix least-squares refinement was carried out with anisotropic thermal parameters for all non-hydrogen atoms. One of the isobutyl groups is disordered. Two sets of isobutyl carbon atoms, "A" and "B", were refined with equal occupancies of 0.5. The structure also contains a molecule of crystallization of hexane which was refined at 0.5 occupancy. All non-hydrogen atoms except those of the disordered isobutyl group and the molecule of hexane were refined with anisotropic thermal parameters. Hydrogen atoms were not included on the disordered atoms, but were otherwise included at calculated positions using a riding model with fixed isotropic thermal parameters of 0.06 Å. Three reflections with severe extinctions were omitted during the refinement. Crystallographic data are presented in Table I, selected bond distances and angles in Table II, and atomic coordinates and isotropic thermal parameters of selected atoms in Table III. Full structure data are given in the supplementary material.

Table I. Summary of Crystallographic Data for [*i*-BuAlNSiPh$_3$]$_4$·0.5hexane (**4**)

empirical formula	$C_{91}H_{103}Al_4N_4Si_4$
mol wt	1473.1
a, Å	13.942(7)
b, Å	14.426(8)
c, Å	21.093(11)
α, deg	93.23(1)
β, deg	98.78(1)
γ, deg	93.84(1)
Z	2
V, Å^3	4174(4)
space group	$P\bar{1}$
d_{calcd}, g cm^{-3}	1.17
radiation (λ, Å)	Mo Kα (0.710 69)
diffractometer	Siemens R3m/V
temp, K	130
scan width, deg	1.20
scan speed, deg min^{-1}	constant; 30.00°/min in ω
scan type	ω
data colln range, deg	0.0–50.0
no. of unique data	14636 (R_{int} = 0.013)
no. of obsd data	8760 [$I > 3\sigma(I)$]
rfln/param ratio	9.5
R^a	0.0710
$R_w^{\,b}$	0.1165
goodness of fit^c	0.78

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = \sum||F_o| - |F_c||\sqrt{w}/\sum|F_o|\sqrt{w}$; $w^{-1} = \sigma^2(|F_o|) + 0.0182(|F_o|^2)$. [c] Goodness of fit $= [\sum(w||F_o| - |F_c||^2)/(M - N)]^{1/2}$, where M is the number of observed reflections and N is the number of parameters refined.

Results and Discussion

Synthesis and Characterization. Thermolyses of alkylaluminum silylamido ring compounds afford alkylaluminum silylimido tetramers:

$$2[R_2AlN(H)SiR'_3]_2 \xrightarrow{\Delta} \underset{\mathbf{2\text{–}6}}{[RAlNSiR'_3]_4} + 4RH \qquad (1)$$

2, R = Me, R′$_3$ = Et$_3$; **3**, R = Me, R′$_3$ = Ph$_3$; **4**, R = *i*-Bu, R′$_3$ = Ph$_3$; **5**, R = *i*-Bu, R′$_3$ = *t*-Bu$_2$H; **6**, R$_2$ = (Cl)(Me), R′$_3$ = Ph$_3$

The products are cubic Al$_4$N$_4$-framework tetramers, as determined by comparison of their IR spectra with that of structurally-characterized **4** (see below), and by NMR spectroscopy and mass

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[12] Sheldrick, G. M. *SHELXTL PLUS, A Program for Crystal Structure Determination*, Version 4.0; Siemens Analytical X-ray Instruments: Madison, WI, 1989.

[13] *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1976; Vol. IV.

[14] Moezzi, B. Ph.D. Dissertation, University of California, Davis, 1987.

Table II. Selected Bond Distances and Angles for $[i\text{-BuAlNSiPh}_3]_4\cdot 0.5$hexane (**4**)

Bond Distances (Å)			
Al(1)–N(1)	1.947(4)	Al(4)–N(4)	1.943(5)
Al(1)–N(2)	1.941(5)	Al(1)–C(1)	1.962(6)
Al(1)–N(4)	1.968(5)	Al(2)–C(23)	1.959(6)
Al(2)–N(1)	1.952(5)	Al(3)–C(45)	1.947(6)
Al(2)–N(2)	1.947(4)	Al(4)–C(67A)	1.953(11)
Al(2)–N(3)	1.959(5)	Al(4)–C(67B)	2.042(11)
Al(3)–N(2)	1.966(5)	Si(1)–N(1)	1.751(4)
Al(3)–N(3)	1.949(5)	Si(2)–N(2)	1.744(5)
Al(3)–N(4)	1.947(5)	Si(3)–N(3)	1.748(5)
Al(4)–N(1)	1.970(5)	Si(4)–N(4)	1.746(4)
Al(4)–N(3)	1.960(5)		
Bond Angles (deg)			
N(1)–Al(1)–N(2)	91.0(2)	N(3)–Al(4)–N(4)	91.0(2)
N(1)–Al(1)–N(4)	92.0(2)	N(1)–Al(4)–C(67A)	138.0(4)
N(2)–Al(1)–N(4)	91.2(2)	N(1)–Al(4)–C(67B)	108.9(3)
N(1)–Al(1)–C(1)	131.2(2)	N(3)–Al(4)–C(67A)	119.4(4)
N(2)–Al(1)–C(1)	125.8(2)	N(3)–Al(4)–C(67B)	125.5(4)
N(4)–Al(1)–C(1)	115.0(2)	N(4)–Al(4)–C(67A)	114.0(3)
N(1)–Al(2)–N(2)	90.7(2)	N(4)–Al(4)–C(67B)	136.1(3)
N(1)–Al(2)–N(3)	91.4(2)	Al(1)–N(1)–Si(1)	130.4(3)
N(2)–Al(2)–N(3)	91.3(2)	Al(2)–N(1)–Si(1)	124.4(2)
N(1)–Al(2)–C(23)	122.2(2)	Al(4)–N(1)–Si(1)	123.8(2)
N(2)–Al(2)–C(23)	130.9(2)	Al(1)–N(2)–Si(2)	125.2(3)
N(3)–Al(2)–C(23)	120.0(2)	Al(2)–N(2)–Si(2)	125.5(2)
N(2)–Al(3)–N(3)	91.0(2)	Al(3)–N(2)–Si(2)	127.2(2)
N(3)–Al(3)–N(4)	91.2(2)	Al(2)–N(3)–Si(3)	128.3(2)
N(2)–Al(3)–N(4)	91.1(2)	Al(3)–N(3)–Si(3)	126.5(2)
N(2)–Al(3)–C(45)	117.6(2)	Al(4)–N(3)–Si(3)	123.4(2)
N(3)–Al(3)–C(45)	129.8(2)	Al(1)–N(4)–Si(4)	122.9(3)
N(4)–Al(3)–C(45)	125.5(2)	Al(3)–N(4)–Si(4)	126.8(2)
N(1)–Al(4)–N(3)	90.8(2)	Al(4)–N(4)–Si(4)	128.8(2)
N(1)–Al(4)–N(4)	92.0(2)		

Table III. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Coefficients (Å × 10^3) for Significant Atoms of $[i\text{-BuAlNSiPh}_3]_4\cdot 0.5$hexane (**4**)

atom	*x*	*y*	*z*	*U*[a]
Al(1)	3518(1)	7600(1)	2025(1)	22(1)
Al(2)	1726(1)	6857(1)	2191(1)	22(1)
Al(3)	2948(1)	7763(1)	3209(1)	23(1)
Al(4)	2116(1)	8752(1)	2232(1)	22(1)
Si(1)	1719(1)	7707(1)	782(1)	25(1)
Si(2)	3550(1)	5662(1)	2761(1)	27(1)
Si(3)	629(1)	8107(1)	3209(1)	26(1)
Si(4)	4380(1)	9523(1)	2869(1)	26(1)
N(1)	2193(3)	7712(3)	1600(2)	23(1)
N(2)	3057(3)	6717(3)	2592(2)	22(1)
N(3)	1611(3)	7892(3)	2811(2)	24(1)
N(4)	3442(3)	8647(3)	2650(2)	23(1)
C(1)	4750(4)	7584(4)	1683(3)	32(2)
C(5)	2034(4)	6716(4)	250(3)	34(2)
C(11)	2103(4)	8799(4)	413(3)	28(2)
C(17)	356(4)	7579(4)	617(3)	29(2)
C(23)	626(4)	5931(4)	1920(3)	36(2)
C(27)	4795(4)	5704(4)	3277(3)	32(2)
C(33)	2767(4)	4913(4)	3207(3)	38(2)
C(39)	3733(4)	4981(4)	2004(3)	33(2)
C(45)	3480(4)	7650(4)	4108(3)	32(2)
C(49)	409(4)	7224(4)	3798(3)	35(2)
C(55)	–610(4)	8140(4)	2702(3)	28(2)
C(61)	802(4)	9288(4)	3649(3)	32(2)
C(67A)	1723(8)	10027(7)	2232(5)	27(2)
C(67B)	1365(8)	9759(8)	1779(5)	27(2)
C(71)	4158(4)	10488(4)	3471(3)	31(2)
C(77)	5507(4)	9078(4)	3300(3)	28(2)
C(83)	4713(5)	10131(4)	2156(3)	34(2)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

spectrometry. Pyrolyses are conducted in the absence of solvent at a temperature slightly below the melting points of the dimers (range 130 °C to 245 °C), with exception of preparation of **2**, which uses molten $[\text{Me}_2\text{AlN(H)SiEt}_3]_2$. Use of higher pyrolysis temperatures or solution pyrolysis still leads to formation of **2**–**6**, as observed by ^{1}H NMR spectroscopy. However, the byproducts formed interfere with crystallization of product. The compound $[\text{MeAlNSiMe}_3]_4$ (**1**) can be obtained by alkylation of $[\text{Cl}_2\text{AlN(H)SiMe}_3]_2$ with methyllithium followed by sublimation at 145 °C and 10^{-2} Torr.[15] The tetramers are unchanged after exposure to dry air for 2 minutes.

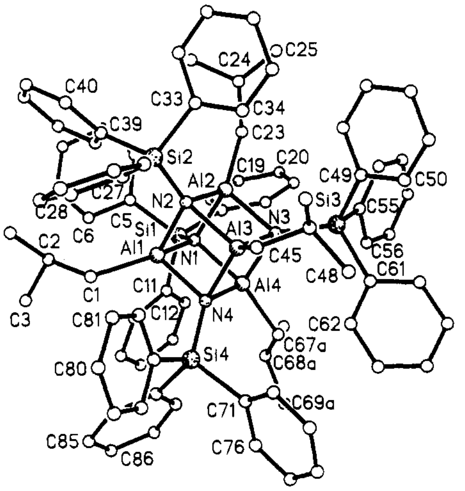

Figure 1. Molecular structure of $[i\text{-BuAlNSiPh}_3]_4$ (**4**).

Structural Studies of $[i\text{-BuAlNSiPh}_3]_4\cdot 0.5$hexane (4). Compound **4** forms a cubic Al_4N_4-framework tetramer (Figure 1), a well-known structure type among alkylaluminum imides. Structurally characterized examples include $[\text{PhAlNPh}]_4$,[16] $[\text{HAlN-}i\text{-Pr}]_4$,[17] $[\text{MeAlN-}i\text{-Pr}]_4$,[17] and $[\text{MeAlN(2,4,6-Me}_3\text{Ph)}]_4$.[18] The degree of oligomerization of alkylaluminum imides ranges from three in the case of $[\text{MeAlN(2,6-}i\text{-Pr}_2\text{Ph)}]_3$[4] to eight for $[\text{MeAlNMe}]_8$.[2f] This degree of oligomerization is most strongly influenced sterically by 1,2-interactions between Al and N substituents, with the smallest substituents generally leading to the highest oligomers.[19] In the case of the less-hindered hydridoaluminum compounds (polyiminoalanes), degrees of oligomerization as high as 16 have been reported.[20]

The structural features of $[i\text{-BuAlNSiPh}_3]_4\cdot 0.5$hexane are similar to those of the above-mentioned tetramers. Its average Al–N bond length of 1.954(4) Å is slightly longer than those of the three tetramers $[\text{PhAlNPh}]_4$,[16] $[\text{HAlN-}i\text{-Pr}]_4$,[17] and $[\text{MeAlN-}i\text{-Pr}]_4$[17] (1.913(2), 1.934(1), and 1.90(1) Å, respectively) but equal within experimental error to the value of 1.948(7) observed for $[\text{MeAlN(2,4,6-Me}_3\text{Ph)}]_4$.[18] This result is rationalized by steric effects, because both $[\text{MeAlN(2,4,6-Me}_3\text{Ph)}]_4$ and $[i\text{-BuAlNSiPh}_3]_4$ have groups on aluminum or nitrogen which are bulkier than the groups in the above three tetramers. Compound **4** shows a distortion observed for other tetramers in which the Al–N–Al bond angles are slightly smaller than the N–Al–N bond angles (average Al–N–Al angle of 88.8(2)° vs average N–Al–N angle of 91.2(2)° in **4**).[21] Further, the C–Al–N angles of **4** vary from 115.0(2) to 131.2(2)° (excluding the angles involving the disordered atoms C(67A) and C(67B)) and the Si–N–Al angles

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(15) In contrast, it is reported that $[\text{Me}_2\text{AlN(H)SiMe}_3]_2$ may be obtained by reaction of MeLi with $[\text{Cl}_2\text{AlN(H)SiMe}_3]_2$: Schmidbaur, H. *Angew. Chem.* **1961**, *73*, 257. We could find no trace of $[\text{Me}_2\text{AlN(H)SiMe}_3]_2$ in the reaction mixture prior to sublimation. Further, addition of MeLi to $[\text{Cl}_2\text{AlN(H)SiMe}_3]_2$, in our hands, causes immediate gas evolution, suggesting deprotonation of the N–*H* of $[\text{Cl}_2\text{AlN(H)SiMe}_3]_2$ and prohibiting formation of $[\text{Me}_2\text{AlN(H)SiMe}_3]_2$.

(16) McDonald, T. R. R.; McDonald, W. S. *Acta Crystallogr.* **1972**, *B28*, 1619.

(17) Del Piero, G.; Cesari, M.; Dozzi, G.; Mazzei, A. *J. Organomet. Chem.* **1977**, *129*, 281.

(18) Waggoner, K. M.; Power, P. P. *J. Am. Chem. Soc.* **1991**, *113*, 3385.

(19) Beachley, O. T.; Coates, G. E. *Inorg. Chem.* **1965**, *5*, 3241.

(20) Cesari, M.; Cucinella, S. *The Chemistry of Inorganic Homo- and Heterocycles*; Haiduc, I., Sowerby, D. B., Eds.; Academic Press: London, 1987; Vol. I, p 167.

(21) Reference 18 and references therein.

vary from 122.9(3) to 130.4(3)°, in a fashion also noted for $[MeAlN(2,4,6\text{-}Me_3Ph)]_4$.[18] The variation of these angles could reflect the steric interactions between corner substituents of the Al_4N_4 cube. Another factor is the electronic preference of aluminum or nitrogen for particular bond angles, which may be affected by the distortion at aluminum and nitrogen required by the cubane structure. With the Al–N bonds at 90° to one another, these bonds can be expected to incorporate more p bonding character from both aluminum and nitrogen. Thus, the Al–C and N–Si bonds can be expected to have more s character from Al or N, respectively, which may reduce their directional preference and therefore make the C–Al–N and Si–N–Al angles more variable.[22]

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Supplementary Material Available: Tables IVS (structure determination summary), VS (bond distances), VIS (bond angles), VIIS (fractional coordinates), VIIIS (thermal parameters), and IXS (H atom coordinates) and Figure 2S (ORTEP drawing) for **4** (17 pages). Ordering information is given on any current masthead page.

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(22) Huheey, J. E. *Inorganic Chemistry*; Harper: Philadelphia, PA, 1983; p 230.