Notiz/Note

Synthesis and Structure of a Silyl-aminoolane Ring

Jurik F. Janik,[1*1], Eileen N. Duesler, and Robert T. Paine*

Department of Chemistry, University of New Mexico, Albuquerque, NM 87131, USA

Received June 21, 1993

Key Words: Alane, amino- / Aluminium nitride

The reactions of hydrazine with tris(trimethylsilyl)aluminum-ether have been studied: Reactant ratios of 0.5:1 and 0.8:1 produce the cyclic aminalane [(Me₅Si)₂AlN(H)[SiMe₃]₂ (I), which is formed by N–N bond cleavage and silyl group migration from aluminum to nitrogen. Pyrolysis under NH₃ of a polymeric product formed from a 1:1 reaction produces an AlN/Si₃N₄ composite.

In earlier reports, we described 1:1 and 1:2 stoichiometry reactions between (Me₅Si)₂Al · OE₂ and NH₃ from which a four-membered aminalane ring compound [(Me₅Si)₂AlNH₂]²⁻ and a trigonal prismatic complex [(Me₅Si)₂Al(NH₂)³]⁺Al⁻ containing a six-coordinate central Al atom were isolated, respectively. Thermolysis of these compounds as well as accompanying polymeric products gave ceramic solid solutions of AlN and SiC. While extending the ceramic precursor aspects of this chemistry, it became an issue to determine if hydrazine could be used as an alternative or supplemental nitridation reagent. Examination of the literature revealed that few reactions of organoaluminum reagents with N₂H₄ have been thoroughly described. For example, Paterson and Onyazchuk[3] reported on a neat reaction of excess Me₅Al with N₂H₄ at 25 °C that produced unreacted Me₅Al, H₂, CH₄, and an intractable nonstoichiometric solid. The reaction in Et₂O solution gave a crystalline solid assumed to be the molecular elimination product Me₅Al(NH)(NH₂)AlMe₅. Like several products from reactions of H₂Al · THF[8] or H₂Al · NMMe₃[9] with hydrazines, this compound is prone to explosive decomposition. As a consequence, the compound was not characterized. In contrast, the reaction of H₂Al · NMMe₃ with Me₅NH·(NH₂)Me₅[3] results in efficient cleavage of the N–N bond and formation of a product described as H₃AlNMMe₅. We report here on aspects of parallel reactions of (Me₅Si)₂Al · OE₂ with N₂H₄ and on the isolation and characterization of a new aminalane ring [(Me₅Si)₂AlN(H)[SiMe₃]₂ (I).

Results and Discussion

As noted above, the reactions of Me₅Al[1], H₂Al · THF[8], or H₂Al · NMMe₃[9] with hydrazine have been reported to form intensely explosive product mixtures under some conditions. More recent studies[10] of the reaction of Me₅Al with N₂H₄ under organometallic vapor phase epitaxy (OMVEPE) conditions suggest that a bis-alane adduct Me₅Al · (N₂H₄)₂ · AlMe₅ is initially formed, and it undergoes methane elimination below 100 °C with formation of Me₅AlN(H)(N₂H₄)AlMe₅. At higher temperatures, AlN is produced. This shows that under these special conditions the beneficial nitridation character of hydrazine can be realized.

In some cases, the elimination reactions of (Me₅Si)₂Al · OE₂ are more sluggish with protic bases than found for Me₅Al; therefore, its chemistry with N₂H₄ was of interest. Unfortunately, we find that these reactions are also very dependent on stoichiometry, reaction time, and solvent. Further, the immiscibility of hydrazine in common solvents contributes to the formation of heterogeneous reaction mixtures and complex reactivity schemes that produce a number of explosive reaction mixtures. For example, 1:1 combinations of N₂H₄ and (Me₅Si)₂Al · OE₂ in pentane or hexane result in violent, exothermic reactions and formation of intractable white solids. The reaction is somewhat moderated by use of Et₂O as the solvent. Infrared spectra from the solids indicate the presence of N–H, Al–H, and Si–H functionalities, which suggests the operation of facile hydride and silyl group transfer chemistry. Pyrolysis of these solids at 930 °C in vacuo gave aluminum nitride, as indicated by XRD powder patterns and infrared spectroscopy. An X-ray amorphous solid is also formed, which is likely silicon nitride or a silicon carbonitride[7]. The reaction of (Me₅Si)₂Al · OE₂ with excess N₂H₄ in several solvents is also found to be unpredictable and hazardous. Consequently, the reactions are of limited practical utility in ceramic precursor synthesis.

The reactions of (Me₅Si)₂Al · OE₂ with a deficiency of hydrazine gave more controlled reactions less prone to explosions. The 0.5:1 and 0.8:1 reactant ratios are chemically significant since these combinations produced a new air-sensitive crystalline molecular product 1 that was isolated and characterized.

2 (Me₅Si)₂Al · OE₂ + N₂H₄ $\xrightarrow{\text{hexane}}$ [(Me₅Si)₂AlN(H)[SiMe₃]₂] (I)

The idealized reaction is summarized in equation (1). Compound 1 and Me₅SiH are the major products of the 0.5:1 reaction; however, several other unidentified compounds are also formed in small amounts, as indicated by the ¹H-NMR spectra of the reaction mixture. Compound 1 is soluble in hexane and benzene, and it begins to decompose with gas evolution at 180 °C. The compound is not adequately characterized by elemental analysis since a ceramic residue is obtained from standard combustion analysis; however, the mass spectrum reveals a clear parent ion corresponding to the dimer. The infrared spectrum displays a band in the N–H stretch…

[1*1] Permanent address: University of Mining and Metallurgy, AGH, B-3, 30-059 Krakow, Poland.

region at 3241 cm$^{-1}$, and the $^1$H- and $^{13}$C-NMR spectra show resonances for (Me$_5$Si)$_2$Al and Me$_5$SiN groups. The most intense $^1$H-NMR resonances appear as singlets at $\delta = 0.30$ and 0.12 in an intensity ratio of $\approx 2.1$. These are assigned to the (Me$_5$Si)$_2$Al and N(H)$_2$SiMe$_2$ methyl groups, respectively, of a trans isomer of I. In addition, two equal intensity singlets at $\delta = 0.36$ and 0.24 are assigned to the (Me$_5$Si)$_2$Al groups in a cis isomer of I. Their intensity relative to the resonance for the trans isomer ($\approx 15:85$) indicates that the trans isomer is heavily favored at 23°C in benzene solution. Planalp and coworkers$^{[8]}$ have reported on a more equal distribution between cis and trans isomers in [Me$_5$Al(H)SiMe$_2$]$^2$; however, a more facile interconversion might be anticipated in this compound with its less sterically demanding Me$_5$Al fragments. No resonance could be unambiguously assigned to the N$-$H groups in either isomer.

A single crystal X-ray diffraction analysis confirms the identity of I, as shown in Figure 1. The compound has a centrosymmetric molecular structure with two exo-Me$_5$Si groups on the Al atoms and one trans-exo-Me$_5$Si group on each N atom. The trans configuration is also found in several related aminoalanes including [Me$_5$Al(N(H)SiPh$_3$)]$_2$$^{[9]}$, [Me$_5$Al(N(H)SiEt$_2$)]$_2$$^{[10]}$, [Cl$_2$Al(N(H)SiMe$_2$)]$_2$$^{[11]}$, and [Me$_5$Al(N(H)(Pr)$_2$)]$_2$$^{[12]}$. The average Al$-$N bond distance in I, 1.974(1) Å, is identical to those reported in the compounds listed except for [Cl$_2$Al(N(H)SiMe$_2$)]$_2$, 1.914(4) Å, which would be expected to have a shorter Al$-$N distance due to the electron-withdrawing chloride substituents. The Al$-$N distance in I is slightly longer than that in [Me$_5$Si$_2$Al(NH)$_2$]$_2$, 1.955(2) Å, and this is likely due to the greater steric congestion around the N atoms in I. The Al-N distance in I is slightly shorter than that reported for [Me$_5$Al(NiSiMe$_2$)$_2$]$_2$, 1.992(3) Å$^{[13]}$, which has two bulky substituents on the N atoms. Planalp$^{[8]}$ has used the magnitude of the dihedral angle between the Al$_2$N$_2$ plane and the Al$-$Si or Al$-$C bond vector to assess the steric interactions in Al$_2$N$_2$ ring compounds, and the dihedral angle in I, 34.4°, falls between the values in [Me$_5$Al(N(H)SiEt$_2$)$_2$], 33.2°, and in [Cl$_2$Al(N(H)SiMe$_2$)$_2$], 36.4°.

![Figure 1. Molecular structure of [Me$_5$Si$_2$Al(N(H)SiMe$_2$)$_2$] (I). Selected bond distances [Å] and angles [°]. Al$-$Si(1) 2.479(1), Al$-$Si(2) 2.501(1), Al$-$N 1.974(3), Al$-$N$^*$ 1.973(3), Al$-$Al 2.844(2), Si(1)$-$N 1.764(3), Si(1)$-$Al$-$Si(2) 109.9(1), Si(1)$-$Al$-$N 108.1(1), Si(2)$-$Al$-$N 121.2(1), N$^*$-Al$-$N 98.7, Al$-$N$-$Si(3) 124.2(1), Al$-$N$-$Al 92.2(1).](image)

The mechanism for the formation of I has not yet been established; however, N-silylation of a weak adduct such as (Me$_5$Si)$_2$Al$^+$N(H)$_2$N$^-$AlMe$_5$, has a parallel in P-silylations of phosphines observed in the reactions of (Me$_5$Si)$_2$Al$^+$OE$_2$ with PH$_3$ and RPH$_2$$^{[14]}$. Such a reaction might also be expected to occur with cleavage of the relatively weak N$-$N single bond.

**Experimental**

Standard inert-atmosphere techniques were used for the manipulation of reactants and products. Solvents were dried with CaH$_2$, LiAlH$_4$, and Na-benzophenone, and they were distilled prior to use. – IR: Mattson 2020 Galaxy Series FTIR. – MS: Finnigan Model 4600 GC/MS. – NMR: Bruker FX250. – XRD: Scintag PAD V diffractometer. – Commercially available anhydrous NH$_4$H$_2$O was additionally dried over KOH and CaO and distilled. (Me$_5$Si)$_2$Al$^+$OE$_2$ was prepared as described$^{[15]}$. All reactions of hydrazine with aluminum reagents should be performed with great care due to the potential for explosive decomposition.

**Reactions of N$_2$H$_4$ with (Me$_5$Si)$_2$Al$^+$OE$_2$, 0.8:1 Ratio**: 0.11 ml of N$_2$H$_4$ (3.37 mmol) was added by syringe to a rapidly stirred solution of 1.28 g of (Me$_5$Si)$_2$Al$^+$OE$_2$ (4.00 mmol) dissolved in 50 ml of hexane at 23°C. A slurry of immiscible droplets formed, and this mixture was refluxed under nitrogen for 20 h, cooled, and then filtered. The filtrate was evaporated to dryness, the residue recrystallized from 3–4 ml of hexane, and 0.30 g (29%) of colorless, crystalline 1 was collected. – 'H NMR (250.133 MHz, CD$_2$CD$_2$, TMS, 25°C): trans $\delta = 0.30$ [36H, H$_2$(C4Al)], 0.12 [18H, H$_2$(C2N)]; cis $\delta = 0.36$ [H$_2$(C4Al), 0.24 [H$_2$(C2N)]. – $^{13}$C NMR (62.896 MHz, CD$_2$CD$_2$, TMS, 25°C): $\delta = 1.9$ [H$_2$(C4Al)], 1.8 [H$_2$(C2N)]. – IR (KBr, cm$^{-1}$): v = 3241 w, 2951 m, 2940 m, 2888 m, 1431 w, 1402 w, 1387 w, 1238 w, 837 s, 812 s, 760 s, 673 m, 619 w, 596 s, 525 s, 515 s. – MS (solid probe, 30 eV), m/z (%): 522 [M$^+$] (10), 507 [M$-$ CH$_3$] (5), 449 [M$-$ SiMe$_3$] (95), 259 (100).

**Reactions of N$_2$H with (Me$_5$Si)$_2$Al$^+$OE$_2$, 0.5:1 Ratio**: 0.065 ml of N$_2$H$_4$ (2.00 mmol) was added by syringe to a stirred solution of 1.28 g of (Me$_5$Si)$_2$Al$^+$OE$_2$ (4.00 mmol) dissolved in 50 ml of hexane. The resulting mixture was refluxed under nitrogen for 20 h, and a milky solution resulted. The mixture was filtered, and the filtrate was evaporated to dryness, leaving an oily solid (0.63 g) that was recrystallized from 3 ml of hexane at −10°C. The resulting crystals were collected, and 'H-NMR spectra confirmed that the material contained 1 (60–70%) as well as several minor products.

**Reactions of N$_2$H$_4$ with (Me$_5$Si)$_2$Al$^+$OE$_2$, 1:1 Ratio**: 1.28 g of (Me$_5$Si)$_2$Al$^+$OE$_2$ (4.00 mmol) was dissolved in 50 ml of hexane and the solution combined with 0.11 ml of N$_2$H$_4$ (4.00 mmol) at 23°C. The resulting slurry was stirred for 24 h, and an insoluble white solid (0.53 g) was collected and vacuum-dried. – IR (KBr): v = 3270 m, 3200 m, 2948 s, 2891 m, 2118 w, 1602 m, 1392 m, 1247 s, 990 m, 905 s, 831 s, 749 s, 673 s, 580 s. – Pyrolysis of the solid under vacuum at 930°C for 24 h gave a gray powder. – XRD (2θ): 33.7, 36.1, 38.4, 50.1, 60.2.

**Crystal Structure Determination for Compound I**: Suitable colorless prismatic (0.27 x 0.46 x 0.51 mm) crystals were obtained from a hexane solution at −10°C. A crystal was sealed in a glass capillary under nitrogen and mounted on a Siemens R3m/V diffractometer. Compound I crystallizes in the tetragonal space group I4/m. – Crystal data: a = 17.690(2), c = 11.271(2) Å, V = 3527(1) Å$^3$, M$_r$ = 261.6, Z = 8, q(calculated) = 0.985 g cm$^{-3}$, $\mu$(Mo-K$_\alpha$) = 0.288 mm$^{-1}$, $T = 20^\circ$C, $\lambda$(Mo-K$_\alpha$) = 0.7073 Å, F(000) = 1152. Data were collected in the 000 scan mode in the range 2$^\circ$.0 $<$ 2$\theta$ $<$ 47.0$^\circ$ as $<$ 19 $<$ h $<$ 19, 0 $<$ k $<$ 19, $-$12 $<$ l $<$ 12. 10816 reflections were collected of which 2612 were independent and 2100 were observed with $F > 3\sigma(F)$. The structure was solved by direct methods and refined by full matrix least-squares methods by using SHELXTL PLUS (VMS version). The non-hydrogen atoms were refined an-
isotropically, and methyl hydrogen atom positions were calculated (riding model). The hydrogen atom on the nitrogen atoms were located from resulting difference maps. The final R (Rw) values were 4.77 (4.27) \[ w = 1/\sigma^2(F) + 0.0003F^2 \] with 130 parameters and largest and mean \( \Delta/\sigma \) 0.018, 0.003. Further information on the X-ray structure determination may be obtained from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, on quoting the depository number CSD-57743, the names of the authors, and the journal citation.

\^ Dedicated to Professor Heinrich Nöth on the occasion of his 65th birthday.


