Notiz/Note

Synthesis and Structure of a Silyl-aminoalane Ring☆

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The reactions of hydrazine with tris(trimethylsilyl)aluminium-ether have been studied: Reactant ratios of 0.5:1 and 0.8:1 produce the cyclic aminoalane $[(Me_3Si)_2AlN(H)(SiMe_3)]_2$ (**1**), which is formed by N–N bond cleavage and silyl group migration from aluminium to nitrogen. Pyrolysis under NH_3 of a polymeric product formed from a 1:1 reaction produces an AlN/Si_3N_4 composite.

In earlier reports, we described 1:1 and 1:2 stoichiometry reactions between $(Me_3Si)_3Al \cdot OEt_2$ and NH_3 from which a four-membered aminoalane ring compound $[(Me_3Si)_2AlNH_2]_2$[1] and a trigonal prismatic complex $[(Me_3Si)_2Al(NH_2)_2]_3Al$[2] 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 organoaluminium reagents with N_2H_4 have been thoroughly described. For example, Paterson and Onyszchuk[3] reported on a neat reaction of excess Me_3Al with N_2H_4 at 25°C that produced unreacted Me_3Al, H_2, CH_4, and an intractable nonstoichiometric solid. The reaction in Et_2O solution gave a crystalline solid assumed to be the molecular elimination product $Me_2AlN(H)N(H)AlMe_2$. Like several products from reactions of $H_3Al \cdot THF$[4] or $H_3Al \cdot NMe_3$[5] with hydrazines, this compound is prone to explosive decomposition. As a consequence, the compound was not characterized. In contrast, the reaction of $H_3Al \cdot NMe_3$ with $Me_2NH(H)Me$[5] results in efficient cleavage of the N–N bond and formation of a product described as H_2AlNMe_2. We report here on aspects of parallel reactions of $(Me_3Si)_3Al \cdot OEt_2$ with N_2H_4 and on the isolation and characterization of a new aminoalane ring $[(Me_3Si)_2AlN(H)(SiMe_3)]_2$ (**1**).

Results and Discussion

As noted above, the reactions of Me_3Al[3], $H_3Al \cdot THF$[4], or $H_3Al \cdot NMe_3$[5] with hydrazine have been reported to form intensely explosive product mixtures under some conditions. More recent studies[6] of the reaction of Me_3Al with N_2H_4 under organometallic vapor phase epitaxy (OMVPE) conditions suggest that a bis-alane adduct $Me_3Al \cdot N(H)_2N(H)_2 \cdot AlMe_3$ is initially formed, and it undergoes controlled methane elimination below 100°C with formation of $Me_2AlN(H)N(H)AlMe_2$. 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 $(Me_3Si)_3Al \cdot OEt_2$ are more sluggish with protic bases than found for Me_3Al; therefore, its chemistry with N_2H_4 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 N_2H_4 and $(Me_3Si)_3Al \cdot OEt_2$ in pentane or hexane result in violent, exothermic reactions and formation of intractable white solids. The reaction is somewhat moderated by use of Et_2O 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 aluminium 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 $(Me_3Si)_3Al \cdot OEt_2$ with excess N_2H_4 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 $(Me_3Si)_3Al \cdot OEt_2$ 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.

$$2\,(Me_3Si)_3Al \cdot OEt_2 + N_2H_4 \xrightarrow[-2\,Me_3SiH]{\text{hexane}} \underset{\mathbf{1}}{[(Me_3Si)_2AlN(H)(SiMe_3)]_2} \quad (1)$$

The idealized reaction is summarized in equation (1). Compound **1** and Me_3SiH 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

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region at 3241 cm^{-1}, and the ^1H- and ^{13}C-NMR spectra show resonances for $(Me_3Si)_2Al$ and Me_3SiN groups. The most intense ^1H-NMR resonances appear as singlets at $\delta = 0.30$ and 0.12 in an intensity ratio of ≈ 2.1. These are assigned to the $(Me_3Si)_2Al$ and $N(H)SiMe_3$ methyl groups, respectively, of a *trans* isomer of **1**. In addition, two equal intensity singlets at $\delta = 0.36$ and 0.24 are assigned to the $(Me_3Si)_2Al$ groups in a *cis* isomer of **1**. 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 $[Me_2AlN(H)SiMe_3]_2$; however, a more facile interconversion might be anticipated in this compound with its less sterically demanding Me_2Al 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 **1**, as shown in Figure 1. The compound has a centrosymmetric molecular structure with two *exo*-Me_3Si groups on the Al atoms and one *trans-exo*-Me_3Si group on each N atom. The *trans* configuration is also found in several related aminoalanes including $[Me_2AlN(H)SiPh_3]_2$[8], $[Me_2AlN(H)SiEt_3]_2$[8], $[Cl_2AlN(H)SiMe_3]_2$[8], and $[Me_2AlN(H)(iPr)]_2$[9]. The average Al–N bond distance in **1**, 1.974(1) Å, is identical to those reported in the compounds listed except for $[Cl_2AlN(H)SiMe_3]_2$, 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 **1** is slightly longer than that in $[(Me_3Si)_2AlNH_2]_2$, 1.955(2) Å, and this is likely due to the greater steric congestion around the N atoms in **1**. The AlN distance in **1** is slightly shorter than that reported for $[Me_2AlN(SiMe_2H)_2]_2$, 1.992(3) Å[10], which has two bulky substituents on the N atoms. Planalp[8] has used the magnitude of the dihedral angle between the Al_2N_2 plane and the Al–Si or Al–C bond vector to assess the steric interactions in Al_2N_2 ring compounds, and the dihedral angle in **1**, 34.4°, falls between the values in $[Me_2AlN(H)SiEt_3]_2$, 33.2°, and in $[Cl_2AlN(H)SiMe_3]_2$, 36.4°.

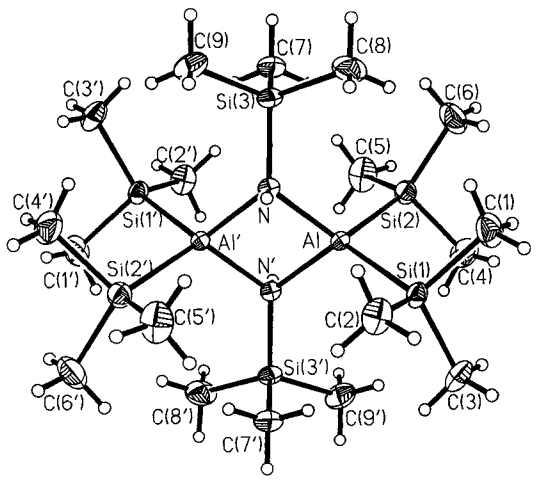

Figure 1. Molecular structure of $[(Me_3Si)_2AlN(H)SiMe_3]_2$ (**1**). Selected bond distances [Å] and angles [°]: Al–Si(1) 2.479(1), Al–Si(2) 2.501(1), Al–N 1.974(3), Al–N′ 1.973(3), Al–Al′ 2.844(2), Si(3)–N 1.764(3); Si(1)–Al–Si(2) 109.9(1), Si(1)–Al–N 108.1(1), Si(2)–Al–N 121.2(1), N–Al–N′ 87.8, Al–N–Si(3) 124.2(1), Al–N–Al′ 92.2(1)

The mechanism for the formation of **1** has not yet been established; however, *N*-silylation of a weak adduct such as $(Me_3Si)_3Al \cdot N(H_2)N(H_2) \cdot Al(SiMe_3)_3$ has a parallel in *P*-silylations of phosphanes observed in the reactions of $(Me_3Si)_3Al \cdot OEt_2$ with PH_3 and RPH_2[11]. 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: Brucker FX250. – XRD: Scintag PAD V diffractometer. – Commercially available anhydrous N_2H_4 was additionally dried over KOH and CaO and distilled. $(Me_3Si)_3Al \cdot OEt_2$ was prepared as described[12]. All reactions of hydrazine with aluminium reagents should be performed with great care due to the potential for explosive decomposition.

Reaction of N_2H_4 with $(Me_3Si)_3Al \cdot OEt_2$, 0.8:1 Ratio: 0.11 ml of N_2H_4 (3.37 mmol) was added by syringe to a rapidly stirred solution of 1.28 g of $(Me_3Si)_3Al \cdot OEt_2$ (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. – ^1H NMR (250.133 MHz, C_6D_6, TMS, 25 °C): *trans* $\delta = 0.30$ [36H, $H_3C(Al)$], 0.12 [18H, $H_3C(N)$]; *cis* $\delta = 0.36$ [$H_3C(Al)$], 0.24 [H_3CAl]. – ^{13}C NMR (62.896 MHz, C_6D_6, TMS, 25 °C): $\delta = 1.9$ [$H_3C(Al)$], 1.8 [$H_3C(N)$]. – IR (KBr, cm^{-1}): $\tilde{\nu} = 3241$ w, 2951 m, 2940 m, 2888 m, 1431 w, 1402 w, 1387 w, 1252 m, 1238 w, 837 s, 812 s, 760 s, 673 m, 619 w, 596 w, 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).

Reaction of N_2H_4 with $(Me_3Si)_3Al \cdot OEt_2$, 0.5:1 Ratio: 0.065 ml of N_2H_4 (2.0 mmol) was added by syringe to a stirred solution of 1.28 g of $(Me_3Si)_3Al \cdot OEt_2$ (4.0 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 ^1H-NMR spectra confirmed that the material contained **1** (60–70%) as well as several minor products.

Reaction of N_2H_4 with $(Me_3Si)_3Al \cdot OEt_2$, 1:1 Ratio: 1.28 g of $(Me_3Si)_3Al \cdot OEt_2$ (4.00 mmol) was dissolved in 50 ml of hexane and the solution combined with 0.11 ml of N_2H_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): $\tilde{\nu} = 3270$ 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 **1**: Suitable colorless prismatic (0.27 × 0.46 × 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 **1** crystallizes in the tetragonal space group $P4_2/n$. – Crystal data: $a = 17.690(2)$, $c = 11.271(2)$ Å, $V = 3527(1)$ Å^3, $M_r = 261.6$, $Z = 8$, $\varrho(\text{calc}) = 0.985$ g cm^{-3}, $\mu(\text{Mo-}K_\alpha) = 0.288$ mm^{-1}, $T = 20$ °C, $\lambda(\text{Mo-}K_\alpha) = 0.71073$ Å, $F(000) = 1152$. Data were collected in the ω scan mode in the range $2.0° < 2\Theta < 47.0°$ 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 Δ/σ 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.

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