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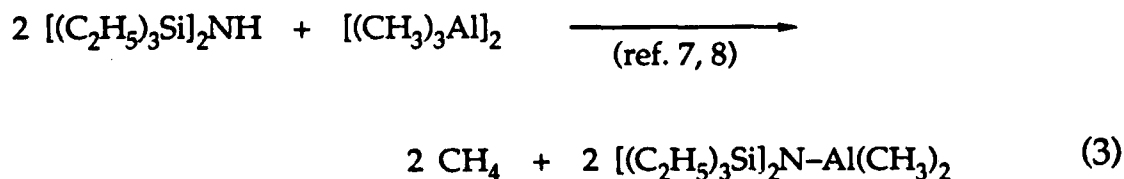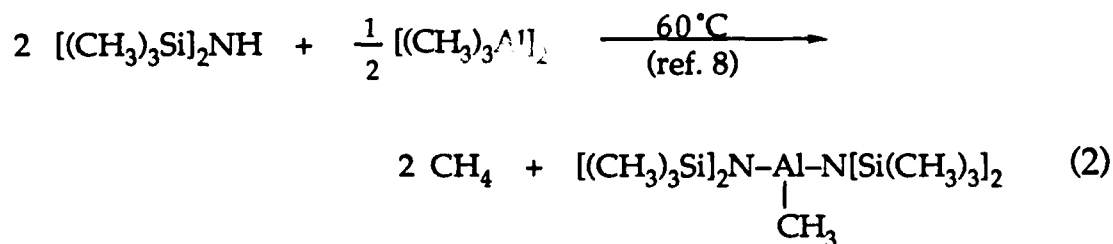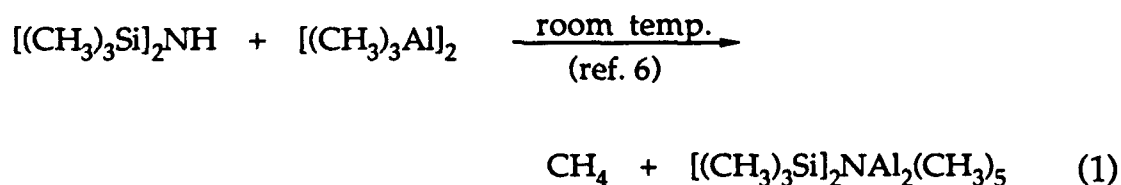Cambridge, Massachusetts 02139

ABSTRACT

The reaction of trimethylaluminum with the $(CH_3SiHNH)_n$ cyclic oligomers obtained by ammonolysis of methyldichlorosilane results in evolution of methane and formation of soluble, cross-linked aluminasilazanes. Pyrolysis of the products in a stream of argon gives a good yield of black aluminosilicon carbonitride, while pyrolysis in a stream of ammonia results in formation of white aluminosilicon nitride.

Silicon nitride and aluminum nitride are useful ceramic materials. Densification of silicon nitride is promoted by addition of aluminum nitride.[1] Films of AlN/Si_3N_4 have been produced by RF sputtering.[2,3] They were found superior (compared to AlN, BN, Si_3N_4 and TiN) as protective layers on magneto-optical recording materials[2] because they were transparent and they protected the TbFe thin films against corrosion. Since one may expect other useful applications of AlN/Si_3N_4 composites, there has been some interest in the preparation of processable (i.e., soluble or fusible) inorganic and organometallic polymers whose pyrolysis under the appropriate conditions will give AlN/Si_3N_4 composites. Thus, Japanese workers[4] treated a polysilazane obtained by ammonlysis of H_2SiCl_2 with aluminum isopropoxide, $Al[OCH(CH_3)_2]_3$, in benzene at 80°C to give what they called a "polyaluminosilazane". A film of this material was pyrolyzed to 1000°C under nitrogen to give a black ceramic film. In other studies, copyrolysis of a polycarbosilane and an organoaluminum amide in the presence of ammonia gave a composite of AlN and Si_3N_4.[5]

We have adapted the simple chemistry that takes place when hexaalkyldisilazanes react with trimethylaluminum (eq. 1-3) to the preparation of useful preceramic polymers by the reaction of $(CH_3)_3Al$ with

$$[(CH_3)_3Si]_2NH \ + \ [(CH_3)_3Al]_2 \ \xrightarrow[\text{(ref. 6)}]{\text{room temp.}}$$

$$CH_4 \ + \ [(CH_3)_3Si]_2NAl_2(CH_3)_5 \quad (1)$$

$$2 \ [(CH_3)_3Si]_2NH \ + \ \frac{1}{2} [(CH_3)_3Al]_2 \ \xrightarrow[\text{(ref. 8)}]{\text{60°C}}$$

$$2 \ CH_4 \ + \ [(CH_3)_3Si]_2N\underset{\underset{CH_3}{|}}{-Al-}N[Si(CH_3)_3]_2 \quad (2)$$

$$2 \ [(C_2H_5)_3Si]_2NH \ + \ [(CH_3)_3Al]_2 \ \xrightarrow[\text{(ref. 7, 8)}]{}$$

$$2 \ CH_4 \ + \ 2 \ [(C_2H_5)_3Si]_2N-Al(CH_3)_2 \quad (3)$$

the ammonolysis product of methyldichlorosilane. This silazane, $(CH_3SiHNH)_n$, is, for the most part, a mixture of cyclic oligomers (n = 3, 4, 5....; average n is 4-5). Since this material is too volatile to serve as a useful ceramic precursor, it must be converted to material of higher molecular weight. In our laboratories we have used the base-catalyzed dehydrocyclodimerization reaction to effect such polymerization,[9] and, more recently, the reaction of this mixture of oligomeric cyclosilazanes with $H_3B \cdot S(CH_3)_2$.[10] The latter process involves the interaction of the cyclosilazane with a Lewis acid, and thus we were led to investigate the reaction of cyclo-$(CH_3SiHNH)_n$ with trimethylaluminum and aluminum hydride, which also are Lewis acids.

In a typical reaction, a 200 ml two-necked Schlenk flask, which was equipped with a rubber septum, a magnetic stir-bar and a gas inlet/outlet tube connected to a Schlenk line, was flushed well with dry argon and charged by syringe with 1.56 g (26.4 mmol) of $(CH_3SiHNH)_n$. While this liquid was stirred, 4.3 ml of a 2$\underline{M}$ solution of trimethylaluminum* (8.6 mmol, hence a Si/Al ratio of 3.1) in toluene was added dropwise by syringe. Ten to fifteen seconds after the first few drops had been added, gas evolution (CH_4) commenced. The reaction mixture was stirred at room temperature for 18 hr. The solvent then was removed at reduced pressure, leaving 2.1 g (94%, based reaction of each $(CH_3)_3Al$ with an N-H fuction with loss of CH_4) of a white solid. (The same result was obtained in a reaction using 46.8 mmol of $(CH_3SiHNH)_n$ and 1.5 ml (15.6 mmol) of neat trimethylaluminum). The product was poorly soluble in aliphatic hydrocarbons and benzene (which precluded a cryoscopic molecular weight determination), but was fairly soluble in toluene. It was sensitive to atmospheric moisture and oxygen. Its analysis showed that aluminum had been incorporated into the silazane: C, 27.01; H, 7.56; N, 17.76; Si, 31.57; Al, 11.67%. The proton NMR spectrum (300 MHz, C_6D_6) showed the presence of Si-H, Si-CH_3 and Al-CH_3 protons in the regions 4.5 to 5.5, 0.0 to 0.8 and -0.6 to 0 ppm, respectively. By TGA (under argon, to 950°C), the ceramic yield obtained on pyrolysis of this product was 77%. A black solid residue remained. Pyrolysis of a bulk sample in a stream

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* CAUTION: Trimethylaluminum is pyrophoric in air and should always be handled and transferred in an inert (argon or nitrogen) atmosphere with rigorous exclusion of atmospheric oxygen and moisture.

of ammonia to 1000°C resulted in a white residue in 76% yield based on the weight of the sample charged. Its elemental analysis showed it to be very nearly carbon-free: C, 0.45; N, 38.31; Si, 44.77; Al, 15.59%, and thus an aluminosilicon nitride had been formed.

Reactions using $CH_3SiHNH/(CH_3)_3Al$ ratios of 6, 3, 2 and 1 were carried out both with $2\underline{M}$ $(CH_3)_3Al$ in toluene and neat $(CH_3)_3Al$. Ceramic yields obtained in pyrolyses of the aluminasilazanes thus prepared, either in a stream of argon or ammonia, decreased somewhat with decreasing Si/Al reactant ratio, but even when this ratio was 1, the ceramic yields in argon and in ammonia were 60% and 63%, respectively. The nominal compositions of the amorphous solids obtained in pyrolyses in ammonia to 1000°C, followed by heating to 1500°C in argon, varied between 1 AlN + 1.48 Si_3N_4 (Si/Al reactant ratio 6) to 1 AlN + 0.52 Si_3N_4 (Si/Al reactant ratio 1).

Similar experiments were carried out using other silazanes, but the results were not as promising as those obtained with $(CH_3SiHNH)_n$. Thus both the 6:1 and 1:1 $(CH_3)_2SiNH/(CH_3)_3Al$ ratio reactions, carried out using $[(CH_3)_2SiNH]_n$ (from ammonolysis of $(CH_3)_2SiCl_2$) for 16 hr at room temperature, gave a very viscous liquid product. The ceramic yields of their pyrolysis (TGA, to 950°C under argon) were only 49% and 33%, respectively.

Aluminum hydride in the form of its diethyl etherate, $H_3Al \bullet O(C_2H_5)_2$, may be used in place of trimethylaluminum. However, in such reactions some or all of the product is insoluble in diethyl ether. For example, in a reaction in which a 3:1 Si/Al reactant ratio was used (6.5 g of $(CH_3SiHNH)_n$ and 70 ml of $0.5\underline{M}$ AlH_3 in diethyl ether for 24 hr at room temperature), an insoluble white solid was obtained in 47% yield. Evaporation of the solution to remove the solvent left a white solid in 41% yield whose proton NMR spectrum showed Si-H, Al-H and Si-CH_3 functionality to be present (δ 5.5 - 4.5, 3.3 - 3.1 and 0.8 - 0 ppm, respectively). Its pyrolysis in a stream of argon (TGA to 950°C) left a black solid in 85% yield, while bulk pyrolysis to 1000°C in a stream of ammonia gave a white solid residue in 86% yield (anal.: C, 0.6; N, 37.24; Si, 45.35; Al, 14.60%). The $(CH_3SiHNH)_n$ + $(CH_3)_3Al$ reaction in which the Si/Al ratio was 1, on the other hand, did not give any soluble product.

The chemistry in this aluminasilazane preparation appears to involve reaction of the trimethylaluminum at the N-H links of the $(CH_3SiHNH)_n$

oligomers to give initially $>$N-Al(CH$_3$)$_2$ or $>$N-Al$_2$(CH$_3$)$_5$ moieties and CH$_4$ (as shown in eq. 1 for hexamethyldisilazane). Further reaction of these methylaluminum amide functions with N-H groups of the silazane leads to cross-linking between silazane rings via N-Al(CH$_3$)-N linkages such that a network polymer is formed. However, it is likely that the chemistry is more complicated than that since Si-N and Al-N bonds are quite labile. Also, methylation of Si-H linkages by reactive metal alkyls is a known reaction,[11] so methylation of some Si-H functions by the trimethylaluminum is a possibility.

The reaction of these aluminasilazanes with ammonia is of some interest. In contrast to methylsilicon compounds, which react with ammonia only at high (>400°C) temperatures, methylaluminum compounds react with ammonia at or slightly above ambient temperature.[12] In the present case, reaction of an aluminasilazane (from a 1:1 CH$_3$SiHNH/(CH$_3$)$_3$Al preparation) with gaseous ammonia was found to take place already at room temperature. Immediate gas evolution occurred and the solid aluminasilazane became liquid. After 2 hr of reaction with ammonia, it resolidified. Removal of all volatiles after a further 6 hr of exposure to ammonia left a glassy white solid which was soluble in toluene. Its proton NMR spectrum still showed Si-H, Si-CH$_3$ and diminished Al-CH$_3$ signals and its pyrolysis to 1000°C in a stream of ammonia gave a white solid, presumably an aluminosilicon nitride, in 63% yield.

The preparative chemistry that we report here is easily effected in high yield using relatively cheap starting materials. The polymeric products, for the most part, are soluble and their pyrolyses in argon and in ammonia give high yields of ceramic product. This chemistry provides an excellent route to aluminosilicon nitrides whose composition can be varied by varying the starting (CH$_3$SiHNH)$_n$/(CH$_3$)$_3$Al stoichiometry. We communicate these preliminary results because of the potential utility of the aluminosilicon nitrides. However, more work is required to delineate the mechanism of formation and the structure of the aluminasilazanes and the mechanism of their pyrolysis in argon and ammonia. In addition, the ceramics issues, which hardly have been touched, must be addressed. Our investigations of these systems are continuing.

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