Dehydrocoupling of Ammonia and Silanes Catalyzed by Dimethyltitanocene

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Received July 29, 1991

The reactions of diphenylmethylsilane and of phenylmethylsilane with ammonia, to give the disilazanes, are effectively catalyzed by dimethyltitanocene (DMT). At longer reaction times, 1,3-dimethyl-1,3-diphenyldisilazane reacts further with excess ammonia to give short oligomers, e.g. $(MePhHSiNH)_3$ and $H(MePhHSiNH)_nH$ (n = 2, 3), but high polymers cannot be made due to the low reactivities of the oligomers. The reactions of primary silanes with ammonia in the presence of DMT are unexpectedly slower than those of tertiary and secondary silanes. In these reactions homodehydrocoupling competes effectively with the amination reaction and physical properties indicate that the products are poly(aminosilanes) $(RSiNH_2)_n$, rather than the expected polysilazanes. Some preliminary results on the pyrolysis of poly(methylaminosilane) are reported.

Introduction

Since Yajima et al. produced silicon carbide fiber by pyrolysis of a polycarbosilane,[1] research on the synthesis of inorganic and organometallic polymers with potential as ceramic precursors has attracted growing attention.[2] Polysilazanes have been extensively studied as precursors for silicon nitride.[3] The classic method for the synthesis of polysilazanes is aminolysis, or ammonolysis, of chlorosilanes.[4,5] This type of reaction has been of very limited value for the production of high-molecular-weight linear polymers, due to the facile formation of cyclic products. In addition, this type of chemistry has the disadvantage, from the standpoint of an industrial process, of generating large amounts of ammonium halides as byproducts. Consequently, there is a continuing need for new synthetic approaches to the Si–N bond, particularly with respect to the synthesis of polymers.

The base-catalyzed dehydrocoupling of cyclic oligomers, $-[MeSiHNH]_n-$, obtained from the ammonolysis of $MeSiHCl_2$, yields fairly high molecular weight polymers, which have proven to be useful precursors for Si_3N_4.[6] In addition, a few catalysts based on transition metals are active for dehydrocoupling hydrosilanes and amines. For example, $Ru_3(CO)_{12}$ was successfully used by Laine et al. for cross-dehydrocoupling polymerization of phenylsilane and either ammonia or 1,3,5-trimethylcyclotrisilazane,[7] whiie $PdCl_2$ was studied by Kinsley and Barton for the reaction of phenylsilane and ammonia.[8] In an earlier publication we explored the use of CuCl and CuH as catalysts for silane/amine coupling.[9] Although these catalysts were useful for the synthesis of simple silazanes and some oligosilazanes, the activity was far too low to be useful for high-polymer synthesis.

Since homodehydrocoupling of hydrosilanes is readily catalyzed by dimethyltitanocene (DMT),[10] and reactions between certain titanocene(III) derivatives and amines are well established,[11,12] we have investigated the cross-dehydrocoupling of silanes and ammonia in the presence of DMT. It was found that DMT is a very good catalyst for the cross-dehydrocoupling reaction, and the results of this study are presented herein.

Results and Discussion

Reactions of Phenylmethylsilane and Diphenylmethylsilane with Ammonia. In contrast to the inactivity of tertiary hydrosilanes toward homodehydrocoupling reactions, they do react with ammonia to give the disilazane. For example, diphenylmethylsilane reacts with ammonia in the presence of titanocene to give $Ph_2MeSiNHSiMePh_2$ (1; see Table I). Heating is necessary to initiate the reaction, and although it then proceeds slowly at room temperature, more convenient rates are achieved by moderate heating. When the reaction was performed at room temperature, after 22 h there was still 30% of monomer unreacted, but at 100 °C a conversion of ca. 60% was obtained after only $^1/_2$ h of reaction.

The product was characterized by GC and NMR spectroscopy (^1H and ^{29}Si) (Tables II and III). At no point during the reaction was any aminosilane detected.

The reactivity of $PhMeSiH_2$ with ammonia was somewhat higher than that for methyldiphenylsilane. This was anticipated, since silane reactivity normally follows the order 1° > 2° > 3°.

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Table I. Cross-Coupling Reactions between Silanes and Ammonia[a]

amt of silane, mmol	amt of Cp_2TiMe_2, mmol	amt of NH_3, mmol	*T*, °C	*t*, h	conversn, %	products[d], (amt, wt %)
Ph_2MeSiH (5.0)	0.06	9	25	22	70	**1** (100)
Ph_2MeSiH (5.0)	0.06	9	100	0.5	60	**1** (100)
$PhMeSiH_2$ (14.6)[b]	0.14	15	35	12	97	**3** (24), **4** (63)
$PhMeSiH_2$ (7.3)[c]	0.10	*e*	100	0.1	100	**2** (80), **5** (10)
				0.5	100	**2** (27), **3** (13), **4** (36), **5** (21)
				1.0	100	**2** (0), **3** (25), **4** (67), **5** (4)

[a] Reactions run in neat silane unless otherwise indicated. [b] Cyclohexene (3.0 mL) added to scavenge hydrogen. [c] Toluene (5 mL) added to reduce viscosity of reaction mixture. [d] Legend: **1**, $Ph_2MeSiNHSiMePh_2$; **2**, PhMeHSiNHSiHMePh; **3**, $H(PhMeSiNH)_3H$ + $(PhMeSiNH)_3$; **4**, $H_2N(PhMeSiNH)_3H$; **5**, $H(PhMeSiNH)_2SiPhMeH$. [e] In this reaction the ammonia was bubbled continuously through the solution at atmospheric pressure.

Table II. Analysis of Coupling Products by GC–MS[a]

product	fw	ion, *m/e* (abundance) [fragmentation]
HPhMeSiNHSiPhMeH	257	256 (4.6) [M^+ – H], 242 (27) [M^+ – Me], 178 (71) [M^+ – PhH_2], 164 (100) [M^+ – $PhCH_3$ – H], 121 (28) [$PhCH_3SiH^+$]
$H(PhMeSiNH)_2SiPhMeH$	392	393 (16.5) [MH^+], 379 (27) [MH^+ – CH_2], 315 (40) [M^+ – Ph], 301 (68) [MH^+ – $PhCH_3$], 238 (81) [M^+ – Ph_2], 197 (100) [M^+ – Ph_2MeSiH], 179 (52) [M^+ – $Ph_2MeSiNH_2$], 135 (48) [$PhMeSiNH^+$], 121 (48) [$PhMeSiH^+$]
$H(PhMeSiNH)_3H$	407	408 (0.5) [MH^+], 392 (100) [M^+ – CH_3], 314 (89) [M^+ – $PhCH_3$ – H], 252 (23) [M^+ – Ph_2 – H]
$(PhMeSiNH)_3$[b]	405	391 (100) [MH^+ – CH_3], 313 (45) (M^+ – $PhCH_3$)
$H_2N(PhMeSiNH)_3H$	422	390 (M^+ – $2NH_2$)

[a] The compounds are listed in their retention time order. [b] This compound was also crystallized as a pure product from the mixture and identified by comparison to an authentic sample.[23]

Table III. ^1H and ^{29}Si NMR Chemical Shifts of the Coupling Products of Phenylmethylsilane and Diphenylmethylsilane with Ammonia

	chem shifts of protons			
product	δ(Si–H)	δ(Si–Me)	δ(N–H)	^{29}Si, δ
$(HPhMeSi)_2NH$	5.0 (m)	0.44 (d)	1.0	
$(PhMeSiNH)_3$		0.50 (s)	1.0	−12.7
$H_2N(PhMeSiNH)_3H$		0.38	1.0	−15.0
$(Ph_2MeSi)_2NH$		0.68 (s)	0.9–1.2	−10.5

The progress of the $PhMeSiH_2$ reaction was followed by GC, and it was observed that the $PhMeSiH_2$ is consumed very rapidly at the beginning of the reaction. For example, at 70 °C, most of the silane was consumed within 10 min after the initiation. The product formed at this point was mainly PhMeSiH–NH–SiHMePh (**2**). At longer times, the reaction leads eventually to higher molecular weight oligomers. Analysis of products by GC–MS indicated that the following oligomers were produced (Table I): $H(PhMeSiNH)_3H$ + $(PhMeSiNH)_3$ (**3**), $H_2N(PhMeSiNH)_3H$ (**4**), and $H(PhMeSiNH)_2SiPhMeH$ (**5**).

The lower aminosilanes PhMeSiH–NH_2 and PhMeSi–NH–SiPhMe–NH_2 never accumulate to a significant degree during the reaction, presumably because the primary amine groups of these two silazanes are more reactive toward silane than is ammonia. The relatively low concentration of ammonia in the reaction solution may also be partly responsible.

The product of the phenylmethylsilane/ammonia reaction was still limited to quite low molecular weight oligomers. The results cited in Table I suggest that this may be mainly due to the facile formation of cyclotrisilazane. The slowness of the reaction of the monosilane with the NH_2 terminus of **4** is also a contributing factor. The analytical data for the characterization of these products are summarized in Tables II and III.

Reactions of Primary Organosilanes with Ammonia. In view of the usual order of reactivity or organosilanes, referred to above, we anticipated that the primary silanes would react much faster than secondary and tertiary silanes. In fact, the opposite turned out to be the case. For phenylsilane, at 95 °C, in the presence of ca. 1 mol % of DMT, complete consumption of the silane required about 6 h. Under similar reaction conditions (see Table I), methyldiphenylsilane and methylphenylsilane required ca. 5 min and 1 h, respectively.

The origin of this unexpected behavior lies in the fact that the homocoupling reaction of phenylsilane and the cross-dehydrocoupling reaction between the silane and ammonia are competing reactions. When the reaction was followed by ^1H NMR spectroscopy, it was found that the disappearance of the Si–H resonance of the phenylsilane (δ 4.2 ppm, $CDCl_3$) was accompanied by the appearance of two sets of new resonances in the ranges of δ 4.6–4.7 and 5.1–5.2 ppm. The higher field resonances are readily attributable to simple oligomers of phenylsilane, particularly 1,2-diphenyldisilane and 1,2,3-triphenyltrisilane. The lower field resonances are assigned to simple oligomers containing the PhSiHN function. This observation leads to the conclusion that there is a competition between homo- and heterocoupling in this case. Furthermore, not only is the heterodehydrocoupling much slower than anticipated, but the rate of homocoupling is also much slower than would normally be observed in the absence of ammonia. It thus seems that not only does the presence of the strongly coordinating NH_3 slow down the homodehydrocoupling but also the presence of a silane, which is highly active toward homodehydrocoupling, severely disrupts the catalytic cycle of the amination reaction.

Some details of the progress of a reaction of phenylsilane and ammonia, in the early stages of the reaction, are given in Table IV. From these results, it is evident that the homocoupling reaction is faster than the amination reaction but that a steady-state concentration of the oligosilanes is reached early in the reaction. Presumably it is the amination of these simple oligomers that is responsible for the major part of the Si–N-containing product, rather than the amination of phenylsilane.

The unique behavior of the primary silane reactions is still more apparent when the later stages of the reaction are studied. At long reaction times, all of the Si–H undergoes reaction to the point that it is no longer detectable by NMR or IR spectroscopy. Despite this, the product remains completely soluble in organic solvents, eliminating the possibility that there is a high degree of reticulation. The product is polymeric with molecular weights corresponding to ca. 15–50 silicon atoms. Some details of re-

Table IV. Cross-Coupling Polymerization of Phenylsilane and Ammonia Catalyzed by Titanocene

amt, mmol			amt, mL				
$PhSiH_3$	Cp_2TiMe_2	p_{NH_3}, psi	cyclohexene	toluene	T, °C	t, h	M_w (M_n)
16	0.12	38		2	90	16	4700 (3500)
8	0.09	12		2	90	17	1900 (1400)
16	0.12	38	3.25		90	16	2800 (1800)
16	0.14	14.7[a]		8	95	16	5000 (3400)
$H(PhSiH)_nH$[b]	0.14	14.7[a]		10	95	16	6900 (3500)

[a] Ammonia was bubbled continuously through the reaction solution at atmospheric pressure. [b] A preprepared polyphenylsilane with the bimodal molecular weight distribution M_{w_1} = 2400 (70%) and M_{w_2} = 400 (30%) was used.

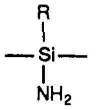
Table V. Coupling Reaction of Phenylsilane and Ammonia Catalyzed by Cp_2TiMe_2 in Toluene at 95 °C[a]

	% of diff Si-H calcd from ^1H NMR		
t, h	$PhSiH_3$	-PhSiH-PhSiH-	$-PhSiH-NH_2$
2.5	37	41	22
4.5	18	41	41
10	0	45	55

[a] Conditions: p_{NH_3} = 1 atm; $[PhSiH_3]$ = 1.6 mol/L; $[Cp_2TiMe_2]$ = 1.4×10^{-2} mol/L.

actions carried out under a variety of conditions are summarized in Table V. In addition to results for products obtained by reaction of phenylsilane with ammonia, some data for a product of reaction of ammonia with a preprepared sample of polyphenylsilane is also included in Table V. In this case, the Si–H groups of the polymer were also no longer detectable by NMR or IR spectroscopy at the end of the reaction. The slight increase in molecular weight (ca ×2.5) might be due to a small amount of cross-linking, but this is far from sufficient to explain the disappearance of the Si–H by formation of Si–NH–Si cross-links.

Elemental analyses carried out on samples of the products of reactions of both $PhSiH_3$ and $MeSiH_3$ with ammonia in the presence of DMT gave a result consistent with a Si:N ratio of unity (see Experimental Section). These results are difficult to interpret in terms other than that the products are polymers based largely on the *mer* unit



$$-\overset{R}{\underset{NH_2}{Si}}-$$

IR spectra of the products are consistent with this formulation, but it is difficult to distinguish definitively between silazanes and aminosilanes by IR spectroscopy, especially if one is dealing with a multifunctional molecule that cannot be freed of hydrogen bonding by dilution.[13] The same is true of the ^1H NMR spectra to some degree. Although the integrals for both the phenyl- and methylsilane products are much closer to those expected for NH_2 rather than NH groups, the extremely broad resonances and very long relaxation times (even with a delay time of up to 20 min, the integrals had not converged to a constant value) make for large uncertainties in the integrals.

The most compelling evidence for the assignment of the polymer structural unit comes from ^{15}N NMR INEPT spectra of poly(aminophenylsilane) and poly(aminomethylsilane). These spectra gave evidence only for NH_2 groups, and NH groups were below the level of detection in both cases.

The behavior of other primary silanes was similar to that of phenylsilane. Ammonia reacts with n-hexylsilane to give a polymer of lower molecular weight than that for phenylsilane (M_n = 1400; M_w = 1700), even though the Si–H groups are completely consumed during the reaction. This parallels the behavior of n-hexylsilane in its homocoupling reaction. All of the IR and NMR evidence supports the conclusion that the product is again a poly(aminosilane).

The cross-coupling reaction between methylsilane and ammonia takes place under conditions similar to those previously described for the homocoupling reaction.[10] The reaction was performed under pressure (ca. 10 atm combined pressure of ammonia and methylsilane), and cyclohexene was used to capture the hydrogen formed during the reaction. As in the case of phenylsilane, all the Si–H groups can be reacted using an excess of ammonia and a long reaction time. In this case, the reaction can eventually lead to cross-linked, insoluble product, as with the homocoupling reaction, if it is continued for too long after

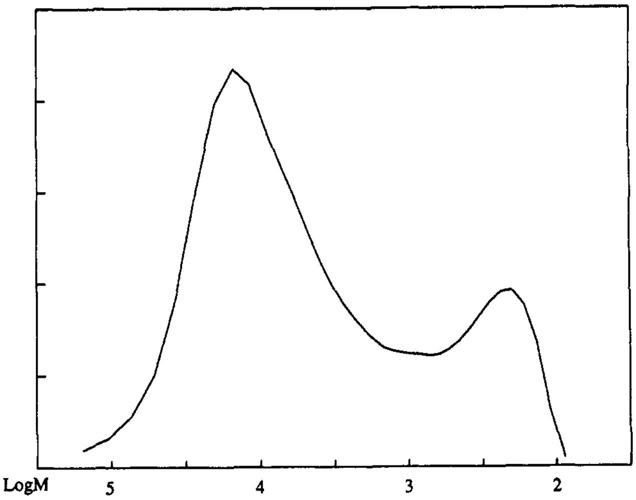


Figure 1. Typical GP chromatogram of poly(methylaminosilane) obtained from the DMT-catalyzed polymerization of methylsilane and ammonia.

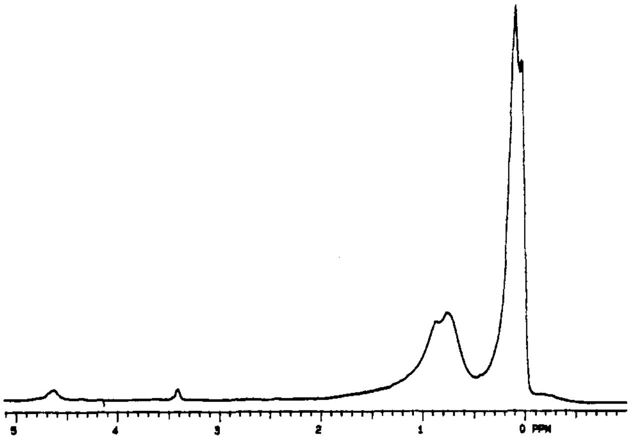


Figure 2. ^1H NMR spectrum of a typical poly(methylaminosilane).

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(13) Marchand, A.; Forel, M.-T.; Metras, F.; Valade, J. *J. Chim. Phys. Phys.-Chim. Biol.* **1964**, *61*(3), 343.

the methylsilane is completely consumed. Under appropriate synthesis conditions the product is soluble in toluene, THF, or chloroform. A typical GPC chromatogram of a completely soluble product is given in Figure 1.

The polymer was analyzed by ^1H and ^{15}N NMR and FTIR spectroscopy. All of the spectroscopic evidence and chemical analysis results again support the conclusion that the predominant unit in the polymer is $-MeSi(NH_2)-$ (see Experimental Section).

We therefore conclude that in the case of primary silanes the reaction mechanism and products are quite different from those of the reactions of secondary and tertiary silanes.

Mechanism of the Reaction. The mechanism of the reactions of primary silanes with ammonia is undoubtedly very complex and can hardly be deduced with any confidence on the basis of presently available evidence. There is, however, a rich known chemistry of related reactions which permits the drawing of some conclusions.

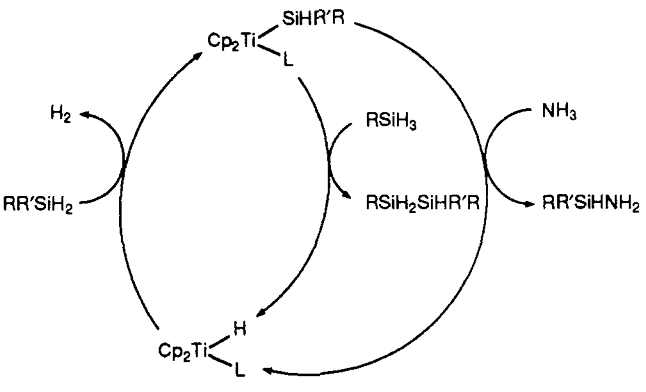
The homocoupling polymerization of hydrosilanes using group 4 metallocenes as catalysts has been investigated in great detail.[10] The most plausible mechanism for the reaction is presently the σ-bond metathesis mechanism proposed by Tilley and co-workers.[14] In its simplest form, this mechanism attributes the catalysis to a sequence of four-center σ-bond metatheses at a metal(IV) center. However, it has also been unequivocally established that the products of reacting DMT with silanes in the presence of donor ligands, L, are ligated silyltitanium(III) complexes of the type $Cp_2TiL(SiRR'R'')$.[15] Although the possibility exists that the Tilley mechanism could involve metal(III) rather than metal(IV) centers, there is as yet no direct evidence of such a mechanism.

A number of reactions of ammonia with titanocene derivatives have been reported. Armor[11] reacted $Cp_2Ti(\mu\text{-}\eta^1{:}\eta^5\text{-}C_5H_4)TiCp$ with ammonia and obtained $(Cp_2TiNH)_2H$. Taken at face value, this suggests that ammonia can be activated by oxidative addition to a Ti(II) center, and there is ample circumstantial evidence for the presence of titanocene as a transient intermediate in organosilane/DMT mixtures.[10] Hillhouse and Bercaw[12] reported that $Cp^*{}_2MH_2$ (M = Zr, Hf) reacts with ammonia to give $Cp^*{}_2MH(NH_2)$. This reaction is almost certainly another example of σ-bond metathesis at a metal(IV) center.

The evidence of the present study shows that the initial reaction is a homocoupling of the silane to small oligomers, particularly the dimer and trimer. This phase of the reaction sequence is consistent with a Tilley-type mechanism, but with the reaction rate greatly diminished because much of the potentially active catalyst is tied up in the form of an ammonia complex. Although the ammonia complex is most likely a Ti(III) species, this does not necessarily mean that the active catalyst is Ti(III). In the first steps, the monosilyl–metal intermediate must react more rapidly with free silane than it does with ammonia. However, as disilyl- and trisilyl–metal species increase in concentration, they react more rapidly with ammonia than with the depleted free monosilane, or the free di- and trisilanes. This results in the appearance of aminated simple oligomers with $-SiRH(NH_2)$ end groups.

Once the aminated oligomers have been produced, they may proceed to higher molecular weight poly(aminosilanes) by further dehydrocoupling, but this would require a high degree of Si–H bond activation by the NH_2 group. While there is no a priori reason for excluding this possibility, we think it more likely that progression to higher molecular weight occurs through redistribution reactions of the oligoaminosilanes. It has been shown previously that DMT is an excellent catalyst for the redistribution of hydrosiloxanes and alkoxysilanes.[16] There is also precedent for the polymerization of disilanes by both dehydrocoupling and redistribution reactions.[10] Some reactions which account for all of the observed details of the DMT-catalyzed reactions of primary silanes with ammonia are summarized in Scheme I. In this scheme, the metal may be either Ti(IV) or Ti(III).

Scheme I. Possible Reaction Loops for $RSiH_3/NH_3$ Reactions[a]



[a] For Ti(IV), L = H; for Ti(III), L = NH_3. R' = H or $RSiH_2(RSiH)_n$-.

The behavior of secondary and tertiary silanes can also be accounted for by such a scheme, if it is assumed that Si–Si bond-forming reactions are negligibly slow compared to reactions of NH_3 and of $RR'SiH(NH_2)$ with the silyl–metal complex. However, it is hard to account for the anomalous order of reactivity of the primary versus secondary and tertiary silanes using common catalytic intermediates. Also, the evidence indicates that, for the reactions of secondary and tertiary silanes, the aminosilane reacts more rapidly than ammonia, since it does not accumulate to an observable concentration during the reaction, while with the primary silanes, the opposite is true. It is evident that there is still much to learn about these reactions before the mechanism can be more clearly defined.

Pyrolysis of Poly(methylaminosilane) (PMAS). One of the goals of making polysilazanes and poly(aminosilanes) was to examine their properties as precursors for SiC/Si_3N_4 ceramic materials. PMAS was the most promising of the materials produced in the present study, and a preliminary investigation of its pyrolysis characteristics was carried out. Earlier studies on the pyrolysis of poly(methylsilane) showed it to be exceptional as a precursor for SiC, in terms of ceramic yield and purity of product.[17]

Samples of PMAS were pyrolyzed under a nitrogen atmosphere at different temperatures, and the changes were monitored by MAS ^{29}Si NMR and PAS FTIR spectroscopy. Some results are summarized in Figures 3 and 4. With increasing pyrolysis temperature from 200 to 1000

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[14] T. D. Tilley, *Comments Inorg. Chem.* **1990**, *10*, 37. Woo, H.-S.; Tilley, T. D. *J. Am. Chem. Soc.* **1989**, *111*, 8043. Woo, H.-G.; Tilley, T. D. *J. Am. Chem. Soc.* **1989**, *111*, 3757.

[15] Samuel, E.; Mu, Y.; Harrod, J. F.; Jeannin, Y.; Dromzee, Y. *J. Am. Chem. Soc.* **1990**, *112*, 3435.

[16] Xin, S.; Aitken, C. T.; Harrod, J. F.; Mu, Y.; Samuel, E. *Can. J. Chem.* **1990**, *68*, 471.

[17] Mu, Y.; Harrod, J. F. In *Inorganic and Organometallic Polymers and Oligomers*; Harrod, J. F., Laine, R. M., Eds.; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1991; p 23.

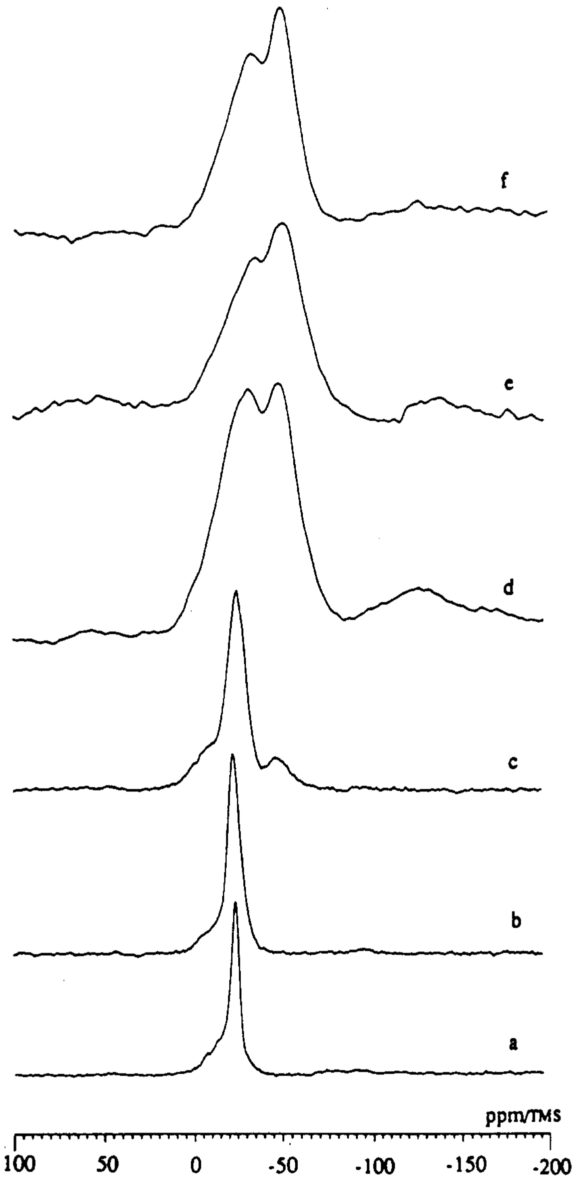


Figure 3. ^{29}Si NMR spectra of poly(methylaminosilane) pyrolyzed at different temperatures (°C): (a) before pyrolysis; (b) 200; (c) 400; (d) 600; (e) 800; (f) 1000.

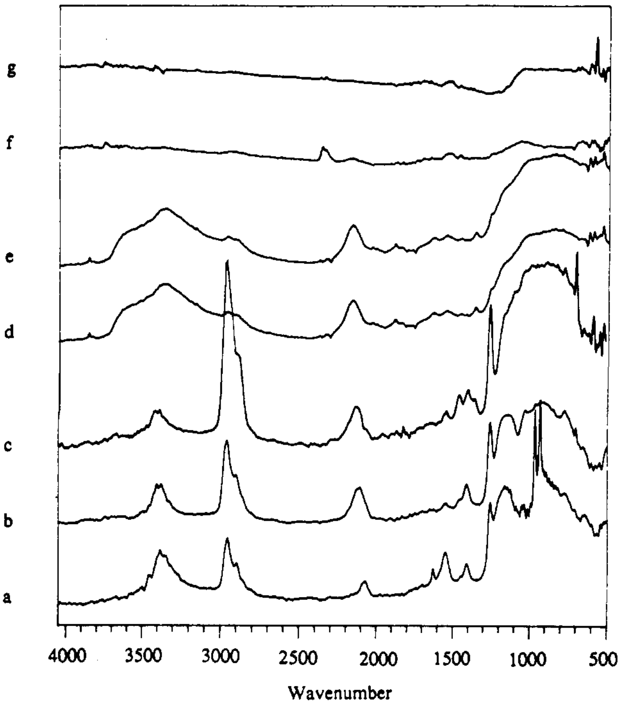


Figure 4. PAS FTIR spectra of poly(methylaminosilane) pyrolyzed at different temperatures (symbols as for Figure 3).

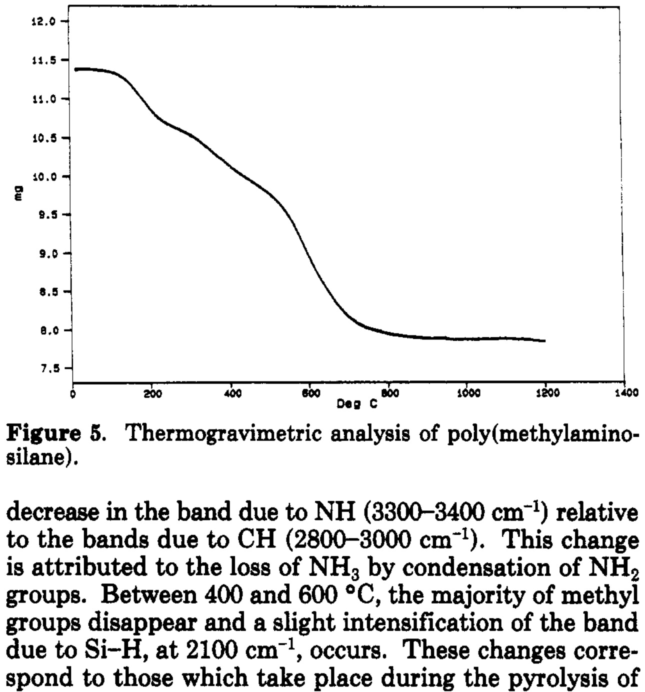
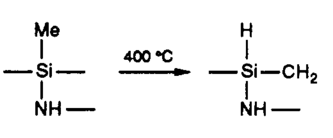


Figure 5. Thermogravimetric analysis of poly(methylaminosilane).

°C, the broad peak at −23 ppm in the ^{29}Si NMR spectrum of the original poly(methylsilazane) was replaced by new peaks at ca. −30 and −45 ppm. The peak at −45 ppm corresponds to amorphous Si_3N_4.[18] A peak at −30 ppm was previously observed by Taki et al.,[19] in a product of pyrolysis of a poly(carbosilane) under a stream of ammonia at moderate temperature. At higher temperature, as nitridation progressed, this peak disappeared. A reasonable inference is that it is due to silicon atoms which have both carbon and nitrogen in their coordination spheres.

Heating the 1000 °C product to 1400 °C transforms the amorphous material into a mixture of crystalline α-Si_3N_4, α-SiC (by X-ray powder diffraction analysis), and carbon.

PAS FTIR analysis of the original PMAS and the pyrolyzed samples obtained at different temperatures reveals important changes between 200 and 600 °C. Between ambient temperature and 400 °C, the main change is a decrease in the band due to NH (3300–3400 cm^{-1}) relative to the bands due to CH (2800–3000 cm^{-1}). This change is attributed to the loss of NH_3 by condensation of NH_2 groups. Between 400 and 600 °C, the majority of methyl groups disappear and a slight intensification of the band due to Si–H, at 2100 cm^{-1}, occurs. These changes correspond to those which take place during the pyrolysis of pure poly(methylsilane)[17] and can be explained by the onset of a Kumada rearrangement to the poly(carbosilane), as shown in eq 1. Subsequent changes in the spectra correlate with the loss of hydrogen to give the final products.



$$-\overset{\displaystyle Me}{\underset{\displaystyle NH-}{\overset{|}{\underset{|}{Si}}}}- \xrightarrow{400\ ^{\circ}C} -\overset{\displaystyle H}{\underset{\displaystyle NH-}{\overset{|}{\underset{|}{Si}}}}-CH_2 \qquad (1)$$

Thermogravimetric analysis of PMAS indicates that weight loss occurs in three stages (see Figure 5). Between room temperature and 200 °C there is a 6% loss and between 200 to 400 °C there is a further 6% loss. The IR results given above suggest that both of these are due to

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partial loss of nitrogen as ammonia. The major weight loss, of nearly 20%, occurs between 400 and 700 °C, the same temperature range in which spectroscopic studies show most of the chemical changes to be occurring. It is probable that some carbon is lost at this stage, since the analysis of the final product indicates that about half of the carbon is lost.

Experimental Section

All the reactions were carried out under air-free conditions. Toluene was freshly distilled from sodium before use. Cyclohexene was distilled from CaH_2. Silanes were synthesized by reduction of the corresponding halides with lithium aluminum hydride, according to a literature method.[21] Dimethyltitanocene was synthesized by following a literature procedure.[22] Ammonia (anhydrous, Matheson) was used as received.

^1H NMR spectra were recorded on a Varian XL-200FT spectrometer and ^{13}C NMR spectra on a Varian XL-300FT spectrometer. MAS ^{29}Si NMR spectra were obtained on a Chemagnetics CMX-300 spectrometer operating at 59.52 MHz. Samples were spun at magic angle at speeds of 3.5–5 MHz. When sufficient ^1H density was present, the cross-polarization technique was used with a contact time of 6 ms and a recycle time of 3–5 s. In those samples which had no protons, single ^{29}Si excitation pulses of 45° were employed with recycle delays of 2 s. All spectra are referenced to external TMS.

Mass spectra were measured on a Du Pont 21-492B spectrometer at a potential of 70 eV and a ZAB-HS mass spectrometer using FAB with an atom energy of 8 kV at 1 mA.

The molecular weights of polymers were measured on a Varian 5000 gel permeation chromatograph, equipped with a Waters Ultrastyragel 1000-Å column or 500- and 100-Å columns at 35 °C and with tetrahydrofuran as solvent. Polystyrene standards were used for calibration. FTIR spectra were measured on an Analect AQS-18 FTIR spectrometer. PAS FTIR spectra were measured on a Cygnus 25 spectrometer.

Gas chromatography (GC) was performed on a Shimadzu GC-8A instrument equipped with a DB-5 capillary column.

Elemental analyses were performed by Galbraith Laboratories, Inc.

Reactions of Diphenylmethylsilane with Ammonia. The reaction was carried out in a 120-mL pressure reactor. After evacuation, the reactor was charged with Ph_2MeSiH (1 mL, 5 mmol), DMT (13 mg, 0.06 mmol) and ammonia (2 atm). The reaction was initiated by gently warming the reactor for a few minutes and the mixture then left at room temperature for 22 h. Analysis by ^1H NMR spectroscopy indicated a conversion of silane of 70%, with diphenylmethyldisilazane as the only product.

Reaction of Phenylmethylsilane with Ammonia. The reaction was carried out either in a pressure reactor, as described above, or in a glass reactor equipped with a condenser, magnetic stirrer, and gas inlet tube. In the latter case, after evacuation, the reactor was charged with $PhMeSiH_2$ (1 mL, 7.3 mmol), DMT (15 mg, 0.07 mmol), and degassed toluene (5 mL). Ammonia was bubbled through the solution at atmospheric pressure, and the mixture was heated to 100 °C. The reaction mixture was periodically sampled and analyzed by ^1H NMR, GC, and GC–MS methods.

Reaction of Phenylsilane and Ammonia at Atmospheric Pressure. The reaction was carried out in a 50-mL glass reactor equipped with a condenser, magnetic stirrer, and gas inlet. After careful evacuation of the flask, toluene (8 mL) and phenylsilane (2 mL, 15 mmol) was introduced. Following degassing of the liquids, dimethyltitanocene (30 mg, 0.15 mmol) was added. Ammonia was then bubbled through the solution, and the temperature was raised to 95 °C. After 16 h, the solvent was evaporated under vacuum and the resulting glassy residue was scraped from the walls of the reactor to give 0.54 g of a brown powder (yield 80%). Anal. Calcd for C_6H_7SiN: C, 59.5; H, 5.78; N, 11.57; Si, 23.14. Found: C, 57.72; H, 5.32; N, 12.51; Si, 22.29. ^1H NMR: 6.8–8.1 ppm (3 H), 0.0–2.0 ppm (1 H); no resonance in Si–H region. IR (NH and SiN modes; cm^{-1}): 3473 (w), 3378 (s), 1171 (vs); no ν_{SiH} at ca. 2100 cm^{-1}.

A similar procedure was employed for reactions that were followed by NMR spectroscopy. Samples were removed by syringe at appropriate intervals, and the NMR spectra were measured directly.

Reactions of Phenylsilane and *n*-Hexylsilane with Ammonia under Pressure. The reactions were carried out in a thick-walled glass pressure vessel of 100-mL capacity and with a pressure rating of 10 atm. After evacuation, phenylsilane (or *n*-hexylsilane) (2 mL, 15 mmol), cyclohexene (3.25 mL; cyclohexene is added as a hydrogen sink to avoid having high pressure at the time that the reactor is opened), and dimethyltitanocene (25 mg, 0.12 mmol) was introduced. The system was completely degassed, and ammonia was introduced at a pressure of 3.6 atm. The reactor was sealed and heated to 90 °C. The reaction was terminated after the appropriate reaction time by venting excess hydrogen and ammonia and pumping off solvent under vacuum.

Reactions of Methylsilane and Ammonia. After evacuation, 10 mL of degassed cyclohexene and 20 mg of Cp_2TiMe_2 was added to a 100-mL pressure flask. Methylsilane was introduced to a pressure of 30 psi followed by 30 psi of ammonia. The reactor was closed and heated to 70 °C. After 2 days of reaction, excess gas was vented and volatiles were removed under vacuum. A brown, brittle solid (0.44 g, 70% yield based on $[MeSiNH_2]_n$) was isolated. Anal. Calcd for CH_5SiN: C, 20.34; H, 8.47; N, 23.73; Si, 47.46. Found: C, 21.34; H, 7.36; N, 21.02; Si, 42.21. ^1H NMR: 0.5–1.5 ppm (1 H), 0.0–0.4 ppm (2.2 H); weak band due to SiH at 4.65 ppm (0.06 H). ^{29}Si NMR −22 ppm. IR (NH and SiH modes; cm^{-1}): 3350 (s), 1157 (vs); weak SiH band at 2066. The analytical deficit is probably due to incomplete combustion of SiC/Si_3N_4, a common problem in the analysis of preceramic polymers.

Pyrolysis of PMAS. Pyrolyses were carried out on pulverized samples (1.0 g) in a quartz tube furnace, under a stream of nitrogen. Samples for the data reported in Figures 3 and 4 were inserted into the furnace, preheated to the requisite temperature, and held at temperature for 1 h. After the sample was quenched to room temperature under nitrogen, it was divided and prepared for the various analyses. A sample pyrolyzed for 1 h at 1200 °C gave a 77% yield of ceramic product (Anal. Found: C, 13.66; H, <0.5; N, 28.91; Si, 51.68). The chemical analysis corresponded to the following nominal composition (weight percent): Si_3N_4, 77; SiC, 13; C, 10.

Acknowledgment. Financial support from the Natural Sciences and Engineering Research Council of Canada and from Fonds FCAR du Québec is gratefully acknowledged. Thanks are also due to Dr. F. Morin for measurement of the solid-state ^{29}Si NMR spectra, Dr. R. Werbowyj for PAS FTIR spectra, and Dr. O Mamer for the mass spectra.

Registry No. 1, 7453-26-1; 2, 25938-40-3; 3, 4222-38-2; 4, 138234-82-9; DMT, 1271-66-5; PMAS, 138234-86-3; H_2N-$(PhMeSiNH)_3H$, 138234-83-0; $H(PhMeSiNH)_2SiPhMeH$, 138234-84-1; Ph_2MeSiH, 776-76-1; $PhMeSiH_2$, 766-08-5; ammonia, 7664-41-7.

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