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The objective of this work was to investigate new transition metal-silicon complexes as precursors to ceramic materials, or as catalysts for the synthesis of silicon-containing polymers. Precursors to metal silicates were based on complexes of the tri(tert-butoxy)siloxy ligand. Very low temperature, clean routes to silicate materials were discovered. The ceramic materials that were investigated in most detail had the compositions $MO_2 \cdot 4SiO_2$ (M = Ti, Zr, Hf). It was shown that these thermolytic methods could be carried out in solution, and used to apply smooth, thin films of the silicate materials. New transition metal silyl complexes were discovered, and some were used in mechanistic studies to demonstrate a mechanism for the d^0 metal-catalyzed dehydrocoupling of silanes to polysilanes. This represents a new polymerization mechanism which shows great promise for the synthesis of new polymers.

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"Surface Modification of Matrix Materials for Oxidation-Resistant Carbon-Carbon Composites." H. Streckert, F. Montgomery, T. D. Tilley, B. K. Campion and R. H. Heyn. In Ultrastructure Processing of Advanced Ceramics, J. A. Mackenzie and D. R. Ulrich, Eds.; Wiley: New York, Chap. 79, p. 963 (1988).

"Transition-Metal Silyl Derivatives." T. D. Tilley. In *The Chemistry of Organic Silicon Compounds*, S. Patai and Z. Rappoport, Eds.; Wiley: New York, Chap. 24, p. 1415 (1989).

"σ-Bond Metathesis Reactions of Si-H and M-Si Bonds. New Routes to d^0 Metal Silyl Complexes." H.-G. Woo and T. D. Tilley. J. Am. Chem. Soc., *111* (1989).

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"Reactivity of a Sc-Si Bond Toward CO and CN(2,6-Me$_2$C$_6$H$_3$). Generation and Reactivity of an Apparent Silene Intermediate Resulting From Isocyanide Coupling at Scandium." B. K. Campion, R. H. Heyn and T. D. Tilley. J. Am. Chem. Soc., *112* (1990).

"Mechanistic Aspects of Transition-Metal Catalyzed Dehydrogenative Silane Coupling Reactions." T. D. Tilley. Comments Inorg. Chem., *10* (1990).

"Trialkoxysiloxy Complexes of Nickel. Crystal and Molecular Structures of Na$_3$(μ_3-I){Ni[μ_3-OSi(O^{t}Bu)$_3$]$_3$I}·0.5THF·0.5C$_5$H$_{12}$ and {(η^3-C$_3$H$_5$)Ni[μ_2-OSi(O^{t}Bu)$_3$]}$_2$." A. K. McMullen, T. D. Tilley, A. L. Rheingold and S. J. Geib. Inorg. Chem., *29* (1990).

"Dehydrogenative Polymerization of Silanes by Sigma-Bond Metathesis." T. D. Tilley and H.-G. Woo. Polym. Prepr., (Am. Chem. Soc. Div. Polym. Chem.), *31* (1990).

"Insertion of Nitriles and Pyridine into the Zr-Si Bond of (η^5-C$_5$H$_5$)(η^5-C$_5$Me$_5$)Zr[Si(SiMe$_3$)$_3$]Me." H.-G. Woo and T. D. Tilley. J. Organomet. Chem., *393* (1990.

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"Transition-Metal Complexes of Reactive Silicon Intermediates." T. D. Tilley, B. K. Campion, S. D. Grumbine, D. A. Straus and R. H. Heyn. In *Frontiers of Organosilicon Chemistry*, A. R. Bassindale and P. P. Gaspar, Eds.; The Royal Society of Chemistry, Thomas Graham House: Cambridge (1991) p. 295.

"Transition-Metal Silyl Derivatives." T. D. Tilley. In *Silicon Heteroatom Bonds*, S. Patai and Z. Rappoport, Eds.; Wiley: New York, in press (1991).

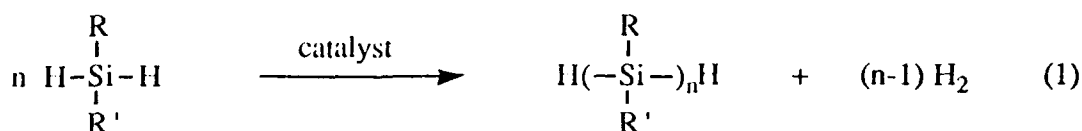## ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The objective of this work was to investigate new transition metal-silicon complexes as precursors to ceramic materials, or as catalysts for the synthesis of silicon-containing polymers. Precursors to metal silicates were based on complexes of the tri(tert-butoxy)siloxy ligand. Very low temperature, clean routes to silicate materials were discovered. The ceramic materials that were investigated in most detail had the compositions MO$_2$·4SiO$_2$ (M = Ti, Zr, Hf). It was shown that these thermolytic methods could be carried out in solution, and used to apply smooth, thin films of the silicate materials. New transition metal silyl complexes were discovered, and some were used in mechanistic studies to demonstrate a mechanism for the d^0 metal-catalyzed dehydrocoupling of silanes to polysilanes. This represents a new polymerization mechanism which shows great promise for the synthesis of new polymers.

Final Technical Report

(Grant No. AFOSR 88-0273)

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The Role of d^0 M-Si Bonds in Polymerizations.

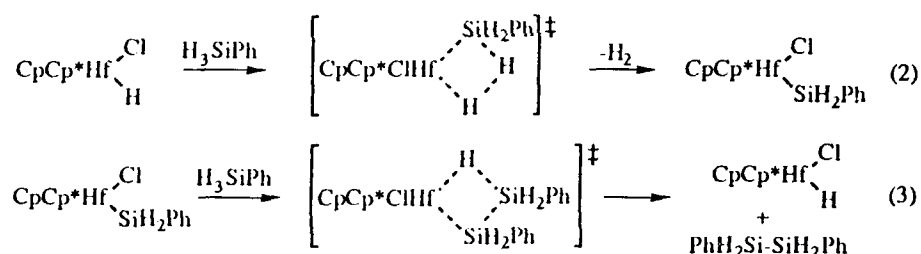The metal-catalyzed dehydropolymerization of silanes is represented generally by eq 1.

$$n \ \underset{\underset{R'}{|}}{\overset{\overset{R}{|}}{H-Si-H}} \quad \xrightarrow{\text{catalyst}} \quad H(\underset{\underset{R'}{|}}{\overset{\overset{R}{|}}{-Si-}})_n H \quad + \quad (n\text{-}1) \, H_2 \qquad (1)$$

It has been known for some time that transition metal catalysts can mediate this disproportionation of σ-bonds, but it was not until 1985 that polysilane chains of significant length (ca. 20-30 Si atoms) were obtained by this method. The latter breakthrough was reported by Harrod and coworkers, who employed titanocene and zirconocene catalysts of the type Cp_2MR_2 ($Cp = \eta^5$-C_5H_5; M = Ti, Zr; R = alkyl, aryl). For this new reaction to find application as a general means for producing new polymers, it is essential to understand how it operates. Mechanisms for such metal-catalyzed reactions have been the subject of much speculation, and a number of possibilities have been suggested. Most speculation has centered on mechanisms involving silylene complexes ($L_nM=SiR_2$) as agents for silylene transfers, but very little experimental evidence for these intermediates exists. Also, it seems likely that different mechanisms can operate, depending upon the nature of the catalyst.

A mechanism for d^0 metal-catalyzed dehydropolymerizations. Our studies in early transition-metal silicon chemistry have produced synthetic routes to the first tractable d^0 metal silyl complexes, and have characterized d^0 M-Si bonds as being highly reactive toward the insertion of unsaturated substrates. Many d^0 M-Si bonds are also reactive toward σ bonds, as exemplified by their facile hydrogenolysis to give M-H and Si-H species. In addition, we have

found that reactions between d^0 M-Si and Si-H bonds can take place, and that the course (and speed) of the reaction is influenced heavily by the nature of the metal silyl complex. Thus, complexes such as $Cp_2Zr[Si(SiMe_3)_3]SiMe_3$ and $CpCp*Zr[Si(SiMe_3)_3]Me$ ($Cp* = \eta^5-C_5Me_5$) are active catalysts for the dehydrocoupling of $PhSiH_3$ to H_2 and $H(SiHPh)_nH$. In general, catalysts based on $CpCp*Zr$ hydrides and silyls are the most active dehydrocoupling catalysts known. Slower reactions are observed between hydrosilanes and hafnium chloro complexes such as $CpCp*Hf[Si(SiMe_3)_3]Cl$ and $CpCp*HfHCl$. Such slow, well-behaved reactions have allowed us to characterize the interactions of d^0 M-Si bonds with hydrosilanes, some of which represent steps in a likely dehydropolymerization mechanism.

In Ti, Zr, Hf, Ta, Sc, Y, Nd and Th complexes, d^0 M-Si bonds undergo facile "σ-bond metathesis" reactions that pass through 4-center transition states containing the d^0 metal, silicon and hydrogen. Two examples of observed, stoichiometric processes are shown in eqs 2 and 3.

$$CpCp*Hf\overset{Cl}{\underset{H}{<}} \xrightarrow{H_3SiPh} \left[CpCp*ClHf \overset{SiH_2Ph}{\underset{H}{\diamond}} H \right]^{\ddagger} \xrightarrow{-H_2} CpCp*Hf\overset{Cl}{\underset{SiH_2Ph}{<}} \quad (2)$$

$$CpCp*Hf\overset{Cl}{\underset{SiH_2Ph}{<}} \xrightarrow{H_3SiPh} \left[CpCp*ClHf \overset{H}{\underset{SiH_2Ph}{\diamond}} SiH_2Ph \right]^{\ddagger} \longrightarrow \underset{\underset{PhH_2Si-SiH_2Ph}{+}}{CpCp*Hf\overset{Cl}{\underset{H}{<}}} \quad (3)$$

Kinetic studies on these and related reactions are consistent with concerted processes in which σ bonds are broken and formed at roughly the same time. Such reactions appear to be characteristic for d^0 transition metal-silicon systems, and further evidence for this is provided by the fact that we have been able to observe every possible σ-bond metathesis reaction involving hydrogen, a d^0 metal center, and a silyl group (Scheme 1).
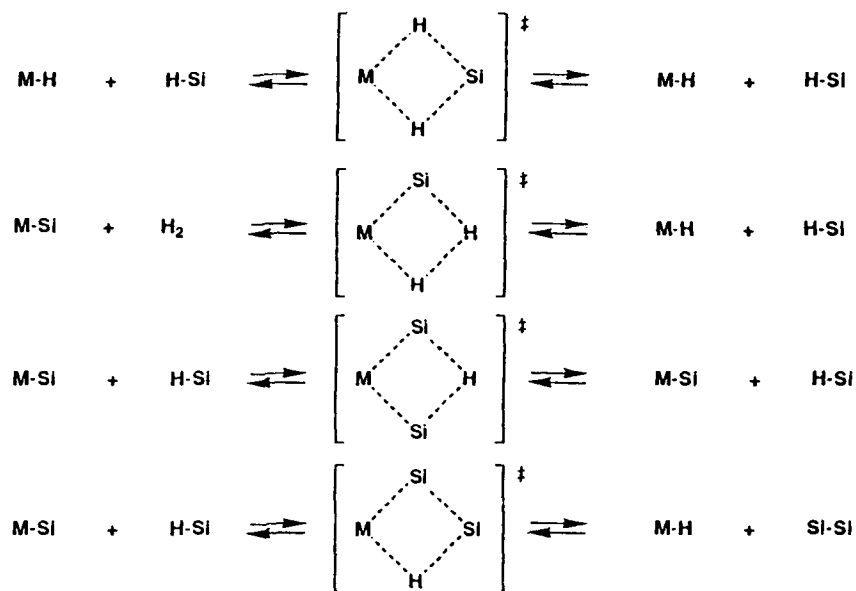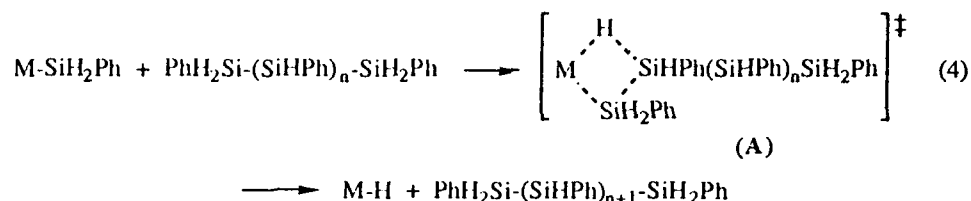
Scheme 1

Such reactions provide the basis for a new polymerization mechanism that accounts for the catalytic action of d^0 metal complexes in the dehydrogenative coupling of hydrosilanes to polysilanes. This mechanism, shown in Scheme 2, is unusual as a metal-mediated, *step-like* polymerization. The slower, more selective catalysts have been effectively used to study isolated, fundamental steps in the various competing processes. Such mechanistic studies have produced a large body of evidence in support of this proposed mechanism.
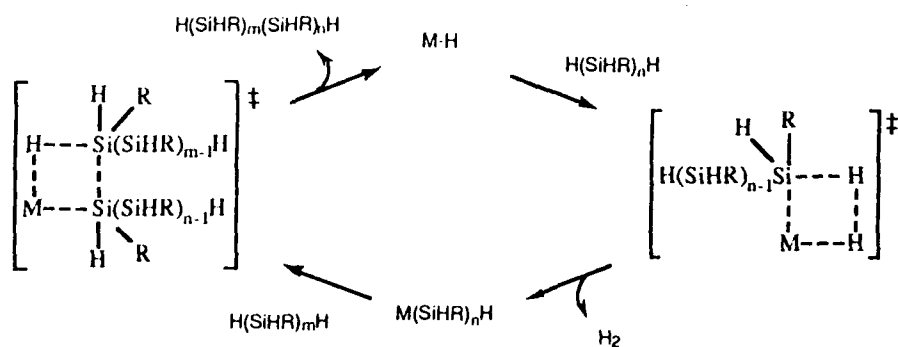
Scheme 2

This evidence includes observation of intermediate species, confirmation of the step-growth nature of chain growth, and identification of the active form of the catalyst as an unsaturated, d^0 metal hydride.

Characteristic features of the mechanism. To a large degree, the rates of the σ-bond metathesis reactions in Scheme 1 are governed by steric effects. Therefore in general, the coupling of silyl groups (last transition state in Scheme 1) is the slowest reaction possible. Using catalysts of low activity such as $Cp*_2HfH_2$, it is possible to monitor the formation and consumption of small polysilanes as the dehydrocoupling proceeds. Under these rather selective conditions, the disilane is not very rapidly coupled to tetrasilane, which appears to be formed predominantly by coupling of $PhSiH_3$ with the trisilane. This and other results indicate that the most facile Si-Si bond-forming reaction involves addition of one silicon at a time to the polysilane chain via a monosilyl $M-SiH_2R$ derivative (eq 4),

$$M\text{-}SiH_2Ph \ + \ PhH_2Si\text{-}(SiHPh)_n\text{-}SiH_2Ph \ \longrightarrow \ \left[M \overset{H}{\underset{SiH_2Ph}{\diagdown}} SiHPh(SiHPh)_nSiH_2Ph \right]^{\ddagger} \quad (4)$$

$$(A)$$

$$\longrightarrow \ M\text{-}H \ + \ PhH_2Si\text{-}(SiHPh)_{n+1}\text{-}SiH_2Ph$$

resulting in *linear chain growth* of the polymer. This selectivity can be understood in terms of steric hindrance in competing 4-center transition states that couple silyl groups together. The least crowded (and presumably lowest energy) transition state is produced by addition of a $M-SiH_2R$ derivative to the end of a polysilane chain, since this places the bulky polysilyl group in the β position relative to the metal center. Therefore, as long as monomer is present, the more important polymerization process corresponds to the case where n = 1 in Scheme 2. Once monomer is consumed, increases in molecular weight require a catalyst active enough to couple chains together via the higher energy transition state. Note however, that such conditions will probably also promote cyclizations, given the $\Delta S^{\ddagger}$ term that contributes to the energy of the latter transition state, which should make the cyclization process somewhat more favorable than the coupling of two chains together.

Factors that control molecular weight distributions. With a likely polymerization mechanism in hand, we have begun to evaluate experimental factors that can be manipulated to

influence molecular weight distributions. We wish to use the available mechanistic information to learn why the observed limitations exist, and how they can be overcome. A fundamental limitation to the polysilane molecular weight results from the step-growth nature of the polymerization, which requires extremely high conversions of Si-H to Si-Si bonds for the production of high polymer.

Attempts to drive the polymerization of PhSiH$_3$ to higher conversion, via heating or longer reaction times, results in degradation of linear chains to the (SiHPh)$_6$ cyclics. Therefore nearly complete conversions of Si-H to Si-Si bonds have been achieved, but only at the expense of converting all the polysilanes to low molecular weight cyclics. Apparently, these cyclic species are thermodynamically preferred over linear chains.

The mechanistic information described above suggests that cyclizations should be suppressed by high monomer concentrations. Such conditions will favor the conversion of metal hydride species to M-SiH$_2$R complexes, which will then react to increment chains. Oligomers such as H(SiHPh)$_6$H will then stand a greater chance of growing linearly relative to undergoing cyclizations catalyzed by M-H. We have determined the influence of initial PhSiH$_3$ concentration on molecular weight distributions, using CpCp*Zr[Si(SiMe$_3$)$_3$]Me as the catalyst. These concentration effects are quite dramatic, and in the absence of solvent, cyclic formation is greatly suppressed. Also, under conditions that yield few cyclic species, the linear chains achieve higher molecular weights. In polymerizations with neat silane, further molecular weight increases are apparently limited only by the high viscosity of the reaction mixture that develops. Consistent with this, the maximum molecular weight is a function of reaction temperature.

It now appears that the major factors which limit chain lengths in metal-catalyzed dehydropolymerizations are: 1) competing cyclic formation, and 2) incomplete conversion of Si-H to Si-Si bonds due to catalyst inactivity, low viscosity reaction media, insufficient removal of hydrogen, etc. Significantly, the results indicate that there is no inherent limitation to molecular weight control via polymerizations of this type, and it should be possible to identify conditions and

catalysts that allow production of high polymers. Future advances may depend largely upon catalyst design, and results so far indicate that the role of the catalyst can be quite dramatic.

The mechanistic information that we have accumulated suggests two approaches for engineering the dehydrocoupling reaction to give higher molecular weights. The first strategy is based on the fact that the preferred dehydrocoupling process is addition of one silicon at a time to the growing chain, via transition state **A**. This result shows that it is kinetically possible, given the right conditions, to selectively produce high molecular weight linear polysilanes. The right conditions correspond to imposed selectivities which partition the polymerization toward the lower energy reactions that pass through transition state **A**. The "higher energy" cyclizations lead to more stable polysilanes, but involve two transition states that have a polysilyl group α to the metal. First, a $M\text{-}(SiHR)_nSiH_2R$ species must be formed via a transition state with the $-(SiHR)_nSiH_2R$ group in the α position, and secondly, a heavily substituted 4-center transition state is involved in the cyclization.

The desired selectivities can be achieved by going to low temperatures, or by using slower (more selective) catalysts which are better at partitioning the various possible dehydrocoupling processes. We have demonstrated this principle, using the $CpCp*Zr[Si(SiMe_3)_3]Me$ catalyst and neat $PhSiH_3$, by showing that cyclic formation is nearly completely suppressed at -25 °C. Alternatively, the selectivity required for exclusive linear chain growth by one silicon at a time can be imposed by use of the more selective (discriminating) catalyst $CpCp*Hf[Si(SiMe_3)_3]Cl$.

An alternative approach that might favor the production of higher molecular weight polysilanes is based on use of highly active catalysts to couple chains. It becomes apparent from an examination of the rate equations for both chain coupling and depolymerization, that the coupling of chains can compete favorably with depolymerization, given the proper balance of competing rates. In particular, coupling appears to be favored by high $[M(SiHR)_nH]/[MH]$ ratios, a higher rate constant for chain coupling vs. chain cleavage, and by rapid removal of H_2 from the system. This kinetic analysis assumes that the rate of chain scissions is slow compared to
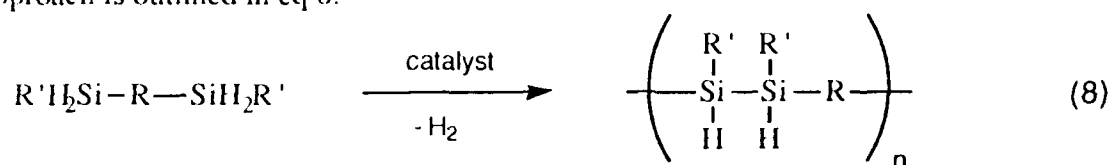
cyclizations by $M(SiHR)_6H$ species, and that all Si-Si bonds are equally reactive toward cleavage by the catalyst.

Higher molecular weight polysilanes via cross-linking agents. Much of the mechanistic work described above is focused toward developing ways to control the dehydropolymerization of hydrosilanes $RSiH_3$, particularly for production of high molecular weight polysilanes. However, the basic dehydrocoupling method can in fact already be employed in slightly modified reactions to produce high molecular weight, silicon-containing polymers. One approach involves use of cross-linking agents containing two or more hydrosilane functionalities.

The copolymerization of primary silanes $RSiH_3$ with disilyl species (e.g., $4,4'$-$(SiH_3)_2C_6H_4$-C_6H_4) as cross-linking agents produces high molecular weight polysilanes. For example, copolymerization of $PhSiH_3$ and $4,4'$-$(SiH_3)_2C_6H_4$-C_6H_4 (5%) gives a soluble polymer ($M_w = 70,000$) with a broad molecular weight distribution ($M_w/M_n = 7$) that tails well beyond 150,000. Interestingly, the high molecular weight properties of this material are reflected in the electronic spectrum ($\lambda = 320$ nm), which shows a red shift relative to the monomers, suggesting some degree of σ-π conjugation.
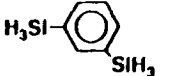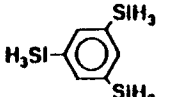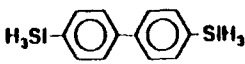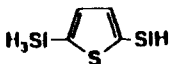
Sigma-pi conjugated polymers. While interest in polysilanes has dramatically increased over the last ten years, there has been comparatively less attention given to other silicon-containing polymers which might have similar properties. Polymers containing both silylene and unsaturated hydrocarbon fragments in the backbone are particularly interesting in this respect, and a few have been synthesized by Wurtz-coupling methods. In some cases the electronic spectra suggest extensive σ-π democratization in the polymer backbone, and oxidative doping has been reported to give conductive or semiconductive materials. For example, Ishikawa and coworkers have reported p-(disilanylene)phenylene polymers, $(-SiMeR-SiMeR-C_6H_4-)_n$ (R = Et, Ph), and investigations into their application as positive deep UV resist materials. Note that polymers of this type are somewhat analogous to polyphenylenevinylenes, given the similar properties of C=C and Si-Si bonds.

We are interested in applying the dehydrocoupling chemistry described above to the synthesis of new silicon-containing polymers with different spacer groups R in the polymer backbone. Much higher molecular weights should in general be possible, since incorporation of two hydrosilyl functionalities into the monomer requires that only one Si-H group per silicon center is required for chain growth. Furthermore, reaction of more than one Si-H group per silicon center should lead to cross-linking of chains, and increased molecular weights. The basic approach is outlined in eq 8.

$$R'H_2Si-R-SiH_2R' \xrightarrow[\text{-}H_2]{\text{catalyst}} \left(\begin{array}{c} R' \quad R' \\ | \quad\quad | \\ -Si-Si-R- \\ | \quad\quad | \\ H \quad\quad H \end{array}\right)_n \qquad (8)$$

A recent communication from our laboratory describes the application of this synthetic method to the synthesis of high molecular weight poly(disilanylenearylene)s from bis-silyl monomers, using [CpCp*ZrH2]2 as a catalyst. This report describes the synthesis of the bis(hydrosilyl) monomers, and their dehydrogenative polymerizations to highly porous, cross-linked polymers (H$_x$Si-R-SiH$_x$)$_n$ (x = 1-2). Empirical formulas for the polymers were determined by combustion analyses and by integration of CRAMPS solid state ^{1}H NMR spectra (Table 1).

Table 1
(Disilanylene)arylene Polymers

Monomer	CRAMPS ^{1}H NMR		Combustion Analysis[a]		UV-vis λ_{max} (nm)[b]
	Formula	% Crosslinking	Formula	% Crosslinking	
H$_3$Si—⬡—SiH$_3$	[H$_{1.4}$SiC$_6$H$_4$Si$_{1.4}$]$_n$	65 %	[H$_{1.5}$SiC$_6$H$_4$Si$_{1.5}$]$_n$	55 %	260 nm
H$_3$Si—⬡(SiH$_3$)	[H$_{1.5}$SiC$_6$H$_4$Si$_{1.5}$]$_n$	55 %	[H$_{1.5}$SiC$_6$H$_4$Si$_{1.5}$]$_n$	55 %	–
H$_3$Si—⬡(SiH$_3$)(SiH$_3$)	[C$_6$H$_3$(SiH$_{1.8}$)$_3$]$_n$	20 %	[C$_6$H$_3$(SiH$_{1.7}$)$_3$]$_n$	27 %	240 nm
H$_3$Si—⬡—⬡—SiH$_3$	[H$_{1.6}$SiC$_6$H$_4$C$_6$H$_4$SiH$_{1.6}$]$_n$	45 %	[H$_{1.6}$SiC$_6$H$_4$C$_6$H$_4$SiH$_{1.6}$]$_n$	45 %	295 nm
H$_3$Si—⟨S⟩—SiH$_3$	[H$_{1.1}$SiC$_4$H$_2$SSiH$_{1.1}$]$_n$	12 %	[H$_{1.8}$SiC$_4$H$_2$SSiH$_{1.8}$]	80 %	295 nm

[a] Hydrogen analysis only. [b] Nujoll mull, ε not calculated.

Despite the large errors inherent in these two methods, there is generally good agreement between them, and both support a high degree of cross-linking.

The polymers are insoluble in organic solvents, and are high melting (mp.> 300 °C). Thermal Gravimetric Analysis (TGA) shows that $[4,4'-H_xSiC_6H_4C_6H_4SiH_x]_n$ is thermally stable under argon, and only 5% of the polymer's initial weight is lost by 350 °C. At 700 °C, the residue remaining is equal to 80% of the initial sample weight, which corresponds to a substantially higher "ceramic yield" than has previously been reported for disilanylene arylene polymers. Differential Scanning Calorimetry (DSC) did not indicate the existence of a glass transition temperature (T_g) for $[1,4-H_xSiC_6H_4SiH_x]_n$, $[1,3-H_xSiC_6H_4SiH_x]_n$, or $[4,4'-H_xSiC_6H_4C_6H_4SiH_x]_n$ between 25 °C and 450 °C. X-ray powder patterns for $[1,4-H_xSiC_6H_4SiH_x]_n$ and $[4,4'-H_xSiC_6H_4C_6H_4SiH_x]_n$ provide no evidence for crystallinity. It therefore appears that these materials adopt amorphous network structures as generalized in eq 9.

$$H_3Si\text{-}R\text{-}SiH_3 \xrightarrow[-H_2]{[CpCp^*ZrH_2]_2} \qquad (9)$$
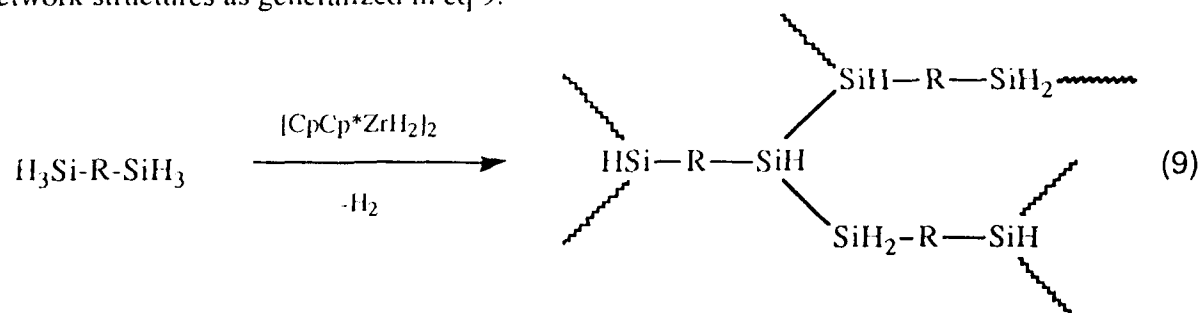
Transmission Electron Microscopy (TEM) analysis of $[1,4-H_xSiC_6H_4SiH_x]_n$ shows a granular structure, with particle sizes ranging from 10 to 400 nm. Similar results were obtained in the TEM analysis of $[1,4-H_xSiC_6H_4SiH_x]_n$, $[1,3-H_xSiC_6H_4SiH_x]_n$, and $[4,4'-H_xSiC_6H_4C_6H_4SiH_x]_n$. All three of these polymers have very high surface areas (BET method, N_2): $[1,4-H_xSiC_6H_4SiH_x]_n$, 420 m^2/g; $[1,3-H_xSiC_6H_4SiH_x]_n$, 380 m^2/g; $[4,4'-H_xSiC_6H_4C_6H_4SiH_x]_n$, 315 m^2/g.
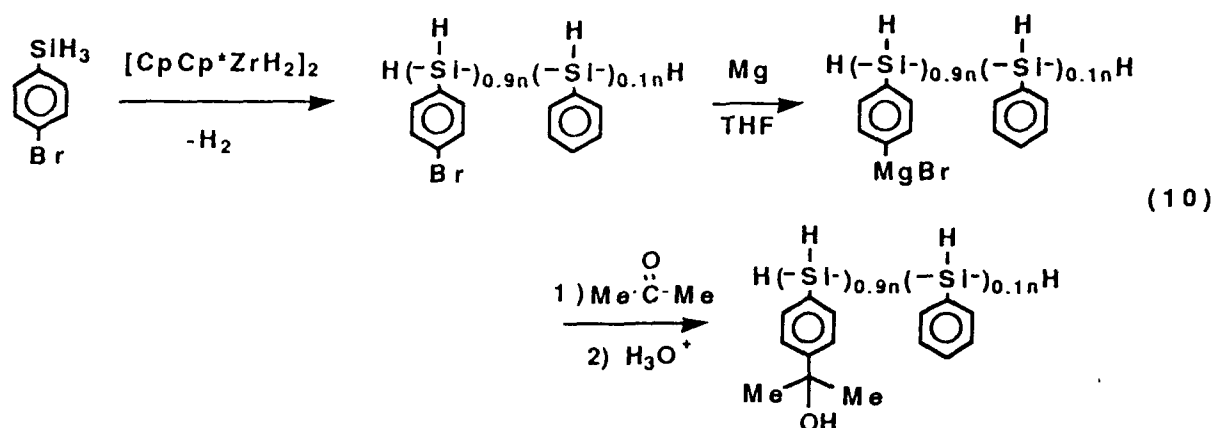
Given the extended σ-π framework present in these polymers, it is not surprising that their UV-vis spectra are red-shifted compared to their respective monomers. Specifically, $[1,4-H_xSiC_6H_4SiH_x]_n$ absorbs at 260 nm compared to $1,4-(H_3SiC_6H_4SiH_3)$, which absorbs at 240 nm, and $[4,4'-H_xSiC_6H_4C_6H_4SiH_x]_n$ absorbs at 295 nm compared with an absorbance of

265 nm for $4,4'$-($H_3SiC_6H_4C_6H_4SiH_3$). The λ_{max} value for $[1,4-H_xSiC_6H_4SiH_x]_n$ is similar to those reported for thin films of $[1,4-MePhSiC_6H_4SiMePh]_n$ (254 nm) and $[1,4-MeEtSiC_6H_4SiEtMe]_n$ (262 nm). In contrast to these materials, however, $[1,4-H_xSiC_6H_4SiH_x]_n$ does not photodegrade upon irradiation with a medium pressure Hg lamp.

Conductivity measurements performed using the four probe method showed that all the polymers synthesized were insulators. Exposure to SbF_5 vapor caused the polymers to darken and turn dark blue or brown, but did not result in measurable conductivity values, except in the case of $[4,4'-H_xSiC_6H_4C_6H_4SiH_x]_n$, which was found to possess a conductivity of ca. 10^{-4} S/cm.

These polymers therefore have properties that are very different from polymers which have been previously prepared by metal-catalyzed dehydropolymerization. Their physical properties are consistent with a substantial degree of cross-linking, and the UV-vis and conductivity data suggest σ-π democratization in the -(Si-Si-Ar)- backbone. Currently we are focussing on modification of this polymerization to produce processible, linear polymers. Initial results indicate that $1,4$-MeH_2Si-C_6H_4-SiH_2Me can be dehydropolymerized to soluble, high polymers with the formula $[1,4-MeHSi-C_6H_4-SiHMe]_n$.

Functionalized polysilanes. In general, the Wurtz method is not useful for the synthesis of functionalized polysilanes, because of the strongly reducing conditions that are employed. We have shown that a variety of functional groups are compatible with dehydropolymerizations using Zr and Hf catalysts. One example is the polymerization of $(p$-$BrC_6H_4)SiH_3$ to $H[-SiH(p-BrC_6H_4)-]_nH$ with only about 10% reduction of the aryl halide functionality by the $[CpCp^*ZrH_2]_2$ catalyst. Reaction of this polymer with magnesium (to form a polymeric Grignard reagent), followed by addition of acetone allows conversion of the bromo group to an alcoholic (-CMe_2OH) functionality (equation 10). Functional groups can be used as cross-linking sites, for formation of block copolymers, for bonding to various matrix materials, and for modifying and introducing electronic properties.

$$SiH_3\text{-}C_6H_4\text{-}Br \xrightarrow[-H_2]{[CpCp^*ZrH_2]_2} H(-Si-)_{0.9n}(-Si-)_{0.1n}H \xrightarrow[THF]{Mg} H(-Si-)_{0.9n}(-Si-)_{0.1n}H$$

with Br and MgBr substituents respectively

(10)

$$\xrightarrow[2)\ H_3O^+]{1)\ Me\text{-}\overset{O}{\overset{\|}{C}}\text{-}Me} H(-Si-)_{0.9n}(-Si-)_{0.1n}H$$

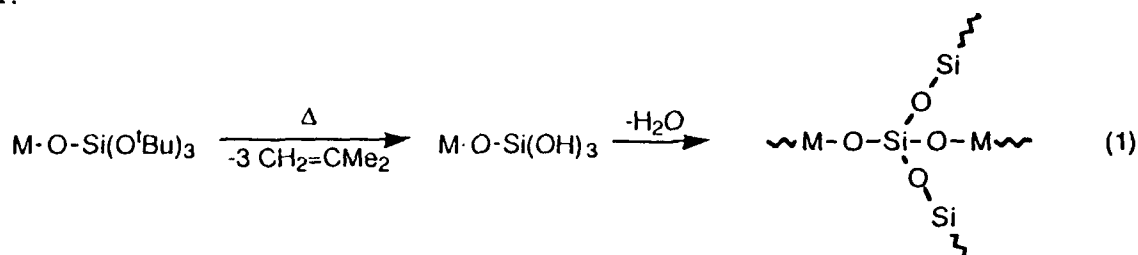with $Me\text{-}\overset{Me}{\underset{OH}{C}}$ substituent

Molecular Precursors to Metal Silicates

Our initial work has concentrated on relatively simple, two-component oxide precursors based on tri(alkoxy)siloxy transition metal complexes as single source precursors to homogeneous, 3-dimensional metal silicate networks. The proposed research is based largely on our initial findings that metal derivatives of $OSi(O^tBu)_3$ eliminate isobutylene and water cleanly at remarkably low temperatures (100-200 °C) to form $M_xSi_yO_z$ materials. Initial experiments also indicate that this chemistry allows for unique control over the microstructure of the resulting oxide materials.
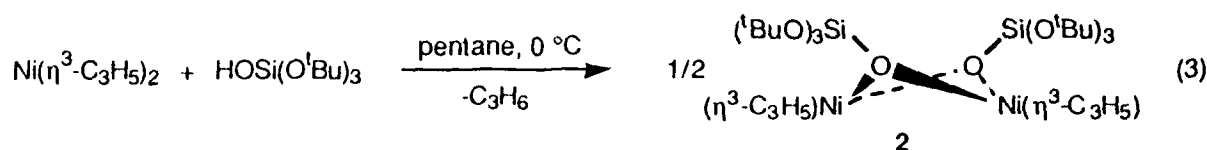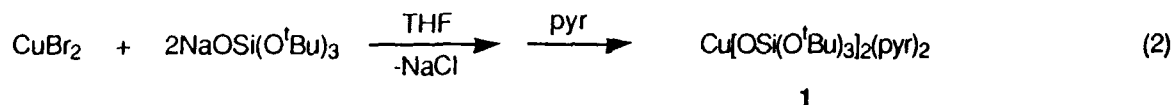
Tri(alkoxy)siloxy complexes represent an interesting class of compounds for study. Whereas metal siloxide chemistry has been developed to some extent, this chemistry primarily involves trialkyl or triaryl derivatives of the type $OSiR_3$. Siloxide ligands of the type $OSi(OR)_3$ have not been extensively employed in transition-metal chemistry, and should differ significantly from previously studied siloxides with regard to the electronic and structural properties that they contribute to a complex. For example, the presence of four donor atoms presents the possibility for these ligands to behave in a multidentate fashion. Also, $M\text{-}OSi(OR)_3$ complexes may exhibit properties that resemble catalytic metal species supported on a silica surface. Our first goal has been to explore the coordination chemistry of these ligands to delineate structural and chemical properties that result from their coordination to transition metals, and to thereby develop precursor compounds.

Simple tri(alkoxy)siloxy derivatives are well suited as precursors to silicate materials, since both the metal and silicon atoms are initially bonded only to oxygen. Also, the ^tBuO groups are

expected to undergo thermal eliminations of isobutylene which cleanly remove all the carbon as volatile material. The chemistry involved in the conversion to solid state materials is summarized in eq 1.

$$M\text{-}O\text{-}Si(O^tBu)_3 \xrightarrow[\text{-3 CH}_2\text{=CMe}_2]{\Delta} M\text{-}O\text{-}Si(OH)_3 \xrightarrow{\text{-H}_2O} \text{\raise1ex\hbox{$\sim$}}M\text{-}O\text{-}\underset{O\,Si}{\overset{Si\,O}{Si}}\text{-}O\text{-}M\text{\raise1ex\hbox{$\sim$}} \quad (1)$$

Synthesis of precursor compounds. We now have considerable experience in the preparation of transition metal derivatives of $OSi(O^tBu)_3$, and have been able to utilize both $NaOSi(O^tBu)_3$ and $HOSi(O^tBu)_3$ in approaches exemplified by eqs 2 and 3.

$$CuBr_2 \;+\; 2NaOSi(O^tBu)_3 \xrightarrow[\text{-NaCl}]{THF} \xrightarrow{pyr} Cu[OSi(O^tBu)_3]_2(pyr)_2 \quad (2)$$
$$\mathbf{1}$$

$$Ni(\eta^3\text{-}C_3H_5)_2 \;+\; HOSi(O^tBu)_3 \xrightarrow[\text{-}C_3H_6]{pentane,\ 0\ ^\circ C} 1/2 \;\; {\substack{(^tBuO)_3Si \\ (\eta^3\text{-}C_3H_5)Ni}}\!\!\!\overset{O}{\underset{O}{\diagdown\diagup}}\!\!\!{\substack{Si(O^tBu)_3 \\ Ni(\eta^3\text{-}C_3H_5)}} \quad (3)$$
$$\mathbf{2}$$

The pentane-soluble complex **1**, a rare example of a copper(II) siloxide, has been crystallographically characterized. Compound **2** has a folded Ni_2O_2 core and bridging siloxides. The reaction of $NiI_2(THF)_2$ with $NaOSi(O^tBu)_3$ in refluxing THF gives blue, pentane-soluble $Na_3(\mu_3\text{-}I)\{Ni[\mu_3\text{-}OSi(O^tBu)_3]_3I\}$ (**3**), which has a $NiNa_3IO_3$ cubelike core. Each $OSi(O^tBu)_3$ ligand is triply bridged to the Ni and two Na ions through the silanolate oxygen, and additionally binds to two Na ions via donation from two butoxy groups.

With respect to pyrolytic conversions to solid state materials, we have thus far examined Ti, Zr, Hf, and Al systems (discussed below) in greatest detail. These systems represent interesting test cases, given the useful materials properties of silicates of these metals, and the large

effort that has gone into obtaining MO_2-SiO_2 (M = Ti, Zr) and Al_2O_3-SiO_2 materials via sol-gel methods.

Titanium, zirconium, and hafnium systems. Sol-gel processes have been utilized to produce TiO_2- or ZrO_2-containing silicates in the form of thin films, fibers, or monoliths. Materials of this type find applications that take advantage of their optical properties, chemical inertness, high melting points, insulating properties, and fracture toughness.

Hrncir has previously shown that zirconium and hafnium siloxides of the type $M(OSiR_3)_4$ ($R_3 = Et_3$, $Me_2{}^tBu$, Me_2Ph, $MePh_2$, Ph_3) decompose over a wide temperature range (350-600 °C) to give MSi_4O_{10} materials. We have obtained crystalline, pentane-soluble $M[OSi(O^tBu)_3]_4$ [M = Ti (**15**), Zr (**16**), and Hf (**17**)] by reactions of the appropriate amido derivatives $M(NEt_2)_4$ with 4 equivs of $HOSi(O^tBu)_3$. In benzene solution, **15** and **17** are monomeric whereas **16** is dimeric. As with the other $OSi(O^tBu)_3$ derivatives that we have examined, these complexes hydrolyze to liberate the silanol and produce metal oxide gels.

Complexes **15-17** undergo clean, low-temperature thermolyses to silicate materials. Thermal gravimetric analysis (TGA) curves for these compounds (Figures 4-6) show
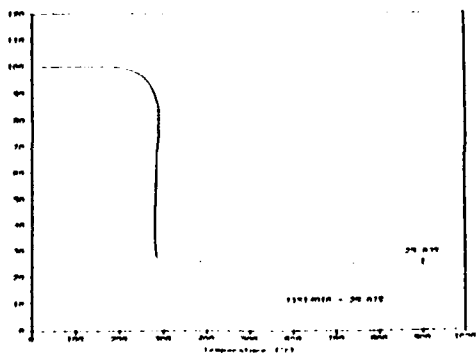

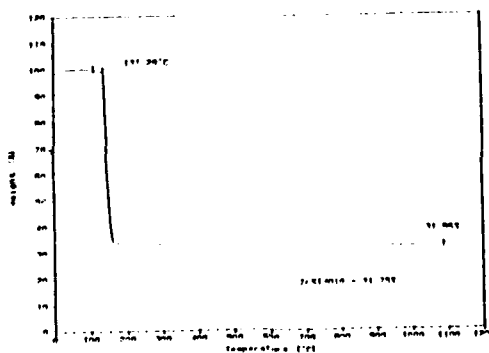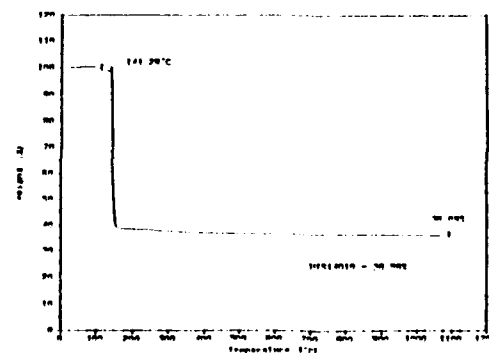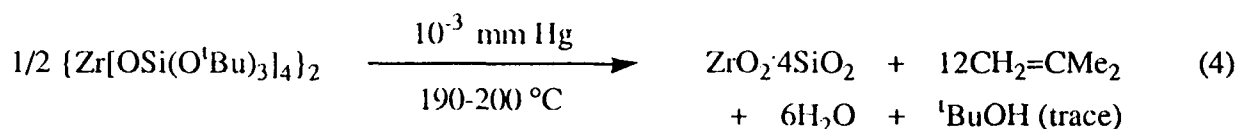Figure 4   Figure 5   Figure 6

precipitous weight losses corresponding to elimination of isobutylene and water. Minimal dehydration continues slowly thereafter, until a constant weight corresponding to quantitative formation of $MO_2\cdot4SiO_2$ is established. These thermolyses occur at remarkably low temperatures, particularly for **16** and **17** which exhibit onset temperatures of 137 and 141 °C, respectively. The higher temperature required for decomposition of **15** may result from greater steric crowding about

the smaller titanium center, which could restrict the molecular motion required for decomposition. The volatile products of thermolysis of **16** at 190-200°C (5 min) were collected by vacuum transfer, and identified as isobutyiene (11.7 equivalents/Zr), water (5.4 equivalents/Zr), and *tert*-butanol (trace). This stoichiometry is approximately represented by eq 4 .

$$1/2 \ \{Zr[OSi(O^tBu)_3]_4\}_2 \ \xrightarrow[190\text{-}200\ ^\circ C]{10^{-3}\ mm\ Hg} \ ZrO_2 \cdot 4SiO_2 \ + \ 12CH_2{=}CMe_2 \quad (4) \\ + \ 6H_2O \ + \ ^tBuOH \ (trace)$$

Surprisingly, crystals of **16** retain their shape and morphology (in going from transparent to opaque) after decomposition at 1200 °C, with very little shrinkage ($\leq$ 10%), despite having lost ca. 2/3 of their weight. Crystallizations and phase transformations for the resulting $MO_2 \cdot 4SiO_2$ materials were followed by X-ray powder diffraction (XRD), differential thermal analysis (DTA), and electron microscopy. The $ZrO_2 \cdot 4SiO_2$ system has been examined in greatest detail. Samples of $ZrO_2 \cdot 4SiO_2$ are amorphous to 1100 °C (by XRD), and an exothermic process at 1150-1400 °C (observed by DTA) corresponds to crystallization of finely dispersed $t\text{-}ZrO_2$. Heating $ZrO_2 \cdot 4SiO_2$ to 1500 °C for 6 h under argon produces a mixture of $m\text{-}ZrO_2$, $t\text{-}ZrO_2$ (1:5 ratio), and cristobalite. Rapid quenching of $ZrO_2 \cdot 4SiO_2$ from 1500 °C to 0 °C gave a material for which the ratio of $m\text{-}ZrO_2$ to $t\text{-}ZrO_2$ was maintained.

Transmission electron micrographs (TEM's) of samples of **16** decomposed at 800 °C (4 h in an O_2 flow) reveal a fibrous structure composed of an ordered, interpenetrating network of thin fibers (Figure 7), which has a surface area of 82 m^2 g^{-1} (BET method). The crystallization of zirconia at 1200 °C (4 h, O_2) is apparent in TEM photographs, which show small crystallites (6-21 nm) embedded in an amorphous silica matrix. The sintering that results from the latter thermal treatment reduces the surface area to 36 m^2 g^{-1}.

Whereas the thermolysis chemistry of **16** and **17** appears to be quite similar (based on TGA's), there are significant differences in the materials that are generated. The $HfO_2 \cdot 4SiO_2$ material produced at 400 °C (2 h, O_2) is composed of 8-32 nm particles. In samples heated to

1000 °C, t-HfO$_2$ (or c-HfO$_2$) is present, and samples taken to 1460 °C contain t-HfO$_2$ (or c-HfO$_2$) and m-HfO$_2$ (in roughly equal amounts), and cristobalite.

Heating 1 to 400 °C results in amorphous TiO$_2$·4SiO$_2$, from which finely dispersed anatase crystallizes at 1000 °C (by XRD). Samples taken to 1400 °C contain anatase, rutile, and cristobalite.

The low temperatures at which 16 and 17 thermally decompose allow for formation of the silicate networks to be conveniently carried out in solution. Refluxing 16 in xylenes for 10 h produces viscous, nearly transparent fluids and small amounts of particulate matter. Removal of the volatiles in vacuo leaves a white, amorphous ZrSi$_4$O$_x$(OH)$_y$ powder that has a BET surface area of 520 m^2 g^{-1}, and looses 27% of its weight when heated to 1150°C (by TGA). This powder is composed of ca. 0.1-3 μm agglomerates (by scanning electron microscopy) made from smaller, non-spherical 30-70 nm particles (by TEM). The dehydration of ZrSi$_4$O$_x$(OH)$_y$ was monitored by ^{29}Si NMR spectroscopy of the isolated powder (dried in vacuo), which revealed a very broad peak which moved from -99 to -110 ppm as the sample was heated from 25 to 1200 °C. Annealing this material at 1200 °C (4 h, O$_2$) results in a significant reduction of the surface area to ca. 3 m^2 g^{-1}. At higher temperatures, the same crystallization behavior described above for ZrO$_2$·4SiO$_2$ is observed.

Hydrocarbon solutions of 2 and 3 have been used to cast thin films of ZrO$_2$·4SiO$_2$ and HfO$_2$·4SiO$_2$ onto quartz. For example, a 1% solution of 2 in benzene was spun onto a quartz disk, and the disk was then heated to 400 °C under O$_2$ for 30 min. Examination of the resulting film by SEM revealed a smooth, crack-free surface. Similar HfO$_2$·4SiO$_2$ films prepared from a 1% solution of 3 in cyclopentanone have thicknesses ranging from 70 to 90 nm (Dektak 3030 profilometer).

In summary, the chemical processes described in this section represent an alternative approach to the synthesis of silicate materials. The solid state conversions produce porous ceramic materials that can have ordered microstructures. Continuing investigations are attempting to probe the possibility that formation of such microstructures may be controlled via directionality imposed

on the condensation process by the crystalline lattice of the precursor compound. The chemistry involved in this process can be applied to sol gel-like processes in non-polar media, and should allow the homogeneous incorporation of a wide variety of dopants (e.g., polymers or additional metal ions).

Aluminum systems. Sol-gel techniques have been widely applied to the generation of aluminosilicates, which have applications as (for example) refractory materials and catalyst supports. We have obtained the precursor complexes **18** and **19** via the reactions in eq 5.
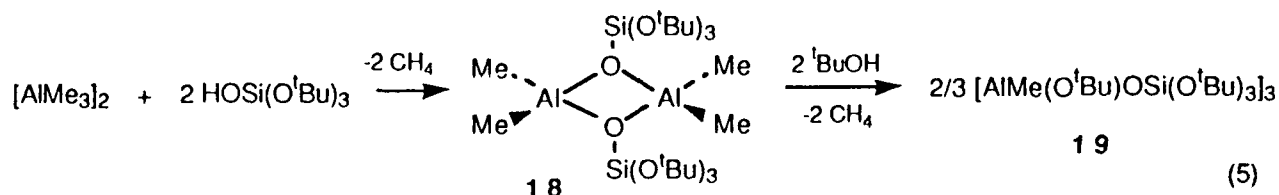
An unusual feature of the structure of **18** is the folded Al_2O_2 core (156 °C). Complex **19** is trimeric in benzene solution, and we are presently attempting to determine the solid state structure of this compound. Compounds **18** and **19** smoothly decompose at low temperatures to give amorphous aluminosilicate materials. In the decompositions of **18** and **19**, crystallization of mullite ($3Al_2O_3 \cdot 2SiO_2$) can be observed by differential thermal analysis and by XRD. Refluxing **18** for 6 h in toluene gave a viscous aluminosilicate gel solution.