Protocol for the Hg Experiments. The catalytic system was generated as in the dct case. Mercury (1 mL, 13.5 g) was then added and the mixture stirred for 12 h. At the end of this time the activity of the catalyst was measured by adding the olefin and observing H_2 absorbtion as above. In the case of the Ir catalyst, which spontaneously deactivates easily,[20] we observed the rate directly after adding mercury.

$RhCl(PPh_3)_3$ Hydrogenations. $RhCl(PPh_3)_3$ (50 mg, 0.054 mmol) was dissolved in degassed benzene (20 mL) and 1-hexene (1 mL) added. H_2 was introduced to a total pressure of 1 atm and the H_2 absorption followed for 5 min at 25 °C. The required amount of dct was added and the solution degassed. The mixture was stirred for 2 h under N_2 and then degassed. H_2 was reintroduced and the rate of uptake observed.

Pd/C Hydrogenations. Pd/C (10%, 25 mg, 0.024 mmol) was added to a hexane (20 mL) solution of cyclohexene (0.8 mL). The mixture was treated as above, but H_2 uptake measurements were made at 0 °C. Measurements in EtOH–H_2O (1:1) and dmf were carried out in the same way, but at 30 °C.

$[Ir(cod)(PMePh_2)_2]PF_6$ Hydrogenations. The title complex (50 mg, 0.059 mmol) was dissolved in CH_2Cl_2 (10 mL), containing cyclohexene (0.8 mL, 8 mmol). H_2 uptake was followed at 0 °C as above.

$RhCl_3(py)_3/NaBH_4$/dmf Hydrogenations. $RhCl_3(py)_3$ (50 mg, 0.11 mmol) was dissolved in degassed dmf (20 mL). $NaBH_4$ (4.2 mg, 0.11 mmol) was added. The solution was degassed and stirred under H_2 at 25 °C for 10 min. Addition of the substrate, 1-hexene (1 mL, 8 mmol), led to H_2 uptake that was followed for 5 min at 25 °C. The degassed mixture was then stirred with dct for 2 h, and H_2 uptake measurements were made as above but at 25 °C.

Pd Colloid.[21] Aqueous solutions of $PdCl_2$ (1%, 2 mL) and Na_2CO_3 (4%, 1 mL) were added to a polyvinyl alcohol (PVA) solution (1%, 50 mL). The mixture was made up to 100 mL with absolute ethanol. A 20-mL aliquot of the above mixture was degassed and stirred under H_2 for 5 min. To the mixture was added 1-hexene (1 mL, 8 mmol), and H_2 uptake was followed for 5 min at 25 °C. The degassed mixture was stirred with dct as above and H_2 uptake determined at 25 °C after 2 h.

Rh Colloid. An 0.5% Rh colloid, stabilized with PVA, was made as follows:[22] to $RhCl_3$ (50 mg) in 1% PVA (50 mL, aqueous solution) was added NaOH (1 N, 1 mL), and the mixture was neutralized with acetic acid. The preparation was then heated to 80 °C for 15 min. H_2 was then passed through the cooled mixture for 15 min to give a color change from yellow to black. The preparation was made up to 100 mL with EtOH, and the hydrogenation experiments were carried out as described above for Pd.

$[Rh(nbd)(PPh_3)_2]PF_6$ Hydrogenations. The title complex (50 mg, 0.058 mmol) in degassed THF (20 mL) was treated with H_2 for 15 min. H_2 uptake with 1-hexene as substrate was measured at 25 °C.

$RuCl_2(PPh_3)_3$ Hydrogenations. The title complex (50 mg, 0.052 mmol) was studied in a mixture of benzene (10 mL) and ethanol (10 mL). After 10 min of stirring under H_2, uptake was determined by using 1-hexene (1 mL, 8 mmol) as substrate at 25 °C.

Polystyrene-Bound $RhCl(PPh_3)_3$ Hydrogenation. Polystyrene-bound $RhCl(PPh_3)_3$ in the form of beads (2.2% Rh, 250 mg, 0.053 mmol) was studied in benzene (10 mL)–ethanol (10 mL) at 25 °C with 1-hexene (1 mL) as substrate.

Light-Scattering Studies. The equipment and methods used have been described.[4] Light absorption by the $RhCl_3(py)_3/NaBH_4$/dmf system prevented measurements from being obtained directly, so the catalyst (5 mL) was diluted to 50 mL with water. A Stokes radius of ca. 2000 A was obtained for the particulate observed.

Results. The results of the experiments are reported in Table I and some typical results shown in Figure 2.

Acknowledgment. We thank the National Science Foundation for support, and R.H.C. thanks the A.P. Sloan and the Henry and Camille Dreyfus Foundations for fellowships. We thank Mr. M. Albaum for some experimental assistance.

Registry No. $RhCl(PoPh_3)_3$, 14694-95-2; $[Ir(cod)(PMePh_2)_2]PF_6$, 38465-86-0; Pd, 7440-05-3; Rh, 7440-16-6; $[Rh(nbd)(PPh_3)_2]PF_6$, 32799-32-9; $RuCl_2(PPh_3)_3$, 15529-49-4; $RuCl_3(py)_3$, 16997-46-9; dct, 262-89-5; 1-hexene, 592-41-6; cyclohexene, 110-83-8.

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Methylchloropolysilanes and Derivatives Prepared from the Redistribution of Methylchlorodisilanes

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A new class of polyfunctional polysilanes has been prepared from the tetrabutylphosphonium chloride catalyzed Si–Si/Si–Cl bond redistribution of methylchlorodisilanes. These materials were shown to have a polycyclic structure with approximately seven rings per molecule when the reaction is carried to 250 °C. Derivatives of the parent polymethylchlorosilane polymer were prepared by modifying the residual silicon–chloride bonds. These reactions include alkylation, arylation, amination, reduction, and alcoholysis.

Introduction

Recently, there has been growing interest to develop polysilanes that can be shaped and thermally decomposed to yield ceramic fibers and other complex articles. The majority of the approaches to date utilize alkali-metal reductions to generate the polysilane backbone. For example, Yajima has prepared carbosilanes through thermolysis of polydimethylsilane.[1] West has reported a ceramic-yielding polymer from phenylmethyl- and dimethylpolysilanes.[2a,b] A series of copolymers were prepared from alkylmethyl- and dimethylsilane polymers by Wesson and Williams.[3] Finally, Shin-Etsu Chemical researchers have coupled disilanes to generate ceramic precursors.[4]

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(1) Yajima, S.; Hayashi, J.; Omori, M.; Okamura, K. *Nature (London)* **1976**, *261*, 683–5.

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(3) Wesson, J. P.; Williams, T. C. ONR Contract No. 014-75-C-1024, Technical Report N. 77-1, Dec 1977

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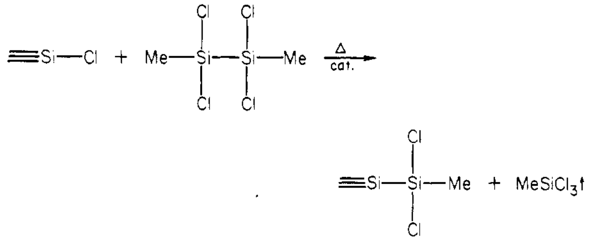
An alternative approach to polysilanes from disilanes involves bond redistribution reactions. A number of reviews on bond redistribution for siloxanes have been published.[5a-c] Frequently, this type of reaction is catalyzed by quaternary phosphonium and ammonium halides and hydroxides, amines, phosphines, and amides. A general review of catalyzed redistribution reactions has been given by Weyenberg et al.[5c]

The redistribution approach was employed by Cooper et al.[6] to catalyze the silicon–silicon, silicon–chlorine bond redistribution to produce monosilanes from disilanes that result from the industrial process to prepare methylchlorosilanes. Polymeric residues were mentioned by Cooper but were not characterized.

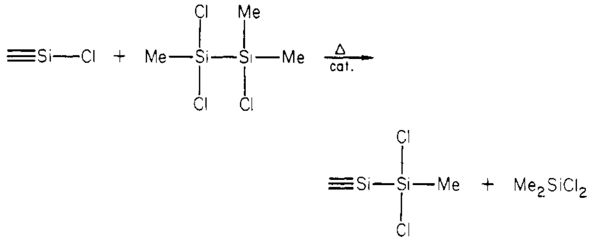
We report here a general method for synthesizing novel preceramic precursors employing silicon–silicon, silicon–chlorine bond redistributions. The characterization and some chemistry of these novel polysilanes are reported. Descriptions of their conversion to ceramic material will be published later.

Results and Discussion

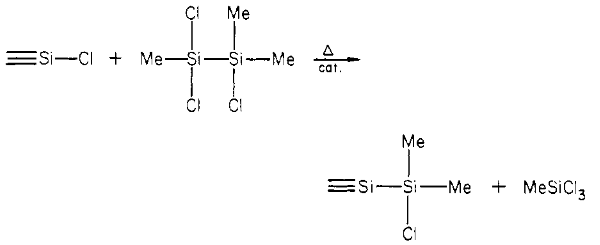
Polymerization. General Reaction. The residues reported by Cooper et al.[6] resulted from $(CH_3)_4NCl$-catalyzed redistribution of mixed disilanes. The disilane cut from the industrial process for the direct synthesis of methylchlorosilanes consists of approximately 55% $(MeCl_2Si)_2$, 35% $Me_2ClSiSiMeCl_2$, and 10% $(Me_2ClSi)_2$. We found that similar polymer residues can be prepared by using tetrabutylphosphonium chloride as the catalyst with pure and mixed disilanes. The proposed redistribution reaction scheme is presented in eq 1–3.



$$\equiv\text{Si}{-}\text{Cl} + \text{Me}{-}\overset{\text{Cl}}{\underset{\text{Cl}}{\text{Si}}}{-}\overset{\text{Cl}}{\underset{\text{Cl}}{\text{Si}}}{-}\text{Me} \xrightarrow[\text{cat.}]{\Delta} \equiv\text{Si}{-}\overset{\text{Cl}}{\underset{\text{Cl}}{\text{Si}}}{-}\text{Me} + \text{MeSiCl}_3\uparrow \quad (1)$$



$$\equiv\text{Si}{-}\text{Cl} + \text{Me}{-}\overset{\text{Cl}}{\underset{\text{Cl}}{\text{Si}}}{-}\overset{\text{Me}}{\underset{\text{Cl}}{\text{Si}}}{-}\text{Me} \xrightarrow[\text{cat.}]{\Delta} \equiv\text{Si}{-}\overset{\text{Cl}}{\underset{\text{Cl}}{\text{Si}}}{-}\text{Me} + \text{Me}_2\text{SiCl}_2 \quad (2)$$



$$\equiv\text{Si}{-}\text{Cl} + \text{Me}{-}\overset{\text{Cl}}{\underset{\text{Cl}}{\text{Si}}}{-}\overset{\text{Me}}{\underset{\text{Cl}}{\text{Si}}}{-}\text{Me} \xrightarrow[\text{cat.}]{\Delta} \equiv\text{Si}{-}\overset{\text{Me}}{\underset{\text{Cl}}{\text{Si}}}{-}\text{Me} + \text{MeSiCl}_3 \quad (3)$$

In this manner, the disilanes are disproportionated into monomers and a polymer. However, rearrangement does not stop at the point where 1 mol of monomer is formed/mol of starting disilane. With continued heating (ultimately to approximately 250 °C), additional monomeric methylchlorosilanes can be generated long after the starting disilanes have reacted. This can be accomplished in a fashion analogous to that in eq 1–3 by the reaction of any Si–Cl bond in the polymer with a terminal Si–Si bond in the polymer backbone. The amount of monomers formed and therefore the extent of the polymerization, can be controlled by the heating schedule and final temperature of the reaction (vide infra).

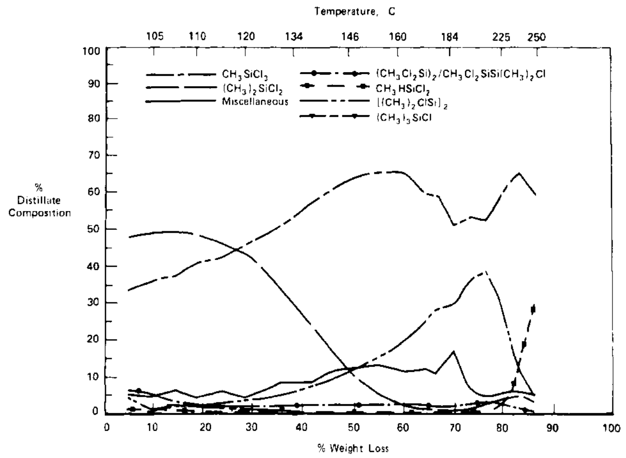


Figure 1. Distillate composition vs. weight percent of distillate removed from the reaction for mixed methylchlorodisilanes $(Me_2ClSi)_2$, $(MeCl_2Si)_2$, and $Me_2ClSiSiMeCl_2$.

In a typical experiment, 100 g of mixed methylchlorodisilanes and 1 wt % catalyst are heated to 250 °C to generate 15 g of a hard, glassy, toluene-soluble resin and 85 g of monomeric methylchlorosilane distillate. Toluene solubility would tend to indicate that a low molecular weight, highly branched polymer is formed. The polymer will be referred to as pre-ceramic polymer or PCP. In this paper, a designation such as PCP-Cl-250 indicates a PCP with chlorine functionality prepared at 250 °C.

As expected, the reaction rate is dependent upon catalyst concentration. Concentrations of catalyst ranged from 0.125% to 5% for studies on the mixed disilanes. Hard, glassy yellow polymers resulted from 1 to 5% catalyst, while incomplete polymerization was observed even after several hours with 0.125% concentration.

Not all of the disilanes were effectively incorporated into the polymer by the Bu_4PCl catalyst. GC analysis of the reaction mixture prior to adding the catalyst indicates a composition comprising a ratio of $MeSi\equiv$ moieties to $Me_2Si=$ moieties of about 2.54/1. It was possible to monitor the polymer composition in terms of these species, assuming no Si–Me bond redistributions, by employing gas chromatography to determine the distillate composition as a function of temperature or the amount of distillate formed. In addition, it was possible to follow the disappearance of the disilanes in the starting material and their reappearance in the distillate to determine the source of the $MeSi\equiv$ vs. $Me_2Si=$ in the polymer.

The studies indicate that $(MeCl_2Si)_2$ and $Me_2ClSiSiMeCl_2$ are consumed completely in the reaction, while $(Me_2ClSi)_2$ remains virtually unreacted. This can be seen by examining Figure 1, in which the instantaneous distillate composition is measured as a function of temperature. From 150 °C and above, the distillate contains increasing percentages of $(Me_2ClSi)_2$ (bp 148 °C). A strict accounting indicates that the moles of $(Me_2ClSi)_2$ distilled from the reaction nearly equals that amount present in the

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(4) Takamizawa, M.; Okamoto, H.; Motakichi, T.; Hoyamu, M. Japanese Patent, OPI No. 101099/78, Sept 1978

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(6) Cooper, G. D.; Gilbert, A. R.; *J. Am. Chem. Soc. 82*, 5042–44.

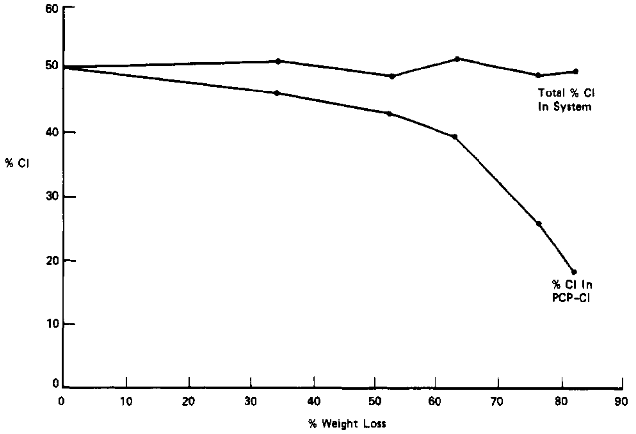


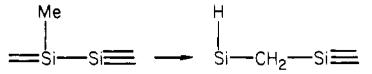
Figure 2. Weight percent of chloride vs. volatile weight loss for preparation of PCP-Cl.

Table I. Mass Balance

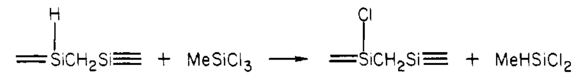
	mole ratios		% wt	
	MeSi	$Me_2Si=$	Cl	yield
disilanes	76	24	52	
distillate	69	31	62	80
polymer	85	15	18	20

starting disilanes, suggesting that $(Me_2ClSi)_2$ is simply distilled unreacted from the reaction mixture.

After approximately 75% weight loss (see Figure 1), a new reaction mechanism becomes prevalent as indicated by the presence of Si–H materials in the distillate. These materials may arise from reactions to form silmethylene-containing SiH moieties[7a,b] followed by SiH/SiCl redistribution to give volatile Si–H containing moieties (eq 4 and 5). Alternatively, the decomposition of $(C_4H_9)_4PCl$ to HCl etc. followed by cleavage of the Si–Si bond also would generate Si–H compounds.



$$=\overset{Me}{Si}-Si\equiv \longrightarrow \overset{H}{Si}-CH_2-Si\equiv \qquad (4)$$



$$=\overset{H}{Si}CH_2Si\equiv + MeSiCl_3 \longrightarrow =\overset{Cl}{Si}CH_2Si\equiv + MeHSiCl_2 \qquad (5)$$

In addition to the distillate composition, the polymer may be characterized by its chlorine content. The graph in Figure 2 illustrates the relationship of the percent chlorine in PCP vs. the percent weight lost as monomers. The total chlorine content was determined by a method that digests the sample with sodium peroxide to form NaCl, followed by silver nitrate titration as described in the Experimental Section. When the chlorine in the polymer and distillate was measured at each temperature, a plot of total chlorine in the system vs. the extent of the reaction can be made. The total chlorine in the system remains constant within expected error, lending confidence to the structural arguments presented below.

Structure of 250 °C Polymerized Mixed Disilane. On the basis of the initial composition of starting disilanes and the final distillate composition, we are able to estimate the final empirical formula for the polymer polymerized to 250 °C. According to the mass balance data in Table I the empirical formula is $(MeSi\equiv)_{5.7}(Me_2Si=)_{1.0}(Cl)_{1.9}$. The average number of silicon–silicon bonds for such a formulation is 2.65/silicon, which represents a high degree of branching. With use of ebulliometry to determine the molecular weight of a permethylated (see Experimental section) PCP (PCP-Me-250), a value of approximately 1000–1300 g/mol has been established. Since the empirical formula corresponds to a molecular weight of 362 g/mol, there are three to four of these units in the actual polymer. Surprisingly, even though the polymer is highly branched, it is completely soluble in toluene, ether, and most other organic solvents.

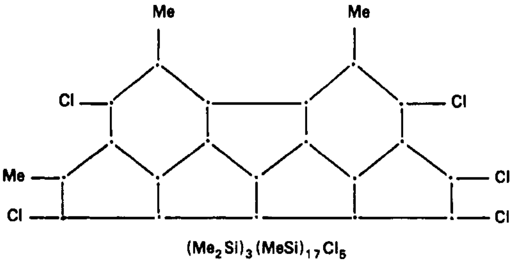


Figure 3. Possible structure for seven-ring polysilane $(Me_2Si)_3(MeSi)_{17}Cl_5$: ●, MeSi.

Conventional spectroscopic techniques such as ^1H and ^{29}Si NMR were unsuccessful in providing much structural information because of broad, ill-defined peaks. The high degree of branching from the empirical formula (2.6 Si–Si bonds/silicon atom) implies the presence of numerous silicon rings. It is consequently possible to draw analogies with the general formulas for rings and unsaturation in alkenes. Since we are dealing with polysilanes, restrictions may be made to rings only.

For linear or branched alkanes, a general formula of C_nH_{2n+2} is observed, while the presence of a ring effects a new formula of C_nH_{2n}. A similar series of formulas may be generated for methylchloropolysilanes, but some initial assumptions are needed. First, rearrangement of methyl groups is forbidden; and second, there is no Si=Si formation. The analogy to alkenes is effected by replacing $-CH_2-$ with $-SiMeCl-$. The relationship of the general formula is given by $(MeSi)_nX_{n+2-2y}$, where y is the number of rings present. The systematics are designed for the moiety $MeClSi=$. PCP-Cl-250, however, also contains $Me_2Si=$ moieties. This was corrected to hypothetically equivalent $MeClSi=$ moieties in order to calculate the probable number of rings. The empirical structure $(Me_2Si)(MeSi)_{5.7}Cl_{1.8}$ has a unit weight of 367 g/mol. Thus, a molecular structure having a weight of approximately 1000 requires multiplication by a factor of 3. The molecular formula becomes $(Me_2Si)_3(MeSi)_{17}Cl_5$ and has a molecular weight of 1101 g/mol. The number of rings present in the structure are derived by replacing the three Me_2Si with MeClSi to give a formula of $(MeSi)_{20}Cl_8$, and therefore, a value of $y = 7$.

If one assumes the primary ring size is limited to five and six members, which are the most thermodynamically stable,[8] one can write numerous hypothetical structures. One example is shown in Figure 3. Obviously, other conceivable structures can be obtained by altering the location of the methyl groups, ring location, as well as size and stereochemistry. The broad NMR peaks are consistent with this hypothesis. The presence of SiH moieties and hypothesized $\equiv SiCH_2Si\equiv$ moieties would also alter conclusions about structures. In view of the errors associated with the number average molecular weight and empirical formulas, actual structures may contain either more or fewer rings.

Structure of Pure Disilanes Polymerized to 250 °C.

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[7] (a) Shinu, K.; Kumada, M. *J. Org. Chem.* **1958**, *23*, 139. (b) Sadurai, H.; Hasomi A.; Kumada, M. *Chem. Commun.* **1968**, *16*, 930–2.

[8] Carberry, E.; West, R. *J. Am. Chem. Soc.* **1969**, *91*, 5440–6.

Table II. Amine Derivatives

		% Cl	reagent	product	% Cl	run time
1	PCP-Cl-250	11.1	NH_2Me	PCP-NHMe-250	...	...
2	PCP-Cl-150	35.7	NH_2Bu	PCP-NHBu-150	...	14 h
3	PCP-Cl-250	10.5	NH_2Bu	PCP-NHBu-250	...	4 days
4	PCP-Cl-250	13.8	NH_2Ph	PCP-NHPh-250	...	14 h
5	$(MeSi)_{3.2}Cl_{1.0}$	18.4[a]	NH_2Ph	PCP-NHPh-250	8.89[a]	

[a] Chloride determination by Na peroxide fusion.

1,2-Dimethyltetrachlorodisilane was also rearranged with catalyst to 250 °C. No dimethyldichlorosilane was detected in the distillate, supporting the contention that there is no Si–Me bond redistribution. However, small amounts of silanes (≡SiH) were present that may also arise from the rearrangement of $CH_3SiSi≡$ groups to give carbosilane structures and SiH-containing species.[7]

Distillate yield and mass balance considerations gave $(MeSi)_{1.0}Cl_{0.31}$ as an empirical formula for the polymer. If it is assumed that chlorine is attached only to difunctional silicon (MeClSi=), then the trifunctional (MeSi≡) to difunctional ratio, i.e., degree of branching, is higher at 2.2/1 than for the mixed disilane polymer, also polymerized to 250 °C, which was 1.3/1.

1,1,2-Trimethyltrichlorodisilane was also rearranged to 250 °C. From mass balance considerations and the assumption that methyl–silicon bond rearrangement did not occur, the empirical formula established for the polymer formed in this reaction was $(CH_3Si)_{11}[(CH_3)_2Si]Cl_4$. If the assumption is made that chlorine is bound only to monomethyl silicon (this assumption is consistent with the observation that MeSi≡ moieties predominate over Me_2Si=) to generate a new species MeClSi=, then the ratio of branch to linear moieties is similar to the mixed disilane materials of 1.4/1.

Derivatives. Polymers were prepared at 150, 200, and 250 °C with mixed disilanes. Nucleophilic substitution of the silicon–chlorine bonds afforded several new polymer structures that were frequently easier to handle and that yielded a range of ceramic compositions when pyrolyzed. The amine derivatives were characterized in more detail to give further structural information about the polysilane polymers. The other derivatives were prepared to illustrate reactivity and ceramic yield and for additional structural information.

Amine Derivatives. Derivatives of the chloropolymer PCP-Cl-250 were prepared by direct amination with excess free amine (i.e., $MeNH_2$, $BuNH_2$, and $PhNH_2$) in solvents such as toluene to facilitate removal of the amine hydrochloride salts. The results are summarized in Table II.

An accurate empirical formula for the aniline derivative was determined by using PCP-Cl-250 that was prepared from pure 1,2-dimethyltetrachlorodisilane described earlier. The ^1H NMR spectrum of PCP-NHPh-250 was nearly identical with that of the polymer prepared from pure $(MeCl_2Si)_2$ in the methyl region. Five signals were observed at 0.40, 0.87, 3.9, 6.7, and 7.1 ppm. The two signals at 0.40 and 0.87 ppm were assigned to the SiMe protons. It should be emphasized that there are two SiMe environments in this polymer, even though the starting disilane $(MeCl_2Si)_2$ contains only one environment. The two signals at 7.1 and 6.7 ppm were assigned to the C_6H_5NH protons. The small signal at 3.9 ppm was potentially attributable to either NH and/or OH.

Integration of the ^1H NMR spectrum allowed determination of the moles of phenyl present (0.15 mol). The moles of OH and/or NH were determined in like manner (0.30 mol). This suggests 0.15 mol of OH and 0.15 mol of NH.

The composition as determined by ^1H NMR spectroscopy is given as $(MeSi)_{1.85}(PhNH)_{0.15}(OH)_{0.15}Cl_{0.27}$. The calculated percent chloride of 9.2 compares very favorable with the independent sodium peroxide analysis of 8.9 wt %. The -O*H* is most likely the result of a small amount of hydrolysis during preparation and workup. A second ^1H NMR spectrum showed the OH content to be increasing slowly, indicative of gradual hydrolysis.

Both PCP-NHBu-250 and PCP-NHPh-250 were isolated as bright yellow solids, and infrared spectra confirmed the presence of the amine groups. The ^1H NMR spectrum of the butylamine compound showed four broad resonances at 0.38, 0.85, 1.32, and 2.64 ppm. The 0.38 and 0.85 ppm signals were assigned to the SiMe protons and include all three possible types ≡SiMe, $=SiMe_2$, and $—SiMe_3$. The uncertainty of the ≡SiMe to $=SiMe_2$ ratio, as well as the residual chloride content, prevents the calculation of an accurate empirical formula. The 1.32 and 2.64 ppm signals were attributed to the butyl protons. The mole ratio of SiMe/NHBu was 1.00/0.086.

The ^1H NMR spectrum of the aniline derivative for the mixed disilane-derived polymer also showed four broad signals at 0.45, 0.83, 6.49, and 6.94 ppm. The first two signals were attributed to SiMe protons and the latter two to phenyl protons. The mole ratio of SiMe/NHPh was 1.00/0.06. Uncertainty in $SiMe/SiMe_2$ ratios and the residual chlorine content prevents calculation of an accurate empirical formula. Ebulliometry of the aniline derivative showed a number average molecular weight of 651 g/mol. Workup was difficult because of large amounts of salt. Adsorption of the higher molecular weight fraction on the salts may account for the lower molecular weight observed for this polymer.

Experiments 2 and 3 in Table II describe butylamine derivatives of two PCP-Cl polymers having different chlorine contents. PCP-NHBu-150 was isolated as a gummy yellow liquid, whereas the PCP-NHBu-250 was a yellow solid. Infrared spectra confirmed the incorporation of the amine. The ^1H NMR spectra of the PCP-NHBu-150 derivatives were similar in appearance to PCP-NHBu-250 (vide supra).

Reaction with Grignard Reagents. As described in the Experimental Section, toluene solutions of the polymers reacted with Grignard reagents (3 M) at around room temperature. One polymer made from the chlorine containing precursors prepared to 275 °C was methylated and then examined by ^1H, ^{13}C and ^{29}Si NMR spectroscopy. The proton NMR spectrum showed only a broad peak at 0–0.75 ppm centered at about 0.4 ppm with three broad shoulders extending to 2.2 ppm. Similarly, very broad, ill-defined peaks were observed in the ^{13}C and ^{29}Si NMR spectra.

Molecular weights were determined on the permethyl derivatives (PCP-Me) by ebulliometry. The chloride derivative had a propensity to hydrolyze easily, and so it was felt that methyl derivatives would reflect more accurate molecular weight data.

The methyl derivatives from the chlorine polymers prepared at 150, 200, and 250 °C had number average

Table III. Derivatives from Alkoxylation

starting chloro polymer	% base titratable chlorine	alkoxylating reagent	reactn time, h	% titratable chlorine reacted
PCP-150	38.4	MeOH	18	gelled
PCP-200	18.0	MeOH	24	69.9
PCP-250	13.1	MeOH	18	67.2
PCP-275	10.9	MeOH	24	47.7
PCP-250	15.9	$HC(OMe)_3$	1.5	92.4
PCP-200	18.0	EtOH	65	63.9
PCP-250	11.3	EtOH	13	54.9
PCP-250	13.0	*i*-PrOH	22	56.9
PCP-250	11.2	PhOH	18	72.3

molecular weights respectively of 657, 1014, and 1267. The monotonically increasing molecular weights with increasing polymerization temperature and lower chlorine content would be expected.

Alkoxylations. By direct reaction with alcohols, alkoxy derivatives (MeO–, EtO–, *i*-PrO–) and an aryloxy group (PhO–) of PCP-Cl were prepared (Table III). In order to prevent hydrolysis of significant quantities of chlorosilanes, anhydrous alcohols were employed. Mixed alkoxy/chloro compounds were frequently obtained. Good yields of alkoxysilanes are seldom obtained by the direct reaction because the production of HCl as the reaction proceeds catalyzes secondary reactions whose magnitude increases as the temperature is raised. Among these are reactions leading to formation of siloxanes and methyl chloride.[9]

A second procedure using alkyl orthoformates[10] was also employed. Very good yields of alkoxysilanes were observed with the added advantage that the reagent and the resulting byproducts were neutral, which eliminated the side reactions mentioned above. In general, the alkoxylations proceeded to a greater extent with higher chlorine containing polymers, with alcohols of lower steric hindrance, and with methyl orthoformate as the methoxylating agent over methanol.

Reduction with Lithium Aluminum Hydride. Lithium aluminum hydride treatment of the PCP-Cl-150 produced a pyrophoric liquid while reduction of PCP-Cl-250 resulted in a pyrophoric solid. A molecular weight of the PCP-H-250 polymer of 1128 compared favorably with the PCP-Me-250. IR confirmed the presence of –SiH moieties.

Experimental Section

General Data. Distillate analysis has been accomplished by using gas chromatography. The gas chromatograph used is a 5710A Hewlett-Packard with a 3380S Hewlett-Packard integrator. Separate columns are needed for the dimers and monomers. The column used for the monomers is a 13 ft × $^1/_8$ in. nickel column packed with OV-210 (15% PAW-DCMS) silane treated. Operating conditions were as follows: He flow, 20 cm^3/s; temperature programed, 75 °C (4 min hold), 16 °C/min to 200 °C (4 min hold); detector sensitivity, 5, detector temperature, = 350 °C, injection temperature, 250 °C, current, 130 mA; sample size, 1–1.5 μL with attenuator setting of 8–16. The column used for dimers was a 13 ft × $^1/_8$ in. nickel column packed with SE-30 (15% PAW-DCMS) silane treated. Operating conditions were as follows: He flow, 20 cm^3/s; temperature program, 145 (8 min hold) to 170 (4 min hold) at 8 °C/min; detector sensitivity, 5; detector temperature, 350 °C; injection port temperature, 250 °C; current, 130 mA; sample size was 1–1.5 μL with an attenuator setting of 8–16.

Elemental analysis was carried out by using classical procedures. Carbon and hydrogen were determined in the usual combustion apparatus by the micro or semimicro process. Carbon analysis by combustion was generally unreliable, due to the high propensity to form ceramic residues that were difficult to completely oxidize.

Total chlorine was determined by digesting the samples in sodium peroxide followed by silver nitrate titration of the formed NaCl. Titratable chloride analysis was also performed by using a modification of the alcoholic/KOH titration of hydrolyzable chloride. A small amount of toluene was used to aid in the dissolution of the polymer. Tetrabromophenolphthalein ethyl ester was used as the indicator.

The chlorine content of the polymers prepared up to 200 °C was found to be the same by each method. Titratable chlorine was reproducible but lower than total chlorine by as much as 50 relative percent for polymers prepared at 250 °C and above. This is presumably due to the formation of insoluble gelled material during titration, limiting reactivity of the remaining SiCl bonds.

Molecular weights were determined on an ebulliometer similar to the one described by Ray.[11]

Nuclear magnetic resonance spectra of the PCP which have been performed include ^1H at Dow Corning, ^{29}Si at the University of Wisconsin, and ^{13}C at the Dow Chemical Co.

Infrared spectra were obtained on a Beckman spectrophotometer as a split mull. The prevalent features are Si–Me peaks 2955, 2892, 1403, 1245, and 770 cm^{-1}. A Si–O–Si band occurs at 1025 cm^{-1}, and the residual chloride is observed at 498 cm^{-1}.

Polymer Preparation from Mixed Disilanes. The preparation of all of the chloropolymers was accomplished in a similar fashion, except that the final temperature differed. A temperature of 250 °C was used for routine polymerization and a detailed procedure follows. In every case, rigorous exclusion of oxygen and moisture was mandatory.

Procedure. Preparation of PCP-Cl-250. A 500-mL three-necked round-bottomed flask was equipped with an air stirrer, heating mantle, thermometer, distilling head, and argon inlet tube. The distillation system was purged with argon for 15 min and then charged with 400.0 g of distilled disilanes obtained from the commercial process for methylchlorosilanes. [This specific distilled mixture contained 12.5% 1,2-dichlorotetramethyldisilane, 31.9% 1,1,2-trichlorotrimethyldisilane, and 56.0% 1,2-dimethyltetrachlorodisilane.] Bu_4PCl, 4.0 g (obtained commercially from Cincinnati Milacron), was added. During the polymerization, the reaction temperature was controlled by a temperature programmer. The initial temperature was set at 90 °C and held there as the solution became cloudy and then slowly cleared. The temperature was raised to 100 °C for 30 min, slowly raised over 1.5 h to 250 °C, and held for 1 h. The reaction mixture then was cooled to room temperature. The distillate yield was 344.3 g (85.2%). The PCP-Cl-250 was recovered (59.7 g, 14.8% yield by weight) as a yellow glassy solid.

Polymer Preparation from 1,2-Dimethyltetrachlorodisilane. One hundred fifty grams of 1,2-dimethyltetrachlorodisilane prepared by the method of Watanabe et al.[12] was rearranged with 1% tetrabutylphosphonium chloride by slowly heating under argon to 250 °C and holding at that temperature for 30 min (GC analysis showed the absence of the starting disilane a few minutes after mixing at room temperature.) As the temperature was increased, methyltrichlorosilane began to distill from the reaction mixture at about 115 °C. A water-white distillate (124.5 g) was shown by GC to contain 98% $MeSiCl_3$ and 2% $MeHSiCl_2$. Seventeen weight percent of a yellow viscous polymer resulted. Mass balance (ignoring the $\equiv$SiH species) gave an empirical formula for the polymer of $(MeSi)_{1.0}Cl_{0.31}$, (Calcd: Cl, 20.4. Found: Cl, 18.4 and 19.8).

Polymer Preparation from 1,1,2-Trimethyldichlorodisilane. 1,1,2-Trimethyltrichlorodisilane, prepared by the method of Matsumoto et al.[13] and containing 8.7% 1,2-dichlorotetramethyldisilane (III), as an impurity polymerized in the presence of 1 wt % tetrabutylphosphonium chloride as a catalyst under a blanket of argon. GC analysis indicated rapid disappearance of 1,1,2-trimethyltrichlorodisilane at room temperature. The

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temperature was slowly raised to 250 °C. Dimethyldichlorosilane and methyltrichlorosilane, along with unreacted 1,2-dichlorotetramethyldisilane (which does not appear to react under our conditions), began to distill from the reaction at 115 °C. Removal of volatiles continued rapidly until 150 °C and slowed as the temperature reached 250 °C. When the reaction mixture had cooled, 20% of the initial reaction mass remained as a viscous yellow polymer. Elemental analysis of the polymer proved difficult due to its high propensity to form silicon carbide. GC analysis of the distillate showed 2.2% methyldichlorosilane, 22.0% methyltrichlorosilane, 66.1% dimethyldichlorosilane, and 9.7% 1,2-dichlorotetramethyldisilane. (A majority of this latter compound was contained in the original mixture.)

Amine Derivatives. All reactions (Table I) were performed by using an argon atmosphere unless otherwise indicated. PCP-Cl was prepared as described above, and the chloride present was determined by alcoholic/KOH titration unless otherwise indicated. (Toluene was dried over Na/benzophenone and freashly distilled prior to use. Methylamine was used as purchased. Aniline and butylamine were dried over KOH pellets and distilled prior to use.)

PCP-NHMe-250. A three-necked two-L flask was equipped with air stirrer, 250-mL addition funnel, and a gas inlet tube. The flask was charged with 176.6 g of toluene and cooled to −78 °C by using a dry ice/2-propanol bath. An excess of monomethylamine was condensed over the toluene. An argon purge was begun, and the addition funnel was loaded with 72 g of PCP-Cl-250 in 64 g of toluene. The PCP-Cl-250/toluene solution was added dropwise. The pot contents were then stirred for 30 min, and the pot was allowed to warm to room temperature. Excess monomethylamine escaped through an oil bubbler. The solution was stirred overnight at room temperature.

The monomethylamine salt was removed by vacuum filtration, and the filtered solution was rotary evaporated. A viscous yellow semisolid was obtained that ignited upon exposure to air.

PCP-NHBu-150. A three-necked 1000-mL flask was equipped with air stirrer, argon inlet, and 125-mL addition funnel. The flask was charged with 181.2 g of PCP-Cl-150/toluene (50 wt %) and the addition funnel with 120.6 g of *n*-$BuNH_2$. Addition was accomplished very slowly, as a violent reaction occurred with crackling and dense white fumes forming. A thick white, gel-like substance formed when over half of the amine had been added. The air stirrer was shut off as the pot became very hot. After the mixture had cooled, an excess of ether was added and the solution was filtered (with great difficulty) through Supercel. The distillate was rotary evaporated overnight to leave a gummy yellow liquid.

PCP-NHBu-250. A 500-mL three-necked flask was charged with 165.6 g of PCP-Cl-250/toluene (50% by weight), and 36.8 g (0.50 mol) of *n*-$BuNH_2$ was slowly added. A white vapor and precipitate formed at each addition, producing a voluminous amount of salt during the reaction. A thick yellow foam resulted, to which 130 mL of dry toluene was added with stirring. The solution was subsequently decanted and rotary evaporated to dryness. Anhydrous ether was added to remove any residual *n*-$BuNH_4Cl$. Filtration was unsuccessful, so the sample was centrifuged, decanted, and rotary evaporated to dryness. A bright yellow solid resulted.

PCP-NHPh-250. To a 500-mL three-necked flask were added 75.0 g of PCP-Cl-250 and 78 g of toluene were added, and 56.7 g (0.61 mol) of aniline was slowly dripped into the solution. The resulting solution stirred at room temperature overnight. Toluene (100 mL) was added prior to filtration and rotary evaporation. The impure PCP-NHPh-250 was dissolved in an excess of ether and filtered through Supercel. The filtrate was rotary evaporated to dryness.

PCP-NHPh-250 from $Me_2Si_2Cl_4$. A 250-mL three-necked round-bottomed flask equipped with an air stirrer, addition funnel, and argon inlet was charged with 37.6 g of the polymer prepared from $(MeCl_2Si)_2$ at 250 °C and 39.4 g of toluene, and 39.7 g (0.43 mol) of freshly distilled aniline was added dropwise. A white precipitate formed as the reaction proceeded. The sample was diluted with additional toluene, filtered twice, and rotary evaporated to dryness. The residue was redissolved in dry ether, centrifuged and rotary evaporated to dryness.

Reaction with Grignard Reagents. The following serves to illustrate the method.

PCP-Me-250, 140 g, was dissolved in 200 mL of dry toluene and added dropwise over 30 min under argon to cold (ice bath) CH_3MgCl (600 mL–1.0 M in THF). The reaction mixture was then warmed and held 4 h at room temperature and 2 h at reflux and cooled again. Water, 50 mL, was added cautiously. Filtration, drying ($MgSO_4$), and rotary evaporation yielded a white solid.

PCP-Ph-250. PCP-Cl-250, 88 g, was dissolved in 179 g of dry toluene and added dropwise under argon to 100 mL of 3.2 M PhMgBr in diethyl ether. The reaction mixture was diluted with 175 mL of diethyl ether, refluxed 6 h, and then stirred overnight at room temperature. H_2O, 250 g, was added over 1 h. The organic layer was filtered, dried ($MgSO_4$), and rotary evaporated to yield a pale yellow solid.

Alkoxylations. The following examples serve to illustrate the alkoxylation experimental procedures.

PCP-OMe-250. A 50 wt % solution of 54.3 g of PCP-Cl-250 and toluene was prepared. An addition funnel was used to add 6.5 g (0.201 mol) of methanol. The solution was heated at reflux for 18 h and rotary evaporated to dryness; yield 51.7 g of PCP-OMe-250.

PCP-OMe-250 Using $HC(OMe)_3$. PCP-Cl-250, 63.5 g, was dissolved in 63.5 g of toluene. Addition of 60.5 g (0.57 mol) of $HC(OMe)_3$ was carried out slowly with ice bath cooling. When the addition was completed, the ice bath was replaced with a heating mantle and the solution was brought to a gentle reflux for 90 min. The solution was cooled and stirred for 48 h. Distillation removed the unreacted $HC(OMe)_3$, toluene, and methyl formate. The polymer slowly turned from yellow to an amber-brown color. The resulting polymer was rotary evaporated and dried under vacuum for 7 h to give 51.1 g of PCP-OMe-250.

Reduction with Lithium Aluminum Hydride. The following are examples of similar procedures used to prepare other PCP-H materials.

PCP-H-150. PCP-Cl-150 (% Cl = 38), 20 g, was dissolved in 125 mL of diethyl ether and added dropwise over several hours to 5.13 g of lithium aluminum hydride ($LiAlH_4$) slurried in 150 mL of ether. This mixture was stirred under argon for 2 days. Water, 5 mL, was then added very slowly, followed by 5 mL of 15% NaOH and 20 mL of H_2O, and stirred several hours. The reaction mixture was filtered, dried (anhydrous Na_2SO_4), and rotary evaporated to yield a clear colorless liquid.

Note! When gravity filtering to remove the drying agent, care should be taken to avoid letting the filter paper dry out. The finely dispersed PCP-H-150 absorbed on the filter paper will undergo autoignition.

PCP-H-250. PCP-Cl-250, 20 g, in 100 mL of dry ether was added to 5.0 g of $LiAlH_4$ in 150 mL of ether over 20 min under an argon atmosphere. After 12 h at room temperature, the excess LAH was destroyed by successive additions of 5 mL of H_2O, 5 mL of 15% NaOH, and 20 mL of H_2O. After being stirred 2 h, the reaction mixture was filtered, dried, and rotary evaporated to yield 10 g of an off-white solid.

Note! This material will also self-ignite if dispersed on filter paper.

Registry No. PCP-Cl-250, 84648-99-7; poly(1,2-dimethyltetrachlorodisilane), 78433-16-6; tetrabutylphoshonium chloride, 2304-30-5; 1,2-dichlorotetramehtyldisilane–1,1,2-trimethyltrichlorodisilane copolymer, 84649-00-3.