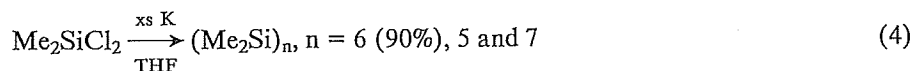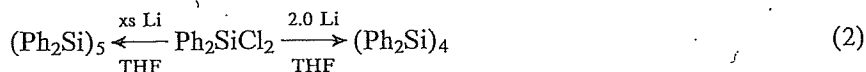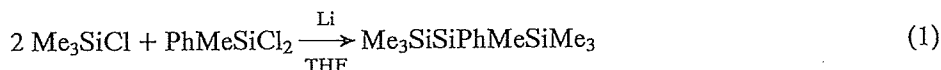# ORGANOPOLYSILANES

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Although the first silicon-silicon bonded compound was prepared as early as 1869,[1] the chemistry of organopolysilanes was largely ignored for nearly a century. Pioneering work by Kumada and Gilman in the early 1960's planted the seeds for the flowering of polysilane chemistry which is now taking place.[2] Polysilanes are of theoretical interest because they show extensive electron-delocalization and can therefore be regarded as molecular analogs to elemental silicon. On the practical side, the polysilane polymers discussed in Part IV seem likely to become important in technology.

Textbooks still state that carbon is unique among the Group IV elements in being capable of extensive catenation. Perhaps the recent syntheses of stable rings containing as many as 35 silicon atoms,[3] and of linear silane polymers with more than 3000 atoms in the chain,[4] will finally dispel this persistent myth.
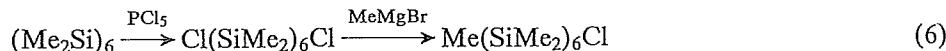
I. **Some Syntheses and Reactions.** Several different methods are available for linking silicon atoms, but by far the most useful and commonly employed is the condensation of halosilanes by active metals. Either linear or cyclic polysilanes can be synthesized in this way, as shown in a few examples in equations 1–4.

$$2\ Me_3SiCl + PhMeSiCl_2 \xrightarrow[THF]{Li} Me_3SiSiPhMeSiMe_3 \qquad (1)$$

$$(Ph_2Si)_5 \xleftarrow[THF]{xs\ Li} Ph_2SiCl_2 \xrightarrow[THF]{2.0\ Li} (Ph_2Si)_4 \qquad (2)$$

$$PhMeSiHCl \xrightarrow[THF]{Mg} (PhMeSiH)_2 \qquad (3)$$

$$Me_2SiCl_2 \xrightarrow[THF]{xs\ K} (Me_2Si)_n,\ n = 6\ (90\%),\ 5\ and\ 7 \qquad (4)$$

Similar condensation reactions have been used by Kumada to build the linear permethylpolysilanes of chain length up to ten silicon atoms (Eq. 5).[2] The lower members of the linear

$$Me_3SiSiMe_2Cl + (ClMe_2Si)_2 \xrightarrow[THF]{Na/K} Me(SiMe_2)_nMe,\ n = 4, 6, 8, 10 \qquad (5)$$
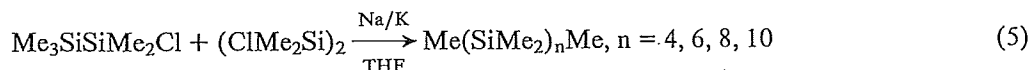
series are liquids, and the higher ones are colorless crystalline solids. In order to make still longer chain molecules it is advantageous to use the cyclic compound $(Me_2Si)_6$, which may be synthesized in good yield according to equation (4). Cleavage of the six-ring compound by PCl_5 or other chlorinating agents provides $Cl(SiMe_2)_6Cl$, which can be methylated and then coupled to yield individual straight-chain molecules up to $Si_{24}Me_{50}$:[5]

$$(Me_2Si)_6 \xrightarrow{PCl_5} Cl(SiMe_2)_6Cl \xrightarrow{MeMgBr} Me(SiMe_2)_6Cl \qquad (6)$$

$$Me(SiMe_2)_6Cl + Cl(SiMe_2)_6Cl \xrightarrow{Na/K} Me(SiMe_2)_nMe,\ n = 12, 18, 24 \qquad (7)$$

The condensation of Me_2SiCl_2 with excess Na/K or potassium gives the equilibrium mixture of crystalline $(Me_2Si)_n$ rings, whose composition at 45° is 90% n = 6, 9% n = 5, and 1% n = 7. The same condensation may however be carried out under kinetically-controlled conditions, for example by adding the chlorosilane slowly to Na/K, or by using only an equivalent amount of potassium. The product mixture then contains all possible ring compounds from n = 5 to n = 35, and these may be separated clearly by HPLC as shown in Figure 1.[3] Recent work in our laboratories provides evidence for still larger cyclic structures, up to n = 42, in the nonequilibrium condensation of $EtMeSiCl_2$ with alkali metals to give $(EtMeSi)_n$ rings.

The condensation of dihalodiorganosilanes to ring compounds is quite general, but the equilibrium product ratio depends both on the reaction conditions and on the steric bulk of the organic groups attached to silicon. For the $(Et_2Si)_n$ and $(Ph_2Si)_n$ series the thermodynamic products are the five-membered rings, while for $(tBuMeSi)_n$ the equilibrium product is the all-*trans* isomer of the four-membered ring, $(tBuMeSi)_4$ (**1**).[6] An interesting recent example of this reaction is the synthesis of organosilicon rotanes such as **2**, from condensation of $(CH_2)_nSiCl_2$ rings:[6]
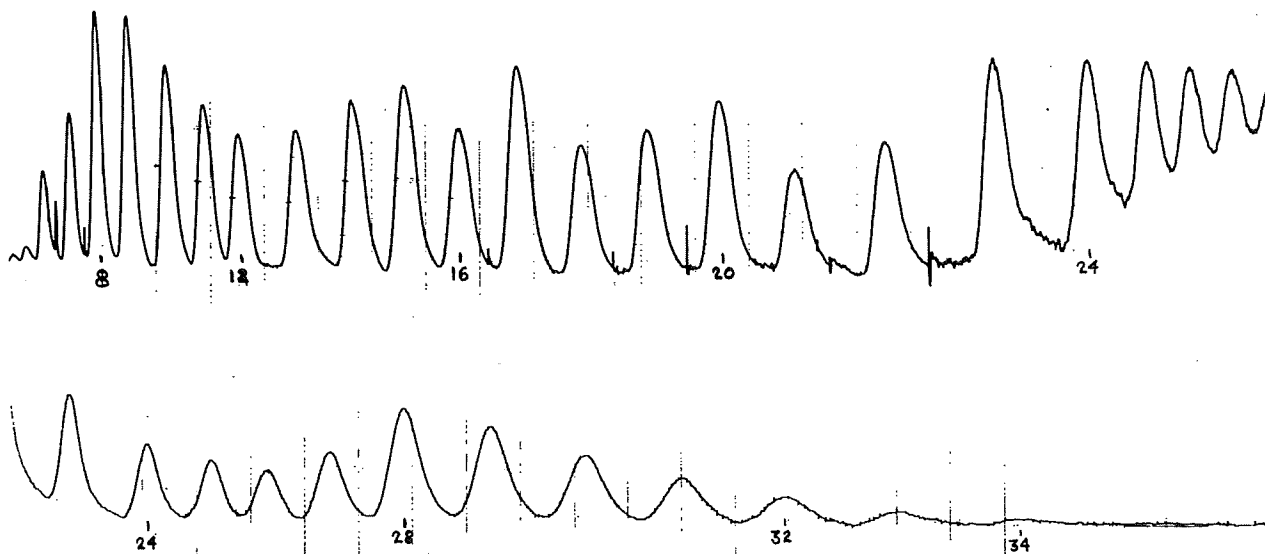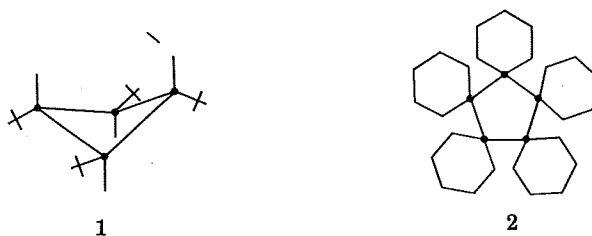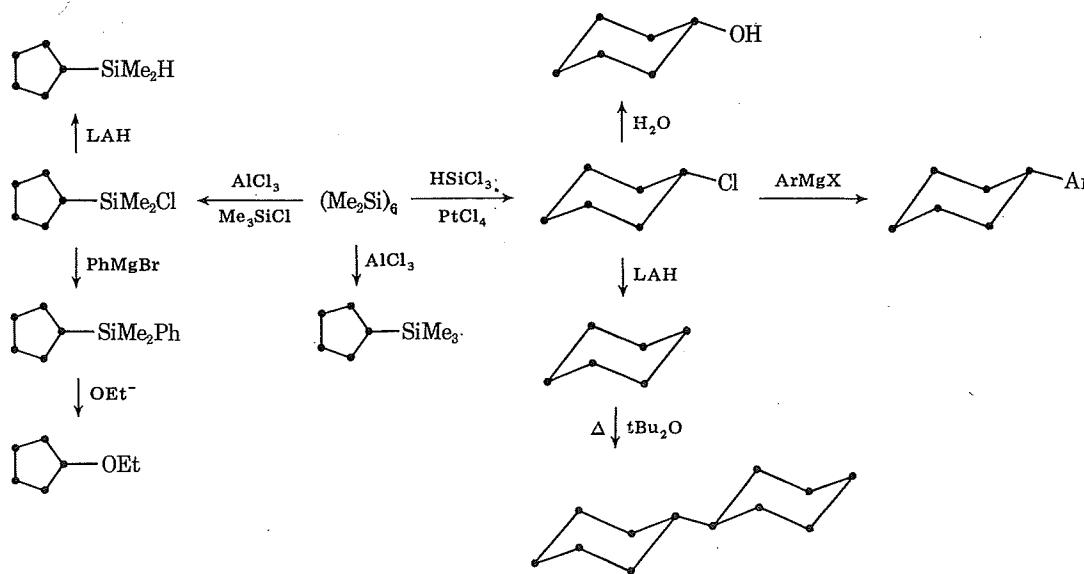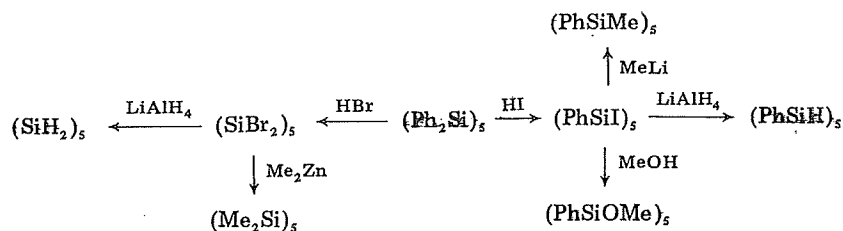
Figure 1. Reversed phase HPLC of cyclic permethylpolysilanes. Each peak consists of a different $(Me_2Si)_n$ oligomer, where n = 5 to 34.

1   2

Further elaboration of structures is possible for both linear and cyclic polysilanes, leading to an extensive chemistry which is only beginning to be explored. Scheme 1 shows examples of reactions which can be carried out starting with $(Me_2Si)_6$. An important method for introducing functionality into polysilanes is selective cleavage of phenyl (or other aryl) groups with HX. Hengge has made good use of this method in the synthesis of the interesting (but intensely reactive) cyclosilanes $(SiH_2)_n$, where n = 4, 5 and 6, from perphenylcyclosilanes.[7] This approach is shown for $(Ph_2Si)_5$ in Scheme 2.


Scheme 1

$$(PhSiMe)_5$$
$$\uparrow MeLi$$
$$(SiH_2)_5 \xleftarrow{LiAlH_4} (SiBr_2)_5 \xleftarrow{HBr} (Ph_2Si)_5 \xrightarrow{HI} (PhSiI)_5 \xrightarrow{LiAlH_4} (PhSiH)_5$$
$$\downarrow Me_2Zn \qquad\qquad\qquad \downarrow MeOH$$
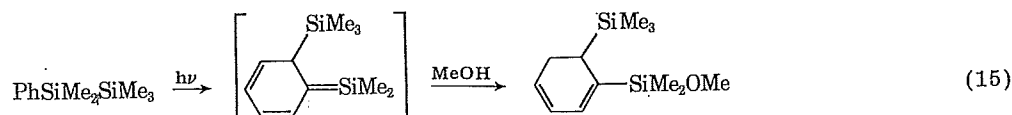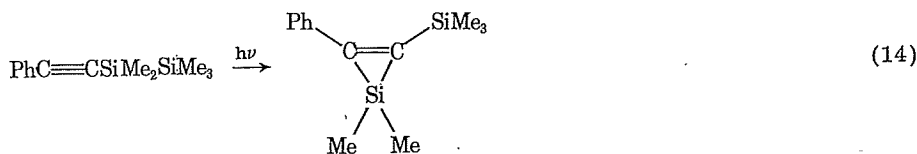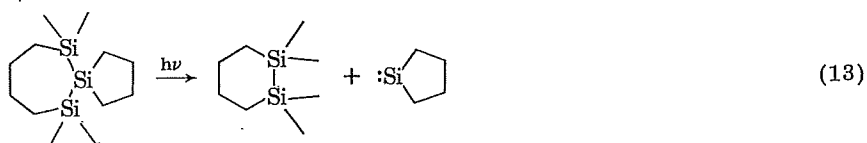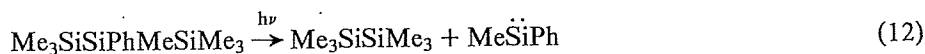$$(Me_2Si)_5 \qquad\qquad\qquad (PhSiOMe)_5$$

Scheme 2

Permethylpolysilanes undergo rearrangement in the presence of aluminum chloride, producing more highly branched isomers. Examples are shown in equations 8–10. The mechanism of these interesting rearrangements has been discussed by Kumada.[8]

$$(8)$$

$$(9)$$

$$(10)$$
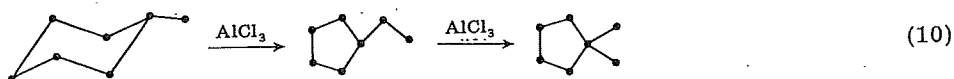
An important reaction of polysilanes is photolysis with elimination of silylenes. The well-known photolysis of $(Me_2Si)_6$ at 254 nm to generate dimethylsilylene is an example of a convenient way to generate Me_2Si. When this photolysis is carried out in a hydrocarbon glass at liquid nitrogen temperature, the silylene can be isolated in the matrix.[9] Other examples[6,10] are shown in equations 11–13. With substituted disilanes, other interesting reactions may take place upon photolysis. Some ethynyldisilanes give silacyclopropenes as in equation 14,[11] and aryldisilanes yield, among other products, compounds derived from Si=C doubly-bonded intermediates (Eq. 15).[12]

$$(Et_2Si)_7 \xrightarrow{h\nu} (Et_2Si)_6 + Et_2Si: \tag{11}$$

$$Me_3SiSiPhMeSiMe_3 \xrightarrow{h\nu} Me_3SiSiMe_3 + MeSiPh \tag{12}$$

$$(13)$$

$$PhC{\equiv}CSiMe_2SiMe_3 \xrightarrow{h\nu}$$

$$(14)$$

$$PhSiMe_2SiMe_3 \xrightarrow{h\nu} \left[\quad \right] \xrightarrow{MeOH}$$

$$(15)$$

II. Electron Delocalization; "Aromatic" Properties of Cyclosilanes. In 1964 Gilman and Schwebke reported that permethylpolysilanes show intense, long-wavelength ultraviolet absorptions, which intensify and shift to lower energy as the length increases.[13] These properties, reminiscent of those of conjugated polyenes, were quite surprising at the time. It now appears that these absorptions reflect electron delocalization, both in the silicon-silicon sigma bonding orbitals and in the unfilled orbitals.

The electron delocalization of polysilanes is manifested most clearly in cyclic alkylpolysilanes such as the permethyl compounds.[14] These compounds show striking resemblances to aromatic hydrocarbons in some of their properties. For instance, they undergo reduction to form brightly-colored anion-radicals in which an electron enters the LUMO,
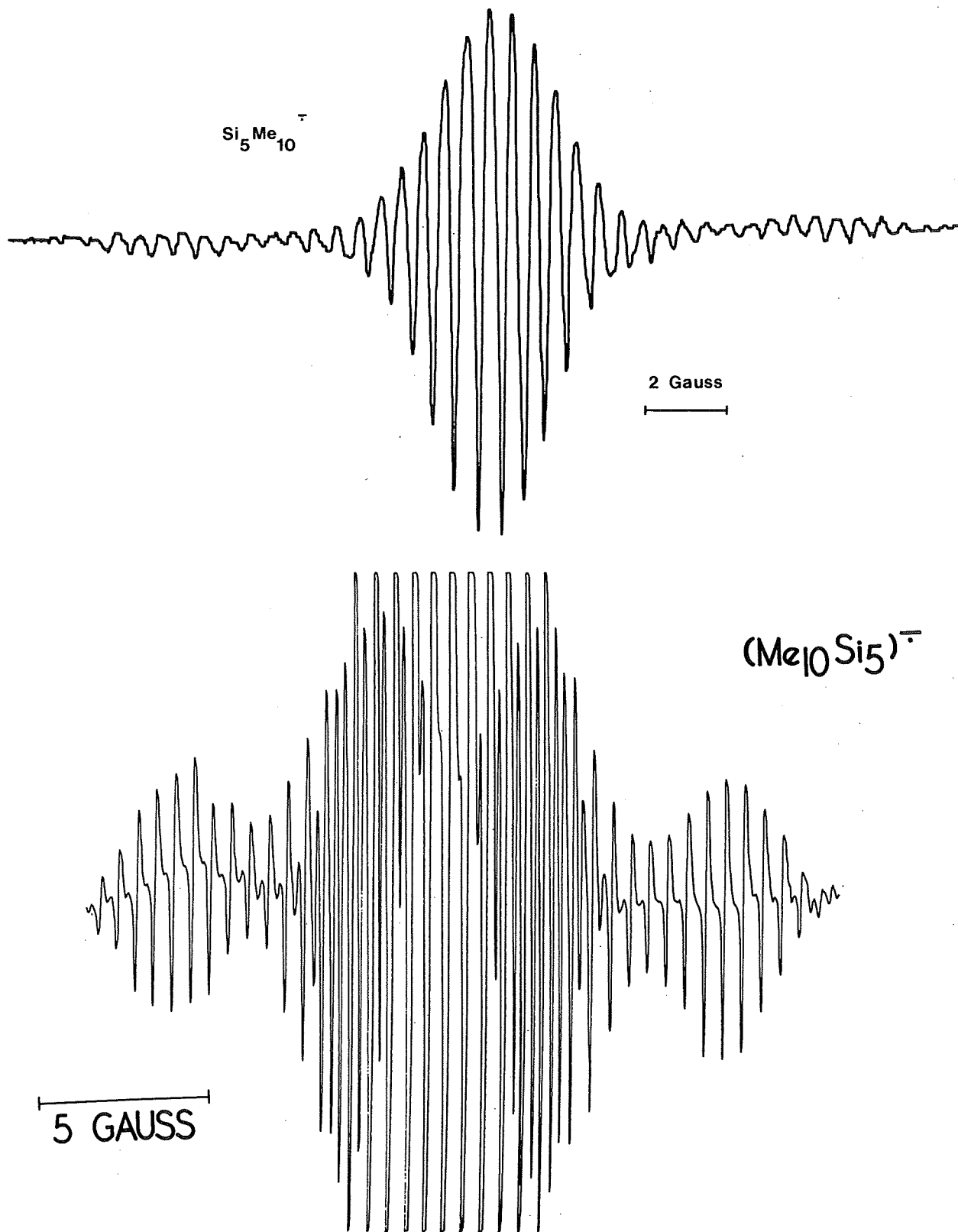
Figure 2. ESR spectra for $(Me_2Si)_5^-$ in THF, $-80°$. The spectrum at top is at low gain; the one at bottom is at high gain and high resolution, showing doublets of multiplets due to molecules containing a ^{13}C or ^{29}Si atom.

in much the same way as benzene, naphthalene and other aromatics do. The electron distribution in these anion-radicals can be studied by electron spin resonance spectroscopy. As an example, the ESR spectrum of the blue anion $(Me_2Si)_5^-$ is shown in Figure 2. The spectrum at low gain (5a) is a multiplet consisting of the center portion of a 31-line pattern, resulting from equivalent coupling of the unpaired electron to each of the 30 protons on the methyl groups. At higher

gain (**5b**) many additional lines appear. Splitting due to carbon-13 and silicon-29 can now be observed in the form of doublet patterns replicating the center portion of the main spectrum. The ^{29}Si splitting constants for polysilane anion-radicals are quite small in every case yet studied, consistent with the electron-nuclear coupling being due to spin polarization only. The implication is that the unpaired electron is in a "π-like" MO which has essentially no s orbital contribution from silicon.[15]
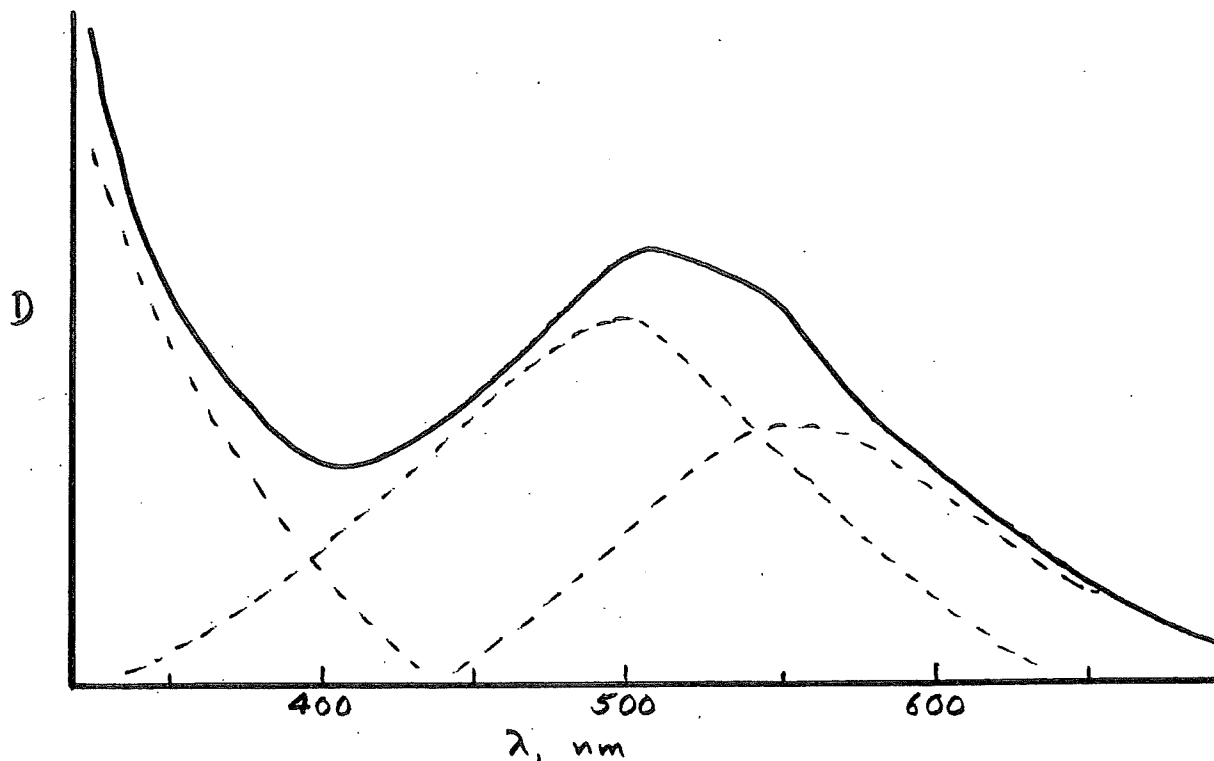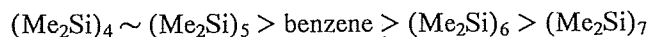

Figure 3. Visible spectrum of charge-transfer complex of (Me$_2$Si)$_6$ with TCNE, in CH$_2$Cl$_2$ solution.

The relative reduction potentials of permethylcyclosilanes have been determined from experiments in which two species are forced to compete for an electron. The order of decreasing tendency to be reduced is:

$$(Me_2Si)_4 \sim (Me_2Si)_5 > benzene > (Me_2Si)_6 > (Me_2Si)_7$$

The four- and five-membered rings have the lowest energies for electronic transitions as well as the lowest reduction potentials. The LUMO in these small rings is apparently stabilized, perhaps because they are nearly planar so that overlap of orbitals on neighboring silicon atoms is favored.

Besides accepting electrons as in forming anion-radicals, the cyclic silanes can also serve as electron donors. Like conventional aromatic compounds, they form colored charge-transfer complexes with powerful electron acceptors such as chloranil or tetracyanoethylene (TCNE). Figure 3 shows the visible spectrum for the lavender complex of (Me$_2$Si)$_6$ with TCNE, in dichloromethane. The absorption can be deconvoluted into two bands, representing electron-transfer in the excited state from the two highest-lying silicon-silicon σ bonding orbitals. Orbital energies for polysilanes estimated from their charge transfer spectra correlate well with ionization potentials determined from photoelectron spectra.[16]

Under more strongly oxidizing conditions (AlCl$_3$ in CH$_2$Cl$_2$) certain cyclosilanes will give up an electron entirely, forming cation-radicals. In the parlance of solid state chemistry such molecules would be "P type", containing a positively charged "hole". Electron spin resonance shows conclusively that the unpaired sigma electron (and hence the hole) is also fully delocalized over the ring, for instance in the cation-radical (Me$_2$Si)$_6^{+\cdot}$.[17]

Finally, the cyclosilanes resemble benzenoid aromatic compounds in their substitution patterns. For example, the chlorodemethylation of (Me$_2$Si)$_6$ shown in Scheme 1 can be repeated to introduce a second chlorine substituent (equation 16).

(16)
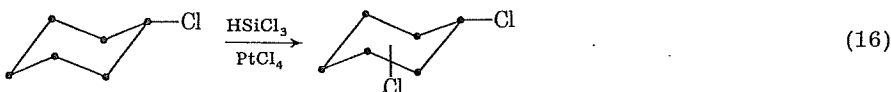
Seven dichloro isomers are possible, but the reaction mixture contains significant quantities of only four isomers, formed in unequal amounts (approximately 4:2:2:1).[6] Although the isomers have not all been identified, it is clear that the presence of one chlorine exerts a directing effect on the entering substituent, resembling the well-known substituent effects in benzene. The substitution chemistry of cyclopolysilanes is perhaps understood about as well as that of aromatic chemistry 80 to 100 years ago.

On the other hand we do have molecular orbital theory which chemists of the last century lacked, and it can be applied in a simple way to polysilanes. A crude MO correlation diagram for $(Me_2Si)_5$, $(Me_2Si)_6$ and benzene is shown in Figure 4. The diagram is helpful in rationalizing some of the similarities in behavior between cyclosilanes and benzenoid aromatics. Both classes of molecules have delocalized filled orbitals at relatively high energy (low ionization potential), as well as delocalized unfilled orbitals at relatively low energy. Consequently cyclosilanes, and aromatics, can readily serve either as charge donors or acceptors.
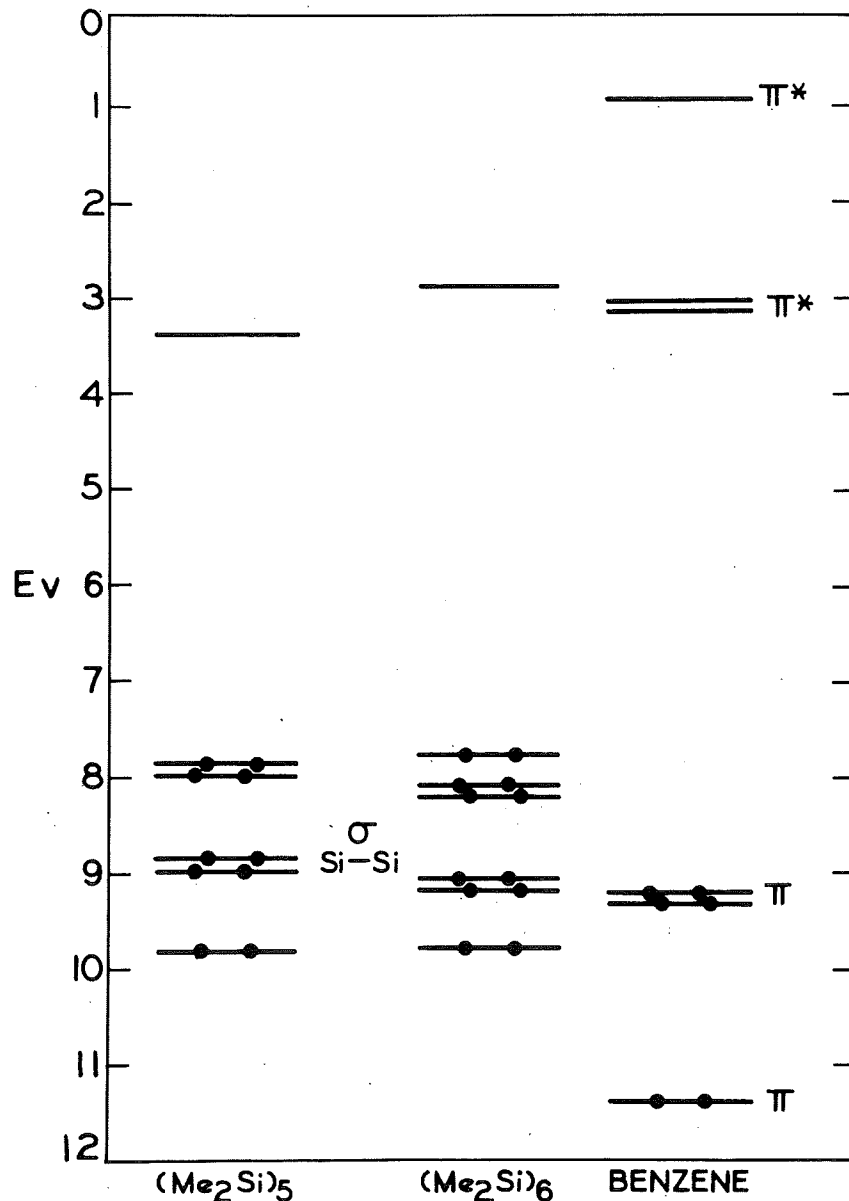

Figure 4. MO correlation diagram for $(Me_2Si)_5$, $(Me_2Si)_6$ and benzene.

III. **Disilanes as Olefin Analogs.** Just as cyclosilanes can be considered as analogs to aromatic hydrocarbons, disilanes can be thought of as pseudo-olefins. The Si-Si bond, with its easily-ionized electrons, behaves in some ways like a C-C pi bond. For example, the reaction of disilanes[6] with perbenzoic acids to form siloxanes (equation 17) is somewhat similar to the epoxidation of olefins.

$$RSiMe_2SiMe_3 + ArCO_3H \rightarrow RSiMe_2OSiMe_3 \tag{17}$$
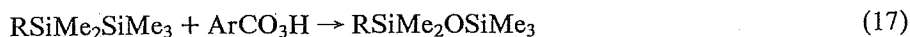
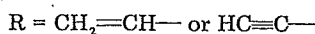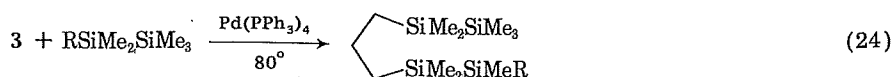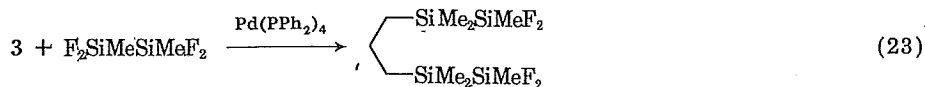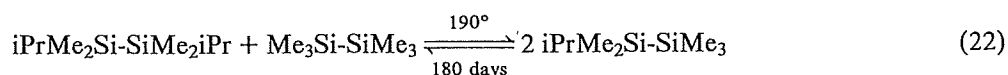Recently, three different groups in Japan have reported a number of olefin-like reactions of disilanes. Addition reactions of disilanes to acetylenes occur with catalysis by palladium complexes.[12,18] The addition of hexamethyldisilane to dimethylacetylenedicarboxylate takes place stereospecifically to give the cis-olefin (equation 18). This reaction is analogous to a $[\sigma_s^2 + \sigma_s^2]$ reaction of carbon chemistry, which is normally forbidden but could become allowed in the presence of a catalyst. Stereospecific cis addition of chlorodisilanes with more than one chlorine atom to acetylene has also been reported.

$$Me_3SiSiMe_3 \; + \; MeO_2CC\!\!\equiv\!\!CCO_2Me \; \xrightarrow{\;PdCl_2(PPh_3)_2\;} \tag{18}$$
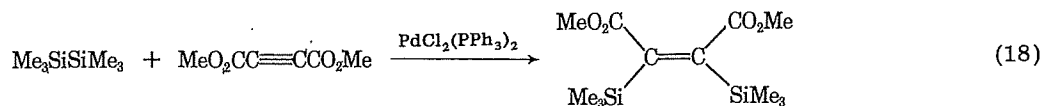
Fluorinated disilanes and ring-strained disilanes such as **3** are more reactive toward acetylenes, and will also give cycloaddition reactions with dienes,[12,19] analogous to the Diels-Alder reaction of organic chemistry. Examples are given in equations 19–21. With **3**, surprising large-ring products are sometimes obtained.

$$\tag{19}$$

$$\tag{20}$$

$$\tag{21}$$
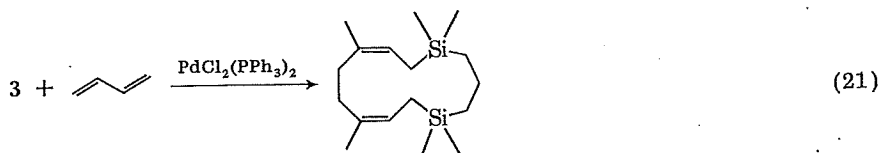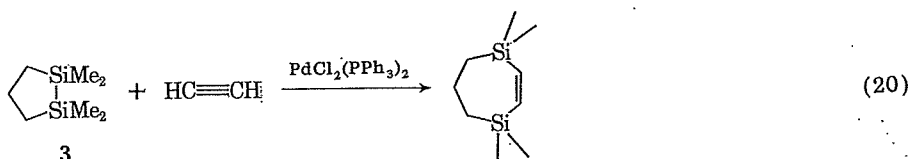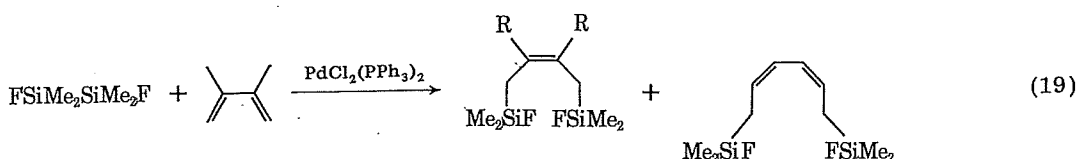
Exchange reactions analogous to olefin metatheses also have been found.[12,18] They take place at high temperatures (equation 22) or at moderate temperatures with palladium catalysis, as shown in equations 23 and 24.

$$iPrMe_2Si\text{-}SiMe_2iPr + Me_3Si\text{-}SiMe_3 \underset{180 \text{ days}}{\overset{190°}{\rightleftharpoons}} 2 \; iPrMe_2Si\text{-}SiMe_3 \tag{22}$$

$$\mathbf{3} + F_2SiMeSiMeF_2 \xrightarrow{\;Pd(PPh_2)_4\;} \tag{23}$$

$$\mathbf{3} + RSiMe_2SiMe_3 \xrightarrow[80°]{\;Pd(PPh_3)_4\;} \tag{24}$$

$$R = CH_2\!\!=\!\!CH\!\!-\!\! \text{ or } HC\!\!\equiv\!\!C\!\!-$$

With the very highly strained disilacyclobutene **4**, insertion of Me_2Si takes place, as shown in equation 25. This reaction is analogous to the addition of carbenes to olefins forming cyclopropanes. (Carbenes might also insert into strained Si-Si bonds, but this has apparently not been reported.)

$$\tag{25}$$

4
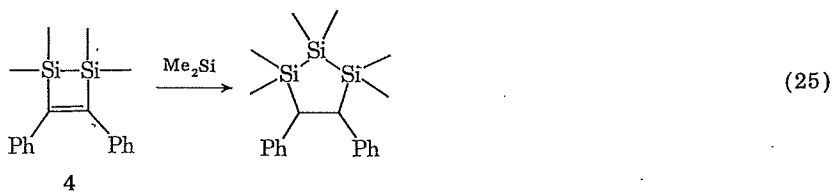
Very recently some remarkable substitution reactions of trimethylsilyl groups from hexamethyldisilane into nitrobenzenes have been discovered,[20] in which the Me_3Si groups replace chlorine. An example is shown in equation 26.

$$O_2N-C_6H_4(Cl)-Cl \xrightarrow[Pd(PPh_3)_4]{(Me_3Si)_2} O_2N-C_6H_4(SiMe_3)-SiMe_3 \qquad (26)$$
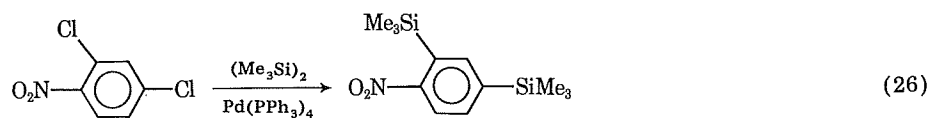
IV. Silane Polymers. Polymeric phenylsilanes were apparently obtained by Kipping early in this century, and permethylpolysilane was prepared as early as 1949 by the sodium condensation of Me_2SiCl_2. However these first silane high polymers were notably intractable, and perhaps as a result the silane polymers were neglected until quite recently. Two new factors have combined to change the situation. First, in 1975 Yajimo and Hayashi discovered that poly(dimethylsilane) can be converted at high temperatures to silicon carbide.[21] Second, recent research has led to organosilane high polymers which are meltable and soluble, and so can be handled by the usual methods of polymer chemistry.[4]

In the Yajima process the polysilane polymer made from Me_2SiCl_2 and sodium is heated under argon at 320°. The changes which take place are probably complex, but among other things insertion of methylene groups into the Si-Si bonds occurs, leading to a polycarbosilane (equation 27). Volatile components of the mixture are then removed by heating under vacuum. The residual carbosilane polymer can be drawn into fibers, heated briefly to 200° in air to give surface oxidation which prevents melting of the fibers, and finally heat-treated in vacuum at temperatures up to 1300°. The resulting fibers, which have high tensile strength and modulus, are mainly β-SiC. This process has been commercialized in Japan, and development quantities of fine silicon carbide fibers are now available from Nippon Carbon Co.

$$Me_2SiCl_2 \xrightarrow{Na} (Me_2Si) \xrightarrow[Ar]{320°} \leftarrow Si(H)(CH_3)-CH_2-Si(H)(CH_3)-CH_2 \rightarrow_n \qquad (27)$$
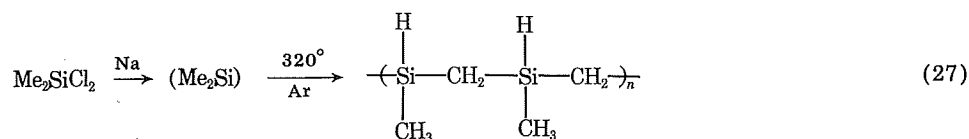
The intractable nature of poly(dimethylsilane) results from its very high crystallinity. Several approaches have been followed to modify the polymer structure so as to reduce crystallinity. Introduction of ethyl or propyl groups into the chain, by co-condensation of $EtMeSiCl_2$ or $nPrMeSiCl_2$ with Me_2SiCl_2, gives polymers with greater solubility, although still highly crystalline.[22] Introduction of phenyl groups from phenylmethyldichlorosilane has a much more dramatic effect on the nature of the polymer.[21] Crystallinity drops sharply with increasing numbers of phenyl groups. At phenyl:methyl ratios near 1:3 the polymer is amorphous, with a melting temperature near 200°, and is highly soluble in organic solvents at room temperature. This material with phenyl groups on one out of every two silicon atoms is structurally similar to polystyrene in the carbon series and has been called informally "polysilastyrene" (5).

$$\leftarrow Si(CH_3)(C_6H_5)-Si(CH_3)(CH_3)-Si(CH_3)(C_6H_5)-Si(CH_3)(CH_3) \rightarrow_n \qquad 5$$
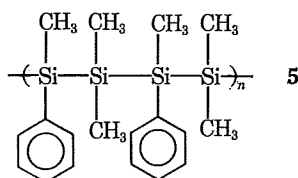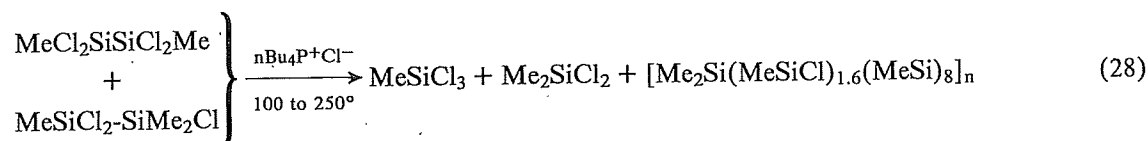
This polymer can be cast into transparent films, and melt- or solution-spun into fibers, which convert to fibrous silicon carbide at high temperatures.
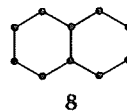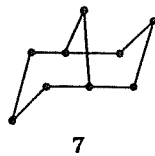
Polysilastyrene is rapidly crosslinked and transformed into an insoluble, rigid form by ultraviolet radiation. This easy change from a soluble to an insoluble form suggests various industrial applications. The polymer is nonconducting, but upon exposure to oxidizing agents it becomes quite a good semiconductor. Thus in the presence of 10 Torr pressure of AsF_5, the conductivity increases by almost 12 orders of magnitude, from $<10^{-11}$ to ~0.5 ohm^{-1} cm^{-1}.[21] Although the mechanism of conduction is not known for certain, it seems likely that the oxidizing agent removes an electron from the polysilane chain to form a hole, as in the formation of cyclosilane cation-radicals. The polysilastyrene would become a p-type semiconductor, with the hole delocalized along the silane chain.

Similar phenylmethylpolysilane polymers have also been used to strengthen silicon nitride ceramic bodies. The silicon nitride is soaked in the melted polymer and then fired, trransforming the polymer to silicon carbide which knits together the silicon nitride particles.[23] Other high polymers based on silicon chains include the homopolymer $(MePhSi)_n$,[6,24] and a block copolymer made from dimethylsilane and diphenylsilane units.

A quite different approach to polysilane polymers has been developed by Baney, starting from the mixed methylchlorodisilanes of the "direct process residue". These are redistributed using a tetraalkylphosphonium chloride as a catalyst, leading to cross-linked or cagelike polysilanes. A typical composition is given in equation (28). At high temperatures these materials readily convert to silicon carbide, which can be obtained as fibers, coatings, bulk objects either dense or foamed, and powder.[25]

$$\left.\begin{array}{c} MeCl_2SiSiCl_2Me \\ + \\ MeSiCl_2\text{-}SiMe_2Cl \end{array}\right\} \xrightarrow[\text{100 to 250°}]{nBu_4P^+Cl^-} MeSiCl_3 + Me_2SiCl_2 + [Me_2Si(MeSiCl)_{1.6}(MeSi)_8]_n \tag{28}$$

V. 3-Dimensional Polysilanes. This class of compounds is almost unexplored, but promises to be quite extensive when it is eventually developed. Only one paper[26] is in print on polycyclicpolysilanes, which were prepared by the co-condensation of Me_2SiCl_2 and $MeSiCl_3$. As seen in equation 29, this reaction yields a mixture containing small amounts of at least eight different polycyclic materials. Although the formulas are well established, the structures are known with certainty only for $Me_{14}Si_8$ (**6**) and $Me_{16}Si_9$ (**7**). The compound $Me_{18}Si_{10}$ is probably the decasila analog to *cis* or *trans* decalin (**8**). Other than

$$\left.\begin{array}{c} Me_2SiCl_2 \\ + \\ MeSiCl_3 \end{array}\right\} \xrightarrow[\text{THF}]{Na/K,\ C_{10}H_8}$$

$Me_{14}Si_8$	5%	6
$Me_{16}Si_9$	2%	7
$Me_{16}Si_{10}$	0.5%	
$Me_{18}Si_{10}$	4%	8
$Me_{18}Si_{11}$	0.5%	
$Me_{22}Si_{13}$	0.1%	

$$\tag{29}$$

6   7   8
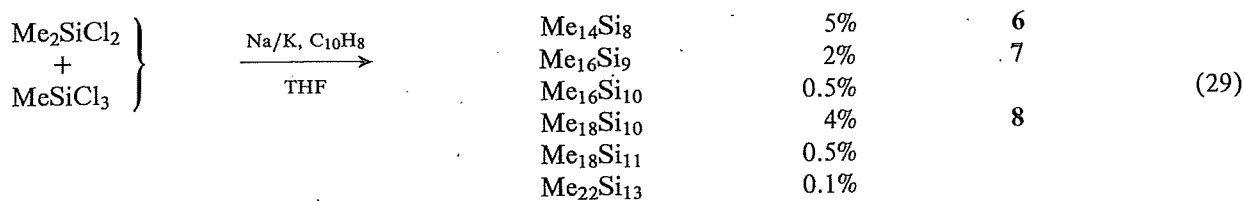
the 3-dimensional polymers mentioned above, no polycyclic silanes bearing functional groups, or with substituents other than methyl groups, have yet been reported.

VI. Further Reading. Polysilane chemistry is the subject of several reviews, either recently published or still in press. The subject is treated in some detail in a chapter in the forthcoming set, "Comprehensive Organometallic Chemistry".[27] Rearrangement reactions of polysilanes are well covered in a review by Kumada,[8] and a chapter by Ishikawa and Kumada will treat their photochemistry.[28] Electron delocalization in polysilanes is the subject of a review now in press[29] as well as an earlier summarizing paper;[14] a more theoretical discussion of chemical bonding in polysilanes appears in a chapter by Pitt.[30] For the NMR of polysilanes, and implications for chemical bonding, see ref. 31.

A recent review by Sakurai describes olefin-like behavior of disilanes, as well as other research by the Tohoku University Group.[12] The chemistry of polysilane polymers, and of cage polysilanes, are so new or sketchily developed that no reviews have yet appeared. Finally, several reviews by Hengge treat aspects of the chemistry of phenylpolysilanes mostly not covered above.[32,33]

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