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Permethylpolysilanes: Silicon Analogs of Hydrocarbons

Cyclic polysilanes resemble aromatic hydrocarbons in electronic and chemical properties.

Robert West and Edward Carberry

The myriad complex molecules of organic chemistry exist in part because of the strong tendency of carbon to form covalent bonds with other carbon atoms. Silicon is the neighboring element below carbon in the periodic table, and chemists have long had fantasies concerning the possibility of an "organic" chemistry based on silicon rather than carbon. Early experiments seemed to show that the tendency toward chain formation, or to catenation, was distinctly less for silicon than for carbon. However, within the last decade evidence has gradually appeared indicating that silicon does have the capability for extensive catenation and that a complex chemistry based on chains and rings of silicon atoms may be possible (*1*).

Another factor essential to the diversity of organic chemistry is the stability and relative inertness of bonds from carbon to hydrogen. In this respect, silicon differs markedly from carbon, for silicon-hydrogen bonds are generally quite susceptible to attack by acidic or basic reagents and sometimes even by oxygen. In contrast to the stable hydrocarbons, the simple hydrosilanes are highly reactive substances, difficult to study because they oxidize spontaneously in air, often with explosive violence. Substitution with atoms or groups other than hydrogen is evidently necessary if stable compounds with chains of silicon atoms are to be made (*2*).

The methyl group, -CH_3 (abbreviated Me) is nearly ideal as a substituent, and recent developments in polysilane chemistry have been concerned mainly with permethylpolysilanes and their derivatives. The basic structure consists of chains of silicon atoms bearing methyl groups: $\cdots SiMe_2\text{-}SiMe_2\text{-}SiMe_2\text{-}SiMe_2\cdots$. The silicon-carbon and carbon-hydrogen bonds are both rather inert, so that these molecules are generally quite stable. Permethylpolysilyl groups behave much as organic alkyl radicals do in that chemical changes involving a functional group in the molecule do not usually disrupt the polysilane chain. Exact structural analogs to permethylpolysilanes are not well known in carbon chemistry, because methyl groups on adjacent carbon atoms interfere sterically leading to severe overcrowding within the molecule. The larger covalent radius of silicon compared to that of carbon (1.17 compared to 0.77 angstrom) moves the methyl groups on adjacent silicon atoms apart just enough so that serious steric crowding does not occur.

Structurally the polysilanes are analogs to saturated hydrocarbons, the alkanes. However, it has become apparent that polysilanes also resemble unsaturated compounds in some of their physical and chemical properties. In particular, the cyclic permethylpolysilanes show some remarkable resemblances to the aromatic rings of organic chemistry. Striking examples are their reduction to form anion-radicals containing delocalized electrons, and their formation of colored charge-transfer complexes with pi-electron acceptors like tetracyanoethylene (TCNE).

In this article, we discuss the unusual properties of the cyclopolysilanes, emphasizing those that have been most important for present understanding of chemical bonding in polysilicon compounds. It is appropriate, however, to begin by considering the simpler and better known linear permethylpolysilanes (*3*).

Permethylpolysilane Chains

Because organosilicon compounds are not found in nature, polysilanes must necessarily be built up from small units. Nowadays the starting material is elemental silicon, which undergoes reaction with methyl chloride in the direct synthesis of methylchlorosilanes, carried out on a very large scale industrially as the first step in the synthesis of silicone polymers. A generally useless by-product of this reaction is "direct process residue," which contains as two of its many constituents 1,1,2-trimethyltrichlorodisilane and 1,2-dimethyltetrachlorodisilane. These two compounds, distilled out together from the residue, can be treated with methyl magnesium halide to give hexamethyldisilane:

$$\left.\begin{array}{l} \mathrm{Cl_2SiMe\text{-}SiMe_2Cl + 3MeMgX} \\ \mathrm{Cl_2SiMe\text{-}SiMeCl_2 + 4MeMgX} \end{array}\right\rangle \rightarrow \mathrm{Me_3SiSiMe_3}$$

$$\mathrm{Me = CH_3,\ X = halogen}$$

Alternatively, at greater convenience but greater cost, commercial trimethylchlorosilane can be coupled with alkali metal to give the same product. Now, in a process worked out by Kumada and his students, a methyl group can be replaced with chlorine, with the use of sulfuric acid and ammonium chloride (*3*). A second coupling reaction yields the linear tetrasilane:

$$\mathrm{Me_3SiSiMe_3} \xrightarrow[2)\,\mathrm{NH_4Cl}]{1)\,\mathrm{H_2SO_4}} \mathrm{Me_3SiSiMe_2Cl}$$

$$\xrightarrow{\mathrm{NaK}} \mathrm{Me_3SiSiMe_2SiMe_2SiMe_3}$$

It is possible gradually to build up chains of silicon atoms by successive demethylation and coupling reactions of this type. To synthesize very long polysilane chains it is preferable to begin with the cyclic permethylpolysilane, $(Me_2Si)_6$, whose prepa-

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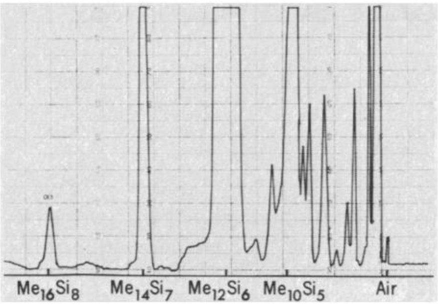


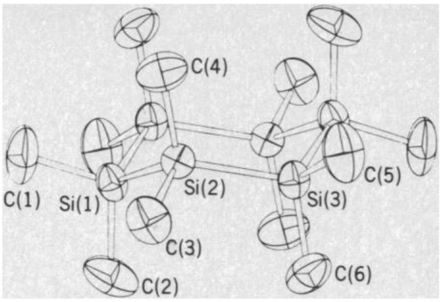


Fig. 1 (left). Temperature-programmed gas chromatograph of crystalline reaction products from condensation of Me_2SiCl_2, with identification of cyclopolysilane peaks. Fig. 2 (right). Structure of $(Me_2Si)_6$ from x-ray crystallographic determination, showing ellipsoids of thermal vibration. [From Carrell and Donahue (*11*); courtesy of International Union of Crystallography]

ration will be described later. This substance can be cleaved with phosphorus pentachloride to a 1,6-dichloro derivative which upon methylation leads to the 1-chlorohexasilane (*4*).

$$(Me_2Si)_6 \xrightarrow{PCl_5} Cl\text{-}(SiMe_2)_6\text{-}Cl$$

$$\xrightarrow{MeMgI} Me_3Si\text{-}(SiMe_2)_5\text{-}Cl$$

Coupling of the latter leads to the 12-silicon chain, and one more demethylation and coupling yields the longest polysilane yet known as a pure compound, Me-$(SiMe_2)_{24}$-Me (*4*). It is a waxy solid, rather like the hydrocarbon of similar chain length. Reactions leading to branched-chain isomers of the permethylsilanes are also known (*3*).

In 1964 it was discovered, apparently independently in several different laboratories, that permethylpolysilanes show strong ultraviolet absorption bands at surprisingly low energies, in the 200- to 300-nm region (*5*). This observation was surprising, for the corresponding hydrocarbons absorb only at very high energies in the vacuum ultraviolet region. Virtually without exception, organic compounds which show absorption above 200 nm contain lone pair electrons or multiple bonds, both of which are lacking in the permethylpolysilanes. This unexpected finding that permethylpolysilanes show low energy electronic transitions prompted our investigation of the cyclic polysilanes.

Permethylcyclosilanes

The first compound of this class (*6*) was the dodecamethylcyclohexasilane $(Me_2Si)_6$ obtained in 1949 by Burkhard in the General Electric Co. Laboratories (*7*). The cyclosilane was obtained in very small yield from the reaction of sodium metal with dimethyldichlorosilane, an intermediate in silicone polymer manufacture. Condensation of Me_2SiCl_2 with alkali metals still provides the only practical route to cyclic permethylpolysilanes, but the procedure has been substantially improved by the use of sodium-potassium (NaK) alloy as the coupling agent and tetrahydrofuran as solvent (*8*, *9*). In our laboratories, $(ME_2Si)_6$ is routinely prepared in 300-gram lots in 70 to 75 percent yield from Me_2SiCl_2.

In our early experiments on the synthesis of $(Me_2Si)_6$, it was observed that other cyclic $(Me_2Si)_n$ compounds accompany its formation (*9*). The fact that a homologous series of permethylcyclosilanes can be obtained has added greatly to the interest in this field. When the crystalline product of the Me_2SiCl_2 condensation was subjected to gas chromatographic analysis after brief (2 hours) reaction time, results shown in Fig. 1 were obtained. At this point the cyclic reaction products consist of about 75 percent $(Me_2Si)_6$, 20 percent $(Me_2Si)_5$, 5 percent $(Me_2Si)_7$, and a trace of $(Me_2Si)_8$. These homologs can be separated by preparative gas chromatography. However, if the reaction mixture is simply allowed to stand in contact with sodium-potassium alloy for 16 hours, the five- and seven-membered ring compounds are slowly converted to $(Me_2Si)_6$ until an apparent equilibrium is reached containing about 95 percent $(Me_2Si)_6$, 4 percent $(Me_2Si)_5$, and < 1 percent $(Me_2Si)_7$. It appears therefore that the five- and seven-membered rings are produced in a kinetically controlled process and subsequent equilibration gradually converts them largely to the thermodynamically more stable six-membered ring.

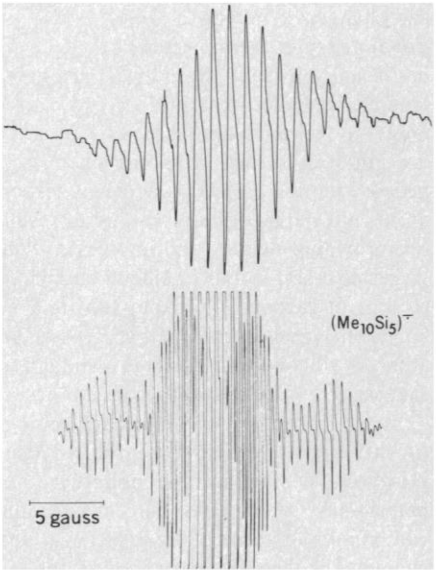


Fig. 3. ESR spectra of $(Me_2Si)_5$ anion radical [electrolytic reduction in a mixture of 2-methyltetrahydrofuran : 1,2-dimethoxyethane (3 : 1) at −75°C]. (Top) Low gain showing center lines; (bottom) high gain showing satellite doublets due to ^{13}C and ^{29}Si.

In practice it is convenient to carry out the reaction so as to produce the maximum amount of $(Me_2Si)_6$. If $(Me_2Si)_5$ is desired it can be obtained by photolysis of the six-membered ring (*10*). This procedure also leads to the four-membered ring $(Me_2Si)_4$ and some by-products:

$$(Me_2Si)_6 \xrightarrow[20\ \text{hours}]{h\nu} \begin{array}{l}(Me_2Si)_5,\ 70\ \text{percent}\\ (Me_2Si)_4,\ 17\ \text{percent}\\ (Me_2Si)_4O,\ 8\ \text{percent}\\ H(Me_2Si)_4H,\ 5\ \text{percent}\end{array}$$

The permethylcyclosilanes are colorless crystalline solids with relatively high melting points. The six- and seven-membered rings are stable in air; but the smaller homologs undergo air oxidation, $(Me_2Si)_5$ slowly and $(Me_2Si)_4$ quite rapidly. The structure is known in detail only for $(Me_2Si)_6$, from an x-ray crystal structure determination (*11*). The molecule exists in a strain-free chair conformation exactly like that of the hydrocarbon analog cyclohexane (Fig 2). In this structure there are two different sets of equivalent methyl groups, six each in the axial and equatorial positions. Nevertheless, the proton magnetic resonance spectrum of $(Me_2Si)_6$ in solution shows only a single line for all 36 hydrogens of the molecule, even at low temperatures (−90°C) (*9*). Unless the axial and equatorial methyl protons are coincidentally equivalent in their nuclear magnetic resonance (NMR) chemical shift, this implies that rapid equilibration between different chair conformations takes place in solutions of $(Me_2Si)_6$. The same kind of conformational equilibration is well known for the carbon analog cyclohexane and its derivatives.

The cyclic compounds show ultraviolet absorption bands between 200 and 300 nm (Table 1). In this they resemble the linear permethylpolysilanes, but there is an important difference. Among the linear compounds the ultraviolet maximum moves to lower energy (longer wavelength) as the chain length increases. But for the five-, six-, and seven-membered rings the opposite is true—the lowest energy transition is found for the five-membered ring, and this shifts to higher energy as ring size increases (*12*). To explain this peculiarity of the ultraviolet absorption it is necessary to consider both the ground state and the first electronic excited state of these molecules.

Table 1. Spectral properties of permethylcyclopolysilanes (λ, wavelength; ϵ, extinction coefficient; ν, frequency).

Silane	Ultraviolet			Photoelectron spectra* (ev)	NMR (δ)	IR νSi-Si (cm^{-1})
	λ_{max} (nm)	λ_{max} (ev)	ϵ			
$(\mathrm{Me_2Si})_5$	210 261 272	5.90 4.75 4.56	Shoulder 1100 970	7.94 8.91 9.80	−0.135	400
$(\mathrm{Me_2Si})_6$	230.5 252.5	5.38 4.91	6000 1200	7.79 8.16 9.12 9.78	−0.132	383
$(\mathrm{Me_2Si})_7$	217 242	5.71 5.12	4500 2100		−0.125	362

*The ionization energy (ev) data for Si-Si bonding electrons are from (*24*).

Table 2. Properties of cyclopolysilane anion radicals (*1*).

Anion radical	*g* value	Splitting constants (gauss)			Color
		$a_{^{29}\mathrm{Si}}$	$a_{^{13}\mathrm{C}}$	a_{H}	
$(\mathrm{Me_2Si})_4^{\dot{-}}$	2.0037		20.97	0.669	Blue
$(\mathrm{Me_2Si})_5^{\dot{-}}$	2.0032	6.13	16.03	0.53	Blue
$(\mathrm{Me_2Si})_6^{\dot{-}}$	2.0028		14.60	0.49	Yellow

Anion Radicals of Cyclopolysilanes

Anion radicals of aromatic hydrocarbons and other species with low-lying antibonding π-molecular orbitals are well known, but formation of anion radicals by molecules lacking unsaturation is not normally observed. The polysilanes are exceptional among formally saturated molecules in that they can be reduced chemically or electrolytically to anion radicals, which can be studied by electron spin resonance (ESR) spectroscopy (*12*). Analysis of the ESR spectrum provides crucial information about the lowest unfilled molecular orbital (LUMO).

The best results have been obtained with cyclopolysilanes, and especially with the five-membered ring decamethylcyclopentasilane. When $(\mathrm{SiMe_2})_5$ is reduced either electrolytically or chemically with NaK alloy in suitable ether solvents at low temperatures (−80° to −100°C), it is reversibly transformed into a dark blue radical anion giving a symmetrical ESR pattern (Fig. 3). At low gain, the spectrum consists of about 15 equally spaced lines separated by 0.53 gauss. The relative intensities of these lines correspond to those of the center portion of a 31-line pattern arising from splitting by 30 equivalent protons, indicating that the unpaired electron contacts each proton in the $(\mathrm{Me_2Si})_5^{\dot{-}}$ anion radical equally, and is fully delocalized over the five-membered ring. The complete electron delocalization in this and other cyclopolysilane anion radicals strongly resembles that in aromatic anion radicals.

Most of the silicon and carbon atoms in $(\mathrm{Me_2Si})_5^{\dot{-}}$ have no nuclear spin and do not affect the ESR pattern, but the isotopes ^{13}C (1.1 percent abundance) and ^{29}Si (4.7 percent) each have spin 1/2, and can therefore split the ESR pattern into a doublet. When the spectrum of $(\mathrm{Me_2Si})_5^{\dot{-}}$ is examined at higher gain, many additional lines are found, including two separate doublet satellite spectra replicating the central, principal spectrum (Fig. 3). Relative intensity measurements establish that radicals containing one ^{13}C atom give rise to the outer doublet (hyperfine splitting constant a = 16.1 gauss) and those with a ^{29}Si atom to the inner doublet (a = 6.13 gauss).

The value of a for ^{29}Si is important because it correlates with an especially significant calculation. Assume that the unpaired electron is in an essentially π-type molecular orbital made up of 3*d* or 4*p* orbitals from the five silicon atoms, a situation analogous to the π^* orbitals of aromatic anion radicals (we will call this the "π^* orbital model"). Since these orbitals have nodes at the silicon nuclei, hyperfine splitting by ^{29}Si would arise only by the mechanism of spin polarization. The amount of splitting due to spin polarization can then be calculated by the method of Hunter and Symons, from the equation (*13*)

$$100a^{\mathrm{x}}/A^{\mathrm{x}} = \rho_{\mathrm{x}}U^{\mathrm{x}} + \rho_{\mathrm{y}}U^{\mathrm{x}}_{\mathrm{yx}}$$

where a^{x} is the observed coupling constant for the atom x; A^{x} is the isotropic one-electron hyperfine constant for atom x; ρ_{x} is the spin density on atom x; U^{x} is the spin polarization constant for atom x; and $U^{\mathrm{x}}_{\mathrm{yx}}$ is the spin polarization constant due to the adjacent atoms. Now supposing that 0.2 electron is on each silicon atom and with the use of Hunter and Symons' values for spin polarization constants and the value 1208 gauss for the isotropic hyperfine splitting constant for ^{29}Si (*14*), we obtain for ^{29}Si, a = 5.6 gauss, in remarkably good agreement with the observed value of 6.1 gauss. Therefore, essentially all of the hyperfine splitting on silicon can be accounted for by spin polarization, as is consistent with the π^* orbital model suggested earlier. If the results are looked at in another way, they indicate that the unpaired electron cannot be in an orbital which has significant *s* atomic orbital character because the hyperfine splitting by silicon would have to be much larger.

The ESR spectrum also shows that spin density at the nucleus is greater for carbon atoms of the attached methyl groups than for silicon atoms in $(\mathrm{Me_2Si})_5^{\dot{-}}$. This result is reasonable if the electron is in a π-type molecular orbital, made up from 3*d* or 4*p* orbitals on the silicons (*15*).

Other permethylcyclopolysilanes can also be reduced to electron-delocalized anion radicals. Upon electrolytic reduction $(\mathrm{SiMe_2})_4$ (*16*) and $(\mathrm{SiMe_2})_6$ give ESR patterns quite similar to that for $(\mathrm{SiMe_2})_5^{\dot{-}}$ but differing in details (Table 2). As ring size decreases, the spin density at each silicon atom must increase. Therefore, increases are expected in all of the hyperfine splitting constants. The ^{29}Si hyperfine splitting constant could not be measured for $(\mathrm{Me_2Si})_6^{\dot{-}}$ and $(\mathrm{Me_2Si})_4^{\dot{-}}$, but the ^{13}C and ^{1}H constants increase with decreasing ring size as predicted (Table 2). However, the differences are much greater between $(\mathrm{Me_2Si})_5^{\dot{-}}$ and $(\mathrm{Me_2Si})_4^{\dot{-}}$ than between $(\mathrm{Me_2Si})_6^{\dot{-}}$ and $(\mathrm{Me_2Si})_5^{\dot{-}}$. A tentative explanation is that rehybridization in the four-membered ring gives the Si-Si bonding orbitals more *p* character leaving more *s* character on silicon for the Si-C bonding orbitals. The result would be to bend the methyl groups away from the plane of the ring and more nearly into the π cloud of the orbital containing the unpaired electron.

The seven-membered ring $(\mathrm{Me_2Si})_7$ does not undergo electrolytic reduction to an anion radical. Surprisingly, chemical reduction of either $(Me_2Si)_6$ or $(Me_2Si)_7$ with NaK gives only the anion radical of the five-membered ring, $(Me_2Si)_5^{\cdot-}$. Moreover, electrolytic reduction of $(Me_2Si)_6$ at temperatures above -100°C gives a mixture of $(Me_2Si)_6^{\cdot-}$ and $(Me_2Si)_5^{\cdot-}$ [the latter radical is more stable, so that, if the solution is allowed to stand until $(Me_2Si)_6^{\cdot-}$ decays away, only $(Me_2Si)_5^{\cdot-}$ can be observed]. Evidently six- (and seven-) membered ring polysilanes are easily transformed to five-membered ring anion radicals on reduction.

These results seem to indicate that $(Me_2Si)_5^{\cdot-}$ is more stable than $(Me_2Si)_6^{\cdot-}$, and independent experiments confirm this deduction (*12*). For example, electrolytic reduction of a mixture of the five- and six-membered rings at low temperature gives only $(Me_2Si)_5^{\cdot-}$. Similar competitive experiments show that $(Me_2Si)_5$, but not $(Me_2Si)_6$, is reduced preferentially to benzene. Therefore, ease of reduction decreases in the order

$$(Me_2Si)_5 > \text{benzene} > (Me_2Si)_6 > (Me_2Si)_7$$

How can this order of "electron affinities" be explained? Ring geometry seems to be crucial. The four- and five-membered rings are probably nearly planar, whereas $(Me_2Si)_6$ has the chair cyclohexane conformation and $(Me_2Si)_7$ is probably even more distorted from planarity. The overlap of silicon atomic orbitals to make up the π^*-like orbital, which contains the unpaired electron in the radicals, may be much better when the Si atoms are coplanar.

Although linear polysilanes as well as cyclopolysilanes capture electrons, the resulting anion radicals are quite unstable even at very low temperatures, and the observed ESR spectra appear to result from unidentified decomposition products.

Photoelectron Spectra and Chemical Bonding

The strong ultraviolet absorption and low ionization potentials of polysilanes have occasioned much speculation about the nature of Si-Si bonding in these molecules. An interpretation has been offered with the use of the "Sandorfy C" model developed for alkanes, in which linear combinations of sp^3 hybrid orbitals on carbon are taken to form σ molecular orbitals (MO's) (*17*). This model has been improved and amplified by recent photoelectron spectral measurements of linear and cyclic polysilanes by Bock and Ensslin (*18*). Photoelectron spectra for $(Me_2Si)_5$ and $(Me_2Si)_6$ are shown in Fig. 4. In these molecules (and in linear polysilanes), the intense band systems above 10 electron volts corresponding to ionization from Si-C and C-H bonding orbitals are preceded by bands of lower energy, due to ionization from polysilane MO's. The polysilane MO's are split according to the symmetry of the molecule. For $(Me_2Si)_5$, assuming D_{5h} symmetry, delocalization of Si-Si bonding electrons should give MO's of symmetry types e_1', e_2', and a_1' and relative weighting 2 : 2 : 1, with the energy increasing in the order given. Similarly $(Me_2Si)_6$ (D_{3d} symmetry) should show a 1 : 2 : 2 : 1 intensity pattern due to Si-Si MO's of symmetry a_{1u}, e_g, e_a, and a_{1g} (*5*, p. 113). These energy levels all appear dramatically in the photoelectron spectra (Fig. 4) (Table 1) although in both cases the highest energy band overlaps the Si-C band and is given an exaggerated intensity.

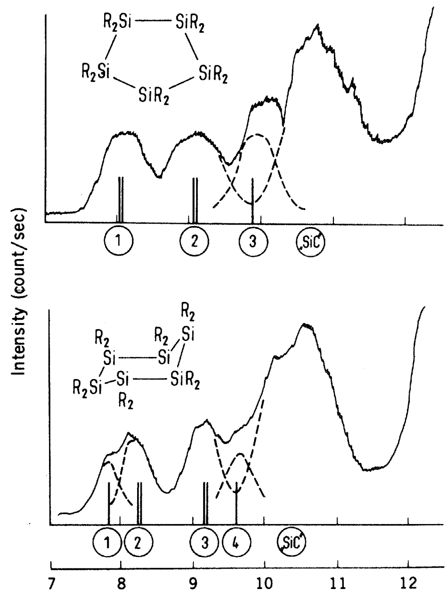


Fig. 4. Photoelectron spectra for $(Me_2Si)_5$ and $(Me_2Si)_6$. [From Bock and Ensslin (*18*); courtesy of Verlag Chemie]

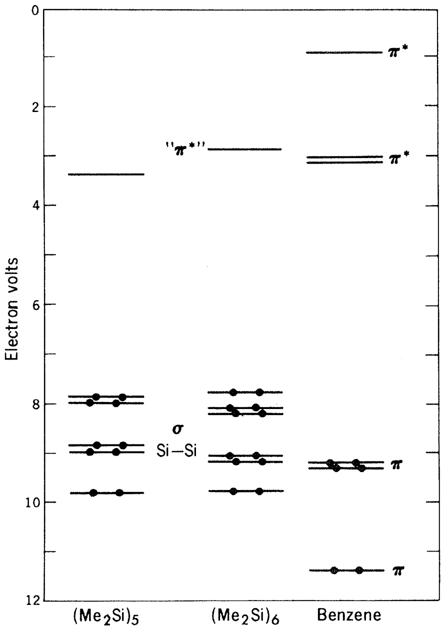


Fig 5. Schematic molecular orbital correlation diagram for $(Me_2Si)_5$, $(Me_2Si)_6$, and benzene. Among bonding orbitals, only the Si-Si σ-bonding orbitals are shown for the polysilanes and only π orbitals for benzene. Energies of LUMO's for polysilanes were estimated from the first electronic transitions whereas the energy for the benzene LUMO is the weighted average of energies of the first excited states. The model, though crude, predicts correctly the relative tendencies of the three species to accept electrons.

The results can be explained by a simple model involving linear combinations of Si-Si bonding orbitals and resultant σ-electron delocalization over the molecule. Orbital eigenvalues are obtained from the equation

$$E_n = \alpha_{\mathrm{SiSi}} + \lambda_n \beta_{\mathrm{SiSi}}$$

in which α_{SiSi} is taken as the ionization energy for hexamethyldisilane, $Me_3SiSiMe_3$ (IE_1 = 8.69 ev), and the coefficients λ_n are obtained from published tables (*18*). An excellent linear relationship is found between ionization energies and λ_n for all polysilanes studied. The model involving σ-electron delocalization beautifully explains the results from photoelectron spectroscopy (*18*). No assumption that *d* orbitals of silicon contribute to the bonding in the occupied orbitals is required.

In organic chemistry, the assumption is usually made that σ electrons in chemical bonds are localized between the atomic nuclei. This approximation is a satisfactory one for most purposes in carbon compounds where the σ-bonding electrons have relatively high ionization potentials (low energies). This certainly does not exclude the possibility of σ-electron delocalization in such carbon compounds, but this model does not usually need to be used to explain observed properties. However, because the polysilanes have Si-Si bonding electrons of relatively high energy, delocalization of σ-bonding electrons must be explicitly considered to explain the chemical and physical properties of these polysilane compounds.

Electronic Spectra

Knowing the energies of the bonding levels from photoelectron studies, we can better understand the electronic spectra of cyclopolysilanes. The highest filled levels in $(Me_2Si)_5$ and $(Me_2Si)_6$ lie quite close in energy with the six-membered ring orbital slightly higher (*18*) (Table 1) (Fig. 5). Thus the 0.35-ev bathochromic shift in the lowest energy electronic transition from $(Me_2Si)_6$ to $(Me_2Si)_5$ must be explained by differences in the excited states of these molecules. These data support the π^* orbital model proposed to explain the stabilities of the anion-radicals. Better overlap of unfilled Si atomic orbitals in the near planar five-membered ring lowers the energy of the LUMO and decreases the transition energy. No such geometrical restriction applies to the linear polysilanes, in which the electronic transitions shift to lower energy with increasing chain length.

The intensities observed for ultraviolet transitions in the cyclic compounds also seem consistent with this model. If the electronic transitions were from σ-bonding orbitals to true π^* orbitals, they would be symmetry-forbidden. In nonplanar molecules σ and π orbitals cannot be strictly separated; thus the LUMO for cyclopolysilanes may not be strictly π^*. The σ-π separation should be most complete in $(Me_2Si)_5$, which should be nearly planar; and indeed this compound shows far lower ultraviolet extinction coefficients (ϵ) than the linear polysilanes (*5*, pp. 113–126). Both $(Me_2Si)_6$ and $(Me_2Si)_7$ have intermediate values of ϵ_{max}

From knowledge of the photoelectron, ESR, and electronic spectra it is possible to develop molecular orbital correlation diagrams for the polysilanes. Such schematic diagrams for $(Me_2Si)_5$, $(Me_2Si)_6$, and benzene, for comparison, are shown in Fig. 5. The reason why the cyclopolysilanes show properties resembling those of aromatic compounds can be seen from the diagrams. In the polysilanes the delocalized Si-Si σ-bonding orbitals take the place of the filled π levels of benzene. In place of the unfilled π^* LUMO of benzene the cyclopolysilanes have delocalized π^*-like orbitals probably constructed from 3*d* atomic orbitals on silicon (*19*).

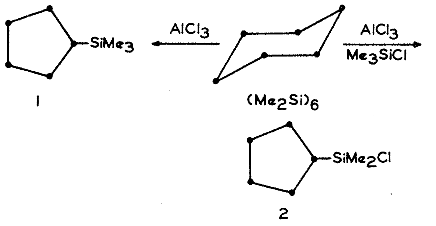
A well-known property of aromatic compounds such as benzene and naphthalene is their action as pi-electron donors in the formation of charge-transfer complexes with pi-acceptors like tetracyanoethylene (TCNE). Recently, it has been discovered that polysilanes will similarly form charge-transfer complexes with pi acceptors in which the delocalized Si-Si σ electrons are the charge source (*20, 21*).

New absorption bands appear in the visible region when polysilanes are mixed with pi acceptors, much like those observed for aromatic pi complexes. Thus when colorless $(Me_2Si)_6$ and TCNE are mixed, a violet color forms due to new absorptions at 477 and 390 nm, which can be associated with charge-transfer transitions from the highest-lying Si-Si MO's. The phenomenon is quite general for polysilanes, linear as well as cyclic, but was long overlooked, probably because the intensity of the charge transfer bands is about an order of magnitude less than for aromatic pi complexes.

Substituted Cyclopolysilanes

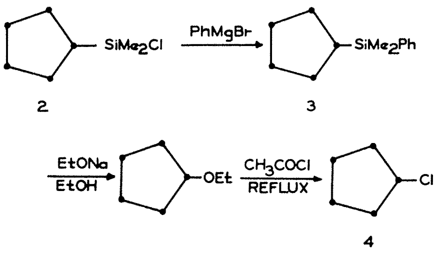
The extensively studied substitution reactions of aromatic compounds provide an important part of organic chemistry. Here too the cyclopolysilanes show some resemblances to aromatic compounds. A wide variety of substituted cyclopolysilanes and a rich chemistry involving their transformations has recently been developed, mainly as a result of studies by Kumada and Ishikawa (*22, 23*). The more interesting and important reactions will be outlined in this section.

A significant reaction is the aluminum chloride–catalyzed ring contraction of $(Me_2Si)_6$ to trimethylsilylnonamethylcyclopentasilane (**1**) which takes place in nearly quantitative yield. This reaction parallels the acid-catalyzed isomerization of cycloheptatriene to toluene known from organic chemistry. If trimethylchlorosilane is present in excess during the reaction, simultaneous exchange of methyl and chlorine takes place yielding **2**, a compound with an exocyclic -$SiMe_2Cl$ group (*22*).

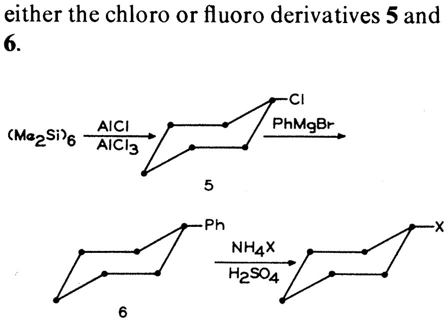


(It is important to recognize here that in these skeletal structures each dot represents a silicon atom, together with enough methyl groups to bring the total valence of silicon to 4.)

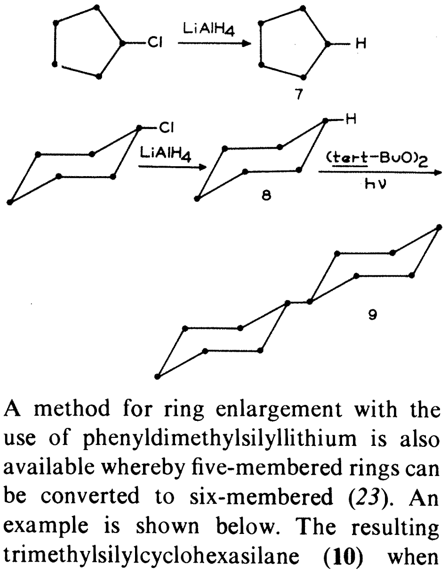
Compounds containing Si-Cl bonds are especially useful as intermediates because the chlorine is easily replaced by a large variety of nucleophilic reagents to give other derivatives. The chlorine in compound **2** can be replaced by phenyl with the use of phenylmagnesium bromide. The phenyl (Ph) substituted silicon is susceptible to cleavage by base, and further reaction leads to the even more useful chloropentasilane **4** (*22*).



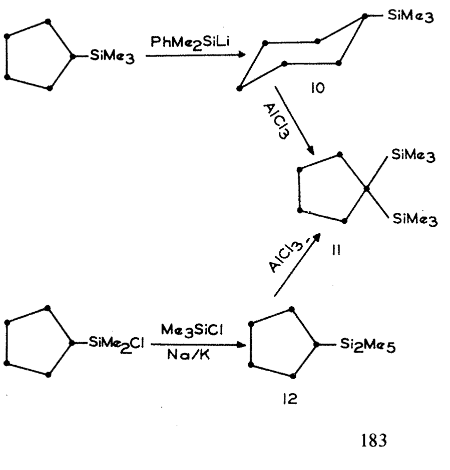
Replacement of methyl groups in $(Me_2Si)_6$ without alteration of the ring can also be carried out with a mixture of hydrogen chloride and aluminum chloride, or antimony pentachloride (*24, 25*). The resulting chloroundecamethylcyclohexasilane (**5**) is, however, contaminated by ring-contracted products that are difficult to separate. Therefore, if the pure chloro compound is needed, it is transformed into the phenyl derivative (**6**), which is easily purified. Cleavage of the phenyl group with ammonium halide and sulfuric acid yields either the chloro or fluoro derivatives **5** and **6**.



The chloro derivatives may be reduced to the corresponding hydrides, **7** and **8**. Coupling of the silyl radicals derived from the six-membered ring monohydride has yielded the first two-ringed cyclopolysilane **9** (*26*).

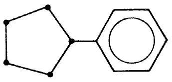


A method for ring enlargement with the use of phenyldimethylsilyllithium is also available whereby five-membered rings can be converted to six-membered (*23*). An example is shown below. The resulting trimethylsilylcyclohexasilane (**10**) when treated with aluminum chloride undergoes ring contraction to give a single bissilylcyclopentasilane isomer, **11**. The same isomer is the only product when the disilanylcyclopentasilane **12** is treated with $AlCl_3$.



These surprisingly specific reactions have been used in developing a mechanism for the ring-contraction process, which appears to proceed through a sequence involving chlorodemethylation, ring-contraction, and chlorine-methyl exchange reactions (*24*).

Study of the physical properties of the substituted cyclopolysilanes is only beginning, but a number of compounds have been reduced to anion radicals (*27*). Among the species whose ESR spectra have been recorded are the anion radicals of **1**, **3**, **6**, **7**, **8**, **11**, and the phenyl- and benzyl-substituted five-membered rings, **13** and **14**.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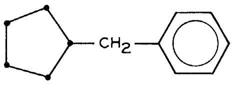

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The anion radicals of the five-membered ring compounds are all blue in color and are relatively stable. The substituted cyclohexasilanes form yellow radical anions which are unstable, usually decomposing to $(\mathrm{SiMe_2})_5^{\cdot-}$. Because the symmetry of the rings is broken by substitution, the methyl groups are nonequivalent, and resolution of methyl proton hyperfine splitting is not expected. Methyl proton splitting is nevertheless observed in the ESR spectra for **1**, **7**, **13**, and **14** (see Fig. 6), suggesting that the corresponding substituents affect the spin density at the various silicon atoms only slightly.

When phenyl-substituted compounds are reduced, an interesting question arises as to whether the unpaired electron will enter the polysilane ring or the phenyl ring. The phenyl and benzyl derivatives of $(\mathrm{Me_2Si})_5$, **13** and **14**, give on electrolytic reduction species with ESR spectra typical for polysilane anion radicals; this shows that the electron enters the silicon ring rather than the aromatic nucleus (the benzyl derivative spectrum is shown in Fig. 6). On the other hand, the phenyl derivative **6** of the six-membered ring, gives an anion radical with a quite different ESR pattern, characteristic of a substituted benzene ring (Fig. 6). Thus the electron is associated with the aromatic ring and not the polysilane ring in the latter case. The results are consistent with the earlier finding that ease of reduction increases from $(\mathrm{Me_2Si})_6$ to benzene to $(\mathrm{Me_2Si})_5$.

Cage Polysilanes

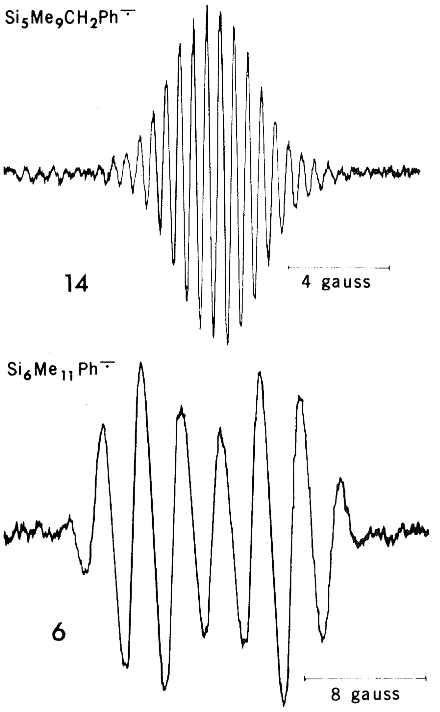


Fig. 6. (Top) ESR spectrum of benzylnonamethylcyclopentasilane anion radical. The pattern is a typical multiplet for a cyclopolysilane anion radical. (Bottom) ESR spectrum of phenylundecamethylcyclohexasilane anion radical. The pattern is a doublet of triplets due to splitting by the para and ortho hydrogens respectively in the benzene ring, showing that the unpaired electron enters the benzene and not the polysilane ring.

In the synthesis of cyclopolysilanes, dialkyldihalosilanes react with alkali metals with elimination of metal halide. If a similar reaction could be carried out on alkyltrihalosilanes, three-dimensional (cage) polysilane structures might result; but in fact this reaction has produced only cross-linked polymers. However, after a lengthy series of unsuccessful attempts, it was found that mixtures of $\mathrm{Me_2SiCl_2}$ and $\mathrm{MeSiCl_3}$ can be co-condensed with sodium-potassium alloy to give small amounts of polycyclic materials—the first cage polysilicon compounds (*28*). In the best conditions found so far for this reaction, a 3 : 1 molar ratio of $\mathrm{Me_2SiCl_2}$ to $\mathrm{MeSiCl_3}$ is treated with Na and K in tetrahydrofuran in the presence of naphthalene. In addition to $(\mathrm{Me_2Si})_6$ and polymer, at least six different polycyclic silanes are formed, all colorless crystalline solids with high melting points:

$$\mathrm{MeSiCl_3} + \mathrm{Me_2SiCl_2} + \mathrm{NaK} \xrightarrow[\text{naphthalene}]{\text{THF}}$$

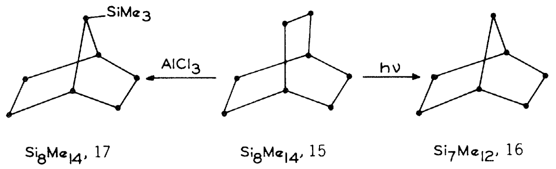
	Yield (%)	m.p. (°C)
$\mathrm{Si_8Me_{14}}$	5.0	>360
$\mathrm{Si_9Me_{16}}$	2.0	279
$\mathrm{Si_{10}Me_{16}}$	0.5	>360
$\mathrm{Si_{10}Me_{18}}$	4.0	195
$\mathrm{Si_{11}Me_{18}}$	0.5	
$\mathrm{Si_{13}Me_{22}}$	0.1	
$(\mathrm{SiMe_2})_6$	10	
Polymer	78	

The reaction mixture can be separated, but only by a tedious, laborious combination of fractional crystallization and preparative gas chromatography. Specific syntheses for cage polysilanes are much needed, and at least one method has been developed (*29*). Condensation of 1,2-dichlorotetramethyldisilane with $\mathrm{MeSiCl_3}$ produces $\mathrm{Si_8Me_{14}}$ in remarkably improved yield:

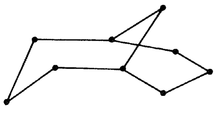
$$\mathrm{MeSiCl_3} + \mathrm{ClMe_2Si\text{-}SiMe_2Cl} \xrightarrow[\mathrm{THF,\,C_{10}H_8}]{\mathrm{NaK}} \mathrm{Si_8Me_{14}}(30\%) + (\mathrm{Me_2Si})_6 + \text{polymer}$$

Also, co-condensation of $\mathrm{Me_2SiCl_2}$ and $\mathrm{MeSiCl_3}$ with lithium metal is reported to give $\mathrm{Si_{10}Me_{18}}$ free of other polycyclic compounds, although accompanied by polymer and $(\mathrm{Me_2Si})_6$ (*30*).

To date, most of the research on cage polysilanes has been directed toward synthesis and purification of these substances and structure determination. The structure of $\mathrm{Si_8Me_{14}}$ has been established from the proton NMR spectrum, which gives just two peaks with an intensity ratio of 6 : 1, and from the ^{13}C and ^{29}Si spectra, both of which show only two resonances. The only structure consistent with these findings is tetradecamethylbicyclo[2.2.2]octasilaoctane, **15**. Photolysis of $\mathrm{Si_8Me_{14}}$ yields, among other products, a compound $\mathrm{Si_7Me_{12}}$, which likewise shows a very simple NMR spectrum uniquely consistent with the [2.2.1]bicycloheptasilane structure **16**. Treatment of $\mathrm{Si_8Me_{14}}$ with aluminum chloride leads also to ring contraction with formation of an isomeric $\mathrm{Si_8Me_{14}}$ having the structure **17**. Both reactions are analogous to those observed for $(\mathrm{Me_2Si})_6$.



The structure of $\mathrm{Si_9Me_{16}}$ is known from single-crystal, x-ray diffraction analysis (*31*) and is remarkable. The compound has the bicyclo[3.3.1]nonasilane structure, which can be regarded as two six-membered rings joined by two common edges. One of the two rings is nearly in the chair form, while the other is in a unique conformation with *five of the atoms nearly planar* (**18**).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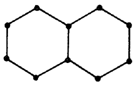
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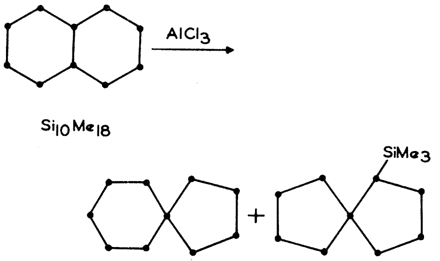
$\mathrm{Si_{10}Me_{18}}$ probably has the noncage [4.4.0]bicyclohexane structure **19**. The proton NMR spectrum does not distinguish between this and other possible structures, but $Si_{10}Me_{18}$ resembles the cyclic polysilanes in showing distinct ultraviolet absorption bands, whereas the known cage compounds show only strong end absorption (Fig. 7) (*28*). Tentatively we believe that the absence of definite ultraviolet bands may be associated with cage structure. In addition, the preferential synthesis of $Si_{10}Me_{18}$ with the use of lithium metal suggests that it contains only six-membered rings, since lithium gives only $(Me_2Si)_6$ with Me_2SiCl_2. Aluminum chloride treatment of $Si_{10}Me_{18}$ yields isomeric compounds believed to have spirosilane structures (*30*).



The physicochemical properties of the cage compounds, as yet little known, are expected to be of much interest. Preliminary experiments indicate that Si_8Me_{14} (**15**) and $Si_{10}Me_{18}$ undergo reduction to anion radicals, which seem to be less stable than anion radicals of cyclopolysilanes. In the radical $Si_8Me_{14}^{\cdot-}$, the unpaired electron may be in a delocalized orbital extending three dimensionally over the entire cage.

Other Groups, Other Metals

Polysilane chemistry offers further potential variability in that the methyl could be replaced by other alkyl groups, and the silicon by other metals. Only a few peralkylpolysilanes other than the methyl compounds are yet known, and their properties have not been fully studied. As the alkyl groups become much larger than methyl, serious steric interactions are likely to occur and may dominate the properties of these molecules.

The perethyl and ethylmethyl compounds $(Et_2Si)_6$ and $(EtMeSi)_6$, the latter probably a mixture of isomers, have been synthesized and reduced to anion radicals (*32*). Decaisobutylcyclopentasilane has been obtained albeit in pitifully small yields (1.6 percent) (*33*). Two isomers of $(tert\text{-}BuMeSi)_4$ have been isolated, both air stable unlike the easily oxidized $(Me_2Si)_4$ (*34*). All of these compounds were produced analogously to the permethylcyclopolysilanes, by alkali metal coupling of the corresponding dialkyldichlorosilanes. Mixed arylalkylcyclopolysilanes such as $(MePhSi)_6$ are also known (*35*). Also, the important "parent" cyclopentasilane, Si_5H_{10}, was recently prepared by the bromination and subsequent reduction of the perphenyl compound (*36*).

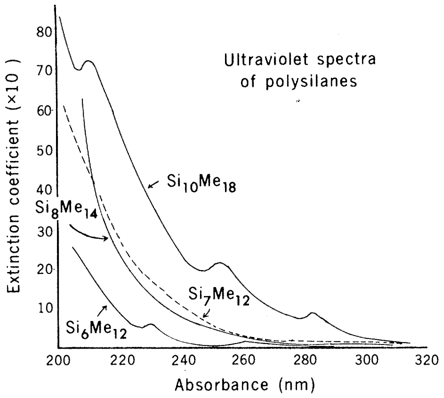
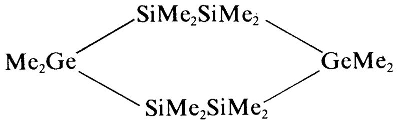


Fig. 7. Ultraviolet spectra of cyclic and cage permethylpolysilanes (*26*). The cyclic, but not the cage, compounds show distinct band maxima.

Some work has also been done on metal replacement, especially with the closely related element germanium. Permethylcyclohexagermane, $(Me_2Ge)_6$, was reported in 1962 by Nefedov and co-workers (*37, 38*) and, more recently, the five- and seven-membered rings have been isolated from lithium condensation of dimethyldichlorogermane (*39*). The cyclopolygermanes appear to resemble the analogous silicon compounds in their physical and chemical properties. For instance, photolysis of the cyclopolygermanes takes place with loss of Me_2Ge units (*39*).

Rings containing both silicon and germanium atoms have also been prepared. Co-condensation of Me_2GeCl_2 and Me_2SiCl_2 with lithium gives all possible types of five-, six-, and seven-membered rings, and the complex mixture of products is separable by gas chromatography (*40*) (Fig. 8). One isomer, dodecamethyl-1,4-digerma-2,3,5,6-tetrasilacyclohexane, has been obtained by a specific synthesis:

$$ClMe_2SiSiMe_2Cl + Me_2GeCl_2 \xrightarrow[THF]{Li}$$



The cyclopolygermanes will probably have ionization potentials at least as low as those for the polysilanes. Like their silicon analogs, $(Me_2Ge)_5$ and $(Me_2Ge)_6$ form charge-transfer complexes with powerful π acceptors. In contrast, attempts to reduce cyclopolygermanes to anion radicals have been unsuccessful (*41*). The LUMO apparently lies at higher energy for the germanium compounds, perhaps because of poorer orbital overlap that could be due to the longer Ge-Ge bonds.

Cyclopolytin compounds have been much less studied. Only one methyl derivative, dodecamethylcyclohexastannane, has been reported, and even this compound was not obtained in pure form (*42*). A series of cyclopermethylpolystannanes, as well as mixed compounds of tin with germanium and silicon, appear possible and will undoubtedly be the subjects of future investigations.

Summary

Studies of the spectra of cyclopolysilanes have led to several significant conclusions. These molecules possess both easily ionized Si-Si bonding electrons and low energy delocalized antibonding orbitals, and can therefore serve either as electron donors or acceptors. This model explains the similarity in properties be-

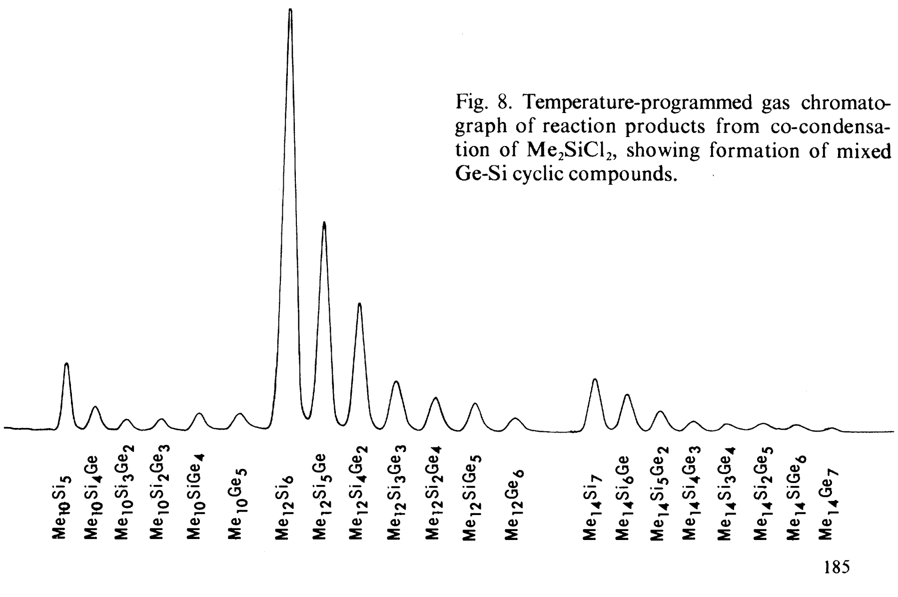


Fig. 8. Temperature-programmed gas chromatograph of reaction products from co-condensation of Me_2SiCl_2, showing formation of mixed Ge-Si cyclic compounds.

tween cyclopolysilanes and aromatic hydrocarbons. Further investigations of cyclopolysilanes seem likely to provide the key to understanding of controversial questions of bonding in metalloid compounds even as studies of their carbon analogs, the cyclic and cage hydrocarbons, have been crucial to present knowledge of organic stereochemistry and reaction mechanisms.

The reactions of cyclopolysilanes are not only interesting in themselves, but have opened the way to the synthesis of complex polysilanes and thus to whole new areas of study. Improved methods of synthesis and isolation are needed, but the number and kinds of compounds that can be prepared seem almost limitless. Perhaps a polymetal chemistry comparable in breadth and variety to carbon chemistry is now developing.

References and Notes

1. Organosilicon compounds of high molecular weight are, however, well known in the form of the siloxanes, whose catenated structures are based on alternating silicon and oxygen atoms; these are the silicone polymers of commerce.
2. The first polysilanes to be systematically studied bore aromatic rings as substituents. In classic researches early in this century, F. S. Kipping prepared compounds such as hexaphenyldisilane ($Ph_3SiSiPh_3$) and octaphenylcyclotetrasilane [$(Ph_2Si)_4$]. The chemistry and physics of arylpolysilanes tends however to be dominated by the aromatic rings, so that the special properties of the catenated silicons are masked. For further information on these compounds H. Gilman and G. L. Schwebke, *Adv. Organometal. Chem.* **1**, 89 (1964); *J. Am. Chem. Soc.* **86**, 2613 (19 *J. Organometal. Chem.* **3**, 382 (1965).
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19. The pattern of Si-Si bonding MO's in these molecules is exactly like that observed for the pi energy levels in the aromatic species cyclopentadienide ($C_5H_5^-$) and benzene. This coincidence arises because the splitting of MO's is symmetry dependent and the symmetries of the polysilanes and the aromatic molecules are sufficiently similar (see Fig. 6).

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43. Supported by the Air Force Office of Scientific Research (NC), Office of Aerospace Research, USAF, grant AF-AFOSR 70-1904; research at Southwest Minnesota State College has been supported by partial grants from the Research Corporation and the donors of the Petroleum Research Fund, administered by the American Chemical Society.

Exploring Cells with a Centrifuge

Christian de Duve

In one of her masterpieces, Nobel Laureate Selma Lagerlöf tells how the little boy Nils Holgersson visited the whole of Sweden, from Skåne to Lappland, on the wings of a friendly white gander. I too have made a wonderful journey, using, like Nils Holgersson, an unconventional mode of travel. For the last 25 years, I have roamed through living cells, but with the help of a centrifuge rather than of a microscope.

On these trips I was never alone. I want to mention this at the onset, since I owe much to my traveling companions. Some of their names will come up as my tale unfolds; but there are so many of them that I will be quite unable to mention them all. My debt goes also to my early mentors in science: Joseph Bouckaert, Joseph Maisin, Hugo Theorell, Carl and Gerty Cori, and Earl Sutherland. Four of them have preceded me on this podium. Three, unfortunately, are not with us any longer.

The Development of Analytical Cell Fractionation

Thirty years ago, much of the living cell still remained virtually unexplored. The reasons for this are simple. Morphological examination was limited downward in the scale of dimensions by the resolving power of the light microscope, whereas chemical analysis stopped upward at the size of the smaller macromolecules. In between, covering almost two orders of magnitude, lay a vast *terra incognita*, impenetrable with the means of the day. Invasion of this terri-