

ELECTRON DELOCALIZATION AND "AROMATIC" BEHAVIOR IN CYCLIC POLYSILANES

Robert West

Department of Chemistry, University of Wisconsin, Madison, WI
53706 USA

Abstract--The cyclic permethylpolysilanes $(\text{Me}_2\text{Si})_n$ and other cyclic alkylpolysilanes have some properties which resemble those of aromatic hydrocarbons: they have strong ultraviolet absorption bands, form electron delocalized anion- and cation-radicals, give charge-transfer complexes with π acceptors, and show substituent effects on disubstitution. The nature of chemical bonding responsible for these effects in polysilanes is discussed.

INTRODUCTION

In recent years we have been studying the chemistry of polysilanes, especially the cyclic polysilanes (1). In these compounds the skeleton is made up entirely of catenated silicon atoms, bonded to other substituents such that their total covalence is four. Although the myth that silicon is not capable of extensive catenation still persists, very large cyclic polysilanes have been synthesized as well as polysilane polymers with molecular weights in the hundreds of thousands (2). These compounds generally are very stable thermally and rather unreactive chemically.

Our interest in chemical bonding in cyclosilanes arose when it was discovered that linear permethylpolysilanes show strong electron absorption bands in the accessible region of the ultraviolet (3). Since these compounds contain only sigma bonding electrons, this finding was quite surprising at the time. Moreover the absorption bands shift to lower energy and become more intense as the polysilane chain becomes longer (Table 1). This behavior is reminiscent of that found for conjugated polyenes, and indeed the same electron-in-a-box model can be used to treat both classes of compounds. However for the permethylsilanes a wavelength limit of about 300 nm is reached for very long chains (4).

A typical example of a cyclosilane is the five-membered ring compound, decamethylcyclopentasilane, $(\text{Me}_2\text{Si})_5$. The cyclosilanes contain only sp^3 hybrid silicon atoms and are therefore structural analogs of saturated alicyclic hydrocarbons. Nevertheless, they show a variety of properties indicative of extensive electron delocalization, and somewhat resembling those of aromatic hydrocarbons. These special properties, and the reasons underlying them, are the subject of this paper.

Synthesis of cyclosilanes

The cyclosilanes are generally prepared by condensation reactions of diorganodihalosilanes. This reaction has been particularly well studied for the case of dimethyldichlorosilane and sodium-potassium alloy (5). With excess NaK an equilibrium mixture is produced consisting of about 9% $(\text{Me}_2\text{Si})_5$, 90% $(\text{Me}_2\text{Si})_6$ and 1% $(\text{Me}_2\text{Si})_7$ (at $\sim 45^\circ$) (5). When the reaction is carried out under kinetically-controlled conditions, the amount of $(\text{Me}_2\text{Si})_6$ is reduced to about 50%; the proportions of $(\text{Me}_2\text{Si})_5$ and $(\text{Me}_2\text{Si})_7$ are somewhat increased; and the reaction mixture contains medium and large rings, including all of the $(\text{Me}_2\text{Si})_n$ oligomers from $n = 5$ up to $n = 35$ (6).

Similar condensation reactions from organosilyl chlorides produce the diphenylsilane oligomers, $(\text{Ph}_2\text{Si})_n$ with $n = 4, 5$ and 6 (7), and the diethyl compounds $(\text{Et}_2\text{Si})_n$ with $n = 4$ through 8 (8). Cyclosilanes with two different organic groups on the silicon can be made similarly, for instance the oligomers $(\text{PhMeSi})_n$ ($n = 5, 6, 7$) and $(\text{tBuMeSi})_n$ ($n = 4, 5$); these compounds

TABLE 1. Ultraviolet spectra of linear permethylpolysilanes (3,4)

<u>n</u>	<u>λ</u>	<u>ε</u>
2	198	8,000
3	215	9,020
4	235	14,700
5	250	18,400
6	220 sh 260	14,000 21,100
8	215 sh 240 272	29,000 18,000 38,000
10	215 sh 230 sh 255 sh 279	28,200 21,000 24,600 42,700
12	221 sh 264 285	43,000 43,500
18	225 sh 270 291	39,800 44,300
24	210 228 293	28,000 27,800 45,500

are formed as mixtures of isomers, which in some cases have been separated and identified.

The cyclosilanes are colorless crystalline compounds, with relatively high melting points. Crystal structure studies show that $(\text{Me}_2\text{Si})_6$ and all-trans $(\text{PhMeSi})_6$ both have a chair conformation like that of cyclohexane (9,10), whereas all-trans $(\text{tBuMeSi})_4$ has a folded, butterfly conformation like that of cyclobutane (11). Nevertheless all three of these compounds, and indeed all of the known $(\text{Me}_2\text{Si})_n$ rings, show only singlets for the methyl groups in their proton and ^{13}C NMR spectra. It follows that rapid interconversion takes place between equivalent chair forms in, for example, $(\text{Me}_2\text{Si})_6$.

UV spectra and ionization potentials

The ultraviolet spectra of the $(\text{Me}_2\text{Si})_n$ and $(\text{Et}_2\text{Si})_n$ series are quite important for the understanding of the electronic structure of these molecules. They show a quite unexpected trend of hypsochromic shifts with increasing ring size. The longest wave-length absorption is found for the four-membered rings, $(\text{Et}_2\text{Si})_4$ and $(\text{tBuMeSi})_4$ (12) and as the ring size increases the absorption bands shift to higher energy (13,14). However at $n = 6$ for the diethyl or $n = 7$ for the dimethyl compounds, the hypsochromic shift is reversed. With further increase in ring size the absorption bands are bathochromically shifted, as expected by analogy with the linear polysilanes. Beyond $n = 10$ the bands for the dimethyl compounds change in a quite regular way, gradually moving to longer wavelength and becoming more intense as the ring size increases to $n = 24$ (6). Representative data and spectra are shown in Figs. 1 and 2 and Table 2.

To explain the electronic absorption and other properties of the cyclosilanes, it is important to have some knowledge of their ionization potentials. Vertical ionization potentials have been determined for a few compounds, mainly by Bock and his group, by photoelectron spectroscopy (15). Data for $(\text{Me}_2\text{Si})_5$ and $(\text{Me}_2\text{Si})_6$ are shown in Fig. 3. The low-energy ionizations all involve Si-Si σ -bonding electrons; these must also be the electrons excited in the ultraviolet transitions. Because of the symmetries of

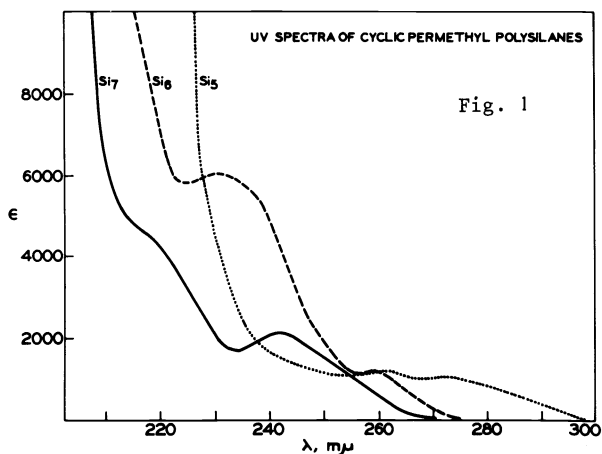


Fig. 1. UV spectra of permethylcyclosilanes
 ... (Me₂Si)₅; --- (Me₂Si)₆; — (Me₂Si)₇

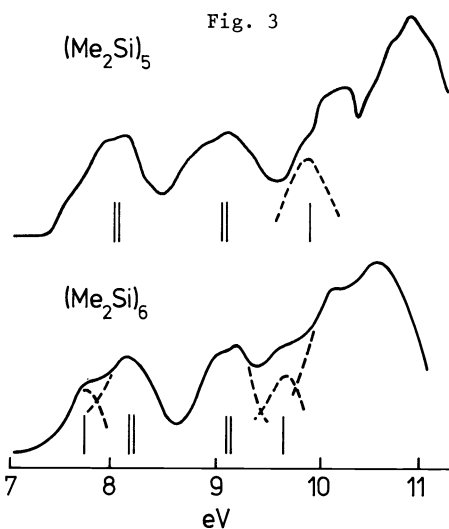
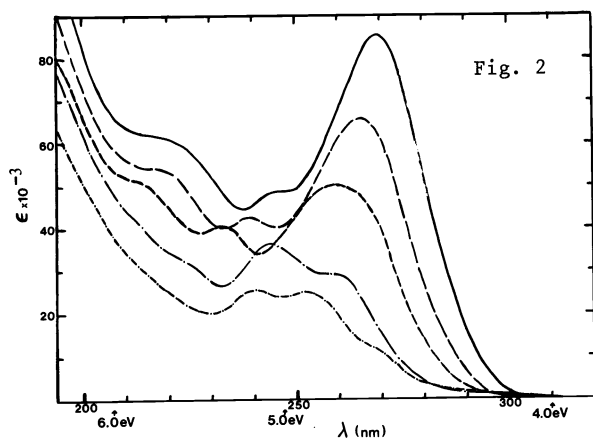


Fig. 3
 Photoelectron spectra and assignments
 for (Me₂Si)₅ (above) and (Me₂Si)₆ (below)

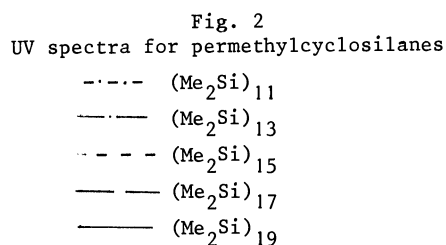


TABLE 2. UV maxima for permethylcyclosilanes, (Me₂Si)_n (6)

n	λ (nm)	ε	n	λ (nm)	ε	
4 ^a	304	180	9	242	13,750	
	228(sh)	14,000		230	17,700	
	211(sh)	23,000		208(sh)	29,000	
5	275(sh)	700	10	285(sh)	3,400	
	264(sh)	800		267(sh)	8,200	
	220	22,600		255	29,800	
	210	24,000		240	17,000	
6	258(sh)	1,100	11	222	17,300	
	240	5,400		205	32,600	
	232	5,900		12	290(sh)	1,700
	197	43,800			268(sh)	12,000
7	249	3,600	252		25,000	
	239	4,600	239		25,400	
	220(sh)	9,200	220(sh)	25,000		
	192	62,000	212(sh)	32,100		
8	246(sh)	7,600	12	288(sh)	1,200	
	235	12,900		266(sh)	16,400	
	212(sh)	18,800		248	33,000	
	193(sh)	91,500		231	29,200	
			211(sh)	39,800		

^aData for (Et₂Si)₄.

these rings, the bonding orbitals are split according to patterns resembling the orbital patterns of aromatic hydrocarbons: 2:2:1 for $(\text{Me}_2\text{Si})_5$ and 1:2:2:1 for $(\text{Me}_2\text{Si})_6$.

Anion-radicals

One way in which the cyclosilanes resemble aromatic compounds is in their formation of anion-radicals. When reduced either electrochemically or in some cases with alkali metals, many cyclosilanes capture electrons to form brightly-colored anion-radicals somewhat resembling the well-known anions of naphthalene, anthracene, etc. For the polysilane anion-radicals, as for their aromatic counterparts, ESR spectroscopy is most useful in elucidating the electron distribution in the LUMO.

As examples, ESR spectra for anion-radicals of $(\text{Me}_2\text{Si})_5^-$ and $(\text{Et}_2\text{Si})_5^-$ are shown in Fig. 4. For $(\text{Me}_2\text{Si})_5$, and indeed for all methylcyclosilane anion-

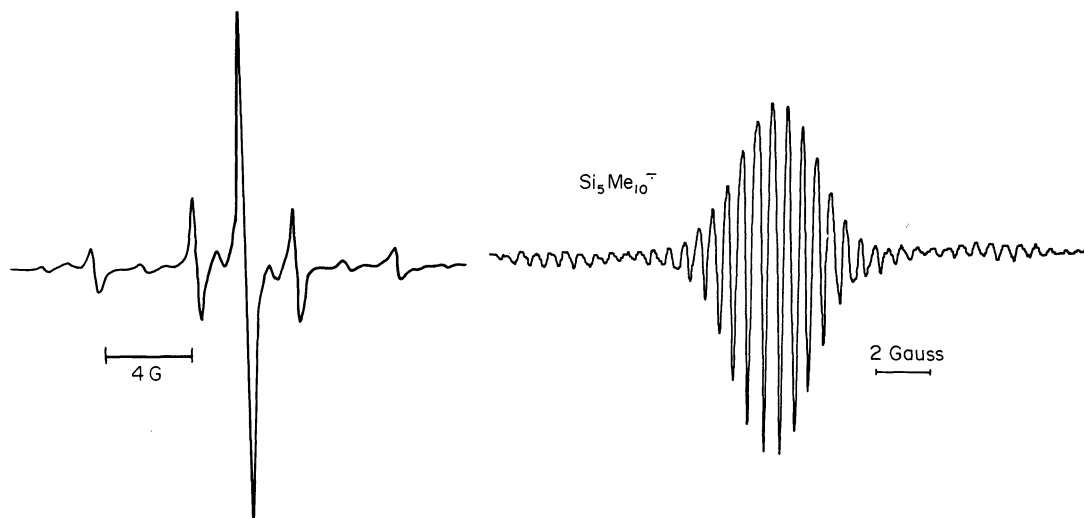


Fig. 4. Electron spin resonance spectra for anion-radicals $(\text{Me}_2\text{Si})_5^-$ (left) and $(\text{Et}_2\text{Si})_5^-$ (right).

radicals, hyperfine splitting for protons is observed (13). The line intensities indicate equal contact with all protons in the molecule, consistent with complete delocalization of the unpaired electron over the rings, exactly as in aromatic anion-radicals (for example, benzene).

Remarkably, the diethylcyclosilane anion-radical $(\text{Et}_2\text{Si})_5^-$ shows no observable proton hyperfine splitting, as seen from Fig. 4 (14). The reason for this difference between the ethyl and methyl compounds is not understood; it is however possible that the conformations of the permethyl and perethyl rings are quite different. The arylcyclosilane anion-radicals also show no proton hyperfine splitting (16).

Properties of some cyclosilane anion-radicals are listed in Table 3. For several of these species, ^{29}Si splitting constants can be determined. These values are significant because they can be calculated independently, according to the method of Symons (17). If the unpaired electron were in an orbital of pure π type, the only coupling to ^{29}Si would be by spin-polarization. The splitting due to spin-polarization is calculated to be 5-6 G, just about the value found for these anion-radicals. If there were appreciable Fermi contact between the electron and the ^{29}Si nucleus, as would be the case if the electron were in an orbital with significant s orbital contribution, the splitting constants should be much larger. We interpret these

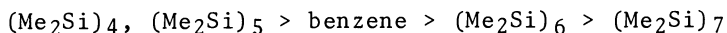
TABLE 3. ESR of some cyclosilane anion-radicals

Anion Radical	g Value	(Splitting Constants(gauss))			Color	Ref
		²⁹ Si	¹³ C	¹ H		
(Me ₂ Si) ₄ ⁻	2.0037	<10	20.97	0.67	blue	1
(Me ₂ Si) ₅ ⁻	2.0032	6.13	16.03	0.53	blue	13
(Me ₂ Si) ₆ ⁻	2.0028	-	14.60	0.44	yellow	13
(Et ₂ Si) ₅ ⁻	-	4.55	13.96 ^a	<0.1	blue	-
(Ph ₂ Si) ₄ ⁻	2.0046	4.4	13.1	<0.1	yellow	16
(Ph ₂ Si) ₅ ⁻	2.0046	3.6	10.0	<0.07	yellow	16

a ¹³CH₃, 2.45 G.

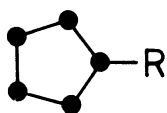
results as showing that the half-filled orbital must be made up almost entirely from p or d atomic orbitals on silicon (13).

The reduction potentials for the cyclosilanes are not known, but relative potentials can be determined by competitive experiments. For the methyl series the order of decreasing ease of reduction is:

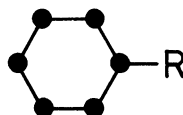


The usually easy reduction of the four- and five-membered rings correlates with the long wave length or absorption shown by the same compounds. Both indicate a low energy for the LUMO in these smaller rings. The underlying reasons are not clear, but may have to do with ring conformations affecting overlap of silicon σ^* (or 3d) orbitals. The conformations for (Me₂Si)₄ and (Me₂Si)₅ are not known, but from structures of analogous compounds it seems certain that they are more nearly planar than the larger rings (18). We propose that overlap of antibonding orbitals on neighboring silicon atoms is favored when they are (nearly) coplanar, leading to a decrease in the excited-state and LUMO energy.

Many substituted cyclosilanes have been made, and quite a few have now been reduced to anion-radicals. Monosubstitution of a methyl group with some other group breaks the symmetry, so that the methyl proton splitting constants become different. In compounds of type 1, five different proton splitting constants are possible.



1a, R = Me₃Si
 1b, R = PhCH₂
 1c, R = Ph
 1d, R = H



2a, R = PhCH₂
 2b, R = Ph

(Dots represent silicon atoms with attached methyl groups sufficient to bring the valence to 4.)

The expected result is overlap of the splittings leading to a single broad ESR line, as observed for 1a (Fig. 5) (19). However for many substituted cyclosilanes, the couplings remain quite closely similar so that they can be resolved. An example is the benzyl-substituted cyclopentasilane, 1b. As seen in Fig. 5, the anion-radical has an ESR spectrum typical for a cyclosilane. A similar ESR spectrum with partial resolution of proton hyperfine splitting is also observed in the anion-radical of the phenyl-substituted compound 1c.

The ESR spectra for 1b and 1c show, among other things, that the unpaired electron is principally associated with the orbitals of the polysilane ring,

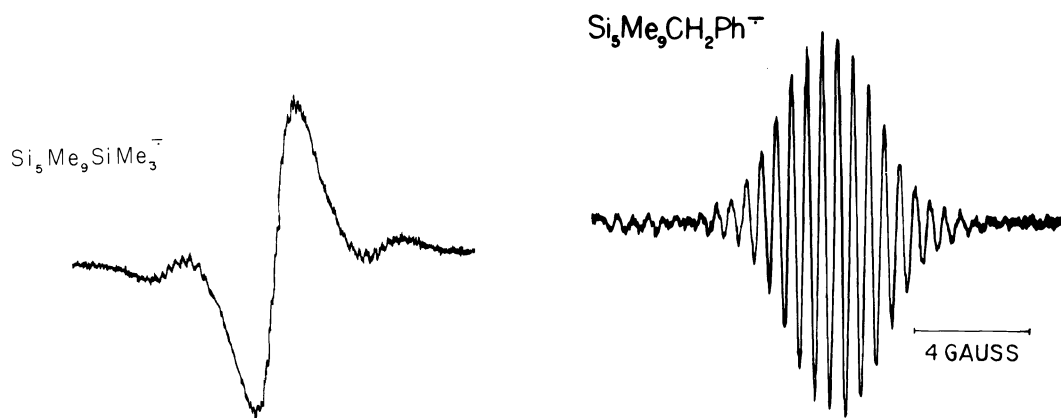


Fig. 5. Electron spin resonance spectra for anion-radicals of cyclo-Si₅Me₉SiMe₃ (**1a**) (left) and cyclo-Si₅Me₉CH₂Ph (**1b**) (right).

and not with the benzene rings. However when the same substituents are attached to the six-membered cyclosilane ring in **2a** or **2b**, the anion-radicals show a totally different ESR spectrum characteristic of a substituted benzene (20). These findings are quite consistent with the observations that (Me₂Si)₅, but not (Me₂Si)₆, is reduced preferentially to benzene (13).

An interesting example of a cyclosilane anion-radical is that from the monohydrogen derivative **1d**. The spectrum shown in Fig. 6 is split into a doublet by coupling with the silicon-bound hydrogen. Further hyperfine coupling is observable in each half of the doublet. Upon detailed examination the spectrum cannot be interpreted on the basis of equal coupling by all of the methyl protons. However the spectrum can be simulated as a superposition of 1.02 Gauss coupling by the 3 protons of the unique methyl group, and (coincidentally equivalent) 0.51 Gauss coupling by the other 24 protons (19). The partly filled orbital in this anion-radical therefore appears to be highly polarized by the hydrogen substituent. Similar polarization is well-known in substituted hydrocarbon anion-radicals.

Charge-transfer complexes and cation-radicals

Because they have relatively low ionization potentials, polysilanes can also serve as electron donors. Such electron donation is observed in the formation of charge transfer complexes between polysilanes and electron deficient pi acids (21,22). For instance, (Me₂Si)₆ forms a green complex with chloranil and a purple complex with tetracyanoethylene (TCNE). These complexes are unusual in that charge is donated from delocalized sigma electrons of the silicon-silicon bonds.

The energies of the CT bands correlate well with the ionization energies of polysilanes. The visible spectrum of the (Me₂Si)₆-TCNE complex is shown in Fig. 7. Note that the charge-transfer absorption can be deconvoluted into two bands; from their relative energies these can be assigned to charge-transfer from the first and second highest occupied orbitals in (Me₂Si)₆.

It should be mentioned that linear polysilanes, as well as cyclic molecules, will serve as electron-donors in charge-transfer complexes. The analogy with polyenes is good here also, since linear as well as cyclic polyenes can similarly form CT complexes. Figure 7 shows the CT complex for the linear

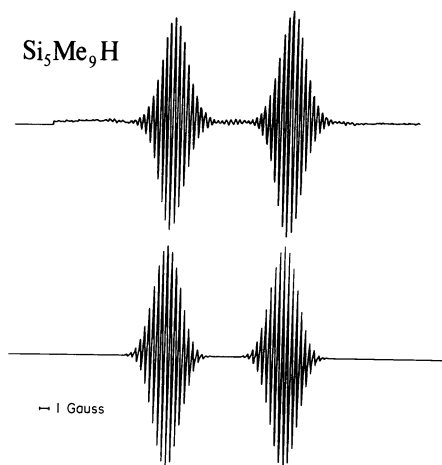


Fig. 6. Electron spin resonance spectrum of anion-radical of cyclo- $\text{Si}_5\text{Me}_9\text{H}$, **1d** (above). Computer-simulated spectrum (below).

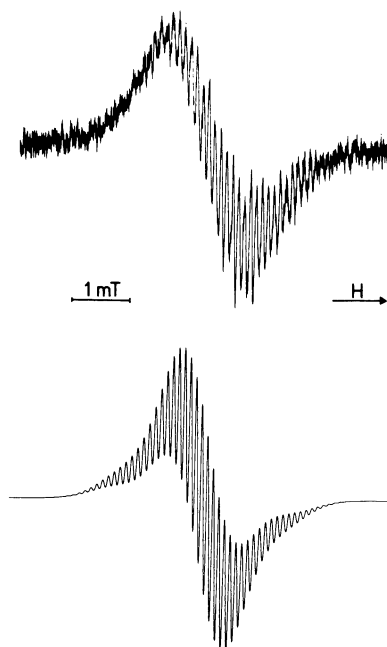


Fig. 8. Electron spin resonance spectrum of cation-radical $(\text{Me}_2\text{Si})_6^+$ (above). Computer-simulated spectrum (below).

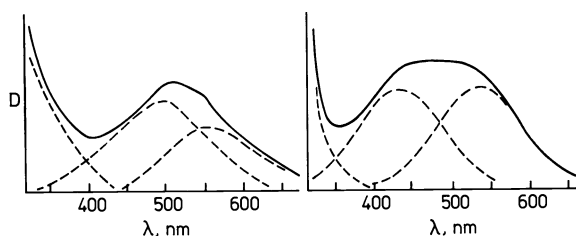


Fig. 7. Visible spectrum of charge-transfer complex of TCNE with $(\text{Me}_2\text{Si})_6$ (left) and with $\text{Me}(\text{SiMe}_2)_6\text{Me}$ (right).

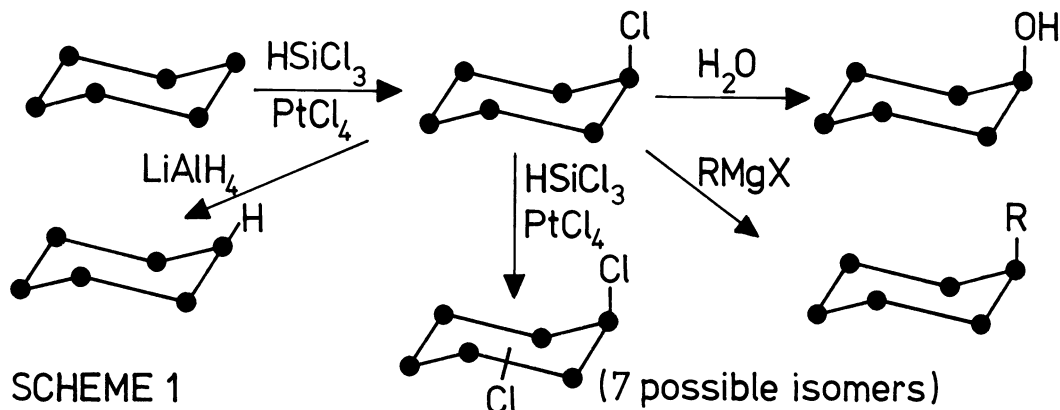
compound $\text{Me}(\text{SiMe}_2)_6\text{Me}$ with TCNE. The absorption evidently contains two maxima, which can be used to estimate the energy of the first two ionizations, predicted by theory but not yet observed.

Certain polysilanes will also give up an electron completely, to form a cation-radical, when oxidized with aluminum chloride in dichloromethane. It is apparently necessary that the polysilane have an ionization potential below ~ 7 eV for a cation-radical to form under these conditions. Such cations, with a singly occupied HOMO, have been observed for **1a**, $(\text{Me}_2\text{Si})_6$, and $(\text{tBuMeSi})_4$ (23). These species have been studied by ESR spectroscopy, but only for $(\text{Me}_2\text{Si})_6$ was a resolved spectrum obtained (Fig. 8). The spectrum is best simulated by assigning two different coupling constants, in a ratio of 3:1, to the axial and equatorial protons. It therefore appears that for $(\text{Me}_2\text{Si})_6^+$, unlike the corresponding anion-radical and neutral molecule, equilibration between equivalent chair forms is slow, at least on the ESR time scale. Further research on these poorly understood polysilane cation-radicals seems highly desirable.

Substitution reactions

Polysilanes are of course very different structurally from true polyene aromatic compounds, and their substitution chemistry bears little resemblance to that of benzenoid hydrocarbons. Nevertheless it is interesting to examine substitution reactions of the polysilanes to see if substituent effects may exist paralleling those so well known in benzene chemistry.

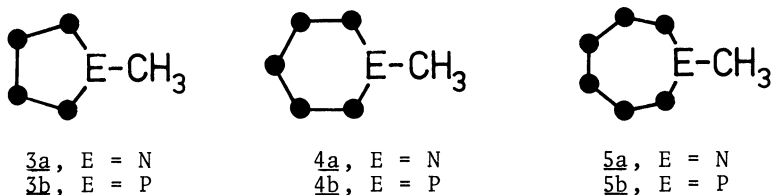
A convenient way to introduce functionality into a peralkylpolysilane is by substituting chlorine for an alkyl group. This may be accomplished with HCl and AlCl_3 , but the reaction is cleaner when carried out using trichlorosilane and platinum tetrachloride (24). The resulting chloro compound is easily converted to other monosubstituted derivatives, as shown in Scheme 1. The chlorodemethylation may be continued to give dichloro and eventually polychloro compounds; exhaustive reaction leads to the hexachloro derivative $(\text{MeSiCl})_6$.



There are seven possible isomers of a disubstituted cyclohexasilane. When the chlorodemethylation of $(\text{Me}_2\text{Si})_6$ is carried out to the disubstitution stage, an isomer mixture is produced. The isomers have not been completely separated, but analysis of the NMR spectra of isomer mixtures indicates the presence of four of the seven possible isomers, in approximate ratio 4:2:2:1 (24). The identity of the isomers is also not known, but the most abundant product is probably the 1,4-trans compound. Although the knowledge of these isomers is in a very early stage, it seems that there is a marked effect of the first chlorine on the position of substitution by the second, reminiscent of substituent effects in benzenoid compounds.

Heterosubstituted cyclosilanes

The unusual properties of the alkylcyclosilanes are attributed to cyclic delocalization of electrons, either in the sigma bonding framework or in the LUMO. What is the effect of introducing a heteroatom into the ring? Evidence is incomplete but one study involving the nitrogen- and phosphorus-containing rings 3-5 is pertinent to this question (25). The nitrogen com-



pounds, 3a-5a, show ultraviolet spectra which are quite unlike those of cyclic polysilanes. Instead, they resemble the spectra observed for linear polysilanes, slowly shifting bathochromically as the number of silicon atoms increases, as if the nitrogen atom were not present. Independent observations show that oxygen atoms and CH_2 groups also interrupt the sigma-delocalization, in that UV bands characteristic of cyclopolysilanes are not observed for these compounds.

The phosphorus compounds 3b-5b, on the other hand, show long-wavelength bands which shift hypochromically as ring size increases from 5 to 7, just like the cyclopolysilanes themselves (Fig. 9). Thus phosphorus seems to participate in sigma-delocalization, at least in the excited states of these molecules. Perhaps phosphorus has orbitals of appropriate energy and symmetry to contribute to the LUMO, whereas nitrogen does not.

Chemical bonding and "aromaticity"

We see that cyclopolysilanes have a number of properties which resemble those of the well-known polyene aromatics. Because they have delocalized, filled orbitals at relatively high energy and unfilled orbitals at relatively low energy, the cyclosilanes, like aromatics, can be either donors or acceptors of electrons. The relative orbital energies for $(\text{Me}_2\text{Si})_5$, $(\text{Me}_2\text{Si})_6$ and benzene are shown in a crude orbital correlation diagram in Fig. 10.

It is appropriate to ask if the cyclosilanes have other properties similar to those of true "aromatic" compounds. There is no reason to believe that they are unusually stable, compared, say, to the linear polysilanes. By a

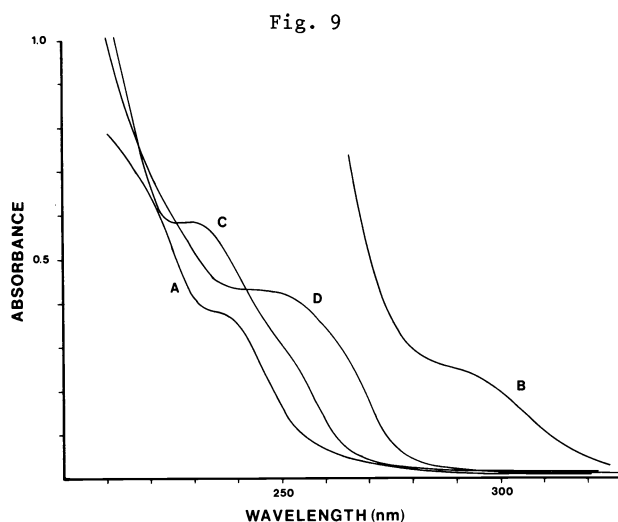


Fig. 9. Ultraviolet spectra of phosphacyclosilanes.
 A, $\text{MeP}(\text{SiMe}_2)_4$, 6.36×10^{-4} M; B, $\text{MeP}(\text{SiMe}_2)_4$, 3.85×10^{-3} M;
 C, $\text{MeP}(\text{SiMe}_2)_5$, 9.66×10^{-4} M; D, $\text{MeP}(\text{SiMe}_2)_6$, 6.00×10^{-4} M.

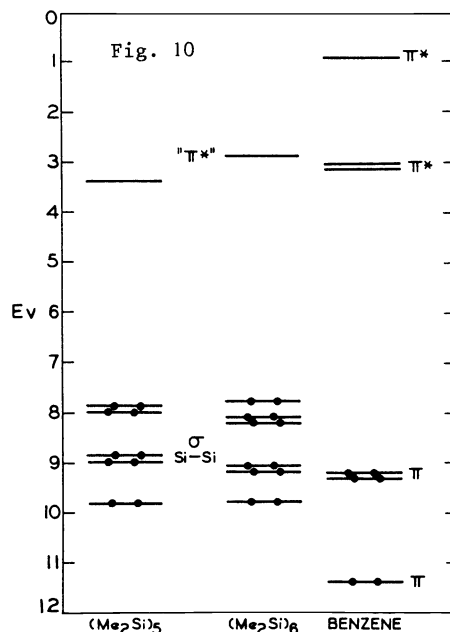


Fig. 10. Simple orbital correlation diagram for $(\text{Me}_2\text{Si})_5$,
 $(\text{Me}_2\text{Si})_6$ and benzene.

thermochemical criterion, the cyclosilanes are almost surely "non-aromatic", like the cycloalkanes.

Another test of "aromaticity" is the ability to sustain a diamagnetic ring current. Ring current effects have been invoked to explain small NMR deshielding in cyclopropanes (26), and because the ionization potentials for the silicon-silicon bonding electrons are rather low, a ring current in the sigma system might conceivably be observable in these molecules. The evidence here is not clear. Alkylpolysilanes lack hydrogens in the plane of the ring, which would be expected to be fully deshielded by any diamagnetic ring current. The only protons are on methyl groups which are angular to the ring; they show no significant chemical shifts which might be evidence for a ring current. It might be better to study hydrogens directly bound to silicon, but for such protons factors determining chemical shifts are not well established. The ^{29}Si chemical shifts for $(\text{Me}_2\text{Si})_6$ and especially $(\text{Me}_2\text{Si})_5$ show deviations otherwise unaccounted for, which might be due to ring current effects (27).

At present our bonding model for the ground states of cyclopolysilanes, though rudimentary, is helpful in correlating quite a lot of information about these molecules. Almost nothing is yet known about the excited states of this fascinating class of substances. It is to be hoped that spectroscopic experiments now underway will expand our knowledge into this unknown territory.

REFERENCES

1. R. West and E. Carberry, *Science*, **189**, 179-186 (1975).
2. R. West, L. D. David, P. I. Djurovič, K. L. Stearley, K. S. V. Srinivasan and H. Yu, *J. Am. Chem. Soc.*, in press.
3. H. Gilman, W. H. Atwell and G. L. Schwebke, *J. Organomet. Chem.*, **2**, 369-371 (1964).

4. W. Boberski and A. L. Allred, J. Organomet. Chem., 88, 65-72 (1975).
5. L. F. Brough and R. West, J. Organomet. Chem., 194, 139-145 (1980).
6. L. F. Brough and R. West, J. Am. Chem. Soc., 103, 3049-3056 (1981).
7. E. Hengge, J. Organomet. Chem. Library, 4, 261-294 (1979).
8. C. W. Carlson, K. Matsumura and R. West, J. Organomet. Chem., 194, C5-C6 (1980).
9. B. H. Carrell and J. Donohue, Acta Cryst. B, 28, 1566-1571 (1972).
10. L. D. David, R. West and K. J. Haller, in press.
11. C. J. Hurt, J. C. Calabrese and R. West, J. Organomet. Chem., 41, 273-278 (1975).
12. M. Biernbaum and R. West, J. Organomet. Chem., 131, 179-188 (1977).
13. E. Carberry, R. West and G. E. Glass, J. Am. Chem. Soc., 91, 5446-5451 (1969).
14. C. W. Carlson and R. West, unpublished.
15. H. Bock and W. Ensslin, Angew. Chem. Int. Ed. Engl., 10, 404-405 (1971).
16. M. Kira, H. Bock and E. Hengge, J. Organomet. Chem., 164, 277-280 (1979).
17. T. F. Hunter and M. C. R. Symons, J. Chem. Soc. A, 1770-1773 (1967).
18. R. West, Comprehensive Organometallic Chemistry, Ch. 9.4, Pergamon Press, Oxford (1982).
19. R. West and E. S. Kean, J. Organomet. Chem., 96, 323-330 (1975).
20. A. C. Buchanan III and R. West, J. Organomet. Chem., 172, 273-283 (1979).
21. V. F. Traven and R. West, J. Am. Chem. Soc., 95, 6824-6826 (1973).
22. H. Sakurai, M. Kira and T. Uchida, J. Am. Chem. Soc., 95, 6826-6827 (1973).
23. H. Bock, W. Kaim, M. Kira and R. West, J. Am. Chem. Soc., 101, 7667-7670 (1979).
24. B. J. Helmer and R. West, unpublished research.
25. T. H. Newman, R. West and R. T. Oakley, J. Organomet. Chem., 197, 159-168 (1980).
26. D. J. Patel, M. E. H. Howden and J. D. Roberts, J. Am. Chem. Soc., 85, 3218-3223 (1963).
27. D. A. Stanislawski and R. West, J. Organomet. Chem., 204, 295-305 (1981).