Cyclic Polysilanes. VI. Bicyclic and Cage Permethylcyclopolysilanes[1,2]

Robert West* and Andris Indriksons

Contribution from the Department of Chemistry, the University of Wisconsin, Madison, Wisconsin 53706. *Received October 21, 1971*

Abstract: Dimethyldichlorosilane and methyltrichlorosilane react with sodium–potassium alloy in the presence of naphthalene in tetrahydrofuran to yield bicyclic and cage polysilanes, Si_8Me_{14}, Si_9Me_{16}, $Si_{10}Me_{16}$, $Si_{10}Me_{18}$, $Si_{11}Me_{18}$, and $Si_{13}Me_{22}$. The photolysis of Si_8Me_{14} in cyclohexane yields Si_7Me_{12}. Structural evidence for these compounds is presented. Anion radicals formed by reduction of several of the polycyclopolysilanes were studied by esr spectroscopy.

Earlier we have reported the synthesis of the series of permethylcyclopolysilanes, $(SiMe_2)_n$ where $n = 5–8$,[3] and the reduction of the five- and six-membered rings to stable anion radicals in which the unpaired electron is fully delocalized over the ring.[4] Subsequent work elsewhere has led to the preparation of Si_4Me_8,[5] $Si_5[(CH_3)_2CHCH_2]_{10}$,[6] and the entire series of mixed silicon–germanium cyclics, $Me_{10}Si_xGe_{5-x}$, $Me_{12}Si_yGe_{6-y}$, and $Me_{14}Si_zGe_{7-z}$.[7]

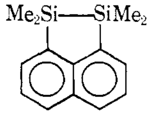
The usual method of synthesis of cyclopolysilanes invovles reductive condensation of a dialkyldihalosilane with an alkali metal. If an alkyltrihalosilane is added in place of some of the R_2SiX_2, cocondensation to form cage polysilanes is possible; but as expected, the cocondensation is much more difficult to effect. In 1970 we communicated the synthesis of the first cage polysilane, tetradecamethylbicyclo[2.2.2]octasilane, Si_8Me_{14}.[1] The synthetic procedure has now been substantially improved, and we report here the isolation of six other polycyclopolysilanes along with a discussion of the spectral properties, probable structures, and the electrolytic and chemical reduction of several of these new compounds.

Ishikawa and Kumada have shown that upon photolysis, the six-membered ring Si_6Me_{12} extrudes dimethylsilene[8] and is converted to Si_5Me_{10}, Si_4Me_8, Si_4Me_8O, and polymer.[5] We have investigated the photolysis of two polycyclopolysilanes. Irradiation of $Si_{10}Me_{18}$ led only to polymer, but Si_8Me_{14} yielded Si_6Me_{12}, Si_5Me_{10}, and a new bicyclopolysilane, Si_7Me_{12}.

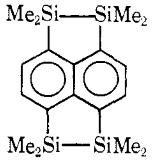
Synthesis. Methyltrichlorosilane and dimethyldichlorosilane were condensed with sodium–potassium alloy in tetrahydrofuran (THF) in the presence of naphthalene.

$$Me_2SiCl_2 + MeSiCl_3 + NaK \xrightarrow[\text{naphthalene}]{\text{THF}} (MeSi)_n(Me_2Si)_m + Na(K)Cl$$

This reaction is deceptively simple; unless very specific reaction conditions are employed only high molecular weight polymers are obtained. A major problem is that methyltrichlorosilane reacts with tetrahydrofuran to give siloxane polymers. A wide variety of other solvents were tried, but successful chlorosilane condensation reactions were observed only in tetrahydrofuran. In diethyl ether, isopropyl ether, *tert*-butyl ether, diglyme, dioxane, cyclohexane, benzene, toluene, *N*-methylmorpholine, ammonia, triethylamine, dimethyl sulfoxide, and acetonitrile, only siloxanes and polymers were formed. When 1,2-dimethyoxyethane (glyme) was used as a solvent, reduction of naphthalene occurred yielding 10% each of the known $C_{10}H_6(SiMe_2)_2$[9] (I) and the new compound $C_{10}H_4(SiMe_2)_4$ (II). (See Experimental Section for discussion of I and II.)



I



II

In 2,2,4,4-tetramethyltetrahydrofuran as solvent a 10% yield of II was obtained along with a trace of Si_8Me_{14}.

When other active metals such as magnesium, lithium wire, and lithium dispersion were substituted for Na–K alloy, no polycyclopolysilanes were obtained, and only polymers were formed.

Earlier work in this laboratory[3] has shown that Na–K alloy in the presence of naphthalene cleaves polysilane polymers, yielding cyclic polysilanes. The presence of naphthalene was crucially necessary for the success of the $MeSiCl_3$–Me_2SiCl_2 condensation reaction; in its absence only high polymer was formed. Napthalene probably functions as an electron carrier in the reaction, undergoing reduction to the anion radical and then transferring an electron to a chlorosilane or to a polysilane chain. When other polycyclic aromatic hydrocarbons such as biphenyl and anthracene were substituted for naphthalene, the reaction yielded only polymers.

Once the reaction conditions were established, a severe problem of purification was encountered. The bicyclopolysilane products are highly comtaminated with siloxanes of similar molecular weight and vapor pressure. It proved necessary to vacuum distill the crude reaction mixture taking fractional cuts every 30°.

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[1] Previous paper in this series: A. Indriksons and R. West, *J. Amer. Chem. Soc.*, **92**, 6704 (1970).

[2] This work was sponsored by the Air Force Office of Scientific Research (NC), Office of Aerospace Research, USAF Grant No. AF-AFOSR-70-1904.

[3] E. Carberry and R. West, *J. Amer. Chem. Soc.*, **91**, 5440 (1969).

[4] E. Carberry, R. West, and G. E. Glass, *ibid.*, **91**, 5446 (1969).

[5] M. Ishikawa and M. Kumada, *Chem. Commun.*, 612 (1970).

[6] G. R. Husk, R. Wexler, and B. M. Kileulen, *J. Organometal. Chem.*, **29**, C49 (1971).

[7] E. Carberry and B. Dombek, *ibid.*, **22**, C43 (1970).

[8] M. Ishikawa and M. Kumada, *Chem. Commun.*, 489 (1971).

[9] I. G. Makarov, V. M. Kazakova, N. G. Tolstikova, and E. A. Chernyshev, *Zh. Strukt. Khim.*, **10**, 495 (1969).

Table I. Yield, Mass Spectra, Melting Point, and Gas Chromatography Retention Time of Cage Polysilanes

Polysilane	Yield, %	Exptl mass	Calcd mass	Mp, °C	Gas chromatography retention time, min
Si_8Me_{14}	5.0	434.1439 ± 0.0043	434.1440	>360	8
Si_9Me_{16}	2.0	492.1673 ± 0.0020	492.1679	279	18
$Si_{10}Me_{16}$	0.5	520.1500 ± 0.0050	520.1449	>360	25
$Si_{10}Me_{18}$	4.0	550.1955 ± 0.0050	550.1918	195	34
$Si_{11}Me_{18}$	0.5	578.1678 ± 0.0020	578.1687		49
$Si_{13}Me_{22}$	0.1	694.2130 ± 0.0040	694.2165		54
Si_6Me_{12}	10.0				
Polymer	78.0				

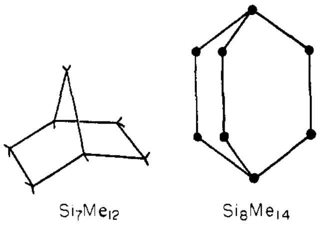

Figure 1. Proposed structure of Si_7Me_{12} and Si_8Me_{14}. The silicon skeleton only is shown.

The bicyclopolysilanes present in these cuts were separated by preparative gas chromatography, recrystallized from an ether–acetone mixture, and sublimed. In most cases this gave a pure product free of siloxane contamination.

Structures. The molecular formulas were established by high resolution mass spectroscopy (Table I). The compounds were shown to be polysilanes, free of siloxane or silanol contamination, by their infrared spectra. There were no absorptions in the 3300 or 1050-cm^{-1} regions which would be indicative of Si–OH or Si–O–Si linkages, nor in the 2050–2300-cm^{-1} region characteristic of Si–H bonds. All polysilanes have very similar infrared spectra. They exhibit a strong band in the 2950-cm^{-1} region (C–H stretch), a medium band at 1400 cm^{-1} (C–H deformation), a strong band at 1250 cm^{-1} (Si–Me deformation), a series of strong bands in the 800-cm^{-1} region (Si–Me rock), and weak to medium bands in the 350–450-cm^{-1} region (Si–Si stretch).[3] Only below 900 cm^{-1} are there noticeable differences in the spectra. The low-frequency bands are listed in Table II for those polycyclopolysilanes for which infrared spectra could be obtained.

Table II. Infrared Spectra[a]

$Me_{14}Si_8$	$Me_{16}Si_9$	$Me_{16}Si_{10}$	$Me_{18}Si_{10}$
840 (m)	840 (m)	835 (m)	840 (m)
			825 (m)
800 (vs)	800 (vs)	800 (vs)	800 (vs)
	780 (w)		770 (w)
725 (m)	730 (m)	735 (w)	720 (m)
685 (w)	685 (m)		680 (m)
670 (m)			
650 (s)			
650 (s)	660 (s)	665 (s)	655 (sh)
630 (w)	650 (sh)	645 (sh)	
	640 (w)		
390 (w)	400 (w)		
375 (m)	370 (s)	360 (w)	440 (w)

[a] Abbreviations used are vs, very strong; s, strong; m, medium; w, weak; and sh, shoulder.

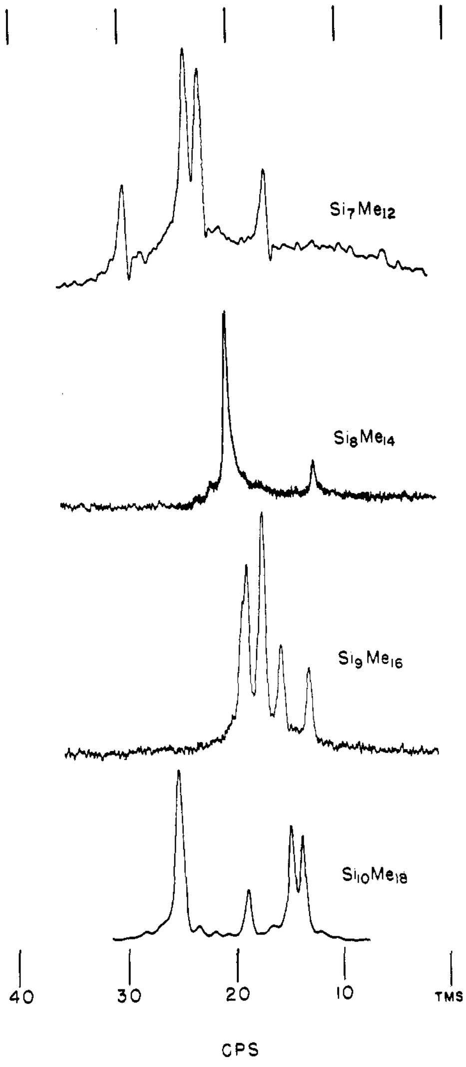

Figure 2. Nmr spectra of polysilanes.

Si_8Me_{14}. The structure of this compound was established as tetradecamethylbicyclo[2.2.2.]octasilane from its proton nmr spectrum (Figure 1), which showed only two peaks, at +0.205 and +0.125 ppm (δ), with a relative intensity of 6:1, respectively (Figure 2). This pattern is consistent with the proposed structure and inconsistent with any other reasonable structure for Si_8Me_{14}.[10] The ultraviolet spectrum of Si_8Me_{14} in

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(10) Other possibilities considered include the bicyclo[3.2.1]- and -[3.3.0]octasilane structures. The 3.2.1 structure can be eliminated because it should give nine different nmr peaks. The 3.3.0 structure should have four or five resonances; accidental degeneracy would be unlikely to occur for all of the nonbridgehead methyl protons in the (hypothetical) 3.3.0 compounds because it is not observed in the related 4,4,0 structure, $Si_{10}Me_{18}$. Other structures are even less likely.

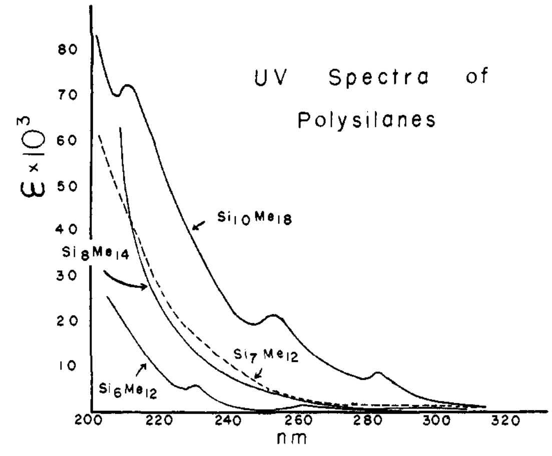

Figure 3. Ultraviolet spectra of polysilanes.

2,2,4-trimethylpentane (Figure 3) showed strong end absorption commencing at 290 nm and an inflection point at 245 nm (ϵ 7500).

Si_7Me_{12}. The nmr spectrum of this compound showed four peaks at +0.30, +0.24, +0.23, and +0.17 ppm in the ratio of 1:2:2:1 (Figure 2). This is entirely consistent with the proposed structure of dodecamethylbicyclo[2.2.1]heptasilane (Figure 1). All other possible structures would necessarily contain four-membered polysilane rings, which are known to be extremely reactive to oxygen whereas Si_7Me_{12} is air stable. Moreover the other possible structures should all give more complex nmr spectra. The 2.2.1 structure could result from the elimination of Me_2Si: from Si_8Me_{14} followed by ring contraction, a reaction pattern observed previously in the formation of $Me_{10}Si_5$ from $Me_{12}Si_6$.[8]

The high-field peak at +0.17 ppm is assigned to the bridgehead methyl groups, consistent with the observed nmr spectrum of Si_8Me_{14}. The low-field peak at +0.30 ppm must be due to the methyl groups of the 1 bridge, while the peaks at +0.24 and +0.23 ppm must come from the *endo*- and *exo*-methyl groups of the two 2 bridges. The ultraviolet spectrum in cyclohexane showed end absorption commencing at 310 nm (Figure 3). The exact mass is 376.1222 ± 0.0020 (calcd 376.1202).

Si_9Me_{16}. This polysilane shows four nmr peaks at +0.19, +0.175, +0.16, and +0.13 ppm in the ratio of 3:3:1:1. Its uv spectrum recorded in cyclohexane showed only strong end absorption commencing at 280 nm. At least four possible structures, A, B, C, and D (Figure 4), must be considered for Si_9Me_{16}. Each of these structures could give rise to the observed nmr spectra if some overlapping of peaks occurred. The shoulder in the peak at +0.19 ppm indicates the presence of two or more overlapping peaks (Figure 2), while the peak at +0.175 could contain two sets of similar methyl groups. The high-field peak at +0.13 ppm probably stems from a bridgehead methyl group. The ultraviolet spectra of Si_7Me_{12}, Si_8Me_{14}, and Si_9Me_{16} are all very similar, showing only end absorption. Therefore it seems likely that Si_9Me_{16} is a cage system with structure B, C, or D and not the nonasilaindan A (Figure 4). The presence of the two peaks at +0.16 and +0.13 ppm can be most satisfactorily explained by a system containing both bridgehead methyls and a 1 bridge. Thus the most likely structure is D, hexadecamethylbicyclo[3.3.1]nonasilane.

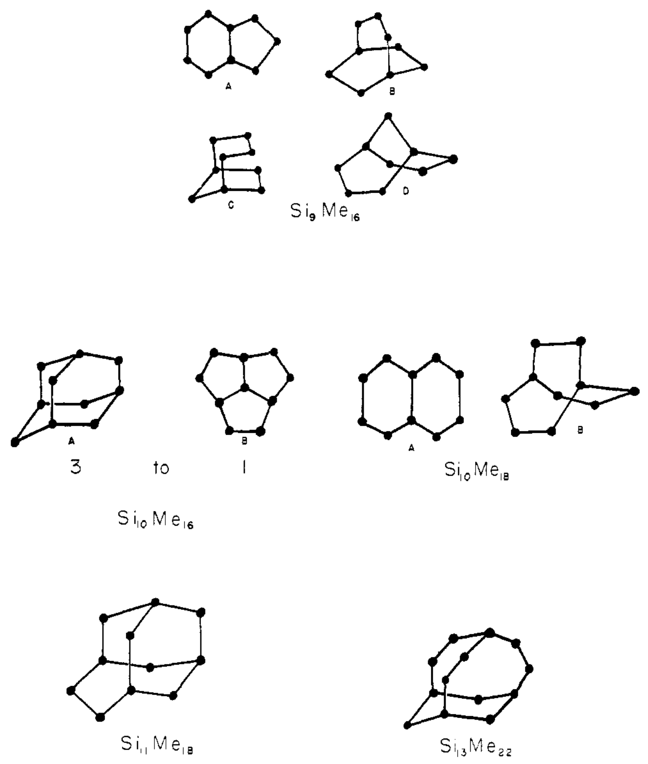

Figure 4. Probable structures of Si_9Me_{16}, $Si_{10}Me_{16}$, $Si_{10}Me_{18}$, $Si_{11}Me_{18}$, and $Si_{13}Me_{22}$.

$Si_{10}Me_{16}$. A conclusive structural assignment for $Si_{10}Me_{16}$ has not been possible. At least seven peaks were present in the nmr, the most intense falling at +0.24, +0.22, +0.17, and +0.13 ppm in the approximate ratio of 3:1:1:1. The melting point is greater than 360°, and polysilanes with such high melting points generally have a high degree of symmetry (Table I). However no reasonably symmetrical structure with the formula of $Si_{10}Me_{16}$ would show seven absorptions in the nmr. Thus, although attempts to separate isomers by gas chromatography and thin-layer chromatography were unsuccessful, it seems likely that more than one structural isomer is present. The peaks at +0.24 and +0.13 ppm could be due to the decasilaadamamtane structure A (Figure 2). The peak ratios of roughly 12 to 4 are in the correct ratio for the bridging methyl groups to the bridgehead methyl groups. Furthermore the bridgehead absorption would be at higher field, consistent with the assignments for Si_7Me_{12} and Si_8Me_{14}. If this assignment is correct, the other five peaks must be due to a second isomer, present in an amount about one-third as great as A. A possible structure is the basket structure B, which could give as many as five nmr peaks. Five-membered rings are well known in polysilane chemistry, and the fused five-membered rings in B might be particularly stable.

$Si_{10}Me_{18}$. The simple nmr spectrum (four peaks at +0.255, +0.19, +0.15, and +0.14 ppm in the ratio of 4:1:2:2) of $Si_{10}Me_{18}$ indicates that only one structural isomer is present (Figure 2). The ultraviolet spectrum recorded in cyclohexane showed three absorptions,

Table III. Electron Spin Resonance Data

Parent bicyclopolysilanes	Si_8Me_{14}	Si_8Me_{14}	$Si_{10}Me_{18}$	$Si_{10}Me_{18}$	Si_6Me_{12}	Si_6Me_{12}
Method of reduction	Elect	Chem	Elect	Chem	Chem	Elect
Observed radical anion	$Si_4Me_8\cdot^-$	$Si_4Me_8\cdot^-$	*a*	$Si_5Me_{10}\cdot^-$	$Si_5Me_{10}\cdot^-$	$Si_6Me_{12}\cdot^-$
g Value	2.0032	2.0032	2.0035	2.0032	2.0032	2.0028
Coupling constants, G						
^1H	0.533	0.533	0.95	0.532	0.53	0.49
^{13}C	16.09	16.09	*c*	16.02	16.06	14.60
^{29}Si	*c*	*c*	*c*	*c*	6.13	*c*
Line width, G	0.137	0.14	*c*	0.137	0.12	0.16
Line intensities center line	1.000[b]	1.000	1.000	1.000	1.000	1.000
2	0.932	0.920	0.75	0.934	0.935	0.94
3	0.725	0.730	0.32	0.787	0.77	0.795
4	0.483	0.480	0.08	0.550	0.545	0.59
5	0.272	0.260		0.378	0.34	0.42
6	0.128	0.130		0.237	0.19	0.24

[a] Inclusive. A weak signal, consisting of doublet (coupling constant 7.01 G) of quintets (coupling constant 0.95 G). The line intensities are given for the quintets. [b] Calculated line intensities assuming complete delocalization over 24 protons: 1.000, 0.923, 0.725, 0.483, 0.272, 0.128; 30 protons: 1.000, 0.935, 0.780, 0.555, 0.350, 0.192; 36 protons: 1.000, 0.947, 0.804, 0.613, 0.418, 0.254. [c] Not observed.

283 (ε 8100), 253 (ε 21,000), and 210 nm (ε 72,000). The presence of distinct uv maxima points to the decasiladecalin structure A (Figure 4) rather than the cage system B, which would probably exhibit only end absorption. Moreover the uv absorption of $Si_{10}Me_{18}$ is similar to that of the structurally related cyclic polysilane $Me_{12}Si_6$ (Figure 3). Therefore we conclude that $Si_{10}Me_{18}$ is octadecamethyl[4.4.0]decasilane.[11] The observed nmr spectrum is consistent with this assignment. The bridgehead methyl groups at the 1 and 6 position could give rise to the peak at +0.19 ppm. The *endo*- and *exo*-methyls at positions 2, 5, 7, and 10 can be assigned to the two peaks at +0.15 and +0.14 ppm, while the protons at positions 3, 4, 8, and 9, being very similar in their chemical environment, give rise to the single observed peak at +0.255 ppm. Cis and trans isomers are possible for this structure, but from the data available there is no way of distinguishing between the two.

$Si_{11}Me_{18}$. Because so little of this compound was available, even after 40 accumulated scans the nmr spectrum was somewhat inconclusive. However four peaks were found at +0.155, +0.135, +0.11, and +0.08 ppm in the approximate ratio of 1:1:4:2. (There is a possible error of ±0.03 ppm in the chemical shifts.) A definite structure cannot be assigned to this molecule. It must have a structure with four fused rings rather than a bicylcic structure (three fused rings), which would require two additional methyl groups. The relatively strain-free homoadamantane-type structure shown in Figure 4 is a likely possibility. Such a molecule could show as many as six peaks in the nmr. However some overlap of peaks is expected because the environment of some of the nonequivalent methyl groups is very similar.

$Si_{13}Me_{22}$. Only a trace amount of $Si_{13}Me_{22}$ was obtained, so no nmr spectrum could be recorded. A reasonable structure is the trishomoadamantane shown in Figure 4.

Reduction to Anion Radicals and Esr Spectra. Earlier work at this laboratory showed that cyclic polysilanes undergo reduction to form cyclic radical anions in which the unpaired electron is completely delocalized over the polysilane ring.[3] We find that polycyclopolysilanes also undergo reduction at − 80° to give radical anions, but not always of the same structures as the starting materials.

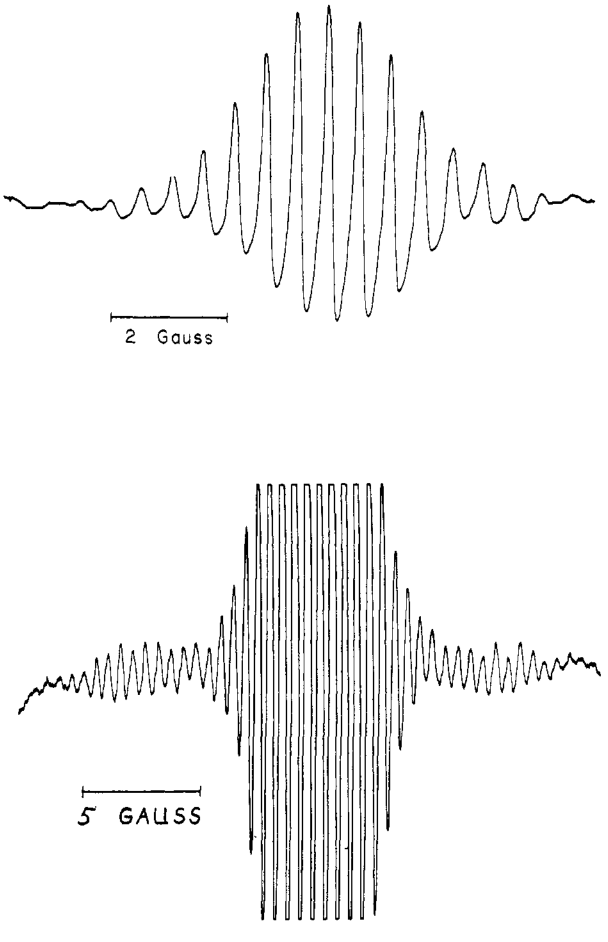

Figure 5. Esr spectra of radical derived from reduction of Si_8Me_{14}, thought to be $Si_4Me_8\cdot^-$.

The reduction of Si_8Me_{14} either chemically or electrically gave a simple esr spectrum consisting of at least 15 symmetrically spaced lines decreasing in intensity from the center line (Figure 5). The simple

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(11) Independent chemical evidence supports the decasiladecalin structure for $Si_{10}Me_{18}$. Unpublished work by M. Ishikawa and M. Kumada, privately communicated by M. Kumada.

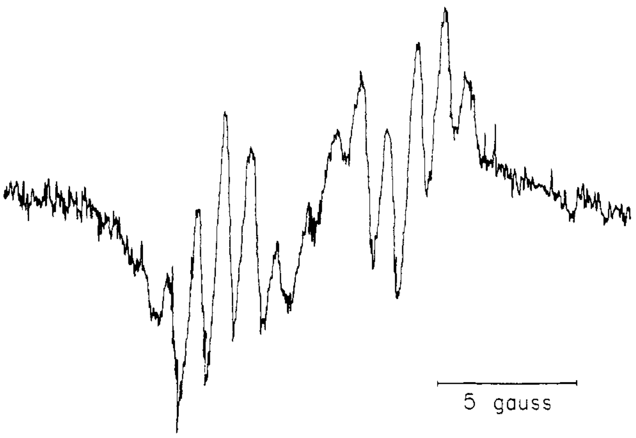

Figure 6. Esr spectrum of radical produced upon electrolytic reduction of $Si_{10}Me_{18}$.

esr spectrum and the presence of only one type of ^1H coupling strongly suggest the presence of a cyclic polysilane radical anion. If delocalization of the electron had taken place within the cage, two proton coupling constants should have been observed. The line intensities most closely fit the delocalization of an electron over 24 equivalent protons (Table III). Therefore the radical anion formed from the reduction of Si_8Me_{14} is believed to be the cyclic four-membered ring, $Si_4Me_8\cdot^-$

The chemical reduction of $Si_{10}Me_{18}$ likewise gave a simple symmetrical esr spectrum. Again the presence of only one type of ^1H coupling strongly indicates that a cyclic polysilane radical anion was formed, and that electron delocalization over the parent $Si_{10}Me_{18}$ molecule did not take place. The relative line intensities, the *g* value, and the ^1H and ^{13}C coupling constants all indicate that the species formed is the $Si_5Me_{10}\cdot^-$ radical anion (Table III).

Electrolytic reduction of $Si_{10}Me_{18}$ gave a completely different esr spectrum than chemical reduction (Figure 6). Instead of a simple symmetric spectrum, a weak apparent doublet with a splitting constant of 7.01 G was observed. Each of the doublets consists of a symmetrically spaced quintet with a coupling constant of 0.95 G (Table III). Since the entire signal was observed to grow in at the same rate, it seems likely that only one chemical species is responsible for the entire esr spectrum. The wide line width of 0.24 G could mean that considerable peak overlap exists. Since this esr spectrum is considerably different from the previously observed spectra of cyclic polysilanes, it could be that of an entirely different radical anion, perhaps a species containing an Si–H bond, which could be responsible for the observed doublet. However because of the weakness of the signal and the resulting poor resolution, no definite structure can be assigned.

After 20 hr of electrolysis, Si_9Me_{16} gave only a weak 11-line pattern with $g = 2.0033$ and an apparent hyperfine splitting constant of 0.51 G. Because the spectrum was symmetric with lines decreasing in intensity going away from the center, we believe that a simple cyclic polysilane was formed upon the reduction of Si_9Me_{16}. However the spectrum was so weak that line intensities could not be measured, so the structure of the radical cannot be determined.

The chemical reduction of Si_9Me_{16} yielded an extremely weak signal with a *g* value of 2.0034. No other information could be derived from the spectrum.

The electrolytic reduction of Si_7Me_{12} gave a weak signal with a ^1H coupling constant of 0.88 G and a *g* value of 2.0035. The relatively high ^1H coupling constant eliminates the possibility of a simple cyclic polysilane radical anion. However the weakness of the esr signal makes the assignment of a conclusive structure for the radical anion impossible. No esr signal was observed upon chemical reduction of Si_7Me_{12}.

In general it is more difficult to reduce the polycyclopolysilanes than the cyclic polysilanes. For many of the polycyclopolysilanes it appears that bond cleavage takes place leading to the formation of simpler cyclic polysilanes, which are then reduced to radical anions.

Experimental Section

Dimethyldichlorosilane and methyltrichlorosilane were obtained from Dow Corning Corp. The chlorosilanes were distilled under nitrogen and kept in sealed glass bottles prior to use. Syringes were employed to transfer the chlorosilanes from the bottles to the reaction vessel. Separation of products was carried out using a Varian-Aerograph Model A-705 gas chromatograph, with 10 ft × 3/8 in. aluminum columns packed with SE-30 or Apiezon L (20% by weight) on 30–60 mesh Chromosorb W. The column temperature was 300° with a helium flow of 140 cc/min. The exact masses of products were determined by high-resolution mass spectrometry, using an Associated Electronics Industries mass spectrometer, Model MS-902. Direct insertion was used to introduce the samples into the mass spectrometer. By this technique, well-resolved mass spectra could be obtained at room temperature in most instances. When it was necessary to heat the samples, the temperature never exceeded 100°. Proton nmr spectra were recorded on the Varian XL-100 nmr spectrometer at room temperature. Samples were run in a solution of 90% CCl_4 and 10% $CHCl_3$. Attempts to record the ^{29}Si nmr spectra of several polycyclopolysilanes as 50% solutions in benzene-d_6 were unsuccessful, perhaps because of unusually long relaxation times or because the nuclei are especially susceptible to power saturation. The chemical shifts for proton nmr are given in parts per million (δ) downfield from tetramethylsilane. Infrared spectra were determined as KBr pellets, on a Perkin-Elmer Model 457 infrared spectrophotometer. All melting points are uncorrected. The ultraviolet spectra were taken on a Cary 14 recording spectrophotometer using spectrograde solvents. Electron spin resonance spectra were recorded on a Varian V-4502-13 spectrometer.

Synthesis of Polycyclopolysilanes. In a typical reaction, a 2000-ml, three-necked round-bottom flask was equipped with a mechanical stirrer, 125-ml vented addition funnel, and a Friedrichs condenser. All glassware was thoroughly dried, and the entire system kept under a nitrogen atmosphere during the course of the reaction. To the flask were added 30 g (0.75 g-atom) of potassium and 6 g (0.26 g-atom) of sodium. Tetrahydrofuran (75 ml), freshly distilled from $LiAlH_4$, was added and the solution was stirred approximately 20 min until silvery beads of sodium–potassium alloy covered the surface of the liquid. An additional 800–1000 ml of THF and 10 g (0.08 mol) of naphthalene were then added.

Into the addition funnel were then syringed 10 ml (0.09 mol) of CH_3SiCl_3, 30 ml (0.25 mol) of $(CH_3)_2SiCl_2$, and 40 ml of THF. The solution containing the alloy was heated, and when refluxing commenced (65°), 1 drop of the chlorosilane mixture was added every 3 or 4 sec. The initial reaction mixture was dark blue, but gradually turned gold-black, and then chocolate brown. If the solution became viscous indicating that polymer formation had started, the addition of chlorosilanes was halted, and the solution was allowed to reflux for 45 min. This usually destroyed the polymer, and the addition of chlorosilanes could then be resumed.

Near the completion of the reaction (4–6 hr) the mixture turned greenish-yellow. When the reaction was completed, the solution was cooled in ice and 100 ml of methanol was slowly added to destroy the excess Na–K alloy. After no trace of alloy remained, 250 ml of water was added to dissolve the salts. The polycyclopolysilanes in solution were extracted with 400 ml of diethyl ether. The yellow organic phase was separated and reduced in volume on a rotary evaporator to a thick viscous syrup, which was vacuum distilled at 0.3 mm from a 250-ml, round-bottom flask, through a short path (3 in.) distillation head. During distillation the temperature was kept constant for at least 4 hr for each fraction. The first fraction to distill at 70° was composed of water, naphthalene, and $Me_{12}Si_6$. The next fraction at 90° was mostly $Me_{12}Si_6$ with some $Me_{14}Si_8$. Raising the temperature to 110° brought off $Me_{14}Si_8$, with traces of $Me_{12}Si_6$. At 140° Si_9Me_{16}, $Si_{10}Me_{16}$, and $Si_{10}Me_{18}$ distilled over. When the temperature was raised to 180–195° more $Si_{10}Me_{18}$ came over, along with small quantities of $Si_{11}Me_{18}$ and $Si_{13}Me_{22}$. Occasionally the polysilanes solidified in the distillation head and were dislodged by melting with a heat gun. Before the receiving flasks were changed, the distillation flask was cooled for 1 hr to prevent the hot polysilanes from inflaming when the vacuum was released. Likewise, the flask was heated slowly to prevent charring of the contents.

After the distillation was completed 15 ml of acetone was added to the 90 and 180° fractions. The contents were placed in the freezer (−10°) overnight causing white precipitates of Si_8Me_{14} and $Si_{10}Me_{18}$ to form in the respective flasks. These precipitates were sometimes quite pure and so required no further treatment. If traces of other polysilanes were detected on the gas chromatograph, the compounds were purified by preparative gas chromatography. The other polysilanes were separated by gas chromatography, recrystallized from an ether–acetone (50:50) mixture, and sublimed. The products and their yields are given in Table I along with high-resolution mass spectral data establishing the formulas.

Anal. Calcd for $C_{14}H_{42}Si_8$: C, 38.63%; H, 9.73%; Si, 51.63%. Found: C, 38.83%; H, 9.48%; Si, 51.38%. Calcd for $C_{18}H_{54}Si_{10}$: C, 39.20%; H, 9.87%. Found: C, 39.41; H, 9.64%.

Other ratios of Me_2SiCl_2 to $MeSiCl_3$ were tried, but the yield of polycyclopolysilanes was much lower. For instance when 20 ml (0.16 mol) of Me_2SiCl_2 and 20 ml (0.18 mol) of $MeSiCl_3$ were treated with NaK alloy the products obtained were 5% $Me_{12}Si_6$, 0.5% Si_8Me_{14}, and 0.5% $Si_{10}Me_{18}$. If the ratio was increased even more in favor of $MeSiCl_3$, as in the case of 10 ml (0.08 mol) of Me_2SiCl_2 and 30 ml (0.27 mol) of $MeSiCl_3$, only polymer and a trace of $Me_{12}Si_6$ was obtained.

The concentration of naphthalene is also crucial to the reaction. The amount of naphthalene was varied from 1.0 (0.008 mol) to 50.0 g (0.40 mol). The best results were obtained when amounts between 5 and 10 g (0.04–0.08 mol) were used. Less than 5 g caused polymer formation, while quantities in excess of 20 g caused excessive siloxane formation.

If the reaction was completed in less than 4 hr excessive amounts of polymer were formed. Taking more than 6 hr led to siloxane formation and decreased polycyclopolysilane content. For example, when the solution was refluxed for 24 hr, no cage polysilanes were detected.

A 10% excess of NaK alloy was used because stoichiometric amounts of Na–K alloy caused the reaction to come to completion before all the chlorosilane was added. Running the chlorosilane condensation reaction at less than reflux temperature (65°) led only to polymer formation.

When dimethoxyethane (glyme) was substituted for THF, two silylnaphthene products, $C_{10}H_6(SiMe_2)_2$ (I) and $C_{10}H_4(SiMe_2)_4$ (II), were obtained. Tetramethyldisilaacenaphthene (I) first reported by Makarov, *et al.*,[9] in 1969 was characterized from its infrared spectrum, which showed a combination of naphthalenic and polysilane absorption bands, from its mass spectrum (calcd 242.0947, found 242.0946 ± 0.0020) and from its nmr. The nmr spectrum showed a multiplet centered at 7.33 ppm and a single peak at +0.12 ppm (δ) in the ratio of 1:2, respectively. Our sample of I showed mp 97°, rather higher than the literature value[9] of 76–77°. Further identification was provided by reduction of I to its anion radical and examination by esr spectroscopy. The anion radical shows a basic triplet with a splitting constant of 5.20 G, which is split twice more into triplets with hyperfine splitting constants of 2.40 and 1.03 G. This spectrum is in good agreement with that reported for tetramethyldisilaacenaphthene at −75° in *N*,*N*-dimethylformamide. The earlier workers give hyperfine splitting constants of 5.30, 2.60, and 1.00 G, respectively.[9]

$C_{10}H_4(SiMe_2)_4$, mp 249–250°, was characterized from its infrared spectrum which showed a combination of naphthalenic and polysilane absorptions and from its mass spectrum (calcd 356.1268, found 356.1226 ± 0.0050). The nmr spectrum showed a multiplet centered at 7.30 ppm and a *singlet* at +0.18 ppm in the ratio of 1:6. Upon electrolytic reduction, II gave an anion radical showing a simple quintet in the esr spectrum, consistent with electron delocalization over the entire carbon skeleton of II. The ^1H coupling constant was 2.05 G. The radical anion was stable from −120 to +20°. All the data are consistent with the indicated structure of octamethyltetrasilapyracene.

Photolysis of Si_8Me_{14}. Si_8Me_{14} (0.4 g) was dissolved in 250 ml of freshly distilled cyclohexane and the solution was photolyzed for either 2 or 4 hr with a low-pressure mercury lamp in a Vycor housing. The solvent was distilled off under reduced pressure on a rotary evaporator and the resulting products were separated gas chromatographically on a 15 ft × $^3/_8$ in. diameter SE-30 column (20% by weight on Chromosorb W) at 265° with a helium flow of 130 cc/min. Results are given in Table IV. The compounds were identified by their mass spectra and gas chromatographic retention time. The photolysis of $Si_{10}Me_{18}$ yielded only polymer.

Table IV. Photolysis Products of Si_8Me_{14}

		Yield, %	
		2 hr	4 hr
	Si_8Me_{14}	35	29
Mass 392	$Si_7Me_{12}O$?	4	0.5
	Si_7Me_{12}	8	14
	Si_6Me_{12}	35	31
Mass 334	$Si_6Me_{10}O$?	4	4
	Si_5Me_{10}	18	22
	Si_4Me_8O	Trace	Trace

Reduction to Anion Radicals and Esr Spectra. Tetrahydrofuran was used as the solvent for electrolytic reductions and a solution of methyltetrahydrofuran and 1,2-dimethoxyethane (2:1) was employed for chemical reduction by sodium–potassium alloy. The solvents were dried by distillation from $LiAlH_4$ under a nitrogen atmosphere, and then stored in the presence of anthracene radical anion. For sample preparation, the solvent was distilled into the esr cell containing the sample and electrolyte on a high vacuum line (2–3 μ). The reductions were carried out at numerous temperatures. The most favorable temperature was −80°. Temperatures below −100° induced the solvent to freeze, while temperatures above −40° caused the signal to decay rapidly.

Electrolytic reduction was accomplished by passing 0.5 μA at 60–120 V through an esr cell containing a 0.5 ml solution of the bicyclopolysilane (2 mg) and 2 mg of tetra-*n*-butylammonium perchlorate as the supporting electrolyte. The esr cell was of 4-mm Vycor tubing with platinum wire electrodes; the cell and our procedure have been described elsewhere.[4,12] The sample and supporting electrolyte were placed in the cell which was then thoroughly degassed on a vacuum line. THF was distilled in and the cell was degassed twice more before being placed in the esr cavity. Current was supplied by means of a 300-V battery equipped with a voltage regulator. This cell and technique were the same as those used in previous preparations of the relatively unstable anion radicals $Me_{10}Si_5\cdot^-$ and $Me_{12}Si_6\cdot^-$.[4]

The chemical reductions were carried out by distilling a mirror of Na–K alloy into the esr cell containing 2–4 mg of bicyclopolysilane in 1.0 ml of solution. The cell was sealed and cooled to −95° in a toluene–liquid nitrogen slush bath. Rapid inversion of the tube caused the polysilane solution to come in contact with the alkali metals and form radical anions. The color of all radical anion solutions was light to medium yellow.

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(12) E. A. Carberry, Ph.D. Thesis, University of Wisconsin, 1968.