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Final Report

Chemical Reactions and Properties of Organosilicon Compounds Related to New Materials

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Principal Investigator and
Author of Report:

Robert West
Department of Chemistry
University of Wisconsin
Madison, WI 53706

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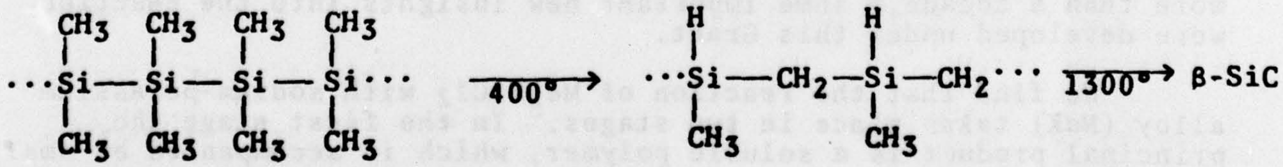
A. INTRODUCTION: TECHNOLOGICAL IMPORTANCE OF POLYSILANES

The current upsurge of interest in polysilanes follows from the discovery that they can be transformed by heat, first to "carbosilanes" (Si-C-Si-C polymers) and then to β-silicon carbide.[1] If the carbosilane polymer is drawn into fibers, the silicon carbide is ultimately obtained as fibers with very high tensile strengths (~300,000 psi).[2] Even without drawing into fibers, thermolysis of polysilanes may give silicon carbide useful for reinforcing other materials such as silicon carbide or silicon nitride ceramics (see section I of this report).



$$\cdots\mathrm{Si(CH_3)_2-Si(CH_3)_2-Si(CH_3)_2-Si(CH_3)_2}\cdots \xrightarrow{400^\circ} \cdots\mathrm{SiH(CH_3)-CH_2-SiH(CH_3)-CH_2}\cdots \xrightarrow{1300^\circ} \beta\text{-SiC}$$

Polysilanes are also of interest presently as analogs to elemental silicon. Transistors and similar solid-state devices made from silicon are the basis of all of modern communications and data processing. Another technological feature of interest in polysilanes is that the bonding in these species provides a model for bonding in elemental silicon, which is poorly understood.[3] Therefore studies of spectroscopy and bonding in polysilanes may have general importance even greater than their intrinsic interest.

In semiconductor technology the properties of elemental silicon are altered by adding other elements as "dopants". With polysilanes, two possibilities for changing the electronic structure exist. An element other than silicon can be included in the polysilane chain or ring; or a substituent can be introduced, changing the electronic nature of one of the silicon atoms. Both of these approaches have been employed. Properties of polysilanes containing one or more phosphorus atoms are described in section IV, and some substituent effects on electric nature of polysilanes are treated in section II.b.

Finally, the polysilanes represent a virtually unexplored class of polymers. Their properties are expected to be intermediate between those of silicones and hydrocarbon polymers, and so may be technologically useful. Polymers from our research are now being investigated as controlled-release agents for example.

B. RESEARCH PROGRESS

This section will describe highlights of research carried out during this Grant period, in the five general areas listed in the Table of Contents. Because of its technological importance, section I on synthesis of cyclic and polymeric silanes will be emphasized. All of the research is discussed in greater detail in journal articles listed in the Cumulative List of Publications at the end of this report.

I. Synthesis of Cyclic and Polymeric Methylsilanes

Fundamental to almost all of our investigations in polysilane chemistry is the synthesis of permethylpolysilanes, accomplished by reduction of dimethyldichlorosilane with alkali metals. Although this reaction has been under investigation in our laboratories for more than a decade,[4] some important new insights into the reaction were developed under this Grant.

We find that the reaction of Me_2SiCl_2 with sodium-potassium alloy (NaK) takes place in two stages. In the first stage the principal product is a soluble polymer, which is accompanied by small amounts of the five-, six- and seven-membered ring cyclic compounds. Typical yields at this stage are:

$$Me_2SiCl_2 + NaK \xrightarrow{THF} (Me_2Si)_5,\ 8\%$$

$$(Me_2Si)_6,\ 18\%$$

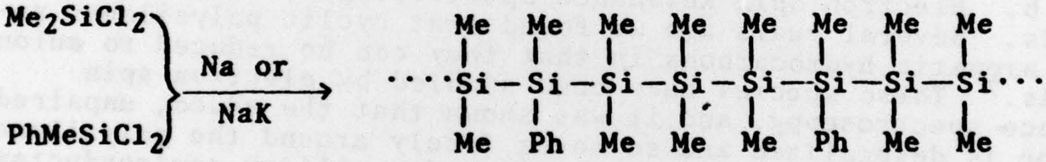
$$(Me_2Si)_7,\ 1\%$$

$$(Me_2Si)_x \text{ polymer},\ 70\%$$

If the reaction mixture is allowed to remain in contact with excess NaK, no change is observed for several hours. Then after an induction period, the polymer undergoes rapid depolymerization to form $(Me_2Si)_6$ almost exclusively. The induction period may be as short as 2 1/2 hours if the reagents are very pure, or as long as 16 hours if rather impure reagents are employed. The depolymerization is complete in about thirty minutes, suggesting that an "unzipping" mechanism must be involved to explain the rapidity of the process.

No further change is observed after unzipping to $(Me_2Si)_6$ is complete. The reaction mixture is thenquenched carefully with 2-propanol and then water, and the $(Me_2Si)_6$ is crystallized from the organic layer. $(Me_2Si)_5$ may be fractionally sublimed from the residue. Eventually, up to 90% of $(Me_2Si)_6$ and 7% of $(Me_2Si)_5$ can be isolated.

The polymer of dimethylsilane, when isolated, is an intractable solid, which does not melt or dissolve in organic solvents. We have found however that solublemeltable polymers can be obtained if a small amount of phenylmethyldichlorosilane is added to the dimethyldichlorosilane. We have used ratios of Me_2SiCl_2 to $PhMeSiCl_2$ varying from 3 to 20, but in the best materials the ratio is between 3 and 5. Useful polymers are obtained using either sodium or NaK as the reducing agent:



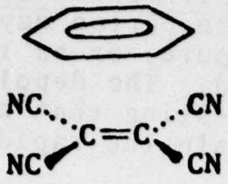
$$\left.\begin{matrix}Me_2SiCl_2\\ \\ PhMeSiCl_2\end{matrix}\right\}\xrightarrow[NaK]{Na\ or}\cdots\underset{Me}{\overset{Me}{Si}}-\underset{Ph}{\overset{Me}{Si}}-\underset{Me}{\overset{Me}{Si}}-\underset{Me}{\overset{Me}{Si}}-\underset{Me}{\overset{Me}{Si}}-\underset{Ph}{\overset{Me}{Si}}-\underset{Me}{\overset{Me}{Si}}-\underset{Me}{\overset{Me}{Si}}\cdots$$

In experiments carried out at the Air Force Materials Laboratory (AFSC), Wright-Patterson Air Force Base, it has been found that phenylmethylpolysilane polymers can decompose to silicon carbide in a matrix of compacted silicon nitride. The resulting threads of β-SiC reinforce and strengthen the Si_3N_4 ceramic structure.[5]

II. Spectroscopic Studies of Polysilanes

a. Charge-Transfer Complexes.

Aromatic compounds generally are known to form charge-transfer complexes with powerful pi-electron acceptors; an example is the complex of benzene with tetracyanoethylene,(TCNE). In such acomplex, contact takes place between the donor (benzene) and the acceptor (TCNE) in which the filled pi-orbitals of the donor interact with the electron-deficient pi-orbitals of the acceptor, as in diagram I. Complex formation is associated with formation of a new electronic absorption band, the charge-transfer band, usually in the visible region. Little charge-transfer takes place in the ground state but charge-transfer from D to A is extensive in the excited state of the new electronic transition.



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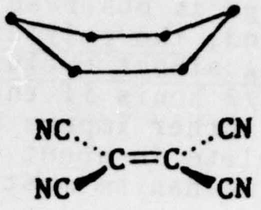


II

We have now found that polysilanes resemble aromatic hydrocarbons on forming charge transfer complexes with pi-acceptors.[6] These are the first examples of such complexes in which the donor employs delocalized sigma electrons (from the Si-Si bonds) for charge-transfer. An example is the purple-colored complex between $(Me_2Si)_6$ and TCNE, which may have the geometry indicated in diagram II.

The charge-transfer complexes of a variety of linear and cyclic polysilanes with TCNE and other acceptors have been studied. The charge-transfer bond energies are related linearly with the ionization potentials, as measured by other methods.

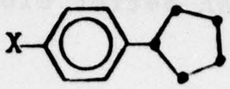
b. Electron Spin Resonance Spectroscopy of Polysilane Anion Radicals. Several years ago we found that cyclic polysilanes resemble aromatic hydrocarbons in that they can be reduced to anion-radicals.[7] These species have been studied by electron spin resonance spectroscopy, and it was shown that the added, unpaired electron is delocalized and so moves freely around the polysilane ring. Thus polysilanes provide a model for silicon semiconductors, in which electron delocalization between silicon-silicon bonds also takes place.

We have carried out a study of aryl-substituted cyclopentasilanes, Si_5Me_9-Ar-X, where X is a variable substituent group. When these compounds are reduced to anion-radicals, in all cases the unpaired electron is associated mainly with the polysilane ring. This indicates that the pentasilane ring is a better electron acceptor than any of the substituted aryl rings. However, the electron spin resonance experiments provide evidence for some electron drift from the pentasilane group to the benzenoid aromatic ring. Data in Table I show that the splitting constants for protons and carbon-13 both decline as the group X on the benzene ring becomes more electron attracting. This subtle substituent effect does then influence the electron affinity of the cyclopolysilane.

When the Si_5Me_9 ring is attached to a biphenyl group, the relative electron affinities are reversed, and the esr splitting constants reflect the fact that the added electron is principally circulating over the biphenyl rings. These results however indicate that the Si_5Me_9 ring is much more electron-attracting than a $SiMe_3$ group.

Table I

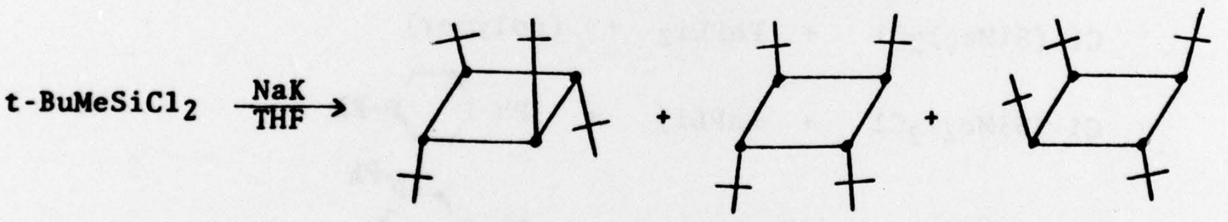
Splitting Constants for Anion-Radicals of p-Substituted Aryl Nonamethylcyclopentasilanes,



X	a_H	$a_{^{13}C}$
CH_3	unres.	20.0
OCH_3	0.61	19.7
H	0.51	14.7
$Si(CH_3)_3$	0.46	13.5

III. tert-Butylmethylcyclotetrasilanes

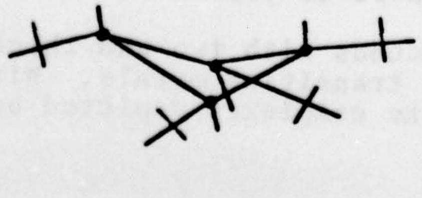
In experiments designed to study the effect of differing substituents on polysilanes, we have carried out the condensation of tert-butylmethyldichlorosilane. The products are a mixture of three different four-membered rings, in approximately a 4:2:1 ratio:[8]



4 : 2 : 1

Unlike the permethyl four-membered ring compound $(Me_2Si)_4$, these tert-butylmethyl compounds are highly unreactive. In fact, they are more resistant to chemical attack than any of the permethylpolysilanes. This suggests that polymers based on the tert-butylmethyl structure might be quite inert also.

The three isomers are drawn in planar from above to show clearly the arrangement of their substituents. However, a x-ray crystal structure study on the all-trans isomer showed that the four-membered ring is strongly bent, in such a way that all of the tert-butyl groups can take up pseudo-equatorial positions:[9]



The electronic properties of these compounds have also been studied. Both *tert*-butyl substitution and ring strain combine to make threse substances even better electron donors than the permethylpolysilanes.[10]

IV. Cyclic Phosphasilanes

Phosphorus is one of the elements frequently added to elemental silicon; the lone pair of electrons forms an "n" site and alters the electronic characteristics of the solid. Under this grant we have introduced phosphorus atoms into polysilane rings, synthesizing a new class of compounds, the cyclic phosphasilanes. As expected, the introduction of a phosphorus atom with its lone pair materially changes the electronic properties of polysilane rings.

The compounds were synthesized from α,ω-dichlorosilanes and lithiophenylphosphines, as shown in the equations:

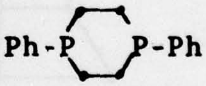
$$Cl\text{-}(SiMe_2)_6Cl \quad + \quad PhPLi_2 \quad \rightarrow \quad (SiMe_2)_6PPh$$

$$Cl\text{-}(SiMe_2)_5Cl \quad + \quad PhPLi_2 \quad \rightarrow \quad (SiMe_2)_5PPh$$

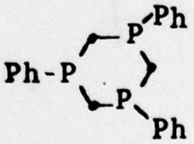
$$Cl\text{-}(SiMe_2)_4Cl \quad + \quad PhPLi_2 \quad \rightarrow \quad (SiMe_2)_4PPh$$

$$Cl\text{-}(SiMe_2)_3Cl \quad + \quad PhPLi_2 \quad \rightarrow \quad \text{(polymer)}$$

$Cl\text{-}(SiMe_2)_2Cl \quad + \quad PhPLi_2 \quad \rightarrow$



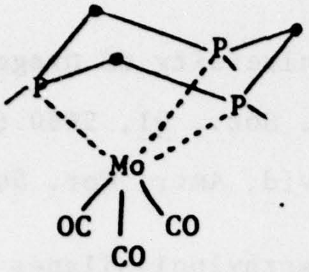
$Cl\text{-}SiMe_2\text{-}Cl \quad + \quad PhPLi_2 \quad \rightarrow$

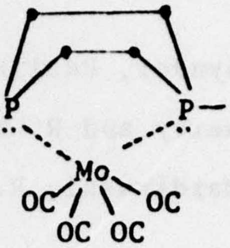


Note that the five, six and seven-membered rings are formed from the appropriate dichloropolysilane and $PhPLi_2$, but that no four-membered ring is formed, the reaction of the dilithiophosphine with $Cl(SiMe_2)_3Cl$ yielding mostly polymeric material. With still shorter polysilane chains, phosphasilane rings are obtained with two or three phosphorus atoms in the ring.

Sharp differences in electronic character from the polysilane rings are indicated from the nmr spectra of the phosphasilanes. In addition the phosphasilanes, unlike the parent cyclosilanes, cannot be reduced to delocalized anion-radicals.

The cyclic compounds with two and three phosphorus atoms are useful ligands for transition metals. With molybdenum carbonyl these compounds form the complexes depicted below:

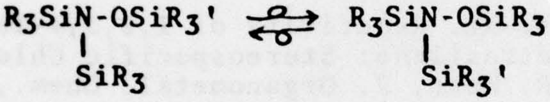




The structure of the diphosphatetrasilane molybdenum tetracarbonyl has been established by single-crystal x-ray investigation.

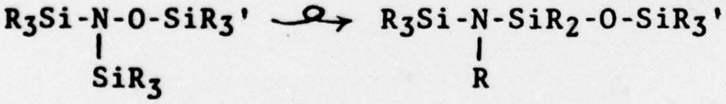
V. Rearrangement Reactions of Silylhydroxylamines

Our investigations of tris(organosilyl)hydroxylamines have been completed. Two new kinds of thermal rearrangement reactions of these compounds have been discovered. The first is a "dyotropic" rearrangement in which the silyl groups on oxygen and nitrogen become interchanged:



$$\underset{\mathrm{SiR_3}}{\mathrm{R_3SiN}}\mathrm{{-}OSiR_3'} \underset{\Delta}{\overset{\Delta}{\rightleftarrows}} \underset{\mathrm{SiR_3'}}{\mathrm{R_3SiN}}\mathrm{{-}OSiR_3}$$

This interchange reaction is reversible, but at a somewhat higher temperature a remarkable irreversible rearrangement takes place in which a silicon atom becomes inserted between the oxygen and nitrogen atom, and an organic group shifts from silicon to nitrogen:



$$\mathrm{R_3Si{-}}\underset{\mathrm{SiR_3}}{\mathrm{N}}\mathrm{{-}O{-}SiR_3'} \xrightarrow{\Delta} \mathrm{R_3Si{-}}\underset{\mathrm{R}}{\mathrm{N}}\mathrm{{-}SiR_2{-}O{-}SiR_3'}$$

These reactions are fully described in two papers which appear in the list of publications.[11,12] The second rearrangement is useful in the preparation of specialized siloxazanes (Si-N-Si-O-Si compounds).

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PERSONNEL

Most of the money spent under this Grant was used for stipends to graduate students at the University. Three individuals supported by this grant were awarded the Ph.D. degree, and all are now employed in chemical research or education. A list of all persons supported by this grant and their present location follows:

Summary of Persons Supported under This Grant

Graduate Students	Degree	Present Location
Peter Nowakowski	Ph.D.	PPG, Pittsburgh, PA
Witta Priester	Ph.D.	Chevron Research Co.,Richmond,CA
Catherine Hurt Middlecamp	Ph.D.	Hobart & Wm.Smith Colleges,Geneva,NY
David Stanislawski	-	Univ. of Wisconsin-Madison
A. C. Buchanan III	-	Univ. of Wisconsin-Madison
Lawrence Brough	-	Univ. of Wisconsin-Madison
Timothy Drahnak	-	Univ. of Wisconsin-Madison
Thomas Newman	-	Univ. of Wisconsin-Madison
Lawrence David	-	Univ. of Wisconsin-Madison
Cynthia Wadsworth	-	Univ. of Wisconsin-Madison
Rodney Schreiner	-	Univ. of Wisconsin-Madison
Postdoctoral Associates		
Michael Biernbaum		Univ. of Wisconsin, Molecular Biol.
Richard Oakley		Stanford Univ., Stanford, CA
Wieslaw Wojnowski		Technical University, Gdansk,Poland
Jamshid Soulati		Univ. of Wisconsin

ACTIVITIES OF THE PRINCIPAL INVESTIGATOR

Professor West served as visiting professor at three different universities during 1974-1978. In 1975, he was awarded a grant from the Knapp Foundation to study the social and human values implications of nucleur power, during which time he spent two months at the University of California-San Diego. In spring 1976 he served as Japan Society for the Promotion of Science Visiting Professor, at Tohoku University in Sendai, Japan. While in Japan he presented lectures on silicon and other chemistry at nine Japanese Universities and research institutes. Finally in the spring of 1977, Dr. West spent three months as visiting professor at the University of California-Santa Cruz.

During 1975 Dr. West was Chairman of the Division of Chemical Education of the American Chemical Society. Since that time he has served on the Board of Publications for the Division, which is the management board of the Journal of Chemical Education.

Continuing responsibilities include Editorship of the annual "Advances in Organometallic Chemistry," now in its 16th volume, and of the monograph series in organometallic chemistry. Dr. West also serves on the International Advisory Committee for the International Symposia on Organosilicon Chemistry and the International Conferences on Organometallic Chemistry.

During the past few years he has served as adviser to the Wisconsin Legislature and to the Department of Natural Resources on environmental legislation. Over the past four years he has presented more than 100 invited lectures in this country and abroad. Many of these were on the organosilicon research under this grant; others concerned oxocarbon, quinone and organolithium chemistry, nuclear energy, education, and environmental problems.

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1) The synthesis of cyclic and polymeric permethylpolysilanes from dimethyldichlorosilane has been studied. Inclusion of small amounts of phenylmethyldichlorosilane gives meltable, soluble silane polymers. 2) Charge transfer complexes of permethylpolysilanes with pi-acceptors have been discovered and investigated. 3) A series of aryl-substituted nonamethylcyclopentasilanes has been prepared and the anion-radicals of these compounds studied by electron spin resonance spectroscopy. 4) Highly stable *tert*-butylmethylcyclotetrasilanes have been

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20. prepared from tert-butylmethyldichlorosilane, and their properties have been investigated. 5) A series of phosphorus-containing permethylpolysilane rings has been prepared and investigated by nmr, esr and electronic spectroscopy. 6) Two new rearrangement reactions of silylhydroxylamines have been discovered.