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New disilenes were synthesized, including the first example of a disilene with a silyl substituent. The oxidation of disilenes by oxygen was investigated and found to produce 1,2-disilaoxetanes which rearrange intramolecularly to 1,3-cyclodisiloxanes. Disilenes were found to react with aldehydes, ketones and thioketones by 2+2 cycloaddition to produce four-membered ring compounds. Reactions of disilenes with ketenes and acid chlorides were also investigated. With white phosphorus, disilenes react to produce nobel bicyclobutane molecules which may be further converted to tricyclic asterane structures. The first platinum derivatives of disilenes were synthesized.

The first siladiimides have been synthesized. These are salts of anions containing partial double bounds between silicon and each of two nitrogen atoms. The chemical reactions, spectroscopy and structure of siladiimides has been investigated.

Final Technical Report

CHEMICAL REACTIONS AND PROPERTIES OF ORGANOSILICON COMPOUNDS RELATED TO NEW MATERIALS

The Air Force Office of Scientific Research

Air Force Systems Command

Grant No. AFOSR-89-0004

Principal Investigator

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Period Covered: October 1, 1988 - September 30, 1991

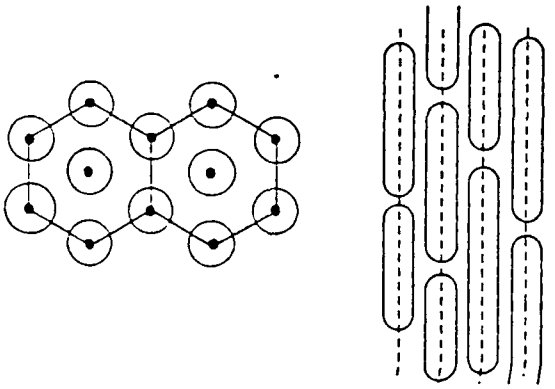
1. Polysilane High Polymers

a. Ordered Polysilane. Polysilane copolymers made by condensing a mixture of two dichlorosilanes have random or blocklike structures. We have made the first ordered polysilane copolymer, by careful condensation of a dibromotrisilane:

$$\underset{1}{BrMe_2Si\text{-}nHex_2Si\text{-}SiMe_2Br} \xrightarrow{Na/K} \underset{2}{(Me_2Si\text{-}nHex_2Si\text{-}SiMe_2)_n}$$

A disordered fraction is also produced in the copolymerization. The ordered, low M_w polymer has a higher melting point than the disordered high M_w fraction, consistent with its greater crystallinity. Also, the ordered polymer shows a new ultraviolet absorption band at low temperature in solution, not observed for the disordered fraction.

b. Symmetrical Dialkylpolysilanes, $(R_2Si)_n$, have crystalline structure of various types. We have synthesized the mixed polymer containing one n-butyl and one n-hexyl group on each silicon, $(n\text{BuSi}n\text{Hex})_n$. This polymer has only two--dimensional order at all temperatures between -50° and +220°C. The x-ray diffraction pattern for this polymer indicates that it exists in a hexagonal lattice and forms columnar liquid crystals, as illustrated in the diagram.

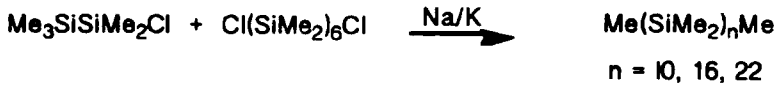


Top View Side View

This kind of liquid-crystalline packing is not unique for $(n\text{BuSi}n\text{Hex})_n$; we find it to be common for many polysilane copolymers of the type $(R_2Si)_n(R'_2Si)_n$, where R and R' are different alkyl groups. The two-dimensional ordering gives $(n\text{BuSi}n\text{Hex})_n$ and related polymers a tough, rubbery nature at ordinary temperatures, which may be useful in technological applications of polysilanes.

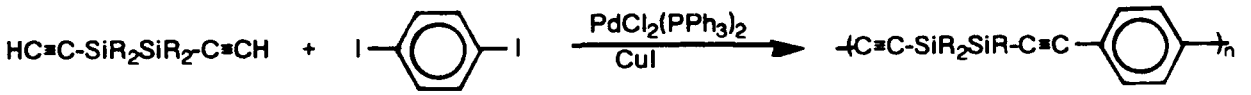
c. Surface Energy of Polysilanes. The surface tensions of 35 polysilane polymers have been determined. The values depend very much on the nature of the grups attached to the polysilane chain, and span the range from 25.0 dyne/cm for $(CF_3CH_2CH_2SiCH_2)_n$, to 52.8 dyne/cm for the copolymer, $[PhCH_2CH_2SiCH_3]_n(Ph_2Si)_m$.

d. Oligomers as Model Compounds. In order to study in detail the conformations of polysilanes in solution, linear oligomers of known structure are needed. We have synthesized several linear permethylpolysilane oligomers by the route



shown. These substances have been thoroughly characterized spectroscopically, and provide important information about the behavior of polysilanes in solution.

e. Acetylene-Disilane Copolymers. Copolymers of the type $(R_2Si\text{-}R_2Si\text{-}C{\equiv}C)_n$ have been synthesized and studied; they show properties consistent with electron delocalization involving both the polysilane and the ethynyl groups. We have made a new family of polyene polysilane copolymers by coupling between ethynyl polysilanes and diiodoaromatics. An example is shown:



Electron-delocalization in these new polymers is being investigated.

2. Multiply-Bonded Silicon Compounds

a. Disilenes, $R_2Si{=}SiR_2$. Disilenes, compounds containing a silicon-silicon double bond, are made by photolysis of trisilanes. This approach was employed to synthesize the first disilene bearing a silicon substituent, 3. This compound, isolated as **Z** and **E** stereoisomers, exhibits a long-wavelength visible absorption band indicating that electron delocalization takes place involving all four silicon atoms.

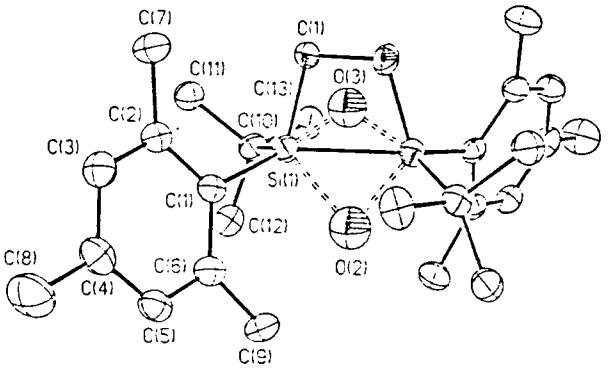
b. Oxidation Products of Disilenes. Oxidation of disilenes by atmospheric oxygen takes place to give 1,2-disiladioxatanes (4) which rearrange into 1,3-cyclodisiloxanes (5).

3

Is = 2,4,6-triisopropylphenyl

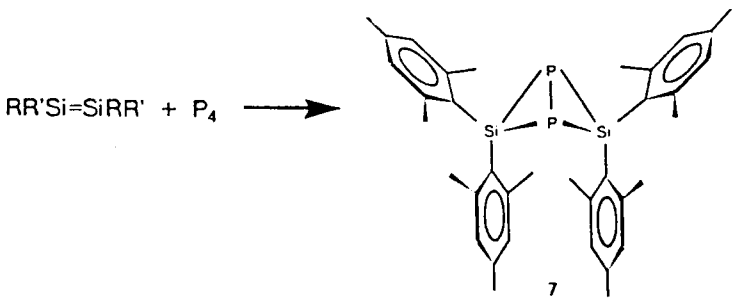
Rate measurements of the 4 — 5 rearrangement in solution show that it is first order. Compound 4 (R = mesityl, R' = t-butyl) was prepared doubly-labelled with ^{18}O. Mixtures of ^{18}O-^{18}O and ^{16}O-^{16}O compounds were allowed to rearrange; examination of the products showed that no ^{18}O-^{16}O was obtained. The rearrangement is therefore fully <u>intramolecular</u> both in solution and in the solid.

An x-ray crystal structure study has now shown that both oxidation and rearrangement both take place with retention of configuration. The x-ray results for 4 showed a striking anomaly, however. Rearranged molecules are evident in the



crystal lattice, which shows evidence for atoms located along the C_2 axis as shown in the figure. This "topotactic", partial rearrangement without disruption of the crystal lattice, is unprecedented.

c. <u>Reactions of Disilenes with Phosphorus</u>. Studies have been carried out on the synthesis, chemistry, spectroscopy and structure of the unusual molecules with bicyclobutane structure (7), obtained by the reaction of disilenes with white phosphorus, P_4. Compound 7 is basic and gives complexes with transition metals.



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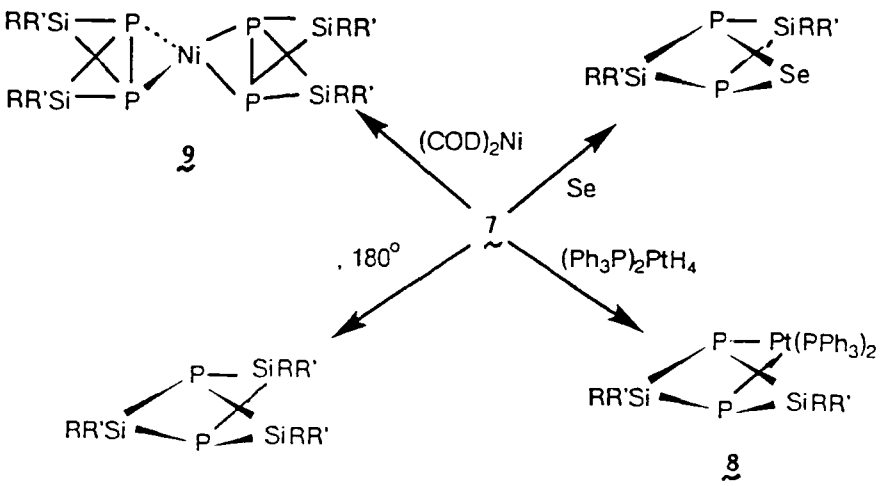
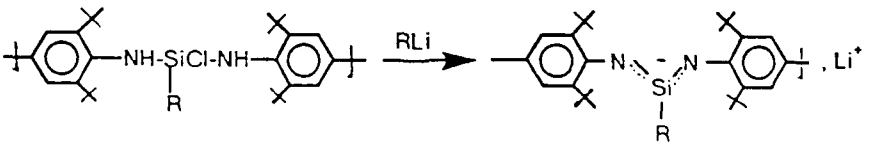
With $[Ph_3P_2Pt(C_2H_4)]$, a tricyclic complex 8 with an "asterane" structure is obtained. Similar asteranes are formed by the reaction of 7 with selenium, and by the thermolysis of 7 at 180°C. However with bis(cyclooctadiene)nickel, a novel bis-propellane structure, 9 is evidently produced.



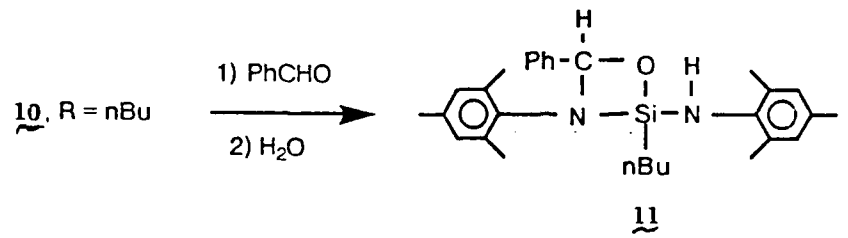
Silaamidide Salts. We have synthesized the first salts of silaamidide ions, (10), and characterized them spectroscopically. The crystal structure of a salt of



10, R = Cl, Ph, nBu, tBu

10 (R = n-Bu) has been determined, and the Si-N bond lengths indicate that partial double bonds exist between the silicon and each of the two nitrogen atoms.

Several chemical reactions of silaamidides have also been investigated. Among the latter is a 2+2 cycloaddition reaction of 10 (R = n-Bu) with benzaldehyde to give a unique silaoxazetane, 11.



11

COMPLETED PROJECT SUMMARY

1. **TITLE:** Chemical Reactions and Properties of Organosilicon Compounds Related to New Materials

2. **PRINCIPAL INVESTIGATOR:** Robert West
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3. **INCLUSIVE DATES:** October 1, 1988 - September 30, 1991

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New 2,4,6-Triisopropylphenyl Substituted Disilenes, R. S. Archibald, Y. van den Winkel, A. J. Millevolte, J. M. Desper and R. West, **Organometallics.**

Linear 2,2-Diaryl-Substituted Trisilanes: Structure and Photolysis to Disilenes, R. S. Archibald, Y. van den Winkel, D. R. Powell and R. West, **J. Organometal. Chem.**

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The Reactions of Tetramesityldisilene with Acid Chlorides and Ketenes, A. D. Fanta, J. Belzner, D. R. Powell and R. West, **Organometallics.**

1,2-Disiladioxetanes: Structure, Rearrangement and Reactivity, K. L. McKillop, G. R. Gillette, D. R. Powell and R. West, **J. Am. Chem. Soc.**

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS

1. Polysilane High Polymers

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