

Organosilicon Chemistry

From Molecules to Materials

Edited by Norbert Auner, Johann Weis



Weinheim · New York · Basel · Cambridge · Tokyo

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Edited by N. Auner, J. Weis



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*Prof. Dr. Dr. h.c. Eugene G. Rochow (left) and
Prof. Dr. Dr. h.c. Richard Müller (right)
at the "Munich Silicon Days" Conference, August 1992*

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PREFACE

Eugene G. Rochow
Professor Emeritus, Harvard University

Professor Müller and I have enjoyed cordial relations for over thirty years, but this is the first time he and I have been honored together for our separate and almost simultaneous discovery of what has become known as the Müller-Rochow Process. It is a great pleasure, and a source of much personal satisfaction to us, that we have both been awarded the "Wacker Silicon-Preis" during the stimulating and enjoyable "Munich Silicon Days '92".

When I realized that the new "methyl silicon oxides" that I developed during the late 1930s could never reach practical application unless an entirely new method of synthesis was devised, entirely outside of the Grignard reagent, it took many experiments before the reaction between methyl chloride and a silicon-copper powder became a demonstrated reality. Then, after the 1940 success and endless laboratory scale-ups, there was an agonizingly long wait while a chemical engineering group under Charles E. Reed devised new equipment for carrying on the reaction, built a pilot plant, and eventually bought land and started full-scale production. Today, the reaction is the basis of a thriving world-wide industry, the products of which are of enormous benefit both to individuals and to commerce.

In the papers presented in the two days of the Munich Silicon Days, representatives from many lands describe what is new and what has been going on in the silicone industry. I join with Prof. Müller in commending these papers, now in book form, to the student and the practitioner in this new, very different, and very exciting field.

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EDITORS' PREFACE

This contribution to the broad field of organosilicon chemistry including molecules and materials, marks a very unusual anniversary, the existence of which effectively contradicts a historical statement by the famous organosilicon pioneer F. S. Kipping, who believed 80 years ago that organosilicon chemistry would never gain industrial and commercial importance. Fifty years after the invention of the Müller-Rochow process, the silicon industry achieved an annual worldwide turnover of US\$ 4.700.000.000. This proves impressively that the basic process - independently developed by R. Müller and E. G. Rochow in 1941/2 - can be considered to be the most important innovation for organosilicon research work in industry and university.

On the occasion of the 50th birthday of the "Direct Synthesis", an organosilicon symposium was held in Munich. Though having been emeriti professors for many years, both pioneers of organosilicon chemistry participated in this symposium, still demonstrating their strong and vivid interest in recent results in this field of research, and thus constituting a notable highlight of the conference. For their outstanding contributions to organosilicon chemistry, both scientists were honored by the conferment of the Wacker Silicon Award 1992.

"Munich Silicon Days '92" proved to be a very effective forum for the exchange of information between university scientists and those from industry, and a stimulus for more intense cooperation between them, enhancing the capability of finding solutions for still open problems in this specific field of chemistry. During the course of the conference it became evident that transitions from basic research work to industrial applications and vice versa are happening more and more; for instance, on the one hand many research scientists dealing originally with molecular organosilicon chemistry have undertaken a second research activity in material science, and on the other hand many material scientists are engaged in finding appropriate molecular precursors.

During the conference many participants asked us to publish the papers presented in a volume of proceedings in order to enable those scientists who could not attend the symposium to have access to the information. As we are convinced that the results presented reflect the most recent aspects of organosilicon chemistry, we have applied ourselves diligently to the task of editing this volume, and would like to thank all authors for their effective and encouraging support.

This conference was a well balanced mixture of plenary and invited lectures as well as poster contributions. They have been arranged in this volume under the following headings:

- I. Tetravalent Organosilicon Compounds: Chemistry and Structure**
- II. Subvalent and Unsaturated Organosilicon Compounds: Formation and Reactivity**
- III. Hypervalent Organosilicon Compounds: Formation, Structure and Chemistry**
- IV. Organosilicon Metal Compounds: Coordination Chemistry and Catalysis**
- V. Silicon Polymers: Formation and Application**

We are confident that "Munich Silicon Days '92", which has had successful predecessors in the USA and Japan, will provide the inspiration for further meetings, and will thereby benefit the organosilicon industry.

Acknowledgment

We would like to thank our coworkers M. Backer, C.-R. Heikenwälder, G. Sommer, H.-U. Steinberger, C. Wagner and especially Dr. W. Ziche, who directed the assisting team, for their excellent engagement in helping us to perform the redactional work.

Contents

Tetravalent Organosilicon Compounds: Chemistry and Structure

Introduction	1
<i>N. Auner, J. Weis</i>	
Structures of Small Silicon Containing Compounds - Why and How?	3
<i>D. W. H. Rankin</i>	
Sterically Overcrowded Organosilicon Compounds and their Properties.....	11
<i>H. Bock, J. Meuret, Ch. Näther, K. Ruppert</i>	
Synthesis of Functionally Substituted Oligosilanes Based on Silyltriflate Derivatives.....	21
<i>W. Uhlig</i>	
Electroreductive Formation of Di- and Polysilanes.....	27
<i>E. Hengge, Ch. Jammegg</i>	
Linear Tetrasilanes with Internal Substituents: Oligosilanes with Optical Activity	31
<i>H. Stüger</i>	
A New Way to Si-Ge and Si-Sn Bonds:.....	35
Hexachlorodisilane Cleavage of Organometal Phosphanes	
<i>R. Martens, W.-W. du Mont</i>	
$^{29}\text{Si}^{29}\text{Si}$ Coupling Constants of Bromo- and Iododisilanes and -trisilanes	37
$\text{X}_n\text{Si}_2\text{H}_{6-n}$ and $\text{X}_n\text{Si}_3\text{H}_{8-n}$ (X = Br, I)	
<i>U. Katzenbeisser, K. Hassler</i>	
Calculation of the ^{29}Si NMR Chemical Shifts in Molecules	39
with SiN, SiCl, and SiSi Bonds	
<i>R. Wolff, R. Radeaglia</i>	
Reactivity of Very Electron-Rich Organosilyl Amines.....	41
<i>W. Kaim, A. Lichtblau, T. Stahl, E. Wissing</i>	
Lithiated Aminofluorosilanes as Precursors for	43
Monomeric and Dimeric Iminosilanes	
<i>K. Dippel, U. Klingebiel, L. Marcus, S. Walter</i>	

XII Contents

Fluorofunctional Silylamines and -Hydrazines -45 Precursors for (Si-N) Ring Systems <i>C. Drost, I. Hemme, B. Tecklenburg, U. Klingebiel</i>	45
New Approaches to (Fluoromethyl)silanes49 <i>H. Bürger, P. Moritz</i>	49
Homo- and heterocyclic Si-O-Systems - Rings and Cages51 <i>U. Klingebiel</i>	51
Silaheterocycles from Intramolecular Reactions of57 Silicon-functionalized Diazoacetic Esters <i>F. Krebs, S. Bender, B. Daucher, T. Werle, G. Maas</i>	57
Synthesis and Reaction Behavior of Organoalkoxysilylphenols61 <i>E. Nietzschmann, O. Böge, Y. Mrestani</i>	61
N-Silylation: New Possibilities for Long-known Amines65 <i>K. Paulini, H.-U. Reißig</i>	65
On the Acid-catalyzed Reaction of Siloxanes with Alcohols67 <i>H. Kelling, D. Lange, A. Surkus</i>	67
On the Reactivity of Chlorosiloxanes69 <i>K. Käppler, U. Scheim, K. Rühlmann</i>	69
Chlorosilanols - more stable than you think - shown with ²⁹ Si NMR71 <i>R. Lehnert</i>	71
Diorganosilyl-bis(O-alkylphosphonates)75 <i>K. Kellner, L. Rodewald</i>	75
Subvalent and Unsaturated Organosilicon Compounds: Formation and Reactivity	
Introduction79 <i>N. Auner, J. Weis</i>	79
Basic Principles of the Theory of Bonding in Silicon Compounds81 <i>R. Janoschek</i>	81

Expectations from an Unusual Compound:	87
The Chemistry of Decamethylsilicocene	
<i>P. Jutzi</i>	
$\text{Cp}^*_2\text{Si}(\text{CO})$ and $\text{Cp}^*_2\text{Si}(\text{N}_2)$: Complexes of Decamethylsilicocene.....	93
<i>M. Tacke, Ch. Klein, D. Stufkens, A. Oskam, P. Jutzi, E. A. Bunte</i>	
Silicon and Phosphinomethanides: A Novel Entry to Hypervalent.....	95
and Low Valent Organosilicon Chemistry	
<i>H. H. Karsch</i>	
Neopentylsilenes: Laboratory Curiosities or Useful Building	103
Blocks for the Synthesis of Silaheterocycles ?	
<i>N. Auner</i>	
Synthesis and Thermolysis Reactions of Si-functionalized 2-Silaazetidines.....	115
<i>A. Weingartner, W. Ziche, N. Auner</i>	
Reactions of Silaethenes in the Gas Phase and in Solution	119
<i>J. Grobe, H. Ziemer</i>	
The Reaction of Vinylsilanes with Lithium Metal	123
<i>A. Maercker, K. Reider</i>	
Small Silicon Ring Compounds: Formation and Reactions.....	125
<i>M. Weidenbruch</i>	
Matrix Photolysis of Simple Azidosilanes	131
<i>G. Maier, J. Glatthaar</i>	
Low-coordinated Si-Compounds:	139
Gas Phase Reactions with Heterosubstituted Silylenes	
<i>J. Heinicke, B. Gehrhus, S. Meinel</i>	
Unusual Coordination in Phosphorus-Silicon Compounds	143
<i>H. R. G. Bender, E. Klein, E. Niecke, M. Nieger, H. Ranaivonjatovo</i>	
Unsaturated Silicon Compounds: Matrix IR Investigations and	147
Quantum Chemical Calculations	
<i>H. Schnöckel, R. Köppe</i>	

XIV Contents

Hypervalent Organosilicon Compounds: Formation, Structure and Chemistry

Introduction	155
<i>N. Auner, J. Weis</i>	
Reactivity of Penta- and Hexacoordinated Silicon Species	157
<i>R. Corriu</i>	
Compounds with High Coordination Numbers at Silicon: Models for the	165
Investigation of the Nucleophilic Substitution Reaction at Silicon Centers	
<i>N. Auner, R. Probst, F. Hahn, E. Herdtweck</i>	

Organosilicon Metal Compounds: Coordination Chemistry and Catalysis

Introduction	167
<i>N. Auner, J. Weis</i>	
A Silane-induced CO-Activation and CC-Coupling Reaction:	169
Modeling of Active Surface Sites	
<i>H. Handwerker, H. Beruda, M. Kleine, Ch. Zybill</i>	
Organometal Fragment Substituted Silanols, Siloxanes and Silylamines	185
<i>W. Malisch, S. Schmitzer, G. Kaupp, K. Hindahl, H. Käb, U. Wachtler</i>	
On the Complex Chemistry of Cyclopentadienyl Ligands with	193
Oligoethylene Glycol Ether Tentacles	
<i>U. Siemeling</i>	
Heterometallic Complexes with a Bridging Alkoxysilyl Ligand:	197
$\eta^2\text{-}\mu_2\text{-Si(OR)}_3$	
<i>M. Knorr, P. Braunstein</i>	
Silicon-containing Main Group Transition Metal Complexes	199
<i>M. Strampfer, M. Knorr, P. Braunstein</i>	
Silicon-containing Bimetallics Fe-M (M = Ni, Pd, Pt) with	201
M-Coordinated Organic Ligands	
<i>T. Faure, M. Knorr, P. Braunstein</i>	

Anionic Transition Metal Silyl Complexes:	205
New Building Blocks in Coordination Chemistry <i>U. Schubert</i>	
Synthesis and Characterization of New Transition Metal-Silicon Compounds	213
<i>E. Hengge, M. Eibl, B. E. Stadelmann, A. Zechmann, H. Siegl</i>	
The Silicon Effect in Metallic Silylamides.....	217
<i>M. Veith, S. Müller-Becker, A. Lengert, N. Engel</i>	
New Chemistry for Reactive Transition-Metal Silicon Bonds	225
<i>T. D. Tilley</i>	
Organosilane Chemistry at Tailor-made Platinum Centers	231
<i>P. Hofmann</i>	
Silicon Polymers: Formation and Application	
Introduction	251
<i>N. Auner, J. Weis</i>	
Regioselectivity in Hydrosilylation Reactions	253
<i>Ch. J. Herzig</i>	
Network Characterization of Photocross-linked Silicone Acrylates	261
<i>U. Müller, S. Jockusch, K.-G. Häusler, H.-J. Timpe</i>	
Photocross-linking of α,ω -Vinyl Terminated Silicones with	263
Silicones Containing Pendant Mercapto Groups <i>A. Füllbier, U. Müller</i>	
Investigations into the Relaxation Behavior of Polymer Siloxanes	265
<i>H. Jancke</i>	
Dicyclopentadienyl Units Containing Silicone Surfactants	267
<i>R. Wagner, G. Sonnek[†]</i>	
Applications of Transition Metal Compounds in the Preparation of	269
Useful Silicon-containing Ceramics <i>D. Seyferth</i>	

New Ways to Polysilanes - Starting Compounds for New Silicon Materials	275
<i>E. Hengge</i>	
Anionic Polymerization of Masked Disilenes:	285
Mechanism, Scope, and Applications	
<i>H. Sakurai</i>	
Ceramic Fibers from Organosilicon Polymers	293
<i>W. Kalchauer, G. Geisberger</i>	
Novel Multifunctional (Meth)acrylate Alkoxysilanes as	301
Precursors for Inorganic-Organic Copolymers	
<i>K. Rose, H. Wolter</i>	
Processing, Properties and Structural Development of	303
Polymer-derived Fiber-reinforced SiC	
<i>T. Haug, H. Knabe, U. Ehrmann</i>	
Metal/SiO ₂ Nanocomposites by Sol-Gel Processing	319
<i>C. Görsmann, B. Breitscheidel, U. Schubert</i>	
Organically Modified SiO ₂ Aerogels	323
<i>F. Schwertfeger, E. Seyfried, U. Schubert</i>	
Spectroscopic Investigations on Silylated Inorganic Substrates	325
<i>J. Grobe, K. Stoppek-Langner, A. Benninghoven, B. Hagenhoff,</i> <i>W. Müller-Warmuth, S. Thomas</i>	
Materials for Optical Data Processing	331
<i>G. Schottner, W. Grond, H. Steins, U. Schubert, D. Haarer, L. Kümmerl</i>	
Thick Siloxane Films from Tetraethoxysilane on Silicon Wafers	333
<i>R. Dietrich, J. Grobe, B. Hagenhoff, K. Meyer, A. Benninghoven</i>	
Chemical Relaxation of SiH ₄ , Si ₂ H ₆ , SiH ₂ , and H ₂ in Low Pressure Discharges.....	337
<i>W. Hallinger, R. Konwitschny, K. Schopper, S. Veprek</i>	
Kinetic and Mass Spectroscopic Investigations of Plasma Induced Deposition of	341
Silicium Dioxide from Tetraethylorthosilicate and Oxygen	
<i>A. Jäger, I. Cermák, V. Windbichler, S. Veprek</i>	
Author Index and Subject Index	343

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Tetravalent Organosilicon Compounds: Chemistry and Structure

N. Auner, J. Weis

Tetravalent silicon is the only structural feature in all silicon sources in nature, e.g. the silicates and silica; even elemental silicon exhibits tetravalency. Tetravalent silicon is considered to be an analogon to its group 14 homologue carbon and in fact there are a lot of similarities in the chemistry of both elements. Furthermore, silicon is tetravalent in all industrially used compounds, e.g. silanes, polymers, ceramics, and fumed silica. Also the reactions of subvalent and / or low coordinated silicon compounds normally lead back to tetravalent silicon species. It is therefore not surprising that more than 90% of the relevant literature deals with tetravalent silicon. The following examples illustrate why "ordinary" tetravalent silicon is still an attractive field for research activities: Simple and small tetravalent silicon compounds - sometimes very difficult to synthesize - are used by theoreticians and preparative chemists as model compounds for a deeper insight into structural features and the study of the reactivity influenced by different substituents on the silicon center. As an example for industrial applications, the chemical vapor decomposition (CVD) of appropriate silicon precursors to produce thin ceramic coatings on various substrates may be mentioned.

Bulky substituents at tetravalent silicon centers are the structural key element of sterically overcrowded compounds with extraordinary properties: Inter- and intramolecular interactions of the bulky ligands can be studied in detail and allow an assessment of the ligands' influence on structure and reactivity.

Silapharmaka often exhibit a stronger drug efficiency compared to the carbon analoga. They are derived from the latter by replacing tetravalent carbon by tetravalent silicon at the bioactive center. This is one more nice example of the analogy between tetravalent carbon and silicon.

Literature on tetravalent silicon has been published to such an extent, that for a good introduction the reader is referred to the basic, comprehensive compendium of Patai & Rappoport.

Reference:

- [1] S. Patai, Z. Rappoport (eds.), *The Chemistry of Organic Silicon Compounds*, John Wiley & Sons, Chichester 1989.

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Structures of Small Silicon-Containing Compounds - Why and How?

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Summary: The importance of structural studies for the identification of small molecules and for the interpretation of their reactivity is illustrated with examples of silicon-containing compounds. Such compounds are best studied in the gas phase, so that their structures are undistorted by intermolecular interactions, and may be compared with those calculated theoretically. Examples are given of silicon compounds which show major differences between their gas and solid phase structures, even when the intermolecular interactions are quite weak.

The methods available for structure determination are surveyed. Those that are applicable to the gas phase, i.e. electron diffraction and rotational spectroscopy, are suitable mainly for small molecules. Data for the crystalline phase are usually relatively straightforward to obtain, but acquiring reliable structural data for silicon compounds as liquids or in solution by diffraction methods or liquid crystal NMR spectroscopy remains a challenge.

Why Study Structures?

Every synthetic chemist needs to have a tame crystallographer available, because crystallography is probably the most important technique for the *identification* of complex or unexpected products. For example, when $(C_5Me_5)Br_2Si-BBr(C_5Me_5)$ is heated, it decomposes to give $BBr_2(C_5Me_5)$ and a colorless compound of composition $BSi_2Br_4(C_5Me_5)_3$ [1]. It was X-ray diffraction which showed that this compound contained a BC_5 fragment, which is best described as an *arachno*- BC_4 fragment with a bridging saturated carbon atom (Figure 1). This unexpected compound would have been extremely difficult to identify by spectroscopic means. Similarly, X-ray diffraction provided evidence for the existence of a stable phosphasilirene, formed by the reaction of di-*t*-butylsilylene with adamantylphosphaethyne [2]. But in this case it was actually the tungsten pentacarbonyl complex (Figure 2) which was studied, and so the geometrical parameters of the phophasilirene itself are still unknown.

Geometrical parameters provide much more information than simple identification. The phosphorus-carbon distance of 1.686(6) Å in this tungsten complex is consistent with there being a double bond, as it is close to those observed in open chain phosphalkenes. But how much better it would have been if the parent compound could have been studied uncomplexed, so that the strain in this unusual ring system could have been investigated. The geometrical parameters would then have provided very useful information about the likely reactivity of the compound, and information about the changes on

coordination would also have been valuable. But presumably it proved impossible to grow crystals of the phosphasilirene, and other structural methods are not suitable for this compound.

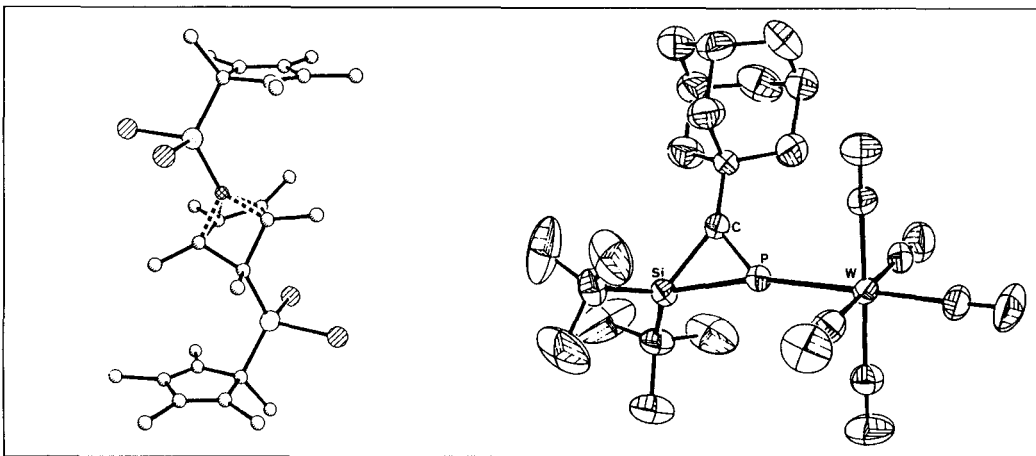


Figure 1. The structure of the compound obtained by heating $(C_5Me_5)Br_2SiBBr(C_5Me_5)$. Adapted from Reference 1.

Figure 2. The structure of the $W(CO)_5$ complex of adamantylphosphadibutylsilirene, determined by X-ray crystallography. Adapted from Reference 2.

In general, structures are best studied in the gas phase if that is possible. The interactions between neighboring molecules in condensed phases may have surprisingly large effects on structural parameters. In an extreme case, silatrane, the Si-N distance changes from 2.45(5) Å in the gas phase to 2.175(4) Å in the solid. Such dramatic changes are of course rare, but significant changes are common, and it is always best to have gas-phase data, particularly if theoretical structural data can be obtained, whether computed *ab initio* or by empirical methods. Use of gas-phase data is most important for conformational analysis, as energy differences are usually small. Thus studies of the conformations of monomethylsilyl and dimethylsilyl ethers [3], which suggested that only one lone pair on oxygen should be regarded as stereochemically significant, could only have been carried out in the gas phase.

It takes more energy to change a valence angle than a torsional angle, but, nevertheless, angles regularly vary by 4 or 5°, and sometimes up to 40°, when the molecular environment is altered. Gasphase data are therefore particularly important for molecules which have large-amplitude bending vibrations. In phenylsilane, the electron-donating silyl group leads to a change of hybridization of the adjacent carbon atom, thereby reducing the energies of structures in which the silicon atom lies out of the ring plane. This change does not result in the potential minimum being at a non-planar structure, but leads to a large-amplitude out-of-plane deformation of the silyl group. Packing the molecules into a crystal will almost certainly lead to a planar structure, but it is quite possible that the molecules could be non-planar. Only weak intermolecular forces would be needed to push it into this unexpected structure. In crystalline $Si(C_5Me_5)_2$ there are no major intermolecular contacts, yet one third of the molecules have parallel

cyclopentadienyl rings, giving a ferrocene-like structure, whereas in the remaining molecules the rings are tilted, giving an angle of 25° between the ring planes [1]. The presence of these two very distinct structures in a single crystal reflects the ease with which the molecule can be deformed. We should not therefore be surprised to find different structures in gaseous and crystalline phases for many compounds, and, if we are interested in more than just identification, we should always consider whether both gas-phase and solid-phase data should be obtained.

Many compounds exhibit strong interactions between molecules in their crystalline phases, and this is a particularly important feature for silicon compounds. In silyl fluoride [4] and silyl iodide [5] the molecules crystallise in chains, with non-bonded silicon...halogen contacts which are shorter than the sums of van der Waals' radii (Figure 3). These contacts are presumed to involve donation of lone pairs of electrons to silicon, and represent the first stages of S_N2 substitution reactions. The X-Si...X angles are invariably very close to 180° , but the Si-X...Si angles reveal the orientation of the donated lone pairs. It is interesting that this angle is 146° in solid silyl fluoride, as this is very close to the SiOSi angle of 144° in gaseous disiloxane.

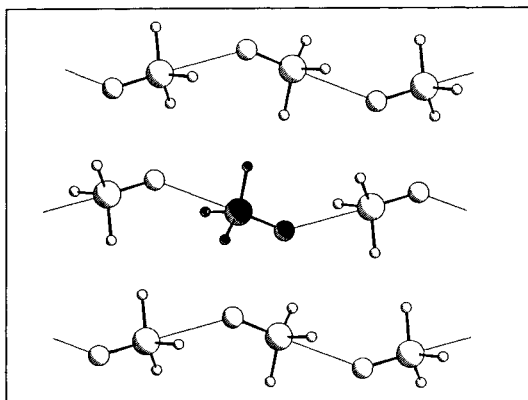


Figure 3. The structure of crystalline SiH_3F . Silyl iodide has a similar packing arrangement, but the chains are much more acutely bent at iodine.

Similarly, the Si-I...Si angle in silyl iodide is 84° , which may be compared with the angle of 88° at tellurium in $\text{Te}(\text{SiH}_3)_2$. Similar comparisons may be made for other silyl compounds, so it seems that these interactions are extremely stereospecific, and that they therefore reveal important information about the distribution of electron density, which is otherwise very difficult indeed to study. Even stronger interactions are observed in other silyl compounds. For example, solid $\text{SiH}_3\text{N}(\text{CH}_3)_2$ is pentameric (Figure 4) and the silicon atoms have regular trigonal bipyramidal structures [6]. Each silicon atom thus corresponds to the transition state of a S_N2 reaction, with one NMe_2 group displacing another. In solid $\text{SiClH}_2\text{NMe}_2$ there are two different Si-N distances [7], and the structure is best regarded as one in which an incoming NMe_2 group is displacing chlorine (Figure 4). If a series of related compounds, such as the silylamines, is studied, it is possible to derive a picture of a typical substitution reaction by plotting the two silicon-nitrogen distances against each other.

There is therefore information to be gained by studying a series of compounds, which cannot be obtained from isolated studies. In general, structures of the same compound in different environments of

the same fragment in different compounds are going to differ by small energies. They may therefore lie along reaction pathways, as in the case of silylamines, or they may give a picture of low-frequency modes of vibration. In addition, studies of a series of compounds will reveal the importance of substituent effects, such as the steric effects of replacing methyl groups by ethyl, *iso*-propyl and then *tert*-butyl groups in the dialkylaminosilanes [8,9].

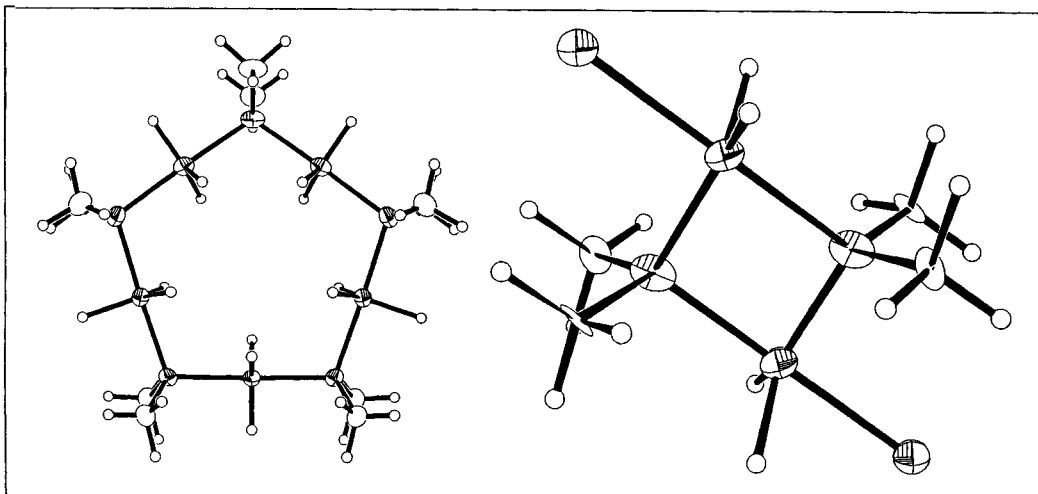


Figure 4. Structures of pentameric SiH_3NMe_2 and dimeric $\text{SiClH}_2\text{NMe}_2$ in the crystalline phase.

Although we are usually most interested in the average geometrical parameters of molecules, we should remember that the atoms move, often by substantial amounts. The ORTEP diagram of the phosphasilirene complex (Figure 2) shows the extent to which different atoms move. In this case the most significant motions appear to involve torsion of the *t*-butyl groups and bending of the carbonyl groups at carbon, so that the oxygen atoms move much more than their neighboring carbon atoms. There is also torsional motion of the adamantyl groups, but the four central atoms, Si, P, C, and W move very little. Studying the motions of atoms in this way may sometimes give a clue about what happens in the course of a chemical reaction, but experimental studies of the structural changes taking place in reactions themselves are extremely difficult to do. Given that most reactions take place in solutions or on surfaces, we are remarkably ignorant about the really important matters of structural chemistry.

Why Study Silicon-Containing Compounds?

That may seem a silly question to ask at a silicon conference! But silicon is of exceptional structural interest. A primary reason is silicon's position in the Periodic Table. In its normal compounds it is 4-coordinate, and so has no vacant s or p orbitals, which would lead to very fast reactions. Compounds of lower coordination number can be made, but they must be stabilized by bulky groups. Silicon also has