Organosilicon Chemistry III

From Molecules to Materials

Edited by Norbert Auner and
Johann Weis

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Preface

This volume summarizes the lectures and poster contributions of the *III. Münchner Silicontage* that were held in April 1996. This symposium as well as the two predecessors (in 1992 and 1994) were again jointly organized by the *Gesellschaft Deutscher Chemiker* and *Wacker-Chemie GmbH*. The number of participants from industry and university, especially of students and young scientists, was again pleasing and is convincing evidence for the great interest in this meeting; in addition it was appreciation for the effort of the organizers. Moreover the book reviews of *Organosilicon Chemistry II - From Molecules to Materials* from all over the world have encouraged us to continue the series with the current issue.

The volumes of *Organosilicon Chemistry* are not considered to be textbooks in a common sense which should help students to pass basic examinations. These contributions from internationally renowned experts and researchers in a fascinating part of the rapidly growing field of main group chemistry describes current trends in organosilicon chemistry and provides summaries of the latest knowledge in this area.

However, in order to facilitate students and "non-silicon" scientists an easier access to the ongoing research on the basis of the relevant historical background, we decided to split this volume in two parts, each with a comprehensive introduction, one on molecular and one on polymer and solid state (organo)silicon chemistry.

During the *I. Münchner Silicontage* the *Wacker Silicon-Preis* was awarded to the two pioneers of silicone chemistry - Prof. Dr. Richard Müller and Prof. Dr. Eugene Rochow on the occasion of the 50th anniversary of the "Direct Process". In the course of the *II. Münchner Silicontage* this award was conferred on Prof. Dr. Edwin Hengge, Technische Universität Graz, for his fundamental work in polysilane chemistry. At the *III. Münchner Silicontage* Prof. Dr. Hubert Schmidbaur was honoured by presenting the *Wacker Silicon-Preis* for his outstanding contributions in the field of the synthesis and characterization of organosilicon "molecules and materials".

Right in the middle of the editorial phase of this volume, we were sad to hear of the unexpected decease of our friend Prof. Dr. Edwin Hengge. With him the organosilicon community has lost a passionate lecturer and researcher, unforgettable for his integrity and charming personality. Therefore it is the editors special wish that this volume shall keep alive the memory of an excellent organosilicon chemist!

Collecting and publishing these papers it is our main intention to encourage students and young scientists to focus on organosilicon chemistry and to continue the work in the future! We want to light a beacon - outstanding success in the last few years should not deceive us, that there are still a lot of challenging problems to be solved in the future: this includes basic research as well as the development of new materials.

In August 1997

Prof. Dr. Norbert Auner *Dr. Johann Weis*

Acknowledgment

First of all we would like to thank the numerous authors for their intense cooperation, which made this overview of current organosilicon chemistry possible. The tremendous work load to achieve the attractive layout of this volume was mainly performed by Dr. Claus-Rüdiger Heikenwälder and Dr. Mathias Kersten. We thank both for their admirable engagement!

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PART I

FASCINATING ORGANOSILICON COMPOUNDS

INTRODUCTION

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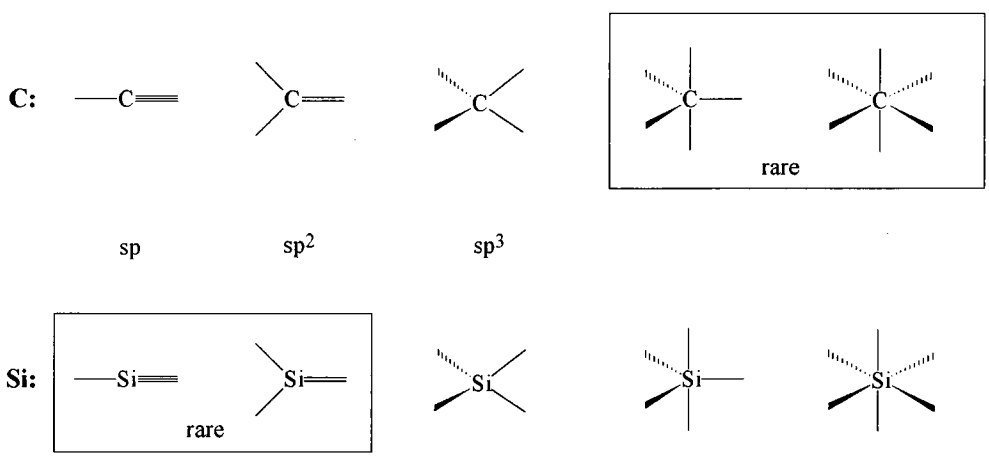
To understand Group 14 - and especially organosilicon - chemistry some comparisons between silicon and carbon have to be considered. There are two major properties that distinguish silicon from carbon. Silicon atoms are about 50 % larger than carbon atoms and this increased size will have some ramifications and consequences, such as lower barriers to silicon-element bond rotations and less stable π-bonds. Furthermore, the smaller Pauling electronegativity of silicon results in differently polar silicon-element bonds compared to carbon and thus will change its reactivity and enable reactions not possible in carbon chemistry.



The common environments exhibited for carbon and silicon show that silicon differs from carbon by its strongly reduced ability to form multiple bonds in comparison to its congener carbon but also in its capacity to form stable derivatives with more than four bonds. Carbon exhibits a maximum of four single covalent bonds, derivatives with more (e.g. five) nearest neighbors only exist in 'non classical (carbon bridged) ions', in a few carbon gold complexes and in some organometallic carbide compounds. The lack of multiple bonds seriously hampers synthetic strategies in silicon chemistry compared to the numerous possibilities available to the organic chemists. But this lack is counterbalanced by the ease of formation of silicon hypervalent species, the low activation energies

for nucleophilic substitution at silicon compared to carbon and the numerous reaction pathways at tetrahedral silicon centers that are not accessible to carbon.

Although over years a hybridization state has often been used to describe the expanded octet geometries of silicon - this is by no means the exclusive bonding view for higher coordinate species - one has to take into account that the participation of d-orbitals in the description of bonding in silicon compounds was a subject of continuing debate and that nowadays an alternative explanation using multicenter bonding has been accepted.

Besides other organizing principles, compounds of silicon might be ordered in terms of oxidation states and coordination numbers at the silicon centers. Tetravalent silicon mostly exhibits the oxidation state +4 (e.g. SiX_4, X = halogen, H, organo group, SiO_2, Si_3N_4, SiC etc.), in Ca_2Si however it is -4. Divalent silicon in the oxidation state +2 is found in compounds such as $:SiX_2$, SiO or SiS which are available only at high temperatures and can be identified spectroscopically in the gas phase at low pressure and/or in low temperature matrices after condensation on a cold surface (T~10K). As examples for tri- and monovalent silicon with positive oxidation numbers +3 and +1 compounds SiX_3 and SiX are named, which are formed competitively to silylenes $:SiX_2$ by photolysis and/or thermolysis of stable precursors SiX_4. Negative oxidation states -3, -2 and -1 with tri-, di-, and monovalent silicon are represented in silicides, as exemplified by $BaMg_2Si_2$, CaSi, and $CaSi_2$.

In its compounds the silicon center is surrounded by at least one up to ten neighbors. Some representative specimens in various coordination numbers are listed below and discussed later in this introduction.

Coordination number	Compound
1	Si≡O, Si≡S
2	O=Si=O, Me_3SiN=Si=$NSiMe_3$, *t*$BuCH_2CH$=Si=$CHCH_2$*t*Bu HSi≡N, PhSi≡N; X_2Si:
3	R_2Si=Y, ·SiX_3, R_3Si^+
4	SiX_4, SiO_2
5	$XSi(1,2\text{-}O_2C_6H_4)_2^-$ (X = Ph, F) $C_9H_6NOSiR_2X$ (X = halogen, SO_3CF_3) (see page 10) $X_3Si(o\text{-}C_6H_4CH_2NMe_2)$
6	SiF_6^{2-} $X_2Si(o\text{-}C_6H_4CH_2NMe_2)_2$
7	$XSi(o\text{-}C_6H_4CH_2NMe_2)_3$ (X = H, F)
8	Mg_2Si $H_2Si\{o,o\text{-}C_6H_3(CH_2NMe_2)\}_2$
10	$(C_5Me_5)_2Si$: (see page 9)

This list of compounds with silicon in the whole range of its coordination numbers and environments, including their synthesis and the investigation of their chemistry gives an impressive overview of organosilicon research currently going on worldwide.