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Structure and Bonding

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Aims and Scope

The series *Structure and Bonding* publishes critical reviews on topics of research concerned with chemical structure and bonding. The scope of the series spans the entire Periodic Table and addresses structure and bonding issues associated with all of the elements. It also focuses attention on new and developing areas of modern structural and theoretical chemistry such as nanostructures, molecular electronics, designed molecular solids, surfaces, metal clusters and supramolecular structures. Physical and spectroscopic techniques used to determine, examine and model structures fall within the purview of *Structure and Bonding* to the extent that the focus is on the scientific results obtained and not on specialist information concerning the techniques themselves. Issues associated with the development of bonding models and generalizations that illuminate the reactivity pathways and rates of chemical processes are also relevant

The individual volumes in the series are thematic. The goal of each volume is to give the reader, whether at a university or in industry, a comprehensive overview of an area where new insights are emerging that are of interest to a larger scientific audience. Thus each review within the volume critically surveys one aspect of that topic and places it within the context of the volume as a whole. The most significant developments of the last 5 to 10 years should be presented using selected examples to illustrate the principles discussed. A description of the physical basis of the experimental techniques that have been used to provide the primary data may also be appropriate, if it has not been covered in detail elsewhere. The coverage need not be exhaustive in data, but should rather be conceptual, concentrating on the new principles being developed that will allow the reader, who is not a specialist in the area covered, to understand the data presented. Discussion of possible future research directions in the area is welcomed.

Review articles for the individual volumes are invited by the volume editors.

In references *Structure and Bonding* is abbreviated *Struct Bond* and is cited as a journal.

David Scheschkewitz
Editor

Functional Molecular Silicon Compounds I

Regular Oxidation States

With contributions by

U. Böhme • G. Kickelbick • E. Kroke • C. Marschner •
T. Müller • J. Wagler

 Springer

Editor
David Scheschkewitz
Chair of General and Inorganic Chemistry
Saarland University
Saarbrücken
Germany

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Preface

Due to its unique properties, elemental silicon is a pivotal material in modern society. Even though a few other semiconductors, e.g., gallium arsenide, rival silicon in some performance indicators such as electron mobility, none of them can equally meet the technological and economic demands of current microprocessor technology: Electronic grade silicon is available at relatively low cost and its native oxide as an insulator is predisposed to effectively separate the conducting zones of microprocessors [1]. In this arguably most important application, silicon is thus present both in the elemental state (oxidation No. 0) and in its most highly oxidized form (oxidation No. +IV). In view of the prominent role of molecular silicon compounds in related industrial processes, this volume of *Structure&Bonding* is devoted to *Functional Molecular Silicon Compounds* with silicon in various oxidation states. It is divided into two sub-volumes: the first covers topics associated to silicon compounds in the “regular” oxidation state of +IV, while the second concerns compounds in lower oxidation states.

All industrial chemical processes involved in the production/purification/transformation of silicon in its elemental form have in common that silicon in lower oxidation states is prevalent in short-lived intermediates such as silylenes and larger unsaturated aggregates [2]. The chapter by Burgert Blom and Matthias Driess (Technical Universität Berlin, Germany) summarizes recent advances in the chemistry of stable silylenes, molecular compounds in the formal oxidation state +II (Volume 2, chapter titled “Recent Advances in Silylene Chemistry: Small Molecule Activation En-Route Towards Metal-Free Catalysis”). Saturated and unsaturated silicon clusters are several steps further on the way towards elemental silicon. Recent years have seen important progress with regard to the functionalization of stable derivatives of such clusters as well as the realization of surprising new structural motifs. In chapter titled “Substituted Polyhedral Silicon and Germanium Clusters” of Volume 2 Masafumi Unno (Gunma University, Kiryu, Japan) gives an account of the developments in this area. It is probably just a question of time before silicon clusters will be routinely connected to extended systems with exciting new properties as novel materials. Oligosilane chains are predisposed as linking

units for such an endeavor. Christoph Marschner (University of Graz, Austria) updates comprehensively on the preparation and functionalization of oligosilane systems in chapter titled “Oligosilanes” of Volume 1.

Initially, the research into molecular silicon compounds was driven by the mostly academic question of how much the chemistry would parallel that of its lighter cousin carbon. Naturally, the stability of unsaturated derivatives was at the center of attention. Frederic Stanley Kipping – generally considered to be one of the most influential pioneers of organosilicon chemistry – eagerly pursued the synthesis of “silico ethylenes” [3] and “silicones” [4] – the heavier analogues of alkenes and ketones, respectively. The first reliable reports on stable compounds with heavier double bonds to silicon, however, only appeared in 1981. Since these milestone achievements on compounds with Si=Si (West et al.) [5] and Si=C bonds (Brook et al.) [6], the chemistry of molecular silicon compounds has matured considerably. Especially during the first decade of the new millennium the focus has shifted from the replication of well-known carbon motifs from organic chemistry to the introduction and tolerance of functional groups. The contribution by Takeaki Iwamoto and Shintaro Ishida (Tohoku University, Sendai, Japan) gives an overview of recent developments regarding Si=Si double bonds (Volume 2, chapter titled “Multiple Bonds with Silicon: Recent Advances in Synthesis, Structure, and Functions of Stable Disilenes”).

With the powerful concept of stabilization of reactive main group species by strongly σ -donating *N*-heterocyclic carbenes pioneered inter alia by Greg Robinson [7], some of Kipping’s initial targets are now available as derivatives stabilized by coordination of *N*-heterocyclic carbenes. Eric Rivard (University of Alberta, Edmonton, Canada) summarizes this emerging new field from the point of view of low valent silicon chemistry in chapter titled “Recent Advances in the *Heterocyclic Carbene-Supported Chemistry of Silicon*” of Volume 2. Interestingly, however, *N*-heterocyclic carbenes were initially employed by Kuhn et al. for the expansion of the coordination sphere of molecular silicon compounds beyond the usual four substituents [8]. Since it is now well established that this expansion does not entail hypervalency, low valent compounds with higher coordination numbers are one possible approach to increase the functionality of hypercoordinate silicon species. The various aspects of higher coordinate silicon compounds are comprehensively reviewed by Jörg Wagler, Uwe Böhme, and Edwin Kroke (Technical University Bergakademie Freiberg, Germany) in chapter titled “Higher-Coordinated Molecular Silicon” of Volume 1.

Having been unsuccessful in the original tasks, Kipping became disillusioned regarding any commercial value of his discoveries towards the end of his career [9]. As Thomas Edison said, however, “just because something doesn’t do what you planned it to do does not mean it’s useless” (As quoted in: [10]). Kipping’s discoveries indeed laid the foundations for the nowadays ubiquitous application of polysiloxanes (colloquially known as silicones) in daily life. Silsequioxanes – already mentioned by Kipping as formally having the empirical formula of an anhydride $(R_2SiO)_2O$ [9] – are increasingly being used as precursors for sophisticated hybrid materials involving polysiloxanes. In his chapter, Guido Kickelbick

(Saarland University, Saarbrücken, Germany) gives an overview of the fundamental sciences and high-end applications of silsequioxanes (Volume 1, chapter titled “Silsequioxanes”).

Finally, two chapters are devoted to the most extreme of functionalization: ionization. The generation of silyl cations and anions provides valuable synthons, e.g., for the further extension of the silicon scaffold. In chapter titled “Silylium Ions” of Volume 1, Thomas Müller (University of Oldenburg, Germany) summarizes the many applications of silylium cations in catalysis and discusses recent trends towards low valent silicon cation chemistry thus completing the full circle to other chapters that are more explicitly devoted to low valent silicon species. Finally, the chemistry of silyl anions is summarized in chapter titled “Silyl Anions” of Volume 2.

Initially, only one volume was envisaged for the topic of functional molecular silicon chemistry, but it rapidly became clear that with the dedicated hard work and enthusiasm of all authors two volumes would be needed to accommodate the vast progress in that area during the last 10 years: the field keeps growing in an exponential manner. The ready availability of this exiting element at very low cost paired with the inquisitiveness and passion of organosilicon chemists will ensure that this trend continues for a long time to come.

Saarbrücken, Germany
September 2013

David Scheschkewitz

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