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Editorial

Coordination Chemistry of Silicon

Shigeyoshi Inoue

WACKER-Institute of Silicon Chemistry and Catalysis Research Center, Technische Universität München, Lichtenbergstraße 4, 85748 Garching, Germany; s.inoue@tum.de; Tel.: +49-89-289-13596

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It is with great pleasure to welcome readers to this Special Issue of *Inorganics*, devoted to "*Coordination Chemistry of Silicon*". Investigations into silicon compounds continue to afford a wealth of novel complexes, with unusual structures and brand-new reactivities. In fact, the ongoing quest for silicon complexes with novel properties has led to a large number of silicon compounds, that contain various types of ligands or substituents. Use of the divergent coordination behavior of silicon to construct sophisticated low- and hyper-valent silicon complexes makes it possible to change their electronic structures and properties. Therefore, progress of the coordination chemistry of silicon can be the key concept for the design and development of next generation silicon compound-based applications. This Special Issue is associated with the most recent advances in coordination chemistry of silicon with transition metals, as well as main group elements, including the stabilization of low-valent silicon species through the coordination of electron-donor ligands, such as *N*-heterocyclic carbenes (NHCs) and their derivatives [1,2]. This Special Issue is also dedicated to the development of novel synthetic methodologies, structural elucidations, bonding analyses, and possible applications in catalysis or chemical transformations, using related organosilicon compounds [3]. Besides, recent years have witnessed great research efforts in silicon-based polymer chemistry, as well as silicon surface chemistry, which have become increasingly important for unveiling the correlations between nanoscopic structural features and macroscopic material properties, including the coordination behavior at silicon.

The 19 articles composing this Special Issue can be considered as a representative selection of the current research on this topic, reflecting the diversity of silicon chemistry and yield an impressive compilation.

Intrinsic coordination behaviors of silanes towards transition metals are the subject of several articles in this issue. For example, Nakata et al. discuss the synthesis and structure of a hydrido platinum(II) complex with a dihydrosilyl ligand that bears a bulky 9-triptycyl group [4]. The ligand exchange reaction of this mononuclear (hydrido)(dihydrosilyl) complex with various phosphines has also been studied. Sunada and coworkers provide an elegant method for accessing planar tetrapalladium clusters starting from octa(isopropyl)cyclotetrasilane through the insertion of palladium atoms into the Si–Si bonds of the cyclotetrasilane [5]. While the ligand exchange reaction with NHCs yields the more coordinatively unsaturated cluster, reaction with a trimethylolpropane phosphite affords a planar tripalladium cluster. Wagler and coworkers demonstrate a striking coordination chemistry of (2-pyridyloxy)silanes with transition metals (Pd, Cu) [6]. The molecular structures of the complexes have been elucidated by crystallographic analysis, and further computational investigations provided an in-depth understanding of the interatomic interaction between transition metals (Pd, Cu) and penta-/hexa-coordinate silicon centers.

Using donor ligands such as NHCs, allowed the stabilization and isolation of reactive low-valent silicon species. For instance, Matsuo and coworkers identified a methodology for accessing the NHC-adduct of arylbromosilylene from the reaction of dibromodisilene with two NHC equivalents [7]. They also discuss the isolation of arylsilyliumylidene ions through the dehydrobromination with four

NHC equivalents. In the course of the reactivity study on the NHC-coordinated silyliumylidene ion, Porzelt et al. describe the activation of the S–H bond in hydrogen sulfide by the arylsilyliumylidene ion, resulting in the formation of an NHC-coordinated thiosilaaldehyde [8]. DFT (density functional theory) calculations have been employed to examine the zwitterionic character of NHC-coordinated thiosilaaldehyde, and the reaction mechanism for the formation has also been computationally investigated. The NHC stabilization method can also be expanded to the heavier congener of silicon, namely, germanium. Egawa, Unno, and coworkers describe the successful isolation of the NHC-adduct of germathioacid from the reaction of corresponding NHC-stabilized chlorogermylene with elemental sulfur [9]. The zwitterionic resonance structures, including the nature of the Ge–S bond have also been analyzed using computational methods.

Several articles comprising this issue focus on molecular silicon clusters and silicon surface chemistry. Jantke and Fässler report computational investigations on polymeric Si_9 clusters [10]. The stability and electronic nature of the related polymeric and oligomeric clusters are discussed. Iwamoto and coworkers describe the intriguing thermal transformation of a Si_8R_8 siliconoid into three novel silicon clusters having unprecedented silicon frameworks [11]. Molecular structures of three obtained clusters have been elucidated by conventional spectroscopic methods and XRD analysis. The absorption of acetylene and ethylene on the surface of Si(001) in the usual bond insertion mode is deeply investigated by implementing DFT calculations by Pecher and Tonner [12]. The distorted and symmetry-reduced coordination of silicon atoms with increased electrophilicity and enhanced reactivity has been shown by molecular orbitals analysis.

The present issue also includes several articles concerning the incorporation of silicon atoms in organic and inorganic ring structures. Ottosson and coworkers provide quantum chemical calculations on the ring-opening ability of silacyclobutene [13]. They show that a silacyclobutene ring fused with a [4n]annulene can be used as an indicator for triplet-state aromaticity. The preparation of a digermadichlorosilane marked by a 5-membered $SiGe_2C_2$ ring is described by Sasamori and coworkers [14]. It was accomplished via double Si–Cl insertion in the reaction between 1,2-digermacyclobutadiene and $SiCl_4$. The enveloped geometry of the $SiGe_2C_2$ ring skeleton was elucidated by XRD analysis. Jana, Scheschkewitz, and coworkers report on the synthesis of an NHC-adduct of chlorogermylene adjacent to an SiN_2C_2 ring [15]. This was produced via the oxidative addition of West's *N*-heterocyclic silylene into the Ge–Cl bond of the NHC-complex of germanium(II) dichloride. Iwamoto and coworkers provide the synthesis of 1,2-bis(trimethylsilyl)-1,2-disilacyclohexene bearing the Si=Si double bond in an Si_2C_4 ring skeleton [16]. The conversion of this disilene into the corresponding potassium disilenide and its reactivity towards various electrophiles are also described. Von Hänisch's group discusses the incorporation of a disilane unit into crown ether, leading the preparation of 1,2-disila[18]crown-6, as well as 1,2-disila-benzo[18]crown-6 [17]. The complexation ability with ammonium cations by these disilane-containing crown ethers is examined, and corresponding complexes are successfully isolated. Pietschnig and coworkers highlight the synthesis of cyclopentyl-substituted silanetriol and its condensation that leads to the isolation of corresponding disiloxanetetrol and also hexameric polyhedral silsesquioxane cage T_6 [18].

The review article by Ohshita and coworkers comprehensively outlines works related to the utilization of disilanylene polymers to modify the TiO_2 surface and their applications in dye-sensitized solar cells [19]. Kanno, Kyushin, and coworkers describe new straightforward synthetic methods for unsymmetrically substituted oligosilanes with various functional groups [20]. Reactions with organolithium or Grignard reagents and ruthenium-catalyzed alkoxylations were employed for the substitution of each functional group. Bauer and Strohmann provide the molecular structures of four enantiomerically pure 2-silylpyrrolidinium salts [21]. XRD analysis unveiled the structures of these compounds, and hydrogen-bond interactions were discussed. The group of Majundar describes the facile one-pot synthesis of *N*-heterocyclic germylene and stannylene using 1,4-bis(trimethylsilyl)-1,4-diaza-2,5-cyclohexadiene as a mild organosilicon reductant [22]. In this

reaction, the volatile byproducts trimethylsilyl chloride and pyrazine can easily be removed under vacuum, and significant over reduction was not observed.

Finally, I wish to express my gratitude to all the authors for their contributions to this Special Issue. I would also like to thank reviewers for their kind, essential advice and suggestions. The contributions of the editorial, as well as the publishing staff at *Inorganics* to this Special Issue are also highly appreciated. I hope readers from different research fields will enjoy this Open Access Special Issue and find a basis for further work in this exciting field of silicon chemistry.

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