Schiegerl, Lorenz J.; Karttunen, Antti J.; Klein, Wilhelm; Fässler, Thomas F.

**Anionic Siliconoids from Zintl Phases**

*Published in:* Chemistry - A European Journal

*DOI:* 10.1002/chem.201805442

Published: 20/12/2018

*Document Version*
Early version, also known as pre-print

*Published under the following license:* CC BY-NC

Anionic Siliconoids from Zintl phases: \( R_2\text{Si}^{9-} \) with Six and \( R_2\text{Si}_9^{2-} \) with Seven Unsubstituted Exposed Silicon Cluster Atoms (\( R = \text{Si(tBu)}_2\text{H} \))

Lorenz J. Schiegerl[ab, Antti J. Karttunen[ac], Wilhelm Klein[b], and Thomas F. Fässler[ab]

Abstract: Neutral and anionic silicon clusters (siliconoids) are regarded as important model systems for bulk silicon surfaces. For 25 years their formation from binary alkali metal silicide phases has been proposed, but experimentally never realized. Herein we report for the first time on the silylation of a silicide leading to the anionic siliconoid \( \text{Si}((\text{Bu})_2\text{H})_2\text{Si}^{9-} \) (1a) and \( \text{Si}((\text{Bu})_2\text{H})_2\text{Si}^{2-} \) (2a) with the highest known number of ligand-free silicon atoms. The new anions are obtained in a one-step reaction of \( K\text{Si}((\text{Bu})_2\text{H})_2\text{Si} \) and \( \text{Si}(\text{Bu})_2\text{H})_2\text{Si} \) with the respective elements in quantitative yields. The synthesis and structural characterization of tetrakis(tert-butylsilyl)-tetrahydro-tetrasilane \( R\text{Si}_6 \) (\( R = \text{Bu}_2\text{Si} \)) featuring a \( \text{Si}_4 \) tetrahedron, obtained by the reaction of \( \text{BRBr}_2\text{SiBr}_2\text{R} \) with \( \text{RNa} \), in his contribution Wiberg also suggested that such compounds should more be straightforwardly accessible through the reaction of alkylsilanes with tetrahedral \( \text{Si}_4 \) cations. Polyanions are present in intermetallic compounds \( R\text{Si}_x \) (\( A = \text{Li–Cs} \)), accessible in a one-step reaction by fusion of the respective elements in quantitative yields. The idea of using so-called Zintl ions as precursors for Si-rich molecules was supported by the synthesis of \( \text{Sekiguchi’s anionic species R}\text{Si}^{9-} \) (\( R = \text{SiMeDis} \), \( \text{Dis} = \text{CH}((\text{SiMe}_3)_2 \)) in 2003 and was for more than two decades frequently considered, but repeatedly discarded due to the high reducing properties of silicides. The development in the synthesis of molecules with low-valent Si atoms as well as with unsubstituted Si atoms triggered again the demand for faster synthetic routes towards molecules with a considerable number of Si–Si bonds and unsubstituted Si atoms. According to a recent definition, such siliconoids require at least one exposed cluster atom with a hemispherical coordination sphere, which forms bonds solely to adjacent Si clusters atoms. Consequently, such units display only homoatomic bonds and are free of ligands (“naked”). Such neutral and anionic silicon clusters (siliconoids) are regarded as important model systems for bulk silicon surfaces. In 2011 our group showed that \( \text{Si}^{9-} \) Zintl clusters are accessible to chemical transformation from solid Zintl phases e.g. by reacting it with \( \text{CuMes} \) (Mes = 1,3,5-trimethylbenzene), thereby giving \( \text{CuMes}_2\text{Si}^{9-} \) whereas in 2016 Scheschkwitz et al. obtained \( \text{LiR}^n\text{Si} \) (\( R = 2,4,6\)-trisopropylphenyl) with one anionic and two neutral unsubstituted vertex atoms by a “purely molecular” approach. However, an approach from Zintl phases with covalently bonded ligands was still missing. By contrast, during the last decade the vinylation, silylation and phosphinylation of polyhedral germanium Zintl anions \( \text{Ge}^{9-} \) with different substituents has been demonstrated by using mainly the Zintl phase \( K_4\text{Ge}_9 \). However, similar reactions of \( \text{Si}^{9-} \) clusters were not yet achieved due to the absence of the corresponding 4:9 phases. Up to date, \( \text{A}_4\text{Si}^{9-} \) (\( A = \text{Li–Cs} \)) and \( \text{A}_4\text{Si}^{11-} \) (\( A = \text{K–Cs} \)) phases that contain either solely \( \text{Si}^{14-} \) units, or \( \text{Si}^{14-} \) beside \( \text{Si}^{12-} \) delacthalic clusters in a 2:1 ratio, are known. \( \text{Si}^{14-} \) and \( \text{Si}^{12-} \) clusters are species which have nucleophilic character due to their highly negative charge but are also electrophilic in character due to the electron-deficient bonding situation of the cluster skeleton. Since the \( \text{A}_4\text{Si}_4 \) phases are rather insoluble in any solvent, the focus was put on the \( \text{A}_4\text{Si}_17 \) phases that are sufficiently soluble in liquid ammonia, and crystal structures of solvates containing \( \text{Si}^{14-} \) and \( \text{Si}^{12-} \) units have been obtained, and subsequent reactions in liquid ammonia as solvent led to the formation of \( \text{(PhZn)}\text{Si}_3^{9-} \) \( \text{(Ni(CO)}_2\text{)}\text{Si}_3^{9-} \) and \( \text{(NHCOPhCu)}\text{Si}_3^{9-} \). Recently, the mono-protonated cluster \( \text{H}_2\text{Si}^{9-} \) was obtained upon the isolation of crystals of \( \text{A}_1\text{Si}_17 \) (\( A = \text{K, Rb} \)) from liquid ammonia with the help of sequestering agents. A subsequent transfer of the extraction products to pyridine yielded the doubly-protonated species, the structure of which was determined for the iso-valence-electronic cluster with mixed tetrel elements \( \text{H}_2\text{Si}^{9-}\text{Ge}^{2-} \) (\( x = 4.1 \)). Both, \( \text{H}_2\text{Si}^{9-} \) and \( \text{H}_2\text{Si}^{2-} \) were fully characterized by \( ^1H \) and \( ^{29}\text{Si} \) NMR spectroscopy in solution. The formation of well-defined solutions that contain nine-atomic silicon clusters after pre-extraction with liquid ammonia finally paved the way for further conversions of these clusters in solution with appropriate reactants. Theoretical studies support the

[a] L. J. Schiegerl, Dr. W. Klein, Prof. Dr. T. F. Fässler
Department of Chemistry
Technical University of Munich (TUM)
Lichtenbergstraße 4, 85748 Garching (Germany)
E-mail: Thomas.Fassler@lrz.tum.de

[b] L. J. Schiegerl, Prof. Dr. T. F. Fässler
WACKER Institute of Silicon Chemistry
Technical University of Munich (TUM)

[c] Prof. Dr. Antti J. Karttunen
Department of Chemistry and Materials Science
Aalto University, 00076 Aalto (Finland)

Supporting information for this article is given via a link at the end of the document.
formation of siliconoids by the attachment of sp³-Si linkers[20] and triggered us to investigate the reactivity of Si⁺⁺ clusters obtained from K₂Si₂²⁺ and chloro-silanes with the ambition to synthesize larger siliconoid units. The experimental results are supported by computational methods (DFT-PBE0/TZVP level of theory).[21]

In analogy to our recent synthesis of H₂Si₂²⁻[19] we dissolved K₂Si₂²⁺/222crypt in liquid ammonia. After removal of the solvent the brown residue was treated with thf under continues cooling in an ice bath, and a pre-cooled solution of Si(tBu)₂HCl in thf was added. After several hours the initially heterogenous reaction mixture gave a red-brown solution, from which after removal of all volatiles and washing with hexane a brown solid was obtained. ESI-MS investigations of the solid in thf solution indicated the presence of (Si(tBu)₂H₂)₂Si⁻ (1a) as the only product species (Figure 1a). ESI-MS fragmentation experiments confirmed the groups in 1a (full ESI-MS and the ESI-MS fragmentation spectra are shown in the Supporting Information).

The ²⁹Si NMR spectrum of 1 shows three resonances at 18.00 (α), 175.16 (β) and 358.81 ppm (γ) which are in considerably good agreement with the calculated values of 21, –184 and –385 ppm, respectively for an optimized structure of 1a with D₃h symmetric cluster core (Figure 1c, NMR calculation details in the Supporting Information). All ¹H and ¹³C NMR chemical shifts were allocated by the quantum chemical shift calculations to the atoms as labeled in Figure 1b. The resonance at 18.00 ppm is attributed to the three equivalent Si(tBu)₂H groups, whereas the strongly high-field shifted signals at –175.16 and –358.81 ppm arise from the three substituted and six unsubstituted Si vertex atoms in the Si₉ polyhedron, respectively. The experimental ²⁹Si NMR signal γ (~358.81 ppm) of the unsubstituted vertex atoms shows a stronger upfield shift as usually observed for prominent siliconoid species[5] and is comparable to the signals for the protonated Si₉ cluster species HSi₉[³⁹] (unsubstituted vertex atoms: –359 ppm) and to the experimental and calculated ²⁹Si NMR average values for H₄Si₂⁹⁻[19] (exp.: –346 ppm; calcd.: –348 ppm).

Since the ligand carries H atoms with different bond separations to the Si atoms of the cluster, a two-dimensional ²⁹Si HMBC NMR spectrum was used to establish the structure of 1a (Figure 1c). Analysis of the cross peaks reveals a strong coupling between the ¹H NMR resonance α (SiH) and the ²⁹Si NMR resonance α (SiH) with a scalar coupling constant J(¹H-²⁹Si) = 177.9 Hz. A cross peak is also observed for α with the ²⁹Si NMR resonance β (silyl-substituted Si vertex atoms) with a decisively smaller scalar coupling J(¹H-²⁹Si) = 8.5 Hz. The detected J and J coupling constants are comparable to the ones in H₂Si₂(Mes)²⁻[20] with J and J values of 207 and 5.5 Hz, respectively. No signal splitting is observed for the ¹J(¹H-²⁹Si) cross peak of α and γ. Cross peaks are also observed for the proton signal b with the silicon signals α and β, but again no ³J(¹H-²⁹Si) and ⁴J(¹H-²⁹Si) signal splitting is observed. Moreover, no cross peak is observed between b and γ which would correspond to a ⁵J(¹H-²⁹Si) coupling. Ligand scrambling as observed for R₂Si₂H[⁴] cannot be excluded for 1a. A fast exchange of the ligands as well as the D₃h symmetry of 1a will both lead to the same number of signals in the NMR spectrum. No NMR-line broadening was observed by decreasing the temperature to –20°C.

Crystallization experiments of 1 from fluorobenzene solutions led to the formation of small amounts of orange needle-shaped crystals, suitable for single-crystal X-ray diffraction (crystallographic details are given in the Supporting Information). The structure determination, however, reveals the composition (K-222crypt)(Si(tBu)₂H₂)₂Si₉ (2) with only two silyl groups attached at the Si₉ cluster core. An Si:K ratio of 9:2 is confirmed by an EDX analysis of the single crystals. A fragmentation product in the ESI spectrum (see Supporting Information) also matches with (Si(tBu)₂H₂)₂Si₂⁹⁻ (2a). A similar transformation of a tris- to a bis-silylated cluster upon the crystallization process has been
detected for (Si(Bu)3)2GeO5−.[23] The molecular structure of the di-anion 2a shows a C2v symmetric cluster that derives from a monocapped square antiprism. The silyl groups are bonded to two opposing vertex atoms of the open face of the polyhedron. The shortest Si–Si distance occurs between the Si atoms of the cluster to the exo-bonded atoms [Si1–Si10: 2.349(2) Å and Si3–Si11: 2.379(2) Å]. However, all bonds between silicon framework atoms and the atoms that carry the silyl groups (Si1 and Si2) are shortened and lie in the narrow range between 2.405(2) and 2.445(2) Å, whereas the two bonds Si5–Si6 and Si7–Si8, the bond vector of which lies perpendicular to the external Si–Si bond, are elongated [2.782(2) and 2.764(2) Å], respectively. The remaining multicenter bonds are also elongated with respect to the localized covalent bonds and are found in the range 2.429–2.534 Å. Polyhedral edges of the unsubstituted Si4+ cluster are overall longer [2.423(4) to 2.881(4) Å].[14a] Longer Si5–Si6 and Si7–Si8 distances compares well to the distances between the unsubstituted bridgehead atoms in the siliconoids [Si–(12crown4)2(Tip)2Si]9 with 2.5506(9) Å, (Tip)2Si24 with 2.7076(8) Å, and (Mes)6Si[22] with a corresponding bond length of 2.636(1) Å.

DFT calculations and structure optimization reveal that the structures 1a and 2a represent minima in energy. All calculated distances of 2a show an almost perfect match with the measured values after structure optimization (Si–Si distances and partial atom charges of 1a and 2a are given in the Supporting Information). Calculation of the partial atom charges reveal that in 1a the extra negative charge is almost equally delocalized over the six siliconoid atoms, whereas in 2a, the two negative charges distribute over the seven siliconoid atoms Si2, Si4, Si5 – Si9, with the square-capping atom Si9 – that carries the third ligand in 1a – having a slightly higher value.

Opening of a novel and relatively simple synthetic protocol to siliconoid clusters will allow for a faster development of the field. The formation of six and seven unsubstituted vertex atoms with hemispherical coordination, which requires a multi-step synthesis through the molecular approach, is achieved in one step synthesis from the Zintl phase K9Si9. The binary phase itself is obtained by simply melting together the elements. The synthetic route is not restricted to the examples shown here, and we will report on the introduction of other ligands in a forthcoming paper. Moreover, we foresee that the manifold chemistry known for Ge9 clusters might now be transferred to Si9.

Acknowledgements

The authors are thankful for the financial support by WACKER Chemie AG and Deutsche Forschungsgemeinschaft (DFG, FA 198/14-1). Further, they thank Prof. Dr. Wolfgang Eisenreich for supporting the 29Si NMR measurements, Maria Müller for the EDX analyses, and Ulrike Ammari for the elemental analyses. A. J. K thanks the Finnish IT Center for Science (CSC) for computational resources.

Keywords: cluster compounds • functionalization • quantum chemical calculations • silicon • siliconoids • synthesis

COMMUNICATION


Closing the gap! 25 years after Wiberg's synthesis of tetrahedro-tetrasilane from molecular precursors, the idea to use binary silicides became true. The direct synthesis of soluble silicon-rich molecules from solid K$_{12}$Si$_{17}$ in a one-step reaction allows now for an easy and direct access to molecules with a large number of ligand-free Si atoms – so-called siliconoids.