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Anionic Siliconoids from Zintl phases: $R_3Si_9^-$ with Six and $R_2Si_9^{2-}$ with Seven Unsubstituted Exposed Silicon Cluster Atoms (R = $Si(tBu)_2H$)

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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 silvlation of a silicide leading to the anionic siliconoids $(Si(tBu)_2H)_3Si_9^{-}$ (1a) and $(Si(tBu)_2H)_2Si_9^{2-}$ (2a) with the highest known number of ligand-free silicon atoms. The new anions are obtained in a one-step reaction of K12Si17/NH3(liq.) and Si(tBu)2(H)Cl/thf. Electrospray ionization spectrometry and ¹H, ¹³C, ²⁹Si as well as ²⁹Si-HBMC NMR spectroscopy confirm in accordance with calculated NMR shifts the attachment of three silyl groups at a [Sig]4- cluster under formation of 1a. During crystal growth the siliconoid di-anion 2a is formed. The single crystal X-ray structure determination reveals that two silyl groups are connected to the deltahedral Si₉ cluster core revealing seven unsubstituted exposed silicon cluster atoms with a hemispheroidal coordination. The negative charges -1 and -2 are delocalized over the six and seven siliconoid Si atoms in 1a and 2a, respectively.

More than two decades ago, the synthesis of polyhedral Si compounds was regarded as the greatest challenge in molecular silicon chemistry.^[1] Shortly later, Wiberg et al. reported in 1993 the synthesis and structural characterization of tetrakis(tri-tertbutylsilyl)-tetrahedro-tetrasilane R₄Si₄ (R = ^tBu₃Si) featuring a Si₄ tetrahedron, obtained by the reaction of RBr₂Si-SiBr₂R with RNa.^[2] In his contribution Wiberg also suggested that such compounds should more be straightforwardly accessible through the reaction of alkylhalides with tetrahedral Si4⁴⁻ polyanions. Such polyanions are present in intermetallic compounds ASi (A = Li-Cs), accessible in a one-step reaction by fusion of the respective elements in quantitative yields.^[3] The idea of using so-called Zintl ions as precursors for Si-rich molecules was supported by the synthesis of Sekiguchi's anionic species R'₃Si₄-[4] (R'= -SiMeDis₂, $Dis = CH(SiMe_3)_2)$ in 2003 and was for more than two decades frequently considered, but repeatedly discarded due to the high

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reducing properties of silicides.^[2, 5] The development in the synthesis of molecules with low-valent Si atoms^[6] as well as with unsubstituted Si atoms^[5, 7] 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,^[5] such siliconoids require at least one exposed cluster atom with a hemispheroidal 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 Si₄⁴⁻ Zintl clusters are accessible to chemical transformation from solid Zintl phases e.g. by reacting it with CuMes (Mes = 1,3,5-trimethylbenzene), thereby giving (CuMes)₂Si₄^{4-,[8]} whereas in 2016 Scheschkewitz et al. obtained LiR"₅Si₆ (R" = 2,4,6-triisopropylphenyl) with one anionic and two neutral unsubstituted vertex atoms^[9] 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 Ge9⁴⁻ with different substituents has been demonstrated by using mainly the Zintl phase K₄Ge₉.^[10] However, similar reactions of Si₉⁴⁻ clusters were not yet achieved due to the absence of the corresponding 4:9 phases. Up to date, $A_4Si_4^{[3]}$ (A = Li–Cs) and $A_{12}Si_{17}^{[11]}$ (A = K–Cs) phases that contain either solely Si₄⁴⁻ units, or Si₄⁴⁻ beside Si₉⁴⁻ deltahedral clusters in a 2:1 ratio, are known. Si₄⁴⁻ and Si₉⁴⁻ 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.^[12] Since the A₄Si₄ phases are rather insoluble in any solvent, the focus was put on the A12Si17 phases that are sufficiently soluble in liquid ammonia, and crystal structures of solvates containing Si_4^{4-} [13] and Si_9^{4-} [14] units have been obtained. and subsequent reactions in liquid ammonia as solvent led to the (PhZn)Si₉³⁻,^[15] ({Ni(CO)₂}₂Si₉)₂⁸⁻ formation of [16] and (NHC^{Dipp}Cu)Si₉³⁻.[17]

Recently, the mono-protonated cluster HSi_{9}^{3-} ^[18] was obtained upon the isolation of crystals of $A_{12}Si_{17}$ (A = K, Rb) from liquid ammonia with the help of sequestering agents. A subsequent transfer of the extraction products to pyridine yielded the doublyprotonated species, the structure of which was determined for the iso-valence-electronic cluster with mixed tetrel elements $H_2Si_{9-x}Ge_x^{2-}$ (x = 4.1).^[18a] Both, HSi_{9}^{3-} ^[18b] and $H_2Si_{9}^{2-}$ ^[19], were fully characterized by ¹H and ²⁹Si 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

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formation of siliconoids by the attachment of sp³-Si linkers^[20] and triggered us to investigate the reactivity of Si₉⁴⁻ clusters obtained from $K_{12}Si_{17}$ 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 $H_2Si_9^{2-}$,^[19] we dissolved $K_{12}Si_{17}/222$ crypt 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_2)HCl 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_2H)₃Si₉⁻ (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).



Figure 1. a) ESI-MS spectrum of $(Si(fBu)_2H)_3Sig^-$ (1a) (m/z = 683; line: measured spectra, bars: simulated isotope distribution); b) atom labelling of the di-anionic siliconoid 1a; c) ²⁹Si HMBC (Heteronuclear Multiple Bond Correlation) NMR spectrum of 1a in thf-*d8* (vertical axis: ²⁹Si NMR; horizontal axis: ¹H NMR; #: 222crypt; +: thf-*d8*; *: silicon grease).

¹H and ¹³C NMR spectra of the brown solid dissolved in thf-*d8* exclusively show one set of signals for (K-222crypt) and the

Si(tBu)₂H groups (Figure 1c, full NMR spectra in the Supporting Information). The integrals of the peaks in the ¹H NMR spectra reveal a ratio of 1:3 as expected for the composition (K-222crypt)(Si(tBu)₂H)₃Si₉ (1). This composition is supported by an elemental analysis (C, H, N) of the solid.

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 D_{3h} 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 Sig polyhedron, respectively. The experimental ²⁹Si NMR signal y (-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 Sig cluster species HSig^{3- [18b]} (unsubstituted vertex atoms: -359 ppm) and to the experimental and calculated ²⁹Si NMR average values for $H_2Si_9^{2-[19]}$ (*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 a (SiH) and the ²⁹Si NMR resonance α (SiH) with a scalar coupling constant ${}^{1}J({}^{1}H-{}^{29}Si) = 177.9$ Hz. A cross peak is also observed for α with the ²⁹Si NMR resonance β (silylsubstituted Si vertex atoms) with a decisively smaller scalar coupling ${}^{2}J({}^{1}H-{}^{29}Si) = 8.5$ Hz. The detected ${}^{1}J$ and ${}^{2}J$ coupling constants are comparable to the ones in $H_2Si_5(Mes)_6^{[22]}$ with ¹J and ²J values of 207 and 5.5 Hz, respectively. No signal splitting is observed for the ${}^{3}J({}^{1}H-{}^{29}Si)$ cross peak of a and γ . Cross peaks are also observed for the proton signal b with the silicon signals a 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 R'₃Si₄-^[4] cannot be excluded for **1a**. A fast exchange of the ligands as well as the D_{3h} 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)₂(Si(*t*Bu)₂H)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(*t*Bu)₂H)₂Si₉²⁻ (**2a**). A similar transformation of a tris- to a bis-silylated cluster upon the crystallization process has been

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detected for (Si(*i*Bu)₃)₃Ge₉^{-.[23]} The molecular structure of the dianion 2a shows a $C_{2\nu}$ symmetric cluster that derives from a monocapped square antiprism. The silvl 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 atoms 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 Si₉⁴⁻ 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 [Li-(12crown4)₂](Tip)₅Si₅^[9] with 2.5506(9) Å, (Tip)₆Si₅^[24] with 2.7076(8) Å, and (Mes)₆Si₅^[22] with a corresponding bond length of 2.636(1) Å.



Figure 2. a) Molecular structure of the siliconoid anion (Si(*t*Bu)₂H)₂Si₉²⁻ (**2a**). Si and C atoms (blue and grey, respectively) are shown as ellipsoids at a 50% probability level; CH₃ groups and H_{SI} atoms are omitted for the reason of clarity. The disorder of one silyl group is shown in the Supporting Information; b) Schematic view of **2a** with emphasis on the seven unsubstituted exposed silicon cluster atoms with a hemispheroidal coordination shown in red.

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 hemispheroidal coordination, which requires a multi-step synthesis through the molecular approach, is achieved in one step synthesis from the Zintl phase $K_{12}Si_{17}$. 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 Ge_9 clusters might now be transferred to Si₉.

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

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Closing the gap! 25 years after Wibergs 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.

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