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## COMMUNICATION

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

Lorenz J. Schiegerl<sup>[a,b]</sup>, Antti J. Karttunen<sup>[c]</sup>, Wilhelm Klein<sup>[b]</sup>, and Thomas F. Fässler<sup>\*[a,b]</sup>

**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 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  $K_{12}Si_{17}/NH_3(liq.)$  and  $Si(tBu)_2H(Cl)/thf$ . Electrospray ionization spectrometry and  $^1H$ ,  $^{13}C$ ,  $^{29}Si$  as well as  $^{29}Si$ -HBMC NMR spectroscopy confirm in accordance with calculated NMR shifts the attachment of three silyl groups at a  $[Si_9]^{4-}$  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  $Si_9$  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 one of the greatest challenge in molecular silicon chemistry.<sup>[1]</sup> Shortly later, *Wiberg et al.* reported in 1993 the synthesis and structural characterization of tetrakis(tri-*tert*-butylsilyl)-tetrahedro-tetrasilane  $R_4Si_4$  ( $R = tBu_3Si$ ) featuring a  $Si_4$  tetrahedron, obtained by the reaction of  $RBr_2Si-SiBr_2R$  with  $RNa$ .<sup>[2]</sup> In his contribution *Wiberg* also suggested that such compounds should more be straightforwardly accessible through the reaction of alkylhalides with tetrahedral  $Si_4^{4-}$  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.<sup>[3]</sup> The idea of using so-called Zintl ions as precursors for Si-rich molecules was supported by the synthesis of *Sekiguchi's* anionic species  $R'_3Si_4^-$ <sup>[4]</sup> ( $R' = -SiMeDis_2$ ,  $Dis = CH(SiMe_3)_2$ ) in 2003 and was for more than two decades frequently considered, but repeatedly discarded due to the high

reducing properties of silicides.<sup>[2, 5]</sup> The development in the synthesis of molecules with low-valent Si atoms<sup>[6]</sup> as well as with unsubstituted Si atoms<sup>[5, 7]</sup> triggered again the demand for faster synthetic routes towards compounds with a considerable number of Si-Si bonds and unsubstituted Si atoms. Hereby, applying of silicon Zintl phases as precursors is of particular interest for the design of well-defined molecular silicon structures with a high number of exposed silicon atoms. According to a recent definition,<sup>[5]</sup> so-called 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  $Si_4^{4-}$  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  $(CuMes)_2Si_4^{4-}$ ,<sup>[8]</sup> whereas in 2016 *Scheschkewitz et al.* obtained  $LiR'_5Si_6$  ( $R' = 2,4,6$ -triisopropylphenyl) with one anionic and two neutral unsubstituted vertex atoms<sup>[9]</sup> 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  $Ge_9^{4-}$  with different substituents has been demonstrated by using mainly the Zintl phase  $K_4Ge_9$ .<sup>[10]</sup> However, similar reactions of  $Si_9^{4-}$  clusters were not yet achieved due to the absence of the corresponding 4:9 phases. Up to date,  $A_4Si_4$ <sup>[3]</sup> ( $A = Li-Cs$ ) and  $A_{12}Si_{17}$ <sup>[11]</sup> ( $A = K-Cs$ ) phases that contain either solely  $Si_4^{4-}$  units, or  $Si_4^{4-}$  beside  $Si_9^{4-}$  deltahedral clusters in a 2:1 ratio, are known.  $Si_4^{4-}$  and  $Si_9^{4-}$  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.<sup>[12]</sup> Since the  $A_4Si_4$  phases are rather insoluble in any solvent, the focus was put on the  $A_{12}Si_{17}$  phases that are sufficiently soluble in liquid ammonia. Crystal structures of solvates containing  $Si_4^{4-}$ <sup>[13]</sup> and  $Si_9^{4-}$ <sup>[14]</sup> units have been obtained, and subsequent reactions in liquid ammonia as solvent led to the formation of  $(PhZn)Si_9^{3-}$ ,<sup>[15]</sup>  $(Ni(CO)_2)_2Si_9^{8-}$ <sup>[16]</sup> and  $(NHC^{Dipp}Cu)Si_9^{3-}$ .<sup>[17]</sup>

Recently, the mono-protonated cluster  $HSi_9^{3-}$ <sup>[18]</sup> 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 transfer of the extraction products from liquid ammonia to pyridine yielded the doubly-protonated species  $H_2Si_9^{2-}$ .<sup>[19]</sup> A similar procedure allowed for the structural characterization of the iso-valence-electronic cluster with mixed tetrel elements  $H_2Si_9-xGe_x^{2-}$  ( $x = 4.1$ ).<sup>[18a]</sup> Both,  $HSi_9^{3-}$ <sup>[18b]</sup> and  $H_2Si_9^{2-}$ <sup>[19]</sup>, were fully characterized by  $^1H$  and  $^{29}Si$  NMR spectroscopy in solution. The formation of well-defined

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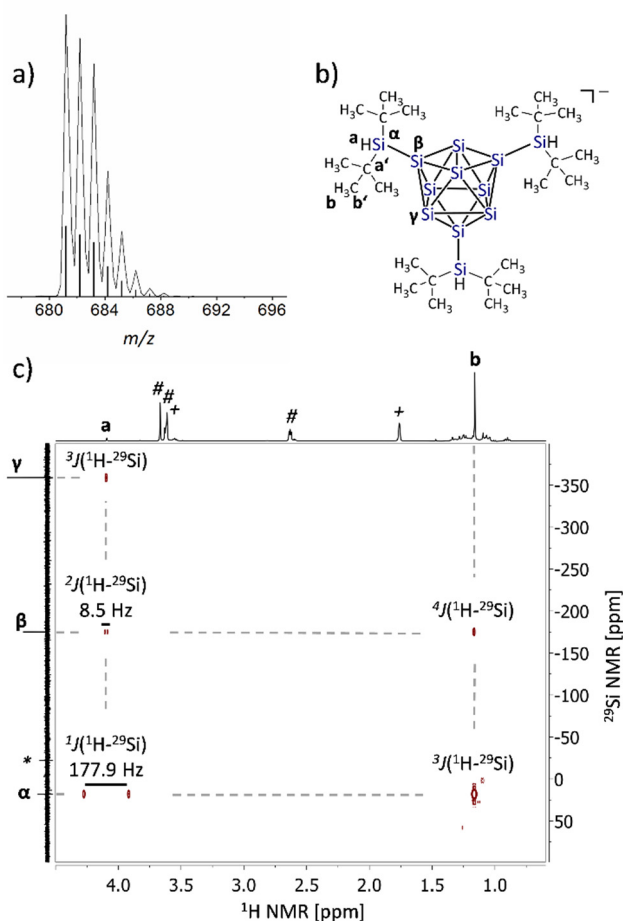
## COMMUNICATION

solutions that contain nine-atomic silicon clusters after activation with liquid ammonia finally paved the way for further conversions of these clusters in solution with appropriate reactants. Theoretical studies support the formation of siliconoids by the attachment of  $sp^3$ -Si linkers<sup>[20]</sup> and triggered us to investigate the reactivity of  $Si_9^{4-}$  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).<sup>[21]</sup>

In analogy to our recent synthesis of  $H_2Si_9^{2-}$ ,<sup>[19]</sup> we dissolved  $K_{12}Si_{17}/222crypt$  in liquid ammonia. After removal of the solvent the brown residue was treated with thf under continuous cooling in an ice bath, and a pre-cooled solution of  $Si(tBu)_2HCl$  in thf was added. After several hours the initially heterogeneous 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  $(Si(tBu)_2H)_3Si_9^-$  (**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).

$^1H$  and  $^{13}C$  NMR spectra of the brown solid dissolved in  $thf-d_8$  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 of (K-222crypt) $(Si(tBu)_2H)_3Si_9^-$  (**1**). This composition is supported by an elemental analysis (C, H, N) of the solid that forms in 36% yield. The  $^{29}Si$  NMR spectrum of **1** shows three resonances at 18.00 ( $\alpha$ ), -175.16 ( $\beta$ ) and -358.81 ppm ( $\gamma$ ) 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  $^{13}C$  NMR chemical shifts were allocated by the quantum chemical shift calculations to the atoms as labeled in Figure 1b. The  $^{29}Si$  NMR 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  $Si_9$  polyhedron, respectively. The experimental  $^{29}Si$  NMR signal  $\gamma$  (-358.81 ppm) of the unsubstituted vertex atoms shows a stronger upfield shift as usually observed for prominent siliconoid species<sup>[5]</sup> and is comparable to the signals for the protonated  $Si_9$  cluster species  $HSi_9^{3-}$ <sup>[18b]</sup> (unsubstituted vertex atoms: -359 ppm) and to the experimental and calculated  $^{29}Si$  NMR average values for  $H_2Si_9^{2-}$ <sup>[19]</sup> (*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  $^{29}Si$  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  $^{29}Si$  NMR resonance  $\alpha$  ( $SiH$ ) with a  $^1J(^1H-^{29}Si) = 177.9$  Hz scalar coupling constant. A cross peak is also observed for  $\alpha$  with the  $^{29}Si$  NMR resonance  $\beta$  (silyl-substituted Si vertex atoms) with a decisively smaller scalar coupling of  $^2J(^1H-^{29}Si) = 8.5$  Hz. The detected  $^1J$  and  $^2J$  coupling constants are comparable to the ones in  $H_2Si_9(Mes)_6$ <sup>[22]</sup> with  $^1J$  and  $^2J$  values of 207 and 5.5 Hz, respectively. No signal splitting is observed for the  $^3J(^1H-^{29}Si)$  cross peak of a and  $\gamma$ . Cross peaks are also observed for the proton signal b with the silicon signals  $\alpha$  and  $\beta$ , but again no  $^3J(^1H-^{29}Si)$  and  $^4J(^1H-^{29}Si)$  signal splitting is observed. Moreover, no cross peak is observed between b and  $\gamma$  which would correspond to a  $^5J(^1H-^{29}Si)$  coupling. Ligand scrambling as observed for  $R'_3Si_4^-$ <sup>[4]</sup> 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  $-20^\circ C$ .

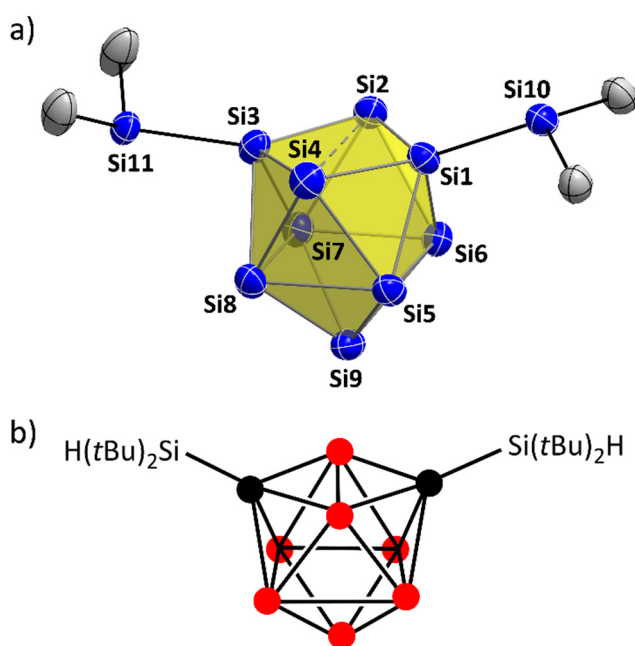
Crystallization experiments of **1** from fluorobenzene solutions led to the formation of small amounts of orange needle-shaped crystals, suitable for single-crystal X-ray diffraction (crystallographic details are given in the Supporting Information). The structure determination, however, reveals the composition (K-222crypt) $_2(Si(tBu)_2H)_2Si_9^-$  (**2**) with only two silyl groups attached at the  $Si_9$  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  $(Si(tBu)_2H)_2Si_9^{2-}$  (**2a**). A similar transformation of a tris- to a bis-silylated cluster upon the crystallization process has also been



**Figure 1.** a) ESI-MS spectrum of  $(Si(tBu)_2H)_3Si_9^-$  (**1a**) ( $m/z = 683$ ; line: measured spectra, bars: simulated isotope distribution); b) atom labelling of the anionic siliconoid **1a**; c)  $^{29}Si$  HMBC (Heteronuclear Multiple Bond Correlation) NMR spectrum of **1a** in  $thf-d_8$  (vertical axis:  $^{29}Si$  NMR; horizontal axis:  $^1H$  NMR; #: 222crypt; +:  $thf-d_8$ ; \*: silicon grease).

## COMMUNICATION

detected for  $(\text{Si}(i\text{Bu})_3)_3\text{Ge}_9^{2-}$ .<sup>[23]</sup> The molecular structure of the dianion **2a** shows a  $C_{2v}$  symmetric cluster that derives from a mono-capped 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 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. In contrast are the two bonds Si5–Si6 and Si7–Si8, of which the bond vector lies perpendicular to the external Si–Si bond, 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  $\text{Si}_9^{4-}$  cluster are overall longer [2.423(4) to 2.881(4) Å].<sup>[14a]</sup> Longer Si5–Si6 and Si7–Si8 distances compares well to the distances between the unsubstituted bridgehead atoms in the siliconoids [Li-(12crown4)<sub>2</sub>](Tip)<sub>5</sub>Si<sub>5</sub><sup>[9]</sup> with 2.5506(9) Å, (Tip)<sub>6</sub>Si<sub>5</sub><sup>[24]</sup> with 2.7076(8) Å, and (Mes)<sub>6</sub>Si<sub>5</sub><sup>[22]</sup> with a corresponding bond length of 2.636(1) Å.



**Figure 2.** a) Molecular structure of the siliconoid anion  $(\text{Si}(t\text{Bu})_2\text{H})_2\text{Si}_9^{2-}$  (**2a**). Si and C atoms (blue and grey, respectively) are shown as ellipsoids at a 50% probability level;  $\text{CH}_3$  groups and  $\text{H}_{\text{Si}}$  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 reveals that in **1a** the extra negative charge is almost equally delocalized over the six siliconoid atoms (partial charge  $-0.13 e^-$  for each atom), whereas in **2a**, the two negative charges distribute over the seven siliconoid atoms Si2, Si4 ( $-0.33 e^-$  each), Si5 – Si8 ( $-0.23 e^-$  each), and the square-capping atom Si9 – that carries the third ligand in **1a** – having a slightly higher value ( $-0.37 e^-$ ). Intrinsic Bond Orbital (IBO) analysis of the Si–Si bonding shows clear differences between the intracluster bonds (delocalized multicenter bonds) and exo-bonds (localized two-center two-electron bonds) (see Supporting Information).

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 activated Zintl phase  $\text{K}_{12}\text{Si}_{17}$ . 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  $\text{Ge}_9$  clusters might now be transferred to  $\text{Si}_9$ .

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

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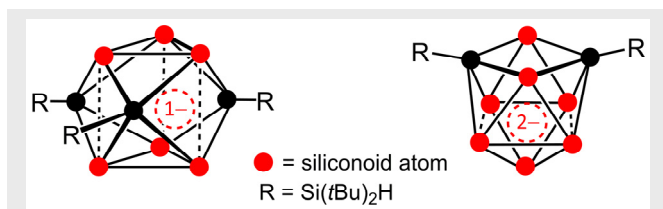
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## COMMUNICATION

## Entry for the Table of Contents

## COMMUNICATION



Lorenz J. Schiegerl, Antti J. Karttunen,  
Wilhelm Klein, and Thomas F. Fässler\*

Page No. – Page No.

Title

**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<sub>12</sub>Si<sub>17</sub> 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.