Showcasing research from Dr. Felicitas Lips’s laboratory, University of Muenster, Inorganic Chemistry, North Rhine-Westphalia, Germany.

A highly unsaturated six-vertex amido-substituted silicon cluster

Thermal treatment of the amido-substituted silicon ring compound with a butterfly-shaped Si₄ ring at 400 °C results in the formation of a highly unsaturated six-vertex silicon cluster with only four amine substituents. This cluster can be considered as the silicon analogue to butalene. In THF the butalene-type silicon cluster is in equilibrium with a minor conformer that is formed either by successively rotating two neighbouring amine substituents or by a twist within the Si₆ cluster scaffold.

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A highly unsaturated six-vertex amido-substituted silicon cluster†

Jan Keuter, a Christian Schwermann, b Alexander Hepp, a Klaus Bergander, c Jörn Droste, b,d Michael Ryan Hansen, b,d Nikos L. Doltsinis, b* and Christian Mück-Lichtenfeld b,*c and Felicitas Lips b,*a

Thermal treatment of the bicyclo[1.1.0]tetrasilaetramide [Si4(N(SiMe3)Dipp)4] 1 resulted in the formation of a highly unsaturated six-vertex silicon cluster [Si6(N(SiMe3)Dipp)4] 2 with only four amine-substituents and two ligand-free silicon atoms. In solution, a major and a minor conformer of this cluster are in equilibrium according to multinuclear NMR spectroscopy, lineshape analysis, DFT calculations and molecular dynamics simulations. The bonding situation in the highly unsaturated cluster features lone pair type character at the ligand-free silicon atoms and partial single and double bond character in the upper butterfly-shaped ring of 2. This allows to consider 2 as the silicon analogue of a butalene isomer.

Introduction

Silicon analogues to benzene were successfully isolated with sterically demanding substituents. Isomers with a prismatic silicon scaffold A, a benzvalene-type isomer B, a tricyclic species C and a propellane-type compound D turned out to be the global minimum structure and to be much lower in energy than benzene-, benzvalene-, prismatic- or Dewar-benzene-type isomers.

In the isolated silicon analogues of benzene as well as in the computationally investigated Si6H6 isomers, silicon atoms with no substituent occur that are only connected to other silicon atoms. These so-called unsubstituted or “naked” silicon atoms display inverted tetrahedral or hemispherical configurations. Therefore, the topology of these clusters resembles surface structures of bulk silicon or silicon nanoparticles. This type of clusters is named siliconoids in analogy to metalloid clusters and can further be considered as model compounds for intermediates of the chemical vapour deposition process of molecular silane precursors.

Besides the six-vertex clusters depicted in Scheme 1, five-vertex silicon clusters with one F21 or two ligand-free atoms F2,13 seven-vertex G14 and H15 and eight-vertex siliconoid clusters P16 and J17 are reported in the literature (Scheme 2).

Recent progress in this field includes a systematic stepwise synthesis from a six- to an eight-vertex siliconoid cluster,14 and thermolysis of a siliconoid cluster into novel seven and eight-vertex silicon clusters.15 Furthermore, functionalization of the benzopolare-type cluster D at different positions and the introduction of boron- and phosphorous-based groups, which corresponds to n- and p-type doping of elemental silicon, was achieved.19

Unsaturated isomers of benzene with the formula C6H4 were considered computationally and feature structural motifs shown in Scheme 3.20

Considering the lower tendency of silicon to form π-bonds and the above mentioned observation for the preference of silicon clusters for spherical scaffolds with a high number of σ-bonds, we expect a silicon analogue to C6H4 to adopt a Si6 structural motif that differs from the carbon-based isomers shown in Scheme 3. Previous computational investigations using Car-Parrinello molecular dynamics simulations21 and

Scheme 1 Six-vertex silicon clusters.
DFT calculations suggested a structure with spherical scaffold for Si₆H₄. However, no such compound has been isolated yet.

Results and discussion

The silicon clusters mentioned in the introduction have the common feature that they are surrounded either by aryl, alkyl or silyl substituents. However, reports on unsaturated main group clusters with higher nuclearity stabilized by amine substituents are rare. One such compound is the metalloid cluster Sn₁₅{N(SiMe₃)Dipp}₆ featuring eight ligand-free tin atoms, that was synthesized in a reductive dehalogenation of the dimeric [{N(SiMe₃)Dipp}SnCl]₂ using KC₈ as the reducing agent. Recently, we reported on the bicyclo[1.1.0]tetrasilate-tramamide Si₄{N(SiMe₃)Dipp}₄ displaying two three-coordinate silicon atoms with different degree of pyramidalization. By thermal treatment of 1 at ca. 400 °C under argon, removal of all volatile components in vacuo at 400 °C, and subsequent extraction of the yellow residue in hexane at room temperature, we were able to synthesize the first amido-substituted highly unsaturated silicon cluster Si₆{N(SiMe₃)Dipp}₄ 2 in form of yellow crystals in ca. 23% yield (see Scheme 4).

Compound 2 was also obtained in much lower yield in a co-reduction of {N(SiMe₃)Dipp}SiBr₃ and SiBr₄ in a 2 : 1 ratio with potassium graphite (KC₈). In this case, however, 2 co-crystallized with 1. The formation mechanism of 2 is unclear due to the difficulty to assign side products at 400 °C. Two possible formation pathways that proceed under release of bis(amido)-substituted silylene are suggested in the ESI (page S48). The formation of siliconoid clusters H and J was also found to proceed with silylene elimination. Single crystal X-ray diffraction revealed that in 2, a Si₆ cluster core with two unsubstituted silicon atoms is surrounded by four {N(SiMe₃)Dipp}-substituents. All silicon atoms in 2 are fourfold-coordinated. The Si₆ cluster core in 2 resembles to the six-vertex propellane- or benzpolarene-type cluster D, but can also be considered as a heavily distorted octahedron missing two edges or as a twisted trigonal prism (see Fig. 1, bottom). The distance between the two unsubstituted silicon atoms (Si2, Si4) amounts to 2.636(6) Å which is very similar to the distance between atoms of this type in the propellane-type clusters D (2.708 Å) and F (2.636 Å). These two unsubstituted silicon atoms are part of a butterfly-shaped moiety of the cluster constituted by Si₁–Si₄. Within this unit the two bond lengths Si₁–Si₂ and Si₃–Si₄ (2.281(5) Å and 2.292(6)) are very short for Si–Si single bonds and approach the value reported for Si==Si double bonds (2.138–2.289 Å). In contrast, the bond lengths Si₂–Si₃ and Si₁–Si₄ (2.502(6) and 2.532(6) Å) are longer than typical single bonds (2.34 Å). The butterfly-shaped moiety is capped by a dumbbell consisting of Si₅ and Si₆ (2.357(1) Å). The bond lengths Si₂–Si₆ and Si₄–Si₅ (2.403(6) and 2.389(6) Å) connecting the butterfly-
type ring and the Si5–Si6-dumbbell are somewhat elongated compared to the standard Si–Si single bond length. All other bond lengths are in the range of usual single bonds. The Si–N bond lengths (1.730(1)–1.740(1) Å) are only somewhat shorter than single bonds (ca. 1.76 Å).27

We were interested to compare the configuration of the unsubstituted silicon atoms in 2 with those in the propellant-type clusters F and D in the solid state (see Fig. 2). In the propellant-type clusters the bond angles around the ligand-free silicon atoms are all ca. 90° in F and 97°, 97°, and 76° in D.

Thus, the configuration at the unsubstituted silicon atoms is inverted tetrahedral or hemispheroidal in F and D. This is a common feature of “naked” Si atoms as it was analyzed by Ishida and Iwamoto⁷ and by Scheschkewitz.⁸

Measuring these angles in 2 results in significantly different angles of 57°, 83°, and 103°, which allows to describe the configuration of the unsubstituted Si atoms (Si2, Si4) in 2 as hemispheroidal with a hemispheroidality parameter φ = 1.45 Å. This represent the highest hemispheroidality parameter so far observed for silicon clusters.⁹ More specifically, the environment at Si2/Si4 can be considered as the apical position of a distorted square-based pyramid. A persila-pyramidane was not reported yet, but was investigated computationally using DFT methods for the compounds Si5H4, Si5(SiH3)4, and Si5(SiMe3)4.²⁸

The C2-symmetric 2 was investigated by multinuclear NMR spectroscopy in PhMe-d8 and THF-d8. The absence of hydride substituents at Si2, Si4 was evidenced by a 2D correlated 29Si/1H experiment (Fig. S26) and by a quantitative 1H NMR spectrum that revealed no hydride signal between 4 and 6 ppm. In the 1H NMR spectrum at 300 K signal broadening is observed indicating dynamic behavior of 2 in solution. In the 29Si NMR spectrum at 300 K signals at 94.2 ppm for Si1 and Si3, at 7.7 ppm for Si5 and Si6 and at −309.4 ppm for Si2 and Si4 appear in THF-d8 besides signals at 7.0 and 7.4 ppm for the two chemically and magnetically different SiMe3 groups. These measured signals are in good accordance with DFT calculated values (see Table S4†). The signal at very high field for the unsubstituted Si atoms at −309.4 ppm is in line with that observed for this type of atoms in F and D (−273.2 and −274.2 ppm, respectively). The dynamic behavior of 2 was analyzed by variable temperature (VT) 1H NMR spectroscopy, 2D NMR experiments and lineshape analysis. This analysis revealed that two species in a 2 : 1 ratio are in equilibrium with each other (see Fig. 3, S19 and page S42†). The minor component has three signals in the 29Si NMR spectrum at 51.3, −5.1 and −294.0 ppm.

Examination of 2 via solid state 29Si[1H] CP/MAS NMR spectroscopy was performed, confirming that only the major component is present in the solid state signals at δ = 98.7, 8.9 and −301.2 ppm, besides two 29Si signals at δ = 7.4 and 6.6 ppm for the SiMe3 groups (see Fig. 4). The solid-state 29Si chemical shifts differ slightly from the solution state shifts, most likely due to ring current effects of the aromatic ligands in the solid, which are averaged out by motion in solution. In the solid-state, the 29Si chemical shift anisotropy (CSA)²⁹ supported by DFT calculations can be used for signal assignment. The 29Si CSAs were determined from analysis of the spinning sidebands at low spinning speed (4.0 kHz MAS, see Fig. 4b). The 29Si signals of the SiMe3 groups at δ = 6.6 and 7.4 ppm show the smallest CSA (δaniso = 20 ± 10 ppm) as expected and in good agreement with DFT calculations (see Table S9†). The two unsubstituted silicon atoms (Si2/4) correspond to the 29Si resonance at δ = −301 ppm. The low 29Si CSA of δaniso = 95 ± 10 ppm with η = 0.25 for these

Fig. 2 Comparison of the configuration of the ligand-free silicon atoms in F, D and 2.

![Fig. 2 Comparison of the configuration of the ligand-free silicon atoms in F, D and 2.](image-url)

![Fig. 3 29Si NMR spectrum of 2 in THF-d8 at 210 K. Δ represents the major component and O the minor component.](image-url)

![Fig. 4 29Si{1H} CP/MAS NMR spectra of 2 recorded at 9.4 T employing (a) 10.0 kHz and (b) 4.0 kHz MAS. The inset in (a) enlarges the chemical shift region of the SiMe3 groups. The corresponding fit is shown in grey in (b). The isotropic 29Si resonances are marked by triangles and spinning sidebands are marked with an asterisk.](image-url)
two atoms suggests only a weak coordination between these silicon atoms, since the distance (2.636(6) Å) is significantly longer than a Si–Si single bond (2.34 Å). The $^{29}$Si signals of Si1/3 at $\delta = 99$ ppm and Si5/6 at $\delta = 9$ ppm show similar $^{29}$Si CSA values ($\delta_{\text{aniso}} = -230 \pm 20$ ppm and $-226 \pm 20$ ppm, respectively) in accordance with DFT calculations ($\delta_{\text{aniso}} = -284$ ppm and $-297$ ppm). Here, Si1/3 have $\eta_s = 0.1$ whereas Si5/6 show an axial symmetric tensor with $\eta_s = 0$. These differences in $^{29}$Si CSA parameters can be understood by comparing the different bonding situations at Si5/6 in contrast to Si1/3.

The bond lengths involving Si5/Si6 are all very similar whereas those of Si1/Si3 include the two short bonds (2.292(6) and 2.281(5) Å) to the adjacent Si2/Si4 atoms and the longer bonds to Si4/Si2 (2.532(6) and 2.502(6) Å), respectively. This results in a non-axial $^{29}$Si CSA tensor for Si1/Si3. The slight discrepancy between experiment and calculations of $^{29}$Si $\delta_{\text{aniso}}$ values for Si1–Si6 may indicate that some residual local mobility is present even in the solid state.

The experimental UVVis spectrum of 2 at room temperature shows a shoulder at 361 nm and at 214 nm. These absorptions can be assigned to a HOMO–† to the adjacent Si2/Si4 atoms and the longer bonds Si2/Si4. This was also observed for the all bonds except for that connecting the two ligand-free silicon atoms (Si2 and Si4). This was also observed for the two ligand-free silicon atoms, since the distance (2.636(6) Å) in accordance with DFT calculations (2.636(6) Å) is consistent with Aromatic characters in29Si NMR spectrum in THF–d8 of the minor component 2-C at 51.3, −5.1 and $-294.0$ ppm indicate that this component is also C5 symmetric. Two of the signals (at −5.1 and at $-294.0$ ppm) are very close to the major component. This provides strong evidence, that the minor component is very similar to the major component. The occurrence of a major and a minor isomer with different chemical shifts in solution was recently also observed for anionic mixed silicon germanium
benzopolarene-type clusters. Lineshape analysis revealed a non-
mutual exchange between the two components and a Gibbs free
energy of activation of 57.2 kJ mol⁻¹ (13.7 kcal mol⁻¹) at 300 K
for the equilibrium between the major and the minor isomer
(see page S42 and S43†).

With this information we generated conformational isomers of
2 by rotating the ligands successively around the Si₆ cluster-N
single bonds in steps of 60° and optimizing the structures with
DFT calculations. From the generated set of conformers, only
the four most stable are reported here (Scheme 5).

Conformer 2-B results from counterclockwise rotation
around the Si₅-N bond. Conformer 2-C is obtained when the Si₆-N bond
from 2-B is rotated clockwise. The enantiomer of 2-A, which is
conformer 2-D, can be generated by a twist within the four-
membered ring Si₂–Si₄–Si₅–Si₆ of the Si₆ scaffold in conformer
2-C (Scheme S1†). This is accompanied by a slight movement of
the amine substituents attached to the butterfly-shaped ring. We
note that both enantiomers 2-A and 2-D are present in the crystal
structure obtained from single crystals grown from hexane.

In this simulation, the necessary structural changes,
rotation of a first ligand, rotation of a second ligand, and
distortion within the Si₆ cluster core, occur sequentially one
after another. This suggests that the transformation 2-A → 2-D
takes place by a stepwise process via structures 2-B and 2-C,
supported by the clearly visible minima in the free energy
profile (Fig. S7†). The barrier heights for the individual
processes (Table S5 and Fig. S8†) are well below ΔF² =
12 kcal mol⁻¹. They are thus easily accessible at T = 300 K. In
particular, if both enantiomers, 2-A and 2-D, are present, two
competing pathways, 2-A → 2-C and 2-D → 2-C, are possible.

The reactivity of 2 with ethylene, CO₂, CCl₄, H₂O, MeOH, I₂,
and NH₄Me (2,3,4,5-tetramethyl-imidazolium-2-ylidene) was
investigated in NMR scale reactions. But, these reagents either
show no reactivity with 2 (ethylene, CO₂, MeOH) or react very
unselectively (CCl₄, H₂O, I₂, NH₄Me) which hinders character-
ization of the products based only on NMR spectroscopy and
the growths of single crystals in solution.

Conclusions

In summary, we synthesized a highly unsaturated Si₆ cluster
with only four amine substituents and two ligand-free silicon
atoms that exhibits an unusual equilibrium in solution between a major and a minor conformer. Variable temperature and 2D-correlated NMR experiments, DFT calculations and molecular dynamics simulations were performed to collect information on this process. These calculations suggest, that the equilibration of the two conformers detected in solution by NMR spectroscopy of 2 (2-A and 2-C) may occur at room temperature by two subsequent ligand rotations or by a twist in the $\mathrm{Si}_6$ core. Analysis of the bonding situation in the $\mathrm{Si}_6$ cluster using the QTAIM method revealed no bond critical point between the ligand-free silicon atoms. Generating intrinsic bond orbitals (IBOs) for the $\mathrm{Si}_6$ cluster core demonstrates lone pair type character at the ligand free silicon atoms and a multi-center bond involving all silicon atoms in the butterfly-shaped ring. In future experiments, the potential of amine substituents for the stabilization of other highly unsaturated silicon clusters will be investigated.

Conflicts of interest

There are no conflicts to declare.

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