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Contraction and Expansion of the Silicon Scaffold of Stable Si_6R_6 Isomers

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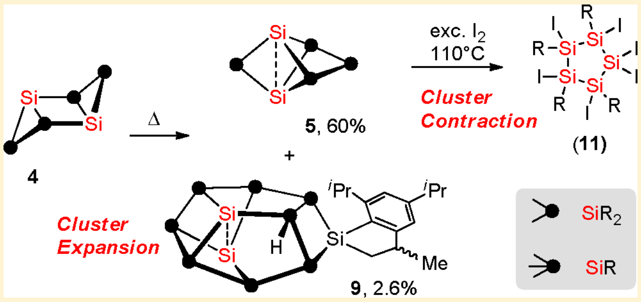
Ⓢ *Supporting Information*



ABSTRACT: The reactivity of two stable Si_6R_6 clusters (**4** and **5**, R = 2,4,6-$^iPr_3C_6H_2$) with unsymmetrical substitution patterns (including Si, SiR, and SiR_2 vertices) is reported. In order to account for the importance of such clusters as model systems for transient intermediates in the deposition of elemental silicon, we here propose the term "siliconoids" for silicon clusters with unsaturated valencies. With the hexasilaprismane **8a**, a saturated—i.e., non-siliconoid—Si_6R_6 isomer is accessible from a suitable Si_3 precursor. Thermal redistribution of the substituents converts 1,1,2-trichlorocyclotrisilane **6** into the corresponding 1,2,3-derivative **7** prior to the requisite reductive coupling step leading to **8a**. On the other hand, a stable expanded Si_{11}-siliconoid **9** was isolated as a minor side product of the thermal isomerization of **4** to **5**, thus providing a first example of siliconoid cluster expansion in the condensed phase. In the solid-state structure, the two unsubstituted vertices of **9** strongly interact in a staggered propellane-like fashion. Oxidative cluster contraction of a siliconoid scaffold is observed upon treatment of siliconoid **5** with a large excess of iodine in refluxing toluene, thus providing access to a highly functionalized hexaiodocyclopentasilane **11** in high yield. Conversely, chlorination of the isomeric **4** with $BiCl_3$ as a mild source of Cl_2 results in a complex mixture of products from chlorination of the unsubstituted vertices as well as σ-bonds of the cluster framework of **4**. The main product, 1,2-dichlorotricyclo[2.2.0.0^{2,5}]hexasilane **12**, undergoes thermal cluster contraction to give tricyclo[2.1.0.0^{2,5}]pentasilane **14** with an exohedral chlorosilyl group.

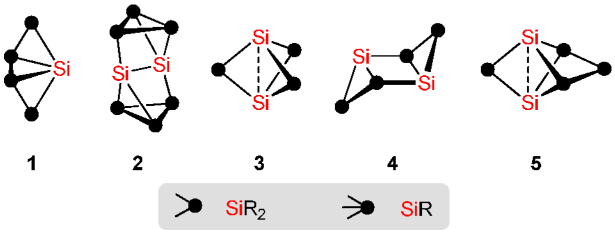
1. INTRODUCTION

Transient silicon clusters with unsaturated vertices are potential intermediates of the gas-phase deposition of elemental silicon.[1] The free valences, also referred to as "dangling bonds" in the context of surface chemistry,[2] are preferred reaction sites for cluster expansion during deposition processes.[3] Furthermore, some of the band-gap-determining defects in hydrogenated amorphous silicon (a-Si:H) closely resemble such unsaturated, low-coordinate sites.[4] The relevance of the defect structure for the undesirable decline in the performance of thin-film solar cells based on a-Si:H, the so-called Staebler−Wronski effect, has been pointed out repeatedly.[4,5]

We now propose to refer to unsaturated molecular silicon clusters as "siliconoids"[6,7] for simplicity and in order to account for their intermediacy in the deposition of elemental silicon from molecular precursors. The term is inspired by the definition of metalloid clusters as introduced by Schnöckel in the context of Group 13 clusters.[8] Accordingly, such metalloid clusters require an average oxidation state between 0 and 1 for the cluster atoms, a notion that has been upheld by Schnepf et al. for the corresponding germanium and tin derivatives.[9] Although the unsubstituted vertex in Group 14 clusters itself certainly requires a formal oxidation state of zero, the average value for the whole cluster is not considered in our proposed definition of siliconoids. The presence of at least one unsubstituted silicon vertex in a neutral molecule with a three-dimensional silicon backbone remains as the sole criterion.

Stable siliconoids—which would allow for the application of the powerful analytical tools of synthetic chemistry to the investigation of structure and reactivity—were unknown until recently. In 2005, the serendipitous synthesis of Si_5R_6 siliconoid **1** was reported by one of us (Chart 1).[10] Just a few months later,

Chart 1. Schematic Representation of Stable Siliconoids[a]



[a]**1**, **4**, **5**: R = Tip = 2,4,6-$^iPr_3C_6H_2$. **2**: R = Si^tBu_3. **3**: R = Mes = 2,4,6-$Me_3C_6H_2$.

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Wiberg and Veith et al. disclosed the synthesis of an Si_8R_6 derivative, **2**, with two unsaturated vertices.[11] Recently, a persilapropellane, **3**, was isolated by Breher et al.,[12] completing the series of group 14 propellanes.[13] The present article describes the reactivity (including cluster expansion) of the Si_6R_6 siliconoids **4** and **5**, which are readily accessible via reduction of 1,1,2-trichlorocyclotrisilane **6**.[14,15] The reaction chemistry of **4** and **5** seemed particularly worth exploring in view of the very unusual electronic situation of both compounds.[15,16] In addition, we now report the thermal isomerization of **6** to the symmetrically substituted 1,2,3-trichloro derivative **7**. Reduction of **7** affords only the second stable hexasilaprismane **8** and thus a non-siliconoid stable isomer within the Si_6Tip_6 manifold.[17]

2. RESULTS AND DISCUSSION

2.1. Non-siliconoid Si_6Tip_6 Isomer.

The reduction of 1,1,2-trichlorocyclotrisilane **6** afforded the dismutational isomer of hexasilabenzene **4**.[14] An alternative, shorter method for the synthesis of **4** employing the reaction of $Tip_2Si{=}Si(Tip)Li$ with Jutzi's $Cp^{*}Si^{+}$ cation was recently reported.[18] Both of these approaches preserve the unsymmetrical substitution pattern of the cyclotrisilane precursor **6** inasmuch as silicon atoms with zero, one, and two substituents are present in **4**, thus constituting the formal dismutation from a hypothetical hexasilabenzene. This substitution pattern persists even during the thermal rearrangement of **4** to the global minimum isomer **5**, which can be distilled at 340 °C and reduced pressure with only minor signs of decomposition.[15]

We anticipated that symmetrization of the substitution pattern might be possible at the stage of the halogenated precursor **6** (solid-state structure in Figure 1a).[14] A strong Lewis acid could facilitate this process through (intermediate) chloride abstraction in view of the ready occurrence of aryl shifts in cationic silicon compounds.[19] Incidently, aluminum(III) chloride had proven suitable to initiate the rearrangement of cyclic silanes.[20] Indeed, the addition of an equimolar amount of $AlCl_3$ to **6** in C_6D_6 led to the appearance of ^{29}Si NMR signals at $\delta = -13.9$ and -18.7 ppm in a ratio of 1:2 after a few hours at ambient temperature, which indicated the formation of a new species with higher symmetry. Conversion to a clean product **7** was completed by heating the mixture to 60 °C for a few hours. The separation of $AlCl_3$ from the product, however, proved tedious. These difficulties prompted us to reinvestigate the decomposition product mixture obtained upon melting of **6**.[14] Indeed, the major product (approximately 70%) present in the melt turned out to be **7**.

By heating a toluene solution of **6** to reflux for 4 days, a more selective conversion of **6** to **7** was achieved (Scheme 1). The resulting crude product contained approximately 6% impurities by NMR. Pale yellow single crystals of the product **7** were obtained at room temperature from an oversaturated hexane solution and analyzed by X-ray diffraction.

The structure in the solid state confirmed the anticipated constitution of a 1,2,3-trichlorocyclotrisilane **7** in the sterically most favorable *cis,trans*-conformation (Figure 1b). Due to the almost identical structural parameters, only one of the four crystallographically independent molecules will be discussed. All Si–Cl bonds are close to the average value of Si–Cl bond of 2.08 Å. The Si–Si bonds are also in the expected region for Si–Si single bonds and vary just by 0.033 Å. The negligible variation of the bond lengths is a result of the equal substitution pattern on each silicon atom in **7**. In unsymmetrically substituted cyclotrisilanes, the substituents exert a considerable electronic influence on the endocyclic Si–Si bonds.[21]

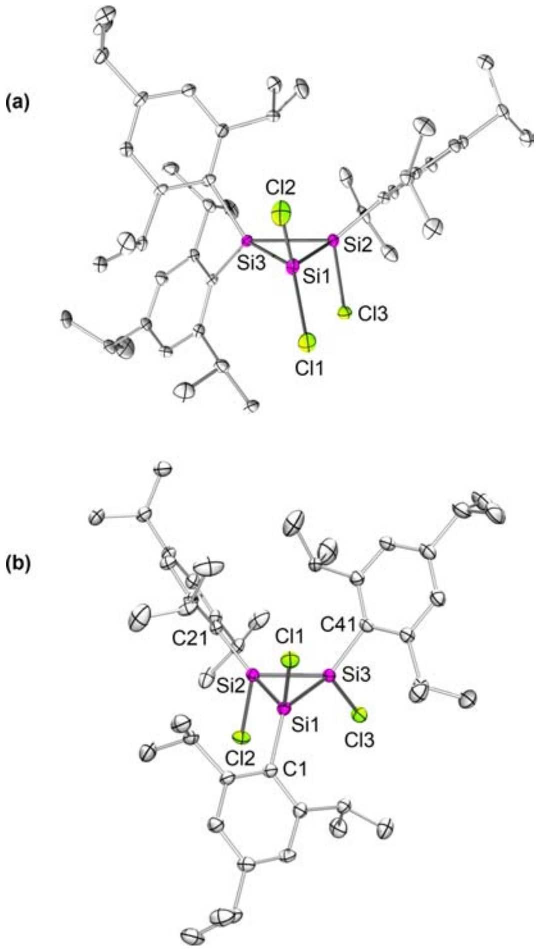
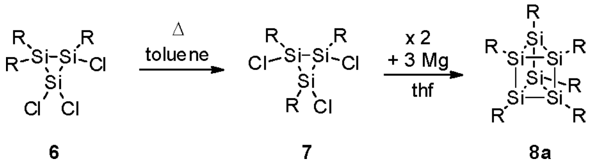


Figure 1. (a) Structure of **6** in the solid state (thermal ellipsoids at 30%).[14] Hydrogen atoms omitted. Selected bond lengths [Å] and angles [°]: Si1–Si2 = 2.2970(6), Si2–Si3 = 2.3908(7), Si3–Si1 = 2.3661(7), Si1–Cl1 = 2.0594(7), Si1–Cl2 = 2.0534(7), Si2–Cl3 = 2.0866(7); Si1–Si2–Si3 = 60.59(2), Si3–Si1–Si2 = 61.67(2), Cl1–Si1–Cl2 = 105.89(3), Si2–Si3–Si1 = 57.744(19). (b) Structure of one of four crystallographically independent molecules of **7** (thermal ellipsoids at 30%). Hydrogen atoms omitted. Selected bond lengths [Å] and angles [°]: Si1–Si2 = 2.3507(15), Si2–Si3 = 2.3490(15), Si3–Si1 = 2.3821(15), Si1–Cl1 = 2.0885(15), Si2–Cl2 = 2.0864(14), Si3–Cl3 = 2.0788(15).

Scheme 1. Thermal Rearrangement of 6 to 7 and Reductive Dimerization to Hexasilaprismane 8[a]



[a] R = Tip = 2,4,6-$^{i}Pr_3C_6H_2$.

Reduction of **7** with magnesium metal in THF at room temperature resulted in a color change from pale yellow to dark red after stirring overnight. Hexasilaprismane **8** can be isolated as orange crystals in 31% yield from hexane (Scheme 1).

With **8b** a very similar hexasilaprismane, Si_6R_6 (R = Dip = 2,6-$^{i}Pr_2C_6H_3$), had been reported by Sekiguchi and Sakurai et al.

in 1993.[17] In that case, the reported yields were just 1% and 7%, depending on the starting material, DipSiCl$_3$ and (DipSiCl$_2$)$_2$, respectively. We conclude that the use of the larger Si$_3$ precursor improves the selectivity of reductive coupling of fragments. Hexasilaprismane **8a** is thermally stable up to temperature of approximately 350 °C. Much like **8b**, **8a** is stable to extended exposure to air and water. The ^{29}Si NMR spectrum of **8a** shows just one chemical shift at $\delta = -23.1$ ppm, as expected from the D_{3h} symmetry of the molecule, in the region for tetracoordinate silicon atoms. The electron impact mass spectrum confirmed the expected formula C$_{90}$H$_{138}$Si$_6$ for **8a** by showing the molecular ion peak at 1388 *m*/*z*.

The structure of **8a** was confirmed by X-ray analysis on suitable single crystals obtained from a concentrated hexane solution (Figure 2). All Si–Si bond lengths are in the typical region for Si–Si single bonds. There are no differences in the Si–Si bond length of the bonds of the three- and four-membered faces of the polyhedron, which is in line with the experimental structure of **8b**[17] as well as with theoretical predictions.[22]

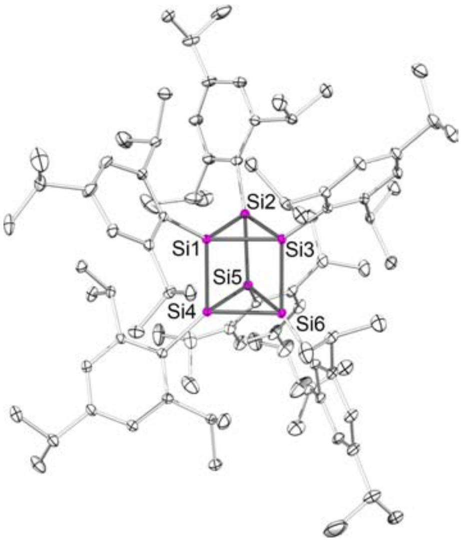


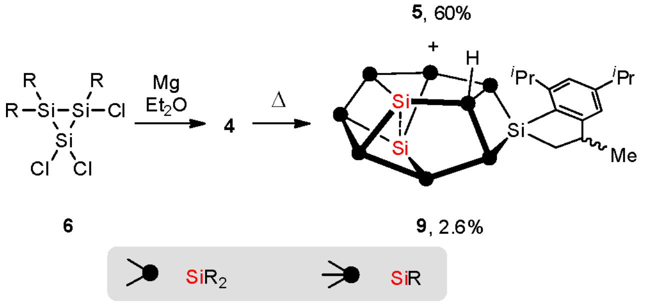
Figure 2. Structure of **8a** in the solid state (thermal ellipsoids at 15%). Hydrogen atoms omitted. Selected bond lengths [Å]: Si1–Si2 = 2.3906(14), Si1–Si3 = 2.3656(14), Si1–Si4 = 2.3789(13), Si2–Si3 = 2.3833(15), Si2–Si5 = 2.3667(14), Si3–Si6 = 2.3718(14), Si4–Si6 = 2.3799(14), Si4–Si5 = 2.3777(14), Si5–Si6 = 2.3868(15).

So far the non-siliconoid isomer **8a** has resisted attempts to rearrange it to other valence isomers of hexasilabenzene or hexasilabenzene itself. Sakurai et al. had suggested the formation of a Dewar benzene isomer from hexasilaprismane **8b** on the basis of a strongly red-shifted longest wavelength absorption after UV irradiation.[17]

2.2. Expanded-Core Siliconoid. The core expansion of silicon clusters is a pivotal process of the chemical vapor deposition of elemental silicon. Despite a large number of experimental gas-phase studies[1] and theoretical investigations,[23] the absence of stable siliconoids prevented the investigation of such processes in the condensed phase until recently.[10−12,14,15]

During the thermal rearrangement of the dismutational isomer **4** to the presumed global minimum **5**, a few side products are formed in very small quantities. The core-expanded Si$_{11}$-siliconoid **9** was thus isolated as orange crystals by crystallization from the hexane mother liquor of **5** in 2.6% yield (Scheme 2) and characterized by multinuclear NMR and UV/vis.

Scheme 2. Isolation of 9 as a Side Product in the Synthesis of the Global Minimum Isomer 5[a]



[a]Indicated yields are isolated. R = Tip = 2,4,6-^{i}Pr$_3$C$_6$H$_2$.

The constitution of **9** was determined by X-ray diffraction of a single crystal (Figure 3). The expanded siliconoid **9** contains a severely disordered Si$_{11}$-cluster core (see Supporting Information). Eight carbon-substituted silicon atoms formally constitute a strongly puckered eight-membered ring about the three central silicon atoms without Si–C connectivity.

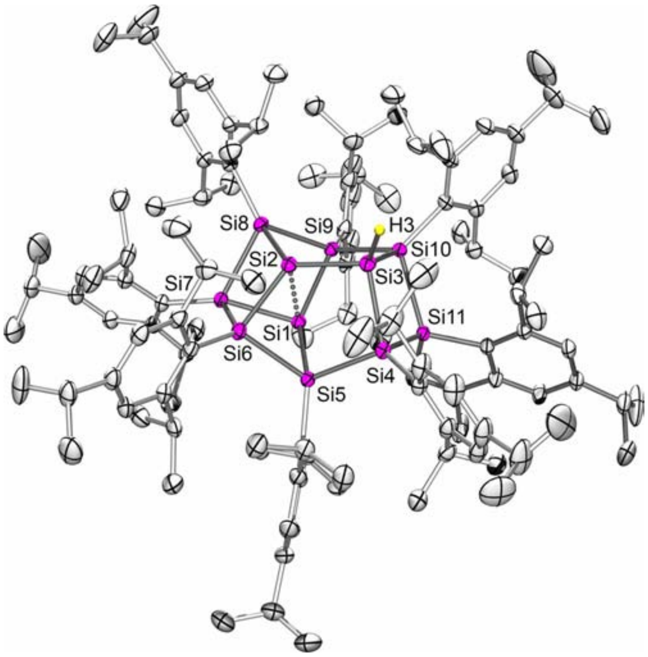


Figure 3. Structure of **9** in the solid state (thermal ellipsoids at 30%). Hydrogen atoms except H3, co-crystallized hexane, and minor position of disorder of the entire molecule omitted. Selected bond lengths [Å]: Si1–Si2 = 2.4976(9), Si1–Si5 = 2.4267(9), Si1–Si9 = 2.4175(9), Si2–Si3 = 2.3196(9), Si2–Si6 = 2.3201(10), Si2–Si8 = 2.3219(9), Si3–Si4 = 2.3580(9), Si3–Si10 = 2.3747(9), Si4–Si5 = 2.3923(9), Si4–Si11 = 2.3888(9), Si5–Si6 = 2.3993(9), Si6–Si7 = 2.3818(9), Si7–Si8 = 2.3816(9), Si8–Si9 = 2.4006(9), Si9–Si10 = 2.3746(9), Si10–Si11 = 2.3926(8).

Two presumably unsubstituted vertices, Si1 and Si2, are arranged in a propellane-like unit, which in contrast to the global minimum isomer **5**[15] and Breher's propellane **3**[12] is arranged in a staggered rather than in an eclipsed manner. Possibly as a consequence of this staggering the distance between the two bridgehead atoms is considerably shorter (**7**, 2.4976(9); **5**, 270.76(8); and **3**, 2.636(1) Å), indicating a much stronger bonding interaction. In order to accommodate this shorter bond, the bridgehead atoms in **9** show a distinctly planarized coordination (sum of angles Si1 343.5°; Si2 354.7°) Conversely, due to the pronounced pyramidalization at Si3 (sum of angles Si3 294.8°) we tentatively assigned H3 as bonded to this atom, although it was not located on the difference electron density map. The position of the Si–H functionality was confirmed by a series of 2D NMR spectra as well as DFT calculations (*vide infra*).

The UV/vis spectrum of **9** shows two absorption maxima at $\lambda = 399$ nm ($\varepsilon = 1650$ M^{-1} cm^{-1}) and $\lambda_{max} = 451$ nm ($\varepsilon = 2455$ M^{-1} cm^{-1}). The longest wavelength absorption is blue-shifted by about 20 nm in comparison with those of **3** and **5**, which is in line with a larger HOMO–LUMO gap and the shorter and therefore presumably stronger bond between the bridgehead atoms Si1 and Si2 as observed in the solid state. The large size of the core-expanded siliconoid **9**, however, precluded the use of TD-DFT to support this assumption.

The ^{29}Si NMR spectrum of **9** exhibits the expected 11 resonances of equal intensity at $\delta = +26.2, +0.1, -0.6, -4.0, -41.2, -43.0, -43.5, -56.0, -62.7, -64.2$, and -78.7 ppm. In the complicated ^{1}H NMR spectrum the isolated singlet at $\delta = 5.68$ ppm can be assigned to the Si-bonded hydrogen H3 on the basis of isotopic satellite peaks with a ^{1}J(Si,H) coupling constant of 194 Hz. Indeed the connectivity of **9** in the solid state proves an insertion reaction of a silicon atom into a methyl C–H bond of an *ortho*-isopropyl group under formation of a spiro-cyclic Si–C bond at Si11. In order to determine the location of H3, full assignment of the ^{29}Si signals by means of 2D NMR spectroscopic analysis was done (see Supporting Information).

For further corroboration of the position of H3, the geometry of the silicon scaffold was partially optimized at the ωB97XD/6-31G(d,p) level of theory with the hydrogen atom H3 alternatively being located on Si3 (**9Dip**), Si2 (**9Dip***), or Si3 (**9Dip****, Figure 4).[24] To economize computational resources the *para*-isopropyl groups of the Tip substituents were replaced by hydrogen atoms, and optimization was halted after convergence of the total energies to the third decimal place. Only the siliconoid **9Dip** bearing the hydrogen atom at Si3 (Figure 4b) matches the structure found experimentally in the solid state (Figure 4a). In contrast to this, the silicon scaffold of **9Dip*** and **9Dip**** visibly distorts as the comparison of the crucial Si–Si distances clearly illustrates (Figure 4c,d).

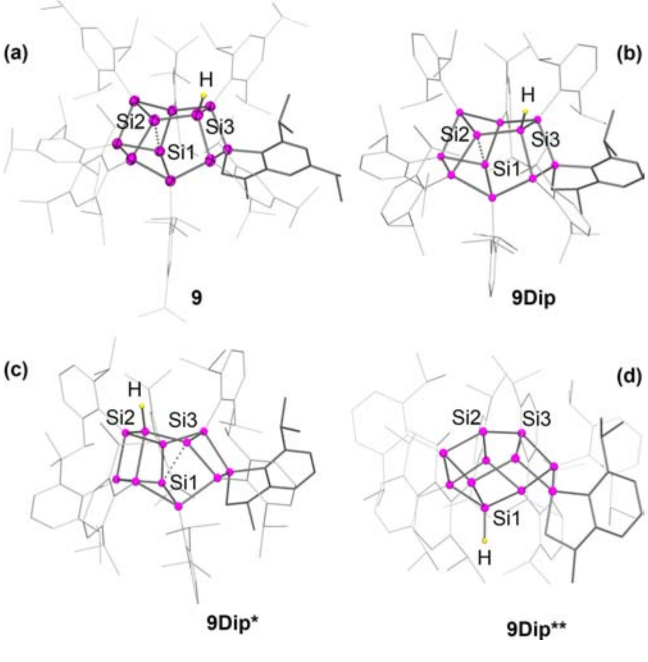
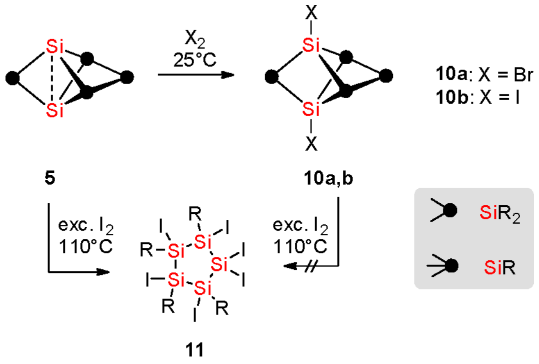


Figure 4. (a) Experimentally determined structure of **9** in the solid state. (b–d) Optimized structures of **9Dip**, **9Dip***, and **9Dip**** at the ωB97XD/6-31G(d,p) level of theory. Distances [Å]: Si1–Si2 = 2.498 (**9**), 2.509 (**9Dip**), 3.302 (**9Dip***), 3.455 (**9Dip****); Si1–Si3 = 3.601 (**9**), 3.643 (**9Dip**), 2.625 (**9Dip***), 3.835 (**9Dip****).

Up to now the mechanism of the formation of **9** has remained obscure. Formally, an $SiTip_4$ unit is expelled from an entirely hypothetical dimerization product, $Si_{12}Tip_{12}$. This would be followed by insertion of one of the resulting three unsubstituted vertices into a CH bond of the substituent. The extrusion of silicon from the Si_6 backbone of **4** or **5**, however, is in principle feasible, as the following results suggest.

2.3. Cluster Contraction of 5 by Iodination. We previously reported that bromination and iodination of the global minimum isomer **5** affords the 1,5-dihalogenated persilatricyclo[2.2.0.0^{2,5}]hexane derivatives **10a,b** by addition of halogen to the bridgehead silicon atoms (Scheme 3).[15]

Scheme 3. Halogenation of Siliconoid 5 to 1,5-Dihalo Derivatives 10a,b[15] and Contraction to Hexaiodocyclopentasilane 11[a]



[a] R = Tip = 2,4,6-$^{i}Pr_3C_6H_2$

Surprisingly, 2 equiv of halogen are required to complete conversion in these reactions. In order to shed light on the nature of the side products during the synthesis of **10b**, the reaction was carried out with a 10-fold excess of iodine in refluxing toluene (instead of benzene at ambient temperature). Notably, a new species, **11**, formed almost quantitatively with three ^{29}Si NMR signals at $\delta = -35.9, -45.3$, and -65.4 ppm in a 1:2:2 ratio, which served as a first indication for the expulsion of one silicon vertex (Scheme 3). Three consecutive crystallizations from toluene were necessary to completely remove excess iodine. Consequently, only 28% of **11** was isolated as colorless crystals.

The constitution of **11** as hexaiodinated cyclopentasilane was determined by an X-ray diffraction study on single crystals obtained from hexane at room temperature (Figure 5). Four Tip substituents are arranged in an *all-trans* fashion on four of the five ring atoms of the silicon backbone. The five-membered ring exhibits a typical envelope confirmation. Si3 lies 0.8281(14) Å out of the plane through Si1, Si2, Si4, and Si5 (max. deviation 0.0848(6) Å for Si1). In comparison with the solid-state structures of cyclopentasilanes Si_5I_{10},[25] all Si–Si bonds of **11** are slightly elongated, reflecting the larger steric bulk of the Tip substituents.

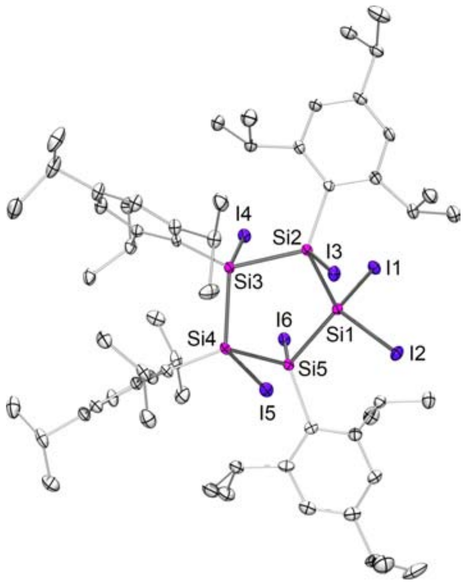


Figure 5. Structure of **11** in the solid state (thermal ellipsoids at 30%). Hydrogen atoms and hexane omitted. Selected bond lengths [Å]: Si1−I1 = 2.4736(9), Si1−I2 = 2.4678(9), Si1−Si5 = 2.4339(13), Si1−Si2 = 2.4369(12), Si2−Si3 = 2.4277(13), Si3−Si4 = 2.3935(13), Si4−Si5 = 2.4145(12).

In order to check whether the 1,5-diiodo derivative **10b** is an intermediate during the formation of **11**, a sample of **10b** was exposed to identical reaction conditions as during the synthesis of **11**, but no reaction occurred even after heating to 110 °C for 15 h. Obviously, the formal expulsion of a “$SiTip_2$” fragment takes place prior to iodination of the unsubstituted vertices. Analysis of the frontier orbitals of **5** reveals that both HOMO and HOMO−1 belong to the cluster’s σ-framework.[15] Accordingly, an initial oxidative expulsion of one of the $SiTip_2$ bridges followed by hexaiodination and rearrangement of the cluster scaffold to the five-membered ring of **11** is plausible.

Compound **11** is the first 1,2,3,4-tetraaryl-substituted cyclopentasilane and therefore inherently suitable for subsequent studies regarding the synthesis of heavier persila analogues of cyclopentadiene and related compounds, which are currently being investigated in our laboratory. It should be noted that the parent cyclopentasilane has been used as a convenient and safe starting material for an inkjet-printable formulation of amorphous silicon precursors.[26]

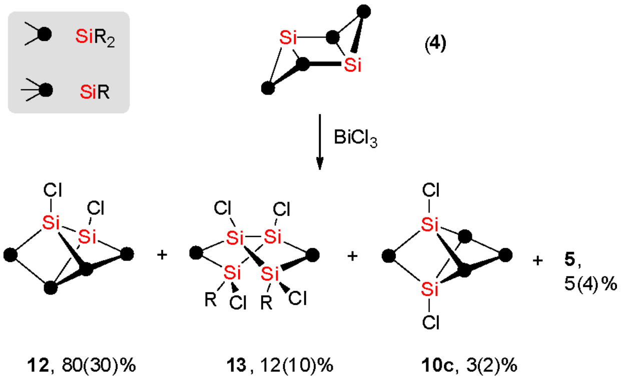
2.4. Reaction of 4 with $BiCl_3$.

Due to its peculiar electronic structure (dismutational aromaticity), we anticipated that the halogenation of **4** might lead to entirely different products. Indeed, the halogenation of **4** with elemental bromine or iodine, unlike that of **5**, resulted in complex reaction mixtures. A milder source of halogen was thus required. Bismuth trichloride ($BiCl_3$) is commonly used as oxidizing agent in synthetic organic synthesis[27] and should act as a mild Cl_2 source.

Similar to the use of elemental halogens, the reaction of **4** with 1 equiv of $BiCl_3$ in benzene at ambient temperature resulted in multiple products. Extraction of the mixture with hexane followed by fractional crystallization, however, allowed for the isolation of most components in this case (Scheme 4).

The main product of the reaction, **12**, which could be isolated in pure form in 30% yield, shows three signals in the ^{29}Si NMR spectrum in the ratio 1:1:1 at δ = 19.1, −25.8, and −69.9 ppm. The electron impact mass spectrum of this compound exhibits the highest mass at 1458.7 m/z, in agreement with the formula $Si_6Tip_6Cl_2$. According to ^1H NMR and 2D $^1H/^{29}Si$ correlation spectra, the silicon scaffold of **12** is formed of six vertices substituted with two, one, and no Tip substituents, respectively. In agreement with the yellow color, the longest wavelength absorption in the UV/vis spectrum of **12** is observed as a shoulder at 396 nm (ε = 850 M^{-1} cm^{-1}) and thus in a similar region as those of **10a,b**.[15] The spectroscopic data therefore initially suggested the formation of the 1,5-substituted derivative **10c** as the main product.

Scheme 4. Products Obtained from Reaction of 3 with $BiCl_3$[a]



[a] Estimated percentage in crude product; isolated yield in brackets. R = Tip = 2,4,6-$^iPr_3C_6H_2$.

Single crystals suitable for X-ray analysis were grown from a concentrated solution in benzene. The unexpected 1,2-dichloro isomer was identified as the main product **12** by an X-ray diffraction study (Figure 6).

The tricyclic silicon scaffold of **12** resembles that of the global minimum isomer **5** rather than the dismutational isomer **4**. The chloro-substituted silicon atoms are adjacent to one another, i.e., in the 1,2-position rather than in the 1,5-position as in **10a,b**. The Si−Cl distances of Si1−Cl1 = 2.0665(6) Å and Si2−Cl2 = 2.0683(6) Å are typical for tetrahedral coordination environ-

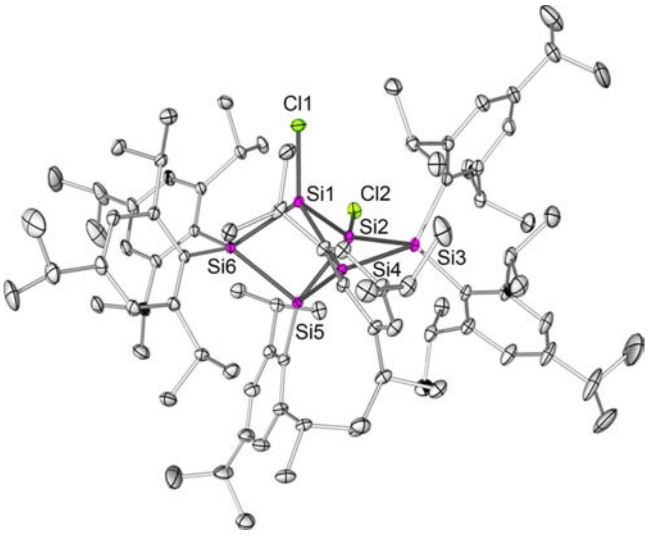


Figure 6. Structure of **12** in the solid state (thermal ellipsoids at 30%). Hydrogen atoms and benzene molecules omitted. Selected bond lengths [Å]: Si1−Si4 = 2.3906(6), Si1−Si2 = 2.3298(7), Si1−Si6 = 2.3428(6), Si2−Si3 = 2.3294(6), Si2−Si5 = 2.3938(6), Si3−Si4 = 2.4157(6), Si4−Si5 = 2.4730(7), Si5−Si6 = 2.4634(7), Si1−Si5 = 2.8229(6), Si2−Si4 = 2.8145(6).

ments of silicon. Most Si−Si bonds are in the range of Si−Si single bonds in saturated small rings.[17,20,21] In marked contrast, the bond between Si4 and Si5 is substantially longer (2.4730(7) Å), presumably due to steric congestion. The two through-space distances of the chlorinated silicon atoms to the opposing silicon atoms (Si1−Si5 = 2.8229(6) Å and Si2−Si4 = 2.8145(6) Å) are approximately 11 pm longer than the distance between the bridgehead atoms in **5**.

Fractional crystallization of the product mixture of the reaction of **3** with $BiCl_3$ also allowed for the isolation of **13** and **10c** as side products in 10% and 2% yield, respectively (Scheme 4). In the electron impact mass spectrum of **13**, the highest mass is observed at 1528.8 *m*/*z*, which is in agreement with the formula $Si_6Tip_6Cl_4$. The additional incorporation of two chlorine atoms in **13** could proceed by oxidative cleavage and chlorination of one Si−Si σ-bond of **12**. However, this assumption was disproven since a solution of **12** and $BiCl_3$ in benzene shows no reaction even after heating to 70 °C for 48 h. Similarly to the reaction of **5** with excess iodine (cf. section 2.3), the chlorination of a Si−Si σ-bond apparently takes place prior to the formation of **12** and therefore possibly in a more reactive transient intermediate.

Colorless crystals of **13**, suitable for X-ray analysis, were grown from a concentrated benzene solution. The solid-state structure contains one molecule benzene in the unit cell (Figure 7). It displays significant disorder of the whole molecule, which was accounted for by refinement on split positions (Supporting Information), preventing a detailed discussion of bonding parameters.

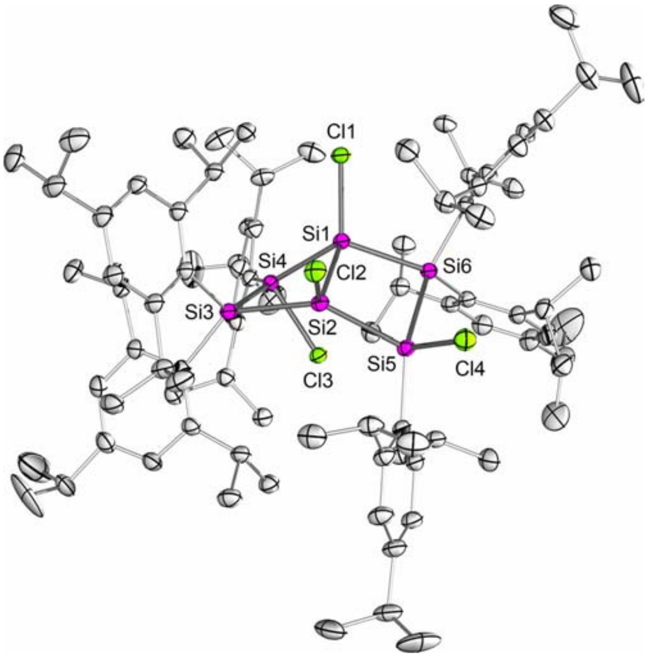


Figure 7. Structure of **13** in the solid state (thermal ellipsoids at 30%). Hydrogen atoms and benzene molecules as well as minor occupation site omitted. Selected bond lengths [Å]: Si1−Cl1 = 2.0831(6), Si1−Si4 = 2.3305(7), Si1−Si2 = 2.4313(6), Si1−Si6 = 2.3749(6), Si2−Cl2 = 2.0797(6), Si2−Si3 = 2.4559(7), Si2−Si5 = 2.4405(6), Si4−Cl3 = 2.1692(8), Si3−Si4 = 2.4102(6), Si5−Cl4 = 2.1015(8), Si5−Si6 = 2.4951(6).

The constitution of **13** as hexasilabicyclo[2.2.0]hexane is formally derived from the tricyclic scaffold of **12** by cleavage of Si4−Si5, i.e., the most congested and thus longest Si−Si σ-bond. The observed Si−Si bonds of **13** are all on the upper end of the typical range observed for Si−Si single bonds, reflecting the high steric strain in the molecule. The two four-membered rings are distorted from planarity, as indicated by the sum of inner angles (Si1−Si2−Si3−Si4 = 350.96°; Si1−Si2−Si5−Si6 = 358.31°).

In the ^{29}Si NMR spectrum six signals at δ = 27.7, 19.0, 18,5, 15.8, 13.2, and −7.8 ppm are observed, reflecting the C_1 symmetry of the molecule. With the help of 2D $^{1}H/^{29}Si$ correlation, the signals at δ = 27.7 and −7.8 ppm are unequivocally assigned to the $SiTip_2$ moieties (Si3 and Si6).

The additional product **10c** (Figure 8) could only be isolated in a mixture with siliconoid **5**. After several crystallizations, the ratio of the mixture was still approximately 1:1, and no further purification could be achieved in this way. Given that the NMR data of the global minimum siliconoid **3** are known,[15] the assignment of the ^{29}Si NMR signals was straightforward. The chemical shifts belonging to **10c** were identified at δ = 21.1, 17.5, 9.8, and −80.3 ppm. They are, with the exception of the signal at 17.5 ppm, very similar to those of **10a,b**.[15] As expected, the latter resonance can be assigned to the halogenated silicon atoms Si1 and Si1′ by 2D $^{1}H/^{29}Si$ correlation. In the electron impact mass spectrum of the mixture of compounds **5** and **10c**, the highest peak, at 1459 *m*/*z*, is the molecular ion peak of **10c** ($Si_6Tip_6Cl_2$).

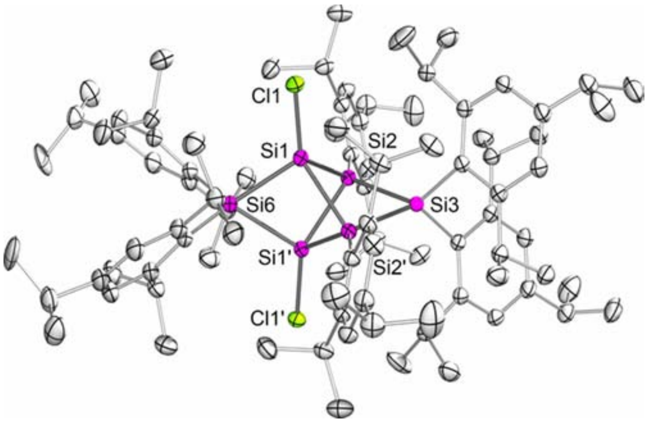


Figure 8. Structure of **10c** in the solid state (thermal ellipsoids at 30%) determined on a crystal with co-crystallized **5** in approximate 1:1 ratio. Hydrogen atoms and hexane molecules omitted.

The orange crystals of the mixture of **5** and **10c** which were obtained from a concentrated hexane solution were analyzed by X-ray diffraction to confirm the presence of **10c** and to get an impression of the structural features. The obtained bond length and angles should just serve as approximate values due to the co-crystallization of two components at the same crystallographic positions.

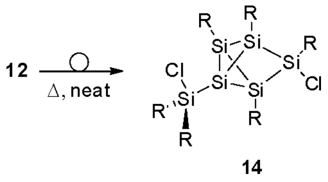
Although the mechanism for this chlorination reaction remains obscure, it is assumed that the presence of subvalent bismuth compounds in the reaction mixture might play an important role in the formation of the reaction products. The assumed "BiCl" intermediate could aggregate, as has been described for the reductive dehalogenation of $BiCl_3$,[28] which would explain the precipitation of an unidentified black material from the reaction mixture.

2.5. Thermal Rearrangement of 12.

The clean thermal isomerization observed upon melting of the 1,2-chlorinated tricyclo[$2.2.0.0^{2,5}$]hexasilane **12** is suitable to shed some further light on the complex rearrangements of the silicon scaffold that take place during the reactions of siliconoids **4** and **5** described above.

Heating of neat **12** to 230 °C until completely melted results in its clean isomerization to a new compound, **14** (Scheme 5). The highest mass in the electron impact mass spectrum of **14** at 1458.7 *m/z* is identical to that of **12**, confirming that no fragmentation occurred during the melting process. The product of thermal rearrangement shows a new set of ^{29}Si NMR signals at δ = 59.4, 5.8, −96.4, −113.2, −151.2, and −151.9 ppm. On the basis of a 2D ^{1}H/^{29}Si correlation NMR experiment, the ^{29}Si signal at δ = 5.8 ppm is assigned to the exocyclic silicon atom. All other ^{29}Si signals are observed at unusual chemical shifts. Four resonances are located at relatively high field, whereas one is significantly deshielded. In the Si_6 siliconoid **5**, the strong deshielding of a tetracoordinate silicon atom had been correlated to the presence of magnetically induced cluster currents.[15]

Scheme 5. Thermal Rearrangement of 12 to 14[a]



[a]R = Tip = 2,4,6-$^{i}Pr_3C_6H_2$.

An X-ray diffraction study on single crystals of **14** allowed for the determination of the molecular structure in the solid state, confirming the contraction of the Si_6-scaffold to the tricyclo[2.1.0.0^{2,5}]pentasilane **14** (Figure 9). The remaining silicon atom is located in an exocyclic chlorosilyl group. It is noteworthy that **14** constitutes a derivative with one SiR_2 moiety, four SiR units, and one silicon atom with no directly attached substituent. In other words, **14** features a substitution pattern halfway between hypothetical hexasilabenzene and its dismutational isomer **4**. In addition, the chlorine functionalities on the cluster core as well as in the side chain provide ample opportunity for further functionalization and modification of the cluster size.

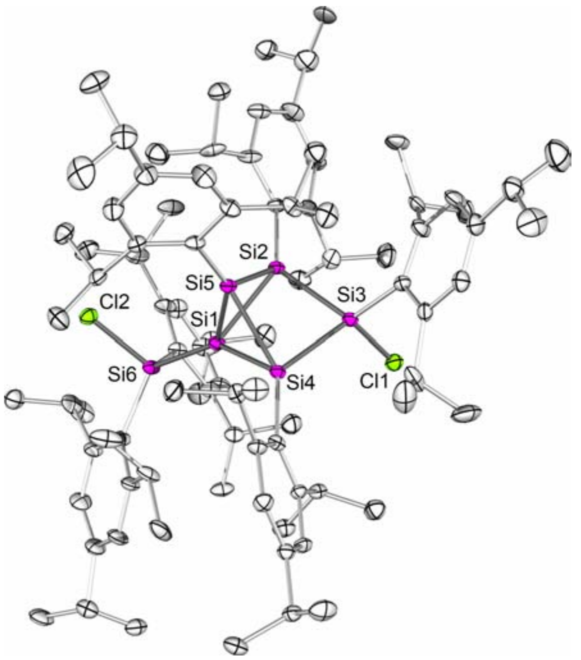


Figure 9. Structure of one of the two independent molecules of **14** in the solid state (thermal ellipsoids at 15%). Second molecule, hydrogen atoms, and hexane molecules omitted. Selected bond lengths [Å]: Si1−Si6 = 2.347(4), Si1−Si2 = 2.355(4), Si1−Si4 = 2.356(4), Si1−Si5 = 2.312(4), Si2−Si5 = 2.334(4), Si2−Si3 = 2.366(4), Si3−Si4 = 2.366(4), Si4−Si5 = 2.334(4).

3. CONCLUSION

The contraction and expansion of unsaturated silicon clusters is pivotal to nucleation processes in the gas-phase deposition of elemental silicon materials. We therefore propose the term “siliconoids” for such clusters. The reactivity of stable siliconoids **4** and **5** in solution phase has been investigated in this regard taking advantage of the powerful preparative and analytical tools of synthetic chemistry. We have thus provided preparative examples of a cluster expansion process of a stable siliconoid in the condensed phase, as well as the thermal or oxidative contraction.

The structure elucidation of transient siliconoids—evident intermediates in important industrial processes (Siemens process, Direct process, CVD of amorphous silicon)—until very recently relied on computational and gas-phase spectroscopic studies alone. Structure−reactivity relationships begin to emerge from the present study. The unusual electronic situation encountered in siliconoids gives rise to a surprisingly rich chemistry that we will continue to study in our laboratories.

4. EXPERIMENTAL SECTION

General Remarks. All manipulations were carried out under a protective atmosphere of argon applying standard Schlenk techniques or in a drybox. Ethereal solvents were refluxed over sodium/benzophenone; toluene over sodium; pentane, hexane, and (deuterated) benzene over sodium/potassium alloy. All solvents were distilled and stored under argon and degassed prior to use. 1,1,2-Trichlorocyclotrisilane (**6**) was prepared following our published procedure.[14] Silicon tetrachloride was purchased from Aldrich, stored over Mg turnings, and distilled prior to use. ^{1}H and ^{13}C{^{1}H} NMR spectra were referenced to external $SiMe_4$ using the residual signals of the deuterated solvent (^{1}H) or the solvent itself (^{13}C). ^{29}Si{^{1}H} NMR spectra were referenced to external $SiMe_4$. UV/vis spectra were recorded on a Perkin-Elmer Lambda 20 UV/vis spectrometer. Melting points were determined under argon in closed NMR tubes and are uncorrected.

1,2,3-Trichlorocyclotrisilane (7). Method 1: In an oil bath, 1.50 g (1.87 mmol) of neat 1,1,2-trichlorocyclotrisilane (**6**) was heated to 185 °C for 5 min. The red melt was cooled to room temperature and dissolved in 5 mL of hexane. The filtrate was reduced to 3 mL, and at room temperature 0.84 g (56%) of 1,2,3-trichlorocyclotrisilane (**7**) crystallized as pale yellow crystals. Method 2: A solution of 7.94 g (9.92 mmol) of **6** in 60 mL of toluene was refluxed for 16 h under a slight overpressure of about 0.2 bar. ^{1}H NMR shows full conversion to **7** along with 6% unidentified side products. ^{1}H NMR (500.13 MHz, C_6D_6, 25 °C): δ = 7.22, 7.14 (each s, altogether 6H, Tip-H), 4.11, 3.39, 2.77, 2.74 (each hept, altogether 9H, iPr-CH), 1.50, 1.34, 1.26, 1.19, 1.16, 1.15 (each d, altogether 54H, iPr-CH_3). ^{13}C NMR (125.76 MHz, C_6D_6, 25 °C): δ = 157.38, 156.79, 153.37, 152.92 (Tip-$C_{o/p}$), 128.62, 127.01 (Tip-C_i), 122.36, 122.16 (Tip-CH), 37.76, 37.09, 34.83 (iPr-CH), 26.44, 25.80, 25.02, 23.98, 23.95, 23.89 (iPr-CH_3). ^{29}Si NMR (99.36 MHz, C_6D_6, 25 °C): δ = −13.9 (1Si), −18.7 (2Si). Exact mass (EI): calcd *m/z* for $C_{45}H_{69}Cl_3Si_3^+$ (M^+), 798.3773; found, 798.3787. MS (EI): *m/z* (%) = 800.4 (14.2, M^+), 757.3 (5.2, M^+ − iPr), 533.2 (16.6, M^+ − iPr), 497.3 (100.0, M^+ − $SiCl_2$ − Tip), 469.3 (43.5), 455.2 (19.5), 433.3 (38.8), 391.3 (10.5), 265.1 (42.9), 251.1 (27.5), 231.1 (88.7), 215.1 (37.0), 203.2 (35.8), 187.1 (42.5), 145.0 (21.4), 43.0 (64.9).

Hexasilaprismane (8a). To a mixture of 7.94 g (9.92 mmol) of **7** and 0.36 g (14.81 mmol) of magnesium powder was added 90 mL of

THF, and the reaction mixture was stirred for 16 h at room temperature. All volatiles were removed under reduced pressure, and the residue was digested in 65 mL of hexane. Insoluble parts were filtered off hot, and the filtrate was reduced until a solid precipitated, which was redissolved by gentle heating. Standing overnight at room temperature gave 2.14 g (31%) of **8a** as small orange crystals (mp >250 °C). ^{1}H NMR (500.13 MHz, C_6D_6, 25 °C): δ = 7.15, 7.03 (each br, altogether 12H, Tip-H), 4.91, 3.54, 2.75 (each hept, altogether 18H, iPr-CH), 1.75, 1.22, 1.18, 1.12, 0.73 (each d, altogether 108H, iPr-CH$_3$). ^{13}C NMR (100.61 MHz, C_6D_6, 25 °C): δ = 156.95, 153.87, 150.37 (Tip-C$_{o/p}$), 133.26 (Tip-C$_i$), 121.65, 121.33 (Tip-CH), 37.18, 36.73, 34.73 (iPr-CH), 27.00, 26.87, 25.60, 24.14 (iPr-CH$_3$). ^{29}Si NMR (99.36 MHz, C_6D_6, 25 °C): δ = −23.1. UV/vis (hexane): λ_{max} (ε) = 264 nm (5550 L mol^{-1} cm^{-1}), 242 nm (7623 L mol^{-1} cm^{-1}), 205 nm (18325 L mol^{-1} cm^{-1}). MS (EI): *m*/*z* (%) = 1388 (100.0, M$^+$), 587 (12.0), 433 (17.8), 231 (46.4), 175 (44.5), 111.0 (63.8), 91 (45.4), 44.0 (38.7).

Si$_{11}$-Siliconoid (9). Siliconoid **9** was formed as a side product during the synthesis of propellane **5** that was described previously.[15] The mother liquor (40 mL) separated from the second batch in the synthesis of **5** was reduced in volume to 25 mL. After 48 h at room temperature, 0.51 g (2.6%) of pure **9** was obtained as orange crystals. ^{1}H NMR (500.13 MHz, C_6D_6, 25 °C): δ = 7.122, 7.119, 7.10, 7.08, 7.05, 7.03, 6.80, 6.75, 6.73, 6.72, 6.68, 6.66, 6.65, 6.64 (each s, altogether 16H, Tip-H), 5.68 (s, 1H, ^1J(Si,H) = 194 Hz, Si−H), 4.88, 4.80, 4.66, 4.51, 4.37, 4.28, 4.20, 3.55 (each hept, altogether 10H, iPr-CH), 3.43 (m, 1H, iPr-CH), 3.27 (m, 1H, CH$_2$), 2.82, 2.80 (each hept, altogether 3H, iPr-CH), 2.69−2.52 (m, altogether 10H, iPr-CH), 2.11, 2.06, 1.89, 1.85 (br, 1H, CH$_2$), 1.82, 1.81, 1.80, 1.79, 1.77, 1.75, 1.73, 1.56, 1.53, 1.52, 1.11, 1.09, 1.08, 1.07, 1.05, 1.03, 0.45, 0.42, 0.39, 0.37, 0.33, 0.31, 0.29, 0.15, 0.13, 0.12, 0.11, 0.09, 0.07, 0.04 (each d, altogether 141H, iPr-CH$_3$). ^{13}C NMR (125.76 MHz, C_6D_6, 25 °C): δ = 158.91, 157.13, 156.95, 156.86, 156.77, 156.25, 156.08, 155.81, 155.71, 155.59, 155.28, 153.62, 153.56, 153.18, 153.02, 152.98, 151.02, 150.50, 150.15, 149.87, 149.84, 149.79 (Tip-C$_{o/p}$), 136.09, 134.19, 134.00, 133.89, 133.80, 132.45, 131.98 (Tip-C$_i$), 123.56, 123.21, 123.08, 122.77, 122.68, 122.56, 122.45, 122.23, 121.69, 121.15, 120.45, 120.41 (Tip-CH), 40.58, 40.55, 37.95, 37.30, 36.71, 36.64, 36.39, 36.14, 36.06, 35.95, 35.88, 35.22, 35.17, 34.99, 34.84, 34.78, 34.75, 34.66, 34.53, 34.47, 34.42 (iPr-CH), 31.46, 30.32, 30.25, 29.30, 29.13, 28.10, 27.69, 27.63, 27.33, 26.47, 26.33, 25.98, 25.71, 25.56, 25.49, 25.44, 25.39, 25.34 (iPr-CH$_3$), 25.24 (CH$_2$), 25.17, 25.12, 24.88, 24.82, 24.26, 24.12, 24.09, 23.99, 23.94, 23.86, 23.79, 23.71, 23.55 (iPr-CH$_3$). ^{29}Si NMR (99.36 MHz, C_6D_6, 70 °C): δ = 26.2 (J(Si,Si) = 58 and 12 Hz, SiTip [Si7]), 0.1 (J(Si,Si) = 71, 64, 42, and 25 Hz, SiTip [Si5/Si9]), −0.6 (J(Si,Si) = 70, 65, 43, and 25 Hz, SiTip [Si5/Si9]), −4.0 (J(Si,Si) = 48, 44, 14, and 11 Hz, SiCH$_2$ [Si11]), −41.2 (J(Si,Si) = 48, 43, 37, 24, and 12 Hz, SiTip [Si4/Si10]), −43.0 (J(Si,Si) = 40, 25, 18, 13, and 8 Hz, Si [Si2]), −43.5 (J(Si,Si) = 43, 37, 24, and 13 Hz, SiTip [Si4/Si10]), −56.0 (J(Si,Si) = 37, 16, and 10 Hz, SiH [Si3]), −62.7 (J(Si,Si) = 71, 64, 58, 23, and 18 Hz, SiTip [Si6/Si8]), −64.2 (J(Si,Si) = 71, 65, 58, 22, and 18 Hz, SiTip [Si6/Si8]), −78.7 (J(Si,Si) = 39, 23, 15, and 10 Hz, Si [Si1]). UV/vis (hexane): λ_{max} (ε) = 399 nm (2460 L mol^{-1} cm^{-1}), 451 nm (1650 L mol^{-1} cm^{-1}).

Hexaiodocyclopentasilane (11). At 110 °C a solution of 18.96 g (12.49 mmol) of **5**·1.5C$_6$H$_{14}$ in 150 mL of toluene was added dropwise to a solution of 29.22 g (115.13 mmol) iodine in 150 mL of toluene during 30 min. Reflux was continued for 15 h before the solution was cooled to ambient temperature. All volatiles were distilled off under reduced pressure. NMR analysis showed a quantitative formation of **11**. Removing the excess of I$_2$ required three consecutive crystallizations from toluene, resulting in 6.35 g (28%) of **11**·C$_7$H$_8$ as colorless crystals (mp 216 °C, dec.). Single crystals suitable for X-ray analysis were obtained from a concentrated hexane solution as **11**·1.5C$_6$H$_{14}$. ^{1}H NMR (400.13 MHz, C_6D_6, 70 °C): δ = 7.26 (br), 7.22, 6.96, 6.95 (br) (each d, altogether 8H, Tip-*H*), 4.62, 4.14, 3.53, 2.93, 2.77, 2.70 (each hept, altogether 12H, iPr-C*H*), 1.95, 1.57, 1.49, 1.44, 1.31, 1.19, 1.13, 1.05, 0.84, 0.29 (each d, altogether 72H, iPr-C*H*$_3$). ^{13}C NMR (100.61 MHz, C_6D_6, 70 °C): δ = 161.47, 159.01, 157.51, 157.39, 152.58, 152.26 (Tip-C$_{o/p}$), 126.54 (Tip-C$_i$), 124.98, 123.99 (Tip-CH), 123.20 (Tip-C$_i$), 123.02, 120.96 (Tip-CH), 38.77, 38.27, 36.56, 36.35, 34.41 (iPr-CH), 30.85, 30.46, 28.19, 27.26, 25.81, 24.39, 24.00, 23.90, 23.86, 23.80, 23.74 (iPr-CH$_3$). ^{29}Si NMR (79.49 MHz, C_6D_6, 70 °C): δ = −35.9 (1Si, *Si*I$_2$), −45.4 (2Si, *Si*TipI), −65.4 (2Si, *Si*TipI). MS (EI): *m*/*z* (%) = 1716 (4, M$^+$), 1588 (27, M$^+$ − I), 1489 (49), 1461 (19, M$^+$ − 2I).

1,2-Dichlorotricyclo[2.2.0.0^{2,5}]hexasilane (12), 1,2,3,5-Tetrachlorobicyclo[2.2.0]hexasilane (13), and 1,5-Dichlorotricyclo[2.2.0.0^{2,5}]hexasilane (10c). A solution of 25.00 g (17.04 mmol) of **3** in 600 mL of benzene was warmed to 50 °C, and 5.39 g (17.09 mmol) of BiCl$_3$ was added in small portions as a solid. Stirring was continued overnight before all solvent was distilled off under reduced pressure. The residue was digested with 750 mL of hexane, and the black precipitate ("BiCl") was filtered off carefully. The filtrate was reduced to 30 mL until **13** started to precipitate as a white solid, which was collected by filtration and recrystallized from benzene, resulting in 2.66 g (10%) of pure **13** as colorless crystals (mp 244 °C). The filtrate was reduced to dryness to yield pure **12** as a pale yellow solid. Crystallization from a concentrated hexane solution afforded 7.54 g (30%) of **12** as pale yellow crystals (mp 219−222 °C, dec.). The initial mother liquor was reduced to 20 mL and stored at room temperature, resulting in the formation of 0.99 g (4%) of orange crystals, which consisted of **10c** and **5** in a 1:1 ratio. A second crop of 0.41 g (2%) of pure **5** was collected from the mother liquor. **12:** ^{1}H NMR (500.13 MHz, C_6D_6, 25 °C): δ = 7.15, 7.05, 6.93 (each br, altogether 12H, Tip-*H*), 4.25, 4.17, 3.60, 3.27, 3.01, 2.76, 2.70 (each br, altogether 18H, iPr-C*H*), 1.62, 1.40, 1.33, 1.25, 1.20, 1.15, 1.10, 0.74, 0.38 (each br, altogether 108H, iPr-C*H*$_3$). ^{13}C NMR (125.76 MHz, C_6D_6, 25 °C): δ = 158.19, 156.90 (br), 155.45, 155.18, 154.92, 154.57 (br), 150.25, 150.15, 150.04, 136.74, 136.40 (Tip-*C*), 124.04, 123.82, 123.69, 123.06, 122.31 (Tip-CH), 39.05, 37.46, 36.70 (br), 36.53, 36.35, 35.97, 34.50, 34.48, 34.46 (iPr-CH), 30.15, 29.08 (br), 28.59 (br), 26.26 (br), 25.80, 25.56, 25.38, 24.88, 24.75, 24.52 (br), 24.10, 24.06, 24.00, 23.99, 23.90, 23.88 (iPr-CH$_3$). ^{29}Si NMR (99.36 MHz, C_6D_6, 25 °C): δ = 19.1 (2Si, *Si*Tip), −25.8 (br, 2Si, *Si*Cl), −69.9 (2Si, *Si*Tip$_2$). UV/vis (hexane): λ_{max} (ε) = 396 nm (850 L mol^{-1} cm^{-1}). MS (EI) *m*/*z* (%) = 1458.7 (24.0, M$^+$), 987.4 (97.0, M$^+$ − SiTip$_2$ − Cl), 721.4 (43.1, Si$_4$Tip$_3$$^+$), 469.3 (67.4, SiTip$_2$Cl). **13:** ^{1}H NMR (400.13 MHz, C_6D_6, 25 °C): δ = 7.32, 7.30, 7.21, 7.13, 7.09, 7.08, 7.00, 6.93, 6.77 (each br, altogether 12H, Tip-*H*), 4.56, 3.91, 3.81, 3.72, 3.56, 3.53, 3.49, 3.35, 3.13, 2.97, 2.80, 2.78, 2.74, 2.73, 2.71, 2.63, 2.33, 2.26 (each hept, altogether 18H, iPr-C*H*), 1.86, 1.80, 1.73, 1.67, 1.61, 1.59, 1.57, 1.44, 1.38, 1.32, 1.31, 1.28, 1.26, 1.23, 1.21, 1.18, 1.16, 1.15, 1.13, 0.84, 0.80, 0.68, 0.66, 0.50, 0.48, 0.32, 0.25, 0.11 (each d, altogether 108H, iPr-C*H*$_3$). ^{13}C NMR (100.61 MHz, C_6D_6, 25 °C): δ = 157.31, 157.13, 156.63, 156.50, 155.58, 155.41, 155.24, 154.09, 153.63, 153.51, 153.20, 152.50, 150.16, 149.97, 149.91, 149.80, 149.70 (Tip-C$_{o/p}$), 139.97, 137.62, 136.13, 136.00, 135.38, 131.83 (Tip-C$_i$), 125.05, 124.49, 124.01, 123.95, 123.42, 123.36, 122.99, 122.85, 122.64, 121.99 (Tip-CH), 41.66, 40.79, 39.10, 38.06, 37.97, 37.27, 36.58, 36.34, 36.15, 36.02, 35.31, 35.15, 34.64, 34.56, 34.47, 34.34, 34.23 (iPr-CH), 31.00, 30.24, 29.79, 28.87, 28.40, 28.34, 28.13, 28.02, 27.84, 27.74, 27.64, 27.58, 27.44, 27.39, 26.97, 26.18, 26.01, 25.97, 25.86, 24.43, 24.20, 24.08, 23.99, 23.92, 23.88, 23.83, 23.80, 23.73, 23.47, 21.92 (iPr-CH$_3$). ^{29}Si NMR (79.49 MHz, C_6D_6, 25 °C): δ = 27.7 (*Si*Tip$_2$), 19.0 (*Si*ClTip), 18.5 (*Si*ClTip), 15.8 (*Si*ClTip), 13.2 (*Si*ClTip), −7.8 (*Si*Tip$_2$). MS (EI): *m*/*z* (%) = 1528.8 (10.0, M$^+$), 1510.8 (4.3), 1262.6 (7.0, M$^+$ − SiClTip), 1227.7 (52.5, M$^+$ − SiCl$_2$Tip), 1059.4 (57.6, M$^+$ − SiClTip$_2$), 959.5 (49.2, M$^+$ − SiTip$_2$ − 3Cl). **10c:** ^{1}H NMR (400.13 MHz, C_6D_6, 70 °C): δ = 7.22, 7.02, 7.00, 6.96, 6.83, 6.77 (each br, each 2H, Tip-*H*), 4.25, 3.822, 3.817, 3.35, 3.34, 3.16 (each hept, each 2H, iPr-C*H*), 2.77−2.56 (m, altogether 6H, iPr-C*H*), 1.71, 1.50, 1.49, 1.47, 1.38, 1.19, 1.16, 1.14, 1.12, 1.08, 1.06, 1.05, 0.49, 0.48, 0.28, 0.27, 0.03 (each d, altogether 108H, iPr-C*H*$_3$). ^{13}C NMR (100.61 MHz, C_6D_6, 70 °C): δ = 157.82, 156.34, 155.21, 154.87, 154.31, 153.38, 151.49, 150.03, 149.56, 140.00, 136.01, 128.71 (Tip-*C*), 124.06, 123.94, 123.78, 123.15, 122.26, 121.75 (Tip-CH), 38.17, 37.67, 37.56, 37.20, 36.63, 35.90, 34.85, 34.58, 34.32 (iPr-CH), 30.62, 29.35, 28.35, 26.69, 25.94, 25.21, 24.92, 24.07, 24.00, 23.86, 23.60, 22.68 (iPr-CH$_3$). ^{29}Si NMR (79.49 MHz, C_6D_6, 70 °C): δ = 21.1 (1Si, *Si*Tip$_2$), 17.5 (2Si, *Si*Cl), 9.8 (1Si, *Si* Tip$_2$), −80.3 (2Si, *Si*Tip). MS (EI): *m*/*z* (%) = 1459 (33.0, M$^+$).

Chlorosilyltricyclo[2.1.0.0^{2,5}]pentasilane (14). A sample of **12** (0.78 g, 0.52 mmol) was heated to 230 °C until all solid had liquefied. After cooling to room temperature, the ^{1}H NMR spectrum showed a quantitative rearrangement to **14**. Single crystals for X-ray analysis were obtained from a concentrated Et$_2$O solution. ^{1}H NMR (500.13 MHz, C$_6$D$_6$, 25 °C): δ = 7.30, 7.27, 7.09, 7.06, 7.03, 7.02, 7.01, 6.99, 6.93 (each br, altogether 12H, Tip-*H*), 4.53, 4.26, 4.17, 4.11, 3.85, 3.52, 3.49, 3.42, 3.39, 3.34 (each hept, altogether 12H, iPr-C*H*), 2.83−2.65 (m, 6H, iPr-C*H*), 1.71, 1.69, 1.62, 1.55, 1.54, 1.46, 1.42, 1.37, 1.26, 1.23, 1.21, 1.19, 1.18, 1.165, 1.157, 1.15, 1.14, 1.05, 1.03, 0.98, 0.76, 0.73, 0.66, 0.59, 0.57, 0.42, 0.37, 0.36 (each d, altogether 108H, iPr-CH_3). ^{13}C NMR (125.76 MHz, C$_6$D$_6$, 25 °C): δ = 159.27, 159.17, 158.83, 156.39, 156.37, 156.29, 156.26, 156.05, 155.00, 154.47, 153.77, 151.42, 151.18, 151.10, 151.06, 150.97, 150.78, 135.85, 134.11, 133.79, 128.57, 128.06, 124.31, 122.70, 122.54, 122.29, 122.24, 122.12, 121.98, 121.90, 121.83, 121.74, 120.06 (Tip-C), 38.36, 38.08, 37.93, 37.89, 37.78, 37.69, 37.48, 36.34, 35.69, 34.81, 34.78, 34.76, 34.67, 34.59, 31.75 (iPr-CH), 31.66, 30.25, 28.39, 28.20, 28.16, 27.85, 27.71, 27.67, 27.49, 27.30, 26.74,26.60, 26.54, 25.99, 25.74, 25.30, 25.19, 24.80, 24.46, 24.37, 24.27, 24.19, 24.16, 24.13, 24.12, 24.08, 24.01, 23.95, 23.85, 23.47, 21.71, 21.63 (iPr-CH$_3$). ^{29}Si NMR (99.36 MHz, C$_6$D$_6$, 25 °C): δ = 59.4 (1Si, *J*(Si,Si) = 37, 17, and 13 Hz, *Si*Tip), 5.8 (1Si, *J*(Si,Si) = 66 and 9 Hz, *Si*Tip$_2$Cl), −96.4 (1Si, *J*(Si,Si) = 51, 36, 23, and 19 Hz, *Si*Tip), −113.2 (1Si, *J*(Si,Si) = 51, 39, 22, and 17 Hz, *Si*Tip), −151.2 (1Si, *J*(Si,Si) = 66, 18, 13, and 9 Hz, *Si*Tip), −151.9 (1Si, *J*(Si,Si) = 23, 17, 13, and 9 Hz, *Si*). MS (EI): *m*/*z* (%) = 1459 (11.4, M$^+$), 988 (42.4, M$^+$ − SiTip$_2$ − Cl), 721 (21.0, Si$_4$Tip$_3$), 469 (37.7, SiTip$_2$Cl).

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Details of X-ray structure determinations, NMR spectroscopic determination of the position of the Si-bonded hydrogen in siliconoid **9**, NMR and UV/vis spectra of all compounds. This material is available free of charge via the Internet at http://pubs.acs.org. Crystallographic data for **7**, **8a**, **9**, **10c·5**, **11**, **12·benzene**, **12·hexane**, **13**, and **14** have been deposited with the Cambridge Structural Database under deposition numbers CCDC 893657−893665.

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Notes

The authors declare no competing financial interest.

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