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Partial Halogenation of Cyclic and Branched Perhydropentasilanes

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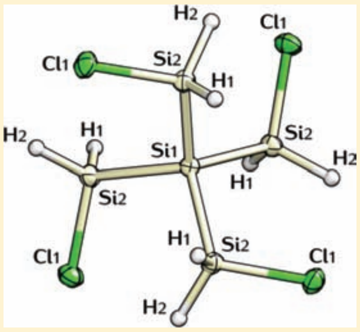
Supporting Information

ABSTRACT: The perhydropentasilanes $(H_3Si)_4Si$ and Si_5H_{10} were chlorinated with $SnCl_4$ to give chlorohydropentasilanes without destruction of the Si−Si backbone. Tetrachloroneopentasilane $(ClH_2Si)_4Si$ (**2**) was prepared in high yield from $(H_3Si)_4Si$ and 3.5 equiv of $SnCl_4$, while Si_5H_{10} and an equimolar amount of $SnCl_4$ afforded a mixture of ~60% of $ClSi_5H_9$ (**1**) with polychlorinated cyclopentasilanes and unreacted starting material, which could not be separated by distillation. The selective monochlorination of Si_5H_{10} was achieved starting from $MesSi_5Cl_9$ (**3**; Mes = 2,4,6-trimethylphenyl) or TBDMP-Si_5Cl_9 (**4**; TBDMP = 4-*tert*-butyl-2,6-dimethylphenyl). **3** or **4** was successfully hydrogenated with $LiAlH_4$ to give $MesSi_5H_9$ (**6**) or TBDMP-Si_5H_9 (**7**), which finally gave **1** along with aryl-H and Si_5H_{10} after treatment with an excess of liquid anhydrous HCl. All compounds were characterized by standard spectroscopic techniques. For Si−H derivatives, the coupled ^{29}Si NMR spectra were analyzed in detail to obtain an unequivocal structural assignment. The molecular structures of **2**−**4** were further confirmed by X-ray crystallography.



■ INTRODUCTION

Solution-based deposition and processing techniques for silicon are of particular interest because they allow significant reduction of processing costs compared to standard vacuum-based approaches. Further advantages of solution methods include suitability for large-area and flexible substrates, increased material utilization efficiency, and lower-temperature processing.[1] Open-chained Si_nH_{2n+2} or cyclic Si_nH_{2n} silicon hydrides are potential precursors in this context because they are liquid at room temperature for $n \geq 3$ and carbon- and oxygen-free and decompose to a-Si:H upon heating to 300 °C and higher. In a pioneering paper, Shimoda et al. describe the fabrication of a thin-film transistor using solution-processed silicon films deposited by pyrolysis of liquid hydrosilane oligomers, which were made by photooligomerization of cyclopentasilane Si_5H_{10}.[2] Later studies revealed that cyclohexasilane Si_6H_{12}[3] or neopentasilane $(H_3Si)_4Si$,[4] which are more easily accessible than Si_5H_{10}, can be used as precursors equally well.[5] n- or p-doped silicon films can also be made using this method if the hydrosilane precursor is mixed with appropriate dopants like P_4 or $B_{10}H_{14}$ prior to photo-oligomerization.[6] The initial studies, however, reported a potential nonuniform dopant distribution within the resulting semiconductor film, which may lead to suboptimal electrical properties. In order to overcome this problem, it has been suggested to use hydrosilane precursors for silicon film deposition, which contain one or more heteroatom dopants covalently linked to the Si−Si backbone (single-source precursors).[7] To the best of our knowledge, compounds of this type have not been described in the literature so far. Therefore, the detailed investigation of the chemical properties of selected higher silicon hydrides with the primary target to elaborate possible pathways to doped single-source precursors for silicon film deposition is one of our main research interests.

Although the synthesis and physical properties of linear[8] and cyclic higher silicon hydrides[9] are well documented, their chemistry is literally unexplored. This is mainly due to their unpleasant properties such as their pyrophoric character upon exposure to air or their thermodynamic and kinetic instability and also due to the lack of suitable synthetic methods for hydrosilane derivatization. Some scattered reports on chemical transformations involving higher silicon hydrides include partial halogenation of di-, tri-, and tetrasilanes with BX_3, HX/AlX_3, AgX, SnX_4, HgX_2, or X_2 (X = Cl, Br, I).[10] These methods usually afford product mixtures that are difficult or even impossible to separate and frequently could only be analyzed after further derivatization of the initial products. More recently, Hassler et al. described the synthesis of a whole series of halohydrodi- and trisilanes by halodephenylation of properly substituted phenyldi- and trisilanes.[11] The challenge of this method, however, is preparation of the starting materials. Redistribution reactions of Si_2H_6 or Si_3H_8 under the influence of $MSiH_3$ (M = Na, K) to give sodium and potassium silanides containing branched oligosilanyl anions such as $(H_3Si)_3Si^-$ are also described.[12] A recent patent claims the synthesis of mixtures of $ClSi_6H_{11}$ and $Cl_2Si_6H_{10}$ by the reaction of Si_6H_{12} with chlorinating agents like AgCl, $HgCl_2$, or $SnCl_4$.[7a] In our laboratories, it was demonstrated some years ago that functionalized linear or branched hydrosilane skeletons,

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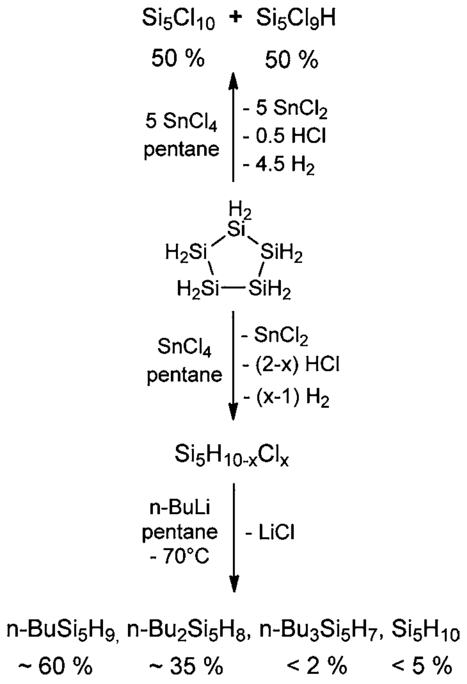
$Si_nH_{m-x}Cl_x$, with $n > 3$, can be assembled stepwise from properly substituted mono- and disilanes employing multistep synthetic procedures.[13] Now we present novel approaches to the preparation of previously unknown partially chlorinated perhydropentasilanes containing the cyclo- or neopentasilane skeleton.

■ RESULTS AND DISCUSSION

Chlorination of Si_5H_{10} with $SnCl_4$. Because of the outstanding reactivity of Si−halogen bonds in nucleophilic substitution reactions, chlorosilanes are widely used as intermediates in the synthesis of functionalized polysilane backbones. The selective introduction of halo substituents into molecules like Si_5H_{10} and $(H_3Si)_4Si$, therefore, might create reactive sites suitable for further derivatization. Ebsworth et al. observed that $SnCl_4$ is an excellent reagent for chlorination of di- and trisilanes.[10j] When roughly equimolar proportions of $SnCl_4$ and Si_2H_6 or Si_3H_8, respectively, were condensed together and allowed to warm to room temperature, a mixture of mono- and dichlorinated compounds was formed along with $SnCl_2$ and HCl. Products resulting from disubstitution at a single Si atom or Si−Si bond scission have not been detected. In close analogy to these findings, we observed that a pentane solution of Si_5H_{10} reacts with an equimolar amount of $SnCl_4$, according to Scheme 1.

Scheme 1. Chlorination of Cyclopentasilane Si_5H_{10} with $SnCl_4$



After 12 h at room temperature, $SnCl_4$ had been completely consumed and the solid $SnCl_2$ was easily removed by filtration. The ^1H NMR spectrum of the resulting solution was consistent with the formation of a mixture of mono- and polychlorinated cyclopentasilanes $Si_5H_{10-x}Cl_x$. At least four broad and poorly resolved signals appeared in the typical range for −SiClH− protons between 5.0 and 5.3 ppm,[13c] while the SiH_2 region showed a superposition of several broad bands between 3.1 and 3.4 ppm, together with the sharp Si_5H_{10} signal near 3.3 ppm. Removal of the solvent at reduced pressure afforded a liquid residue, which is highly pyrophoric upon exposure to air. In order to enable quantitative analysis, the crude mixture of partially chlorinated cyclopentasilanes was reacted with *n*-BuLi at −70 °C to give the corresponding *n*-butyl derivatives (Scheme 1) with higher thermal and hydrolytic stability. According to gas chromatography (GC)/mass spectrometry (MS) analysis performed after aqueous workup and removal of the solvents at 25 °C and 0.05 mbar, $n\text{-BuSi}_5H_9$ (∼60%) had been formed as the major product along with $n\text{-Bu}_2Si_5H_8$ (∼35%) and minor amounts of $n\text{-Bu}_3Si_5H_7$ (<2%) and residual Si_5H_{10} (<5%). However, pure $ClSi_5H_9$ (**1**) could not be isolated by distillation or recondensation because of insufficiently different boiling points of the single components present in the crude product mixture.

The treatment of Si_5H_{10} with 5 equiv of $SnCl_4$ produces Si_5Cl_{10} and HSi_5Cl_9 in an approximate molar ratio of 1:1 instead of the expected product $Si_5H_5Cl_5$ (Scheme 1). The high chlorine content in the final products is easily understood, taking into account the ability of HCl to chlorinate Si−H bonds especially in the presence of Lewis acids.[10c,d]

$$Si_5H_{10} \xrightarrow[-SnCl_2 \atop -HCl]{SnCl_4} Si_5H_{10-x}Cl_x \qquad (1)$$

$$Si_5H_{10} \xrightarrow[-H_2]{HCl} Si_5H_{10-x}Cl_x \qquad (2)$$

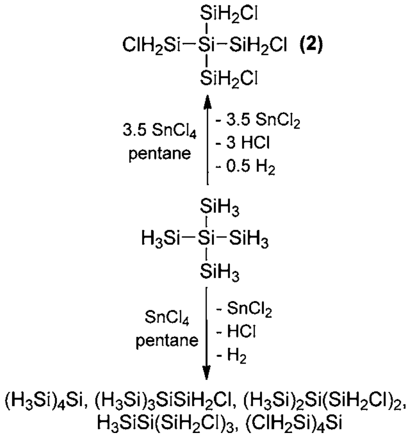
HCl, which is formed as a primary product from Si_5H_{10} and $SnCl_4$ (eq 1), acts as an additional chlorinating agent under the influence of the Lewis acid $SnCl_4$ (eq 2), giving rise to the formation of further Si−Cl bonds. The coupled ^{29}Si NMR spectrum of the reaction mixture obtained after stirring Si_5H_{10} with a 5-fold excess of $SnCl_4$ for 160 h showed a singlet at −2.7 ppm, which is easily assigned to Si_5Cl_{10}.[14] Additional lines at −27.9 ppm (doublet, $^1J_{Si-H} = 248.5$ Hz), 1.1 ppm (doublet, $^2J_{Si-H} = 8.2$ Hz), and −3.0 ppm (doublet, $^3J_{Si-H} = 7.3$ Hz) match data previously reported for Si_5Cl_9H.[15] Shorter reaction times or reduced amounts of $SnCl_4$ lead to the formation of complicated mixtures of chlorohydrocylopentasilanes without any noticeable selectivity; longer reaction times and a larger excess of $SnCl_4$ increase the relative amount of Si_5Cl_{10}.

Chlorination of $(H_3Si)_4Si$ with $SnCl_4$. The treatment of $(H_3Si)_4Si$ with 1 equiv of $SnCl_4$ did not result in the exclusive formation of $(H_3Si)_3SiSiH_2Cl$. Just as observed in the analogous reaction of Si_5H_{10}, mono- and polychlorinated products were formed along with unreacted starting material. The ^1H NMR spectrum of the reaction mixture obtained after stirring equimolar amounts of $(H_3Si)_4Si$ and $SnCl_4$ at room temperature for 120 h showed four different SiH_3 and four different SiH_2Cl proton environments between 3.9 and 4.1 ppm and 5.4 and 5.7 ppm, respectively, which is in accordance with the formation of $(H_3Si)_3SiSiH_2Cl$, $(H_3Si)_2Si(SiH_2Cl)_2$, $H_3SiSi(SiH_2Cl)_3$, and $(ClH_2Si)_4Si$ (**2**).

When we reacted $(H_3Si)_4Si$ with 3.5 equiv of $SnCl_4$, exactly one H atom per SiH_3 group was exchanged with chlorine and tetrakis(chlorosilyl)silane (**2**) was formed (Scheme 2). Because of the chlorinating ability of the byproduct HCl already mentioned above, less than the stoichiometric amount of $SnCl_4$ was necessary to achieve complete conversion. Significantly increased reaction times gave rise to formation of a higher chlorinated byproduct such as $Cl_2HSiSi(SiH_2Cl)_3$.

In the ^{29}Si NMR spectrum of a mixture obtained after stirring $(H_3Si)_4Si$ and $SnCl_4$ in a molar ratio of 1:3.5 in pentane for 72

Scheme 2. Chlorination of Neopentasilane $(H_3Si)_4Si$ with $SnCl_4$



h at room temperature and removal of solid $SnCl_2$, only two signals at −24.6 and −124.9 ppm appeared, while the signals of $(H_3Si)_4Si$ at −89.6 and −165.9 ppm[16] disappeared. The observed ^{29}Si and ^{1}H chemical shift values, splitting patterns, and Si−H coupling constants are completely in line with the exclusive formation of **2**, as depicted in Scheme 2. In the coupled ^{29}Si NMR spectrum, the resonance line at −24.6 ppm exhibited triplet splitting with $^{1}J_{Si-H} = 236.9$ Hz, while the signal at −124.9 ppm was split into nine lines with a coupling constant of $^{2}J_{Si-H} = 12.6$ Hz. ^{1}H NMR data were also consistent with the formation of one distinct product. Besides the signals of the solvent, only one line at 4.85 ppm appeared, which is shifted to lower field by 1.4 ppm compared to $(H_3Si)_4Si$.[12a] Chlorohydrooligosilanes described in the literature exhibit ^{29}Si NMR signals for ClH_2Si groups between −24 and −32 ppm with unusually large coupling constants $^{1}J_{Si-H} > 225$ Hz.[13b,17] Downfield-shifted β-Si resonances in hydrosilanes upon chlorination are also evident. For **2**, the signal of the central Si atom is shifted tremendously by 41 ppm to lower field relative to unsubstituted $(H_3Si)_4Si$.

Pure **2** could be isolated by crystallization from the crude reaction mixture at −70 °C as a moisture-sensitive but nonpyrophoric liquid in ∼50% yield. Crystals of **2** suitable for single-crystal X-ray crystallography could be grown at −70 °C using an optical heating and crystallization device (OHCD) laser system. A graphical representation of the molecular structure is given in Figure 1, along with key bond lengths and angles.

Compound **2** crystallizes in the tetragonal space group $I\bar{4}$. The Si−Si distance of 2.346 Å is slightly longer than the Si−Si bond length of 2.332 Å observed for $(H_3Si)_4Si$ in the gas phase.[12f] The Si−Cl bond length of 2.074 Å is close to the Si−Cl distance in H_3SiCl (2.06 Å),[18] which is markedly shorter than the Si−Cl bond length of 2.16 Å estimated from the sum of the covalent radii of silicon and chlorine. The tetrahedral geometry around Si1 is slightly distorted with Si−Si−Si bond angles of 111.4° and 105.7°. It is interesting to compare the structure of **2** with the structure of its carbon analogue $(ClH_2C)_4C$. Gaseous $(ClH_2C)_4C$ has been studied by electron diffraction[19] and showed small, but significant, deviations of the C atom framework from a tetrahedral arrangement, just as observed for the silicon skeleton of **2** in the crystal. However, two conformers with D_{2d} and S_4 symmetry, respectively, were detected in equal amounts for $(ClH_2C)_4C$ in the gas phase, whereas only the S_4 conformer of **2** is observed in the solid state. If the molecule is viewed along the 4-fold rotoinversion axis of symmetry passing through Si1, all Cl atoms are oriented in the same direction relative to Si2.

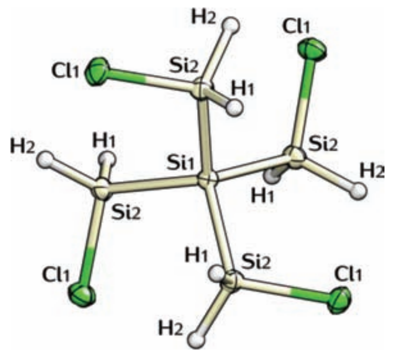
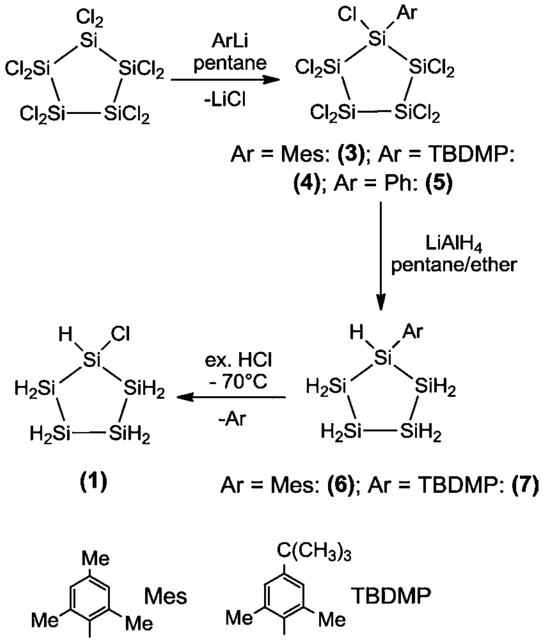


Figure 1. Molecular structure of **2** in the crystal (50% thermal probability ellipsoids). Selected bond lengths (Å) and angles (deg) with estimated standard deviations: Si1−Si2 2.346(1), Si2−Cl1 2.074(1); Si2−Si1−Si2 111.4(1), 111.4(1), 111.4(1), 105.7(1), 105.7(1), Cl1−Si2−Si1 108.8(1).

Selective Monofunctionalization of Si_5H_{10}. Because pure **1** was not accessible by direct halogenation of Si_5H_{10} with $SnCl_4$, we developed an alternative preparative approach using protective groups (Scheme 3). In the first step, one aromatic side group was attached to the cyclopentasilane ring by reacting Si_5Cl_{10} with appropriate aryllithium compounds in order to protect one of the Si−Cl bonds during the subsequent hydrogenation step. Substituted aromatics like mesityl (Mes = 2,4,6-trimethylphenyl) or 4-*tert*-butyl-2,6-dimethylphenyl (TBDMP) were better suited for this purpose than unsubstituted phenyl rings because they greatly facilitate crystallization of the resulting arylnonachlorocyclopentasilanes. Thus, pure $MesSi_5Cl_9$ (**3**) and $(TBDMP)Si_5Cl_9$ (**4**) crystallized at −30 °C in >85% yield from the crude product mixtures,

Scheme 3. Selective Monofunctionalization of Cyclopentasilane Si_5H_{10}



obtained after Si_5Cl_{10} had been reacted with 1 equiv of MesLi or TBDMPLi. $PhSi_5Cl_9$ (**5**) synthesized under similar conditions from Si_5Cl_{10} and PhLi, however, was reluctant to crystallize and, therefore, could not be isolated in a pure state. In all cases, it was necessary to perform the reaction strictly under ether-free conditions. Traces of ethers readily react with Si_5Cl_{10} to give undesired byproducts.

The treatment of **3** and **4** with $LiAlH_4$ in diethyl ether afforded the corresponding hydrocyclopentasilanes $MesSi_5H_9$ (**6**) and $(TBDMP)Si_5H_9$ (**7**). Analytically pure samples of **6** and **7** were obtained after removal of all volatile components at 0.05 mbar and 25 °C. GC/MS analysis of the resulting colorless and moderately air-sensitive oils exhibits just one signal with M^+ ions at *m*/*e* 268 and 310, respectively, and other ions consistent with the proposed structures.

Finally, the aryl protective groups of **6** or **7** were easily removed with HCl. According to ^1H and ^{29}Si NMR analysis, the colorless highly air-sensitive liquid obtained after stirring a pentane solution of **6** with an excess of anhydrous liquid HCl at −95 °C and removal of pentane and residual HCl at reduced pressure contained **1**, mesitylene, and up to 30% Si_5H_{10} formed as a byproduct. Once again, it was not possible to isolate pure **1** by fractional condensation because of insufficiently different boiling points of the single components present in the crude product mixture.

Compounds **3**−**7** were characterized by usual spectroscopic techniques and by elemental analysis, the corresponding data can be found in the Experimental Section. The fully coupled ^{29}Si NMR spectra of the monofunctionalized cyclopentasilanes **1**, **6**, and **7** show characteristic splitting patterns due to extensive $^{29}Si-^{1}H$ coupling, which greatly facilitates structural assignment. All chemical shifts and coupling constants were consistent with the proposed structures. Furthermore, excellent agreement with literature data of open-chained hydrosilanes containing aryl or chloro substituents was observed.[11a,13a,17a,20] The −arylSiH− and −ClSiH− resonances exhibit doublet splitting and characteristic low-field shifts relative to the triplets arising from the endocyclic $-SiH_2-$ groups. The exceptionally large value of $^1J(^{29}Si-^{1}H) = 231.3$ Hz observed for the −SiHCl group in **1** is typical for silicon hydrides bearing electronegative substituents.[21] Additionally, all signals exhibit significant line broadening due to extensive long-range coupling. The complex endocyclic spin systems, however, prevent resolution of the individual resonance lines, which is frequently observed in open-chained silicon hydrides.[16]

The molecular structures of **3** and **4** as determined by single-crystal X-ray crystallography are depicted in Figures 2 and 3 together with selected bond lengths and angles.

The average Si−Si bond distances of ∼2.36 Å within the Si5 rings of **3** and **4** are close to the values reported for Si_5Br_{10} (2.35 Å), Si_5I_{10} (2.36 Å),[22] and Si_6Cl_{12} (2.34 Å).[23] The Si−Cl bond lengths within the $SiCl_2$ units are ∼2.05 Å, while the Si1−Cl1 bond is significantly elongated to 2.12 Å in **3** and to ∼2.08 Å in **4**. The cyclopentasilane rings adopt conformations close to the envelope form with dihedral angles ∠Si2−Si3−Si4−Si5 of 5.4° for **3** and 9.2° for **4**. Intermediate conformations closer to the envelope than the twist form have been observed earlier for the cyclopentasilanes Si_5Br_{10} and Si_5I_{10}. The conformations of five-membered rings are frequently described in terms of a puckering amplitude *q* (eq 3):

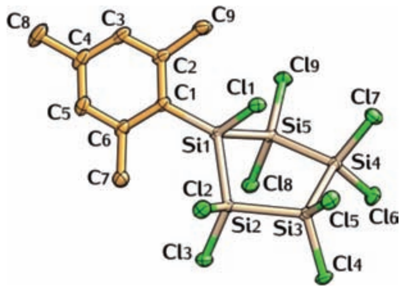


Figure 2. Molecular structure of **3** in the crystal (50% thermal probability ellipsoids). Selected bond lengths (Å), angles (deg), and torsion angles (deg) with estimated standard deviations: Si1−Si2 2.365(1), Si1−Si5 2.353(1), Si2−Si3 2.367(1), Si3−Si4 2.360(1), Si4−Si5 2.352(1), Si1−C1 1.867(2), Si1−Cl1 2.123(1), Si*n*−Cl (mean) 2.050; Si5−Si1−Si2 98.7(1), Si1−Si2−Si3 103.2(1), Si4−Si3−Si2 106.4(1), Si5−Si4−Si3 103.4(1), Si4−Si5−Si1 103.8(1); Si1−Si2−Si3−Si4 24.7(1), Si2−Si3−Si4−Si5 5.4(1), Si3−Si4−Si5−Si6 33.8(1), Si4−Si5−Si1−Si2 48.7(1), Si5−Si1−Si2−Si3 44.3(1).

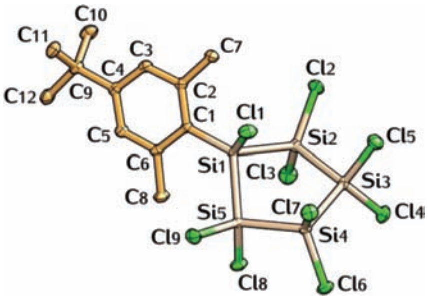


Figure 3. Molecular structure of **4** in the crystal (50% thermal probability ellipsoids). Selected bond lengths (Å), angles (deg), and torsion angles (deg) with estimated standard deviations: Si1−Si2 2.339(1), Si1−Si5 2.359(1), Si2−Si3 2.361(1), Si3−Si4 2.367(1), Si4−Si5 2.359(1), Si1−C1 1.862(2), Si1−Cl1 2.085(1), Si2−5−Cl (mean) 2.043; Si5−Si1−Si2 99.2(1), Si1−Si2−Si3 105.2(1), Si4−Si3−Si2 106.2(1), Si5−Si4−Si3 103.1(1), Si4−Si5−Si1 104.1(1); Si1−Si2−Si3−Si4 20.1(1), Si2−Si3−Si4−Si5 9.2(1), Si3−Si4−Si5−Si1 35.1(1), Si4−Si5−Si1−Si2 47.0(1), Si5−Si1−Si2−Si3 40.7(1).

$$q = \sqrt{\sum_{i=1}^{5} z_i^{\,2}}$$

$$z_i = \text{perpendicular out-of-plane deviations of atom } i \text{ from a least-squres plane through the ring} \qquad (3)$$

Values for *q* for **3** and **4** are summarized in Table 1, together with literature data for Si_5Br_{10} and Si_5I_{10}. Because of the presence of the sterically demanding aromatic side groups, **3** and **4** are significantly more puckered than Si_5Br_{10} and Si_5I_{10}.

Table 1. Summary of Five-Membered-Ring Parameters for Halocyclopentasilanes

		3	4	Si_5Br_{10}[22]	Si_5I_{10}[22]
z_i[a]	Si1	0.478	0.446	0.065	0.064
	Si2	−0.339	−0.294	−0.249	−0.249
	Si3	0.183	0.049	0.346	0.348
	Si4	0.093	0.212	−0.300	−0.300
	Si5	−0.415	−0.413	0.138	0.137
q[a]		0.747	0.709	0.543	0.544

[a] For definitions of z_i and *q*, see eq 3.

■ CONCLUSION

In conclusion, we have successfully demonstrated that the perhydropentasilanes $(H_3Si)_4Si$ and Si_5H_{10} can be chlorofunctionalized without destruction of the Si−Si backbone. The selectivity of higher silicon hydrides in the chlorination reaction with $SnCl_4$ has been shown to be strongly dependent on the molecular structure of the hydrosilane substrate and on the stoichiometric ratio of the reactants. Thus, tetrachloroneopentasilane **2** could be prepared in high yield from $(H_3Si)_4Si$ and 3.5 equiv of $SnCl_4$, while Si_5H_{10} and an equimolar amount of $SnCl_4$ afforded mixtures of **1** with polychlorinated cyclopentasilanes and unreacted starting material, which could not be separated by distillation. In order to selectively monofunctionalize Si_5H_{10}, a multistep synthetic procedure using bulky Mes or TBDMP protective groups had to be applied. Additional studies concerning chemical transformations involving **1** and **2** are currently in progress.

■ EXPERIMENTAL SECTION

All experiments were performed under a nitrogen atmosphere using standard Schlenk techniques. Solvents were dried using a column solvent purification system.[24] $SnCl_4$ (99%) and *n*-BuLi (1.6 M in hexane) were used as purchased. Solid $LiAlH_4$ was dissolved in diethyl ether and filtered prior to use, and anhydrous HCl (99.8%) was passed through $AlCl_3$ to remove traces of moisture. Si_5H_{10},[9a] Si_5Cl_{10},[25] $Si(SiH_3)_4$,[4a] ether-free PhLi,[26] MesLi,[27] and TBDMPLi[28] were synthesized as previously reported. ^1H (299.95 MHz) and ^{29}Si (59.59 MHz) NMR spectra were recorded on a Varian INOVA 300 spectrometer in a C_6D_6 solution and referenced versus tetramethylsilane (TMS) using the internal ^2H-lock signal of the solvent. MS spectra were run either on a HP 5971/A/5890-II GC/MS coupling [HP 1 capillary column, length 25 m, diameter 0.2 mm, 0.33 μm poly(dimethylsiloxane)] or on a Kratos Profile mass spectrometer equipped with a solid probe inlet. Melting points were determined using a Buechi 535 apparatus and are uncorrected. Elemental analyses were carried out on a Hanau Vario Elementar EL apparatus.

Table 2. Crystallographic Data and Structure Refinement for 2−4

	2	**3**	**4**
empirical formula	$Cl_4H_8Si_5$	$C_9H_{11}Cl_9Si_5$	$C_{12}H_{17}Cl_9Si_5$
fw	290.31	578.68	620.76
cryst syst, space group	tetragonal, $I\bar{4}$	monoclinic, $P2(1)/c$	triclinic, $P\bar{1}$
unit cell dimens	$a = 9.182(3)$ Å	$a = 11.8326(8)$ Å	$a = 9.2711(3)$ Å
	$b = 9.182(3)$ Å	$b = 22.1445(2)$ Å	$b = 11.4701(4)$ Å
	$c = 7.035(2)$ Å	$c = 8.6689(6)$ Å	$c = 13.3919(5)$ Å
	$\alpha = 90°$	$\alpha = 90°$	$\alpha = 66.415(1)°$
	$\beta = 90°$	$\beta = 92.067(2)°$	$\beta = 84.353(1)°$
	$\gamma = 90°$	$\gamma = 90°$	$\gamma = 84.666(1)°$
volume [$Å^3$]	593.1(3)	2270.0(3)	1296.56(8)
Z, calcd density [$g \cdot cm^{-3}$]	2, 1.626	4, 1.693	2, 1.590
abs coeff [mm^{-1}]	1.439	1.368	1.203
F(000)	292	1152	624
cryst size [mm]	1.34 × 0.25 × 0.25	0.60 × 0.41 × 0.32	0.64 × 0.59 × 0.56
θ range [deg]	3.14−29.69	2.52−28.00	2.677−33.338
limiting indices	$-12 \leq h \leq 11$, $-12 \leq k \leq 12$, $-9 \leq l \leq 8$	$-15 \leq h \leq 15$, $-26 \leq k \leq 29$, $-11 \leq l \leq 11$	$-12 \leq h \leq 12$, $-14 \leq k \leq 15$, $-18 \leq l \leq 18$
reflns collected/unique	793/773 [*R*(int) = 0.0218]	5473/4950 [*R*(int) = 0.0661]	6869/6411 [*R*(int) = 0.0273]
completeness to θ [%]	99.7	99.9	99.5
max and min transmn	0.698−0.656	0.645−0.515	0.5522−0.5131
data/restraints/param	793/0/29	5473/0/210	6869/0/240
GOF on F^2	1.112	1.051	1.124
final *R* indices [$I > 2\sigma(I)$]	R1 = 0.0182, wR2 = 0.0407	R1 = 0.0282, wR2 = 0.0799	R1 = 0.0224, wR2 = 0.0568
R indices (all data)	R1 = 0.0192, wR2 = 0.0411	R1 = 0.0319, wR2 = 0.0815	R1 = 0.0249, wR2 = 0.0584
largest diff peak and hole [$e \cdot A^{-3}$]	0.287 and −0.222	0.672 and −0.483	0.641 and −0.279

Reaction of Si_5H_{10} with $SnCl_4$ (1:1). A total of 2.84 g (10.9 mmol) of $SnCl_4$ dissolved in 40 mL of pentane was slowly added to a solution of 1.64 g (10.9 mmol) of Si_5H_{10} in 40 mL of pentane at −30 °C. After stirring at room temperature overnight and removal of the white precipitate, the resulting solution was cooled to −70 °C and 6.8 mL of a 1.6 M solution of *n*-BuLi (10.9 mmol) in hexane was added. After stirring for an additional 1 h at room temperature, the resulting mixture was cooled to −30 °C and hydrolyzed with 20 mL of deoxygenated 10% H_2SO_4. Drying over Na_2SO_4 and removal of the solvents in vacuo afforded 1.3 g of a clear and colorless liquid containing *n*-$BuSi_5H_9$ and *n*-$Bu_2Si_5H_8$ in a approximate molar ratio of 2:1 along with minor amounts of *n*-$Bu_3Si_5H_7$ and residual Si_5H_{10} according to GC/MS analysis.

n-$BuSi_5H_9$. MS [*m*/*e* (relative intensity)]: 206 (71%, M^+).

n-$Bu_2Si_5H_8$. MS [*m*/*e* (relative intensity)]: 262 (80%, M^+).

n-$Bu_3Si_5H_7$. MS [*m*/*e* (relative intensity)]: 318 (88%, M^+).

Reaction of Si_5H_{10} with $SnCl_4$ (1:5). A total of 7.35 g (28.2 mmol) of $SnCl_4$ dissolved in 50 mL of pentane was slowly added to a solution of 0.84 g (5.6 mmol) of Si_5H_{10} in 50 mL of pentane at −30 °C. After stirring at room temperature for 160 h, the resulting mixture was filtered and concentrated in vacuo. The coupled ^{29}Si NMR spectrum of the resulting sticky residue was consistent with the formation of an approximately 1:1 mixture of Si_5Cl_{10} and Si_5Cl_9H.

^{29}Si NMR (C_6D_6, TMS, ppm): −2.7 (s, Si_5Cl_{10}, *Si*Cl_2),[14] 1.1 (d, $^3J_{Si-H}$ = 8.2 Hz, Si_5Cl_9H, *Si*Cl_2), −3.0 (d, $^2J_{Si-H}$ = 7.3 Hz, Si_5Cl_9H, *Si*Cl_2), −27.9 (d, $^1J_{Si-H}$ = 248.5 Hz, Si_5Cl_9H, *Si*ClH).[15]

Reaction of $Si(SiH_3)_4$ with $SnCl_4$ (1:1). A total of 3.40 g (13.2 mmol) of $SnCl_4$ was added via a syringe to a solution of 2.00 g (13.2 mmol) of $Si(SiH_3)_4$ in 30 mL of pentane at 0 °C. After stirring at room temperature for 120 h, the resulting mixture was filtered and concentrated in vacuo. ^1H and ^{29}Si NMR data of the resulting liquid residue were consistent with the formation of $(H_3Si)_3SiSiH_2Cl$, $(H_3Si)_2Si(SiH_2Cl)_2$, $H_3SiSi(SiH_2Cl)_3$, and $(ClH_2Si)_4Si$ along with unreacted $Si(SiH_3)_4$.

^{29}Si NMR (INEPT dec, C_6D_6, TMS, ppm): 18.7, −21.0, −23.1, −25.1 (*Si*H_2Cl), −90.3, −93.5, −96.5, −99.3 (*Si*H_3). ^1H NMR (C_6D_6, TMS, ppm): 5.61, 5.56, 5.51, 5.47 (s, Si*H_2*Cl), 4.03, 3.99, 3.96, 3.94 (s, Si*H_3*).

Synthesis of Tetrachloroneopentasilane (2). A total of 7.50 g (28.8 mmol) of $SnCl_4$ was added via a syringe to a solution of 2.20 g (14.4 mmol) of $Si(SiH_3)_4$ in 30 mL of pentane at 0 °C. After stirring at room temperature for 12 h, another 5.60 g (21.6 mmol) of $SnCl_4$ was added, and the resulting mixture was stirred for 48 h. Subsequent filtration and concentration in vacuo afforded a colorless liquid residue containing residual pentane, **2**, and minor amounts of byproduct according to ^1H and ^{29}Si NMR spectroscopy. Crystallization of the crude material from pentane at −70 °C gave 2.0 g (48%) of pure **2**.

Bp: 36−38 °C (0.01 mbar). Anal. Found: H, 2.70. Calcd for $Cl_4H_8Si_5$: H, 2.78. ^{29}Si NMR (C_6D_6, TMS, ppm): −24.6 (t, $^1J_{Si-H}$ = 236.9 Hz, *Si*H_2Cl), −124.9 (m, $^2J_{Si-H}$ = 12.6 Hz, *Si*Si_4). ^1H NMR (C_6D_6, TMS, ppm, rel intens): 4.85 (s, Si*H_2*Cl). HRMS. Calcd for $[Cl_4H_6Si_5]^{\bullet *}$ ($M^+ - 2H$): *m*/*e* 285.8070. Found: *m*/*e* 285.8092.

Synthesis of Nonachloromesitylcyclopentasilane (3). A total of 5.60 g (44.2 mmol) of ether-free mesityllithium was added to a solution of 21.90 g (44.2 mmol) of Si_5Cl_{10}, and the resulting mixture was stirred for 6 days at room temperature. After filtration of the salts and concentration of the solution, 12.50 g (48%) of pure **3** could be isolated after crystallization at −30 °C.

Mp: 55−58 °C. Anal. Found: C, 18.16; H, 1.81. Calcd for $C_9H_{11}Cl_9Si_5$: C, 18.68; H, 1.92. ^{29}Si NMR (C_6D_6, TMS, ppm): 3.3 (s, *Si*Cl$_2$), 2.0 (s, *Si*Cl$_2$), −17.9 (s, Mes*Si*Cl). ^{1}H NMR (C$_6$D$_6$, TMS, ppm, rel intens): 6.53 (s, 2 H, C*H* aromatic), 2.48 (s, 6 H, *o*-C*H*$_3$), 1.95 (s, 3 H, *p*-C*H*$_3$). MS [*m*/*e* (relative intensity)]: decomposes prior to evaporation.

Synthesis of (4-*tert*-Butyl-2,6-dimethylphenyl)-nonachlorocyclopentasilane (4). **4** was synthesized according to the procedure followed for compound **3** with 4.22 g (25.1 mmol) of ether-free 4-*tert*-butyl-2,6-dimethylphenyllithium and 12.40 g of Si$_5$Cl$_{10}$ (25.1 mmol). Yield: 17.70 g (49%).

Mp: 124−28 °C. Anal. Found: C, 23.68; H, 2.73. Calcd for C$_{12}$H$_{17}$Cl$_9$Si$_5$: C, 23.22; H, 2.76. ^{29}Si NMR (C$_6$D$_6$, TMS, ppm): 3.2 (s, *Si*Cl$_2$), 2.0 (s, *Si*Cl$_2$), −18.0 (s, aryl*Si*Cl). ^{1}H NMR (C$_6$D$_6$, TMS, ppm, rel intens): 6.85 (s, 2 H, C*H* aromatic), 2.49 (s, 6 H, *o*-C*H*$_3$), 1.14 (s, 9 H, C(CH$_3$)$_3$). MS [*m*/*e* (relative intensity)]: decomposes prior to evaporation.

Synthesis of Nonachlorophenylcyclopentasilane (5). Synthesized according to the procedure followed for compound **3** with 5.54 g of ether-free PhLi (66 mmol) and 24.24 g of Si$_5$Cl$_{10}$ (49 mmol). After removal of the solvent, 24.50 g of a slightly yellow oil was obtained containing **5** and unreacted Si$_5$Cl$_{10}$ from which pure **5** could not be separated.

^{29}Si NMR (dec, C$_6$D$_6$, TMS, ppm): −2.7 (Si$_5$Cl$_{10}$, *Si*Cl$_2$),[14] 2.0, −1.0 (Si$_5$Cl$_9$Ph, *Si*Cl$_2$), −18.1 (Si$_5$Cl$_9$Ph, *Si*ClPh).

Synthesis of Mesitylcyclopentasilane (6). A total of 27.6 mL of a 2.3 M solution of LiAlH$_4$ (64.0 mmol) in diethyl ether was slowly added to a solution of 12.40 g (21.4 mmol) of **3** in 200 mL of pentane at 0 °C. After the resulting mixture was stirred overnight at room temperature and aqueous workup with 100 mL of deoxygenated 10% H$_2$SO$_4$, drying over Na$_2$SO$_4$, and removal of the solvents and volatile components in vacuo (0.05 mbar, 25 °C), 5.30 g (91%) of spectroscopically pure **6** was obtained as a colorless and slightly viscous liquid that decomposed during distillation at 0.05 mbar and 70 °C.

Bp: 70 °C dec (0.05 mbar). Anal. Found: C, 40.58; H, 7.60. Calcd for C$_9$H$_{20}$Si$_5$: C, 40.23; H, 7.50. ^{29}Si NMR (C$_6$D$_6$, TMS, ppm): −82.1 (d, $^1J_{\text{Si−H}}$ = 185.6 Hz, Mes*Si*H), −102,2 (t, $^1J_{\text{Si−H}}$ = 194.0 Hz, *Si*H$_2$), −106.8 (t, $^1J_{\text{Si−H}}$ = 194.7 Hz, *Si*H$_2$). ^{1}H NMR (C$_6$D$_6$, TMS, ppm, rel intens): 6.67 (s, 2 H, C*H* aromatic), 4.65 (m, 1 H, MesSi*H*), 3.4−3.5 (m, 8 H, Si*H*$_2$), 2.33 (s, 6 H, *o*-C*H*$_3$), 2.08 (s, 3 H, *p*-C*H*$_3$). MS [*m*/*e* (relative intensity)]: 268 (40%, M$^+$).

Synthesis of (4-*tert*-Butyl-2,6-dimethylphenyl)-cyclopentasilane (7). **7** was synthesized according to the procedure followed for compound **6** with 3.30 g (5.3 mmol) of **3** and 8.0 mL of 2.0 M LiAlH$_4$ (15.9 mmol) in diethyl ether. Yield: 1.40 g (85%) of spectroscopically pure **7**, which decomposed during distillation.

Bp: 70 °C dec (0.05 mbar). Anal. Found: C, 46.16; H, 8.47. Calcd for C$_{12}$H$_{26}$Si$_5$: C, 46.38; H, 8.43. ^{29}Si NMR (C$_6$D$_6$, TMS, ppm): −69.3 (d, $^1J_{\text{Si−H}}$ = 185.0 Hz, aryl*Si*H), −98.8 (t, $^1J_{\text{Si−H}}$ = 195.0 Hz, *Si*H$_2$), −94.2 (t, $^1J_{\text{Si−H}}$ = 198.0 Hz, *Si*H$_2$). ^{1}H NMR (C$_6$D$_6$, TMS, ppm, rel intens): 6.99 (s, 2 H, C*H* aromatic), 4.62 (m, 1 H, arylSi*H*), 3.3−3.5 (m, 8 H, Si*H*$_2$), 2.34 (s, 6 H, arylC*H*$_3$), 1.19 (s, 9 H, C(CH$_3$)$_3$). MS [*m*/*e* (relative intensity)]: 310 (45%, M$^+$).

Synthesis of Chlorocyclopentasilane (1). A solution of 2.56 g (9.5 mmol) of **6** in 20 mL of pentane was slowly added to 30 mL of liquid anhydrous HCl at −95 °C. After stirring for 1 h at −95 °C, the mixture was allowed to come to room temperature in order to evaporate excess HCl. After removal of pentane and residual HCl at reduced pressure (25 °C, 100 mbar), a colorless liquid mixture of mesitylene, **1**, and up to 30% of Si$_5$H$_{10}$, which could not be separated because of the similar boiling points of **1** and the byproduct, was obtained.

*ClSi$_5$H$_9$ (**1**).* ^{29}Si NMR (C$_6$D$_6$, TMS, ppm): −12.7 (d, $^1J_{\text{Si−H}}$ = 231.3 Hz, Cl*Si*H), −100.9 (t, $^1J_{\text{Si−H}}$ = 205.1 Hz, *Si*H$_2$), −108.7 (t, $^1J_{\text{Si−H}}$ = 203.9 Hz, *Si*H$_2$). ^{1}H NMR (C$_6$D$_6$, TMS, ppm, rel intens): 5.22 (m, 1 H, ClSi*H*), 3.2−3.6 (m, 8 H, Si*H*$_2$).

X-ray Crystallography. Crystals suitable for X-ray structural analyses of compounds **3** and **4** were immersed in inert oil under a nitrogen atmosphere, selected, and mounted on the tip of a glass fiber. Diffraction data were collected at 100 K on a Bruker D8 Kappa diffractometer equipped with a SMART APEX II CCD detector with Mo Kα (λ = 0.71073 Å) radiation. Crystals of **2** were grown in situ on the same diffractometer by using the OHCD[29] setup equipped with a CO$_2$ laser (λ = 10640 nm) in combination with an Oxford cryostream cooling system set to a temperature of 150 K.

Data were integrated with *SAINT*,[30] and empirical methods as implemented in *SADABS*[31] were used to correct for absorption effects. Structures were solved with direct methods using *SHELXS-97*. *SHELXL-97* was used for refinement against all data by full-matrix least-squares methods on F^2.[32] All non-H atoms were refined with anisotropic displacement parameters. H atoms of compounds **3** and **4** were refined isotropically on calculated positions using the riding model implemented in *SHELXL-97*. H atoms attached to Si in compound **2** were located at the Fourier difference map and refined without constraints. The X-ray diffraction crystallographic data are summarized in Table 2. The files CCDC 863713 (**2**), 863714 (**3**), and 863715 (**4**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, U.K.; fax +44 1223 336033; e-mail deposit@ccdc.cam.ac.uk).

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

X-ray crystallographic data of **2**−**4** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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