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Polysilane Reactions

Cationic Si–H–Si Bridges in Polysilanes: Their Detection and Targeted Formation in Stable Ion Studies

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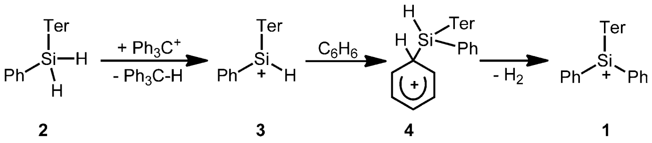
Abstract: The ionization of 1,1-dihydridocyclopentasilane **7** has been found to yield the cyclic polysilanylsilyl cation **8** instead of the expected hydrogen-substituted silylium ion **6**. The silyl cation **8** is stabilized by the formation of an intramolecular Si–H–Si bridge, which also provides the thermodynamic driving force for its formation. In general, the preference for the formation of Si–H–Si bridges can be used to scavenge and identify transient intermediates in the Lewis acid induced rearrangement of polysilanes. The validity of this concept has been demonstrated for one central step in this chemistry, the ring-contraction reaction of cyclohexasilanes to form silylcyclopentasilanes.

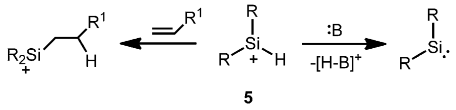
Introduction

Several well-characterized examples of silylium ions, tricoordinated silyl cations of the general formula R_3Si^+, are known.[1–8] Commonly, all of these cations are substituted with three bulky aryl groups to prevent bimolecular reactions with nucleophiles.[9] Even the replacement of only one of the aryl groups by a smaller alkyl or even a hydrogen substituent triggers a rich consecutive chemistry.[1,2] For example, in a previous investigation we noticed the surprising formation of the triaryl-substituted silyl cation **1** from the reaction of dihydridosilane **2** with the trityl cation.[10] Cation **1** is formed presumably by the reaction of the incipiently formed cation **3** with the solvent benzene and arenium ion **4** is a likely intermediate (Scheme 1).



Scheme 1. Reaction of dihydridosilane **2** with the trityl cation to give the silylium ion **1** according to ref. [10] (Ter = 2,6-bis(2,4,6-trimethylphenyl)phenyl).

This observation clearly reveals the principal difficulties in the synthesis of hydrogen-substituted silylium ions of type **5**.[11–13] Nevertheless, the secondary silylium ions **5** are an interesting class of compounds. On the one hand, being isoelectronic with hydridoboranes, they are perfect reagents for hydrosilylation reactions. On the other hand, in principle, secondary silylium ions can be regarded as protonated silylenes, which opens the field for a complementary chemistry based on proton-transfer reactions to sterically hindered Lewis bases (Scheme 2).



Scheme 2. Possible reactivity of secondary silylium ions **5** (:B = sterically hindered Lewis base).

Hence, the above-mentioned reactivity was our impetus for an investigation into the synthesis of secondary silylium ions of type **5**. As a viable target cation, we chose the oligosilanylsilyl cation **6**. The results of density functional calculations[14,15] predicted a substantial stabilization of the cation **6** through a combination of favorable α- and β-silyl effects. In detail, according to isodesmic reaction (1), the cyclic cation **6** is more stable than dimethylsilylium, $Me_2Si^+–H$, by $\Delta E = 141\ \mathrm{kJ\,mol^{-1}}$ (at the M06-2X/6-311+G(d,p) level of theory). Moreover, in the past, the 1,1,4,4-tetrakis(trimethylsilyl)tetrasilane-1,4-diyl unit proved to be a well-suited scaffold for the steric protection of reactive main group centers.[16–19]

Although the number of applications of silyl cations in synthesis and catalysis has increased in recent years,[1,2,20,21] experimental investigations of polysilanyl-substituted silyl cations,

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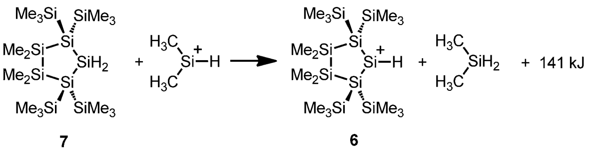
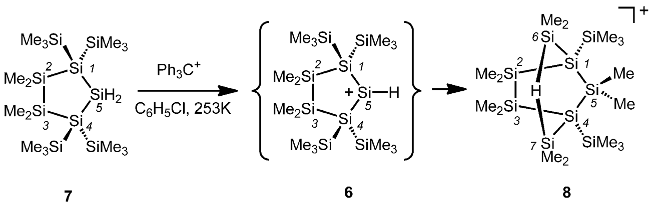


(1)

such as cation **6**, are rather scarce. This is even more surprising as these cations are believed to be important intermediates in skeletal rearrangement reactions of oligosilanes[22] and a deeper understanding of their nature and reactivity could pave the way to a controlled and directed modification of oligo- and polysilanes.[23–30] Exploratory investigations by Lambert and Zhang revealed the thermolability of even such small representatives as tris(trimethylsilyl)silylium, $(Me_3Si)_3Si^+$.[31–34] Subsequently, Sekiguchi and co-workers demonstrated the tendency of dialkyl-oligosilyl cations to undergo 1,2-methyl shifts[35] and our group reported recently on the involvement of polysilanylsilyl or germapolysilanylsilyl cations as intermediates in sila-Wagner–Meerwein rearrangements of polysilanes and germapolysilanes.[36,37] Common to all the studied polysilanyl compounds is their high reactivity, their thermolability, unusual for silyl cations, and their pronounced tendency to undergo skeletal rearrangement reactions. The only examples of polysilanyl cation salts that are stable at room temperature are the highly stabilized representatives of aromatic[38,39] and homoaromatic species[40,41].

Against this background, we describe herein our attempts to prepare the secondary silylium ion **6** and its unexpected rearrangement reaction to give the intramolecular hydrogen-bridged silyl cation **8** (Scheme 3). As the main driving force for the rearrangement reaction we identified the formation of the Si–H–Si linkage in cation **8**.[1,2,42,43] In addition, we will demonstrate that the targeted formation of this type of intramolecular Si–H–Si bridge can be used for the stabilization and verification of cationic intermediates in the skeletal rearrangements of oligosilanylsilyl cations.



Scheme 3. Reaction of dihydridosilane **7** to give the bis-silylated hydronium ion **8**.

Results and Discussion

The reaction of cyclo-oligosilane **7** with trityl tetrakis(pentafluorophenyl)borate, $[Ph_3C][B(C_6F_5)_4]$ (**9**), in benzene under ambient conditions resulted in the formation of a mixture of products, as indicated by numerous signals of variable intensity in the $^{29}Si\{^1H\}$ INEPT NMR spectrum. However, a set of five ^{29}Si NMR signals ($\delta^{29}Si = 95.5$, -4.6 -14.9, -31.2, and -126.3 ppm) dominated. To prevent side-reactions due to the reactivity demonstrated by other secondary silylium ions (Scheme 1), we changed the solvent to chlorobenzene. Chlorobenzene is known to coordinate to silylium ions through the chlorine atom, which excludes arenium-ion-like reactivity.[1] After changing the solvent to chlorobenzene and lowering the temperature ($T = -20\,^\circ C$), the same reaction gave a set of NMR spectra that indicated the selective formation of a single compound (see Figure 1). The polysilanylsilyl cation formed was identified by five ^{29}Si NMR signals with chemical shifts very close to those obtained in benzene ($\delta(^{29}Si) = 95.3$, -4.6, -15.2, -31.7, and -127.7 ppm). In the ^1H–^{29}Si HMQC spectrum, the most deshielded resonance at $\delta(^{29}Si) = 95.3$ ppm shows a cross-peak with a broad ^1H NMR signal at $\delta(^1H) = 1.10$ ppm (1 H; Figure 1). In the proton-coupled ^{29}Si INEPT NMR spectrum, this resonance appears as a doublet of multiplets with a coupling constant of $J(SiH) = 46$ Hz. The deshielded ^{29}Si NMR resonance and the size of the Si–H coupling constant (J) are characteristic of Si–H–Si linkages in silicon cations.[43] In addition, the high-field signal at $\delta(^{29}Si) = -127.7$ ppm indicates the presence of tetrasilyl-substituted silicon atoms.[44] These distinctive ^{29}Si NMR spectroscopic features clearly rule out the targeted formation of the hydrogen-substituted silyl cation **6**. The additional ^{29}Si NMR resonances at $\delta(^{29}Si) = -15.2$ and -31.7 ppm could be assigned to $SiMe_2$ groups by their characteristic NMR chemical shifts and by their correlation with ^1H NMR signals with a relative intensity of six hydrogen atoms. Additional NMR spectroscopic analysis of the silicon cation formed finally revealed the bicyclic structure **8** with the bridging Me_2Si–H–$SiMe_2$ unit as the most prominent structural feature.

Further support for the identification of cation **8** came from the close agreement between calculated ^{29}Si NMR chemical shifts (GIAO/M06 L/6-311G(2d,p)) for a molecular structure optimized by DFT calculations at the M06-2X/6-311+G(d,p) level of theory (see Figure 2) and the experimental data (see Table 1).[14,15,45] In particular, the calculated ^{29}Si NMR chemical shifts and $^1J(SiH)$ coupling constants of the characteristic symmetric $SiMe_2$–H–$SiMe_2$ unit ($\delta(^{29}Si)^{calcd} = 99.5$ ppm; $^1J(SiH)^{calcd} = 44$ Hz) agree convincingly with the experimental parameters obtained in chlorobenzene ($\delta(^{29}Si)^{exp} = 95.3$ ppm; $^1J(SiH)^{exp} = 46$ Hz). Even though solutions of polysilanylsilyl cation **8** with different weakly coordinating anions, such as $[B(C_6F_5)_4]^-$, $[B_{12}Cl_{12}]^{2-}$, or $[Al\{OC(CF_3)_4\}_4]^-$, in several arenes or halogenated arenes were prepared, no single crystals suitable for X-ray crystal analysis were obtained.

The isomerization reaction of silylium ion **6** to give the hydrogen-bridged cation **8** was further investigated by means of DFT calculations.[14,15] Although the secondary silylium ion **6** was found to be a minimum, the hydrogen-bridged cation **8** was predicted to be significantly more stable (by $\Delta E = = -67\ kJ\,mol^{-1}$, Figure 3). The formation of the Si–H–Si linkage is the main thermodynamic driving force for this reaction as its formation from its non-bridged isomer **10e** was calculated to be exothermic by $\Delta E = = -77\ kJ\,mol^{-1}$. In addition, we identified a possible reaction channel connecting both cations (Figure 3). Along this reaction path we located five intermediate silyl cations, **10a–e**, which are interconverted by 1,3-methyl shifts (Figure 3). These interconversions proceed via

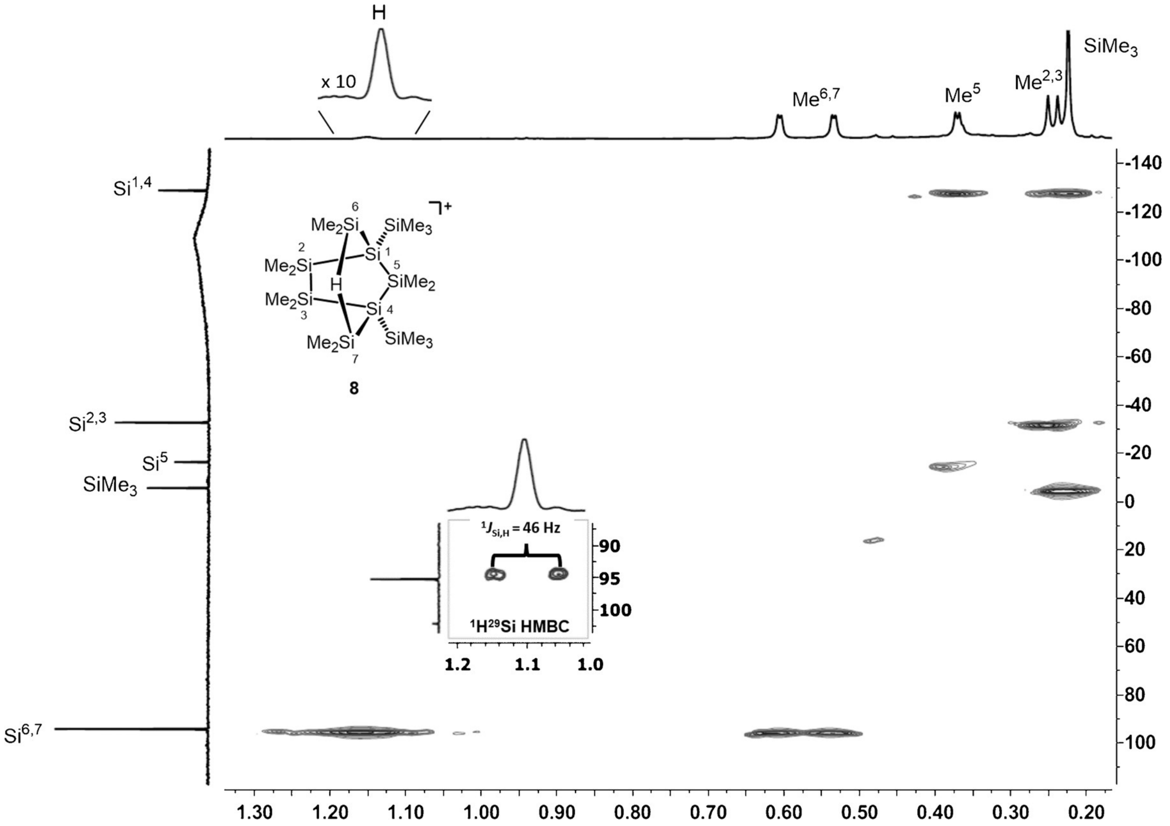


Figure 1. ^{1}H–^{29}Si HMQC NMR spectrum of cation **8** (499.87/99.31 MHz, 253 K, C_6H_5Cl).

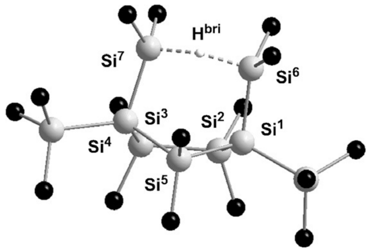
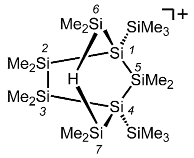


Figure 2. Calculated molecular structure of cation **8** (M06-2X/6-311+G(d,p)). Only the hydrogen atom bridging Si^6 and Si^7 is shown, all other hydrogen atoms have been omitted for clarity. Selected atom distances [pm] and bond angles [°]: Si^6–Si^7 = 317.8, Si^6–H = 163.6, Si^7–H = 163.9, Si^6–H–Si^7 = 151.8.

four-membered cyclic transition states. Transfer of the methyl group may occur in an antara- or suprafacial manner with regard the migrating methyl group. The antarafacial transition states are very high in energy, with energy barriers of $\Delta E = 98$–$113\ \mathrm{kJ\,mol^{-1}}$. In contrast, a possible reaction channel connecting the cations **6** and **8** in which the methyl groups shift in a suprafacial way reveals barriers of only $\Delta E = 25$–$33\ \mathrm{kJ\,mol^{-1}}$ (Figure 3, see the Supporting Information for the predicted structures of the transition states and intermediates). Such 1,3-methyl shifts are common in silyl cation chemistry. Seminal contributions by Eaborn et al. disclosed the occurrence of such 1,3-methyl shifts during the solvolysis of tris(trimethylsilyl)methylsilyl halides.[46]

Table 1. Experimental and calculated (italic) NMR parameters for polysilanyl cations **8** and **19**. Calculated data for the secondary silylium ion **6** and the hydrogen-bridged cation **18** are provided for comparison.



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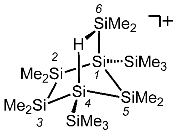

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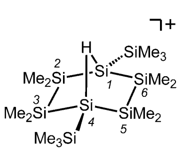


18

Compd	δ [ppm] (^1J(SiH) [Hz])								
	δ_{Si}(Si^1)	δ_{Si}(Si^2)	δ_{Si}(Si^3)	δ_{Si}(Si^4)	δ_{Si}(Si^5)	δ_{Si}(Si^6)	δ_{Si}(Si^7)	δ_{Si}(SiMe$_3$)	δ_H(H^{br})
8[a]	−127.7	−31.7	−31.7	−127.7	−15.2	95.3 (46)	95.3 (46)	−4.6	1.10 (46)
8[b]	−128.8	−32.9	−32.9	−128.8	−16.4	94.1 (45)	94.1 (45)	−5.9	
8[c]	−126.2	−31.2	−31.2	−126.2	−14.9	95.5 (46)	95.5 (46)	−4.6	1.01 (46)
8[d]	*−135.1*	*−25.9*	*−25.9*	*−135.1*	*−5.7*	*99.5* *(44)*[e]	*99.5* *(44)*	*−2.0*	*1.81*
6[e]	*−43.3*	*−24.9*	*−24.9*	*−43.3*	*594.5*			*2.8*	
19[f]	−107.5	−35.3	−33.0	64.1 (43)	−33.4	78.1 (39)		−0.7 −4.2	−1.07 (40)
19[d]	*−120.8*	*−32.4*	*−34.3*	*61.2* *(37)*[e]	*−34.7*	*66.7* *(39)*[e]		*0.7* *−2.3*	*−0.14*
18[d]	*52.2*	*−19.8*	*−32.9*	*52.2*	*−19.8*	*−32.9*		*1.0*	*−1.75*

[a] At 253 K in C_6D_5Cl. [b] At 258 K in o-$C_6H_4Cl_2$ with [D$_6$]acetone capillary. [c] At 303 K in C_6D_6. [d] Calculated at M06L/6-311G(2d,p)//M06-2X/6-311+G(d,p). [e] Calculated at the B3LYP/IGLOIII//M06-2X/6-311+G(d,p) level. [f] At 233 K in C_6D_5Cl.

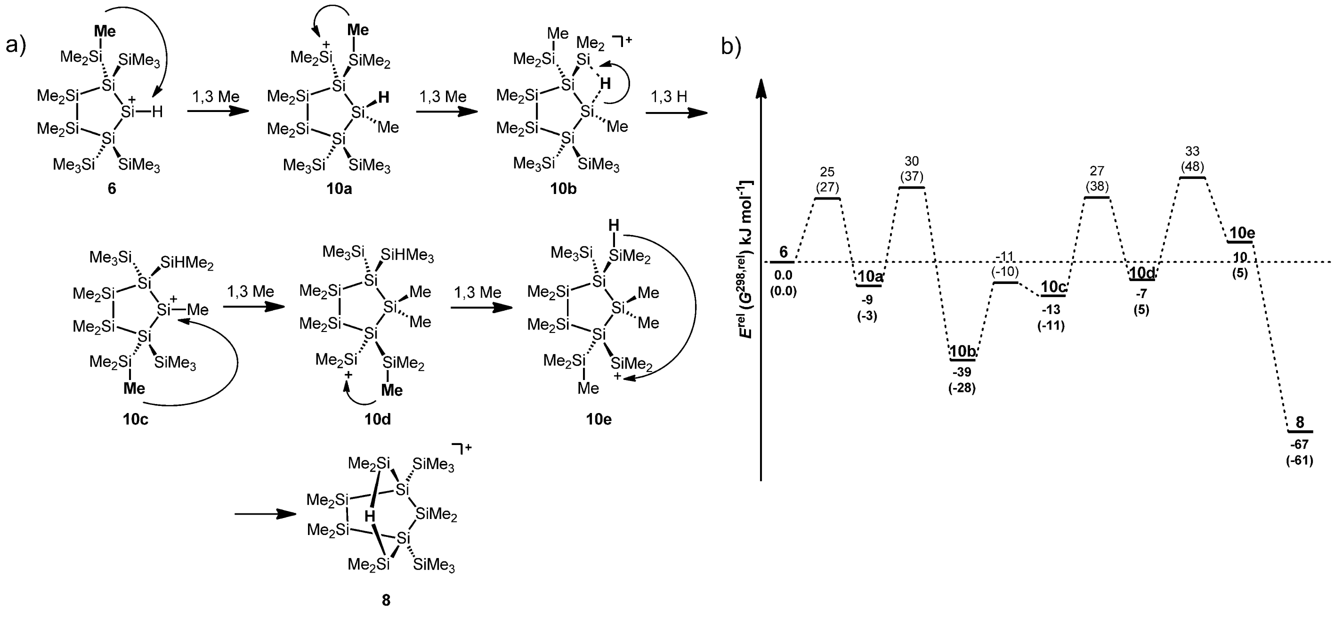
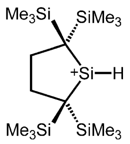


Figure 3. a) Suggested reaction path for the isomerization reaction of the secondary silylium ion **6** to give the bicyclic bis-silylhydronium ion **8**. b) Calculated reaction coordinate for this reaction (energies E^{rel} and free enthalpies $G^{298\ \text{rel}}$ (in kJ mol^{-1}) at 298 K and 0.1013 MPa are computed relative to compound **6** at the M06-2X/6-311+G(d,p) level of theory).



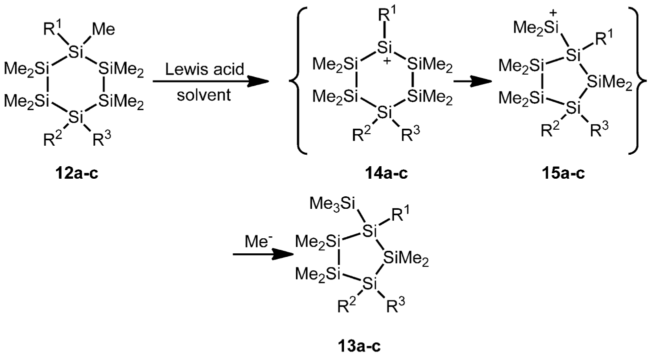
11

Related 1,3-methyl migrations are important steps in skeletal rearrangement processes of polysilanyl cations and in inter- and intramolecular substituent exchange reactions in silylium ions.[7,8,36,37] Recently, we disclosed a similar rearrangement of the closely related silyl cation **11**.[42]

In general, the potential energy surface along the reaction coordinate is predicted by the calculations to be rather shallow with only small activation barriers for the subsequent methyl shifts (Figure 3). The rate-determining step is the exothermic formation of cation **8**. This step involves an overall energy barrier of $\Delta E = 33$ kJ mol^{-1}, which is in qualitative agreement with the fast formation of cation **8** at temperatures as low as $T = -20\,^{\circ}\text{C}$. These experiments are interesting in their own right as they clearly demonstrate the high reactivity of secondary silylium ions, which prevents their detection, isolation, and characterization even under carefully controlled reaction conditions. They also indicate the high mobility of alkyl groups in polysilanyl cations. In addition, a more general implication of this chemistry emerges. There is a clear preference for polysilanyl cations to form Si–H–Si bridges, which stabilize these systems significantly, allow their spectroscopic characterization, and in some cases even their isolation. For example, silyl cation **10e**, a conformer of cation **8** that does not contain the Si–H–Si unit, is markedly less stable than cation **8** by $\Delta E = 77$ kJ mol^{-1}.

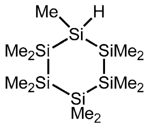
This fact suggests that the lifetime of fleeting intermediates in this type of rearrangement can be extended significantly by using appropriately designed starting materials, which allow the formation of Si–H–Si linkages in an auto-scavenge reaction. These intermediates then can be verified and identified spectroscopically. Such experiments would provide important insights into the actual rearrangement mechanism.

This concept has been demonstrated for the rearrangements of cyclohexasilanes **12** to yield silylcyclopentasilanes **13** (Scheme 4).[26,28–30] This reaction is a prototype for ring-contraction reactions mediated by strong Lewis acids, which are important tools for the skeletal modification of polysilanes. The reaction is thought to proceed via cyclohexasilanyl cations **14**, which undergo ring contraction to cyclopentasilanylsilyl cations **15**, followed by trapping by a nucleophile to give neutral cyclopentasilane derivatives **13**.[29] Although we found that the reaction of **12a** to **13a** is also catalyzed by 1 mol% of trityl tetrakis(pentafluorophenyl)borate (**9**) in dichloromethane or benzene as solvent (Scheme 4), we were unable to detect cationic intermediates in stoichiometric reactions with trityl borate **9** under ambient conditions at $T = -20\,^{\circ}\text{C}$. Subsequently, we studied the reaction of hydrogen-substituted cyclohexasilane



Scheme 4. Lewis acid-catalyzed rearrangement of cyclohexasilanes **12** to give silylcyclopentasilanes **13** (**a**: $R^1 = R^2 = R^3 = Me$; **b**: $R^1 = R^2 = SiMe_3$, $R^3 = Me$; **c**: $R^1 = R^2 = R^3 = SiMe_3$). Reaction conditions for **12a**: Lewis acid: Ph_3C^+, solvent: CD_2Cl_2 or C_6D_6; for **12b**: Lewis acid: $AlCl_3$, solvent: cyclohexane; for **12c**: Lewis acid: $AlCl_3$, solvent: cyclohexane).[14b]

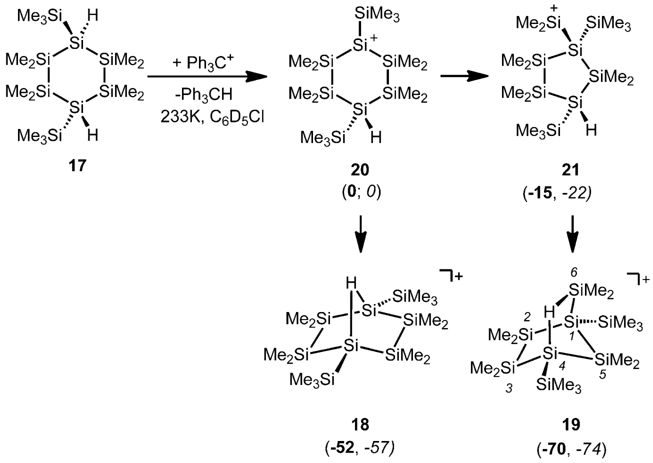
16, which smoothly generated the cation even at low temperatures. The ^{29}Si NMR spectra of the reaction of compound **16** with trityl borate **9** in toluene recorded at $T = -40\,^{\circ}$C suggest the generation of cationic species. The number of ^{29}Si NMR signals and their NMR chemical shifts indicate the formation of toluene complexes of rearranged silylcyclopentasilanyl cations as the main products in this reaction. Significant formation of side- or decomposition products prevented, however, a reliable structural assignment (see the Supporting Information).



16

Finally, the use of 1,4-dihydridocyclohexasilane **17** as the starting material for cation generation provided deeper insights into the rearrangement of the cyclohexasilanes (Scheme 5). The ionization of compound **17** was easily accomplished by removal of the first hydride with trityl tetrakis(pentafluorophenyl)borate (**9**) in chlorobenzene at low temperatures. Based on the previously suggested mechanism (Scheme 4), the formation of two different cations, the symmetric cyclohexasilanyl cation **18** and the cyclopentasilanylsilyl cation **19**, could be expected as a result of the auto-scavenge reaction by the remote Si–H functionality (Scheme 5).

The ^{29}Si NMR spectra recorded at $T = -40\,^{\circ}$C clearly show the predominant formation of one cationic compound. The number and intensity of the ^{29}Si NMR signals in the inverse-gated ^{29}Si{^{1}H} NMR spectrum indicate that this compound contains seven different silicon atoms. Two low-field doublets at $\delta(^{29}\text{Si}) = 78.1$ and 64.1 ppm with characteristic small J coupling constants of $^1J(\text{SiH}) = 39$ and 43 Hz show the formation of a cation with an unsymmetrically substituted Si–H–Si bridge (see Figure 4 and Table 1). In addition, the ^{1}H–^{29}Si HMQC NMR spectrum shows a correlation between both low-field resonances with a broad ^{1}H NMR signal at an unusually high field for Si–H and Si–H–Si groups ($\delta(^1\text{H}) = -1.07$ ppm).[15] Analysis of the signal multiplicity resulting from long-range Si–H couplings and of the $\delta(^{29}\text{Si})$-NMR chemical shifts of the remaining signals suggest the structure of cyclopentasilanylsilyl cation **19** as the predominantly formed cation. This assignment is supported by the close agreement between calculated ^{29}Si NMR chemical shifts (GIAO/M06 L/6-311G(2d,p)) and the experimental data (see Table 1).[47] Solutions of **19**[B(C$_6$F$_5$)$_4$] in chloroben-



Scheme 5. Reaction of 1,4-dihydridocyclohexasilane **17** with the trityl cation and the possible formation of hydrido-bridged cations **18** and **19** in auto-scavenge reactions. Calculated energy differences (ΔE, bold) and free enthalpy differences at 298 K (ΔG^{298}, italics) for cations **18**–**21** relative to cation **20** are given in parentheses (in kJ mol^{-1}, calculated at the M06-2X/6-311+G(d,p) level).

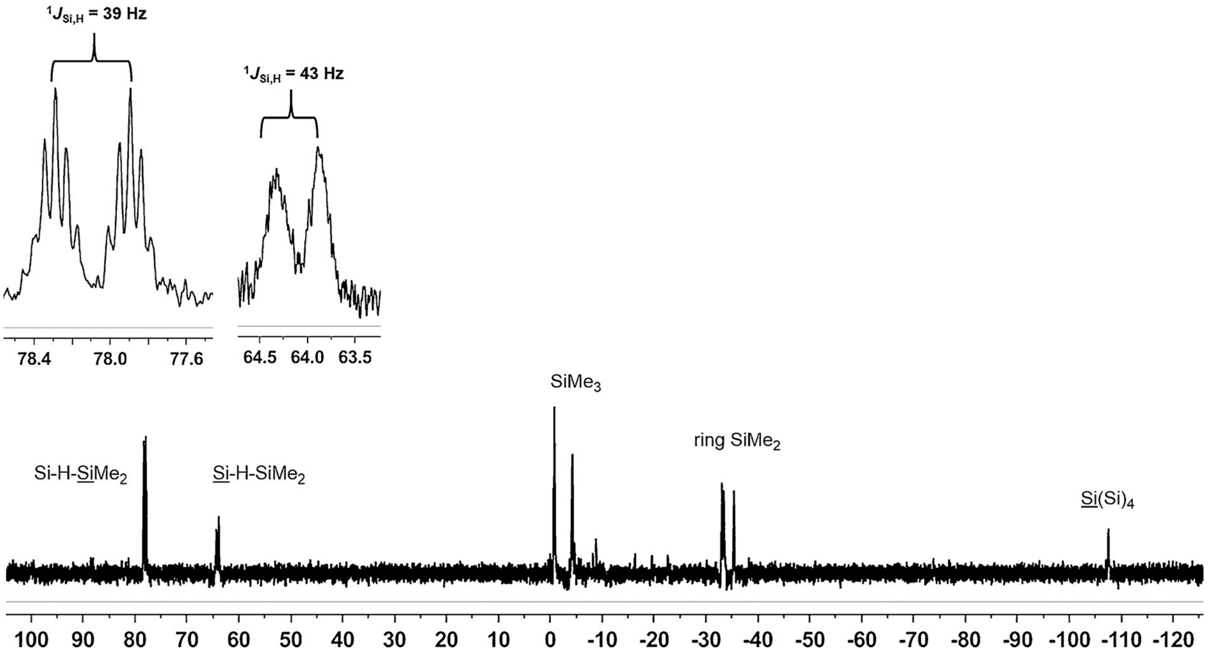


Figure 4. ^{29}Si INEPT NMR spectrum (99.31 MHz, 233 K, C$_6$D$_5$Cl) of cyclopentasilanylsilyl cation **19** obtained from the reaction of cyclohexasilane **17** with trityl tetrakis(pentafluorophenyl)borate **9**.

zene are marginally stable at temperatures around $T=-40\,^{\circ}\mathrm{C}$. After several hours and at higher temperatures, significant decomposition occurs.

It is particularly noteworthy that no characteristic ^{29}Si NMR signals due to the formation of the symmetric cation **18** were detected (see Table 1 for the theoretical prediction). The absence of significant amounts of cation **18** in the reaction mixture is interesting, because the results of calculations suggest that its formation from the primarily formed cyclohexasilanyl cation **20** is exothermic by $\Delta E=-52\ \mathrm{kJ\,mol^{-1}}$ (Scheme 5). Evidently, the ring contraction reaction of cation **20** to give the five-membered ring cation **21** is faster than the formation of the Si–H–Si linkage to form the symmetric cation **18**. In contrast, the lifetime of compound **21** is longer, which allows for the formation of the unsymmetrical Si–H–Si-bridged cation **19**, which is the most stable isomer in the series of cations **18**–**21**. As a consequence, the predominant formation of cation **19** indicates that cation **20** is either not an intermediate in this reaction and the ring contraction to form cation **21** occurs simultaneously with ionization or, at most, it is a high-lying intermediate with a very low barrier to rearrangement to give cyclopentasilanylsilyl cation **21**. This example shows that the formation of cations with an intramolecular Si–H–Si linkage can be detected straightforwardly by NMR spectroscopy and that this feature can be applied in auto-scavenge reactions to reveal important details of otherwise complex reaction sequences in cationic rearrangement reactions of oligo- and polysilanes.

Conclusion

Our attempts to synthesize the hydrogen-substituted polysilanyl silylium ion **6** by hydride transfer reaction from the corresponding cyclic dihydrido-oligosilane **7** resulted in the selective and clean formation of the rearranged bis-silylated hydronium ion **8**. This result demonstrates the strong tendency of polysilanyl cations to undergo skeletal rearrangement reactions and indicates the superior thermodynamic stability of polysilanylsilyl cations stabilized by the formation of a Si–H–Si linkage. In addition, our findings suggest that the lifetime of fleeting intermediates in skeletal rearrangement reactions of polysilanylsilyl cations can be extended significantly by using appropriately designed starting materials, which allow the targeted formation of Si–H–Si bridges in an auto-scavenge reaction. This concept has been successfully demonstrated for one of the key steps in the Lewis acid catalyzed rearrangement reactions of poly- and oligosilanes, the cyclohexasilane/silylcyclopentasilane ring-contraction reaction. By using the appropriately substituted dihydridocyclosilane **17** as the starting material, we identified solely the product **19** of the auto-scavenge reaction of the cyclopentasilanylsilyl cation **21**. This result provides strong evidence for a synchronous ionization/rearrangement reaction pathway without passing through a cyclohexasilanyl cation intermediate. We are currently investigating the scope of the targeted formation of cations featuring a Si–H–Si bridge for mechanistic studies in Lewis acid initiated skeletal rearrangement reactions of poly- and oligosilanes.

Experimental Section

General

All manipulations of air- and moisture-sensitive compounds were carried out under an argon or nitrogen atmosphere using Schlenk techniques or in a standard glovebox (Braun Unilab). NMR spectra were recorded on Bruker Avance 500, Bruker Avance III 500, and Varian Inova 300 spectrometers. ^{1}H NMR spectra were calibrated against the residual proton signal of the solvent as internal reference ([D$_5$]chlorobenzene: $\delta(^{1}\mathrm{H})\,(C_6D_4HCl)=7.14$ ppm; [D$_6$]acetone: $\delta(^{1}\mathrm{H})$ $((CD_3)(CD_2H)CO)=2.05$ ppm) and ^{13}C NMR spectra by using the central line of the solvent signal ([D$_5$]chlorobenzene: $\delta(^{13}\mathrm{C})$ $(C_6D_5Cl)=134.2$ ppm; [D$_6$]acetone: $\delta(^{13}\mathrm{C})$ $((CD_3)_2CO)=29.8$ ppm). ^{29}Si{^{1}H} NMR spectra were calibrated against an external standard (Me_2SiHCl: $\delta(^{29}\mathrm{Si})=11.1$ ppm versus tetramethylsilane (TMS)). The inverse-gated ^{29}Si{^{1}H} NMR spectra were recorded with a relaxation delay $D1$ of 10 s. Based on our experience, at $T=-20$ or $-40\,^{\circ}\mathrm{C}$ this delay is long enough to allow a reliable integration of the peaks. The ^{29}Si{^{1}H} INEPT spectra were recorded with the following delays: $D3=D4=0.0056$ s for cation **8** and $D3=D4=0.0061$ s for cation **19**.

Triphenylmethyl tetrakis(pentafluorophenyl) borate ([Ph_3C][$B(C_6F_5)_4$], **9**) was used as hydride abstraction reagent and prepared according to a modified literature procedure.[48,49] The silyl cations were obtained as salts of the tetrakis(pentafluorophenyl)borate. The NMR characterization data for the anion are given below and not repeated for each cation preparation reaction. Negligible differences were found for the NMR chemical shifts and coupling constants of the anion depending on the solvent or temperature. Data for $[B(C_6F_5)_4]^-$: ^{13}C{^{1}H} NMR (125.71 MHz, 243.1 K, C_6D_5Cl): $\delta=148.9$ (d, $^{1}J_{C,F}=239$ Hz, CF^{ortho}, $[B(C_6F_5)_4]^-$), 138.8 (d, $^{1}J_{C,F}=235$ Hz, CF^{para}, $[B(C_6F_5)_4]^-$), 136.9 (d, $^{1}J_{C,F}=233$ Hz, CF^{meta}, $[B(C_6F_5)_4]^-$), 123.7–125.6 ppm (m, C^{ipso}, $[B(C_6F_5)_4]^-$); ^{19}F{^{1}H} NMR (470.28 MHz, 243.1 K, C_6D_5Cl): $\delta=-131.9$ (br s, 2 F; CF^{ortho}, $[B(C_6F_5)_4]^-$), -161.9 (br s, 1 F; CF^{para}, $[B(C_6F_5)_4]^-$), -165.8 ppm (br s, 2 F; CF^{meta}, $[B(C_6F_5)_4]^-$); ^{11}B{^{1}H} NMR (160.38 MHz, 243.1 K, C_6D_5Cl): $\delta=-16.8$ ppm ($[B(C_6F_5)_4]^-$).

Cation preparation

Synthesis of hydrogen-bridged bis-silyl borate 8[$B(C_6F_5)_4$] from dihydridocyclopentasilane 7 in chlorobenzene: Dihydridocyclopentasilane **7** (87 mg, 1 equiv, 0.18 mmol) and trityl tetrakis(pentafluorophenyl)borate (**9**; 0.162 g, 1 equiv, 0.18 mmol) were evacuated in different Schlenk tubes for 1 h and then each dissolved in chlorobenzene or [D$_5$]chlorobenzene (0.5 mL). The solution of trityl tetrakis(pentafluoro)phenyl borate (**9**) was cooled to $T=-20\,^{\circ}\mathrm{C}$ in an EtOH/N$_2$ bath. The silane was added through a Teflon tube and the reaction mixture was stirred at $T=-20\,^{\circ}\mathrm{C}$ for 1.5 h. The solution was then transferred into an NMR tube and stored at $T=-60\,^{\circ}\mathrm{C}$ overnight. The NMR spectra were recorded at $T=-20\,^{\circ}\mathrm{C}$. Data for cation **8**: ^{1}H NMR (499.87 MHz, 253.0 K, C_6H_5Cl, [D$_6$]acetone lock): $\delta=1.10$ (m, $^{1}J_{Si,H}=46$, $^{3}J_{H,H}=2.3$ Hz, 1 H; Si–H–Si), 0.56 (d, $^{3}J_{H,H}=2.3$ Hz, 6 H; $(H_3C)MeSi^{6,7}$), 0.48 (d, $^{3}J_{H,H}=2.3$ Hz, 6 H; $Me(H_3C)Si^{6,7}$), 0.32 (2 s, 2×3 H; $Si^{5}(CH_3)_2$), 0.20 (s, 6 H; $Si^{2,3}Me(CH_3)$), 0.19 (s, 6 H; $Si^{2,3}(CH_3)Me$), 0.17 ppm (s, 18 H; $Si(CH_3)_3$); ^{13}C{^{1}H} NMR (125.71 MHz, 253.0 K, C_6H_5Cl, [D$_6$]acetone lock): $\delta=1.8$ ($Si(CH_3)_3$), 1.8 ($(H_3C)MeSi^{6,7}$), 1.1 ($Me(H_3C)Si^{6,7}$), -0.9 ($Me(H_3C)Si^{5}$), -1.0 ($(H_3C)MeSi^{5}$), -2.6 ($Si^{2,3}Me(CH_3)$), -3.5 ppm ($Si^{2,3}(CH_3)Me$); ^{29}Si{^{1}H} NMR (99.31 MHz, 253 K, C_6H_5Cl, [D$_6$]acetone lock): $\delta=94.2$ ($Si^{6,7}$), -5.7 (2×SiMe$_3$), -16.3 (Si^{5}), -32.8 ($Si^{2,3}$), -128.8 ppm ($Si^{1,4}$); ^{29}Si INEPT NMR (99.31 MHz, 253 K, C_6H_5Cl, [D$_6$]acetone lock): $\delta=94.2$ (dsept., $^{1}J_{Si,H}=46$, $^{2}J_{Si,H}=6$ Hz, $Si^{6,7}$), -5.7 (m, 2×SiMe$_3$), -16.3

(sept., $^{2}J_{\mathrm{Si,H}}=6$ Hz, Si^{5}), -32.8 (m, Si^{2,3}), -128.8 ppm (s, Si$^{1,\ 4}$); ^{29}Si{^{1}H} NMR (99.31 MHz, 253 K, C_6D_5Cl): $\delta=95.3$ (Si^{6,7}), -4.6 (2× SiMe$_3$), -15.2 (Si^{5}), -31.7 (Si^{2,3}), -127.7 ppm (Si^{1,4}).

Synthesis of hydrogen-bridged bis-silyl borate 8[B(C_6F_5)$_4$] from dihydridocyclopentasilane 7 in *o*-dichlorobenzene: Dihydridocyclopentasilane **7** (50 mg, 1 equiv, 0.10 mmol) and trityl tetrakis(pentafluorophenyl)borate (**9**; 92 mg, 1 equiv, 0.10 mmol) were evacuated in different Schlenk tubes for 1 h and then each dissolved in *o*-dichlorobenzene (1 mL). The solution of trityl tetrakis(pentafluoro)phenyl borate (**9**) was cooled to $T=-15\,^{\circ}$C in an EtOH/N$_2$ bath. The silane was added through a Teflon tube and the reaction mixture stirred at $T=-15\,^{\circ}$C for 2 h. The solution was then transferred into an NMR tube and stored at $T=-25\,^{\circ}$C overnight. The NMR spectra were recorded at $T=-15\,^{\circ}$C with an external [D$_6$]acetone lock. Data for cation **8**: ^{29}Si{^{1}H} NMR (99.31 MHz, 253 K, $C_6H_4Cl_2$, [D$_6$]acetone lock): $\delta=94.1$ (Si^{6,7}), -5.9 (2×SiMe$_3$), -16.4 (Si^{5}), -32.9 (Si^{2,3}), -128.8 ppm (Si^{1,4}); ^{29}Si INEPT NMR (99.31 MHz, 253 K, $C_6H_4Cl_2$, [D$_6$]acetone lock): $\delta=94.1$ (dsept., $^{1}J_{\mathrm{Si,H}}=46$, $^{2}J_{\mathrm{Si,H}}=6$ Hz, Si^{6,7}), -5.9 (m, 2×SiMe$_3$), -16.4 (m, Si^{5}), -32.9 (m, Si^{2,3}), -128.8 ppm (s, Si^{1,4}).

Synthesis of hydrogen-bridged bis-silyl borate 19[B(C_6F_5)$_4$] from 1,4-dihydridocyclohexasilane 17: Trityl tetrakis(pentafluorophenyl)borate (**9**; 92 mg, 1 equiv, 0.10 mmol) was evacuated in an NMR tube and cooled to $T=-80\,^{\circ}$C. A solution of 1,4-dihydridocyclohexasilane **17** (44 mg, 1 equiv, 0.10 mmol) in [D$_5$]chlorobenzene (0.7 mL) was added to the cold trityl borate through a syringe. The addition was performed slowly enough that the solution froze before it reached the trityl borate. The NMR tube was carefully warmed until the solvent melted and the silane **17** slowly reached the trityl borate **9**. At that point, the NMR tube, which was wrapped in a gauze bandage soaked in $T=-70\,^{\circ}$C cold ethanol, was quickly shaken with a vortex mixer and then quickly transferred to the NMR spectrometer precooled to $T=-40\,^{\circ}$C. Data for cation **19**: ^{1}H NMR (499.87 MHz, 233.0 K, C_6D_5Cl): $\delta=0.62$ (Si^{6}(CH_3)$_2$), 0.50 (Si^{3}(CH_3)$_2$), 0.32 (Si^{5}(CH_3)$_2$), 0.23 (Si^{2}(CH_3)$_2$), 0.20 (Si^{4}Si(CH_3)$_3$), 0.17 (Si^{1}Si(CH_3)$_3$), -1.07 ppm (br, $^{1}J_{\mathrm{Si,H}}=40$ Hz, Si–H–Si); ^{13}C{^{1}H} NMR (125.71 MHz, 233.0 K, C_6D_5Cl): $\delta=1.8$ (SiMe$_3$), 0.2 (SiMe$_3$), -0.9 (SiMe$_2$), -1.6 (SiMe$_2$), -2.4 (SiMe$_2$), -2.5 (SiMe$_2$), -2.7 (SiMe$_2$), -3.4 (SiMe$_2$), -5.0 ppm (SiMe$_2$); ^{29}Si{^{1}H} NMR (99.31 MHz, 233 K, C_6D_5Cl): $\delta=78.1$ (Si^{6}), 64.1 (Si^{4}), -0.7 (Si^{4}-*Si*Me$_3$), -4.2 (Si^{1}-*Si*Me$_3$), -33.0 (Si^{3}), -33.4 (Si^{5}), -35.3 (Si^{2}), -107.5 ppm (Si^{1}); ^{29}Si INEPT NMR (99.31 MHz, 233 K, C_6D_5Cl): $\delta=78.1$ (dsept., $^{1}J_{\mathrm{Si,H}}=39$, $^{3}J_{\mathrm{Si,H}}=5$ Hz, Si^{6}), 64.1 (d, $^{1}J_{\mathrm{Si,H}}=43$ Hz, Si^{4}), -0.7 (oct., $^{3}J_{\mathrm{Si,H}}=7$ Hz, (Si^{4}-*Si*Me$_3$)), -4.2 (m, Si^{1}-*Si*Me$_3$), -33.0 (m, Si^{3}), -33.4 (m, Si^{5}), -35.3 (m, Si^{2}), -107.5 ppm (m, Si^{1}).

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