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Thermal Synthesis of Perchlorinated Oligosilanes: A Fresh Look at an Old Reaction

Felix Neumeyer, Julia I. Schweizer, Lioba Meyer, Alexander G. Sturm, Andor Nadj, Max C. Holthausen,* and Norbert Auner*[a]

Dedicated to Prof. Nino Russo on the occasion of his 70th birthday

Abstract: A combined experimental and theoretical study of the high-temperature reaction of $SiCl_4$ and elemental silicon is presented. The nature and reactivity of the product formed upon rapid cooling of the gaseous reaction mixture is investigated by comparison with defined model compounds, i.e. *cyclo*-Si_5Cl_{10}, *n*-Si_5Cl_{12} and *n*-Si_4Cl_{10}. A DFT assessment provides mechanistic insight into the oligosilane formation. Experimental ^{29}Si NMR investigations, supported by quantum-chemical ^{29}Si NMR calculations, consistently show that the reaction product is composed of discrete molecular perchlorinated oligosilanes. Low-temperature chlorination is an unexpectedly selective means for the transformation of cyclosilanes to acyclic species by endocyclic Si–Si bond cleavage, and we provide a mechanistic rationalization for this observation. In contrast to the raw material, the product obtained after low-temperature chlorination represents an efficient source of *neo*-Si_5Cl_{12} or the amine-stabilized disilene $EtMe_2N\bullet SiCl_2Si(SiCl_3)_2$ through reaction with aliphatic amines.

Introduction

Chlorosilanes are key substances used at large scales for the production of elemental silicon from $HSiCl_3$ in the Siemens process,[1] or for silicone synthesis starting from Me_2SiCl_2 obtained in the Müller-Rochow process.[2] Silylenes are considered key intermediates in both processes[3] and the reactivity of the dichlorosilylene ($SiCl_2$) in particular has been widely investigated for over a century. Gaseous $SiCl_2$ is formed quantitatively at temperatures above 1200 °C in the reaction of elemental silicon with tetrachlorosilane.[4] In the chemical transport reaction[5] this comproportionation is reversed under equilibrating cooling conditions and disproportionation of $SiCl_2$ leads back to $SiCl_4$ and deposition of (purified) silicon. Inhibition of equilibration by rapid cooling, however, yields a polymeric $(SiCl_2)_n$ residue, which has served as starting material for the preparation of varying perchlorosilane mixtures.[6] Despite the fact that this approach, together with the alternative chlorination of calcium silicide,[7] is still one of the few preparative routes to perchlorinated oligosilanes, neither the chemical nature nor the reactivity of the polymer have received widespread attention.[8] At the same time, the chemical properties of the $SiCl_2$ building block have spurred considerable research activities over decades.[9] Today the ambiphilicity of silylenes represents one of the most exciting topics explored in contemporary main-group chemistry[10] and the bearing of $SiCl_2$ as synthon has been emphasized lately.[10b]

Here we report an experimental reinvestigation of the high temperature reaction of $SiCl_4$ and elemental silicon. The nature and reactivity of the product formed upon rapid cooling of the gaseous reaction mixture (hereafter referred to as perchlorinated polysilane; PCS) was studied in detail by comparison with defined model compounds. An accompanying quantum-chemical assessment provides mechanistic insight into the formation of cyclic and acyclic oligosilanes from $SiCl_2$, whose ^{29}Si NMR chemical shift values are predicted computationally to aid product assignments. In search of procedures for the preparation of defined oligosilanes, we identified low-temperature chlorination as an unexpectedly selective means for ring-opening of cyclosilanes. We provide a mechanistic rationalization for this observation.

Results and Discussion

Synthesis and Composition of PCS

PCS was obtained by the high-temperature comproportionation reaction of gaseous tetrachlorosilane and elemental silicon. Specifically, a gas stream of $SiCl_4$ was passed over granular silicon at 1250 °C and low pressure. The hot reaction mixture was subsequently led, after passage of a non-heated equilibration zone (20 cm, see Figure S1 in the Supporting Information for schematic of the apparatus), into a cold trap at –196 °C. The solution obtained upon thawing contains about 50 w-% PCS dissolved in unreacted $SiCl_4$, which was evaporated under vacuum. Isolated PCS is a yellow to green/grey, highly viscous material with a mean molecular weight of about 800 g mol^{-1} (approximately $(SiCl_2)_8$, cryoscopy in benzene). It is air- and water sensitive and prone to thermolysis when heated above 200 °C.

Earlier mechanistic suggestions for this reaction involve silyl radicals[6c, 11] or silylenes[4a, 4e, 12] as key reactive intermediates, yet photoelectron spectroscopy has shown that it is actually $SiCl_2$ which forms under the reaction conditions.[9a] While this view appears now generally accepted[10c] detailed insight into the polymer formation reaction is unavailable to date. We therefore evaluated the gas-phase oligomerization processes of dichlorosilylene in a detailed density functional theory (DFT) investigation.[13]

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[a] F. Neumeyer, J. I. Schweizer, L. Meyer, A. G. Sturm, A. Nadj, Prof. M. C. Holthausen, Prof. N. Auner
Institut für Anorganische Chemie, Goethe-Universität
Max-von-Laue-Str. 7, 60438 Frankfurt/Main (Germany)
E-mail: Max.Holthausen@chemie.uni-frankfurt.de
Auner@chemie.uni-frankfurt.de

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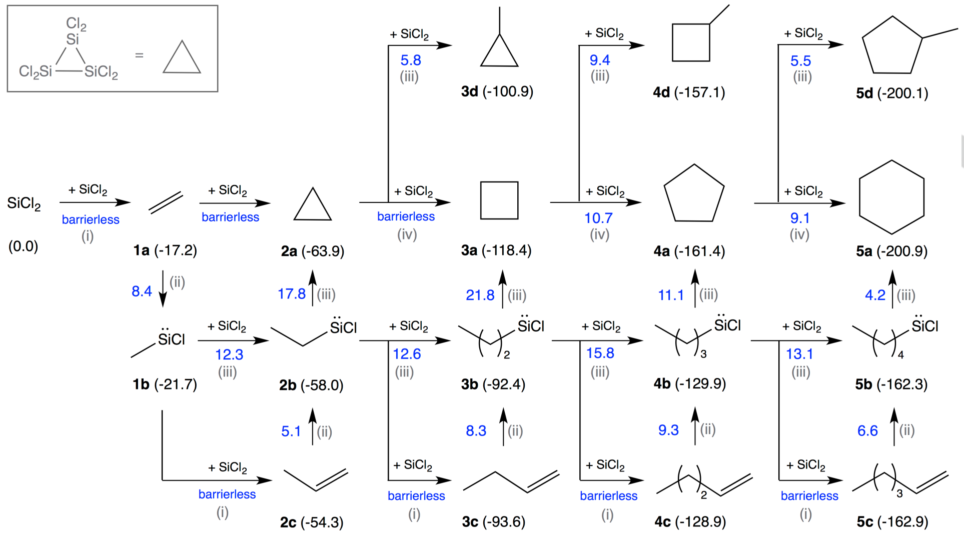
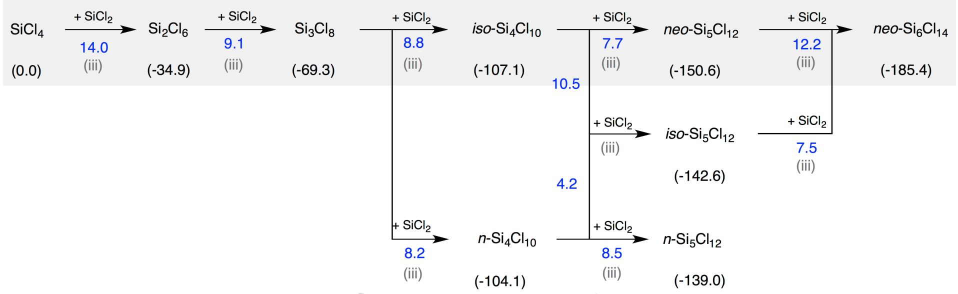
(a) Formation of cyclic silanes



(b) Formation of acyclic silanes



Scheme 1. Schematic gas-phase reactivity of $SiCl_2$. (a) Formation of 3-, 4-, 5- and 6-membered cyclic perchlorosilanes by $SiCl_2$ oligomerization; (b) reaction of $SiCl_2$ with unreacted $SiCl_4$ through silylene insertion. Key elementary steps: (i) silylene dimerization, (ii) disilene/silylene isomerization, (iii) $SiCl_2$ insertion into Si–Cl and (iv) into Si–Si bonds. ΔH^0 in kcal mol^{-1}; RI-M06-L/6-311++G(2d,2p)//RI-M06-L/6-31+G(d,p), activation barriers for individual steps (in blue) are given relative to preceding minima. Encounter complexes formed in most bimolecular steps not shown; a full presentation of results is provided in the Supporting Information. In addition to processes for which no transition state exists, such as the initial dimerization of $SiCl_2$, elementary steps with marginal activation barriers below $\Delta^{\ddagger}H^0 < 0.5$ kcal mol^{-1} are also considered barrierless.

Assuming a gas phase consisting of $SiCl_2$ and unreacted $SiCl_4$ under the reaction conditions[14] we explored all conceivable reaction paths of these species. As condensation reactions occur after the heating zone in a region with strong temperature gradient, we limit the discussion below to enthalpies at zero Kelvin (enthalpies and free energies computed at 298 K are given in the Supporting Information).

The evolving mechanistic scenario is shown in Scheme 1a and comprises four elementary steps, i.e. (i) silylene dimerization to disilenes, (ii) disilene/silylene isomerization by silyl migration, (iii) $SiCl_2$ insertion into Si–Cl and (iv) Si–Si bonds (transition state geometries are shown in the Supporting Information). Initial interaction between two $SiCl_2$ molecules leads to dimerization to the disilene $Cl_2Si{=}SiCl_2$ (**1a**) with its characteristic *trans*-bent geometry. **1a** can isomerize to the more stable silylsilylene **1b** with moderate barrier. We explored three conceivable routes for the subsequent addition of a third $SiCl_2$ equivalent. Reaction of **1b** with $SiCl_2$ leads to disilene **2c** and silyl migration leads to the more stable higher silylene **2b**. This species can also be reached by $SiCl_2$ insertion into a Si–Cl bond of the $SiCl_3$ group in **1b**. Cyclotrisilane **2a** represents the thermodynamically most stable species in this part of the potential energy surface and can be formed either via intramolecular ring-closing Si–Cl insertion of the silylene terminus in **2b** or, kinetically unhindered, directly from **1a** and $SiCl_2$. Buildup of the higher silylene **3b** and disilene **3c** by $SiCl_2$ addition to **2b** involves the same elementary steps. Starting from cyclotrisilane **2a**, $SiCl_2$ can insert without barrier into a Si–Si bond to furnish the thermodynamically stable cyclotetrasilane **3a** Alternative insertion into a Si–Cl bond yielding the $SiCl_3$-substituted cyclotrisilane **3d** is connected with a barrier of 6 kcal mol^{-1} and thermodynamically disfavored. The buildup of the higher (substituted) penta- and hexasilanes shown in Scheme 1a involves the same elementary steps as above with similar activation barriers and reaction energies.

Up to this point, we have identified cyclosilane formation as a thermodynamically dominant process. From **3a** on, ring-expansion by $SiCl_2$ insertion into the Si–Si bond competes with silyl-substitution by Si–Cl insertion, and the thermodynamic preference for the unsubstituted isomers vanishes with larger ring size. Given the cryoscopically determined average PCS composition of $(SiCl_2)_8$, it is thus reasonable to assume that $SiCl_2$ condensation leads to a broad variety of (silyl-substituted) cyclosilanes with varying ring-sizes.

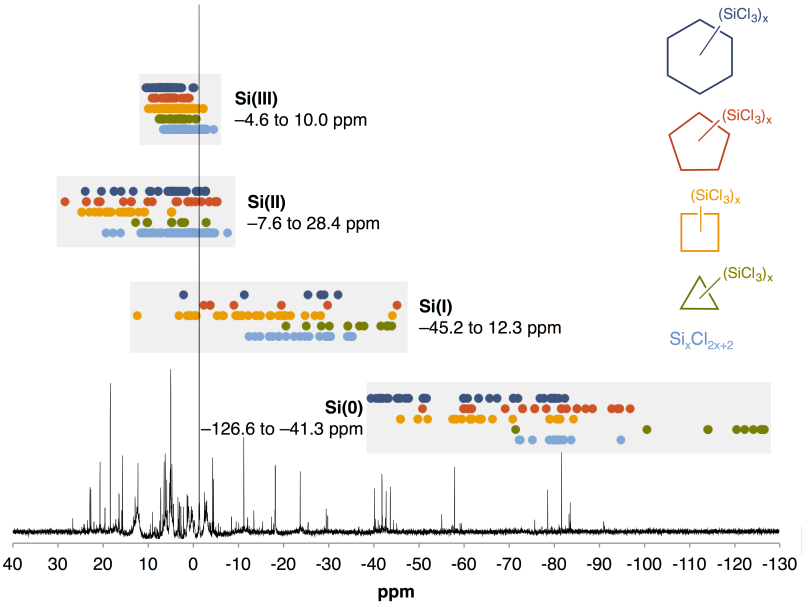


Figure 1. Experimental ^{29}Si NMR spectrum of PCS after removal of $SiCl_4$[16] and ^{29}Si NMR chemical shifts of perchlorinated cyclic and acyclic silanes obtained by DFT calculations (chemical shift values in ppm relative to tetramethylsilane (TMS, δ^{29}Si = 0 ppm); COSMO-SO-ZORA-RPBE/TZ2P//SMD-RI-M06-L/6-31+G(d,p); solvent toluene). Selected constitutional and conformational isomers of penta- and hexacyclosilanes have been evaluated, cf. the Supporting Information.

In a plausible alternative scenario dichlorosilylene can also undergo Si–Cl bond insertion with unreacted $SiCl_4$ left in the gas mixture. Initially, this gives rise to exothermic Si_2Cl_6 formation with an activation barrier of 14 kcal mol^{-1} (Scheme 1b).[15] Each subsequent $SiCl_2$ insertion step en route to higher silanes is equally exothermic (by 35 to 44 kcal mol^{-1}) and generation of branched isomers is thermodynamically favored. Yet, cyclosilane formation by oligomerization of $SiCl_2$ is both, kinetically and thermodynamically favored over formation of acyclic silanes at 0 K. This preference might change, however, upon inclusion of thermal and entropic effects, but in view of the fact that the condensation reactions occur in the temperature gradient zone of the apparatus we refrain from a discussion of relative free energies here.[16]

In summary, the mechanistic picture for the formation of PCS involves four elementary steps. The condensation of $SiCl_2$ leads to cyclosilanes whereas acyclic, preferentially branched oligosilanes might form in the presence of residual $SiCl_4$. The individual build-up sequences are highly exothermic and irreversible, and give rise to a variety of molecular compounds. Correspondingly, the ^{29}Si NMR spectrum of PCS shown in Figure 1 reveals numerous sharp resonances, indicative of distinct molecular compounds, and few broadened domains between +15 and –5 ppm that imply presence of oligomeric silicon chains. The specific composition of PCS, however, escapes detailed identification by NMR spectroscopy as reported ^{29}Si NMR chemical shift values of characterized perchlorinated silanes are scarce.[17] The only species unambiguously identifiable in the product mixture is *cyclo*-Si_5Cl_{10}, which we isolated from PCS by sublimation at 140 °C and 10^{-6} mbar (Si_2Cl_6 and Si_3Cl_8 were collected in the cold trap during sublimation). Accordingly, the dominant NMR signal at δ^{29}Si = –1.7 ppm in Figure 1 perfectly matches the chemical shift value for *cyclo*-Si_5Cl_{10} reported by Hengge and coworkers.[18]

In view of the glaring lack of experimental data we set out to quantum-chemically establish ^{29}Si NMR chemical shifts for a large set of cyclic and acyclic perchlorosilanes, which were chosen based on the formation mechanism discussed above. To this end, we performed spin-orbit relativistic ^{29}Si NMR calculations at the COSMO-SO-ZORA-RPBE/TZ2P//SMD-RI-M06-L/6-31+G(d,p) level of DFT,[10e, 19] a pleasingly accurate approach as documented in the Supporting Information for a set of experimentally characterized compounds (Table S9; 1.3 ppm mean absolute error, –3.1 ppm maximum deviation). Confirmatively, the ^{29}Si NMR chemical shift value computed for *cyclo*-Si_5Cl_{10} (δ^{29}Si = –1.7 ppm) perfectly matches experiment. Irrespective of the evident predictive capability of this approach for individual species, comparison of the experimental PCS NMR spectrum with the collected theoretical data superimposed in Figure 1 illustrates that detailed assignments are precluded by a prohibitive degree of ambiguity. The quantum-chemical results, however, provide a useful categorization of typical ^{29}Si NMR shift domains by formal silicon oxidation state for a large set of hitherto unknown perchlorosilanes (see Supporting Information for a full presentation of individual results): With a narrow spread between δ^{29}Si = +10 and –5 ppm the signal domain for Si(III) centers inseparably coincides with the Si(II) and Si(I) domains, which extend from δ^{29}Si = +28 to –8 ppm and δ^{29}Si = +12 to –45 ppm, respectively. Si(0) centers in turn resonate between δ^{29}Si = –45 and –127 ppm, partly overlapping with the Si(I) domain in the low-field region.

PCS as source of defined oligosilanes

Historically, the use of PCS-analogous materials as source of perchlorinated oligosilanes was exploited in detail.[6, 8a, 8b] To this end, PCS was typically subjected to thermolysis and smaller oligosilanes were isolated by careful distillation. Such an approach, however, lacks efficiency as well as selectivity. More efficient access to smaller silanes should reportedly be possible through breakdown of PCS by reaction with elemental chlorine.[8a, 20] The outcome of the chlorination, however, strongly depends on the reaction temperature as detailed in the following ^{29}Si NMR spectroscopy, used to monitor the chlorination of PCS in the temperature range between 20 °C and 120 °C, reveals significant conversion of PCS already at room temperature (r.t.). Specifically, the dominant NMR signal attributable to *cyclo*-Si_5Cl_{10} (δ^{29}Si = –1.7 ppm) vanishes completely and smaller amounts of Si_2Cl_6 and Si_3Cl_8 are formed (Figure 2). Resonances of the latter gain intensity with increasing reaction temperature.

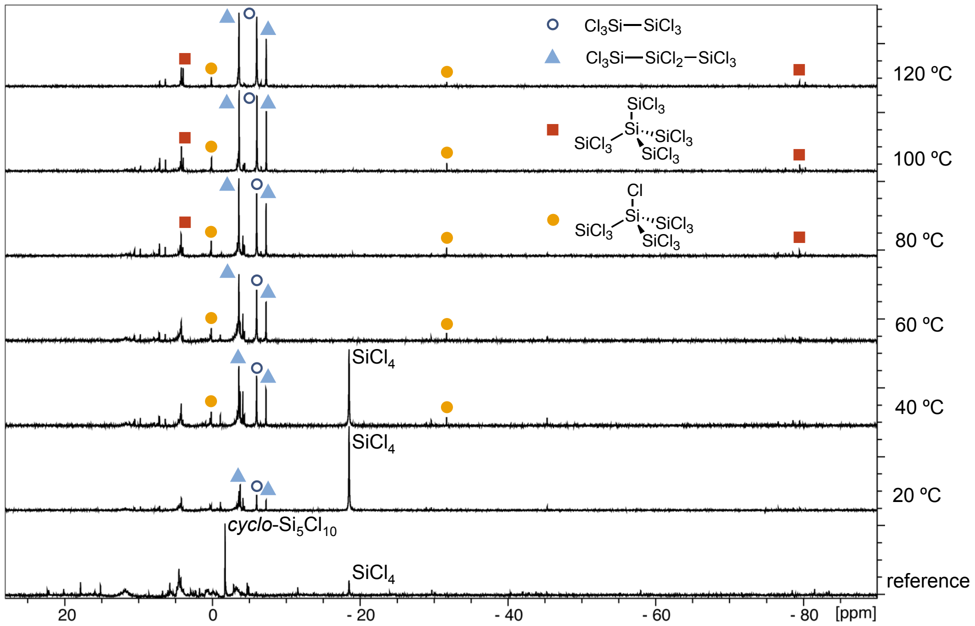
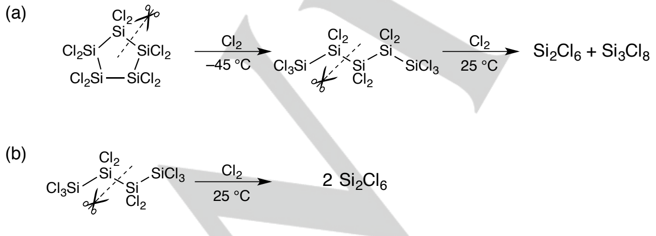


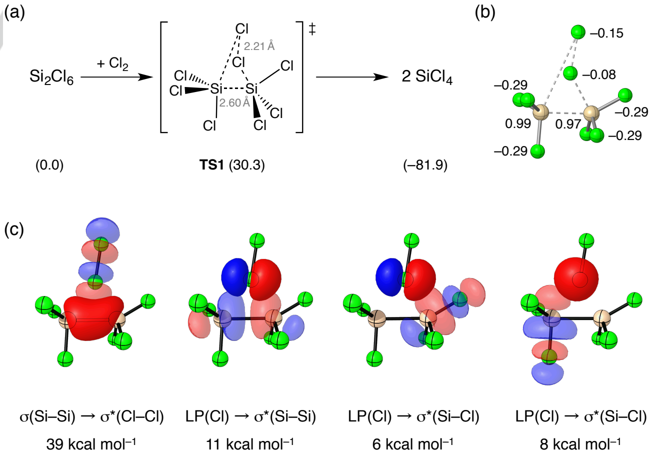
Figure 2. ^{29}Si NMR spectra of PCS chlorination at different reaction temperatures (20–120 °C, top); Reference spectrum of unreacted PCS (bottom).

Signatures of *iso*-Si_4Cl_{10} (δ^{29}Si = –31.8 and 0.0 ppm)[17] appear from 40 °C on, while $SiCl_4$ boils off at 58 °C. Within a set of spurious high-field signals between –76 and –81 ppm present in the spectra, *neo*-Si_6Cl_{14} (δ^{29}Si = +6.3, +4.1, –3.5, –79.5 ppm, from 20 °C on)[17] and *neo*-Si_5Cl_{12} (δ^{29}Si = –80.4 and +4.0 ppm, $T > 80$ °C)[17] can be assigned according to their literature-known chemical shift values (see Supporting Information for further details). Overall, chlorination of PCS at lower temperatures results in marked changes observable by ^{29}Si NMR spectroscopy, but the reaction mixture still remains complex and unambiguous identification of other individual silanes is unfeasible.

For further insight we studied the chlorination reaction of the authentic oligosilanes *cyclo*-Si_5Cl_{10}, *n*-Si_5Cl_{12} and *n*-Si_4Cl_{10}, which were synthesized according to published procedures.[21] Warming of a solution of *n*-Si_4Cl_{10} in liquid chlorine from –35 °C to r.t. led to evaporation of excess chlorine and quantitative formation of Si_2Cl_6. For both, *n*-Si_5Cl_{12} and *cyclo*-Si_5Cl_{10}, the same procedure resulted in a 1:1 mixture of Si_2Cl_6 and Si_3Cl_8. Selective ring opening of *cyclo*-Si_5Cl_{10} was observed at –45 °C and *n*-Si_5Cl_{12} was isolated in quantitative yield after removal of excess chlorine under vacuum (Scheme 2). We note in passing that *cyclo*-Si_5Cl_{10} and *n*-Si_5Cl_{12} swiftly react with chlorine gas at r.t. to the same products, whereas *neo*-Si_5Cl_{12} is known to react only slowly even at elevated temperatures.[22] Formation of significant amounts of $SiCl_4$ was not observed in any case.



Scheme 2. (a) Ring-opening of *cyclo*-Si_5Cl_{10} and subsequent cleavage of *n*-Si_5Cl_{12} to hexachlorodisilane and octachlorotrisilane. (b) Cleavage of *n*-Si_4Cl_{10} to hexachlorodisilane.



Scheme 3. Chlorination of Si_2Cl_6. a) Computed reaction pathway (ΔG^{298} in kcal mol^{-1}); b) NPA charges (**TS1**); c) dominant NBO interactions (occupied NBOs solid, vacant NBOs faded) and corresponding perturbative interaction energies; SMD-M06-L/6-311++G(2d,2p)//SMD-M06-L/6-31+G(d,p) (solvent toluene).

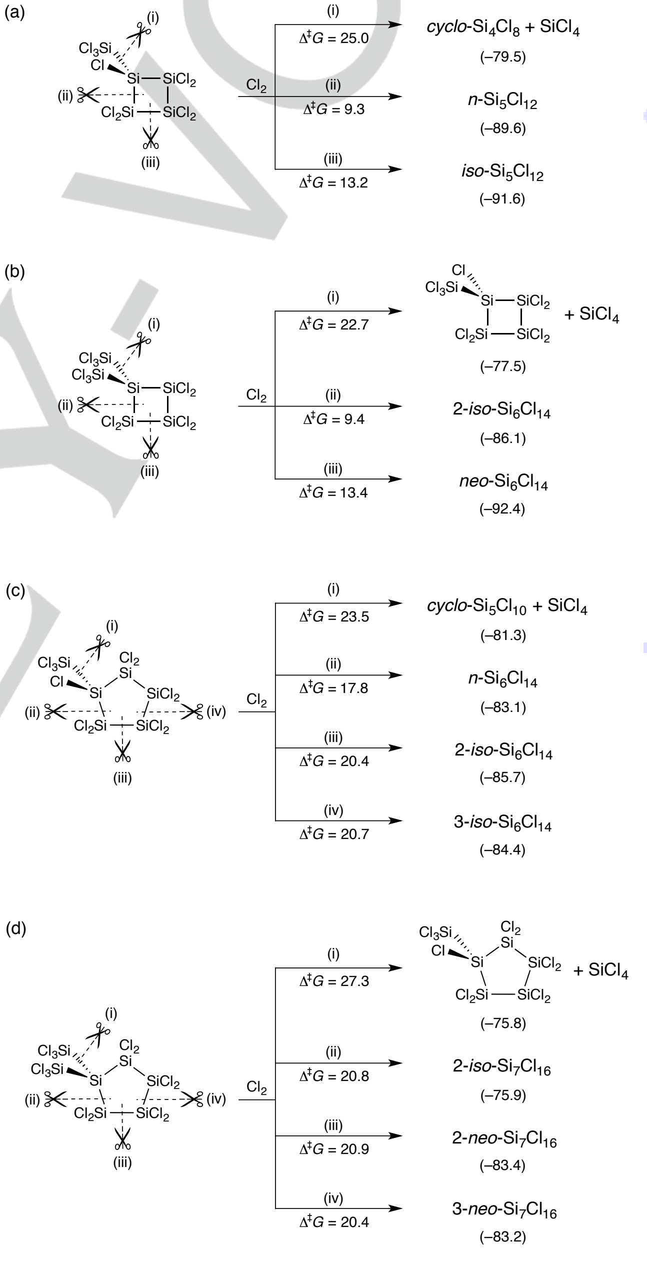
We evaluated the underlying reaction mechanism by quantum-chemical means for various oligosilanes.[23] Si–Si bond cleavage is exergonic in all cases (Table 1 and Scheme 4) and involves the same concerted elementary step, which we exemplarily discuss here for Si_2Cl_6. In the transition state geometry (**TS1**, Scheme 3a), the chlorine fragment is oriented perpendicular to the Si–Si bond broken and both, the Si–Si (2.60 Å) and Cl–Cl bonds (2.21 Å) are elongated with respect to the corresponding bond lengths in the separated reactants (Si_2Cl_6: 2.33 Å, Cl_2: 2.01 Å). Natural population analysis (NPA) indicates Cl–Cl bond polarization with negative charge accumulated at the terminal chlorine atom (Scheme 3b). Natural bond orbital (NBO) analysis discloses four significant donor/acceptor interactions in the transition state: Activation of the Si–Si and Cl–Cl bonds arises dominantly from σ(Si–Si)→σ*(Cl–Cl) donation and LP(Cl)→σ*(Si–Si) back-donation (Scheme 3c). Secondary interactions involve LP(Cl)→σ*(Si–Cl) donation.

The corresponding transition states for chlorination of the higher silanes all exhibit very similar structural characteristics (see Supporting Information for further details). The computed activation barrier of $\Delta^{\ddagger}G$ = 30 kcal mol^{-1} for the chlorination of Si_2Cl_6 via **TS1** is consistent with the experimentally observed lack of reactivity at moderate temperatures. Chlorination of Si_3Cl_8, *iso*-Si_4Cl_{10} and *neo*-Si_5Cl_{12}[22] only occurs at elevated temperatures, which is in line with calculated activation barrier heights above 25 kcal mol^{-1} (Table 1). In agreement with experimental observation, cleavage of the central Si–Si bonds in *n*-Si_4Cl_{10} and *n*-Si_5Cl_{12} is kinetically and thermodynamically favored over cleavage of terminal Si–Si bonds by 5 kcal mol^{-1}. Ring opening of *cyclo*-Si_4Cl_8 to *n*-Si_4Cl_{10} by Cl_2 is by far the kinetically least demanding reaction and should be fast even at very low temperatures. With a computed activation barrier of 21 kcal mol^{-1} ring opening of *cyclo*-Si_5Cl_{10} to *n*-Si_5Cl_{12} is slightly more demanding than subsequent chlorination of the latter. We attribute the obvious contrast to experiment to solid-state and concentration effects not accounted for in the calculations.

Table 1. Chlorination of selected perchlorinated oligosilanes. Reaction energies and activation barrier heights given in kcal mol^{-1} at 298 K (SMD-M06-L/6-311++G(2d,2p)//SMD-M06-L/6-31+G(d,p); solvent toluene).

			$\Delta_R G$	$\Delta^{\ddagger}G$
Si_2Cl_6	→	2 $SiCl_4$	–81.9	30.3
Si_3Cl_8	→	Si_2Cl_6 + $SiCl_4$	–83.3	24.9
n-Si_4Cl_{10}	→	2 Si_2Cl_6	–85.0	20.6
	→	Si_3Cl_8 + $SiCl_4$	–83.7	25.0
iso-Si_4Cl_{10}	→	Si_3Cl_8 + $SiCl_4$	–81.2	25.6
n-Si_5Cl_{12}	→	Si_3Cl_8 + Si_2Cl_6	–85.5	19.9
	→	*n*-Si_4Cl_{10} + $SiCl_4$	–84.0	24.2
neo-Si_5Cl_{12}	→	*iso*-Si_4Cl_{10} + $SiCl_4$	–76.7	29.8
cyclo-Si_4Cl_8	→	*n*-Si_4Cl_{10}	–94.1	11.4
cyclo-Si_5Cl_{10}	→	*n*-Si_5Cl_{12}	–85.4	21.3

As detailed in Scheme 4, chlorination of silyl-substituted cyclosilanes can occur via several routes. For the mono- and disubstituted cyclotetra- and pentasilanes studied here, ring opening is kinetically preferred proximal to the Si(I) or Si(0) ring atoms. Cleavage of exocyclic Si–Si bonds is disfavored in all cases.



Scheme 4. Chlorination of (a) *cyclo*-$Si_4Cl_7(SiCl_3)$, (b) *cyclo*-$Si_4Cl_6(SiCl_3)_2$, (c) *cyclo*-$Si_5Cl_9(SiCl_3)$, and (d) *cyclo*-$Si_5Cl_8(SiCl_3)_2$ (ΔG^{298} in kcal mol^{-1}; SMD-M06-L/6-311++G(2d,2p)//SMD-M06-L/6-31+G(d,p); solvent toluene).

Based on our experimental and quantum-chemical model studies we conclude that any amount of (possibly silyl-substituted) cyclosilanes present in PCS readily undergoes ring opening by reaction with Cl_2. At temperatures below 0 °C this should result in selective and quantitative conversion to acyclic *n*-, *iso*-, and *neo*-silanes, the distribution being dependent on the degree of $SiCl_3$ substitution at the silacycles. To corroborate this hypothesis further, we performed low temperature chlorination of PCS strictly at –35 °C. After removal of chlorine ^{29}Si NMR spectroscopy of the resulting, ring-opened product mixture (ro-PCS) reveals complete disappearance of low-field signals attributable to cyclosilanes together with the break-down of a number of other compounds. From this mixture we directly isolated 63 w-% acyclic oligosilanes of the composition Si_nCl_{2n+2} (n = 1–6) by multi-step low-pressure fractional distillation. Renewed chlorination of the distillation residue at 120 °C increases the total yield of lower oligosilanes to 97 w-%. Detailed results are presented in the Supporting Information.

To further scrutinize the differences in chemical composition introduced by chlorination we reacted samples of PCS and ro-PCS with NMe_2Et. The reaction of perchlorinated oligosilanes with catalytic amounts of aliphatic amines has long been established as one of the few selective procedures for the quantitative transformation of smaller perchlorinated oligosilanes, such as Si_2Cl_6 and Si_3Cl_8, into *neo*-Si_5Cl_{12}.[10f, 22, 24] Furthermore, we have recently shown that treatment of Si_2Cl_6 or *neo*-Si_5Cl_{12} with equimolar amounts of NMe_2Et quantitatively yields the amine-stabilized disilene $EtMe_2N{\bullet}SiCl_2Si(SiCl_3)_2$.[10e] Notably, reactions of PCS with both catalytic and equimolar amounts of NMe_2Et led, apart from the expected products, to significant formation of side-products with unprecedented ^{29}Si NMR signatures. We observed the same signatures in reactions of authentic samples of *cyclo*-Si_5Cl_{10} with amine base under identical conditions (see Supporting Information). It is hence obvious that these resonances originate from yet unknown species formed in characteristic reactions of cyclosilanes. In contrast, ring-opened PCS samples react with NMe_2Et selectively to *neo*-Si_5Cl_{12} and $EtMe_2N{\bullet}SiCl_2Si(SiCl_3)_2$. Additional experiments, in which we reacted Si_3Cl_8, *n*-Si_4Cl_{10} and *n*-Si_5Cl_{12} with equimolar amounts of NMe_2Et, gave the same results. These findings clearly illustrate the absence of cyclosilanes in ro-PCS.

Conclusions

In this work, we revisited the high-temperature synthesis of PCS from $SiCl_4$ and elemental silicon at 1250 °C. PCS is an oligomeric material composed of mostly discrete silanes as consistently shown by experimental ^{29}Si NMR investigations, supported by quantum-chemically derived ^{29}Si NMR chemical shift values. The suggested formation mechanism of cyclosilanes involves oligomerization of $SiCl_2$, the key reactive species present in the gas phase. Reaction of $SiCl_2$ with unreacted $SiCl_4$ leads to build-up of acyclic oligosilanes. High-temperature chlorination of PCS affords improved access to smaller oligosilanes, which need to be separated by fractional distillation. We identified low-temperature chlorination as an unexpectedly selective means for the transformation of cyclosilanes to acyclic species by endocyclic Si–Si bond cleavage, and we provide a mechanistic rationalization for this observation. In contrast to the raw material, the ring-opened PCS can be used as efficient source of *neo*-Si_5Cl_{12} or the amine-stabilized disilene $EtMe_2N{\bullet}SiCl_2Si(SiCl_3)_2$, which are formed quantitatively in the reaction with aliphatic amines.

Experimental Section

All reactions were performed employing standard Schlenk techniques using N_2 or Ar as inert gases. Solvents were dried over appropriate drying agents, distilled and stored in PTFE-valved flasks. NMR spectra were recorded on a Bruker AV-500 spectrometer equipped with a Prodigy BBO 500 S1 probe. ^1H NMR spectra were calibrated to the residual solvent proton resonance ([D$_6$]benzene δ_H = 7.16 ppm). ^{29}Si NMR chemical shifts are referenced internally to $SiCl_4$ (–18.5 ppm)[17] or Si_2Cl_6 (–6.1 ppm).[17]

Synthesis of PCS. Granular silicon (35.86 g, 1.28 mol), fixed in place by quartz wool inside a quartz tube, was heated to 1250 °C in a tubular oven at 10 mbar with an Argon gas flow of 20 mLn/min. After temperature equilibration (60 minutes), the Argon gas flow was stopped and gaseous $SiCl_4$ was led over the heated silicon at 80 mLn/min. After leaving the heating zone, the product gas mixture was led through an approx. 20 cm long non-heated equilibration zone into a receiving flask cooled with liquid nitrogen. $SiCl_4$ supply was stopped after 6.5 h and the apparatus was cooled to r.t. under Argon flow while the product flask remained frozen. After thawing, the product solution was heated to reflux washing down all remaining viscous substances formed inside the quartz tube (221.6 g of product solution in $SiCl_4$, 51 w-% products).

Further experimental details are provided in the Supporting Information.

Acknowledgements

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Keywords: silylenes • perchlorinated oligosilanes • Si–Si bond cleavage • reaction mechanisms • density functional calculations

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[13] Geometry optimizations were performed at the RI-M06-L/6-31+G(d,p) level of theory; improved energies and wave functions were obtained from subsequent RI-M06-L/6-311++G(2d,2p) single point calculations. See Supporting Informations for full computational details.

[14] This assumption is motivated by the presence of a temperature gradient in our flow reactor operated at a maximum temperature of 1250 °C; for a simulation of the temperature dependent partial pressures of $SiCl_4$ and $SiCl_2$ comprising the gas phase in the $SiCl_4$/Si system see ref. 10c.

[15] A reviewer raised the question whether $SiCl_3$• radicals formed by Si_2Cl_6 fragmentation under the reaction conditions might become involved in the overall reaction. According to a theoretical assessment at the W1 level of theory, however, homolysis of the Si–Si bond is thermodynamically strongly disfavored compared to the reverse reaction here, that is, fragmentation into $SiCl_2$ and $SiCl_4$: E. M. L. Fink, A. Schießer, R. Berger, M. C. Holthausen, *Int. J. Mass. Spectrom.* **2013**, *354–355*, 378-390.

[16] ^{29}Si NMR signals for Si_2Cl_6 and Si_3Cl_8 are clearly visible in the experimental NMR spectrum of the raw reaction product (Figure S4 in the Supporting Information). The NMR spectrum displayed in Figure 1 was obtained after removal of $SiCl_4$ ($p = 0.1$ mbar, $T < 100$ °C) and does not include the corresponding NMR signals for Si_2Cl_6 and Si_3Cl_8, which were removed together with excess $SiCl_4$.

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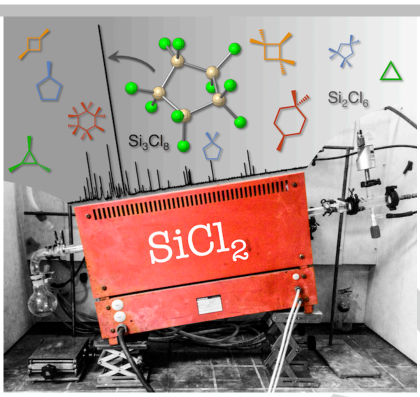
FULL PAPER

Not much of a polymer but rather a complex mixture of small oligosilanes results from quenching the thermal reaction of $SiCl_4$ and elemental silicon. A combined theoretical and experimental reinvestigation of the long-known $(SiCl_2)_x$ synthesis sheds new light on the reaction product and its reactivity.



Felix Neumeyer, Julia I. Schweizer, Lioba Meyer, Alexander G. Sturm, Andor Nadj, Max C. Holthausen, and Norbert Auner**

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Thermal Synthesis of Perchlorinated Oligosilanes: A Fresh Look at an Old Reaction