Disilane Cleavage with Selected Alkali and Alkaline Earth Metal Salts

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Abstract: The industry-scale production of methylchlorosilanes in the Müller–Rochow Direct Process is accompanied by the formation of a residue, the direct process residue (DPR), comprised of disilanes Me₂SiCl₃₉₊ₙ (n = 1–6). Great efforts have been devoted to the recycling of these disilanes into monosilanes to allow reintroduction into the siloxane production chain. In this work, disilane cleavage by using alkali and alkaline earth metal salts is reported. The reaction with metal hydrides, in particular lithium hydride (LH), leads to efficient reduction of chlorine containing disilanes but also induces disproportionation into monosilanes and oligosilanes. Alkali and alkaline earth chlorides, formed in the course of the reduction, specifically induce disproportionation of highly chlorinated disilanes, whereas highly methylated disilanes (n > 3) remain unreacted. Nearly quantitative DPR conversion into monosilanes was achieved by using concentrated HCl/ether solutions in the presence of lithium chloride.

Introduction

Methylchlorosilanes Me₂SiCl₃₉₊ₙ (n = 1–3) are produced in the Direct Process (DP)[1] at large scales by reaction of elemental silicon with chloromethane. The production of the main product Me₂SiCl₃ has, however, been accompanied by the formation of an unwanted residue (the DPR) comprised of methylchlorodisilanes, Me₂SiCl₃₉₊ₙ (n = 1–6) and, in minor amounts, of carbodisilanes, which accumulate in the overall DP significantly.3Dedicated to Professor Bernhard Rieger on the occasion of his 60th birthday

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A number of earlier studies by others have shown that the hydrogenation of chlorosilanes can efficiently be achieved by using complex reducing agents, such as LiAlH₄, NaBH₄, and LiBH₄. Also the alkali metal hydrides LiH[15] and NaH[16] as well as alkaline earth metal hydrides such as MgH₂[17] have been used for chlorosilane reduction. Polyether solvents have been often used to activate LiBH₄ and NaBH₄ for reduction of, for example, SiCl₄, Me₂SiCl₄, or GeCl₄.[18] Chlorosilane reductions are generally performed at ambient temperatures (20–25 °C) as temperatures above 100 °C often cause decomposition of the reducing agents or the desired product.[18] Moreover, calcium and titanium hydrides,[19] or mixtures of NaH/NaBH₄,[20] have been found effective in reduction reactions, but all synthetic routes reported thus far are lacking selectivity and yield the perhydrido-substituted derivatives as main products.

Bifunctional monosilanes represent fundamentally important building blocks in silicon technology. Utilizing 1) the Si–H functionality for hydrosilylation reactions to create silicon-carbon bonds[21] and 2) the Si–Cl functions for hydrolysis or alcoholysis provides access to the corresponding silanols or alkoxysilanes employed in condensation reactions to form the siloxane Si–O–Si bonding motif.[22,23] For the synthesis of bifunctional monosilanes, some preparative protocols have been reported: As shown by D’Errico and Sharp for a variety of halosilanes, the selective reduction of a single Si–Cl bond is possible by using alkyltin hydrides.[23] Further, the Roewer group converted Me₃SiCl₂ to Me₂SiHCl with organotin hydrides in the presence of phosphonium chlorides or amine bases.[24] More recently, Ir-mediated synthetic protocols utilizing H₂ as hydrogen source have been reported.[25] Alternatively, efficient access to monosilanes R₂SiHCl and R₂SiHCl₂ has been established by selective chlorination of hydridomonosilanes with HCl in the presence of catalytic amounts of Lewis acids[26] or Lewis-bases such as ethers.[27]

The efficient cleavage of silicon-silicon bonds with alkali metal salts has been first reported by Ring and co-workers.[28] This group studied reactions of Si₃H₄ with alkali metal chlorides and hydrides to yield SiH₄, “SiH₃,” polymers and metal silanides,[29] and also the cleavage of some alkylsilanes was investigated.[30] Furthermore, the pertinent patent literature reports on metal-salt-catalyzed cleavage of different disilanes present in the DPR and disclosed alkali metal halides to form complexes with various tertiary amines, which are effective in cleavage reactions.[31] We here report the cleavage reactions of different methylchlorosilanes with alkali and alkaline earth metal salts to give monosilanes in high yields. We focus in particular on the synthesis of bifunctional monosilanes, bearing both hydrido and chloro substituents, formed by simultaneous cleavage and reduction of the disilanes present in the DPR.[28–30]

### Results and Discussion

Highly chlorinated disilanes such as Cl₃MeSi–SiMeCl₂ (1, 50–75 wt% of the DPR) and ClMe₃Si–SiMeCl₂ (2, 20–40 wt%) are referred to in the literature as “cleavable fraction” of the DPR, because they can be thermally cleaved by amine catalyzed reduction with HCl.[104] In contrast, the term “uncleavable fraction” has been coined for the highly methylated disilanes ClMe₃Si–SiMeCl₂ (3, 4–10 wt%), Me₂Si–SiMeCl₂ (4, 2–4 wt%), Me₂Si–SiMeCl₂ (5, 3–6 wt%) and Me₂Si–SiMe₃ (6, 0–1 wt%) as their cleavage requires harsh conditions.[3b,c, 4a,c, 32] Only recently cleavage of these disilanes has been reported, but yields of bifunctional monosilanes were low.[4b] In principle, the “uncleavable” fraction of the DPR can be transformed into “cleavables” by high temperature Si–Cl/Si–Me redistribution reactions with HCl in the presence of AlCl₃,[33] but clearly this process is cumbersome.

Table 1 lists the numbering scheme of starting materials and products relevant in this study, procedures as well as NMR spectroscopic data are provided as Supporting Information. Disilanes were separated from authentic industrial DPR samples and hydridodisilanes and hydridocarbodisilanes were obtained by reduction of chlorinated precursors with LiAlH₄ maintaining the Si–Si and the Si–C–Si backbone.

### Table 1. Numbering scheme of silanes reacted and reaction products formed.

| No. | Compounds | No. | Compounds | No. | Compounds |
|-----|-----------|-----|-----------|-----|-----------|
| 1   | Cl₃MeSi–SiMeCl₂ | 14 | Me₂SiCl₂ | 27 | Cl₃MeSi–SiMe₃H |
| 2   | ClMe₃Si–SiMeCl₂ | 15 | Me₂SiH₂ | 28 | ClMe₃Si–SiMe₃H |
| 3   | ClMe₃Si–SiMeCl₂ | 16 | H₂MeSi–SiMe₃H | 29 | H₂MeSi–SiMe₃ClH |
| 4   | Me₂Si–SiMeCl₂ | 17 | H₂MeSi–SiMe₃H | 30 | H₂MeSi–SiMe₃ClH |
| 5   | Me₂Si–SiMeCl₂ | 18 | H₂MeSi–SiMe₃H | 31 | Cl₂MeSi–SiMe₃Cl |
| 6   | Me₂Si–SiMeCl₂ | 19 | Me₂Si–SiMe₃H | 32 | Cl₂MeSi–SiMe₃Cl |
| 7   | Me₂SiCl₂ | 20 | Me₂Si–SiMe₃H | 33 | Me₂Si–SiMe₃Cl |
| 8   | Me₂SiCl₂ | 21 | Cl₂MeSi–SiMe₃ClH | 34 | Me₂Si–SiMe₃Cl |
| 9   | Me₂SiCl₂ | 22 | Cl₂MeSi–SiMe₃ClH | 35 | Me₂Si–SiMe₃Cl |
| 10  | Me₂SiCl₂ | 23 | HClMe₃Si–SiMe₃ClH | 36 | Me₂Si–SiMe₃Cl |
| 11  | Me₂SiCl₂ | 24 | Cl₂MeSi–SiMe₃H | 37 | H₂MeSi–SiMe₃H |
| 12  | Me₂SiCl₂ | 25 | Cl₂MeSi–SiMe₃H | 38 | H₂MeSi–SiMe₃H |
| 13  | Me₂SiCl₂ | 26 | Cl₂MeSi–SiMe₃H | 39 | H₂MeSi–SiMe₃H |

To study the reduction and cleavage of disilanes with lithium hydride, we chose tetramethylchlorodisilane (3) as a representative model compound for the “uncleavable” fraction of the DPR. 3 was quantitatively reduced at room temperature (RT) to tetramethyldisilane 18 with two equivalents of lithium hydride [Eq. (1)].

\[
\text{ClMe}_3\text{Si} - \text{SiMeCl}_2 + 2 \text{LiH} \rightarrow \text{HMe}_3\text{Si} - \text{SiMe}_3\text{H} + 2 \text{LiCl}
\]

Increase of the reaction temperature to 140 °C with excess of LiH led to cleavage of 18 to form dimethylsilane (94%) together with the NMR-detectable oligosilanes HMe₃Si–(SiMe₂)ₙ–SiMe₃H (n = 1–3, 6%, cf. the Supporting Information).[34] In contrast to the mechanistic picture recently established,[35] we found that lithium chloride does not afford disilane cleavage: in a set of NMR experiments, no reaction with lithium chloride was observed for disilanes 16[40] and 18 even at elevated temperatures. Also in contrast to earlier reports,[28a,30] both disilanes were efficiently cleaved into silane monomers with lithium hydride. Already at RT the reaction with 16 afforded Me₂SiH₃ (44%) along with oligosilanes (4%), 52% of disilane 16 re-
mained uncleaved. Upon increasing the reaction temperature to 60 °C, only MeSiH₄ was identified by ²⁹Si NMR spectroscopy. The reaction of 18 with excess LiH was studied further in variable-temperature NMR experiments: Me₅SiH was, apart from traces of oligosilanes, the only product detectable up to 140 °C.³³

Based on earlier detailed studies on the chloride-induced aufbau of higher perhalogenated oligosilanes from SiₓClₓ,³⁴ we devised a tentative reaction mechanism for the cleavage of disilane 18 (Scheme 1). As the initial step, we assume the formation of a silicate DH⁻ by attachment of a hydride ion, released from the LiH solid, to one of the silicon centers in disilane 18 (D), which subsequently undergoes Si–Si bond cleavage to give Me₃SiH (M) and the silanide anion HMe₅Si⁻ (A⁻).³⁵ The silanide A⁻ can then abstract a proton from another equivalent of D to yield monosilane Me₅SiH thieves yield by using substoichiometric amounts of LiH: The reaction with 4 equiv LiH but undergoes quantitative cleavage of multiply methylated disilanes with lithium hydride at elevated reaction temperatures. We note in passing that neither 3 nor 18 react with LiCl, even at temperatures as high as 220 °C.³⁵

Much to our surprise, dimethyldichlorodisilane 15, chosen as a representative model for the “cleavable” fraction of the DPR, does not form dimethyldichlorodisilane 16 upon reaction with 4 equiv LiH but undergoes quantitative cleavage into monosilanes. Most notably, the industrially important bifunctional silanes Me₂SiHCl₂ and Me₃SiHCl comprise almost 80% of the product mixture obtained at RT. We optimized their yield by using substoichiometric amounts of LiH: The reaction with 1.3 equiv LiH yields 8 in almost 90%, with 8 in significant excess (Table 2).

In contrast to our observations for 18 detailed above, the analogous reduction of disilane 1 to yield 16 is not possible with LiH. Instead, Si–Si bond cleavage interferes and 1 is quantitatively converted into monosilanes already at RT (Table 2; oligo-

Table 2. Reaction products from Cl₂Me₂Si–SiMe₂Cl (1) and different molar amounts of LiH (mol%).

| Compound | 1.3 equiv LiH, RT | 1.3 equiv LiH, 60 °C | 2.7 equiv LiH, RT | 2.7 equiv LiH, 60 °C | 4.0 equiv LiH, RT | 4.0 equiv LiH, 60 °C |
|----------|------------------|---------------------|------------------|---------------------|------------------|---------------------|
| MeSiCl₂ (7) | 11 | 1 | 2 | – | 1 | – |
| MeSiH₃Cl (8) | 74 | 49 | 47 | 15 | 32 | 8 |
| MeSiH₂Cl (9) | 15 | 40 | 40 | 44 | 46 | 35 |
| MeSiH (10) | – | 10 | 11 | 41 | 21 | 57 |
gosilanes necessarily formed in this process are not NMR visible. Evidently, partial reduction of 1 has taken place already with 1.3 equiv LiH at RT giving rise to the formation of LiCl, which might trigger chloride-induced disilane disproportionation under these conditions.\(^{[35]}\) This supposition was corroborated in further experiments: treatment of 1 with catalytic amounts of LiCl at RT in polar solvents, such as glymes, THF or 1,4-dioxane, resulted in MeSiCl\(_3\) formation, comprising 50% of the reaction mixture along with unreacted 1 and oligosilanes according to \(^{29}\)Si NMR analysis. Full consumption of 1 is observed at longer reaction times and higher temperatures (Table 3).\(^{[34]}\) This observation contrasts the inability of LiCl to induce cleavage of highly methylated disilane 3; also the fully reduced dimethylsilsilane 16 shows no sign of Si–Si bond cleavage in the presence of LiCl (cf. the Supporting Information).

We thus conclude that reaction of disilane 1 with LiH initially leads to partial reduction and kinetically favored Si–Si bond cleavage sets in, once sufficient amounts of LiCl have formed. The resulting monosilanes, in turn, are then partially reduced by LiH to yield the bifunctional monosilanes observed in the experiments. These findings complement our related study on the disilane cleavage with phosphonium chlorides (cf. section 6 in the Supporting Information). Heating the sample to 180 °C led to carbodisilane reduction and Si–C cleavage to give MeSiH\(_3\) (37%) and Me\(_2\)SiH\(_2\) (31%) as main products, along with the hydridocarbodisilanes 36–39 (32%).\(^{[41]}\) Scheme 2 illustrates a tentative mechanistic suggestion that involves initial hydride-induced Si–C bond cleavage resulting in formation of methylsilanes together with lithium silanides. The latter undergo coupling with chlorinated monosilanes to form disilanes,\(^{[42]}\) which are subsequently cleaved in the presence of excess LiH.\(^{[43]}\)

The suitability of other alkali and alkaline earth metal chlorides to induce disilane disproportionation was investigated in reactions with an industrial DPR mixture (Table S29, Supporting Information). Although disilane conversion was found most effective with LiCl in diglyme, the use of NaCl, KCl, CaCl\(_2\), and MgCl\(_2\) is impeded by their lower solubility. Acceptable reaction rates, however, were found in tetraglyme at 140 °C and above. In exemplary reactions performed at a preparative scale with both, LiCl and KCl, the DPR mixture was efficiently converted: with a maximum theoretical yield of 50% the disproportionation led to 42% monosilanes (predominantly MeSiCl\(_3\) and Me\(_2\)SiCl\(_2\)) (cf. Supporting Information). The residue remaining after distillation of the monosilanes consists of highly methylated disilanes, carbodisilanes and oligosilanes. A broad signal at +35 ppm in the \(^{29}\)Si NMR spectrum of the sample was assigned to branched oligosilanes with terminal Cl\(_2\)MeSi groups. Slightly higher conversion ratios were obtained with LiCl at 220 °C.\(^{[44]}\)

Conclusions

In summary, we have shown that chlorosilane reduction is possible with lithium hydride, which thereby is established as economically favorable alternative to LiAlH\(_4\). We have further shown that LiCl, formed in the course of the reduction of chlorinated disilanes with LiH, acts as an efficient catalyst to trigger disproportionation of disilanes bearing SiMe\(_X\) groups (X=H, Cl) into the corresponding mono- and higher oligosi-
lanes.[45] Si–Si bond cleavage of highly methylated as well as perhydrogenated disilanes was not observed with lithium chloride. We found, however, that lithium hydride efficiently triggers disproportionation of perhydrogenated disilanes into MeSiH₃, Me₂SiH₂, and Me₃SiH and oligosilanes.

**Experimental Section**

**General procedure for disilane cleavage reactions**

For the elucidation of the reaction conditions, disilanes Me₂SiCl₂ₙ (ₙ = 2–6) were isolated from the DFR by fractional distillation and investigated as pure model compounds or in complex mixtures. The reactants for example, HCl/ether solutions, catalysts and solvents were placed in an NMR tube under nitrogen atmosphere and investigated to avoid losses of low boiling monosilanes, such as MeSiH, (b.p. 28 °C), Me₂SiH₂, (b.p. 20 °C), Me₃SiH₃, (b.p. 46 °C), Me₄SiH₄, (b.p. 41 °C) and Me₅SiH₅, (b.p. 35 °C). After warming the mixture to RT the reaction temperatures were increased, and the course of reaction was followed by NMR spectroscopy, especially by ²⁵²⁹Si NMR. The molar ratios of products formed were determined by integration of product specific NMR signals of the resulting mixtures. According to the optimum reaction conditions evaluated for the experiments in sealed NMR tubes, alternatively, upscaling was performed in open systems. This procedure is described in the Supporting Information.[46]

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**Conflict of interest**

The authors declare no conflict of interest.

**Keywords:** alkali and alkaline earth metal salts • disilane cleavage • lithium chloride • lithium hydride • monosilanes.
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[37] We note in passing that additional formation of Me3SiH sets in upon heating the same sample to 160 °C and becomes more prominent at 200 °C (cf. Supporting Information). It is tempting to assume that this process involves decomposition of higher oligosilanes, but in the absence of further spectroscopic evidence we refrain from mechanistic speculations.

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[43] The general applicability of the procedure was demonstrated for an authentic industrial DPR mixture representing the conventionally “un cleavable” fraction as detailed in the Supporting Information. Alternative hydride donors such as sodium or calcium hydride require higher temperatures to induce the same reactivity.

[44] In case LiH was used for oligosilane cleavage at 180 °C, MeSiH3 (10) was formed in 52 %, MeSiH2Cl (9) in 28 % as NMR detectable thermolysis products. The oligosilanes were cleaved as indicated by the disappearance of the corresponding 29Si NMR signal of the sample (SI 9).

[45] We have shown in earlier work that highly chlorinated disilanes can efficiently be cleaved with concentrated ether/HCl solutions in the presence of catalytic amounts of phosphines and phosphonium chlorides (ref. [40]). In the present context, we have found that this cleavage reaction can be catalyzed by LiCl instead of phosphonium chlorides with equal efficiency. Reaction of a disilane mixture mainly consisting of 1 (50 %) and 2 (33 %) with a 12 m diglyme/HCl solution (1:1 molar ratio disilanes/HCl) in the presence of catalytic amounts of LiCl led to nearly quantitative monosilane formation (97 %, 80 °C). The corresponding reaction with KCl yielded monosilanes but was less efficient (70 % conversion to monosilanes, 100 °C; cf. SI 12 and 13).

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