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# Unusually selective synthesis of chlorohydrooligosilanes†

Thomas Lainer,[a] Roland Fischer,[a] Mario Leypold,[a] Michael Holthausen,[b] Odo Wunnicke,[b] Michael Haas *[a] and Harald Stueger *[a]

**New pathways towards molecular chlorohydrooligosilanes enable their one-pot synthesis in preparative amounts either by the selective chlorination of the corresponding perhydrosilanes with HCl/$AlCl_3$ or by the partial hydrogenation of perchlorooligosilanes with substoichiometric amounts of $iBu_2AlH$. The unexpected selective formation of $Cl_3Si$-substituted species in the partial hydrogenation reactions could be related to mechanistic aspects.**

Chlorosilanes, especially chlorohydrosilanes, are ideal precursors for the generation of hyperpure polycrystalline silicon. Because of the dramatic rise of photovoltaic applications, the production capacity of polysilicon reached 600 kton per year at the end of 2018.[1] The vast majority of polycrystalline Si produced worldwide is made by the chemical vapor deposition of $HSiCl_3$.[2] Less than 10% of all solar grade silicon is currently manufactured from silicon hydrides such as $SiH_4$ in spite of their lower decomposition temperatures and the resulting lower energy cost incurred during the deposition process. The major drawbacks of silicon hydrides are their high production costs and difficulty in handling because of their pyrophoric nature. Therefore, the search for alternative precursor materials for silicon deposition is still an issue of primary importance.[3]

Based on calculations, two mechanisms for the deposition of silicon from $HSiCl_3$ are possible. The disilane mechanism proposed by Swihart and Carr *et al.*[4] and the radical mechanism by Cavallotti *et al.*[5] In both mechanisms, the formation of disilanes as reaction intermediates plays a crucial role by enhancing the gas phase reactivity. This is due to their increased reactivity, determined by the relatively low Si–Si bond energy and small barriers for Cl and H intramolecular transfers. Therefore, it can be anticipated that chlorohydrooligosilanes will outperform the state-of-the-art precursors concerning their film deposition properties. A recently published study actually showed the formation of higher quality films at higher deposition rates using atomic layer deposition (ALD) processes for the precursor molecule $HSi_2Cl_5$ as compared to $Si_2Cl_6$.[6]

However, the state-of-the-art synthetic protocols of chlorohydrooligosilanes are not straightforward. Partial halogenation reactions of di-, tri- and tetrasilane with $BX_3$, $HX/AlX_3$, AgX, $SnX_4$, $HgX_2$ or $X_2$ (X = Cl, Br, I) afforded product mixtures which could only be analyzed after further derivatization of the initial products.[7] The partial hydrogenation of perchlorooligosilanes by treatment with substoichiometric amounts of $LiAlH_4$ or $Bu_3SnH$ was also found to be rather unselective.[8,9] Additionally, selected halohydrooligosilanes were prepared by the halodephenylation of appropriately substituted phenylated precursors with anhydrous HX.[10] The challenge of this method is the preparation of the starting materials which frequently involves tedious multi-step procedures. In a more recent study, we observed the clean formation of 1,2,3,4-tetrachloroneopentasilane **2** after treatment of neopentasilane **1** with 3.5 equivalents of $SnCl_4$.[11] To the best of our knowledge this was the first example of a direct and selective functionalization of a higher silicon hydride on a preparative scale.

A major disadvantage of $SnCl_4$ as a halogenating reagent is the formation of huge amounts of $SnCl_2$, which are difficult to remove completely, particularly on a larger scale. Thus, we investigated the chlorination of neopentasilane with gaseous HCl in the presence of $AlCl_3$ as the catalyst. When dry HCl gas was bubbled through a benzene solution of neopentasilane containing catalytic amounts of $AlCl_3$ at 70 °C for 15 minutes, compound **2** was obtained with remarkable selectivity along with 1,2,3-trichloroneopentasilane **3** as the by-product (Scheme 1). Removal of the solvent and the catalyst and recondensation of the crude product afforded a mixture of **2** (85%) and **3** (15%) in >60% yield. Attempts to separate both components using distillation or crystallization were unsuccessful.

An even more appealing approach to chlorohydrooligosilanes is the partial hydrogenation of perchlorooligosilanes with substoichiometric amounts of $iBu_2AlH$. This pathway enables the

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[a] *Institute of Inorganic Chemistry, Technische Universität Graz, Stremayrgasse 9/IV, Graz 8010, Austria. E-mail: michael.haas@tugraz.at, harald.stueger@tugraz.at*
[b] *Evonik Creavis GmbH, Paul-Baumann-Strasse 1, Marl 45772, Germany*

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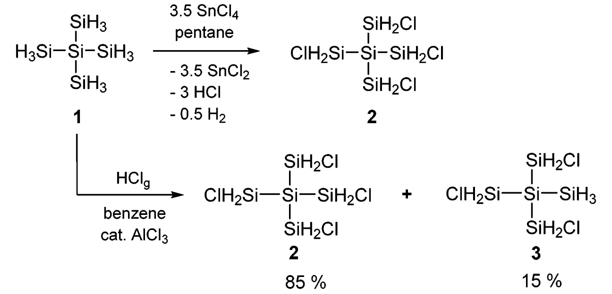
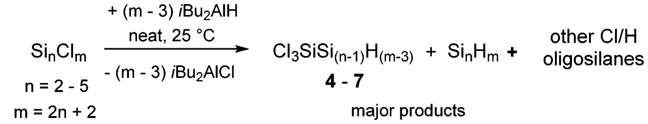


Scheme 1 Partial chlorination of neopentasilane with SnCl$_4$ and HCl/AlCl$_3$.



Scheme 2 General scheme for the partial hydrogenation of perchloro-oligosilanes with iBu$_2$AlH.

synthesis of chlorohydrooligosilanes on a broader scope. In recent studies it has been found that iBu$_2$AlH is suitable for the hydrogenation of linear and branched chlorooligosilanes under mild reaction conditions without the formation of any Si–Si bond scission products.[12] When we reacted hexachlorodisilane (Si$_2$Cl$_6$), octachlorotrisilane (Si$_3$Cl$_8$), nonachloroisotetrasilane ClSi(SiCl$_3$) or dodecachloroneopentasilane Si(SiCl$_3$)$_4$ with sub-stoichiometric quantities of iBu$_2$AlH, we observed the predominant formation of the corresponding 1,1,1-trichlorooligosilanes **4–7** with unexpected selectivity (Table 1). SiHCl$_2$- and SiH$_2$Cl-moieties were only detected in minor side products. Based on screening experiments, we determined that the ideal amount of iBu$_2$AlH equals the number of chlorine atoms minus three. If more equivalents of iBu$_2$AlH were used, the completely hydrogenated species were formed as the major products. Application of less equivalents of iBu$_2$AlH afforded increasing portions of higher chlorinated polysilanes.

This new synthetic method can be performed in the absence of any solvent at room temperature, which enabled the isolation of **4–7** along with the corresponding perhydrogenated species and small amounts of other Cl/H silanes using trap-to-trap distillation under vacuum. The structures and relative quantities of the individual species present in the volatile fraction were assigned using NMR spectroscopy. (The corresponding experimental data and procedures are included in the ESI.†) If Si$_2$Cl$_6$ was used as the precursor the volatile fraction additionally contained considerable amounts of 1,1,1,2-tetrachlorodisilane. In all other cases, higher chlorinated species could not be separated from iBu$_2$AlCl and ended up in the high boiling residue of the vacuum condensation along with some unreacted starting material. For Si$_3$Cl$_8$ the addition of excess iBu$_2$AlH to the higher boiling product fraction afforded a further 0.6 g of Si$_3$H$_8$ which means a more or less quantitative conversion of the starting material to chlorohydrotrisilanes. Extensive side reactions such as Si–Si bond scission or oligomerization, thus, can be ruled out. Yields calculated for **4–7** on the basis of the relative intensities of $^1$H-NMR signals range between 28 and 39%.

Very recently, neopentasilane and its derivatives have attracted considerable attention as precursors for the deposition of silicon and silicon heterostructures.[13] Thus, we decided to study compound **7** in more detail. **7** could be isolated from the crude product mixture obtained according to Scheme 2 from the reaction of Si(SiCl$_3$)$_4$ with 9 equiv. of iBu$_2$AlH by fractional distillation as a colorless oil in about 20% yield and characterized by comparing its NMR data with literature values.[14] The resulting samples were reasonably pure but still contained small amounts of neopentasilane **1** and iBu$_2$AlCl. For the isolation of pure **7** the application of more sophisticated distillation techniques would be necessary, which was beyond the scope of this study.

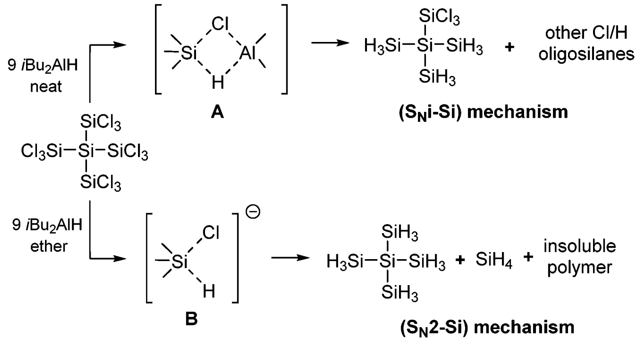
For nucleophilic substitution reactions of chlorosilanes a reactivity order of R$_3$SiCl < R$_2$SiCl$_2$ < RSiCl$_3$ < SiCl$_4$ is usually found due to the impact of the electronegative Cl substituents at the silicon center.[15] Attempts to partially hydrogenate polychlorosilanes with substoichiometric amounts of LiAlH$_4$, thus, only afforded more or less statistical mixtures of various chlorohydrosilanes.[8]

The unexpected selectivity of the hydrogenation reactions with iBu$_2$AlH towards the formation of 1,1,1-trichlorosilanes **4–7** as described above can be easily rationalized if mechanistic aspects are taken into account. Based on stereochemical arguments it has been proposed that the hydrogenation of chlorosilanes with iBu$_2$AlH in non-coordinating solvents like hexane follows a S$_N$i–Si-mechanism involving a four-center transition state **A**. In diethyl ether, on the contrary, the same hydrogenation reaction proceeds *via* a pentacoordinated transition state **B** typical for S$_N$2 reactions (Scheme 3).[16]

Table 1 Summary of experimental results of the partial hydrogenation of perchlorooligosilanes with iBu$_2$AlH

| Precursor | Equiv. iBu$_2$AlH | Molar ratio of main products[a] | Yield of Cl$_3$SiSi$_n$H$_m$[a] (%) |
|---|---|---|---|
| Si$_2$Cl$_6$ | 3 | Cl$_3$SiSiH$_3$ (**4**) (54%); ClH$_2$SiSiCl$_3$ (40%); Si$_2$H$_6$ (6%)[b] | 39 |
| Si$_3$Cl$_8$ | 5 | Cl$_3$SiSiH$_2$SiH$_3$ (**5**) (67%); Si$_3$H$_8$ (33%)[b] | 36 |
| ClSi(SiCl$_3$)$_3$ | 6 | Cl$_3$SiSiH(SiH$_3$)$_2$ (**6**) (57%); HSi(SiH$_3$)$_3$ (43%)[c] | 28 |
| Si(SiCl$_3$)$_4$ | 9 | Cl$_3$SiSi(SiH$_3$)$_3$ (**7**) (11%); Si(SiH$_3$)$_4$ (89%)[d] | 2 |
| | | Cl$_3$SiSi(SiH$_3$)$_3$ (**7**) (67%); Si(SiH$_3$)$_4$ (33%)[e] | 28 |

[a] Calculated by integrating $^1$H-NMR signals of the volatile fraction after trap-to-trap distillation. [b] Trap-to-trap distillation at room temperature and 0.01 mbar. [c] Trap-to-trap distillation at 50 °C and 0.01 mbar. [d] Fraction 1: trap-to-trap distillation at 50 °C and 0.01 mbar. [e] Fraction 2: subsequent trap-to-trap distillation of the high boiling fraction at 80 °C and 0.01 mbar.



Scheme 3 Mechanism of partial hydrogenation of **7**.

DFT calculations at the SMD (pentane) M06-2X-D3/aug-cc-pVTZ level of theory were performed on the reaction of $Cl_3SiSiCl_3$, $H_3SiSiCl_3$, $H_3SiSiHCl_2$, and $H_2SiSiH_2Cl$ with $HAlMe_2$. For $Cl_3SiSiCl_3$ which is the best suited test system, we were not able to locate all structures (ground states and transition states) on the energy surface. For $H_3SiSiCl_3$, $H_3SiSiHCl_2$, and $H_2SiSiH_2Cl$ the reaction path *via* intermediate/transition state **A** did not show any selectivity in terms of calculated activation energies ((1) reduction step: $\Delta\Delta G^0_{AE}$ = 8.6 kcal mol$^{-1}$; (2) reduction step: $\Delta\Delta G^0_{AE}$ = 9.6 kcal mol$^{-1}$; (3) reduction step: $\Delta\Delta G^0_{AE}$ = 11.6 kcal mol$^{-1}$). In contrast, the calculated activation energies would favor a slightly preferred reaction at the higher chlorinated Si atom, contradicting our experimental observations. Thus, we attribute the unexpected selectivity of our hydrogenation reactions in non-coordinating solvents more to a steric than to an electronic effect. We reasoned that due to the presence of the sterically demanding iBu-groups in transition state **A** further substitution preferably occurs at the sterically less encumbered Si-center, which is the Si atom bearing already one or two hydrogens leaving the residual $SiCl_3$ groups rather untouched. This steric effect more or less outperforms the electronic influence of the Cl substituents mentioned above leading to the predominant formation of products **4–7** containing exclusively $Cl_3Si$- and $H_3Si$-moieties. Further support for this picture was gained from the observation that the reduction of **7** with $iBu_2AlH$ in diethyl ether does not show any selectivity. When **7** was reacted with substoichiometric amounts of $iBu_2AlH$ in diethyl ether solution only small amounts of neopentasilane **1** were formed along with insoluble polymeric material and $SiH_4$. In this case the hydrogen atom in $iBu_2AlH–Et_2O$ containing formally tetravalent aluminum is far more hydridic and nucleophilic and the reaction proceeds *via* a $S_N2$ mechanism.[16b] As a consequence the reduction is accompanied by Si–Si bond scission and redistribution reactions and occurs rather unselectively just as found for the hydrogenation of chlorosilanes with $LiAlH_4$ in diethyl ether.

In conclusion, we have introduced two new innovative strategies for the synthesis of chlorohydrooligosilanes in gram quantities. In particular, it has been discovered that substoichiometric amounts of neat $iBu_2AlH$ react with perchlorooligosilanes, resulting in the formation of products containing exclusively $Cl_3Si$- and $H_3Si$-moieties. Si–Si bond scission and oligomerization reactions do not occur at all which contrasts the behavior of the more common hydrogenation reagent $LiAlH_4$/diethyl ether described in the literature. Different reaction mechanisms ($S_N2$–Si and $S_Ni$–Si) operative in polar and unpolar environments could be made responsible for this unexpected discrepancy. The target molecules of this study are of particular importance for potential applications as alternative precursors for the deposition of hyperpure polycrystalline silicon. Corresponding experiments are currently underway in our laboratories.

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## Conflicts of interest

There are no conflicts to declare.

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