Unusually selective synthesis of chlorohydrooligosilanes†

Thomas Lainer, Roland Fischer, Mario Leypold, Michael Holthausen, Odo Wunnicke, Michael Haas and Harald Stueger

New pathways towards molecular chlorohydrooligosilanes enable their one-pot synthesis in preparative amounts either by the selective chlorination of the corresponding perhydrosilanes with HCl/AlCl3 or by the partial hydrogenation of perchlorooligosilanes with substoichiometric amounts of iBu2AlH. The unexpected selective formation of Cl3Si-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 HSiCl3.2 Less than 10% of all solar grade silicon is currently produced 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 SnCl4.11 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 SnCl4 as a halogenating reagent is the formation of huge amounts of SnCl2, 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 AlCl3 as the catalyst. When dry HCl gas was bubbled through a benzene solution of neopentasilane containing catalytic amounts of AlCl3 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 iBu2AlH. This pathway enables the...
synthesis of chlorohydrooligosilanes on a broader scope. In recent studies it has been found that iBu2AlH 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 (Si2Cl6), octachlorotrisilane (Si3Cl8), nonachlorotetrasilane ClSi(SiCl3)2 or dodecachloropentasilane Si3Cl13 with substoichiometric quantities of iBu2AlH, we observed the predominant formation of the corresponding 1,1,1-trichlorooligosilanes 4–7 with unexpected selectivity (Table 1). SiHCl2- and SiH2Cl-moieties were only detected in minor side products. Based on screening experiments, we determined that the ideal amount of iBu2AlH equals the number of chlorine atoms minus three. If more equivalents of iBu2AlH were used, the completely hydrogenated species were formed as the major products. Application of less equivalents of iBu2AlH 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 ESL†) If Si2Cl6 was used as the precursor the volatile fraction addition contained considerable amounts of 1,1,1,2-tetrachlorodisilane. In all other cases, higher chlorinated species could not be separated from iBu2AlCl and ended up in the high boiling residue of the vacuum condensation along with some unreacted starting material. For Si3Cl8 the addition of excess iBu2AlH to the higher boiling product fraction afforded a further 0.6 g of Si3H8 which means a more or less quantitative conversion of the starting material to chlorohydrosilanes. 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 1H-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 Si3Cl13 with 9 equiv. of iBu2AlH 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 iBu2AlCl. 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 R3SiCl < R2SiCl2 < RSiCl3 < SiCl4 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 LiAlH4, thus, only afforded more or less statistical mixtures of various chlorohydrosilanes.8

The unexpected selectivity of the hydrogenation reactions with iBu2AlH towards the formation of 1,1,1-trichlorooligosilanes 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 iBu2AlH in non-coordinating solvents like hexane follows a Sn2-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 Sn2 reactions (Scheme 3).16

Table 1  Summary of experimental results of the partial hydrogenation of perchlorooligosilanes with iBu2AlH

| Precursor                | Equiv. iBu2AlH | Molar ratio of main products$^a$ | Yield of ClSiSiHmHn$^a$ (%) |
|-------------------------|---------------|----------------------------------|-----------------------------|
| Si2Cl6                  | 3             | Cl2SiSiH4 (4) [54%]; CH3SiSiCl4 (40%); Si3H6 (6%)$^b$ | 39                          |
| Si3Cl8                  | 5             | Cl2SiSiH4SiH3 (5) [67%]; Si3H6 (33%)$^f$ | 36                          |
| ClSi(SiCl3)3            | 6             | Cl2SiSiH(3)SiH3 (6) [37%]; HSi(SiH3) (43%)$^e$ | 28                          |
| Si(SiCl4)4              | 9             | Cl3SiSi(3)SiH3 (7) [11%]; Si(SiH3)4 (89%)$^d$ | 2                           |
|                         |               | Cl2SiSiH(3)SiH3 (6) [67%]; Si(SiH3)4 (33%)$^e$ | 28                          |

$^a$ Calculated by integrating 1H-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.
DFT calculations at the SMD (pentane) M06-2X-D3/aug-cc-pVTZ level of theory were performed on the reaction of Cl₃SiSiCl₃, H₂SiSiCl₃, H₂SiSiHCl₂, and H₂SiSiH₂Cl with HAlMe₂. For Cl₃SiSiCl₃ 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 H₂SiSiCl₃, H₂SiSiHCl₂, and H₂SiSiH₂Cl the reaction path via intermediate/transition state A did not show any selectivity in terms of calculated activation energies ((1) reduction step: ΔΔG°AE = 8.6 kcal mol⁻¹; (2) reduction step: ΔΔG°AE = 9.6 kcal mol⁻¹; (3) reduction step: ΔΔG°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 SiCl₃ 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 Cl₂Si- and H₂Si-moieties. Further support for this picture was gained from the observation that the reduction of 7 with iBu₂AlH in diethyl ether does not show any selectivity. When 7 was reacted with substoichiometric amounts of iBu₂AlH in diethyl ether solution only small amounts of neopentasilane 1 were formed along with insoluble polymeric material and SiH₄. In this case the hydrogen atom in iBu₂AlH–Et₂O containing formally tetravalent Cl₃SiSiCl₃ which is the best suited test system, we were not able to show any selectivity in terms of calculated activation energies ((1) reaction path to locate all structures (ground states and transition states) on the energy surface. For H₂SiSiCl₃, H₂SiSiHCl₂, and H₂SiSiH₂Cl the reaction path via intermediate/transition state A did not show any selectivity in terms of calculated activation energies ((1) reduction step: ΔΔG°AE = 8.6 kcal mol⁻¹; (2) reduction step: ΔΔG°AE = 9.6 kcal mol⁻¹; (3) reduction step: ΔΔG°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 SiCl₃ 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 Cl₂Si- and H₂Si-moieties. Further support for this picture was gained from the observation that the reduction of 7 with iBu₂AlH in diethyl ether does not show any selectivity. When 7 was reacted with substoichiometric amounts of iBu₂AlH in diethyl ether solution only small amounts of neopentasilane 1 were formed along with insoluble polymeric material and SiH₄. In this case the hydrogen atom in iBu₂AlH–Et₂O containing formally tetravalent aluminum is far more hydridic and nucleophilic and the reaction proceeds via a S₈2 mechanism. 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 LiAlH₄ 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 iBu₂AlH react with perchloro-oligosilanes, resulting in the formation of products containing exclusively Cl₂Si- and H₂Si-moieties. Si–Si bond scission and oligomerization reactions do not occur at all which contrasts the behavior of the more common hydrogenation reagent LiAlH₄/diethyl ether described in the literature. Different reaction mechanisms (S₈2-Si and S₈-I-Si) operative in polar and unpolared 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.

This work was supported via a government financed project by the “Austrian Klima und Energiefonds” in the framework of the Austrian energy research project 2015 (FFG Project No. 858491 “Liquid Silicon 2.0”) and the NRW Ministry of Economic Affairs of the state North Rhine-Westphalia (funding code W49, “Liquid Silicon 2.0”). We gratefully acknowledge additional financial support from the Evonik Creavis GmbH.

Conflicts of interest

There are no conflicts to declare.

Notes and references
1. Research Report on Global and China’s Polysilicon Industries, 2019–2023, available athttp://www.researchandmarkets.com.
2. [a] F. Chigondo, Silicon, 2018, 10, 79–79; [b] S. Yadav, K. Chattopadhyay and C. S. Virg, Renewable Sustainable Energy Rev., 2017, 78, 1288–1314.
3. [a] W. O. Filletvdt, A. Holt, P. A. Ramachandran and M. C. Melaen, Sol. Energy Mater. Sol. Cells, 2012, 107, 188–200; [b] G. Bye and B. Ceccaroli, Sol. Energy Mater. Sol. Cells, 2014, 130, 634–646; [c] K. Yasuda, K. Morita and T. H. Okabe, Energy Technol., 2014, 2, 141–154.
4. [a] M. T. Swihart and R. W. Carr, J. Phys. Chem. A, 1997, 101, 7434–7445; [b] M. T. Swihart and R. W. Carr, J. Phys. Chem. A, 1998, 102, 775–792; [c] M. T. Swihart and R. W. Carr, J. Phys. Chem. A, 1998, 102, 1542–1549.
5. S. Ravasio, M. Masii and C. Cavallotti, J. Phys. Chem. A, 2013, 117, 5221–5231.
6. X. Meng, H. S. Kim, A. T. Lucero, S. M. Hwang, J. S. Lee, Y.-C. Byun, J. Kim, B. K. Hwang, X. Zhou, J. Young and M. Telgenhoff, ACS Appl. Mater. Interfaces, 2018, 10, 14116–14123.
7. [a] M. Abedini, C. H. van Dyke and A. G. MacDiarmid, J. Inorg. Nucl. Chem., 1963, 25, 307–309; [b] R. P. Hollandsworth and M. A. Ring, Inorg. Chem., 1968, 7, 1635–1637; [c] E. D. Drake and N. Goddard, J. Chem. Soc. A, 1970, 2587; [d] F. Feher, P. Plichta and R. Guillery, Chem. Ber., 1970, 103, 3028–3033; [e] E. Benthom, S. Cradock and E. A. V. Esbworth, Inorg. Nucl. Chem. Lett., 1971, 7, 1077–1079; [f] F. Feher, P. Plichta and R. Guillery, Inorg. Chem., 1971, 10, 606–608; [g] T. C. Geisler, C. E. Cooper and A. D. Norman, Inorg. Chem., 1972, 11, 7170–7171; [h] N. S. Hosmane, Inorg. Nucl. Chem. Lett., 1974, 10, 1077–1079; [i] F. Feher and F. Oekelenburg, Z. Anorg. Allg. Chem., 1984, 515, 35–40; [j] E. D. Drake, N. Goddard and N. P. C. Westwood, J. Chem. Soc. A, 1971, 3305–3308.
8. U. Herzog, G. Roewer and U. Pätzold, J. Organomet. Chem., 1995, 494, 143–147.
9. U. Herzog and G. Roewer, J. Organomet. Chem., 1997, 544, 217–223.
10. [a] K. Hassler and M. Pöschl, J. Organomet. Chem., 1990, 398, 225–227; [b] K. Hassler and W. Köll, J. Organomet. Chem., 1997, 540, 113–118; [c] H. Stüger, J. Organomet. Chem., 1992, 433, 11–19; [d] H. Stüger, J. Organomet. Chem., 1993, 458, 1–7; [e] H. Stüger and P. Lassacher, J. Organomet. Chem., 1993, 450, 79–84.
11. H. Stueger, T. Mitterfellner, R. Fischer, C. Walker, M. Patz and S. Wieber, Inorg. Chem., 2012, 51, 6173–6179.
12. [a] H. Stueger, T. Mitterfellner, R. Fischer, C. Walkner, M. Patz and S. Wieber, Chem. – Eur. J., 2012, 18, 7662–7664; [b] J. P. Cannady and X. Zhou, WO2008/051328, 2008; [c] V. Christopoulos, M. Rotzinger, M. Gerwig, J. Seidel, E. Kroke, M. Holthausen, O. Wunnicke,
A. Torvisco, R. Fischer, M. Haas and H. Stueger, Inorg. Chem., 2019, 58, 8820–8828.

13 (a) F. Porrati, B. Kämpfe, A. Terfort and M. Huth, J. Appl. Phys., 2013, 113, 53707; (b) F. Porrati, R. Sachser, G. C. Gazzadi, S. Frabboni and M. Huth, J. Appl. Phys., 2016, 119, 234306; (c) M. Winhold, C. H. Schwalb, F. Porrati, R. Sachser, A. S. Frangakis, B. Kämpfe, A. Terfort, N. Auner and M. Huth, ACS Nano, 2011, 5, 9675–9681; (d) T. Bronger, P. H. Wöbkenberg, J. Wördener, S. Muthmann, U. W. Paetzold, V. Smirnov, S. Traut, Ü. Dagkaldiran, S. Weißen, M. Cölle, A. Prodi-Schwab, O. Wunnicke, M. Patz, M. Trocha, U. Rau and R. Carius, Adv. Energy Mater., 2014, 4, 1301871.

14 M. Haas, V. Christopoulos, J. Radebner, M. Holthausen, T. Lainer, L. Schuh, H. Fitzek, G. Kothleitner, A. Torvisco, R. Fischer, O. Wunnicke and H. Stueger, Angew. Chem., 2017, 129, 14259–14262.

15 Compare. (a) I. Fleming, Comprehensive organic chemistry, in The synthesis and reactions of organic compounds, ed. D. Neville Jones, D. H. R. Barton and D. N. Jones, Pergamon Press, Oxford, 1st edn, 1979, pp. 541–686; (b) A. F. Holleman, E. Wiberg and N. Wiberg, Lehrbuch der anorganischen Chemie, de Gruyter, Berlin, 101st edn, 1995, p. 908.

16 (a) L. H. Sommer, J. McLick and C. M. Golino, J. Am. Chem. Soc., 1972, 94, 669–670; (b) L. H. Sommer, C. M. Golino, D. N. Roark and R. D. Bush, J. Organomet. Chem., 1973, 49, C3–C5.