Convenient Synthesis of Si_6H_{12} from Si_2Cl_6

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Introduction

Thin films of nano-crystalline, micro-crystalline and amorphous silicon (Si) are and will be an important element of present and future semiconductors. Until today such Si-films are made through gas-phase deposition of smaller silanes. Those silanes are obtained from the reduction of the corresponding chlorosilanes. A promising approach to improve the manufacturing of Si-films are solution-based methods, such as spin-, spray- or printing-processes. Therefore, higher oligosilanes with boiling points significantly higher than their deposition temperatures are in demand. It is expected that silanes consisting of 10 or more Si-atoms meet those requirements best. Known synthetic routes are much too laborious and expensive to be used in large-scale production, it is a necessity to develop synthesis strategies that give easy access to precursor oligochlorosilanes.

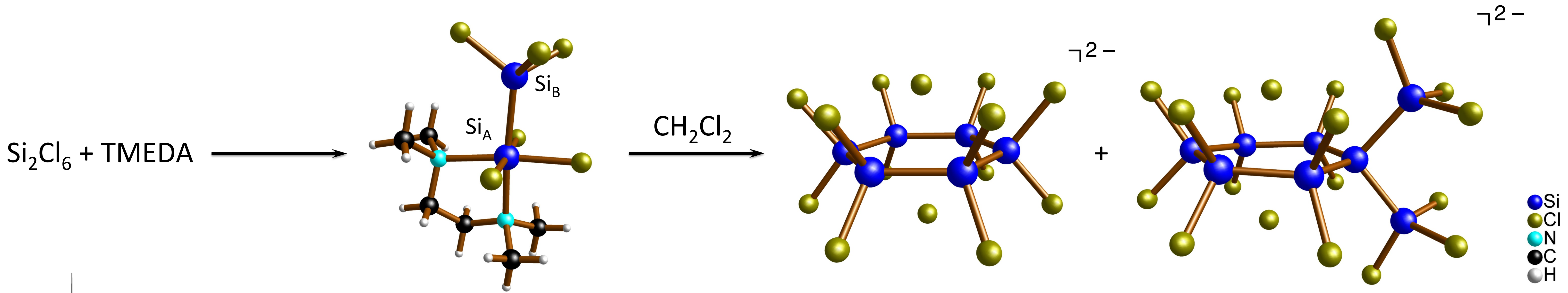
$$Si_xCl_y \xrightarrow{\text{reduction}} Si_xH_y \xrightarrow{\text{deposition}} \text{thin Si-films}$$

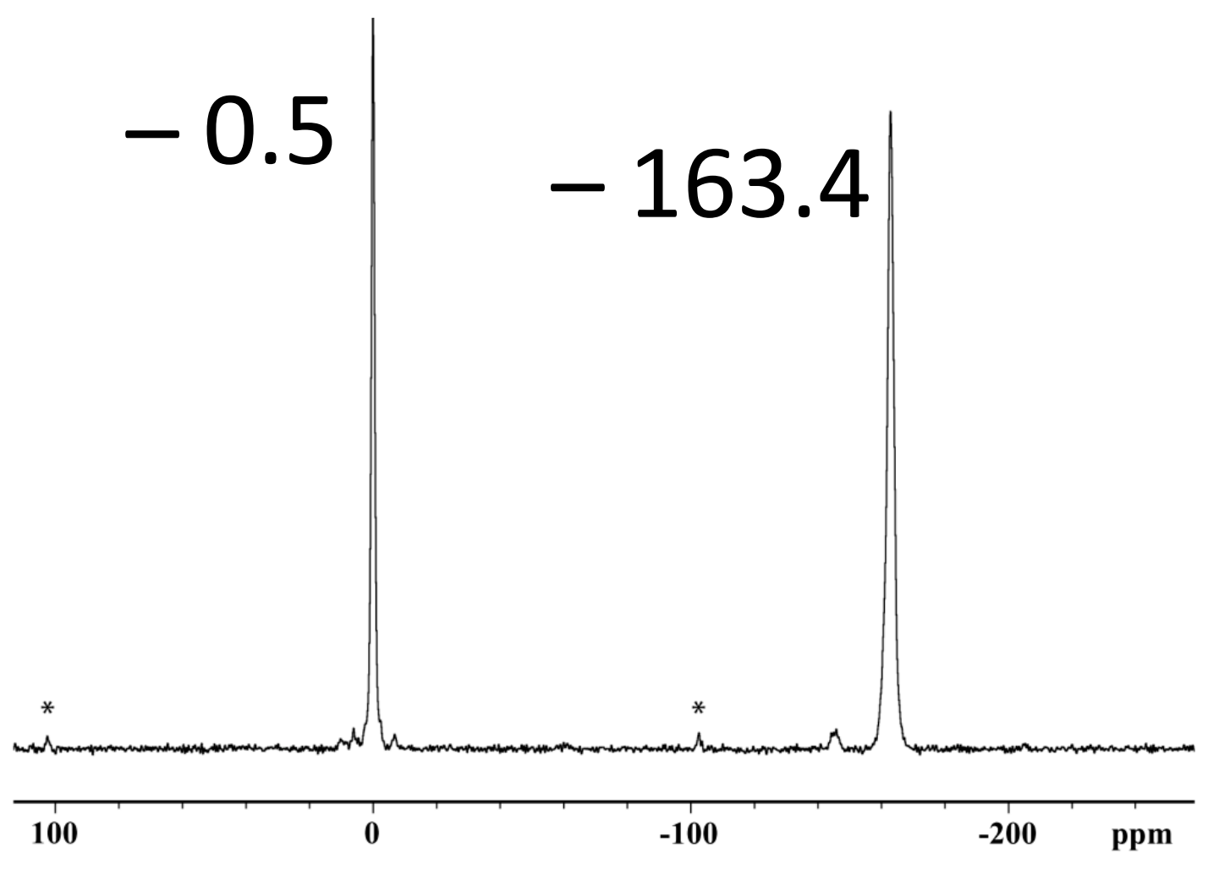
Past and Present (x: 1–4; y: 4–10)
- silanes are pyrophoric gases / low-boiling liquids
- gas-phase deposition methods
- large-scale production is not possible

Future (x: 10–14; y: 20–30)
- silanes are rather stable liquids
- solution-based deposition methods
- high-throughput production

Disproportionation of $Si_2Cl_6 \cdot$ TMEDA

The amine-induced disproportionation of Si_2Cl_6 leading to $Si(SiCl_3)_4$ and $SiCl_4$ has been known for years.[1] In contrast to this we have recently shown that tetramethylethylenediamine (TMEDA) forms the stable adduct $Si_2Cl_6 \cdot$ TMEDA.[2] This new compound dissolves in CH_2Cl_2 and undergoes redistribution and disproportionation to give (silylated) Si_6Cl_{12}-rings. These rings are coordinated at both faces by chloride ions and therefore show inverse sandwich structure. This structural motif was first described by Boudjouk *et al.*[3]





^{29}Si CP/MAS NMR spectrum of $Si_2Cl_6 \cdot$ TMEDA

$Si_2Cl_6 \cdot$ TMEDA

$Si_A - Si_B$	2.405 Å
$Si_A - N_{equatorial}$	2.113 Å
$Si_A - N_{axial}$	2.064 Å
average Si_A – Cl	2.188 Å
average Si_B – Cl	2.062 Å

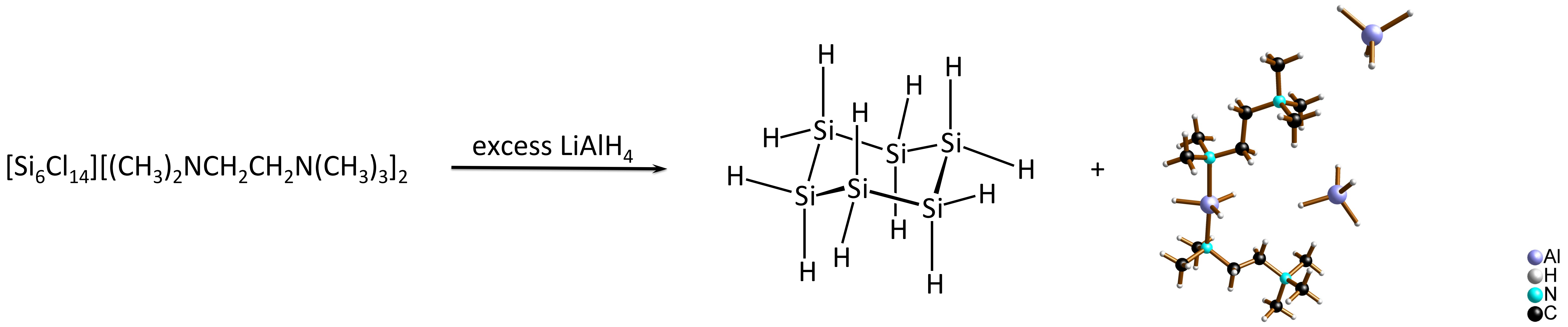
$[Si_6Cl_{14}]^{2-}$
$[(CH_3)_2NCH_2CH_2N(CH_3)_3]^+_2$

average Si – Si	2.322 Å
average Si – Cl	2.075 Å
average Si ····· Cl⁻	3.020 Å
Cl⁻ ····· Cl⁻	3.860 Å

$[Si_8Cl_{18}]^{2-}$
$[(CH_3)_2NCH_2CH_2N(CH_3)_3]^+_2$

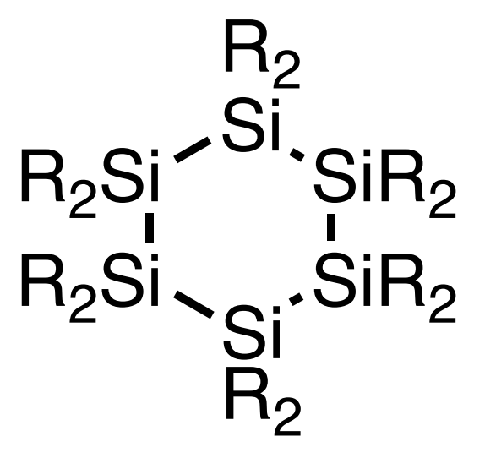
average $Si_{cyc} - Si_{cyc}$	2.322 Å
average Si_{cyc} – Cl	2.079 Å
average Si_{cyc} ····· Cl⁻	3.014 Å
Cl⁻ ····· Cl⁻	3.864 Å
average $Si_{cyc} - Si_{term}$	2.361 Å
average Si_{term} – Cl	2.036 Å

Hydrogenation of $[Si_6Cl_{14}][(CH_3)_2NCH_2CH_2N(CH_3)_3]_2$



Summary / Outlook

Through disproportionation of $Si_2Cl_6 \cdot$ TMEDA we were able to assemble Si_3-bridged-neopentasilane. Currently, efforts are made to isolate $Si_{10}Cl_{20}$ and $Si_{12}Cl_{24}$. Evidence for their existence was found (as $Si_{10}Cl_{22}^{2-}$ and $Si_{12}Cl_{26}^{2-}$) in the MALDI⁻ spectra of the reaction mixture.
The question why the substitution of the Si_6-ring occurs at least twice and at the same Si-atom remains to be answered.



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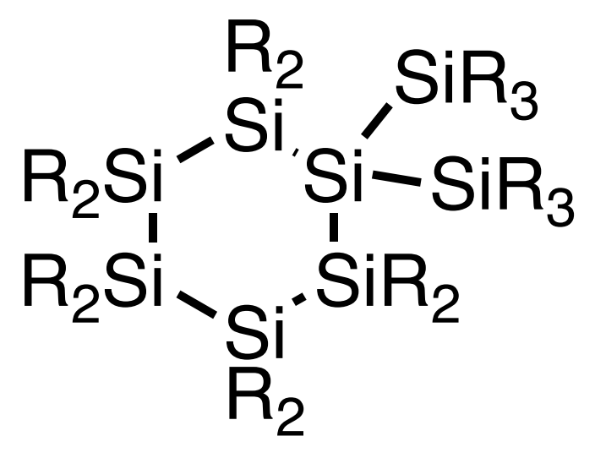
Si_6R_{12}



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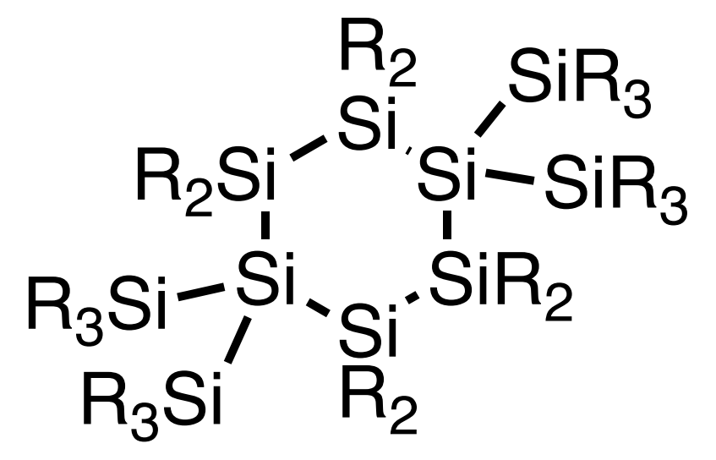
Si_8R_{16}



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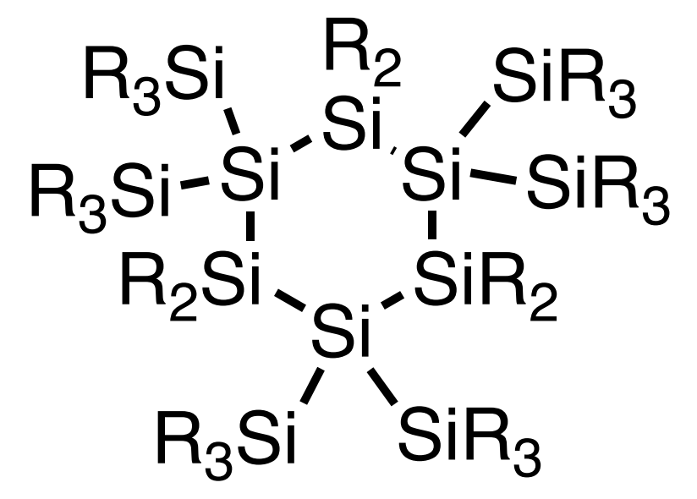
$Si_{10}R_{20}$



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$Si_{12}R_{24}$

R: Cl / H

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[1] F. Meyer-Wegner, A. Nadj, M. Bolte, N. Auner, M. Wagner, M. C. Holthausen, H.-W. Lerner, *Chem. Eur. J.* **2011**, 17, 4715 – 4719
[2] J. Tillmann, F. Meyer-Wegner, A. Nadj, J. Becker-Baldus, T. Sinke, M. Bolte, M. C. Holthausen, M. Wagner, H.-W. Lerner, *Inorg. Chem.* **2012**, 51, DOI: 10.1021/ic301283m
[3] S.-B. Choi, B.-K. Kim, P. Boudjouk, D. G. Grier, *J. Am. Chem. Soc.* **2001**, 123, 8117 – 8118

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