

Density Functional Theory: Study on the Mechanism of the Chloride-Induced Aufbau of Perchlorinated Cyclohexasilanes

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Clusters
LOEWE CSC Cluster Frankfurt

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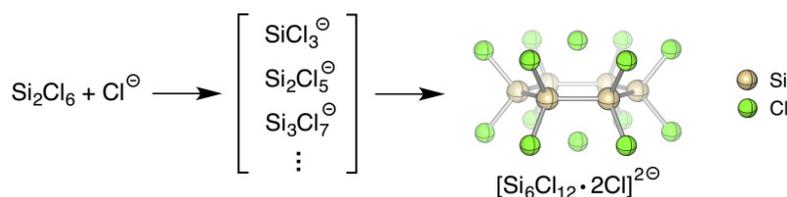


Fig. 1: Chloride induced formation of $[\text{Si}_6\text{Cl}_{12}\cdot 2\text{Cl}]^{2-}$.

Introduction

Nano- and micrometer-scaled silicon structures are essential components not only in microelectronic but also in photovoltaic and opto-electronic applications. Oligo- and polymeric (perchloro)silanes are suitable precursors for the formation of silicon wires or thin silicon films.

Methods

The mechanism of the amine-induced disproportionation of perchlorinated silanes affording neo-Si₅Cl₁₂ was recently established.[1,2] A surprisingly simple preparative procedure, the addition of Si₂Cl₆ to a solution of [nBu₄N]Cl in dichloromethane, leads to the formation of a chloride-complexed cyclic dianion $[\text{Si}_6\text{Cl}_{12}\cdot 2\text{Cl}]^{2-}$ and a variety of its silyl-substituted structural analogs, depending on the reaction conditions. The underlying reaction mechanism has been elucidated by DFT calculations (Fig. 1).

Results

It reveals the chloride ion itself as a Lewis base to trigger a disproportionation of perchlorinated silanes with a subsequent buildup of dianions containing up to eight silicon atoms.[3]

Outlook

The mechanistic insights gained provide the fundament required for the targeted synthesis of oligosilane precursors suitable for microelectronic applications.

Reference

[1] F. Meyer-Wegner, A. Nadj, M. Bolte, N. Auner, M. Wagner, M.C. Holthausen, and H.-W. Lerner (2011), The Perchlorinated Silanes Si_2Cl_6 and Si_3Cl_8 as Sources of SiCl_2 , Chem.-Eur. J. 17, 4715-4719. <https://doi.org/10.1002/chem.201003654>

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[3] J. Tillmann, L. Meyer, J.I. Schweizer, M. Bolte, H.W. Lerner, M. Wagner, and M.C. Holthausen (2014), Chloride-Induced Aufbau of Perchlorinated Cyclohexasilanes from Si_2Cl_6 : A Mechanistic Scenario, Chem.-Eur. J. 20, 9234-9239. <https://doi.org/10.1002/chem.201402655>

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