Chloride-Induced Aufbau of Cyclohexasilanes from Si_2Cl_6

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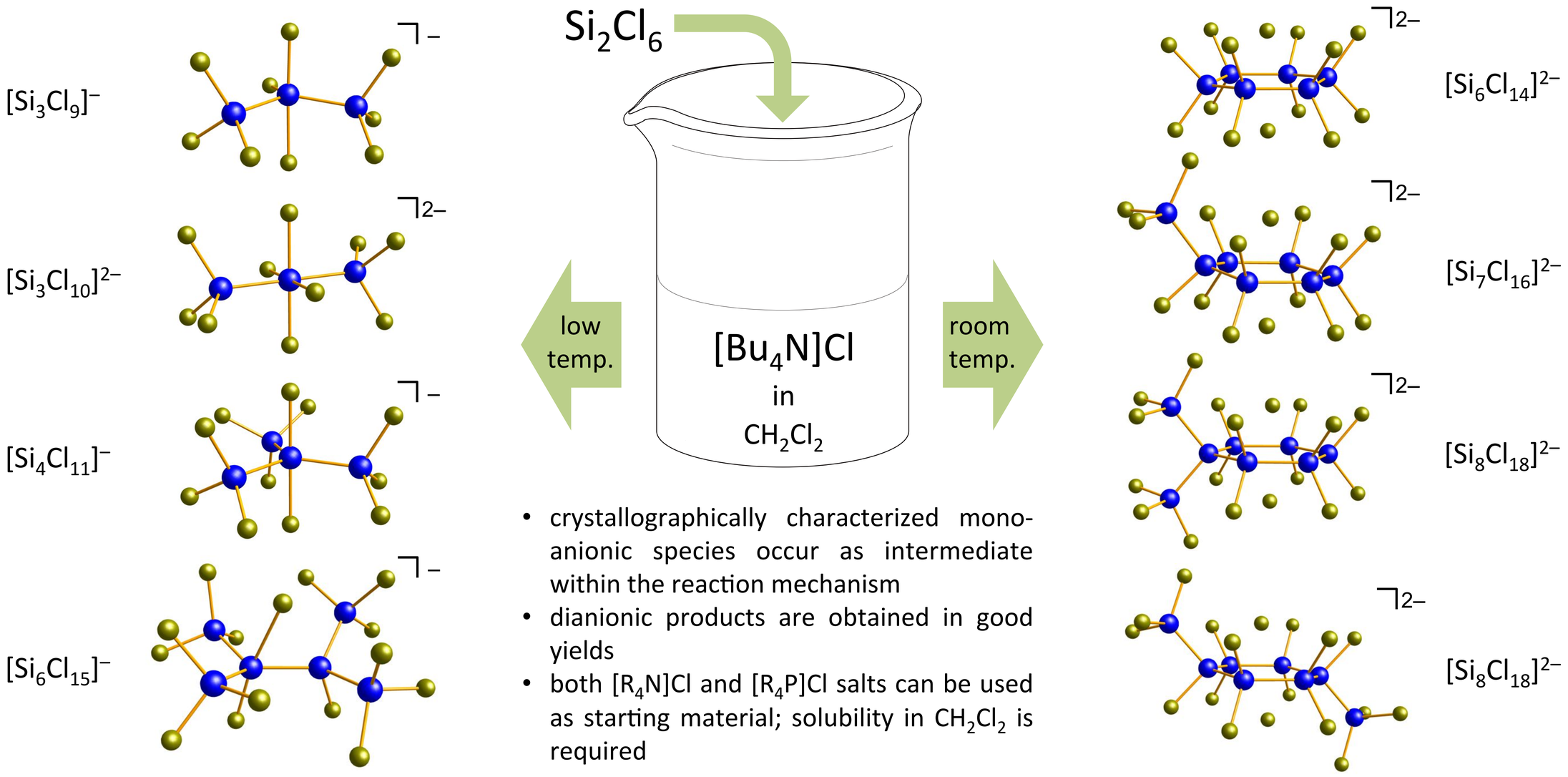
Introduction

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 fabricated through gas-phase deposition of smaller silanes, originating from the reduction of the corresponding chlorosilanes. Solution-based methods, such as spin-, spray- or printing processes, provide a promising approach to improve the manufacturing of Si-films. Therefore, higher oligosilanes with boiling points above their deposition temperatures are in demand. Known synthetic routes are too laborious and expensive to be used in large-scale production. We therefore suggest a synthesis strategy offering convenient access to oligochlorosilane precursors: the chloride-induced formation of chloride-complexed cyclic dianions upon addition of Si_2Cl_6 to a solution of $[Bu_4N]Cl$ in CH_2Cl_2.[1]

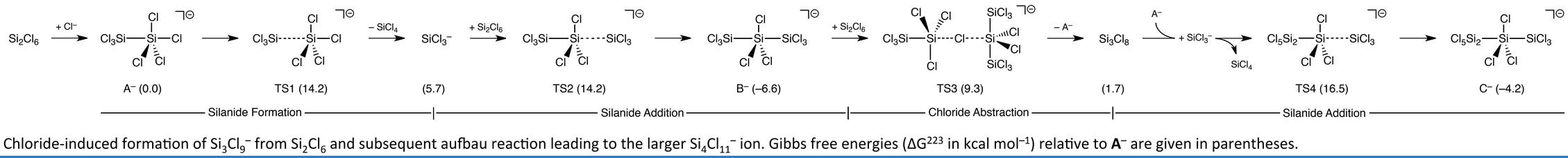
Chloride-Induced Aufbau of Higher Perchlorinated Silanes



- crystallographically characterized mono-anionic species occur as intermediate within the reaction mechanism
- dianionic products are obtained in good yields
- both $[R_4N]Cl$ and $[R_4P]Cl$ salts can be used as starting material; solubility in CH_2Cl_2 is required

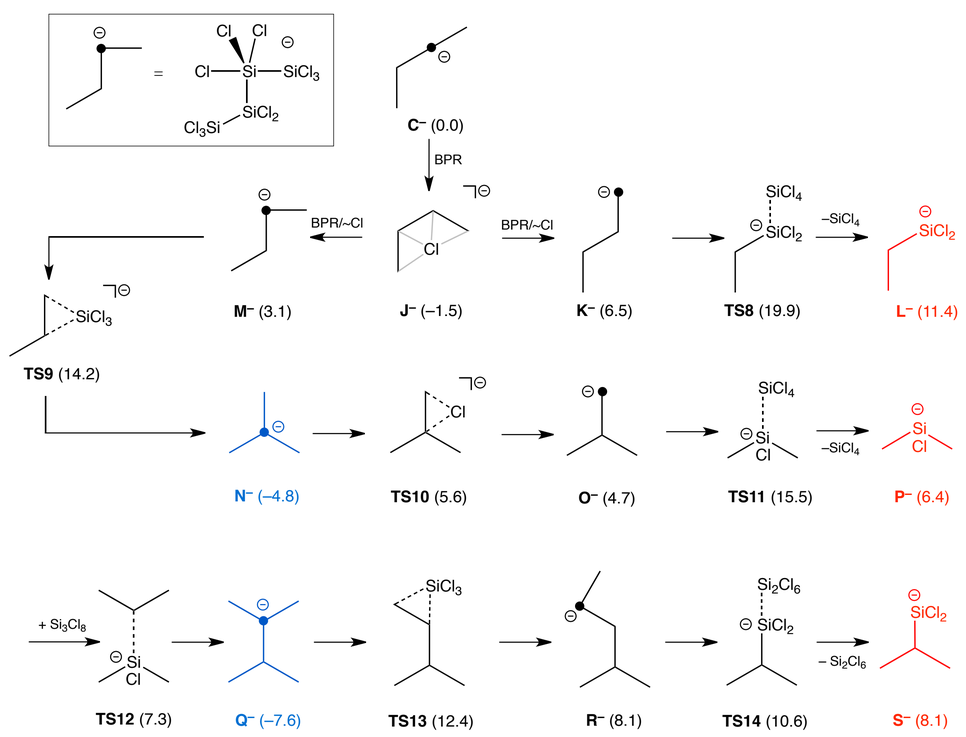
Mechanistic Scenario According to Experimental and Quantum-Chemical Studies

Elementary Steps of the Aufbau Reaction



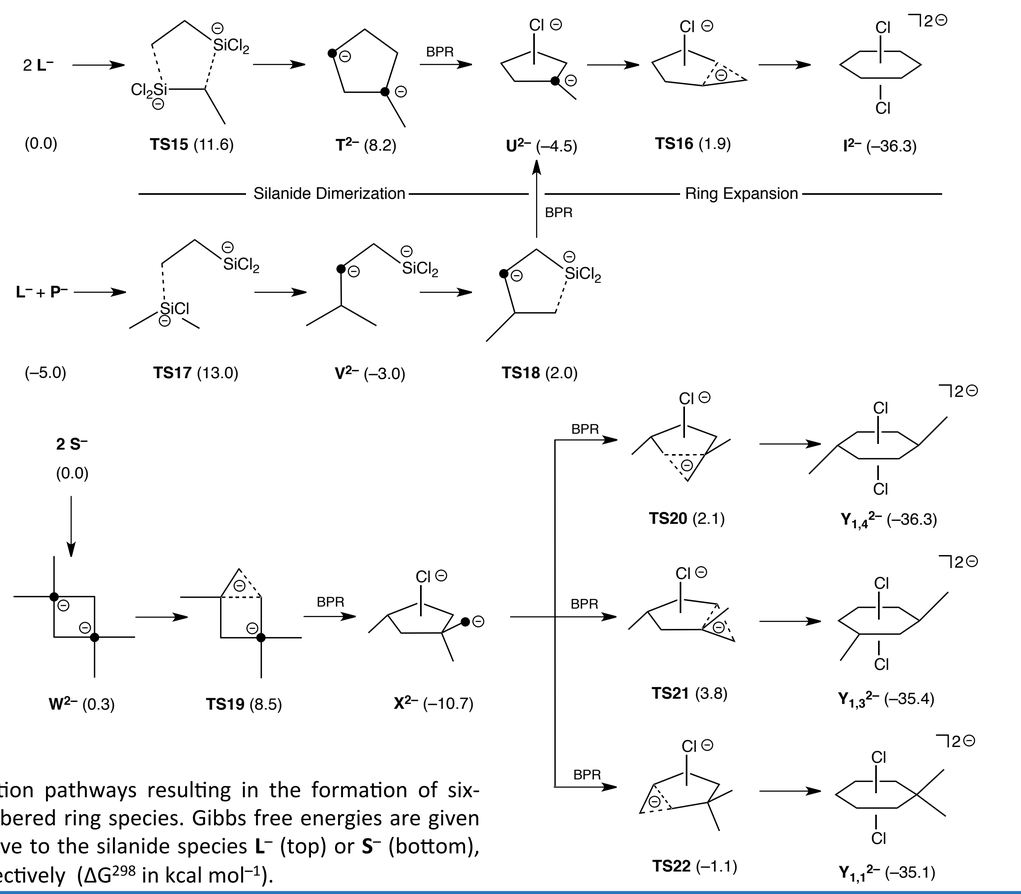
Chloride-induced formation of $Si_3Cl_9^-$ from Si_2Cl_6 and subsequent aufbau reaction leading to the larger $Si_4Cl_{11}^-$ ion. Gibbs free energies (ΔG^{223} in kcal mol^{-1}) relative to **A**$^-$ are given in parentheses.

Aufbau Reaction of Higher Silanides



Reaction pathways resulting in the formation of the experimentally observed species **N**$^-$ and **Q**$^-$ (highlighted in blue) leading to the precursors **L**$^-$, **P**$^-$ and **S**$^-$ (highlighted in red) for the formation of hexachlorosilane rings. Gibbs free energies are given relative to **C**$^-$ (ΔG^{223} in kcal mol^{-1}).

Formation of (Silyl-Substituted) Hexasilanes



Reaction pathways resulting in the formation of six-membered ring species. Gibbs free energies are given relative to the silanide species **L**$^-$ (top) or **S**$^-$ (bottom), respectively (ΔG^{298} in kcal mol^{-1}).

Reference: [1] J. Tillmann, L. Meyer, J. I. Schweizer, M. Bolte, H.-W. Lerner, M. Wagner, M. C. Holthausen, *Chem. Eur. J.* **2014**, *20*, DOI: 10.1002/chem.201402655