

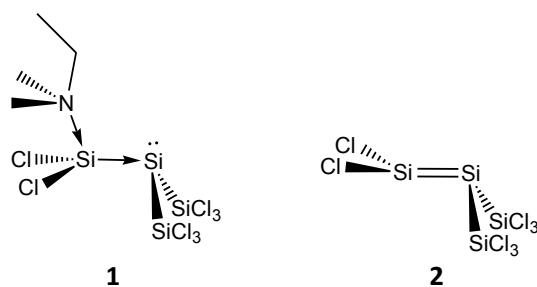
A Disilene Base Adduct with a Dative Si–Si Single Bond

Julia I. Schweizer, Martin Diefenbach and Max C. Holthausen

Goethe-University, Institute of Inorganic Chemistry, Frankfurt/Main, Germany

The base-stabilized disilene **1** forms at low temperatures in the amine-induced disproportionation of Si_2Cl_6 and of *neo*- $\text{Si}_5\text{Cl}_{12}$.^[1] NBO, QTAIM, and EDA-NOCV bonding analyses disclose an unprecedented structure in silicon chemistry featuring a dative Si→Si single bond between two silylene moieties, $\text{EtMe}_2\text{N} \rightarrow \text{SiCl}_2 \rightarrow \text{Si}(\text{SiCl}_3)_2$. The rather unusually bent arrangement of the two silylene moieties in **1** is retained in the computed structure of the base-free disilene **2**, resulting in a partial Si=Si double bond. Based on experimental and theoretical investigations a formation mechanism is presented that involves an autocatalytic reaction of the intermediately formed anion $\text{Si}(\text{SiCl}_3)_3^-$ with *neo*- $\text{Si}_5\text{Cl}_{12}$ to yield **1**. DFT-based NMR calculations fully support the mechanistic picture.

Computed ^{29}Si NMR chemical shifts in chlorosilanes displayed large deviations from experiment in earlier work^[2], which was traced back to the neglect of relativistic spin-orbit effects – a somewhat unexpected result in view of the moderate atomic masses involved.^[1, 3–5] We show here that application of the relativistic SO-ZORA operator yields results of acceptable accuracy for predicting ^{29}Si NMR chemical shifts of perchlorinated silanes.



- [1] J. I. Schweizer, M. G. Scheibel, M. Diefenbach, F. Neumeyer, C. Würtele, N. Kulminkaya, R. Linser, N. Auner, S. Schneider, M. C. Holthausen, *Angew. Chem. Int. Ed.* **2015**, in print. DOI: 10.1002/anie.201510477.
- [2] F. Meyer-Wegner, A. Nadj, M. Bolte, N. Auner, M. Wagner, M. C. Holthausen, H.-W. Lerner, *Chem. Eur. J.* **2011**, *17*, 4715–4719.
- [3] L. A. Truflandier, E. Brendler, J. Wagler, J. Autschbach, *Angew. Chem.* **2011**, *123*, 269–273.
- [4] K. A. Chernyshev, L. B. Krivdin, *Russ. J. Org. Chem.* **2012**, *48*, 1518–1525.
- [5] C. Zhang, P. Patschinski, D. S. Stephenson, R. Panisch, J. H. Wender, M. C. Holthausen, H. Zipse, *Phys. Chem. Chem. Phys.* **2014**, *16*, 16642–16650.