

An NHC-Stabilized Disilavinylidene: Synthesis, Structure and Reactivity

P. Ghana, S. Krämer, G. Schnakenburg, A. C. Filippou*

Institut für Anorganische Chemie, Rheinische Friedrich-Wilhelms Universität Bonn
 Gerhard-Domagk-Strasse 1, GER-53121, Bonn, e-mail: filippou@uni-bonn.de, pghana@uni-bonn.de

Introduction

The behavior of silicon in multiply bonded compounds differs markedly from that of its lighter homologue carbon. This is exemplified by the presence of four energetic minimum structures **A** – **D** for Si_2H_2 (Chart 1) on the potential energy hypersurface (PES), in contrast to only two minimum structures ($\text{HC}\equiv\text{CH}$ and $\text{H}_2\text{C}=\text{C}$) for C_2H_2 .^[1] The dibridged (**A**) and monobridged (**B**) Si_2H_2 molecules were identified by spectroscopic studies,^[2] and *trans*-bent disilynes Si_2R_2 of type **D** with bulky substituents were isolated in the condensed phase.^[3] However, no experimental evidence for disilavinylidenes (**C**) has been reported to date. Using N-heterocyclic carbenes (NHCs), we herein present an efficient two-step synthesis and some initial reactivity studies of the first NHC-stabilized disilavinylidene.^[4]

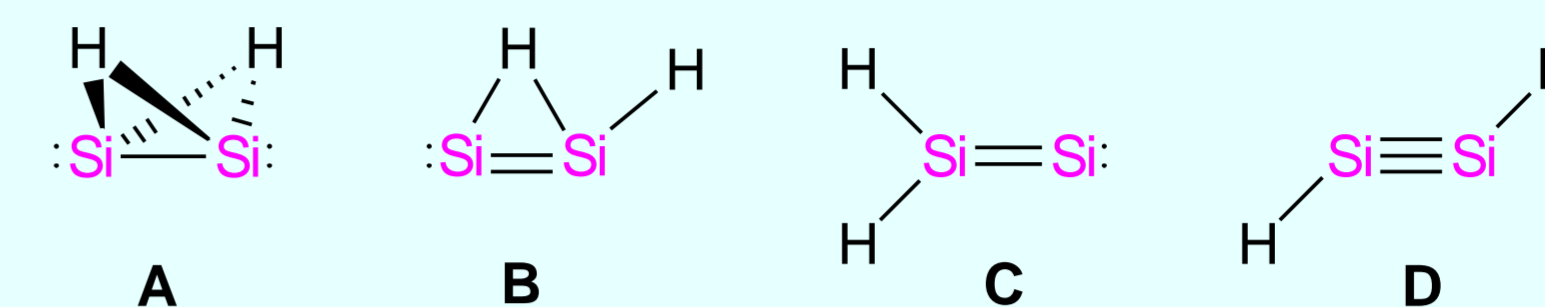
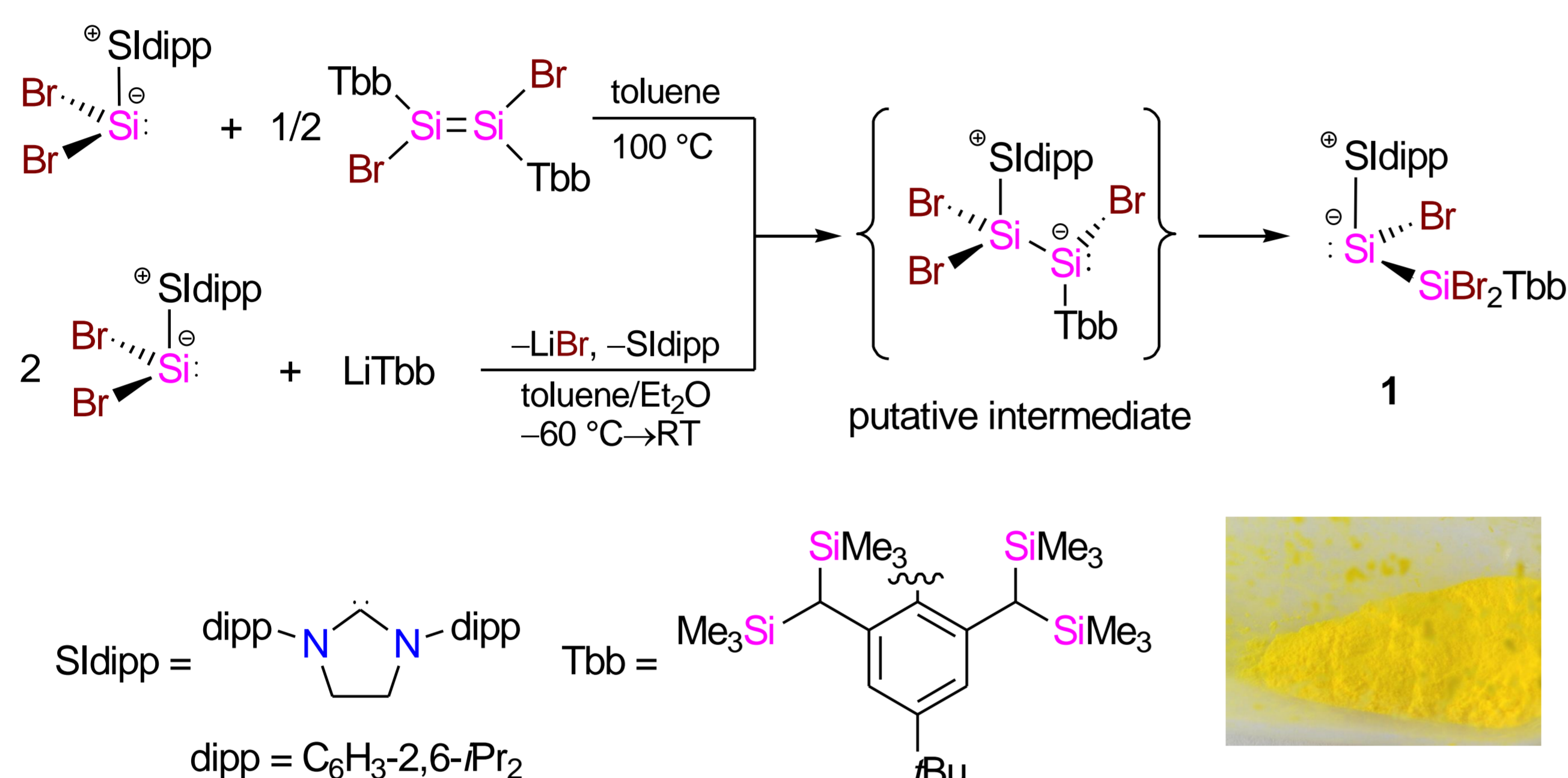


Chart 1. Calculated minimum structures of Si_2H_2 .

Results

NHC-Stabilized Bromo(silyl)silylenes

The entry into this chemistry was provided by the NHC-stabilized Si(II) dibromide $\text{SiBr}_2(\text{Sldipp})$, which upon reaction with (*E*)- $\text{Tbb}(\text{Br})\text{Si}=\text{Si}(\text{Br})\text{Tbb}$ or LiTbb afforded the first NHC-stabilized bromo(silyl)silylene $\text{SiBr}(\text{SiBr}_2\text{Tbb})(\text{Sldipp})$ (**1**) (Scheme 1). Compound **1** was isolated as an extremely air-sensitive, yellow solid in 50 – 61 % yield.



Scheme 1. Synthesis of the NHC-stabilized bromo(silyl)silylene **1** starting from $\text{SiBr}_2(\text{Sldipp})$.

The ^{29}Si NMR spectrum of **1** displays four characteristic singlets at $\delta = -11.3$, -1.9 , 2.45 and 2.64 ppm, among which the first two signals were assigned by ^1H - ^{29}Si correlation spectroscopy to the SiBr_2 and SiBr nuclei, respectively.

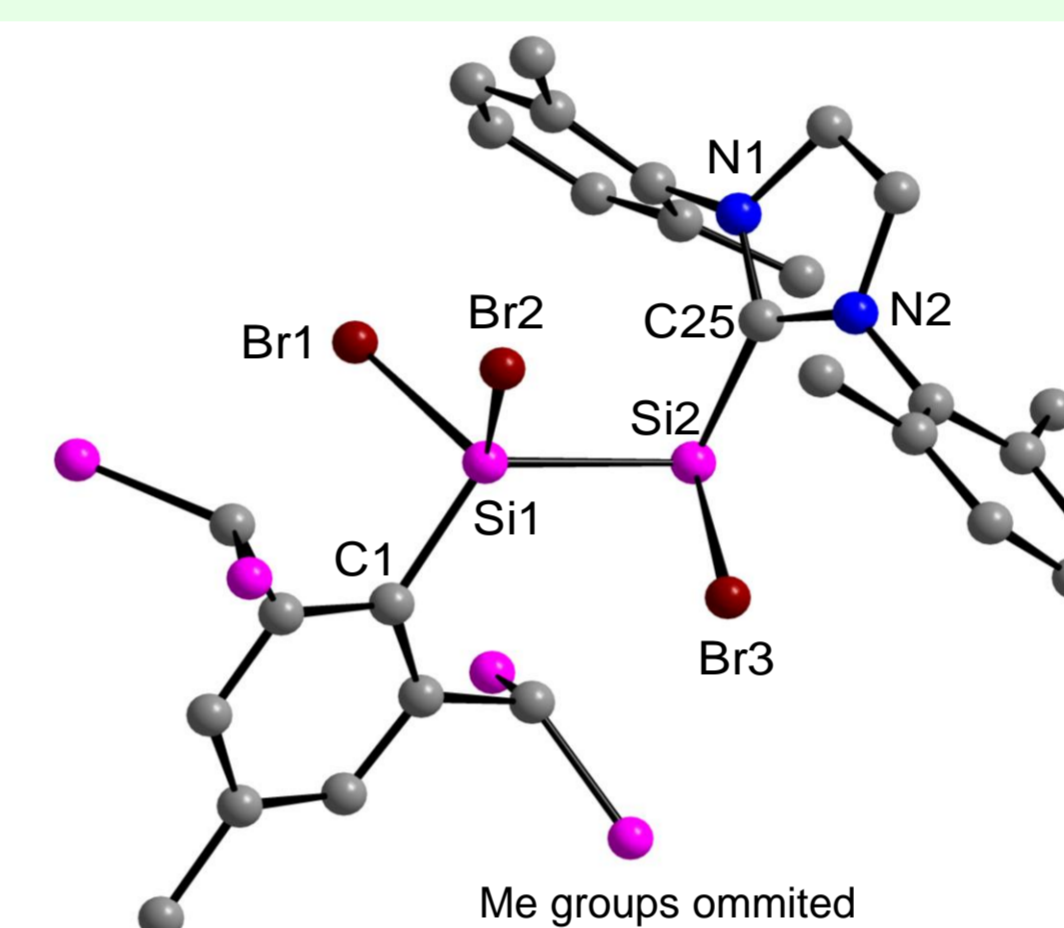
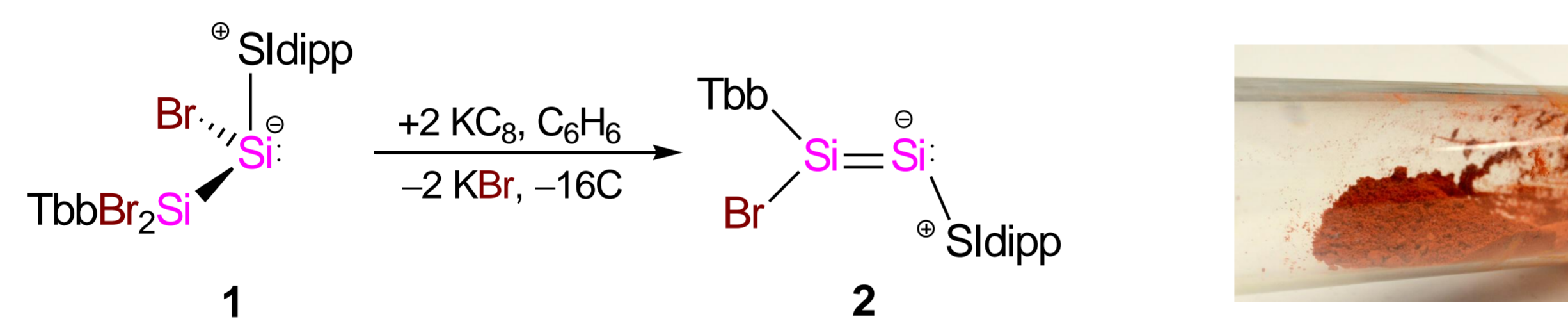


Figure 1. Molecular structure of compound **1**.

The molecular structure of **1** reveals an antiperiplanar conformation of the bulky Tbb and Sldipp groups, a tetrahedral geometry at the Si1 atom and a trigonal-pyramidal geometry at the Si2 center. The Si1–Si2 bond length is $2.391(1)$ Å, which is expected for a Si–Si single bond.

NHC-Stabilized Disilavinylidenes

The reduction of **1** with two equivalents of KC_8 in benzene leads to the first NHC-stabilized disilavinylidene (*Z*)- $\text{Si}(\text{Sldipp})=\text{Si}(\text{Br})\text{Tbb}$ (**2**) (Scheme 2), which after work-up was isolated as an extremely air-sensitive, bright-red solid in 60 % yield.



Scheme 2. Synthesis of the NHC-stabilized disilavinylidene **2** upon two-electron reduction of **1**.

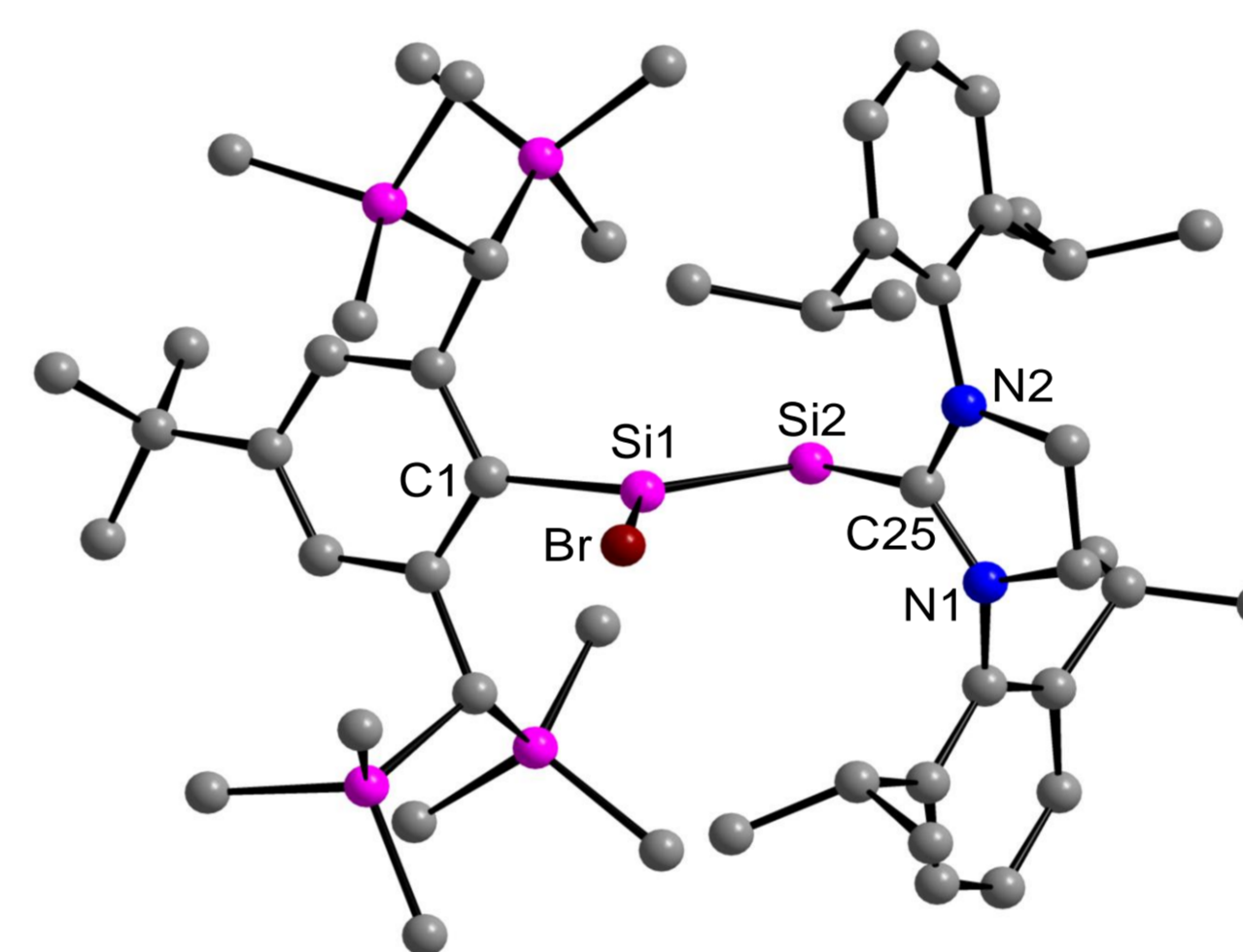


Figure 3. Molecular structure of compound **2**.

The molecular structure of **2** reveals a planar core composed of the atoms C1, Si1, Br, Si2 and C25, and a *trans*-arrangement of the bulky Tbb and Sldipp groups (Figure 3). The Si1–Si2 bond of **2** ($2.167(2)$ Å) is markedly shorter than that observed in **1** ($2.391(1)$ Å) and indicates the presence of a Si–Si double bond.

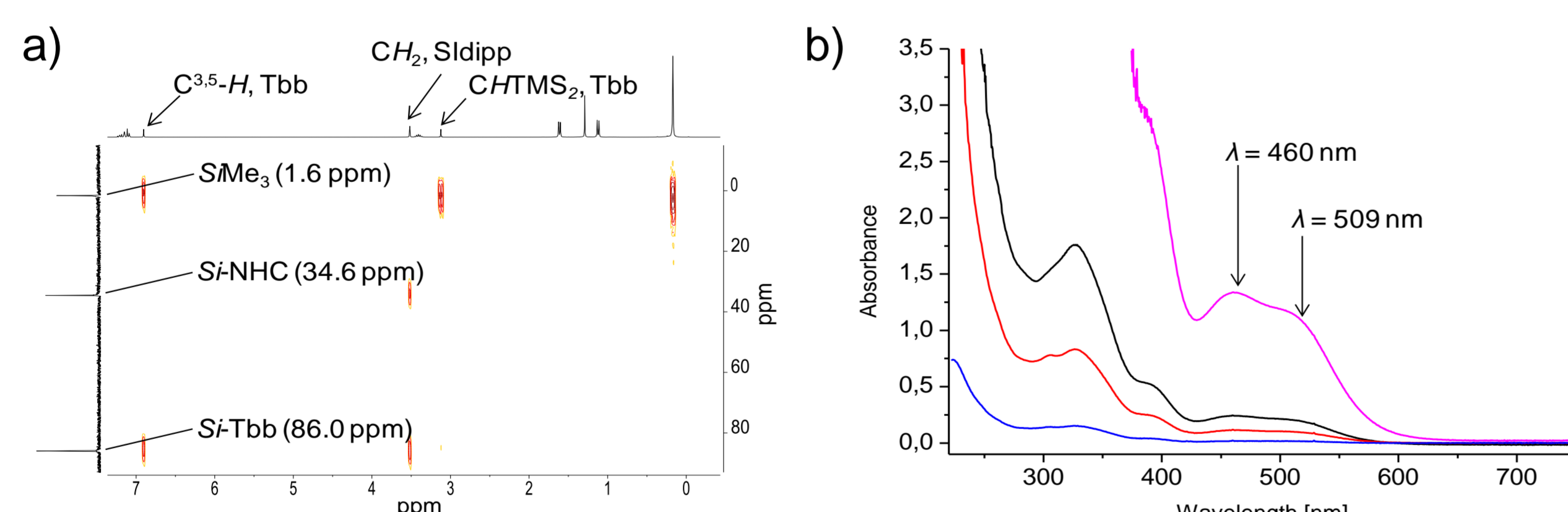


Figure 2. a) ^1H - ^{29}Si HMBC correlation spectrum of **2**; b) UV-Vis spectrum of **2** in *n*-hexane.

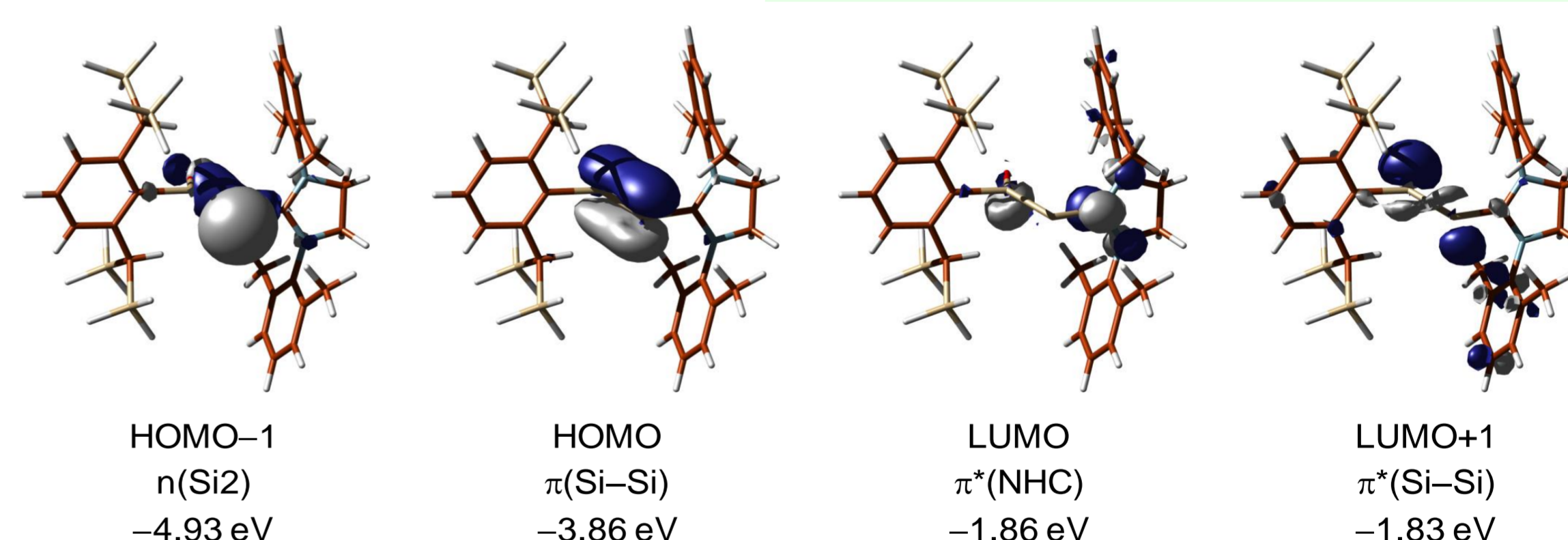
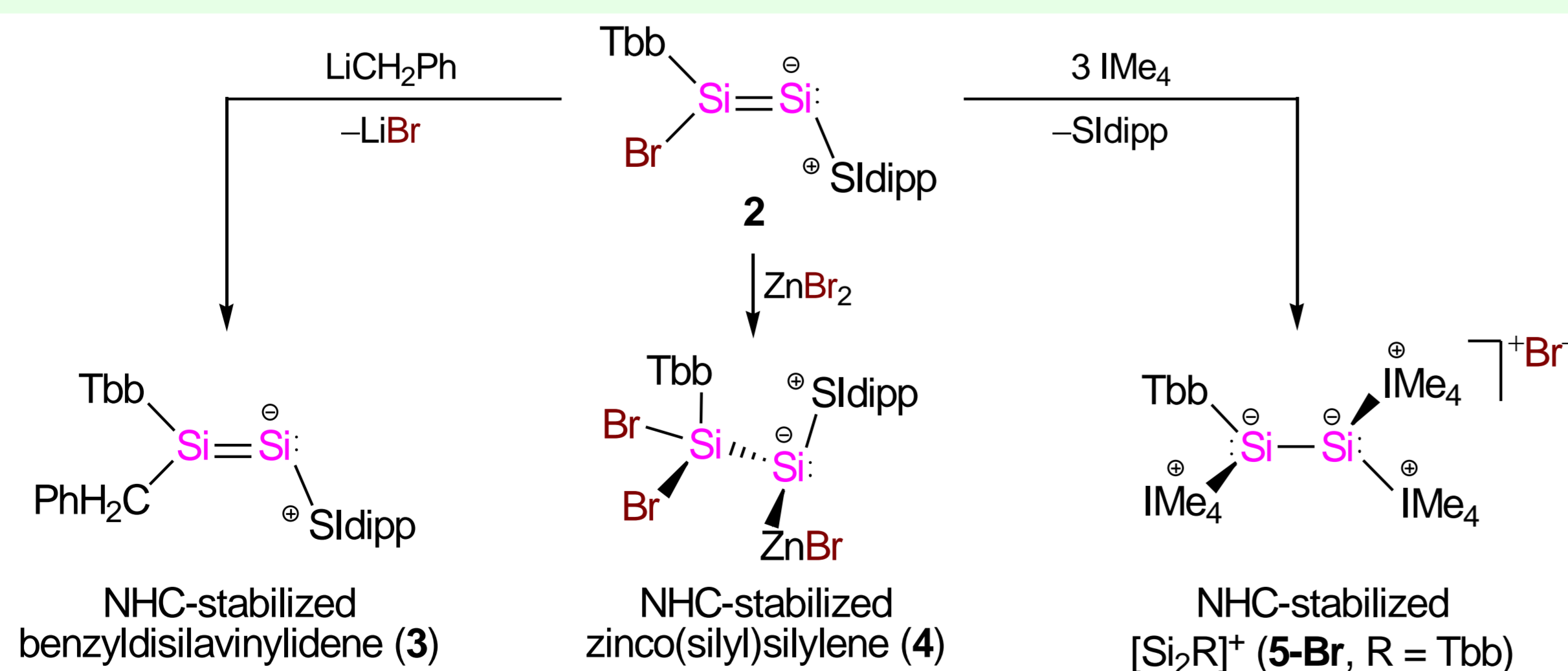


Figure 4. Selected Kohn-Sham orbitals of (*Z*)- $\text{R}(\text{Si})=\text{Si}(\text{NHC})$ ($\text{R} = \text{C}_6\text{H}_3-2,6-[\text{CH}(\text{SiH}_3)_2]_2$, $\text{NHC} = \text{C}[\text{N}(\text{C}_6\text{H}_3-2,6-\text{Me}_2)]_2$; isosurface value $0.05 e \text{ bohr}^{-3}$).

Reactivity of the NHC-Stabilized Disilavinylidene **2**

The NHC-stabilized disilavinylidene **2** contains multiple reactive sites, such as the Si–Br and Si=Si bonds, the Si lone pair or the displaceable NHC group, which opens up many potential reaction pathways. Some initial results of the exploration of the fascinating reactivity of **2** are presented in Scheme 3 and Figure 5.



Scheme 3. Initial reactivity studies of compound **2**; $\text{IME}_4 = \text{C}[\text{N}(\text{Me})\text{C}(\text{Me})_2]$.

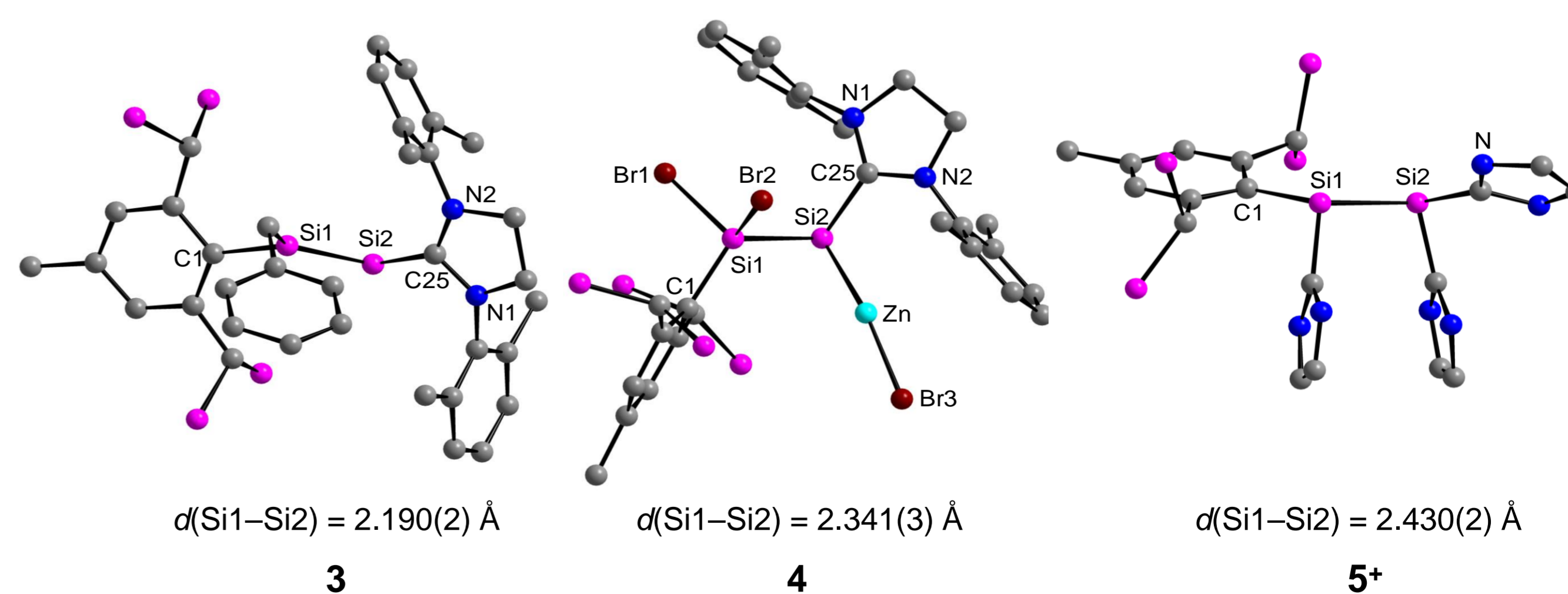


Figure 5. Molecular structures of **3**, **4** and **5**⁺; methyl groups were omitted for clarity.

Summary

The first NHC-stabilized bromo(silyl)silylenes and disilavinylidenes (**1**, **2**) were isolated and fully characterized by X-ray diffraction analysis, NMR spectroscopy and quantum chemical calculations. Both compounds feature many reactive sites, which facilitated the isolation of many novel and exciting low-valent Si compounds.

References

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