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ARTICLE

# Reactions of $Si_2Br_6$ with N-Heterocyclic Carbenes

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*Dedicated to Prof. Alexander C. Filippou on the Occasion of his 60th Birthday*

**Abstract**. A combined experimental and theoretical study on the reaction of $Si_2Br_6$ with N-heterocyclic carbenes is reported. Employment of an imidazole-2-ylidene with methyl groups in $C^4$- and $C^5$-position results in the disproportionation of $Si_2Br_6$ into the adducts $NHC \rightarrow SiBr_2$ and $NHC \rightarrow SiBr_4$. According to expectation, the hydrogenated derivative 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene forms analogous disproportionation products of $Si_2Br_6$ at low temperatures, whereas reaction at higher temperatures furnishes the 4-$SiBr_3$-substituted NHC. The underlying formation mechanism explored by means of density functional theory calculations features an abnormal carbene intermediate.

## Introduction

The isolation of low-valent silicon compounds has long intrigued chemists,[1] particularly in view of the distinct differences to the corresponding carbon analogs. In defiance of *Mulliken's*[2] and *Pitzer's*[3] (putatively universal) double-bond rule,[4] *Brook* and *West* heralded a new era of intense research activities in main group chemistry in 1981 by characterization of the first stable Si=C and Si=Si double bond, respectively.[5] After exploiting possibilities for the intramolecular stabilization of such bonding motifs,[6,7] the use of N-heterocyclic carbenes (NHC) for trapping of otherwise fleeting reactive main group species has proven exceptionally well suited over the last decade[8] and spurred a “renaissance in main group chemistry”.[9] Utilization of these strong σ-donors has successfully led to the isolation and characterization of a variety of compounds with silicon in unusual oxidation states and coordination environments,[10] including NHC adducts of transient dihalosilylenes.[11]

Bare $SiX_2$ ($X$ = H, F, Cl, Br, I) is a highly reactive species with pronounced ambiphilic character.[12] Coordination of a Lewis base (LB) effectively saturates the electrophilicity of the subvalent silicon atom and the resulting adduct exhibits an enhanced Lewis basic character,[11a–11c,12d,13] enabling subsequent transformations with Lewis acids (LA) to push-pull compounds of the type $LB \rightarrow SiX_2 \rightarrow LA$.[14] In 2009, *Roesky*, *Stalke*, and co-workers isolated an $NHC \rightarrow SiCl_2$ adduct by reaction of $HSiCl_3$ with NHC or, alternatively, by reduction of $NHC \rightarrow SiCl_4$ with $KC_8$.[11a] Both, $NHC \rightarrow SiCl_2$ and $NHC \rightarrow SiCl_4$ can also be obtained through base-induced disproportionation of $Si_2Cl_6$.[15] The same groups recently reported the isolation of a stable, biradicaloid $SiF_2$ base adduct[16] employing cyclic alkyl(amino) carbenes, which were first synthesized by *Bertrand* and co-workers.[17] In 2013, *Filippou* et al. reported formation of $NHC \rightarrow SiI_2$ en route to an NHC stabilized $Si^{2+}$ ion.[11c]

Also in 2009, the first stable adduct of $SiBr_2$ was prepared by *Filippou* et al.[11b] Reaction of $SiBr_4$ with one equivalent of 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene ($NHC_H$) in hexane led to formation of ion-pair $\mathbf{B_{H,ion}}$, which was subsequently reduced with two equivalents of $KC_8$ in THF to give $\mathbf{A_H}$ in 48 % isolated yield (Figure 1). $\mathbf{A_H}$ is a yellow, air-sensitive solid soluble in THF and benzene. The reasonably short Si–C bond in $\mathbf{A_H}$ was characterized as a strong C→Si donor-acceptor single bond by quantum-chemical means. Formation of the neutral pentacoordinate $NHC \rightarrow SiBr_4$ adduct $\mathbf{B_H}$ in toluene was described by *Ghadwal* et al. in 2009 (Figure 1).[18] Starting from $NHC \rightarrow SiBr_2$, *Filippou's* group was recently able to synthesize an NHC-stabilized disilavinylidene,[10k] and only few other reports on NHC adducts of silicon bromides exist.[10i,19] However, the reactivity of higher bromosilanes towards NHCs remains elusive to date.

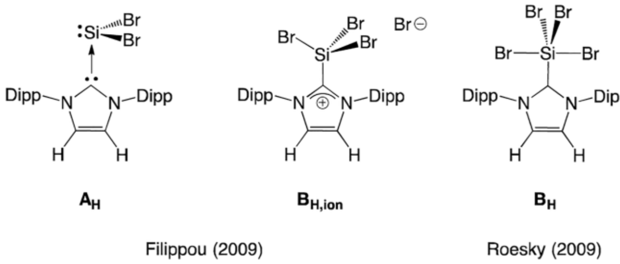

**Figure 1.** Reported products of the reaction of 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene with $SiBr_4$.

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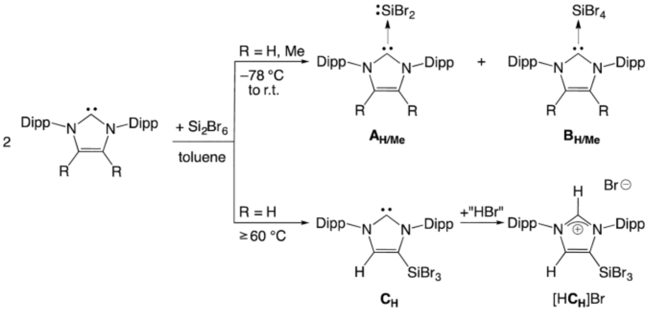
Herein, we report a combined experimental and theoretical study on the reactions of $Si_2Br_6$ with $NHC_H$ and 1,3-bis(2,6-diisopropyl)-4,5-methyl-imidazole-2-ylidene ($NHC_{Me}$, Scheme 1). According to expectation, the disproportionation products $NHC{\rightarrow}SiBr_2$ (**A**) and $NHC{\rightarrow}SiBr_4$ (**B**) form at moderate temperatures, whereas reaction at higher temperatures furnishes a 4-$SiBr_3$-functionalized NHC ($\mathbf{C_H}$). The formation mechanism for all experimental products detailed in the following involves an abnormal carbene intermediate occurring along the path to $\mathbf{C_H}$.



**Scheme 1.** Products formed in the reaction of $Si_2Br_6$ with 1,3-bis(2,6-diisopropyl)-4,5-methyl-imidazole-2-ylidene ($NHC_{Me}$: $\mathbf{A_{Me}}$, $\mathbf{B_{Me}}$) and 1,3-bis(2,6-diisopropyl)imidazole-2-ylidene ($NHC_H$: $\mathbf{A_H}$, $\mathbf{B_H}$, $\mathbf{C_H}$, $[\mathbf{HC_H}]$Br), respectively.

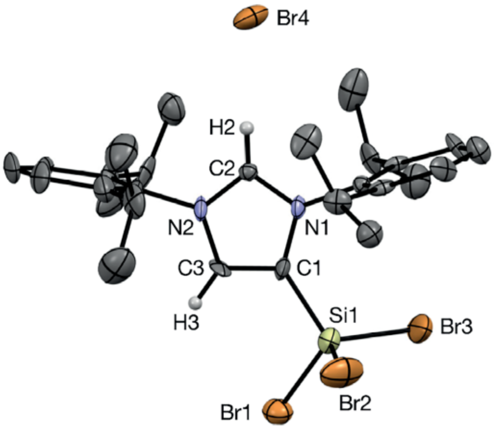


**Figure 2.** Molecular structure of $[\mathbf{HC_H}]$Br with thermal ellipsoids shown at the 50 % probability level. Hydrogen atoms on the substituents are omitted for clarity. Selected experimental bond lengths /Å and angles /°: Si1–C1 1.863(10), Si1–Br1 2.160(4), Si1–Br2 2.182(4), Si1–Br3 2.174(3), C1–C3 1.350(12), C1–N1 1.379(13), C3–N2 1.352(12), C2–N1 1.324(12), C2–N2 1.324(12), C1–Si1–Br1 107.0(4), C1–Si1–Br2 111.4(4), C1–Si1–Br3 112.2(4), N1–C1–Si1 131.3(7).

## Results and Discussion

The reaction of two equivalents of $NHC_H$ with $Si_2Br_6$ at room tempeature in toluene selectively gives $\mathbf{A_H}$ ($C_6D_6$: $\delta^{29}Si$ = 10.9 ppm[11b]) and $\mathbf{B_H}$ ($C_6D_6$: $\delta^{29}Si$ = –90.2 ppm[18]). In agreement with *Filippou*, NMR spectroscopic analyses of $\mathbf{B_H}$ in $CD_2Cl_2$ show a singlet resonance at $\delta^{29}Si$ = –63.9 ppm,[11b] corresponding to the $\mathbf{B_{H,ion}}$ salt (Scheme 1, top). Warming the reaction mixture to 60 °C or above leads to carbene $\mathbf{C_H}$, which is $SiBr_3$-functionalized in 4-position ($D_6D_6$: $\delta^{29}Si$ = –49.9 ppm; Scheme 1, bottom), and $[HNHC_H]$Br, which we suggest as HBr source for the transformation of $\mathbf{C_H}$ to $[\mathbf{HC_H}]$Br. $\mathbf{C_H}$ is detectable as a dominant species in solution, whereas single crystals of $[\mathbf{HC_H}]$Br and $[HNHC_H]$Br suitable for X-ray diffraction analysis were obtained from crystallization experiments. The molecular solid-state structure of $[\mathbf{HC_H}]$Br is shown in Figure 2. While these results add to the overall mechanistic picture (see below), we did not attempt to obtain $[\mathbf{HC_H}]$Br in quantitative yields.

$[\mathbf{HC_H}]$Br crystallizes as ion pair in the orthorhombic space group $P2_12_12_1$. The imidazolium ring unit is planar and the bond lengths C2–N1 and C2–N2 are identical (1.324 Å). Compared to *Filippou's* ionic complex $\mathbf{B_{H,ion}}$ the Si–C bond in $[\mathbf{HC_H}]$Br (1.863 Å) is slightly shortened by 0.017 Å and generally in the range of Si–C($sp^2$) single bonds.[11b] The Si1 atom in $[\mathbf{HC_H}]$Br is almost tetrahedral with angles between 107–112° and the average Si–Br bond length of 2.172 Å is comparable to the averaged values of $\mathbf{B_{H,ion}}$ (2.175 Å[11b]) and $SiBr_4$ (2.183 Å[20]).

The activation of the $C^4$–H bond (C1 in Figure 2) in $\mathbf{C_H}$ is intriguing as the acidity of $C^4$ protons in NHCs is minute compared to protons attached to the $C^2$ position (calculated $pK_a$ difference of 9 units).[21] Notably, *Gates* and co-workers synthesized a 4-phosphino-substituted NHC in 2009 and postulated involvement of an abnormal carbene intermediate in its formation mechanism.[22] These so-called "abnormal carbenes" (*a*NHCs), which bear the carbene center in 4- or 5-position, have long been fleeting curiosities in main-group chemistry[23] until *Bertrand* and co-workers isolated the first crystalline *a*NHC in 2009.[24] *a*NHCs are stronger σ-donors than normal NHCs;[25] reactions with silanes lead to formation of 4-silyl-functionalized imidazolium salts.[26] To date, a variety of 4-silyl-substituted NHCs and their corresponding imidazolium salts have been reported (Figure 3),[26b,27] most of which result from reactions of an NHC with the corresponding silane upon addition of a strong base. *Robinson* and co-workers have established more convenient access to this compound class through $C^4$-lithiated NHCs.[27f,28]

Dimethylation of the NHC backbone inhibits the formation of $C^4$-functionalized products. In fact, reaction of $NHC_{Me}$ with $Si_2Br_6$ in *n*-hexane at –78 °C yields a mixture of $\mathbf{A_{Me}}$ and $\mathbf{B_{Me,ion}}$ as pale yellow precipitate, from which $\mathbf{A_{Me}}$ was isolated by washing with benzene. The NMR spectrum of the concentrated filtrate shows a single signal at $\delta^{29}Si$ = 14.0 ppm, similar to the NMR signal of $\mathbf{A_H}$ ($\delta^{29}Si$ = 10.9 ppm[11b]). This assignment is supported by the $^{13}C$ NMR signal for the $C^2$ atom at $\delta$ = 162.5 ppm ($\mathbf{A_H}$: $\delta^{13}C$ = 164.5 ppm[11b]). Colorless crystals suitable for X-ray diffraction analysis were obtained from a solution of $\mathbf{A_{Me}}$ in benzene at 5 °C (Figure 4).

$\mathbf{A_{Me}}$ crystallizes in the monoclinic space group $P2_1/c$ with one benzene molecule in the unit cell. The molecular structure is very similar to that of the stable carbene adduct $\mathbf{A_H}$.[11b] The $SiBr_2$ group shows a significant torsion to the essentially planar imidazolium ring, as seen by the quite different torsion angles Br1–Si1–C1–N1 [83.6(7)°] and Br2–Si1–C1–N2 [–17.1(9)°]. The silicon center is distinctly trigonal pyramidal (sum of angles at Si = 297.2°) and the Si–C bond length of

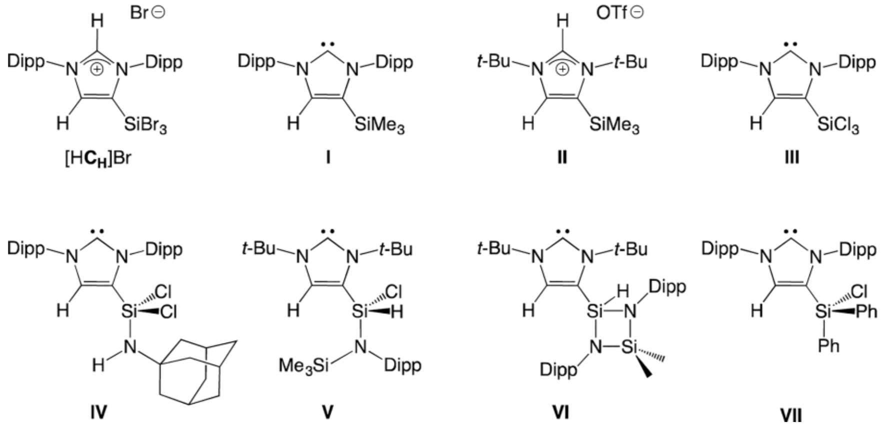


**Figure 3.** Examples of 4-silyl-functionalized NHCs.

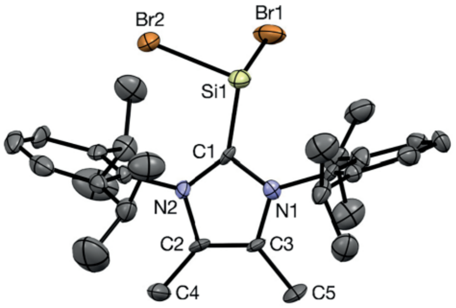


**Figure 4.** Molecular structure of $\mathbf{A_{Me}}$ with thermal ellipsoids shown at the 50 % probability level. Hydrogen atoms and benzene are omitted for clarity. Selected experimental bond lengths /Å and angles /°: Si1–C1 2.008(8), Si1–Br1 2.326(3), Si1–Br2 2.336(3), C2–C3 1.349(11), C1–N1 1.336(9), C1–N2 1.351(10), C3–N1 1.387(9), C2–N2 1.406(9), C1–Si1–Br1 97.2(3), C1–Si1–Br2 102.8(2), Br1–Si1–Br2 97.23(10), N1–C1–N2 104.9(6).

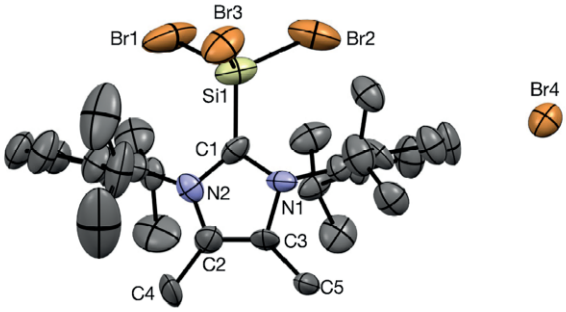


**Figure 5.** Molecular structure of $\mathbf{B_{Me,ion}}$ with thermal ellipsoids shown at the 50 % probability level. Hydrogen atoms are omitted for clarity. Selected experimental bond lengths /Å and angles /°: Si1–C1 1.900(18), Si1–Br1 2.178(6), Si1–Br2 2.161(7), Si1–Br3 2.171(6), C2–C3 1.35(2), C1–N1 1.34(2), C1–N2 1.42(2), C3–N1 1.459(19), C2–N2 1.31(2), C1–Si1–Br1 107.6(6), C1–Si1–Br2 111.7(6), C1–Si1–Br3 112.2(6), N1–C1–Si1 122.6(12), N1–C1–N2 105.5(15).

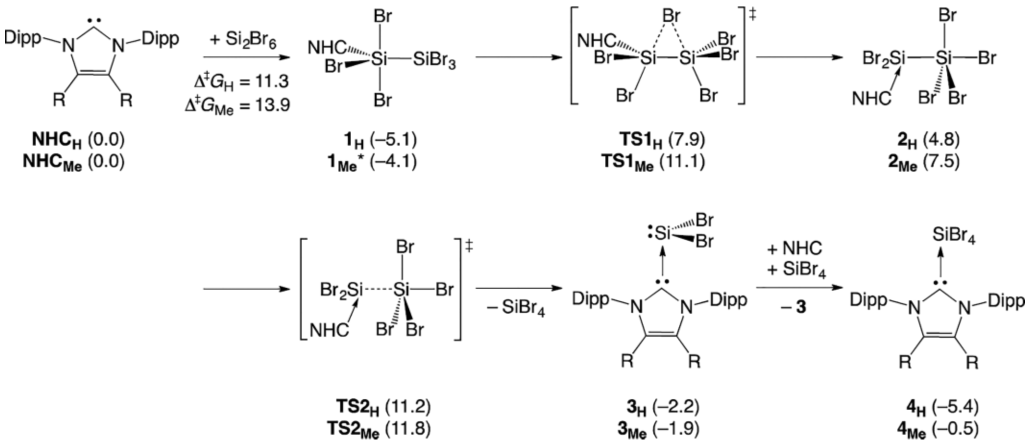
2.008 Å is slightly elongated compared to $\mathbf{A_{H}}$ (1.989 Å[11b]). Both Si–Br bond lengths (2.326 Å and 2.336 Å) are in good agreement with the values determined for $\mathbf{A_{H}}$ (2.338 Å and 2.361 Å[11b]).

The colorless residue that remained after washing with benzene is readily dissolved in dichloromethane. One main $^{29}$Si NMR signal is detected at $\delta$ = –63.4 ppm, compatible with the chemical shift of the ionic salt $\mathbf{B_{H,ion}}$. The same holds for the characteristic $^{13}$C NMR chemical shift for the C$^2$ atom at $\delta^{13}$C = 138.2 ppm vs. 136.3 ppm in $\mathbf{B_{H,ion}}$.[11b,29] The identical NMR signature was observed in an additional experiment employing NHC$_{Me}$ and SiBr$_4$. $\mathbf{B_{Me,ion}}$ was obtained from CD$_2$Cl$_2$ at –20 °C as a white powder with single-crystals of low quality (Figure 5).

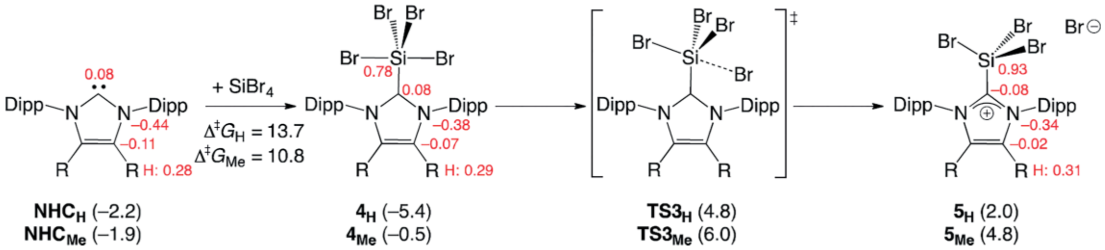
$\mathbf{B_{Me,ion}}$ crystallizes as ion pair in the monoclinic space group *Cc* with four imidazolium cations, four bromine anions, and two benzene molecules in the asymmetric unit. The N-heterocycle is planar in all four molecules. The silicon atom in $\mathbf{B_{Me,ion}}$ is almost tetrahedral with angles between 107–112° analogously to [H$\mathbf{C_{H}}$]Br and $\mathbf{B_{H,ion}}$[11b] and the Si–C bond is in the same range (1.880 Å vs. 1.900 Å in $\mathbf{B_{H,ion}}$). The average Si–Br bond length of 2.170 Å compares well with that in $\mathbf{C_{H}}$, $\mathbf{B_{H,ion}}$ (2.175 Å[11b]) and SiBr$_4$ (2.183 Å[20]).

The formation mechanisms of **A**, **B**, and **C** were explored by means of density functional theory calculations, which were benchmarked against high-level coupled-cluster theory.[30] Initial interaction between Si$_2$Br$_6$ and NHC$_H$ leads to exergonic adduct formation with a moderate activation barrier ($\Delta^{\ddagger}G_{H}$ = 11.3 kcal·mol$^{-1}$, Scheme 2). In the presence of excess NHC, adduct $\mathbf{1_{H}}$ thus is the resting state of Si$_2$Br$_6$. Subsequent [1,2]-bromide migration furnishes $\mathbf{2_{H}}$ that carries the pentacoordinate silicon site in terminal position; in other words, $\mathbf{2_{H}}$ represents an adduct of the NHC-stabilized silylene with SiBr$_4$. Liberation of the former via $\mathbf{TS2_{H}}$ is rate-limiting with an effective activation barrier of 16 kcal·mol$^{-1}$. With respect to $\mathbf{1_{H}}$, formation of the experimentally observed products NHC$_H$→SiBr$_2$ ($\mathbf{3_{H}}$) and NHC$_H$→SiBr$_4$ ($\mathbf{4_{H}}$) is thermoneutral. The corresponding pathway for the reaction of NHC$_{Me}$ with Si$_2$Br$_6$ is closely related, with the NHC$_{Me}$·SiBr$_4$ adduct $\mathbf{4_{Me}}$ slightly disfavored.

Overall, the reaction sequences leading to silylene extrusion from Si$_2$Br$_6$ bear close resemblance to the mechanism of the amine-induced disproportionation reaction of Si$_2$Cl$_6$ reported recently.[12d] At variance with the reactivity of Si$_2$Cl$_6$, primary adduct formation is exergonic here, presumably resulting from the strongly σ-donating character of the NHC base.[17b,31] Con-



**Scheme 2.** NHC-induced formation of NHC→SiBr$_2$ and NHC→SiBr$_4$ from Si$_2$Br$_6$ ($\Delta G^{298}$ in kcal·mol$^{-1}$). * **1**$_{\mathbf{Me}}$: different isomer (see Supporting Information).



**Scheme 3.** NHC-induced formation of [NHC–SiBr$_3$]Br from SiBr$_4$; NPA charges of **NHC**$_{\mathbf{H}}$, **4**$_{\mathbf{H}}$, and **5**$_{\mathbf{H}}$ in red ($\Delta G^{298}$ in kcal·mol$^{-1}$).

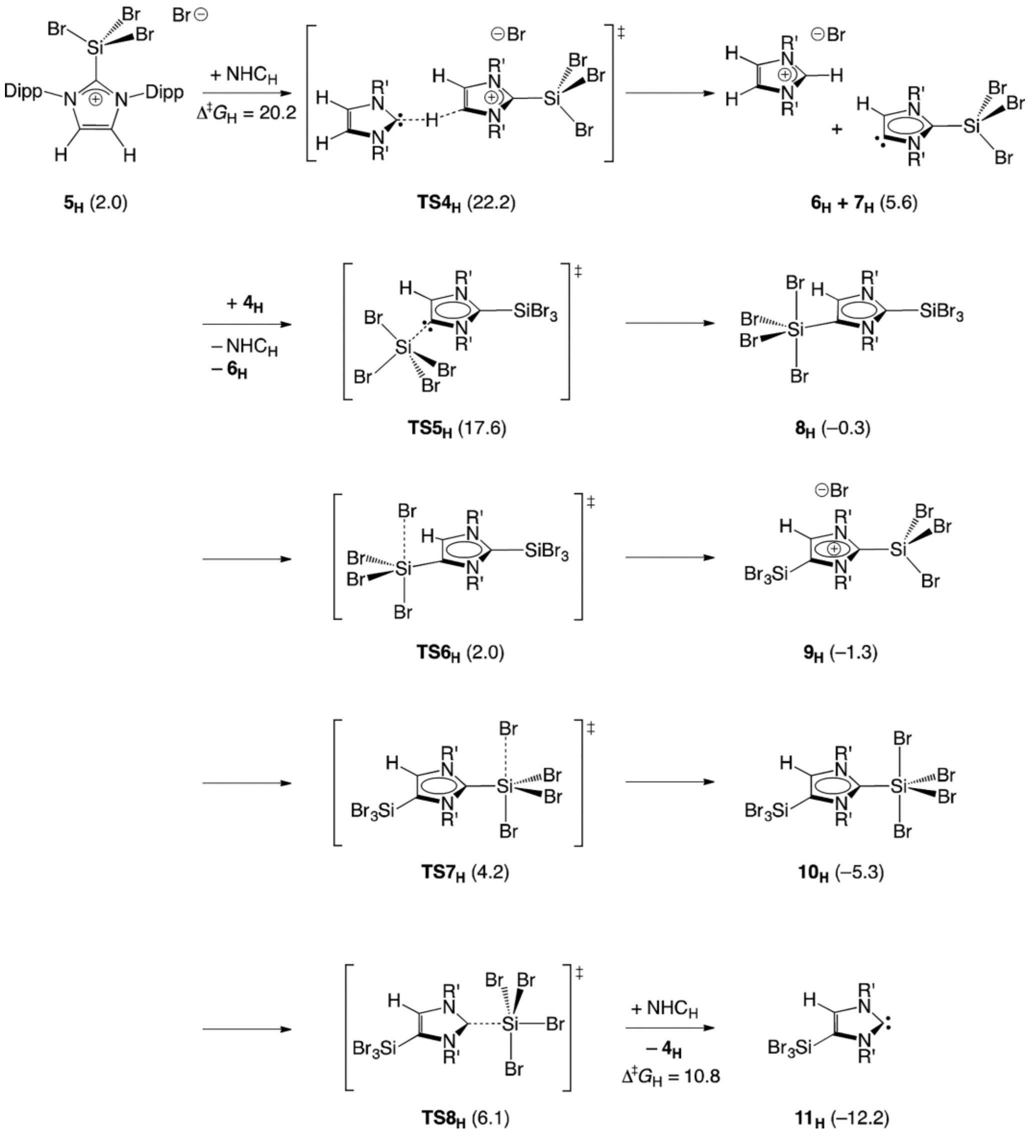
sequently, adduct **1** and NHC-stabilized **3** and **4** are predicted to exist in equilibrium, although NMR signatures of **1** were not detected in our experiments.

In line with earlier experimental work of *Ghadwal* et al.,[18] in which the NHC$_H$ adduct of SiBr$_4$ was characterized crystallographically, **4**$_{\mathbf{H}}$ forms exergonically from the reactants with a low activation barrier (Scheme 3). Formation of **4**$_{\mathbf{Me}}$ is kinetically slightly more feasible, but thermodynamically disfavored. Subsequent dissociation of a bromide ion yielding **5** is endergonic for both NHCs. We attribute the experimental observation of **B**$_{\mathbf{ion}}$ corresponding to **5** to solvent and crystallization effects not accounted for in our calculations.

According to natural population analysis (NPA), the acidity of the hydrogen atoms in the NHC backbone is enhanced by partial delocalization of the positive charge within the imidazolium ring-system in ion-pair **5**$_{\mathbf{H}}$. Consequently, the most favorable route to the 4-substituted NHC **C**$_{\mathbf{H}}$ is initiated by deprotonation of **5**$_{\mathbf{H}}$ in C$^4$-position by another equivalent of NHC$_H$ via **TS4**$_{\mathbf{H}}$ (Scheme 4).[32] The effective activation barrier of 28 kcal·mol$^{-1}$ (computed with respect to **4**$_{\mathbf{H}}$) for the formation of imidazolium salt **6**$_{\mathbf{H}}$ and the abnormal carbene **7**$_{\mathbf{H}}$ is in line with a reaction taking place only at elevated temperatures. Alternative deprotonation of **3**$_{\mathbf{H}}$ is kinetically feasible ($\Delta^{\ddagger}G_H = 26$ kcal·mol$^{-1}$), but thermodynamically strongly disfavored ($\Delta_R G = 20$ kcal·mol$^{-1}$, see Supporting Information). Addition of SiBr$_4$ to *a*NHC **7**$_{\mathbf{H}}$ leading to **8**$_{\mathbf{H}}$ is kinetically and thermodynamically favored. A sequence of low-barrier bromide dissociation and association reactions shifts the pentacoordinate silicon center from C$^4$- to C$^2$-position. The resulting isomer **10**$_{\mathbf{H}}$ can undergo SiBr$_4$ elimination via **TS8**$_{\mathbf{H}}$ to furnish carbene **11**$_{\mathbf{H}}$, which bears a SiBr$_3$-group in 4-position, in an overall exergonic reaction. This scenario is supported by the NMR spectroscopic detection of **C**$_{\mathbf{H}}$ in solution. Formation of the [H**11**$_{\mathbf{H}}$]Br salt, corresponding to crystallized product [H**C**$_{\mathbf{H}}$]Br, can either proceed via HBr transfer from **6**$_{\mathbf{H}}$ or by deprotonation of **5**$_{\mathbf{H}}$ in 4-position (see Supporting Information for details). A related mechanistic picture has been put forth by *Bertrand* and co-workers, who postulate formation of an abnormal carbene as fleeting intermediate in the reaction between NHC$_H$ and benzoyl chloride.[27b]

## Conclusions

In this work, we investigated the reaction of Si$_2$Br$_6$ with N-heterocyclic carbenes. Employment of an imidazole-2-ylidene with methyl groups in C$^4$- and C$^5$-position results in the disproportionation of Si$_2$Br$_6$ into adducts NHC$_{Me}$→SiBr$_2$ and NHC$_{Me}$→SiBr$_4$. Reaction of the disilane with the corresponding NHC$_H$ at room temperature leads to formation of the analogous products NHC$_H$→SiBr$_2$ and NHC$_H$→SiBr$_4$, which were isolated in earlier work by Filippou and Roesky from the reaction of NHC$_H$ with SiBr$_4$ and further treatment with KC$_8$.[11b, 18] However, the reaction at elevated temperatures yields a 4-SiBr$_3$-substituted carbene, which we characterized by single-



**Scheme 4.** H-abstraction from $\mathbf{5_H}$ by NHC$_H$; $R'$ = Dipp ($\Delta G^{298}$ in kcal·mol$^{-1}$).

crystal X-ray diffraction analysis. We elucidated the underlying reaction mechanism by DFT calculations. The quantum-chemical results are in line with the experimental observations and suggest formation of an abnormal carbene intermediate en route to the experimentally characterized C$^4$-functionalized NHC.

## Experimental Section

All reactions were performed employing standard Schlenk techniques using $N_2$ as inert gas. Solvents were dried with appropriate drying agents, distilled and stored in PTFE-valved flasks. NMR spectra were recorded with a Bruker AV400 equipped with a TXI 5N zgrad ATMA probe and a Bruker AV-500 spectrometer equipped with a Prodigy BBO 500 S1 probe. $^1$H NMR spectra were calibrated to the residual solvent proton resonance ([D$_6$]benzene $\delta^{1H}$ = 7.16 ppm, $CD_2Cl_2$ $\delta^{1H}$ = 5.32 ppm). $^{13}$C{$^1$H} NMR spectra were calibrated to the solvent resonance ([D$_6$]benzene $\delta^{13C}$ = 128.06 ppm, $CD_2Cl_2$ $\delta^{13C}$ = 53.84 ppm). $^{29}$Si NMR chemical shifts are referenced to tetramethylsilane.

**Supporting Information** (see footnote on the first page of this article): ORTEP and crystallographic data of [HC$_H$]Br (CCDC 1025332), $A_{Me}$ (CCDC 1025333), and $B_{Me}$ (CCDC 1025334). Details to the chemicals, syntheses, and general procedures. $^{29}$Si NMR spectra of the product mixtures. Computational details and additional information on the reaction mechanism. XYZ coordinates of all computed structures.

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**Keywords:** N-heterocyclic carbenes; Bromosilanes; Silylenes; Reaction mechanism; Density functional theory

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