Silicon Compounds

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Si=Si Double Bonds: Synthesis of an NHC-Stabilized Disilavinylidene[**]

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Abstract: *An efficient two-step synthesis of the first NHC-stabilized disilavinylidene (Z)-(SIdipp)Si=Si(Br)Tbb (**2**; SIdipp = $C[N(C_6H_3\text{-}2,6\text{-}iPr_2)CH_2]_2$, Tbb = $C_6H_2\text{-}2,6\text{-}[CH(SiMe_3)_2]_2\text{-}4\text{-}tBu$, NHC = N-heterocyclic carbene) is reported. The first step of the procedure involved a 2:1 reaction of $SiBr_2$(SIdipp) with the 1,2-dibromodisilene (E)-Tbb(Br)Si=Si(Br)Tbb at 100°C, which afforded selectively an unprecedented NHC-stabilized bromo(silyl)silylene, namely SiBr($SiBr_2$Tbb)(SIdipp) (**1**). Alternatively, compound **1** could be obtained from the 2:1 reaction of $SiBr_2$(SIdipp) with LiTbb at low temperature. **1** was then selectively reduced with C_8K to give the NHC-stabilized disilavinylidene **2**. Both low-valent silicon compounds were comprehensively characterized by X-ray diffraction analysis, multinuclear NMR spectroscopy, and elemental analyses. Additionally, the electronic structure of **2** was studied by various quantum-chemical methods.*

The heavier Group 14 homologues of alkynes E_2R_2 are of considerable interest in theoretical and experimental chemistry.[1] Calculations of the potential energy surface (PES) of the parent silicon compound Si_2H_2 revealed that the energetic minima in order of increasing energy are: a structure bridged by two hydrogen atoms, a structure bridged by one hydrogen, a disilavinylidene, and a *trans*-bent disilyne structure (Figure 1).[2]

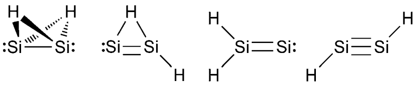

Figure 1. Calculated minimum structures of Si_2H_2. The relative energy increases for the structures from left to right. The bonds to the bridged H atoms correspond to three-center two-electron bonds and two dots represent a lone pair of electrons.

The PES calculated for Si_2H_2 is markedly different to the calculated PES of C_2H_2 which shows the vinylidene $H_2C{=}C$ as the only higher-energy minimum structure, a species that rapidly isomerizes by quantum-mechanical tunneling to the global energy minimum acetylene $HC{\equiv}CH$.[3,4] Both hydrogen-bridged structures of Si_2H_2 were detected by rotational spectroscopy in low-temperature matrices.[5] The derivatives Si_2R_2 with bulky substituents (R = silyl,[6a,b,d] aryl,[6c] alkyl[6e]) were isolated as stable compounds in the condensed phase and found to adopt a *trans*-bent disilyne structure.

Although the chemistry of disilynes has flourished since the isolation of the first stable derivatives,[7] experimental studies on disilavinylidenes have not been reported. We aimed to control the high reactivity of these species by trapping with N-heterocyclic carbenes (NHCs). This concept proved to be particularly successful in recent years leading to a renaissance of low-valent silicon chemistry.[8] Remarkable examples for the thermodynamic stabilization provided by N-heterocyclic carbenes are the Si(0) compounds Si_2(Idipp)$_2$ (Idipp = $C[N(C_6H_3\text{-}2,6\text{-}iPr_2)CH]_2$)[9] and Si(bNHC) (bNHC = chelating bis-*N*-heterocyclic carbene),[10] the NHC-adducts of the Si(II) compounds SiX_2 (X = Cl, Br, I),[11] Si(X)R (X = Cl, Br; R = aryl, amino),[12] and SiR(Si=SiR_2),[13] the NHC-stabilized 1-silacyclopenta-2,4-dienylidenes $(RC)_4Si$,[14] or the NHC-trapped $[SiR]^+$[11d,12d,15] and Si^{2+} ions.[11d] The same concept was recently employed to trap a silagermenylidene ($R_2Si{=}Ge$)[16] and a phosphasilenylidene (RP=Si).[17] Notably, an NHC-stabilized disilavinylidene was recently presumed to be one of the intermediates during the formation of an NHC-stabilized trisilacycloprop-1-ylidene, but no experimental evidence was provided.[18] Also recent theoretical work predicted that NHC-stabilized silavinylidenes and the heavier homologues should be stable and isolable molecules.[19] We set out to combine the well-known Lewis base character of ECl_2(NHC) (E = Si, Ge)[8b,20] with the electrophilicity of multiply bonded low-valent silicon compounds, such as the 1,2-dihalodisilenes,[6c,12d,21,22] and envisaged that this approach might lead to new interesting silicon chemistry. Herein, we report the realization of this approach with the syntheses and full characterization of an unprecedented NHC-stabilized bromo(silyl)silylene and its reduction product, an NHC-stabilized disilavinylidene.

$SiBr_2$(SIdipp)[11c] and (*E*)-Tbb(Br)Si=Si(Br)Tbb[12d] (SIdipp = $C[N(C_6H_3\text{-}2,6\text{-}iPr_2)CH_2]_2$, Tbb = $C_6H_2\text{-}2,6\text{-}[CH(SiMe_3)_2]_2\text{-}4\text{-}tBu$; see Scheme 1 for the substituent structures) were chosen as promising starting materials to test our concept. Heating of a 2:1 mixture of $SiBr_2$(SIdipp) and (*E*)-Tbb(Br)Si=Si(Br)Tbb in toluene at 100°C for 5 h was accompanied by a color change from yellow to orange.

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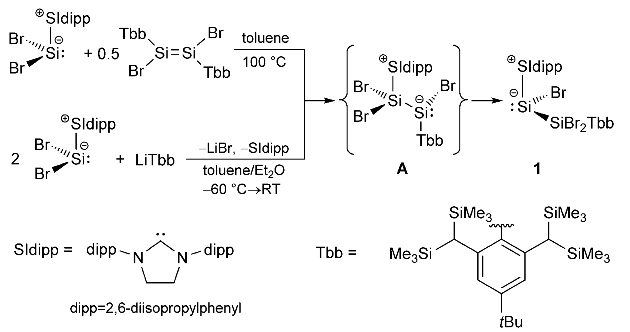


Scheme 1. Syntheses of **1** starting from $SiBr_2$(SIdipp) via the putative intermediate (SIdipp)Br_2SiSi(Br)Tbb (**A**) and the structures of the groups SIdipp and Tbb.

Monitoring of the reaction progress by ^{1}H NMR spectroscopy revealed a selective conversion into the NHC-stabilized bromo(silyl)silylene **1**, which after workup was isolated as a yellow, extremely air-sensitive solid in 61% yield (Scheme 1).[23] Compound **1** decomposes upon melting at 122–125 °C.

A two-step reaction pathway can be suggested for the formation of **1** given the Lewis basic character of $SiBr_2$(SIdipp)[11c] and the propensity of 1,2-dibromodisilenes (*E*)-R(Br)Si=Si(Br)R to act as precursor for the synthesis of bromosilylenes Si(Br)R.[21b,22] In the first step, the base-stabilized silylene intermediate **A** is slowly formed, which then rapidly rearranges via a 1,2-migration of bromine from the four- to the three-coordinate Si center to give the final product **1** (Scheme 1). Indirect evidence for this pathway was provided by the reaction of $SiBr_2$(SIdipp) with Ge(Br)R (R = C_6H_3-2,6-Mes_2, Mes = C_6H_2-2,4,6-Me_3), which was found to stop at the base-stabilized aryl(bromo)germylene (SIdipp)Br_2SiGe(Br)R.[24]

With the goal of expanding the range of accessible NHC-stabilized bromo(silyl)silylenes, a second method for the synthesis of **1** was devised starting from LiTbb (generated in situ) and $SiBr_2$(SIdipp). Indeed, addition of a diethyl ether/*n*-pentane solution of LiTbb to a toluene solution of $SiBr_2$(SIdipp) (2 equiv) at −60 °C followed by slow warming to room temperature afforded a mixture of **1** and SIdipp, as evidenced by ^{1}H NMR spectroscopy. After trapping the released SIdipp with BPh_3 as the less-soluble adduct SIdipp·BPh_3, compound **1** could be easily separated upon extraction with *n*-pentane and isolated as a spectroscopically pure yellow solid in 50% yield. Although no intermediates could be detected in this reaction, a plausible pathway to **1** could start with a metathetical exchange of LiTbb with $SiBr_2$(SIdipp) to give, after elimination of SIdipp, a bromosilylene (Si(Br)Tbb) or a lithium silylenoid (LiSiBr_2(Tbb))[22,25] intermediate. These intermediates are then rapidly trapped by the second equivalent of $SiBr_2$(SIdipp) to give **A**, which finally rearranges as described above to **1** (Scheme 1). Alternatively, the second step might involve an oxidative addition of $SiBr_2$(SIdipp) to the bromosilylene Si(Br)Tbb to give **1**.

This reaction offers a more general approach to NHC-stabilized bromo(silyl)silylenes SiBr($SiBr_2$R)(NHC) since it can be applied to a wider range of bulky organyl substituents R, for which the corresponding 1,2-dibromodisilenes (*E*)-R(Br)Si=Si(Br)R are presently unknown. In fact, current studies in our group have confirmed that the reactions of LiC_6H_3-2,6-Mes_2 and $LiC(SiMe_3)_3$ with two equivalents of $SiBr_2$(SIdipp) proceed smoothly to give the corresponding NHC-stabilized bromo(silyl)silylenes.

Compound **1** is the first NHC-stabilized bromo(silyl)silylene to be reported and was characterized by single-crystal X-ray diffraction analysis, multinuclear NMR spectroscopy, and elemental analysis.[23] In fact, silylsilylenes are an interesting class of very reactive Si^{II} compounds, which have been suggested as transient intermediates in silylsilylene–disilene rearrangement reactions.[6c,26] Only recently one stable amido(silyl)silylene, specifically Si[Si$(SiMe_3)_3$][N$(SiMe_3)$(dipp)] (dipp = C_6H_3-2,6-*i*Pr_2), was reported.[27] Base-stabilized silylsilylenes are also very rare and only three examples have been reported: the amidinato-stabilized derivative Si[SiX{(N*t*Bu)$_2$CHPh}][(N*t*Bu)$_2$CPh] (X = H, Cl),[28] the NHC-stabilized disilylsilylene Si(Si*t*Bu_3)$_2$(IMe_4) (IMe_4 = C[N(Me)C(Me)]$_2$)[29] and the NHC-stabilized hydrido(silyl)silylene SiH(Si*t*Bu_3)(IMe_4).[30]

The molecular structure of **1** features a trigonal-pyramidal geometry at the Si2 center, indicating the presence of a stereochemically active lone pair of electrons at Si2, and tetrahedral geometry at the Si1 atom, as expected for a silyl substituent (Figure 2). The sum of angles at Si2 (287.4°) compares well with that of $SiBr_2$(SIdipp) (sum of angles = 290°)[11c] and corresponds to a pyramidalization degree of 81%.[31] The bulky SIdipp and Tbb substituents as well as the bromine atoms Br1 and Br3 adopt an almost antiperiplanar

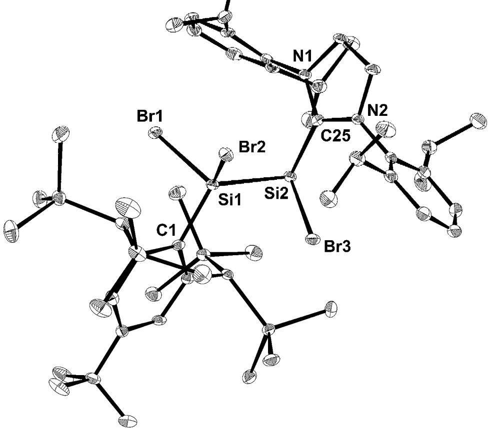
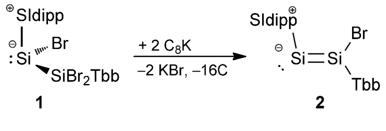


Figure 2. DIAMOND plot of the molecular structure of compound **1** in the crystal lattice of the *n*-pentane solvate **1**·(*n*-C_5H_{12}). The thermal ellipsoids are set at 30% probability at 123(2) K. Hydrogen atoms and the solvent molecule are omitted for clarity. Selected bond lengths [Å], bond angles [°], and torsion angles [°]: Si1−Si2 2.391(1), Si1−C1 1.921(3), Si2−C25 1.978(3), Si1−Br1 2.2634(9), Si1−Br2 2.286(1), Si2−Br3 2.342(1); C1-Si1-Si2 119.7(1), C1-Si1-Br1 101.24(9), C1-Si1-Br2 116.1(1), C25-Si2-Si1 102.1(1), C25-Si2-Br3 100.7(1), Si1-Si2-Br3 84.59(4), Si2-Si1-Br1 114.94(5), Si2-Si1-Br2 102.68(4); C1-Si1-Si2-C25 −159.5(2), C1-Si1-Si2-Br3 −59.6(1), C25-Si2-Si1-Br1 79.7(1), C25-Si2-Si1-Br2 −29.0(1), Br1-Si1-Si2-Br3 179.48(5).

conformation along the Si1−Si2 single bond as evidenced by the torsion angles C1$_{(\mathrm{Tbb})}$-Si1-Si2-C25$_{(\mathrm{NHC})}$ and Br1-Si1-Si2-Br3, which have the values −159.5(2)° and 179.48(5)°, respectively. The Si1−Si2 bond length (2.391(1) Å) compares well with that of the amidinato-stabilized silylsilylene Si[SiX{(N*t*Bu)$_2$CHPh}][(N*t*Bu)$_2$CPh] (X = H, *d*(Si−Si) = 2.377(5) Å; X = Cl, *d*(Si−Si) = 2.381(7) Å)[28] or the amido(silyl)silylene Si[Si(SiMe$_3$)$_3$][N(SiMe$_3$)(dipp)] (*d*(Si−Si) = 2.386(1) Å),[27] but is slightly longer than the Si−Si single bond length in α-Si (2.352 Å).[32] The Si−C$_{\mathrm{NHC}}$ bond length (Si2−C25 = 1.978(3) Å) compares well with those of other NHC-stabilized Si$^{\mathrm{II}}$ bromides, such as SiBr$_2$(SIdipp) (2.007(5) Å),[33] or SiBr$_2$(Idipp) (1.989(3) Å).[11b] Similarly, the Si$^{\mathrm{II}}$−Br bond length of **1** (*d*(Si2−Br3) = 2.342(1) Å) is found in the range of other Si$^{\mathrm{II}}$ bromides (2.3201(7)–2.3607(8) Å),[11b,c] whereas the Si1−Br1 (2.2634(9) Å) and Si1−Br2 (2.286(1) Å) bonds are considerably shortened and close in value to the mean Si−Br bond length of bromosilanes (2.243 Å).[34]

The ^{29}Si NMR spectrum of **1** displays two characteristic singlets at $\delta = -11.3$ and −1.9 ppm, which were assigned by ^{1}H–^{29}Si correlation spectroscopy to the *Si*Br$_2$ and *Si*Br nuclei, respectively. The silylene (*Si*Br) resonance signal in the ^{29}Si NMR spectrum appears at a slightly higher field than that of SiBr$_2$(SIdipp) ($\delta = 10.8$ ppm).[11c] Two additional singlets are detected in the ^{29}Si NMR spectrum of **1** for the SiMe$_3$ substituents of the Tbb group at $\delta = 2.45$ and 2.64 ppm, indicating the presence of a stereogenic trigonal-pyramidal Si2 center with a high racemization barrier, which is typical for three-coordinate Si$^{\mathrm{II}}$ compounds.[12a] This barrier renders the two SiMe$_3$ groups in the 2,6-bonded CH(SiMe$_3$)$_2$ substituents of the Tbb group diastereotopic despite the rapid rotation of the Tbb group about the Si1−C1$_{(\mathrm{Tbb})}$ bond on the NMR timescale.

Compound **1** contains several reactive sites for further functionalization. Reduction of **1** with two equivalents of C$_8$K in benzene was accompanied by a color change from orange to red and proceeded smoothly, according to ^{1}H NMR spectroscopy, to afford selectively the NHC-stabilized disilavinylidene **2** (Scheme 2). Compound **2** was isolated after



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

crystallization from *n*-pentane as a bright-red, microcrystalline solid in 60% yield.[23] Compound **2** is extremely air sensitive and decolorizes instantaneously upon exposure to air. It is remarkably stable to heat and starts to decompose upon melting at 237–238 °C.

Compound **2** was fully characterized.[23] Its molecular structure reveals a planar core composed of the atoms C1, Si1, Br, Si2, and C25 (sum of angles at Si1 = 360.1(1)°; Figure 3). The bulky Tbb and SIdipp groups are *trans*-arranged at the Si1=Si2 double bond (torsion angle C1$_{(\mathrm{Tbb})}$-Si1-Si2-C25$_{(\mathrm{NHC})}$ = 177.3(2)°) and orthogonally oriented with respect to the planar core of the molecule, as evidenced by the dihedral angles between the Tbb and NHC central ring least-square planes and the least-square plane passing through the atoms C1, Si1, Si2, Br, and C25, which have values 83.8(1) and 92.9(1)°, respectively. The Si1−Si2 bond of **2** (2.167(2) Å) is significantly shorter than the Si−Si single bond in **1** (2.391(1) Å), which in combination with the results of the electronic structure analysis (see below) corroborates the presence of a Si=Si bond in **2**.[35] Notably, the Si=Si bond of **2** is shorter than that of Si$_2$(Idipp)$_2$ (2.229(1) Å)[9] and Si$_2$(SIdipp)$_2$ (2.2323(8) Å),[36] and is also shorter than that of (*E*)-Tbb(Br)Si=Si(Br)Tbb (2.216 Å).[33] This trend can be rationalized with the increased s character (50%) of the hybrid orbital of the Si1 atom used for the Si1−Si2 σ-bonding in **2** (Table 1). Another salient structural feature of **2** is the narrow angle at the two-coordinate Si2 atom of 97.6(1)° (for C25-Si2-Si1), which has a similar value to that in Si$_2$(Idipp)$_2$ (C$_{\mathrm{NHC}}$-Si-Si 93.37(5)°),[9] Si$_2$(SIdipp)$_2$ (C$_{\mathrm{NHC}}$-Si-Si 93.07(5)°),[36] and (Idipp)Si=PMes* (C$_{\mathrm{NHC}}$-Si-P 96.90(6)°; Mes* = C$_6$H$_2$-2,4,6-*t*Bu$_3$).[17] A rationale for the narrow angle at Si2 is provided by the natural bond orbital (NBO) analysis of the model compound (*Z*)-**2′**$_{\mathbf{calc}}$ (Figure 4, Table 1). NBO analysis indicates a stereochemically active lone pair of electrons of high s character (77%) at Si2, and further shows that the Si2 atom uses hybrid orbitals of high p character for the σ bonding to the Si1 atom and the C$_{\mathrm{NHC}}$ atom (89% and 90%, respectively). The Si2−C25$_{(\mathrm{NHC})}$ bond length of **2** (1.937(4) Å) compares well to that of Si$_2$(SIdipp)$_2$ (1.924(2) Å)[36] or Si$_2$(Idipp)$_2$ (1.927(2) Å)[9] and is only slightly longer than the Si1−C1$_{(\mathrm{Tbb})}$ bond (1.882(4) Å).

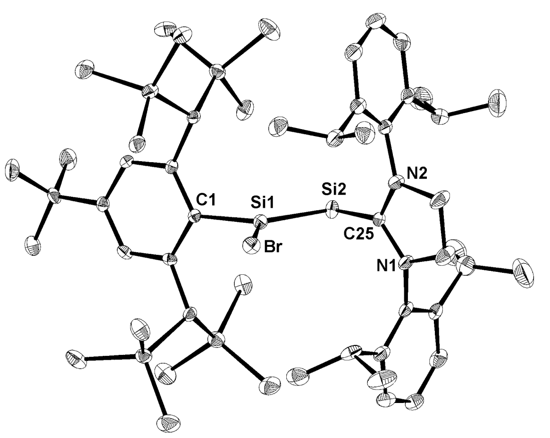


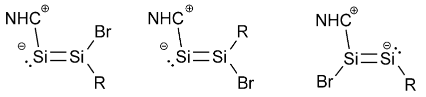
Figure 3. DIAMOND plot of the molecular structure of **2** in the crystal lattice of the *n*-pentane solvate **2**·(*n*-C$_5$H$_{12}$). Thermal ellipsoids are set at 30% probability. Hydrogen atoms and the solvent molecule are omitted for clarity. Selected bond lengths [Å], bond angles [°], and torsion angles [°]: Si1−Si2 2.167(2), Si1−C1 1.882(4), Si2−C25 1.937(4), Si1−Br 2.286(1); C1-Si1-Si2 123.4(1), C1-Si1-Br 109.5(1), C25-Si2-Si1 97.6(1), Si2-Si1-Br 127.16(5); C1-Si1-Si2-C25 177.3(2), C25-Si2-Si1-Br −4.0(2).

The ^{1}H, ^{13}C, and ^{29}Si NMR spectra of **2** indicate an overall *C*$_s$-symmetric structure in solution and a rapid rotation of the bulky Tbb and SIdipp groups about the respective Si−C bonds. In contrast to **1**, this leads to equivalent SiMe$_3$ groups on the Tbb substituent and to equivalent C2/C6- and C3/C5-

Table 1: Selected results of the natural bond orbital (NBO) and natural resonance theory (NRT) analyses of (*Z*)-**2′**$_{calc}$.[a]

	NBO analysis[b]				NPA partial charges[c]		NRT analysis[d]	
	occ.	pol. [%]	hyb.	WBI	atom	charge	bond	tot/cov/ionic
σ(Si1–Si2)	1.92	60.8 (Si1)	sp$^{1.01}$ (Si1)	1.79			Si1–Si2	1.91/1.61/0.30
		39.2 (Si2)	sp$^{8.27}$ (Si2)		Si1	0.52		
π(Si1–Si2)	1.84	51.1 (Si1)	sp$^{26.11}$(Si1)		Si2	0.03		
		48.9 (Si2)	sp$^{38.59}$(Si2)					
σ(Si1–C$_{aryl}$)	1.94	29.4 (Si1)	sp$^{2.36}$ (Si1)	0.78	C$_{aryl}$	−0.46	Si1–C$_{aryl}$	0.96/0.57/0.40
		70.6 (C$_{aryl}$)	sp$^{2.53}$ (C$_{aryl}$)		Σ(aryl)	−0.62		
σ(Si2–C$_{NHC}$)	1.93	22.6 (Si2)	sp$^{9.05}$ (Si2)	0.84	C$_{NHC}$	0.17	Si2–C$_{NHC}$	1.13/0.47/0.66
		77.4 (C$_{NHC}$)	sp$^{1.38}$ (C$_{NHC}$)		Σ(NHC)	0.42		
σ(Si1–Br)	1.97	26.6 (Si1)	sp$^{4.75}$ (Si1)	0.79	Br	−0.36	Si1–Br	0.94/0.49/0.45
		73.4 (Br)	sp$^{4.48}$ (Br)					
n(Si2)	1.78		sp$^{0.3}$		Σ(Si$_2$Br)	0.19		

[a] Atom numbers used in the experimental structure were employed also in the calculated structure (*Z*)-**2′**$_{calc}$. [b] occ. = occupancy, pol. = polarization, hyb. = hybridization, WBI = Wiberg bond index. [c] Partial charges obtained by natural population analysis (NPA). [d] A local NRT analysis was carried out including the Br, Si1, Si2, N, C$_{aryl}$, and C$_{NHC}$ atoms, tot/cov/ionic: total bond order/covalent bond order/ionic bond order.



(*Z*)-**2'**$_{calc}$ 0.00 kJ mol^{-1} (*E*)-**2'**$_{calc}$ 43.4 kJ mol^{-1} (*Z*)-**2''**$_{calc}$ 33.0 kJ mol^{-1}

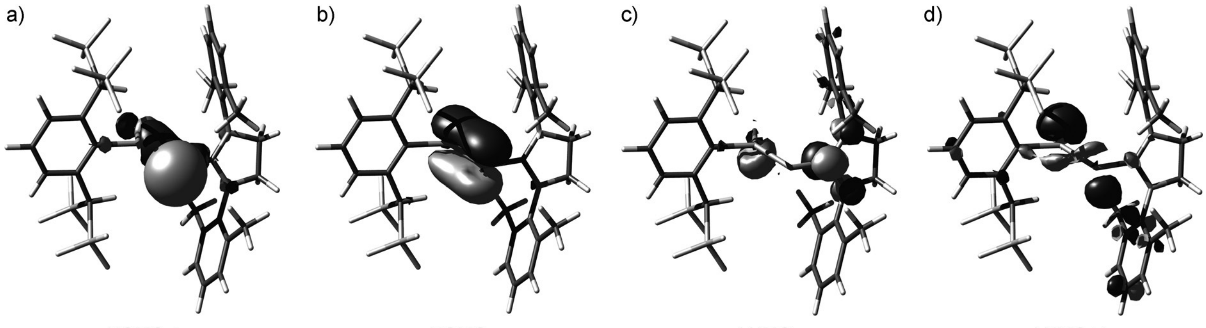
Figure 4. Isomers of the model system (NHC)Si=Si(Br)R (**2′**$_{calc}$: NHC = C[N(C$_6$H$_3$-2,6-Me$_2$)CH$_2$]$_2$, R = C$_6$H$_3$-2,6-[CH(SiH$_3$)$_2$]$_2$) with the corresponding relative Gibbs energies.

positions in the peripheral dipp substituents of the SIdipp group. Most distinctive are the signals for the double bonded Si atoms in the ^{29}Si NMR spectrum of **2** in C$_6$D$_6$ solution which appear at $\delta = 86.0$ and 34.6 ppm. These signals were assigned by ^{1}H–^{29}Si correlation spectroscopy. While the chemical shift of the three-coordinate Si atom (δ(Si1) = 86.0 ppm) compares well with that of (*E*)-Tbb(Br)Si=Si(Br)Tbb ($\delta = 84.12$ ppm in C$_6$D$_6$),[12d] the ^{29}Si NMR signal for the two-coordinate Si atom (δ(Si2) = 34.6 ppm) appears at much higher field than that of Si$_2$(SIdipp)$_2$ (δ(^{29}Si) = 215.2 ppm in C$_6$D$_6$ at 348 K),[36] Si$_2$(Idipp)$_2$ (δ(^{29}Si) = 224.5 ppm in C$_6$D$_6$),[9] or (Idipp)Si=PMes* (δ(^{29}Si) = 267.3 ppm in C$_6$D$_6$).[17]

Geometric optimization of **2** at the RIJ-B97-D3/TZVP level of theory afforded a minimum structure with an excellent agreement between the calculated and experimental bonding parameters (see Table S1 in the Supporting Information).[23] Furthermore, a search for other possible isomers of **2** was carried out for the smaller model system (*Z*)-(NHC)Si=Si(Br)R ((*Z*)-**2′**$_{calc}$: NHC = C[N(C$_6$H$_3$-2,6-Me$_2$)CH$_2$]$_2$, R = C$_6$H$_3$-2,6-[CH(SiH$_3$)$_2$]$_2$; Figure 4). Two additional minimum-energy structures were found on the potential energy hypersurface at the same level of theory, the one corresponding to the (*E*)-diastereomer ((*E*)-**2′**$_{calc}$) and the other to the structural isomer (*Z*)-**2″**$_{calc}$, an NHC-stabilized bromodisilyne (Figure 4).[37] Both isomers were found to be less stable than (*Z*)-**2′**$_{calc}$ by 43.4 and 33.0 kJ mol^{-1}, respectively.

A look at the Kohn–Sham frontier orbitals reveals that the HOMO of (*Z*)-**2′**$_{calc}$ is the Si=Si π-bonding orbital, which is followed by the Si2 lone-pair orbital (HOMO-1) at considerably lower energy (Figure 5).

A natural bond orbital analysis (NBO) of the wave function of (*Z*)-**2′**$_{calc}$ suggests a high localization of the orbitals



HOMO-1 –4.93 eV HOMO –3.86 eV LUMO –1.86 eV LUMO+1 –1.83 eV

Figure 5. Selected Kohn–Sham orbitals of (*Z*)-**2′**$_{calc}$ and their corresponding energy eigenvalues; isosurface value 0.05 e bohr^{-3}.

describing the Si=Si, Si–C_{NHC}, Si–C_{aryl}, and Si–Br bonds (Table 1). For example the Si–Si σ-bond NBO is occupied with 1.92 electrons and the Si–Si π-bond NBO with 1.84 electrons. Whereas the Si–Si σ bond is slightly polarized towards the Si1 atom, the Si–Si π bond is not polarized and is formed from almost pure Si p orbitals. The moderate polarization of the Si–Si bond and the high occupancies of its NBO lead to a high Wiberg bond index (WBI) of 1.79, suggesting the presence of a quite covalent Si=Si bond. Additional support was provided by the high covalent contribution to the overall Si–Si bond order of 1.91 obtained by natural resonance theory (NRT) (Table 1), which furthermore showed that the canonical formula depicted in Scheme 2 contributes to 67% to the resonance hybrid.[23] Finally, a natural population analysis (NPA) of (Z)-**2′**$_{\mathrm{calc}}$ indicates a considerable charge flow from the NHC to the disilavinylidene fragment as evidenced by the overall NPA charge of the NHC ($q(\Sigma(\mathrm{NHC}))=0.42$). Remarkably, the two-coordinate Si2 atom is almost electroneutral ($q=0.03$), whereas the three-coordinate Si1 atom bears a positive partial charge of 0.52.

In conclusion, the first NHC-stabilized bromo(silyl)silylene and disilavinylidene **1** and **2** were reported in this work. Their isolation and full characterization corroborates the potential of N-heterocyclic carbenes (NHC) to stabilize compounds of low-valent silicon in unusual bonding environments. Both compounds contain many reactive sites, such as the Si lone pair, the Si–Br bonds, or the displaceable NHC group, opening up many potential reaction pathways that are currently under investigation in our laboratory.

Keywords: disilavinylidenes · multiple bonds · N-heterocyclic carbenes · quantum-chemical calculations · silicon

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