Silicon Compounds Hot Paper

International Edition: DOI: 10.1002/anie.201504489
German Edition: DOI: 10.1002/ange.201504489

# From Silylone to an Isolable Monomeric Silicon Disulfide Complex**

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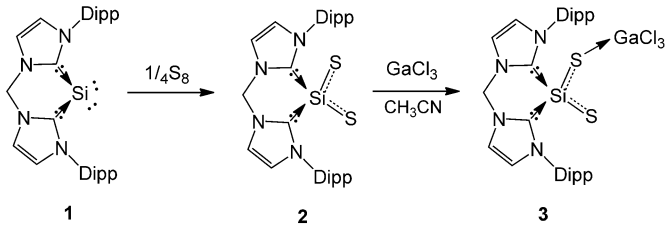
*Dedicated to Professor Manfred Scheer on the occasion of his 60th birthday*

***Abstract:*** *The synthesis and characterization of the first bis-N-heterocyclic carbene stabilized monomeric silicon disulfide (bis-NHC)SiS$_2$* **2** *(bis-NHC = $H_2C[\{NC(H)C(H)N(Dipp)\}C:]_2$, Dipp = 2,6-iPr$_2$C$_6$H$_3$) is reported. Compound* **2** *is prepared in 89 % yield from the reaction of the zero-valent silicon complex ('silylone')* **1** *[(bis-NHC)Si] with elemental sulfur. Compound* **2** *can react with GaCl$_3$ in acetonitrile to give the corresponding (bis-NHC)Si(S)S→GaCl$_3$ Lewis acid–base adduct* **3** *in 91 % yield. Compound* **3** *is also accessible through the reaction of the unprecedented silylone-GaCl$_3$ adduct [(bis-NHC)Si→GaCl$_3$]* **4** *with elemental sulfur. Compounds* **2**, **3**, *and* **4** *could be isolated and characterized by elemental analyses, HR-MS, IR, $^{13}$C- and $^{29}$Si-NMR spectroscopy. The structures of* **3** *and* **4** *could be determined by single-crystal X-ray diffraction analyses. DFT-derived bonding analyses of* **2** *and* **3** *exhibited highly polar Si–S bonds with moderate $p_\pi$–$p_\pi$ bonding character.*

Silicon disulfide SiS$_2$ is a textbook compound which was first prepared from elemental silicon and sulfur by Berzelius in 1824.[1] Under normal conditions SiS$_2$ adopts a polymeric structure owing to the extremely high polarity of the Si–S bond.[2] Monomeric SiS$_2$ (S=Si=S) is a heavier analogue of CO$_2$ and CS$_2$ but far more reactive, and it undergoes spontaneous polymerization as a result of the relatively weak $p_\pi$–$p_\pi$ bond between the silicon and sulfur atoms. Since monomeric SiS$_2$ is metastable its isolation requires the utilization of particular experimental techniques and methods. Schnöckel and co-workers showed that molecular SiS$_2$ can be synthesized and isolated under matrix isolation conditions at very low temperatures and studied spectroscopically.[3] In an alternative approach, the isolation of monomeric SiS$_2$ even at room temperature could be envisaged by taking advantage of the concept of donor–acceptor stabilization and formation of a L→SiS$_2$ complex with L acting as a donor ligand towards the strongly electrophilic silicon atom in S=Si=S. To our knowledge, such a complex is currently unknown.

The concept of kinetic and/or thermodynamic stabilization has enabled great achievements in the chemistry of low-coordinate silicon compounds as shown through the isolation and structural characterization of disilenes, Ar$_2$Si=SiAr$_2$ (Ar = 2,4,6-Me$_3$C$_6$H$_2$), by West et al.[4] Remarkable examples also include the isolation of stable silylenes,[5] disilynes,[6] and other interesting low-coordinate silicon species.[7a–c] Moreover, a striking N-heterocyclic carbene (NHC) supported disilicon(0) complex could be synthesized by Robinson et al. by taking advantage of the concept of donor–acceptor stabilization.[7d] Unusual silicon species featuring elusive terminal Si=O and Si=S moieties[4a,8] and E=Si=E bonds (M = C, Si, Ge)[9] could as well be stabilized using Lewis donors. Very recently, Roesky et al. and our group successfully isolated the first zero-valent silicon complexes ('silylones') by utilizing two cyclic alkyl(amino) carbenes (cAACs)[10a] and the bis-NHC chelating ligand (bis-NHC = $H_2C[\{NC(H)C(H)N(Dipp)\}C:]_2$, Dipp = 2,6-*i*Pr$_2$C$_6$H$_3$),[10b] respectively. Owing to the stronger σ-donor but weaker π-acceptor character of the bis-NHC ligand, the silylone **1** bearing two lone pairs of electrons on the silicon atom (Scheme 1) is more electron-rich than Roesky's (cAAC)$_2$Si as confirmed by DFT calculations. The presence of an electron-rich silicon(0) atom in the pocket of the sterically protecting bis-NHC ligand of **1** prompted us to investigate whether the monomeric silicon disulfide complex **2** could be synthesized by direct oxidation of **1** with elemental sulfur. Herein we report the synthesis and characterization of the first SiS$_2$ complex (bis-NHC)SiS$_2$ **2** and its GaCl$_3$ adduct **3**, (bis-NHC)Si(S)S→GaCl$_3$, starting from silylone **1** (Scheme 1).



***Scheme 1.*** Formation of the SiS$_2$ complex **2** and its GaCl$_3$ adduct **3**, starting from the bis-NHC stabilized silylone **1** (Dipp = 2,6-*i*Pr$_2$C$_6$H$_3$).

Treatment of a dark red solution of **1** in THF with 0.25 molar equivalents of elemental sulfur (S$_8$) at room temperature leads immediately to a color change of the

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[**] We are grateful to the Deutsche Forschungsgemeinschaft (Sonderforschungsbereich 1109) for financial support. We thank Dr. Vladimir Pelmenschikov for providing the Q-Spector program.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201504489.

reaction mixture to pale orange, and subsequent formation of a colorless precipitate (Scheme 1). Filtration and washing of the precipitate with small amounts of THF affords the desired (bis-NHC)$SiS_2$ compound **2** as a colorless powder in 89% yield. The compound is insoluble in hydrocarbons and ethereal solvents. Its composition has been confirmed by correct elemental analysis and high-resolution (HR) electrospray ionization (ESI) mass spectrometry (MS; see Supporting Information). The HR-ESI-MS spectrum of **2** shows the molecular ion peak at *m*/*z* 561.25220 (calcd 561.25364). The solid state CP/MAS $^{29}Si\{^1H\}$ NMR spectrum of **2** displays a signal at $\delta = -32.5$ ppm which is in good agreement with the value of $\delta = -29.8$ ppm predicted by DFT calculations (Table 1). The experimental $^{29}Si\{^1H\}$ NMR chemical shift is upfield from the value of $\delta = -19.5$ ppm observed for polymeric and polycrystalline $SiS_2$.[11] However, it is very close to the chemical shifts of $\delta = -33.5$ and $-34.9$ ppm observed for the NHC-stabilized Si=S complexes L(NHC)SiS (L = N(Dipp)C(=$CH_2$)CH=C(Me)N(Dipp)) with four-coordinate silicon centers.[12a]

***Table 1:*** Calculated $^{29}Si$ NMR chemical shifts (in ppm vs. TMS; experimental values are given in parentheses),[a] NPA charges (*q*),[b] Wiberg bond indices (WBI),[b] and Mayer bond orders (MBO)[b] for compounds **2′**, **3′**, and **4′**.

| Parameter | **2′** | **3′** | **4′** |
|---|---|---|---|
| $\delta(^{29}Si)$ | −29.8 (−32.5) | −42.0 (−40.0) | −131.3 (−119.0) |
| *q*(Si) | +1.14 | +1.17 | +0.17 |
| $q(S_{ax/1})$ | −0.85 | −0.69 | – |
| $q(S_{eq/2})$ | −0.84 | −0.77 | – |
| $q(GaCl_3)$ | – | −0.46 | −0.73 |
| WBI(Si-$S_{ax/1}$) | 1.19 | 0.97 | – |
| WBI(Si-$S_{eq/2}$) | 1.34 | 1.41 | – |
| MBO(S-$S_{ax/1}$) | 1.65 | 1.24 | – |
| MBO(Si-$S_{eq/2}$) | 1.75 | 1.86 | – |

[a] B3LYP/IGLO-III(H,C,Si,N,S,Cl)/def2-TZVPP(Ga)//B3LYP-D3(BJ)/def2-TZVPP results. [b] B3LYP/def2-TZVPP results. As expected, owing to the different definitions of bond orders, MBOs exhibit a larger overall weight of covalent σ-bonding than WBIs, but the same trends when going from **2′** to **3′**.

Compound **2** is almost insoluble in common organic solvents, presumably due to the extremely high polarity of the two Si=S moieties. Thus attempts to grow single crystals of **2** for X-ray diffraction analysis failed. However, complexation of **2** with $GaCl_3$ in acetonitrile at ambient temperature leads to the formation of the soluble (bis-NHC)Si(S)S→$GaCl_3$ Lewis acid–base adduct **3** in 91% yield after work-up. Single crystals of **3** suitable for X-ray diffraction analysis were obtained in a THF solution at −30°C. Complex **3** crystallized in the monoclinic space group *Cm*. The analysis revealed the presence of a bis-NHC-ligand-supported monomeric silicon disulfide molecule which is coordinated to the $GaCl_3$ Lewis acid by a S→Ga bond (Figure 1). Accordingly, the Si atom adopts a distorted tetrahedral geometry and is in a slightly puckered six-membered $C_3N_2Si$ ring with the chelating bis-NHC ligand. The C1-Si1-C1′angle of 92.5(2)° is slightly larger than the corresponding angle in silylone **1** (89.1(2)°).[10b] The Si−C distances of 1.930(4) Å are elongated compared with the value observed for **1** (1.869 Å). As expected, the two Si−S distances are significantly different owing to the coordination of the $GaCl_3$ moiety to the S1 atom. While the Si1−S2 bond length of 2.006(2) Å is identical to the value of 2.006(1) Å found for the Si=S bond in L(NHC)Si=S mentioned above,[12a] the Si1−S1 bond of 2.106(2) Å is only slightly shorter than the Si−S single bond in [{PhC(N*t*Bu)$_2$}Si(S)S*t*Bu] (2.131(7) Å).[12b] In addition, the S-Si-S angle of 115.03(8)° in **3** deviates pronouncedly from the value of 180° for a linear S=Si=S structure of "free" $SiS_2$, apparently because of the coordination of the bis-NHC ligand to the highly electrophilic silicon center.

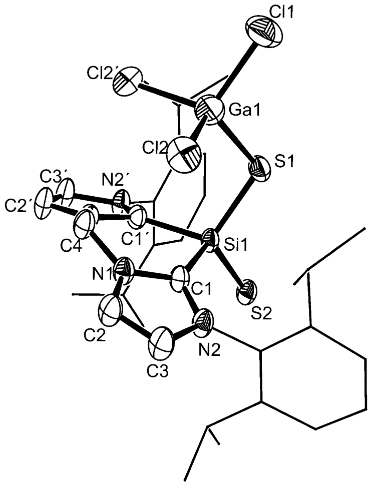
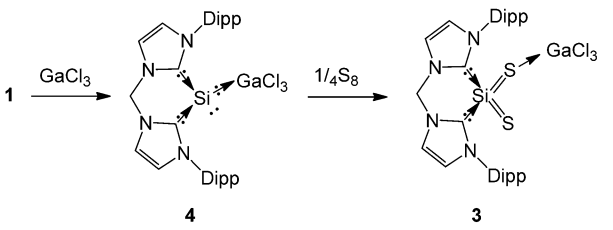


***Figure 1.*** Molecular structure of **3**. Thermal ellipsoids are set at 50% probability. H atoms and one THF lattice solvent molecule are omitted for clarity. Symmetry transformations used to generate equivalent atoms with (′): *x*,−*y*,*z*. Selected interatomic distances [Å] and angles [°]: S1-Si1 2.106(2), Ga1-S1 2.262(2), Si1-S2 2.006(2), Ga1-Cl1 2.169(2), Ga1-Cl2 2.190(1), Si1-C1 1.930(4), N1-C1 1.352(4), N1-C2 1.378(5), N1-C4 1.454(4), C1-N2 1.338(5), N2-C3 1.396(5), C2-C3 1.351(6); Si1-S1-Ga1 109.32(7), C1-Si1-C1′ 92.5(2), C1-Si1-S2 113.3(1), C1-Si1-S1 110.3(1), S2-Si1-S1 115.03(8), Cl1-Ga1-Cl2 109.28(5), Cl2-Ga1-Cl2′ 106.97(7), Cl1-Ga1-S1 107.86(8), Cl2-Ga1-S1 111.71(4).

Complex **3** is insoluble in hexane, toluene, and diethyl ether, but sparingly soluble in THF and acetonitrile which enabled us to record its $^1H$ NMR spectrum in $CD_3CN$ solutions (see Supporting Information). In the HR-ESI-MS spectrum of **3**, only the molecular ion peak of **2** at *m*/*z* 561.25470 (calcd 561.25364) could be observed. The solid-state CP/MAS $^{29}Si\{^1H\}$ NMR spectrum of **3** shows a signal at $\delta = -40.0$ ppm which is upfield shifted compared with **2** ($\delta = -32.5$ ppm). The change of the $^{29}Si$ shift of **3** is somewhat unexpected because $GaCl_3$ coordination withdraws charge from the silicon center (cf. more positive Si NPA charge in Table 1). Analysis of molecular-orbital (MO) contributions in this context (see below) show that changes in the $^{29}Si$ shielding are dominated by Si−S σ-bonding MOs (these have far larger MO coefficients at Si than the very polar Si−S π-bonding MOs; cf. Supporting Information for details), resulting in an overall stronger shielding of silicon in **3**.

Akin to **2**, the electron-rich zero-valent Si atom in silylone **1** is able to form a Lewis acid–base adduct with $GaCl_3$. Accordingly, treating a THF solution of **1** with one molar



***Scheme 2.*** Formation of the silylone–$GaCl_3$ adduct **4**, starting from silylone **1** and $GaCl_3$, and its direct oxidation with elemental sulfur to **3**.

equivalent of $GaCl_3$ results in the formation of the (bis-NHC)Si→$GaCl_3$ complex **4**, which precipitates from the reaction solution as a yellow solid and can be isolated in 58 % yield (Scheme 2). Even with molar excess of $GaCl_3$, only compound **4** is formed ($^1$H NMR). Compound **4** is the first Lewis acid–base adduct of a silylone. It crystallized as yellow blocks in the monoclinic space group $P2_1/c$ in acetonitrile solutions (Figure 2). X-ray diffraction analysis revealed a monomeric structure with the $GaCl_3$ moiety directly coordinated to the zero-valent Si atom. Thus the three-coordinate silicon atom features a pseudotetrahedral coordination geometry with a lone pair of electrons occupying the vertex. This implies that one of the lone pairs of the silicon center donates charge to the $GaCl_3$ molecule. The C-Si-C angle of 88.59(9)° is quite close to the corresponding angle found in silylone **1** (89.1(2)°). The sum of the bond angles around the silicon atom is 273.17°. The Si–C distance of 1.942(2) Å is slightly longer than the value in **1** (1.869 Å),[10b] but similar to the distance observed in **3**. The Si1–Ga1 distance of 2.4588(6) Å is similar to the Si–Ga values observed in a hypersilylated polygallium cluster [$Ga_{10}\{Si(SiMe_3)_3\}_9$] (2.443(1) to 2.468(1) Å).[13]

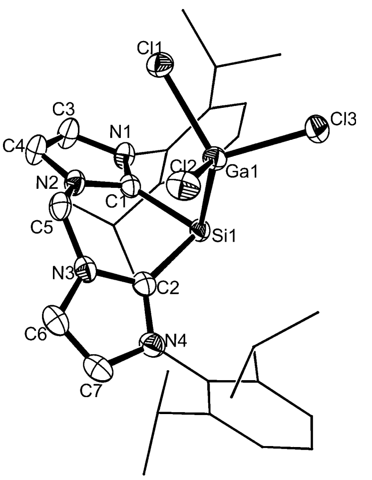
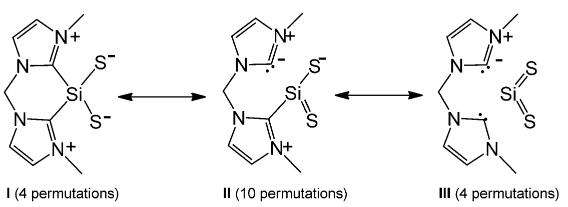


***Figure 2.*** Molecular structures of **4**. Thermal ellipsoids are set at 50 % probability. H atoms are omitted for clarity. Selected interatomic distances [Å] and angles [°]: Ga1-Cl3 2.2319(6), Ga1-Cl2 2.2516(6), Ga1-Cl1 2.2884(5), Ga1-Si1 2.4588(6), Si1-C2 1.942(2), Si1-C1 1.942(2), N1-C1 1.351(3), N1-C3 1.390(3), C1-N2 1.351(3), N2-C4 1.377(3), N2-C5 1.445(3), C2-N4 1.346(3), C2-N3 1.351(3), N3-C5 1.450(3), C3-C4 1.340(3); Cl3-Ga1-Cl2 102.42(2), Cl3-Ga1-Cl1 104.55(2), Cl2-Ga1-Cl1 97.45(2), Cl3-Ga1-Si1 113.32(2), Cl2-Ga1-Si1 120.82(2), Cl1-Ga1-Si1 115.83(2), C2-Si1-C1 88.59(9), C1-Si1-Ga1 92.16(9), C2-Si1-Ga1 92.42(9).

The $^1$H NMR spectrum of **4** shows one doublet and one broad signal for the methyl groups of the isopropyl substituents, presumably, caused by the coordination of $GaCl_3$ and the associated steric congestion which hinders the free rotation of the isopropyl groups. In line with this, the $^{29}Si\{^1H\}$ NMR spectrum exhibits a broad signal at $\delta = -119.0$ ppm, strongly upfield from that of **1** ($\delta = -83.8$ ppm). Interestingly, the reaction of **4** with elemental sulfur enables an alternative approach to **3** (Scheme 2). In fact, mixing **4** with 0.25 molar equivalent of $S_8$ in THF at room temperature affords **3** in 50 % yield after work-up.

To elucidate the electronic structure of **2** and **3**, DFT calculations at the B3LYP level of theory have been performed for truncated model systems (**2′**, **3′**, cf. Supporting Information for details). Table 1 lists the calculated $^{29}$Si chemical shifts (which are close to the computed values for the full, untruncated systems), as well as NPA charges and Wiberg/Mayer bond orders.

To achieve closer insight into bonding in **2′** and **3′** in terms of resonance, analyses based on natural resonance theory (NRT)[14] have been performed. Detailed NRT analyses are provided in Schemes S1 and S2 in the Supporting Information. Concisely summarizing the main results, Scheme 3 shows that the electronic structure is best described by semi-polar Si–S bonds and a delocalization of positive charge into the bis-carbene ligand framework. The underlying NRT structures account for about 80–85 % of the one-particle density matrix. Si–S multiple-bonding character is built in through no-bond/double-bond resonance structures (Scheme S1, S2; cf. Ref. [15] for related analyses in main-group chemistry). These contributions correspond to the notion of negative hyperconjugation in MO language. The overall weight of such resonance structures is about 11–13 % in **2′** and **3′**, consistent with relatively polar Si–S π-bonding ($S_1$ = the axial S atom, $S_2$ = the equatorial S atom). In **2′**, such resonance structures pertaining to the equatorial Si–$S_2$ bond contribute 9 %, those to the axial Si–$S_1$ bond approximately 4 %. $GaCl_3$ coordination to the axial $S_1$ (made favorable by its more negative sulfur charge, Table 1) eliminates the Si–$S_1$ contributions but enhances the weight of equatorial Si–$S_2$ multiple-bonding NRT structures to 11 %. These observations are fully consistent with Wiberg bond indices (WBI, Table 1), which



***Scheme 3.*** Predominant electronic-structure situation for compound **2′** (**I**) and no-bond/double-bond resonance structures (**II**, **III**). Permutation numbers include only resonance structures above 0.5 % weight.

exhibit moderate $\pi$ bonding for both Si–S bonds in **2′** (more for Si-S$_2$) but a clear reduction of bond order for Si-S$_1$ and a slight increase for Si-S$_2$ in **3′** (note also the large negative charges on sulfur). NPA charges clearly confirm the expected charge donation to the GaCl$_3$ Lewis acid (Table 1).

In summary, the first isolable monomeric silicon disulfide complex **2** could be synthesized by taking advantage of the donor–acceptor concept, starting from the electron-rich silylone **1** and elemental sulfur. One of the highly polar Si–S bonds in **2** is able to form a Lewis acid–base adduct, as shown by the reaction with GaCl$_3$ to give the (bis-NHC)Si(S)S$\rightarrow$Ga complex **3**. Compound **3** is also accessible from direct oxidation of the unprecedented silylone–GaCl$_3$ adduct **4** with elemental sulfur. Bonding analyses indicated highly polar Si–S bonds with moderate multiple-bonding character made possible by negative hyperconjugation ( no-bond/double-bond resonance). Notably, the multiple bonding character of the axial Si-S$_1$ bond in **2′** is lower than that of the equatorial Si-S$_2$ bond. In **3′**, GaCl$_3$ coordinates to the more negatively charged axial S$_1$. This quenches much of the $\pi$-bonding character in the Si-S$_1$ bond but enhances that in the Si-S$_2$ bond. Featuring a zero-valent silicon atom, the silylone **1** and its adduct **4** are also very sensitive towards other oxidation reagents such as dioxygen and N$_2$O which may enable the synthesis of isolable complexes of monomeric silicon oxides.[16] Respective investigations are currently in progress.

**Keywords:** hyperconjugation · multiple bonds · N-heterocyclic carbenes · silicon · sulfur

**How to cite:** *Angew. Chem. Int. Ed.* **2015**, *54*, 10254–10257
*Angew. Chem.* **2015**, *127*, 10392–10395

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Received: May 18, 2015