Facile Conversion of Bis-Silylene to Cyclic Silylene Isomers: Unexpected C−N and C−H Bond Cleavage

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Ⓢ *Supporting Information*

ABSTRACT: Reaction of thiolate **1** with carbene-stabilized diiodo-bis-silylene (**2**) (in a 2:1 ratio) in THF unexpectedly gives both the first five-membered, sulfur-containing, zwitterionic silylene ring (**3**) via insertion of the "Si$^I_2$" unit of **2** into the olefinic C−H bond of the imidazole ring of **1** and four-membered cyclic silylene (**4**) via insertion of a silicon(I) atom of **2** into the C$_{phenyl}$−N bond of the carbene ligand. The parallel reaction in toluene only gives **3** as the major product. The nature of the bonding in isomeric **3** and **4** was probed by experimental and theoretical methods.

Silylenes (R$_2$Si:), highly reactive divalent silicon species, are remarkable reaction intermediates.[1−3] In particular, the parent silylene (H$_2$Si:)[4] and chlorosilylenes[5−7] have been observed as reactive intermediates in chemical vapor deposition (CVD) of silicon from silane and chlorosilanes, respectively. Since the seminal discoveries of the siliconocene[8] and diamidosilylene,[9] a number of stable silylenes have been synthesized and employed in a variety of chemical processes including organic syntheses, transition-metal coordination, catalysis, and small-molecule activation.[10−18]

N-Heterocyclic silylenes have emerged as the most extensively studied cyclic silylenes (Figure 1a−c).[9,19,20] In
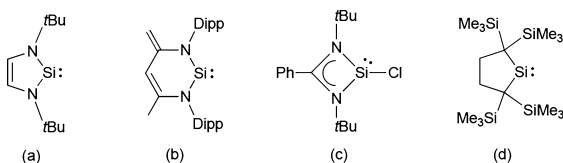

Figure 1. Representative cyclic silylenes.

contrast, cyclic alkyl silylenes (Figure 1d)[21] have been reported to be less persistent than those with stabilizing π-donor substituents. Acyclic silylenes are usually stabilized by Lewis base coordination.[22] Notably, stable, acyclic, two-coordinate silylenes have only recently been reported.[23−27] Among these acyclic two-coordinate silylenes, boryl(amino)silylene and diaminosilylene have been utilized in H$_2$, O$_2$, and NH$_3$ activations.[26,27]

This laboratory prepared an *N*-heterocyclic carbene (NHC)-stabilized bis-silylene [L:(Cl)Si−Si(Cl):L] via KC$_8$ reduction of L:SiCl$_4$ [L: = :C{N(2,6-Pr$^i_2$C$_6$H$_3$)CH}$_2$].[28] The synthesis of

[L:(X)Si−Si(X):L, X = Cl, Br, and I (**2**)] by combining L:Si═Si:L [L: = :C{N(2,6-Pr$^i_2$C$_6$H$_3$)CH}$_2$][28] with 1,2-dihaloethanes was subsequently reported.[29] Reaction of dihalo(bis-silylenes) with anionic ligands may provide an efficient route to aggregate the bis-silylene moiety into a variety of organic and organometallic substrates, rendering unusual low-oxidation-state organosilicon species. Herein, we report thiolate (**1**)-mediated conversion of bis-silylene (**2**) to five- and four-membered cyclic silylene isomers (**3** and **4**) via unexpected C−H and C−N bond cleavage, respectively.[30] Compounds **3** and **4**, notably, are the first cyclic silylenes containing a silicon−silicon bond. Although silylenes have been reported to participate in C−H bond activation of various organic substrates,[31−37] Compound **3** represents the first "Si$^I_2$" insertion into an olefinic C−H bond. Recently, main group species-mediated C−N bond activation of NHCs have begun to receive increased attention.[38,39] In addition to alkali metal-mediated C−N bond cleavage of saturated NHCs[40,41] and *N*-heterocyclic guanidine,[42] a series of main group (i.e., beryllium, silicon, boron, and aluminum) hydrides and Lewis acids have been reported to involve imidazole ring expansion reactions (RERs) via C$_{NHC}$−N bond activation.[43−51] Notably, reactive borylene intermediates have been proposed to insert into a C$_{phenyl}$−N bond of *N*-heterocyclic olefins.[52] To the best of our knowledge, **4** represents the first silicon(I)-mediated C−N bond cleavage of NHCs.

Recently, we synthesized an imidazole-based thiolate (**1**) by disulfurization of anionic *N*-heterocyclic dicarbene (Scheme 1).[53] Reaction of **1** with carbene-stabilized diiodo(bis-silylene) (**2**) in a 2:1 ratio in toluene gave **3** in 52.5% yield, whereas the parallel reaction in THF afforded a mixture containing cyclic silylene isomers **3** and **4** in a molar ratio of 7:1 (based on ^{1}H NMR data) (Scheme 1). Compounds **3** and **4** may be isolated as yellow and colorless crystals, respectively. Notably, we did not observe the interconversion between isomeric **3** and **4**.

The core of **3** contains a five-membered silylene ring (Figure 2), which is achieved via the "Si$^I_2$" insertion into the imidazole C−H bond of the complexed thiolate **1**. The C$_2$Si$_2$S ring in **3** (the Si−S−C−C torsion angle = −30.2°) is obviously bent, which may be due to the spatial repulsion between the bulky ligands in **3** (Figure S1).[30] Indeed, the doubling of the resonance of the NHC ring protons (7.98 and 8.06 ppm) of **3** may be attributed to the slow rotation of the C$_{NHC}$−Si bond,

Scheme 1. Thiolate (1)-Mediated Conversion of Bis-Silylene (2) to Cyclic Silylene Isomers (3 and 4)[a]

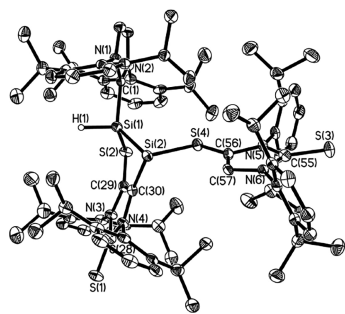[a][L: = :C{N(2,6-Pr$^i_2$C$_6$H$_3$)CH}$_2$; R = 2,6-Pr$^i_2$C$_6$H$_3$].

Figure 2. Molecular structure of **3**. Thermal ellipsoids represent 30% probability. Hydrogen atoms attached to the carbons have been omitted for clarity. Selected bond distances (Å) and angles (deg): Si(1)—H(1), 1.441(19); Si(1)—Si(2), 2.349(2); Si(1)—C(1), 1.909(6); Si(1)—S(2), 2.183(2); Si(2)—S(4), 2.263(2); Si(2)—C(30), 1.941(6); C(1)—Si(1)—Si(2), 123.89(18); S(2)—Si(1)—Si(2), 106.57(9); Si(1)—Si(2)—S(4), 93.40(8); Si(1)—Si(2)—C(30), 77.33(17).

which is also caused by the steric bulk of the ligands.[54] The Si—Si bond distance for **3** [2.349(2) Å] is almost equal to the sum of silicon covalent radii (2.34 Å),[55] however, somewhat shorter than those [2.385(1)−2.393(3) Å] for [L:(X)Si—Si(X):L, X = Cl, Br, and I (**2**)][28,29] and that (2.428 Å) for **3-Ph**.[30] Natural bond orbital (NBO) analysis of **3-Ph** indicates that the Si—Si σ bond (Figure S2) polarization is 64.4% toward Si(1) (32.7% s-, 67.1% p-, 0.2% d-character) and 35.6% toward Si(2) (8.6% s-, 90.7% p-, 0.7% d-character).[30] The Si(1) atom bears a positive charge of +0.63, while the C(30) atom bears a negative charge of −0.34. The H(1) atom bound to the four-coordinate Si(1) atom in **3** renders 4.61 ppm ^{1}H NMR resonance, which was located in the difference Fourier map. The Si—H coupling constants ($^1J_{Si-H}$ = 195 Hz and $^2J_{Si-H}$ = 20 Hz) shown in the proton-coupled ^{29}Si NMR spectrum of **3** (Figure 3) compares well to those obtained from low-intensity ^{29}Si satellites in the ^{1}H NMR spectrum of **3** ($^1J_{Si-H}$ = 196 Hz and $^2J_{Si-H}$ = 20 Hz) and the average $^1J_{Si-H}$ value (195 Hz) observed in the ^{29}Si NMR spectrum of a "push−pull"-stabilized
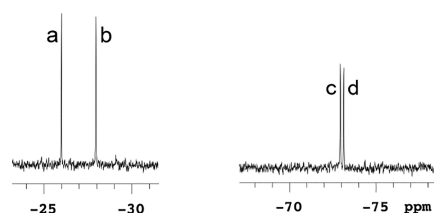

Figure 3. Proton-coupled ^{29}Si NMR spectrum of **3**. [δ (ppm): for Si(1), a = −26.00, b = −27.96; for Si(2), c = −72.93, d = −73.13].

parent monochlorosilylene [:Si(H)Cl] (**5**).[56] The Si—H IR stretching band (ν = 2109 cm^{-1}) for **3** is between that (ν = 2103 cm^{-1}) for **5** and that (ν = 2118 cm^{-1}) for L$_2$SiH$_2$Cl$_2$ [L: = :C{N(2,6-Pr$^i_2$C$_6$H$_3$)CH}$_2$].[57] In addition, the distorted trigonal pyramidal geometry around the Si(2) atom of **3** is consistent with the existence of the Si(2)-based lone pair (Figure S2).[30] Both C(30)—Si(2) [1.941(6) Å] and C(1)—Si(1) [1.909(6) Å] bond distances in **3** are comparable with those [1.929(7)− 1.943(2) Å] of the C$_{NHC}$—Si bonds in [L:(X)Si—Si(X):L, X = Cl, Br, and I (**2**)].[28,29] The S—Si bonds in **3** [2.183(2) and 2.263(2) Å] are somewhat longer than those in Si(SAr)$_2$ [Ar = C$_6$H$_3$-2,6(C$_6$H$_2$-2,4,6-Me$_3$)$_2$] [2.1560(5) and 2.1607(5) Å].[24]

The X-ray structure[30] of **4** (Figure 4) suggests the insertion of one silylene center into the C(16)—N(1) bond of the
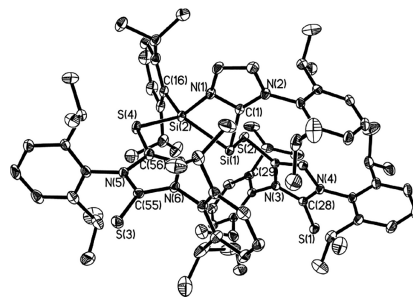

Figure 4. Molecular structure of **4**. Thermal ellipsoids represent 30% probability. Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (deg): Si(1)−Si(2), 2.4164(11); Si(1)−C(1), 1.952(3); Si(1)−S(2), 2.2181(11); Si(2)−N(1), 1.838(3); Si(2)−C(16), 1.889(3); C(1)−Si(1)−Si(2), 67.84(9); C(1)−Si(1)−S(2), 100.20(9); N(1)−Si(2)−Si(1), 78.78(9); Si(1)−Si(2)−S(4), 125.49(5); Si(1)−Si(2)−C(16), 126.58(10).

carbene ligand, giving a nonplanar four-membered CNSi$_2$ silylene ring with two thiolate ligands residing above and below the ring. Indeed, in contrast to only one imidazole ^{1}H NMR resonance observed for **3** (6.30 ppm), compound **4** exhibits two imidazole ^{1}H NMR resonances at 5.20 and 6.16 ppm. Similar to **3**, the distorted trigonal pyramidal geometry around Si(1) atom in **4** is due to the presence of Si(1)-based lone pair of electrons (Figure S3).[30] The Si—Si bond in **4** is predominantly polarized toward the four-coordinate Si(2) atom [62.9% toward Si(2) and 37.1% toward Si(1) for **4-Ph** model (Figure S3)].[30] Although comparable to that in the **4-Ph** model (2.463 Å), the Si—Si bond distance in **4** [2.4164(11) Å] is ca. 0.07 Å longer than that in **3** [2.349(2) Å], which is in accordance with the corresponding WBI$_{Si-Si}$ values (0.82 for **4-Ph** and 0.85 for **3-Ph**).[30] The two ^{29}Si NMR resonances (+2.21 and −56.73 ppm), which are assigned to the four- and three-coordinate silicon atoms [i.e., Si(2) and Si(1)] in **4**, respectively, shift downfield compared with the corresponding resonances for **3** [−27.00 ppm for Si(1) and −72.98 ppm for

Si(2)] (Figure 3). Both C_{NHC}—Si [1.952(3) Å] and S—Si [2.1502(11) and 2.2181(11) Å] bond distances in **4** compares to those for **3** ($d_{C(1)-Si(1)}$ = 1.909(6) Å, d_{S-Si} = 2.183(2) and 2.263(2) Å]. Additionally, the Si—N bond distance of **4** [1.838(3) Å] is comparable to the reported Si—$N_{imidazole}$ bond distances [1.759(1)−1.837(3) Å].[58,59]

The mechanism of thiolate (**1**)-mediated conversion of bissilylene (**2**) into two cyclic silyene isomers (**3** and **4**) remains obscured. However, it is plausible to propose **6a** and **6b** (Figure 5), as possible intermediate precursors of **3** and **4**, which could
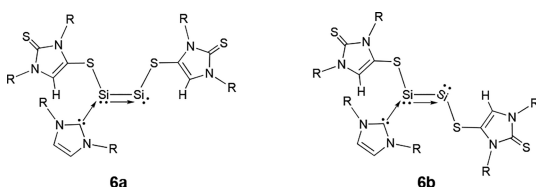
Figure 5. Proposed intermediates (**6a** and **6b**) containing a Si^I_2 unit with an asymmetric Si=Si double bond.

be achieved via double thiolate ligand coordination and subsequent release of one carbene ligand in **2**. The nature of intermediates **6a** and **6b** was investigated by performing B3LYP/6-311G** DFT computations on the simplified models (**6a-Me** and **6b-Me**, R = Me).[30] Computations suggest that both **6a-Me** and **6b-Me** are nearly equal in energy (energy difference = ca. 0.5 kcal/mol). Given their similar structural parameters, only the bonding of **6a-Me** is discussed herein. Interestingly, the silicon−silicon bond distance in **6a-Me** (2.309 Å) is only 0.08 Å longer than the reported Si=Si double bond distance [2.2294(11) Å] in L:Si=Si:L [L: = :C{N(2,6-$Pr^i_2C_6H_3$)CH}_2],[28] and 0.08 Å shorter than the Si—Si single bond in **2** [2.3909(9) Å].[29] The relatively short silicon−silicon bond in **6a-Me**, coupled with the 1.33 Si—Si Wiberg bond index (WBI), suggests that the silicon−silicon bond in **6a-Me** possesses a measure of multiple bond character. NBO analysis of **6a-Me** (Figure 6) shows that the Si—Si σ bonding orbital
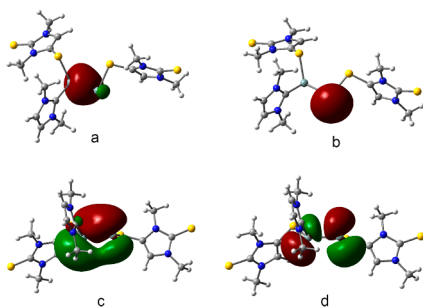
Figure 6. Natural bond orbitals of the simplified model **6a-Me**. (a) Si—Si σ bonding orbital; (b) silicon-based lone pair orbital; (c) Si—Si π bonding orbital; (d) Si—Si π* antibonding orbital.

(67.8%) and π bonding orbital (69.9%) are polarized toward the three-coordinate Si(1) atom.[30] While the Si—Si π bonding orbital (Figure 6c) has overwhelmingly p-character [99.2% p of Si(1) and 94.7% p of Si(2)], the Si—Si σ bonding orbital (Figure 6a) involves the overlap of the approximately sp-hybridized Si(1) atomic orbital (47.2% s, 52.5% p, 0.3% d) with the Si(2) atomic orbital bearing mostly p-character (8.8% s, 90.3% p, 0.9% d). Moreover, the two-coordinate Si(2)-based lone pair orbital (Figure 6b) has mainly s-character (77.5% s,

22.5% p, 0.0% d). Considering that two-coordinate acyclic silylenes have been utilized in H_2, O_2, and NH_3 activation,[26,27] the presence of two different types of reactive sites in both **6a** and **6b** intermediates (i.e. asymmetric and polarized Si=Si double bond and the two-coordinate acyclic silylene center) could play a role in the unexpected C—H and C—N cleavage involved in the formation of **3** and **4**, respectively.

■ ASSOCIATED CONTENT

ⓈSupporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.7b10325.

> Syntheses, computations, X-ray crystal determination (PDF)
> Crystallographic data for **3** (CIF)
> Crystallographic data for **4** (CIF)

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Notes

The authors declare no competing financial interest.

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