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A C_2-Linked Bis-silene Formed without Using Metals and the Transformation into the Bis-silyl and Bis-silylium C_4-Cumulenes

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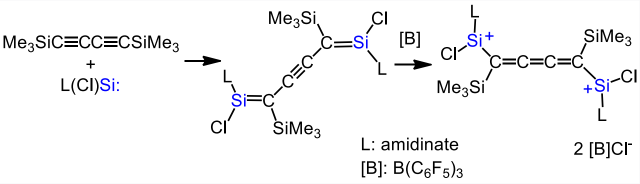
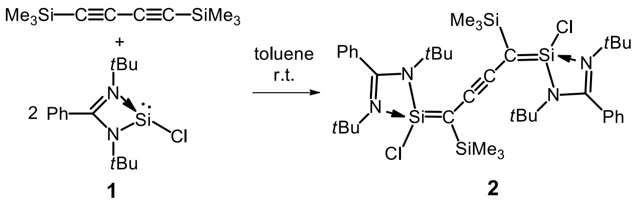


ABSTRACT: Reaction of silylene L(Cl)Si: (**1**; L = PhC(N*t*Bu)$_2$) with 1,3-diyne $Me_3SiC{\equiv}CC{\equiv}CSiMe_3$ produced bis-silene $L(Cl)Si{=}C(SiMe_3)C{\equiv}C(SiMe_3)C{=}Si(Cl)L$ (**2**). This shows a route by oxidative coupling reaction to silenes. Reaction of **2** with $AgOSO_2CF_3$ resulted in $[L(Cl)(F_3CO_2SO)Si](Me_3Si)C{=}C{=}C{=}C(SiMe_3)[Si(OSO_2CF_3)(Cl)L]$ (**3**) and a silver mirror. From the reaction of **2** and $B(C_6F_5)_3$ were isolated compounds $\{[L(Cl)Si](Me_3Si)C{=}C{=}C{=}C(SiMe_3)[Si(Cl)L]\}^{2+}{\cdot}2[ClB(C_6F_5)_3]^-$ (**4**) and $\{LSi[\mu_2\text{-}C_2(SiMe_3)(C{\equiv}CSiMe_3)]\}_2$ (**5**). When **2** was treated with $[Ph_3C]^+[B(C_6F_5)_4]^-$, compounds $[L_2(Cl)Si]^+[B(C_6F_5)_4]^-$ (**6**) and $Ph_2C{=}$*cyclo*-$C(CH{=}CH)_2CHCPh_3$ (**7**) were formed. These reactions exhibit reduction of the polar Si=C bond to create unusual species of neutral and dicationic C_4-cumulenes. The formation, bonding, and reactivity of compound **2** is explored by the computational quantum mechanical calculations.

Silylenes and silenes both are the unique organosilicon species.[1] They are highly reactive, and either syntheses or reactions of them exhibit unpredictable but exciting chemistry.[1,2] Silylenes have an ambiphilic character and behave as Lewis acids as well as Lewis bases due to a lone pair of electrons in the HOMO and an empty p orbital as the LUMO. This feature shows nucleophilic as well as electrophilic reactive sites at the silicon atom.[1a,b,3] In addition, silylenes function as two-electron reducing species.[1a,b,4] Silenes exhibit a polar silicon−carbon double bond although with lower Si−C π-bond energy due to electronic deficiency at the Si atom.[1c] They easily form addition products, when substrates contain polar bonds.[2] Therefore, owing to the inherent reactivity, syntheses of these two species are often difficult, and the thermodynamic and kinetic stabilization by using either electronic or steric demanding organic ancillary substituents is highly required.

To date, synthesis of silenes is still scarce due to fulfilling of the requirement by stabilization at both the Si and C atoms. Experimental and theoretic studies have indicated that substituents at the silicon are better with π-electron acceptor and σ-electron donor character, while at the carbon atom substituents are preferred to have π-electron donor and σ-electron acceptor properties.[1c,2] The selection of suitable precursors is therefore responsible for a successful silene synthesis. Currently, efficient routes are available by Brook's photochemical isomerization of oligosilanes[5] and the classical 1,2-salt elimination of organolithium with chlorosilanes.[6] Furthermore, the Sila−Peterson reaction has been documented using silyllithium and adamantanone.[7] In most syntheses the silenes were formed as the transient intermediates.[1c] In recent years, we have published efficient methods for preparing L(Cl)Si: (**1**; L = PhC(N*t*Bu)$_2$). The HCl elimination from $LSiHCl_2$ proceeds with *N*-heterocylic carbene (NHC) as HCl scavenger. This experiment demonstrates that silylene L(Cl)Si: can be formed in high yield without using any alkaline metals as reducing agent.[8] We envisioned that **1** may be a good precursor for synthesizing the silene when the selected substrate on account of the preferring amidinate stabilization of the silylene alternatively favors the silene formation. The silene-directed synthesis route has not been reported so far.[1c] A test investigation using the 1,4-bis(trimethylsilyl)buta-1,3-diyne successfully resulted in the formation of an acetylene-linked bis-silene $L(Cl)Si{=}C(SiMe_3)C{\equiv}C(SiMe_3)C{=}Si(Cl)$-L (**2**) (Scheme 1). Interestingly, further reactions of **2** with $AgOSO_2CF_3$ and $B(C_6F_5)_3$ produced the C_4-cumulenes $[L(Cl)(F_3CO_2SO)Si](Me_3Si)C{=}C{=}C{=}C(SiMe_3)[Si$-

Scheme 1. Synthesis of Bis-silene 2



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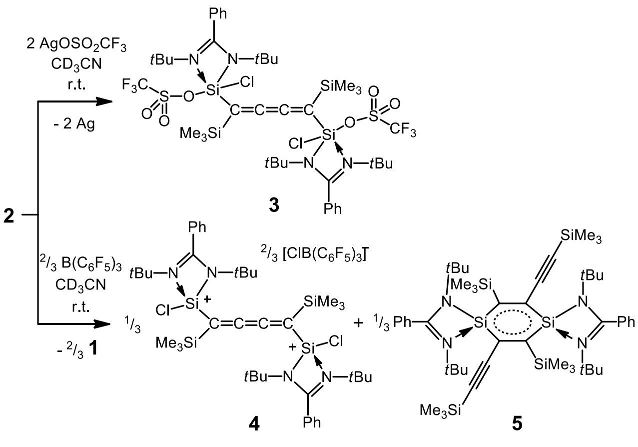
$(OSO_2CF_3)(Cl)L]$ (**3**) with four silyl and $\{[L(Cl)Si](Me_3Si)C{=}C{=}C{=}C(SiMe_3)[Si(Cl)L]\}^{2+}\cdot 2[ClB(C_6F_5)_3]^-$ (**4**) having two silyl and two silyliumyl substituents, respectively (Scheme 2). Both these transformations are unknown in the field of silene reaction chemistry.

Scheme 2. Reactions of 2 with $AgOSO_2CF_3$ and $B(C_6F_5)_3$



C_6D_6 was added to a mixture of **1** and 1,4-bis(trimethylsilyl)-1,3-butadiyne in a 2:1 molar ratio at room temperature, immediately forming a deep brown solution. After storing the flask for 1 h, the ^1H NMR data confirmed the reaction came to completion. Large-scale reaction in toluene formed **2** as a red-brown solid (81% yield) by removal of toluene followed with washing using *n*-hexane (Scheme 1). X-ray quality single crystals of **2** were obtained by storing the solution in solvent mixture of toluene and *n*-hexane at −20 °C for 24 h. Compound **2** has a good solubility in aromatic solvent (benzene and toluene), but is sparingly soluble in *n*-hexane. It is highly air- and moisture-sensitive. Under inert atmosphere like N_2 and Ar, it can be stored for a long time at room temperature. The melting point measurement indicated that upon heat treatment up to 150 °C **2** started to decompose as indicated by its color change from brown to black. Compound **2** has been characterized by NMR (^1H, ^{13}C, ^{29}Si), CHN elemental analysis, and X-ray crystallography. The ^{29}Si NMR spectrum shows two resonances, and the small broad one at δ −6.38 ppm is assignable to the *Si*=C which appears upfield when compared with that of L(Cl)*Si*: in **1** (δ 14.6 ppm).[8a] Actually, the ^{29}Si NMR resonances are shown in a wide range for the silenes (δ −59.9 to −78.7 and 17.5−144.2 ppm),[1c,5−7,9] and the value for **2** is comparable to that of $Tip_2Si{=}C[\eta^2\text{-}Si(Tip)(Ph)N(tBu)]$ (δ −6.9 ppm, Tip = 2,4,6-$i$$Pr_2C_6H_2$).[9b] However, the ^{13}C NMR spectrum does not display the Si=*C* resonance, although the acetylenic carbon resonance is clearly found at δ 82.19 ppm. X-ray single-crystal diffraction study of **2** clearly discloses the composition and structure (Figure 1). The Si(1)−C(1) and Si(2)−C(4) bond lengths are 1.723(2) and 1.724(2) Å, which are a little longer than that in Wiberg's $Me_2Si{=}C(SiMe_3)SiMe\textit{t}Bu_2$ (1.702(5) Å)[10] but shorter than those of other silenes (1.726(4)−1.778(3) Å).[1c,9] The C(1)−C(2) and C(3)−C(4) bond lengths are 1.437(3) and 1.434(3) Å, whereas the C(2)−C(3) bond length exhibits 1.214(3) Å. The former two are a little shorter than that of the C−C single bond, while the latter is a little longer than that of the C≡C triple bond. It is noteworthy that the C(1)−C(2)−C(3)−C(4) unit is in an almost linear array (C(1)−C(2)−C(3) = 178.6(2)° and C(2)−C(3)−C(4) = 179.1(2)°). This array is coplanar to Si(1) (the least-squares plane Δ = 0.0027 Å) and according to Si(2) (Δ = 0.0017 Å), but these two planes have a torsion angle of 32.5°. These data indicate clearly π-electrons' conjugation over the two terminal Si=C bonds and one central C≡C bond.

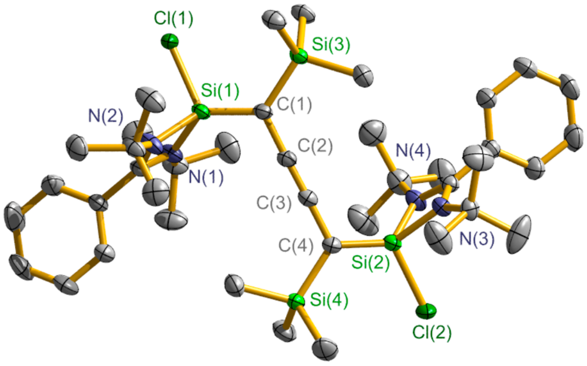


Figure 1. X-ray crystal structure of **2** with thermal ellipsoids at 30% probability level. The hydrogen atoms are omitted for clarity.

Oxidative addition reactions of the silylenes with alkynes are well-known.[1a,b,4a] tBu_2Si:, *in situ* generated, reacts with $tBuC{\equiv}CC{\equiv}CtBu$ to produce sequentially [1 + 2] oxidative cycloaddition compound $[tBu_2Si(\eta^2\text{-}C_2)tBu]_2$.[4a] It is then reasoned that the formation of **2** from **1** and $Me_3SiC{\equiv}CC{\equiv}CSiMe_3$ might proceed through a similar route to form $[L(Cl)Si(\eta^2\text{-}C_2)SiMe_3]_2$ which underwent further bond isomerization over the two jointed $Si(\eta^2\text{-}C_2)$-cycles. This shows a route different from *hv*-induced conversion of $[tBu_2Si(\eta^2\text{-}C_2)tBu]_2$ to 2,5-disilabicyclohexadiene.[4a] This might be due to the different reactivities, when tBu_2Si: is compared with silylene **1**. In the latter the amidinate donor ligand at the Si atom strongly promotes the stable Si=C bond formation. A comparable case is known for a smooth synthesis of the *N*-donor stabilized silene $(Me_3Si)(9\text{-}NMe_2C_{10}H_6)Si{=}C(SiMe_3)_2$.[6]

The Si=C bond in the silenes is known to be highly polarized indicative of a high reactivity.[1c,2] We performed further reactions using **2** with $AgOSO_2CF_3$, $B(C_6F_5)_3$, and $[Ph_3C]^+[B(C_6F_5)_4]^-$, respectively. At room temperature, CD_3CN was added to a mixture of **2** and 2 equiv of $AgOSO_2CF_3$. After 10 min the ^1H NMR spectrum indicated that the reaction was complete. It was clearly observed that the silver mirror was spontaneously generated. The following filtration to remove the mirror and then storing the filtrate at −20 °C in a freezer for 24 h led to formation of complex **3** (Scheme 2) as light-yellow crystals (68% yield). Reaction of **2** and 2/3 equiv of $B(C_6F_5)_3$ was conducted in a mixture of $CDCl_3$ and C_6D_6 at room temperature and finalized within 10 min. However, the ^1H NMR data indicated formation of a mixture of products. The flask was stored in a freezer at −20 °C for 2 weeks to produce **4** as light-pink crystals (19% yield). Interestingly, the mother solution after separation of **4** was again kept at −20 °C for 2 days affording compound **5** as purple crystals (30% yield) (Scheme 2). For comparison, the reaction of **2** with $[Ph_3C]^+[B(C_6F_5)_4]^-$ in CD_3CN was accomplished. The reaction also occurred immediately at room temperature and was complete within 10 min. The ^1H NMR data showed formation of several new species. Storing the solution after addition of pyridine and *n*-hexane at −20 °C in a freezer for 2 weeks resulted in products $[L_2(Cl)Si]^+[B-$

$(C_6F_5)_4]^-$ (**6**) and $Ph_2C{=}$*cyclo*-$C(CH{=}CH)_2CHCPh_3$ (**7**) as a mixture of crystals. The light-yellow crystals were determined to be **6**, while the colorless crystals were **7**·C_5H_5N.[11] Both were characterized by single-crystal X-ray structural analysis (Figures S2-3−S2-5). Obviously, this reaction proceeds in a complicated way; however, it does not lead to formation of the C_4-cumulene-like species although $[Ph_3C]^+[B(C_6F_5)_4]^-$ is known to be of a stronger Cl^- abstraction ability.

The X-ray single-crystal structure of **3** (Figure 2) shows oxidative addition of one OSO_2CF_3 group at each Si center (1.8361(15) Å) of **3**. However, the Si(1)−C(1) bond length is 1.864(2) Å, and this bond is of single-bond character. Meanwhile, the C(1)−C(2) and C(2)−C(2A) bond lengths are 1.324(3) and 1.276(4) Å, respectively, with the C(1)−C(2)−C(2A) bond angle of 179.1(3)°. This indicates that the central C_4 array definitely is a cumulenyl group and compares well with those found in $R_2C{=}C{=}C{=}CR_2$ (R_2 = $(Me_3Si)_2$, Ph_2, $CMe_2CH_2CH_2CH_2CMe_2$, and N(2,6-*i*$Pr_2C_6H_3$)-$CMe_2CH_2CMe_2$; 1.319(6)−1.345(3) and 1.246(3)−1.276(8) Å).[12] Compound **4** is composed of the $\{[L(Cl)Si](Me_3Si)C{=}C{=}C{=}C(SiMe_3)[Si(Cl)L]\}^{2+}$ dication and two $[ClB(C_6F_5)_3]^-$ anions (Figures 3 and S2-1). This dication appears to be an isomer to **2**, but it displays the Si(1)−C(1) (1.830(4) Å) single bond and the central C_4-cumulenyl feature (C(1)−C(2) 1.316(6) Å, C(2)−C(2A) 1.278(9) Å, and C(1)−C(2)−C(2A) 178.0(6)°).

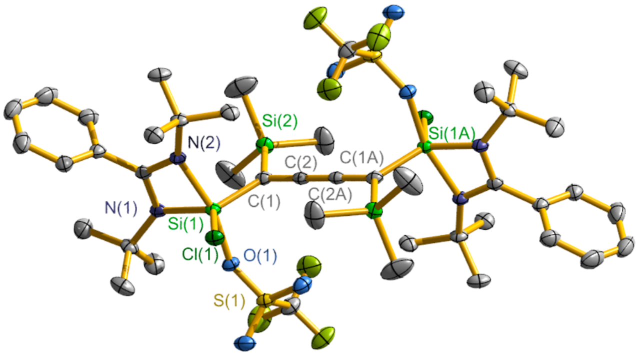


Figure 2. X-ray crystal structure of **3** with thermal ellipsoids at 50% probability level. The hydrogen atoms are omitted for clarity.

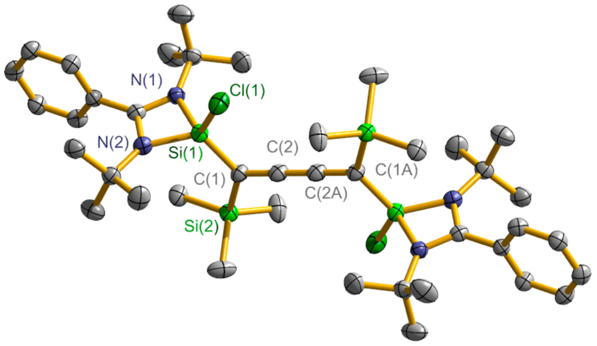


Figure 3. X-ray crystal structure of the dication in **4** with thermal ellipsoids at 50% probability level. The hydrogen atoms are omitted for clarity.

For the reaction of **2** and $B(C_6F_5)_3$ to obtain **4**, in the first step we assume that abstraction of two Cl^- from **2** occurred to form two anions of composition $[ClB(C_6F_5)_3]^-$. The intermediate dication $[LSi{=}C(SiMe_3)C{\equiv}C(SiMe_3)C{=}SiL]^{2+}$ might be formed. The latter oxidized a second molecule of **2** to generate the dication of **4**. With the isolation and characterization of compound $\{LSi[\mu_2\text{-}C_2(SiMe_3)(C{\equiv}C\text{-}SiMe_3)]\}_2$ (**5**, Figure S2-2), we were able to infer that the Cl^- abstraction could take place between $B(C_6F_5)_3$ and **1**. The two-electron transfer between a second molecule of **2** and the intermediate $[LSi{=}C(SiMe_3)C{\equiv}C(SiMe_3)C{=}SiL]^{2+}$ generated compound **4**. Compound **5** might be formed during the coupling of two radicals under Si−Si bond formation.[13] Two [LSi:]· radicals coupled to give [LSi:]−[:SiL], a known compound that was prepared from the potassium reduction of **1**.[13] and [LSi:]−[:SiL] further reacted with $Me_3SiC{\equiv}CC{\equiv}CSiMe_3$ to yield **5** (Scheme S3-1). A similar reaction has been reported for [LSi:]−[:SiL] with $PhC{\equiv}CPh$ to $[LSi(\mu_2\text{-}C_2Ph_2)]_2$.[14]

Quantum mechanical calculations at the M06/def2-TZVPP//BP86/def2-SVP level of theory were carried out to explore the formation and reactivity of the acetylene linked bis-silene **2** (Figure S5-1).[15] The compound **2** is formed by the reaction of 1,4-bis(trimethylsilyl)-1,3-butadiyne with silylene **1**. The tri−coordinated silicon center in silylene **1** is pyramidal with pyramidalization angle 94°, indicating an active lone pair on the silicon.[16] The highest occupied molecular orbital (HOMO) is mainly localized on the silicon atom with a little contribution from nitrogen and chlorine atoms (Figure 4a). The natural bond orbital (NBO) analysis indicates a lone pair on silicon atom with 76.9% contributions from 3s-orbital and 23.1% contribution from 3p-orbitals. Hence, the silicon atom in **1** is a nucleophilic center. Each carbon atom in 1,4-bis(trimethylsilyl)-1,3-butadiyne is sp-hybridized with two-sets of orthogonal π-type p-orbitals. The linear combination of these π-type p-orbitals results in two-sets of orthogonal π-MOs (Figure S5-2). Two of the molecular orbitals from each set are doubly occupied. The third set of π-MOs are degenerate LUMOs, which has nodal planes perpendicular to each terminal C≡C bonds (Figure 4b,c). These MOs have a relatively higher coefficient on the terminal carbon atoms.

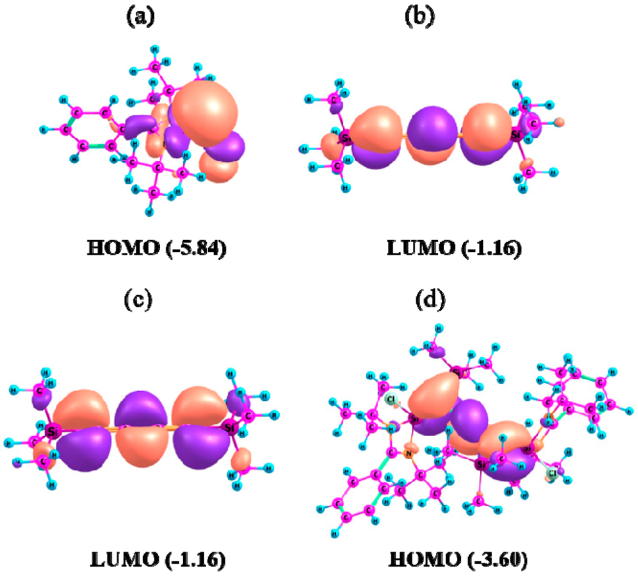
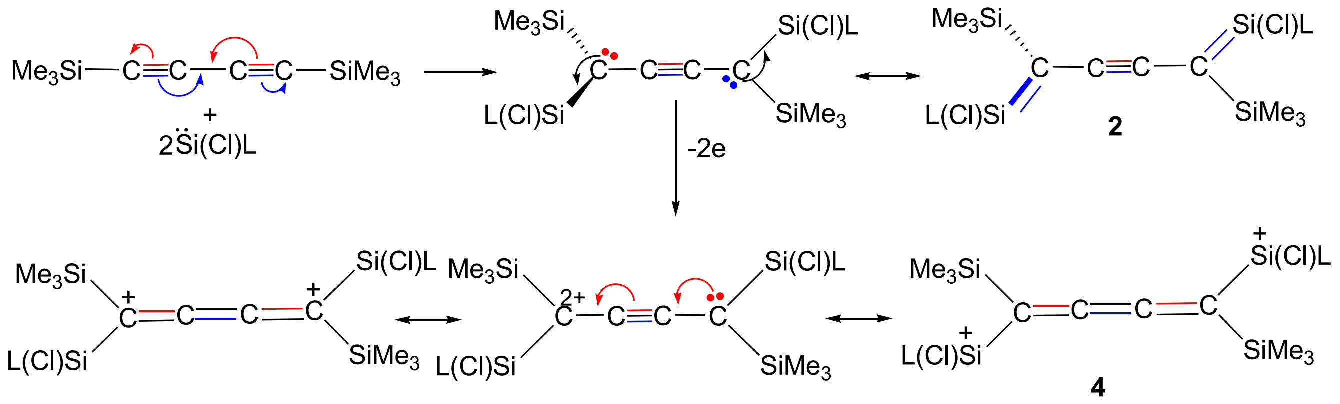


Figure 4. (a) HOMO of **1**, (b, c) degenerate LUMOs of 1,3-diyne, and (d) HOMO of **2**. Energies are given in eV.

Scheme 3. Schematic Representation of the Bonding Pattern of Compounds 2−4



Hence, the π-type p-orbitals of the terminal carbon atoms are relatively electrophilic, which corroborates well with the molecular electrostatic potential (MESP) values on the van der Waals surface of the terminal carbon atoms (Figure S5-3, Table S5-1). The MESP values on the terminal carbon atoms C1 and C4 (−13.2 kcal/mol) has slightly less negative potential as compared to middle carbon atoms C2 and C3 (−14.3 kcal/mol). Thus, the formation of compound **2** can be explained by the donation of lone pair electron from silicon atom of two molecules of silylene **1** to the mutually orthogonal LUMOs of 1,4-bis(trimethylsilyl)-1,3-butadiyne which are majorly localized on the terminal carbon atoms (Figure 4b,c). The reaction energy for the formation the compound **2** is highly exothermic by 38.6 kcal/mol and exergonic by 18.9 kcal/mol.

Accordingly, the silenyl fragments in compound **2** are not in the same plane, which is evident from the Si1−C1−C4−Si4 torsion angle of 142°. The coordination of silylene **1** to 1,4-bis(trimethylsilyl)-1,3-butadiyne alters the geometrical and bonding pattern, as shown qualitatively in Scheme 3. Consequently, the central C−C bond in **2** becomes a triple bond, and the terminal carbon atoms possess a lone pair of electrons. The lone pair of electrons on the terminal carbon atoms can be back-donated to the Si−N σ^*-orbital resulting in partial double character to Si−C bond. Si1−C1/Si2−C4 bonds (Figure S5-1) are much shorter than Si3−C1/Si4−C4 bonds. The HOMO shows significant back-donation from the terminal carbon atoms to Si−N σ^*-orbital. The NBO data indicates that Si1−C1/Si2-C4 π-bonds are majorly localized on the carbon atom (88.7% on C). This is well-supported by NBO charge data, which indicates that the Si atoms of silenyl fragment in **2** are highly positively charged and that the terminal carbon atoms are highly negatively charged (Table S5-2). Accordingly, the Si═C bond in bis-silene **2** can be considered to be highly polar. Thus, there are three π-MOs delocalized over diyne-C_4 skeleton which are filled. The third π-MO (Figure 4) has nodal planes across the terminal C−C bonds, which results in the distortion of silyl group attached to the terminal carbons leading to the Si1−C1−C4−Si4 torsion angle of 142°. The instability of bis-silene **2** can be attributed to these two additional π-electrons, which is reflected in the reactivity.

These additional electrons in compound **2** can be removed by the oxidative addition with $AgOSO_2CF_3$ resulting in compound **3** having a cumulenic C_4-skeleton. The formation of **3** is exothermic by 34.4 kcal/mol and endergonic by 2.6 kcal/mol. Compound **2** can also be oxidized to compound **4** by the reaction with $B(C_6F_5)_3$. Compound **4** is a dicationic form of oxidized bis-silene **2** having a cumulenic C_4-skeleton as well. The change in the bonding pattern by two-electron oxidation of compound **2** is qualitatively shown in Scheme 3. The two-electron oxidation of compound **2** can be understood from the very low first (105.4 kcal/mol) and second vertical ionization energies (200.4 kcal/mol). The energy difference between **2** and **4** is only 262 kcal/mol.

To summarize, we have prepared C_2-linked bis-silene **2** starting from silylene **1** and 1,3-diyne. This is a new route to silenes.[1c,2] The reaction of **2** with $AgOSO_2CF_3$ led to bis-silyl C_4-cumulene **3** and a deposit of silver. Furthermore, **2** reacted with $B(C_6F_5)_3$ to bis-silylium C_4-cumulene **4** and 1,4-disilabenzene **5**, respectively. These reveal the unusual reaction patterns of **2** at the reactive Si═C double bond. The theoretical calculations confirmed that the high reactivity of bis-silene **2** is mainly attributed to the high polarity of the silicon−carbon double bond.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.organomet.0c00368.

Detailed synthetic procedures, analytical and characterization data of **2**−**7**, details of crystal structure refinements, and details of computational methodology (PDF)

Cartesian coordinates of all calculated molecules (PDF)

Accession Codes

CCDC 1976767, 1976780−1976782, 1978353, and 1980547 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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