

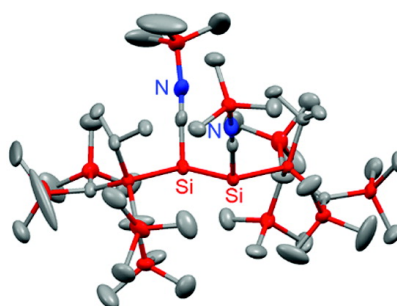
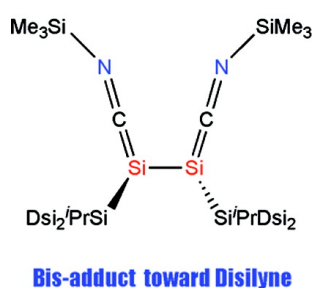
Communication

Reactivity of the Disilyne $\text{RSi}\equiv\text{SiR}$ ($\text{R} = \text{SiPr}[\text{CH}(\text{SiMe}_3)]$) toward Silylcyanide: Two Pathways To Form the Bis-Adduct $[\text{RSiSiR}(\text{CNSiMe}_3)]$ with Some Silaketenimine Character and a 1,4-Diaza-2,3-disilabenzene Analogue

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Reactivity of the Disilyne $\text{RSi}\equiv\text{SiR}$ ($\text{R} = \text{Si}^i\text{Pr}[\text{CH}(\text{SiMe}_3)_2]_2$) toward Silylcyanide: Two Pathways To Form the Bis-Adduct $[\text{RSiSiR}(\text{CNSiMe}_3)_2]$ with Some Silaketenimine Character and a 1,4-Diaza-2,3-disilabenzene Analogue

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Since the discovery of the stable tetramesityldisilene $\text{Mes}_2\text{Si}=\text{SiMes}_2$ ($\text{Mes} = 2,4,6\text{-trimethylphenyl}$)¹ and the silene $(\text{Me}_3\text{Si})_2\text{Si}=\text{C}(\text{OSiMe}_3)\text{Ad}$ ($\text{Ad} = 1\text{-adamantyl}$),² numerous alkene analogues of heavier group 14 elements have been isolated and characterized.³ However, compounds with a silicon–silicon triple bond were unknown until reports from our group⁴ and Wiberg's group.⁵ Very recently, Tokitoh et al. also reported a 1,2-diaryldisilyne.⁶ The first stable crystalline disilyne **1**,⁴ bearing two bulky substituents, $\text{Si}^i\text{Pr}[\text{CH}(\text{SiMe}_3)_2]_2$ groups, at the triply bonded silicon atoms shows that the silicon–silicon triple bond is not linear but trans-bent, which results in two nondegenerate occupied π -MOs and two unoccupied antibonding π^* -MOs.⁴ Upon bending, the energy of the LUMO is significantly lowered. Indeed, we found an unusual reaction of **1** with $t\text{BuLi}$, alkenes, and alkynes, producing a disilyllithium, 1,2-disilacyclobutenes, and 1,2-disilabenzene derivatives, respectively.⁷

Disilenes with a silicon–silicon double bond are known to react with various compounds, such as alcohols, alkenes, alkynes, carbonyl compounds, dienes, etc.³ However, to the best of our knowledge, there is only one previous paper on the reactivity of disilenes toward cyanides; Weidenbruch et al. reported the [2 + 2] cycloaddition of tetra-*tert*-butyldisilene and tri-*tert*-butylsilylcyanide.⁸ To understand the nature of the π bond of a silicon–silicon triple bond, we examined the reaction of the disilyne **1** with trimethylsilylcyanide and unexpectedly found two types of products: the bis-adduct **2** with some silaketenimine character and the 1,4-diaza-2,3-disilabenzene analogue **3**, in which two isomers of trimethylsilylcyanide, the isocyanide and cyanide forms, compete to react with **1**.

Disilyne **1** was allowed to react with 2 equiv of trimethylsilylcyanide in hexane to give **3** in 84% yield, together with a small amount of purple crystalline compound **2**, a bis-adduct (Scheme 1).^{9,10} The product ratio depends strongly on the concentration of the reaction mixture, and the yield of **2** increased to 58% in the absence of solvent. In the formation of **3**, two molecules of silylcyanide coordinate with the sp-silicon atoms of **1**, enabling C–C bond formation to take place.¹¹ On the other hand, the bis-adduct **2** is formed by a different mode of coordination: two molecules of the silylisocyanide form bond to the sp-silicon atom in **1**.¹² It is known that silylcyanide exists as an equilibrium mixture with the N-bonded silylisocyanide form and they can interconvert

each other.¹³ Therefore, the isocyanide and cyanide forms compete to react with **1**, depending on the reaction conditions.

In the ^{29}Si NMR spectrum of **2**, measured by an inverse-gate pulse sequence, a characteristic signal of skeletal Si is observed at -172.0 ppm as a broad signal,¹⁴ significantly upfield shifted relative to those of the recent report on dialkylsilaketenimines ($15.9\text{--}23.9$ ppm for $\text{Si}=\text{C}=\text{N}$ in toluene- d_6)¹⁵ and silylene–isocyanide complexes (-48.6 to -57.4 ppm in C_6D_6).¹⁶ The structure of **3** was determined by ^1H , ^{13}C , ^{29}Si NMR spectroscopic data, as well as mass spectrometry.⁹ In the ^{29}Si NMR spectrum of **3**, the $\text{sp}^2\text{-Si}$ signal was observed at 40.2 ppm, significantly shifted upfield because of the influence of the lone-pair electrons of the neighboring nitrogen atoms.

The molecular structure of **2** was unambiguously determined by X-ray crystallography.⁹ As shown in Figure 1, the $\text{Si3}\text{--Si1}\text{--Si2}\text{--Si8}$ skeleton of **2** has a *trans*-bent geometry, which is similar to that of **1**, and has silylisocyanide molecules bound to each of the skeletal silicon atoms, Si1 and Si2, from the same side.¹² The central $\text{Si1}\text{--Si2}$ bond length is $2.3655(9)$ Å, which lies within the normal range for Si–Si single bond lengths. The $\text{Si1}\text{--C35}$ and $\text{Si2}\text{--C39}$ bond lengths are $1.826(3)$ and $1.830(2)$ Å, respectively, which are shorter than the normal Si–C single bond length (1.860 Å).¹⁷ The $\text{Si13}\text{--N1}\text{--C35}$ ($174.1(2)^\circ$) and $\text{Si14}\text{--N2}\text{--C39}$ ($172.1(2)^\circ$) moieties are not linear, being slightly bent away from each other. The $\text{N1}\text{--C35}$ ($1.185(3)$ Å) and $\text{N2}\text{--C39}$ ($1.179(3)$ Å) bond lengths are longer than that of the C–N bond of *meso*-**4** ($1.151(3)$ Å) (see the Supporting Information, SI).⁹ The bond angles of $\text{Si2}\text{--Si1}\text{--Si3}$

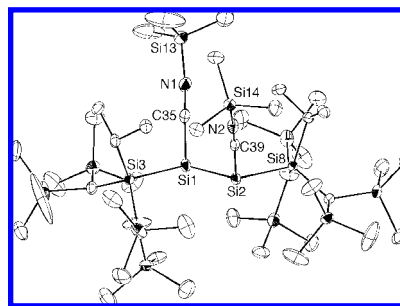
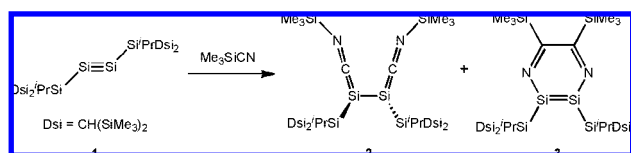


Figure 1. ORTEP drawing of **2** (30% probability level). H atoms are omitted for clarity. Selected bond distances (Å): $\text{Si1}\text{--Si2} = 2.3655(9)$, $\text{Si1}\text{--Si3} = 2.4054(8)$, $\text{Si1}\text{--C35} = 1.826(3)$, $\text{Si2}\text{--Si8} = 2.4012(8)$, $\text{Si2}\text{--C39} = 1.830(2)$, $\text{Si13}\text{--N1} = 1.754(2)$, $\text{Si14}\text{--N2} = 1.764(2)$, $\text{N1}\text{--C35} = 1.185(3)$, $\text{N2}\text{--C39} = 1.179(3)$. Selected bond angles (deg): $\text{Si2}\text{--Si1}\text{--Si3} = 113.48(3)$, $\text{Si2}\text{--Si1}\text{--C35} = 103.72(8)$, $\text{Si3}\text{--Si1}\text{--C35} = 101.88(7)$, $\text{Si1}\text{--Si2}\text{--Si8} = 113.94(3)$, $\text{Si1}\text{--Si2}\text{--C39} = 104.48(7)$, $\text{Si8}\text{--Si2}\text{--C39} = 101.46(7)$, $\text{Si13}\text{--N1}\text{--C35} = 174.1(2)$, $\text{Si14}\text{--N2}\text{--C39} = 172.1(2)$, $\text{N1}\text{--C35}\text{--Si1} = 171.1(2)$, $\text{Si2}\text{--C39}\text{--N2} = 170.8(2)$. Selected torsion angles (deg): $\text{Si3}\text{--Si1}\text{--Si2}\text{--Si8} = 178.82(4)$, $\text{Si3}\text{--Si1}\text{--Si2}\text{--C39} = -71.36(8)$, $\text{C35}\text{--Si1}\text{--Si2}\text{--Si8} = -71.48(8)$, $\text{C35}\text{--Si1}\text{--Si2}\text{--C39} = 38.34(11)$.

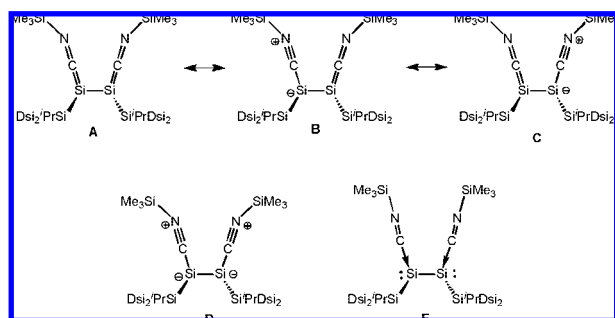
Scheme 1



(113.48(3)°) and Si1–Si2–Si8 (113.94(3)°) in **2** are contracted by more than 20° in comparison with that of **1** (137.44(4)°),⁴ indicating substantial lone-pair electron character on both Si1 and Si2 atoms.

Concerning the bis-adduct **2**, the possible resonance structures are depicted in Chart 1. Two important structural features for **2** should be pointed out: (1) short Si–C bond lengths (1.826(3) and 1.830(2) Å) relative to the normal Si–C single bond length (1.860 Å);¹⁷ (2) significant pyramidalization around the central Si atoms (the sum of the bond angles: 319.1° for Si1 and 319.9° for Si2). These results indicate that the bis-adduct **2** has the silaketenimine structure **A** with very important zwitterionic contributions from **B** and **C**, as demonstrated by the large pyramidalization around the Si1 and Si2 atoms and large shielding of their ²⁹Si NMR resonances (–172.0 ppm). The resonance structure **D** is less likely because of the electrostatic repulsion between the two central silicon atoms. The bis(silylene–isocyanide) complex, represented by **E**, is also unlikely because of the lack of the silylene-type reactivity, as described below.

Chart 1

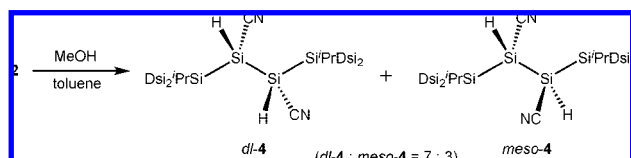


To clarify the bonding nature in **2**, we performed a theoretical calculation at the HF/6-31G(d) level using experimental atomic coordinates. The highest occupied molecular orbital (HOMO) and the second-highest orbital (HOMO-1) are mainly derived from the in-plane π^* - and π -orbitals of **1**, respectively, and the additional π -bonding interactions with the π^* -orbital of the C–N moieties also participate to a minor extent, thereby contributing to the double-bond nature of the Si–C bond (see the SI). The out-of-plane π^* - and π -orbitals of **1** participate in the formation of the σ -bond of the Si–C bond. Therefore, structural parameters obtained from both X-ray crystallographic analysis and molecular orbital considerations suggest that the best description of compound **2** is a bis(silaketenimine) character with zwitterionic contributions.¹⁸

When **2** was allowed to react with MeOH at room temperature in toluene, the purple color of the solution disappeared immediately to give *dl*-**4** (70%) and *meso*-**4** (30%) along with elimination of MeOSiMe₃ (Scheme 2).⁹ In contrast to the reaction of silylene–isocyanide complexes,^{16a} insertion of central Si atoms into the O–H bond was not observed. The preferential formation of *dl*-**4** is also explained by the absence of any reactive silylene-type intermediate in our present case.

The molecular structure of *meso*-**4** was determined by X-ray crystallography⁹ and the central Si–Si bond length in *meso*-**4** is

Scheme 2



2.3723(10) Å, which is longer than that of **2** (2.3655(9) Å). The Si–C bond length (1.857(2) Å) is elongated compared with those of **2** (1.826(3) and 1.830(3) Å), because of the disappearance of the silaketenimine character.

In summary, it has been shown that the disilyne **1** can form the bis-adduct **2** with some bis(silaketenimine) character and 1,4-diaza-2,3-disilabenzene analogue **3** with trimethylsilylcyanide. The structural parameters of **2** and theoretical studies show that compound **2** has the silaketenimine structure **A** with strong ionic contributions from **B** and **C**, as depicted in Chart 1.

Supporting Information Available: The experimental procedure of **2**, **3**, *dl*-**4**, and *meso*-**4**, MO diagram of **2**, tables of crystallographic data including atomic positional and thermal parameters for **2** and *meso*-**4**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- For the experimental procedures and spectral data of **2**, **3**, *dl*-**4**, and *meso*-**4** and crystal data of **2** and *meso*-**4**, see the SI.
- When organic nitriles, such as acetonitrile and benzonitrile, were used instead of silylcyanides, entirely different products were produced. The reaction of **1** with an isocyanide such as mesityl isocyanide also yielded a different type of product. These results will be reported elsewhere.
- Power et al. first reported the formation of a 1,4-diaza-2,3-digermylenebenzene analogue by reaction of the digermene ArGeGeAr (Ar = C₆H₃-2,6-(C₆H₃-2,6-Pr₂) with benzonitrile; see: Cui, C.; Olmstead, M. M.; Fettingler, J. C.; Spikes, G. H.; Power, P. P. *J. Am. Chem. Soc.* **2005**, *127*, 17530.
- Power and Spikes reported that the reaction of the digermene ArGeGeAr (Ar = C₆H₃-2,6-(C₆H₃-2,6-Pr₂) with mesityl isocyanide yielded the bis-adduct [ArGeGeAr(CNMe₃)₂]; see: Spikes, G. H.; Power, P. P. *Chem. Commun.* **2007**, 85. The structure of the adduct is similar to that of our compound **2**, in which mesityl rings are oriented parallel to each other. However, they represented the structure of the adduct as type **E**, rather than **A–C**, depicted in Chart 1.
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- Very recently, Robinson and co-workers reported the synthesis of the bis(silylene–carbene) complex **5** L:(Cl)Si–Si(Cl):L (L: is: C[N(2,6-Pr₂C₆H₃)CH]₂). Except for the reversed orientation of substituent and ligand, the molecular structure of **2** is similar to that of L:(Cl)Si–Si(Cl):L **5**. However, the bond lengths between skeletal Si atoms and carbenic C atoms of **5** (1.939(6) and 1.929(7) Å) are significantly longer than those of **2** (1.826(3) and 1.830(2) Å), because of the lack of any contribution from the silaketenimine character in the case of **5**; see: Wang, Y.; Xie, Y.; Wei, P.; King, R. B.; Schaefer, H.F., III; Schleyer, P. v. R.; Robinson, G. H. *Science* **2008**, *321*, 1069.

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