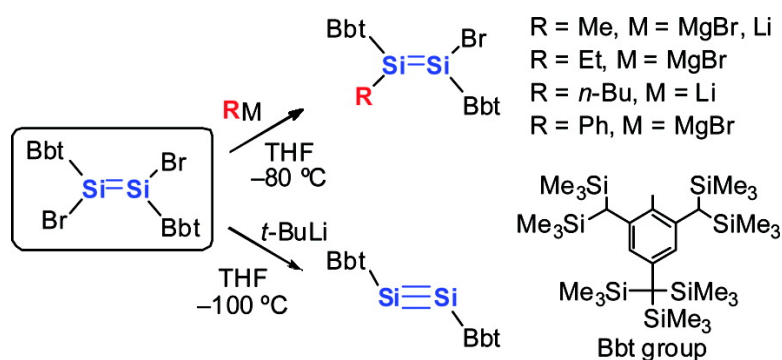


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Synthesis and Reactions of a Stable 1,2-Diaryl-1,2-dibromodisilene: A Precursor for Substituted Disilenes and a 1,2-Diaryldisilyne

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There has been much interest in the chemistry of multiply bonded organosilicon compounds, *i.e.*, disilenes and disilynes.^{1–4} While numbers of kinetically stabilized disilenes have been synthesized and characterized since the isolation of the first stable disilene, $\text{Mes}_2\text{Si}=\text{SiMes}_2$ (Mes = mesityl), by West and his co-workers,² only two examples of stable disilynes have been known up to now. Wiberg *et al.*³ and Sekiguchi *et al.*⁴ independently reported the synthesis of disilynes bearing bulky silyl groups, while theoretical studies suggest that a silyl group should afford thermodynamic stabilization toward the low-coordinated organosilicon compounds due to the electropositive silicon atom.⁵ Although a carbon-substituted disilyne has been desired as a new standard of a $\text{Si}\equiv\text{Si}$ triple-bond compound, no example has been reported so far for a diaryl- or dialkyl-substituted disilyne. On the other hand, unique properties of disilenes prompted many chemists to explore the chemistry of novel systems containing $\text{Si}=\text{Si}$ units with extended π -conjugation from the standpoint of material science.⁶ Accordingly, a proper disilene unit as a “building block” has been desired for the synthetic studies of functionalized disilenes. Recently, the stable disilyne, $\text{R}_{\text{Si}}\text{Si}\equiv\text{SiR}_{\text{Si}}$ ($\text{R}_{\text{Si}} = \text{Si}[\text{CH}(\text{SiMe}_3)_2](i\text{-Pr})$), was evidenced to afford unique disilenes by addition reactions.⁷ Although $\text{R}^*(\text{Cl})\text{Si}=\text{Si}(\text{Cl})\text{R}^*$ [$\text{R}^* = \text{SiMe}(\text{Si}(t\text{-Bu})_3)_2$],^{3,8} which has been known as the only stable dihalodisilene, should be of great interest as a good precursor for the functionalized disilenes via substitution reaction, it is too protected to undergo substitution reaction on the central silicon atoms. We report here the synthesis and structure of a new, stable 1,2-dibromodisilene **1**. Furthermore, it was demonstrated that **1** was transformed into a variety of substituted disilenes and the corresponding stable 1,2-diaryldisilyne by reaction with alkyl metals.

Reduction of tribromosilane **2** with lithium naphthalenide afforded dibromodisilene **1** as stable yellow crystals (Scheme 1).⁹ X-ray crystallographic analysis (Figure 1a) revealed the structural parameters of **1** with a highly trans-bent structure (trans-bent angles = 32.4°, 39.8°) and a relatively longer $\text{Si}=\text{Si}$ double bond [2.2264(8) Å], which are in sharp contrast to the planar structure and a relatively shorter $\text{Si}=\text{Si}$ bond length [2.163(4) Å] of $\text{R}^*(\text{Cl})\text{Si}=\text{Si}(\text{Cl})\text{R}^*$,⁸ where the central $\text{Si}=\text{Si}$ moiety might be sterically perturbed by the bulky silyl substituent. In the solid state Raman spectra, **1** exhibited an intense Raman line at 541 cm^{-1} , which should predominantly correspond to the $\text{Si}=\text{Si}$ vibration.¹ In the ^{29}Si NMR spectrum (C_6D_6) of **1**, the characteristic, low-field shifted signal was observed at 79.4 ppm, indicating its $\text{Si}=\text{Si}$ double-bond character. Although the ^1H NMR spectrum (toluene- d_8) of **1** suggested that the Bbt groups should freely rotate without any steric restriction at rt and even at $-40\text{ }^\circ\text{C}$, two independent

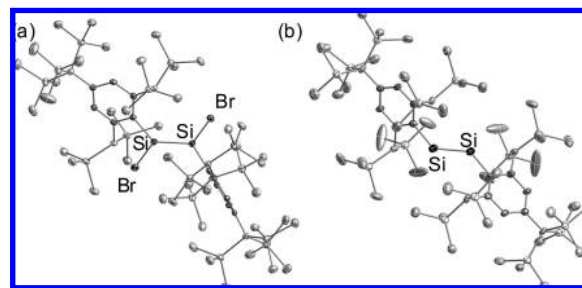
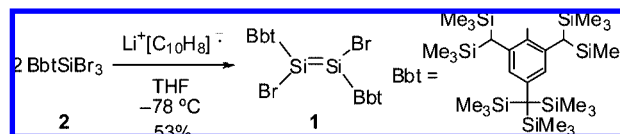
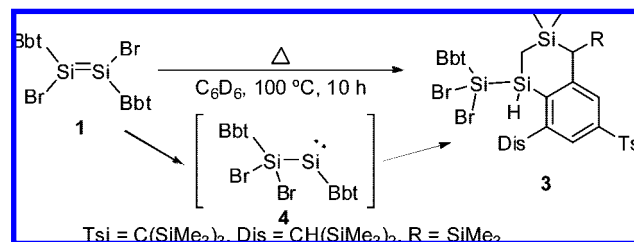


Figure 1. Structures of (a) dibromodisilene **1** and (b) diaryldisilyne **9**. Displacement ellipsoids were drawn at the 30% probability level.

Scheme 1



Scheme 2



signals were observed for the SiMe_3 groups at the *ortho*-positions of Bbt groups even at $60\text{ }^\circ\text{C}$, suggesting the trans-bent structure of **1** in solution. The UV–vis spectra of **1** in hexane showed characteristic absorption at $\lambda_{\text{max}} = 434\text{ nm}$ ($\epsilon = 25\,000$) assignable to the $\pi-\pi^*$ transition, which did not change at variable temperature (-60 to $40\text{ }^\circ\text{C}$). Thus, dibromodisilene **1** did not undergo any thermal dissociation into the corresponding silylenes in contrast to the case of the germanium analogue, $\text{Bbt}(\text{Br})\text{Ge}=\text{Ge}(\text{Br})\text{Bbt}$.¹⁰ However, dibromodisilene **1** was found to start gradual decomposition at $60\text{ }^\circ\text{C}$ (Scheme 2), and further heating of **1** at $100\text{ }^\circ\text{C}$ for 10 h afforded the cyclization product **3** quantitatively. The formation of **3** is most likely interpreted in terms of the intermediacy of dibromodisilylene **4** generated by the migration of the bromine atom.¹¹

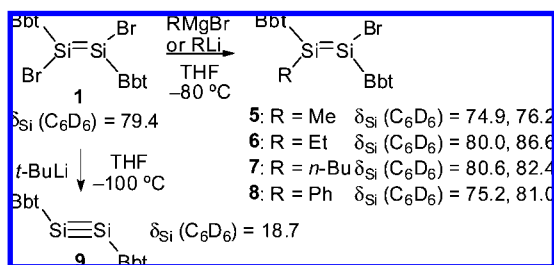
Interestingly, the reaction of dibromodisilene **1** with MeLi in THF at $-80\text{ }^\circ\text{C}$ resulted in the formation of bromomethyldisilene **5**, $\text{Bbt}(\text{Me})\text{Si}=\text{Si}(\text{Br})\text{Bbt}$, in 48% yield (Scheme 3). The treatment of **1** with MeMgBr , EtMgBr , $n\text{-BuLi}$, and PhMgBr under the same conditions also afforded the corresponding substituted disilenes, **5**

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Scheme 3



(46%), **6** (ca. 40%), **7** (ca. 50%), and **8** (ca. 20%), respectively. The formal substitution reaction on the sp^2 -silicon atom of **1** may occur via the addition–elimination mechanism, where RM undergoes an addition reaction toward the $\text{Si}=\text{Si}$ bond of **1** leading to the formation of $\text{Bbt}(\text{Br})(\text{R})\text{Si}-\text{Si}(\text{M})(\text{Br})\text{Bbt}$ followed by the 1,2-elimination of MBr .¹² Thus, it was demonstrated that **1** should be a candidate for the building block of novel disilenes by reactions with nucleophiles. Since it is well-known that bromoethene derivatives undergo no substitution reaction with an organometallic reagent such as MeLi or MeMgBr , the observed substitution reactions of dibromodisilene **1** should reflect unique properties of a low-coordinated organosilicon species, i.e., lower LUMO of a disilene.¹ However, further addition of MeLi toward bromomethyldisilene **5** under the same conditions afforded a complicated mixture without any disilene species probably due to the slightly higher LUMO of **5** than that of **1**.¹³

When dibromodisilene **1** was treated with $t\text{-BuLi}$ at $-100\text{ }^\circ\text{C}$ in THF, not t -butyl-substituted disilene but 1,2-diaryldisilyne **9** was obtained (55% yield as judged by ^1H NMR spectra).¹⁴ In this case, $t\text{-BuLi}$ may attack not the sp^2 -silicon atom but the bromine atom of **1** due to the bulkiness of t -butyl group (halophilic reaction) to afford **9** via the elimination of LiBr from the intermediately formed $\text{Bbt}(\text{Li})\text{Si}=\text{Si}(\text{Br})\text{Bbt}$.¹⁵ In the ^{29}Si NMR spectrum, diaryldisilyne **9** showed a singlet signal for the triply bonded silicon atoms at 18.7 ppm, the chemical shift of which is in the apparently upper field than that of the silyl substituted disilynes (91.5 and 89.9 ppm).^{3,4} Similarly, tetraaryl disilenes were reported to show their ^{29}Si NMR chemical shifts in the upper field than those of tetrasilyl-substituted disilenes.¹ Since the slightly remaining **1** and the slow decomposition of **9** prevent **9** from further purification, disilyne **9** could not be completely purified. However, patient efforts to recrystallize **9** gave us the single crystals of **9** for X-ray crystallographic analysis.

Diaryldisilyne **9** has a crystallographic C_2 axis through the central $\text{Si}\equiv\text{Si}$ bond; that is, the two BbtSi units of **9** are inherently identical. As in the case of the previously reported disilyldisilyne, $\text{R}_3\text{SiSi}\equiv\text{SiR}_3$,⁴ **9** exhibited a bent structure with the $\text{Si}-\text{Si}-\text{C}$ bond angles of $133.0(3)^\circ$ and the $\text{C}-\text{Si}-\text{Si}-\text{C}$ dihedral angle of $164.1(8)^\circ$. The $\text{Si}\equiv\text{Si}$ bond length of **9** [$2.108(5)\text{ \AA}$] is reasonably shorter than the typical $\text{Si}-\text{Si}$ and $\text{Si}=\text{Si}$ bond lengths, featuring its triple-bond character. In addition, the slightly longer $\text{Si}\equiv\text{Si}$ bond length of **9** than that of $\text{R}_3\text{SiSi}\equiv\text{SiR}_3$ [$2.0622(9)\text{ \AA}$]⁴ should reflect the electronic feature of the aryl substituents on the triply bonded silicon atoms. Theoretical calculations (B3PW91/6-311+G(2df) for Si; 6-31G(d) for C,H) for 1,2-diaryldisilyne **9** strongly supported the observed structure and chemical shifts in the ^{29}Si NMR spectrum. The structural parameters of **9** optimized with C_2 symmetry exhibits the $\text{Si}=\text{Si}$ bond length of 2.119 \AA and $\text{Si}-\text{Si}-\text{C}$ bond angles of 135.9° . The ^{29}Si NMR chemical shift for the triply bonded silicon atoms was computed as 16.7 ppm, supporting the observed value in C_6D_6 . That is, diaryldisilyne **9** should feature a

triple-bond character even in solution, though the ^{29}Si NMR signal for the triply bonded silicon atoms of **9** was observed in relatively upper field region as compared with those of the silyl-substituted disilynes and tetraaryldisilenes probably due to the large contribution of the paramagnetic terms in **9**.¹⁶

In summary, the synthesis and isolation of stable diaryldibromodisilene **1** has been accomplished for the first time. It should be noted that **1** was found to undergo substitution reactions with organometallic reagents on the low-coordinated silicon atom to afford the corresponding substituted disilenes. Furthermore, the reaction of **1** with $t\text{-BuLi}$ afforded the corresponding 1,2-diaryldisilyne, $\text{BbtSi}=\text{SiBbt}$ (**9**), the structure and properties of which were established by X-ray crystallographic and spectroscopic analyses together with theoretical calculations.

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Supporting Information Available: Experimental procedures and spectral data for new compounds. These materials are available free of charge via the Internet at <http://pubs.acs.org>.

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- (14) Compound **9** obtained here is not $\text{Bbt}(\text{H})\text{Si}=\text{Si}(\text{H})\text{Bbt}$, since it was preliminarily synthesized as a stable compound, the NMR chemical shifts of which ($\delta_{\text{Si}} = 61.1$ and $\delta_{\text{H}} = 6.10$) are apparently different from those of BbtSiSiBbt (**9**).
- (15) Although the generation of **9** may be initiated by the electron transfer reaction from $t\text{-BuLi}$ to **1**, the reaction of **1** with a reductant such as lithium naphthalenide or KC_8 afforded a complicated mixture without **9**.
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