This article is published as part of the *Dalton Transactions* themed issue entitled:

New Horizon of Organosilicon Chemistry

Guest Editor: Professor Mitsuo Kira
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Published in issue 39, 2010 of *Dalton Transactions*

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Reactivity of an aryl-substituted silicon–silicon triple bond: 1,2-disilabenzenes from the reactions of a 1,2-diaryldisilyne with alkynes†

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Received 11th March 2010, Accepted 9th June 2010
DOI: 10.1039/c0dt00115e

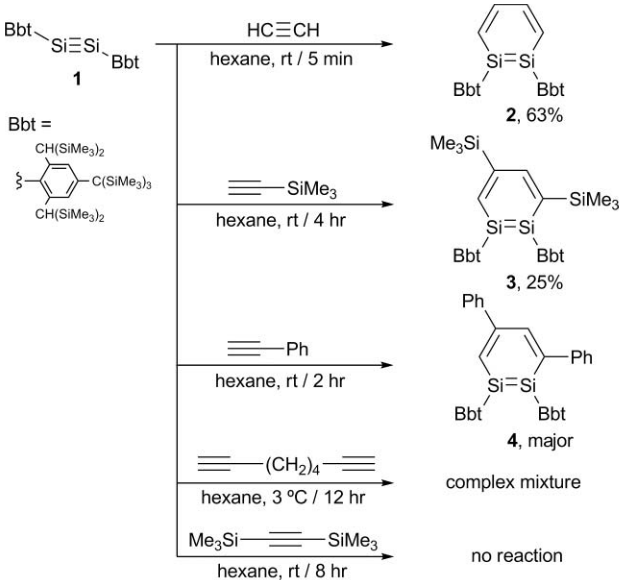
The reactivity of a diaryl-substituted disilyne, Ar–Si≡Si–Ar, with alkynes was examined. Reaction of the disilyne with acetylene yielded a 1,2-disilabenzene as the sole product.

In 2004, the groups of Sekiguchi and Wiberg independently reported a successful synthesis of overcrowded silyl-substituted disilynes (RSi≡SiR: R = Si(i-Pr)[CH(SiMe$_3$)$_2$]$_2$ (**I**),[1a] R = SiMe[Si(t-Bu)$_3$]$_2$ (**II**)[1b]). Although more than 6 years have passed since then, only a few reactions of disilynes are known.[1–3] Recently, we reported the synthesis and isolation of a stable 1,2-diaryldisilyne, BbtSi≡SiBbt (**1**, Bbt = 2,6-bis[bis(trimethylsilyl)methyl]-4-[tris(trimethylsilyl)methyl]-phenyl), along with its unique properties.[3] In addition, we demonstrated that the 1,2-diaryldisilyne **1** has a reactivity with alkenes similar to that of the silyl-substituted disilynes **I** and **II**, with the exception of its unique reactivity towards a conjugated diene.[3c]

Since our successful synthesis of a stable 2-silanaphthalene in 1997, we have continued to explore the chemistry of group 14 metallaaromatic compounds (*heavy aromatics*).[4] Recently, Sekiguchi *et al.* reported the first synthesis of diphenyl-substituted 1,2-disilabenzene derivatives from the reaction of 1,2-bis(silyl)disilyne **I** with phenylacetylene.[2c] They reported that **I** reacted with 2 equivalents of phenylacetylene to produce a mixture of two regioisomers, 4,5-diphenyl-1,2-disilabenzene (**IIIa**) and 3,5-diphenyl-1,2-disilabenzene (**IIIb**) in 2 : 3 ratio. On the other hand, Power and co-workers reported that the reaction of a digermyne bearing bulky terphenyl substituents underwent [2 + 2] cycloaddition with alkynes, such as diphenylacetylene or trimethylsilylacetylene, to give the corresponding 1,2-digermacyclobutadiene derivatives.[5]

Following these results, we turned our attention to the reactions of diaryldisilyne **1** with several alkynes, from which the corresponding 1,2-diaryl-1,2-disilabenzenes were obtained as major products. Herein, we report the preliminary results obtained for 1,2-diaryl-1,2-disilabenzene **2**, which exhibits the interesting *trans*-bent nature of the Si–Si bond.

The reactivity of **1** with various alkynes is summarized in Scheme 1. When a hexane solution of **1** was treated with 1 atm acetylene gas at room temperature for 5 min, the dark-yellow colour of **1** immediately disappeared and a light-yellow solution was obtained. Using NMR analysis, it was evidenced that 1,2-disilabenzene **2** was produced as the sole product. From the concentrated hexane solution, pure 1,2-disilabenzene **2** was isolated in 63% yield as light-yellow needles.



Scheme 1 Reactivity of **1** towards alkynes.

Treatment of **1** with trimethylsilylacetylene gave 3,5-bis(trimethylsilyl)-1,2-disilabenzene **3** as the major product. Two peaks at 64.1 and 65.4 ppm (C$_6$D$_6$) were observed for Si atoms of the central ring in the ^{29}Si NMR spectrum. While a product mixture of 4,5- and 3,5-substituted isomer (2 : 3) has been reported from the reaction of silyl-substituted disilyne **I** with phenylacetylene,[2c] no significant signals for the 4,5- or 3,6-substituted isomer could be observed in the NMR spectra of the crude product. Although **3** was formed as the major product, pure **3** could be isolated in only 25% yield due to its low crystallinity and high solubility in organic solvents. Reaction of **1** with phenylacetylene in hexane gave an orange solution after 2 h at room temperature, where the complete consumption of **1** was confirmed by NMR analysis of the reaction mixture. As in the reaction of Sekiguchi's disilyne (**I**) with phenylacetylene,[2c] two peaks at 55.0 and 61.7 ppm (C$_6$D$_6$) in ^{29}Si NMR spectra strongly suggested the formation of the corresponding 3,5-diphenyl-1,2-disilabenzene **4** as the major product. However, the isolation of **4** as a pure compound was unsuccessful due to its low crystallinity. Although a light-yellow solution was obtained from the reaction of **1** with 1,7-octadiyne, the resulting NMR spectra suggested the formation of a complex mixture. On the other hand, no reaction was observed when **1** was treated with bis(trimethylsilyl)acetylene for 8 h at room temperature, likely due to the steric hindrance.

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† Electronic supplementary information (ESI) available: Experimental details, characterization data, and NMR spectra for **2** and **6**. CCDC reference numbers 768830 and 768831. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c0dt00115e

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Single crystals of **2** were obtained by recrystallization from toluene and its molecular structure is shown in Fig. 1.§ The central ring skeleton of 1,2-disilabenzene **2** has an almost planar structure (the sum of the internal bond angles = 719.8°). One of the most unique structural features of **2** is the large torsion angle of C(Bbt)–Si–Si–C(Bbt) (45.6°), which is likely due to the *trans*-bent character of the Si–Si bond (*trans*-bent angles = 12.1°, 13.7°). The sums of the bond angles around skeletal Si atoms are 357.5° and 356.9°. Such feature is in sharp contrast to that of 1,2-bis(silyl)-4,5-diphenyl-1,2-disilabenzene **IIIa**, showing virtually planar geometries around the two skeletal Si atoms [Si–Si–Si–Si = 13.1(2)°].[2c]

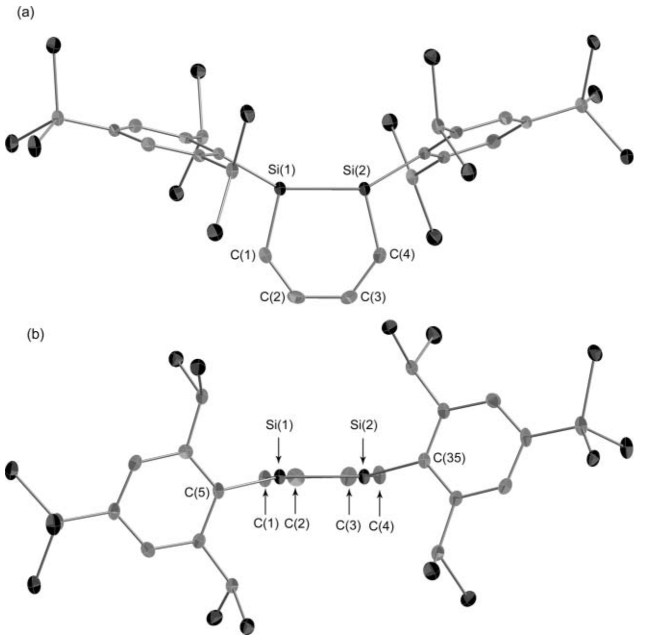
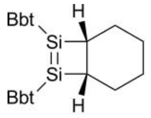


Fig. 1 Thermal ellipsoid (50%) drawing of $[\mathbf{2}\cdot 0.5(C_7H_8)]$ [(a) top view of the disilabenzene ring; (b) side view of the disilabenzene ring]. Hydrogen atoms, solvate, and methyl groups on the Bbt groups have been omitted for clarity. Selected bond lengths (Å) and angles (°): Si(1)–Si(2) 2.2334(7), Si(1)–C(1) 1.8047(19), C(1)–C(2) 1.377(3), C(2)–C(3) 1.400(3), C(3)–C(4) 1.372(3), C(4)–Si(2) 1.806(2), Si(1)–C(1)–C(2) 131.04(15), C(1)–C(2)–C(3) 126.51(18), C(2)–C(3)–C(4) 126.02(18), C(3)–C(4)–Si(2) 130.90(15), C(4)–Si(2)–Si(1) 102.98(7), Si(2)–Si(1)–C(1) 102.37(6), C(1)–Si(1)–C(5) 106.48(8), C(5)–Si(1)–Si(2) 148.67(6), C(4)–Si(2)–C(35) 106.96(8), C(35)–Si(2)–Si(1) 146.98(6), C(5)–Si(1)–Si(2)–C(35) 45.6(2).

In our previous studies, we reported the structure of 1,2-disilacyclobutene **5**, which has two Bbt groups in *cis* geometry, a *trans*-bent structure with a Si=Si bond distance of 2.213(3) Å, and a C(Bbt)–Si=Si–C(Bbt) torsion angle of 103.3(8)°.[3c]



5

d Si=Si	2.213 (3) Å
bent angle	26.4°
δ Si (C_6D_6)	92.3 ppm
λ_{max}	419 nm (ε 16000)

Although **2** has a similar *cis*-1,2-bis(Bbt) geometry as **5**, the Si–Si bond distance [2.2334(7) Å] is slightly longer than those of disilenes having aromatic substituents in *cis* geometry, which vary from 2.140 to 2.21 Å.[3c,6] Therefore, the Si–Si bond of **2** can be seen as an intermediate of a single and a double bond. Previously, we reported the structure of 1-Tbt-silabenzene (Tbt = 2,4,6-$[CH(SiMe_3)_2]_3$-C_6H_2), showing C–C bond lengths of 1.381(6)–1.399(6) Å.[4c] The skeletal C–C bond lengths of **2** are in the range of 1.37–1.40 Å and closely resemble that of silabenzene, suggesting the magnitude of the π-electron delocalization is similar to the case of a monosilabenzene. The longest wavelength absorption maxima of **2** in *n*-hexane was observed at 378 nm (ε 11 000), which is further red-shifted than the value of 1-Tbt-silabenzene (331 nm).[4c]

The disilabenzene **2** is highly oxygen-sensitive. Exposure of **2** under 1 atm molecular oxygen produced a colourless product **6** in quantitative yield (Scheme 2). Single crystals suitable for X-ray structure analysis§ were obtained from a toluene and hexane solution, and its crystal structure is shown in Fig. 2. Based on the analysis, it was evident that the Si–Si bond was oxidized to form a 1,3,2,4-dioxadisiletane ring, which is bridged by a butadiene chain. Consistent with previous findings,[1b,7] a short distance [2.3777(7) Å] between the two Si atoms in the 1,3,2,4-dioxadisiletane ring was observed, which is comparable to a typical Si–Si single bond length (2.34 Å). Although the ring connected with the butadiene chain is slightly distorted,[8] the relatively short distance between the two Si atoms and symmetrical structure of **6** provide a good model to compare with **2**. We also performed theoretical calculations for 1,2-diaryl-1,2-disilabenzene **2-A**, which has two 2,6-bis[bis(trimethylsilyl)methyl]benzene groups instead of Bbt groups of **2**.

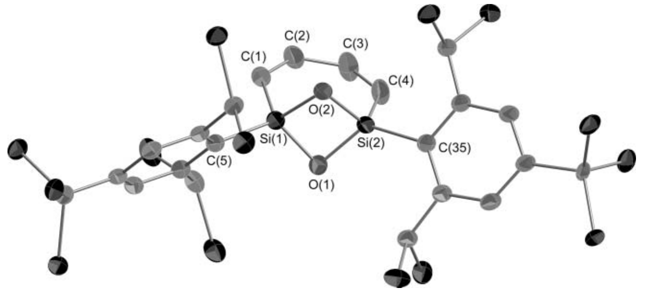
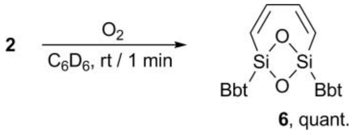


Fig. 2 Thermal ellipsoid (50%) drawing of $[\mathbf{6}\cdot C_7H_8\cdot C_6H_{14}]$. Hydrogen atoms, solvates, and methyl groups on the Bbt groups have been omitted for clarity. Selected bond lengths (Å) and angles (°): Si(1)–O(1) 1.6910(14), O(1)–Si(2) 1.6904(14), Si(2)–O(2) 1.6931(14), O(2)–Si(1) 1.6888(13), Si(1)–Si(2) 2.3777(7), Si(1)–C(1) 1.862(2), C(1)–C2 1.342(3), C(2)–C(3) 1.467(3), C(3)–C(4) 1.343(3), C(4)–Si(2) 1.857(2), Si(1)–C(1)–C(2) 127.45(16), C(1)–C(2)–C(3) 129.3(2), C(2)–C(3)–C(4) 129.7(2), C(3)–C(4)–Si(2) 127.84(18), C(4)–Si(2)–Si(1) 101.93(7), Si(2)–Si(1)–C(1) 102.58(7), Si(1)–O(1)–Si(2) 89.37(7), O(1)–Si(2)–O(2) 87.77(7), Si(2)–O(2)–Si(1) 89.35(7), O(2)–Si(1)–O(1) 87.89(7), C(1)–Si(1)–C(5) 109.78(9), C(5)–Si(1)–Si(2) 147.56(6), C(4)–Si(2)–C(35) 109.32(9), C(5)–Si(1)–Si(2)–C(35) 18.16(19).



Scheme 2 Oxidation of **2**.

In Table 1, selected structural features and chemical shifts were compared among **2**, **2-A**, and **6**. Although optimized geometry of **2-A** has asymmetrical Si atoms, the calculated ^{29}Si chemical

Table 1 Selected chemical shifts (ppm), bond lengths (Å), and dihedral angles (°)

	2	**2-A**[a]	**6**
δ Si[b]	57.1	61.40, 63.43	−10.1
$\delta_H(1)$[b]	7.73–7.79 (m)	8.40, 8.33	6.64–6.71 (m)
$\delta_H(2)$[b]	7.61–7.68 (m)	8.02, 8.06	6.12–6.19 (m)
*d*Si(1)–Si(2)	2.2334(7)	2.245	2.3777(7)
*d*Si(1)–C(1)	1.8047(19)	1.812	1.862(2)
*d*Si(2)–C(4)	1.806(2)	1.813	1.857(2)
*d*C(1)–C(2)	1.377(3)	1.383	1.342(3)
*d*C(3)–C(4)	1.372(3)	1.383	1.343(3)
*d*C(2)–C(3)	1.400(3)	1.414	1.467(3)
∠Ar–Si–Si–Ar	45.6(2)	60.597[10]	18.16(19)

[a] For calculations, 2,6-bis[bis(trimethylsilyl)methyl]benzene group was substituted instead of Bbt; structural optimizations: B3PW91/6-311G(3d) for Si, 6-31G(d) for C, H; GIAO calculations: B3PW91/6-311+G(3df) for Si, 6-311G(2d,p) for C, H. [b] 300 MHz for ^{1}H and 59 MHz for ^{29}Si; C_6D_6 was used as a solvent for **2** and **6**.

shifts of the central silicon atoms of **2-A** are close to the signal observed from **2** (δ 57.1). As expected, a ^{29}Si NMR signal of the ring Si atoms of **6** was observed at highly upfield region (δ −10.1). The central ring protons of **2** were observed more than 1 ppm downfield compared to **6**. These downfield shifts should be interpreted as a result of ring current effect of the 1,2-disilabenzene ring. Although, the central rings of **2** and **6** have structural similarities, remarkable differences in the bond distances of their central rings were observed. Compared to **6**, **2** has significantly shortened Si–C and C(2)–C(3) bond distances, which can be interpreted as indicative of its aromatic property. Furthermore, the good agreement in bond distances with the theoretical calculations supports the delocalization of π-electrons of **2**. The calculated NICS(1) (nucleus-independent chemical shift)[9] values of **2-A** are −8.15 and −8.14 of which the significant negative values provide evidence for its aromaticity.

Gathering all spectral and structural features of **2** discussed above, it is clear that **2** has delocalized π-electrons. Because **2** is the first example of 1,2-disilabenzene having the *trans*-bent structural feature, it will be interesting to study how the conjugation takes place through a *trans*-bent bond. In ^{1}H and ^{13}C NMR spectra, two independent signals were observed for the $SiMe_3$ groups at the *ortho*-positions of Bbt groups even at 70 °C, suggesting that **2** retains the *trans*-bent conformation even in warm solution.[11]

In summary, the 1,2-diaryldisilyne **1** showed high reactivity with alkynes, especially unhindered alkynes. Both polar and non-polar alkynes reacted with **1** to give 1,2-disilabenzene as the major product. Crystal structure analysis showed that the central ring of 1,2-diaryl-1,2-disilabenzene **2** is almost planar, and most notably, the Si–Si bond has significant *trans*-bent character. Evidence supporting the aromatic structure of **2** was collected by both experimental and theoretical means.

Acknowledgements

This work was supported by Grants-in Aid (17GS0207 and 20036024) and the Global COE Program from the Ministry of Education, Culture, Sports, Science and Technology (MEXT), Japan.

Notes and references

§ Crystal data for [**2**·0.5(C_7H_8)]. $C_{67.5}H_{142}Si_{16}$, $M = 1403.25$, monoclinic, $a = 18.524(2)$, $b = 12.0037(14)$, $c = 40.568(5)$ Å, $U = 8836.5(19)$ Å^3, $T = 103(2)$ K, space group $P2_1/c$ (no. 14), $Z = 4$, 80 148 reflections measured, 15 370 independent reflections ($R_{int} = 0.0709$), $R_1 = 0.0441$ [$I > 2\sigma(I)$], w$R_2 = 0.1284$ (all data).
Crystal data for [**6**·C_7H_8·C_6H_{14}]. $C_{77}H_{160}O_2Si_{16}$, $M = 1567.49$, triclinic, $a = 16.8221(2)$, $b = 17.7685(2)$, $c = 18.7611(2)$ Å, $U = 4879.28(10)$ Å^3, $T = 103(2)$ K, space group $P\bar{1}$ (no. 2), $Z = 2$, 40 744 reflections measured, 16 924 independent reflections ($R_{int} = 0.0296$), $R_1 = 0.0452$ [$I > 2\sigma(I)$], w$R_2 = 0.1244$ (all data).

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10 The theoretically optimized structure of the less hindered model, 1,2-diphenyl-1,2-disilabenzene, exhibits completely planar structure with C(Ph)–Si–Si–C(Ph) torsion angle of 0°, suggesting the *trans*-bent structure of **2** would be due to the severe steric repulsion of extremely bulky Bbt groups.

11 When a Bbt group is connected directly to a chiral center, the two trimethylsilyl groups at the *ortho*-benzyl position are in diastereomerically non-identical situation in NMR spectroscopy, see ref. 3a.