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Addition of Amines and Hydroborane to the Disilyne RSi≡SiR (R = Si^{i}Pr[CH(SiMe$_3$)$_2$]$_2$) Giving Amino- and Boryl-Substituted Disilenes

Katsuhiko Takeuchi, Masao Ikoshi, Masaaki Ichinohe, and Akira Sekiguchi*

Department of Chemistry, Graduate School of Pure and Applied Sciences, University of Tsukuba,
Tsukuba, Ibaraki 305-8571, Japan

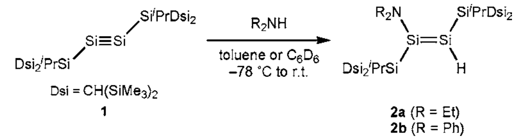
Received December 1, 2009; E-mail: sekiguch@chem.tsukuba.ac.jp

Since the isolation of the first stable tetramesityldisilene Mes$_2$Si=SiMes$_2$ (Mes = 2,4,6-trimethylphenyl) in 1981,[1] numerous disilene derivatives containing a silicon−silicon double bond have been isolated and characterized.[2] There are several methods for the synthesis of stable disilenes:[2] dimerization of silylenes, photochemical cleavage of cyclotrisilanes, reductive coupling of dihalosilanes, and the reaction of dilithiosilanes with dihalosilanes, giving disilenes of the types A$_2$Si=SiA$_2$ or A$_2$Si=SiB$_2$. The reaction of disilenides with aryl halides leads to the formation of the type A$_2$Si=SiAB (B = aryl group).[3] The reduction of L:SiCl$_4$ (L = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene) to afford a new type of a disilene, L:Si=Si:L, was also recently reported.[4] However, methods for the synthesis of heteroatom-substituted disilenes are currently very limited.[5]

Recently, heavier group 14 alkyne analogues have been synthesized and isolated.[6−9] Among them, the silicon−silicon triply bonded compounds, disilynes, have been prepared by our and Wiberg's groups[7,8] using bulky silyl groups, and we reported a full characterization of the first isolable crystalline disilyne **1**, RSi≡SiR (R = Si^{i}Pr[CH(SiMe$_3$)$_2$]$_2$), with a *trans*-bent structure. Tokitoh's group also recently reported a disilyne derivative with bulky aryl groups.[9] The disilyne **1** is very reactive toward alkenes,[10] alkynes,[10] ^{t}BuLi,[11] alkali metals,[11b] nitriles,[12] and silylcyanides[13] to give a disilenyllithium, 1,2-disilacyclobutenes, 1,2-disilabenzene derivatives, triaza-1,4-disilabicyclo[2.2.2]oct-2,5,7-triene derivatives, disilyne-silylisocyanide adduct, and 1,4-diaza-2,3-disilabenzene derivatives, respectively. We report here a new highly effective route for the synthesis of a type of heteroatom-substituted disilenes R(R′$_2$E)Si=SiHR **2a**, **2b**, and **3** (R′$_2$E = Et$_2$N (**2a**), Ph$_2$N (**2b**), and 9-borabicyclo[3.3.1]nonan-9-yl (**3**)) by the reaction of disilyne **1** with diethylamine, diphenylamine, or 9-borabicyclo[3.3.1]nonane (9-BBN), respectively.[5] We also discuss the π-conjugation between the Si=Si double bond and the lone pair on the nitrogen atom or the vacant 2p orbital on the boron atom, correlated with the dihedral angle between the Si=Si double bond and the plane of the amino or boryl group.[5]

The reaction of disilyne **1** with an excess amount of diethylamine in toluene from −78 °C to room temperature gave an orange solution, from which amino-substituted disilene **2a** was isolated as orange crystals in 78% yield (Scheme 1).[14] The reaction of **1** with diphenylamine in C$_6$D$_6$ also afforded amino-substituted disilene **2b**; however, the reaction was very slow and it took 1 month for the completion because of steric hindrance. Neither **2a** nor **2b** reacted with excess amine, in contrast to the reaction of **1** with alcohols, which only gave the 1:2 adduct dialkoxydisilane.[15] The molecular structures of **2a** and **2b** were determined by X-ray crystallography, their crystal structures are shown in Figure 1 (**2a**: left; **2b**: right).[14] The sums of the bond angles around the nitrogen atoms are nearly 360° in both **2a** and **2b**, which is common among monosilyl-substituted amines.[16] However, the orientation of the amino substituents is dramatically different in **2a** and **2b**. The Si=Si double bond plane and amino group plane of **2a** are almost parallel to each other with the torsion angle Si2−Si1−N1−C1 of ca. 7°, which allows conjugation between the Si=Si double bond and the lone pair on the nitrogen atom. On the other hand, in **2b**, the orientation of the amino substituent to the Si=Si double bond plane is close to perpendicular with the torsion angle Si2−Si1−N1−C1 of ca. 67°, because of the two bulky phenyl groups. Thus, **2b** has almost no π-conjugation between the Si=Si double bond and the amino group. The shorter Si1−N1 bond length of **2a** (1.717(2) Å) compared with that of **2b** (1.775(9) Å) also reflects the presence or absence of π-conjugation. The Si=Si double bond length of **2b** (2.1790(14) Å) is slightly longer than that of **2a** (2.1647(2) Å), but this can be explained by assuming that the effect of steric hindrance of the bulky diphenylamino group is larger than the π-conjugation effect.

Scheme 1



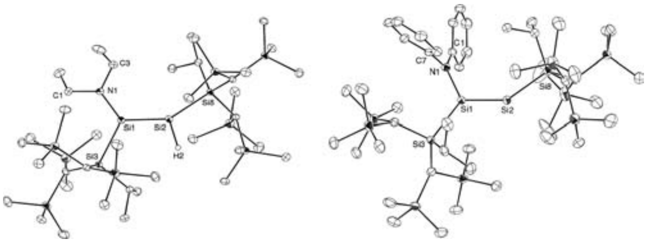


Figure 1. ORTEP drawing of **2a** (left) (30% thermal ellipsoids). Hydrogen atoms except for H2 on Si2 are omitted for clarity. Selected bond lengths (Å): Si1−Si2 = 2.1647(10), Si1−Si3 = 2.3966(9), Si1−N1 = 1.717(2), Si2−Si8 = 2.3550(10), Si2−H2 = 1.45(4). Selected bond angles (deg): Si2−Si1−Si3 = 116.14(4), Si2−Si1−N1 = 122.41(8), Si3−Si1−N1 = 120.10(8), Si1−Si2−Si8 = 141.72(4), Si1−Si2−H2 = 104.8(17), Si8−Si2−H2 = 108.4(17), Si1−N1−C1 = 123.46(17), Si1−N1−C3 = 120.72(18), C1−N1−C3 = 115.8(2). ORTEP drawing of **2b** (right) (30% thermal ellipsoids). Hydrogen atoms are omitted for clarity. Selected bond lengths (Å): Si1−Si2 = 2.1790(14), Si1−Si3 = 2.4320(14), Si1−N1 = 1.775(3), Si2−Si8 = 2.3723(15). Selected bond angles (deg): Si2−Si1−Si3 = 122.60(6), Si2−Si1−N1 = 116.92(12), Si3−Si1−N1 = 118.31(12), Si1−Si2−Si8 = 143.36(6), Si1−N1−C1 = 121.0(3), Si1−N1−C7 = 122.0(2), C1−N1−C7 = 116.5(3).

The NMR spectra of **2a** and **2b** also showed the presence or absence of π-conjugation between the Si=Si double bond and the amino group. Thus, the ^{29}Si NMR spectrum of **2a** showed characteristic signals of low-coordinate silicon atoms at 170.5 (N−*Si*=Si) and −39.3 ppm (H−*Si*=Si); the latter is greatly upfield shifted relative to those of the disilenes reported so far (63.3−154.5 ppm).[2a] On the other hand, the ^{29}Si NMR spectrum of **2b** showed resonance signals at 136.4 (N−*Si*=Si) and 66.6 ppm (H-*Si* = Si), both of which lie in the range of typical unsymmetrical disilenes.[17] The ^{1}H NMR spectrum of **2a** also showed the characteristic signal

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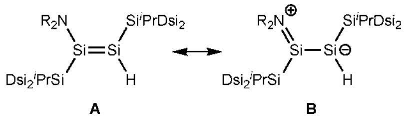
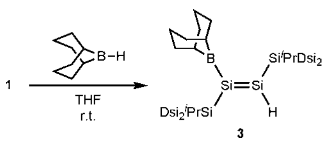
of Si—H at 2.97 ppm, which is high-field shifted compared with that of **2b** (4.54 ppm). The contribution of zwitterionic structure **B**, which has anionic character on the H-substituted Si atom, accounts for the significantly high-field shifts of the Si—H unit of **2a** compared with that of **2b** (Chart 1).

Chart 1



Although the boryl-substituted disilene is also expected to have π-conjugation between the Si═Si double bond and the vacant 2p orbital on the boron atom, the first boryl-substituted disilenes $(^t\mathrm{Bu_2MeSi})_2\mathrm{Si{=}Si(SiMe^tBu_2)(BR^*_2)}$ **4a**, **b** ($\mathrm{R^*_2}$ = pinacol (**4a**), catechol (**4b**)), which we reported recently, have no π-conjugation because of the almost perpendicular orientation of the boryl substituent to the Si═Si double bond plane.[5e] However, we were able to synthesize a boryl-substituted disilene with π-conjugation by the reaction of **1** with hydroborane.

Scheme 2



The reaction of **1** with 1 equiv of 9-BBN in dry THF at room temperature afforded boryl-substituted disilene **3**, which was isolated as orange crystals in 53% yield (Scheme 2).[14] The molecular structure of **3** determined by X-ray crystallography is shown in Figure 2.[14] The dihedral angle between the boryl substituent plane and the Si═Si double bond plane is ca. 11°. The Si1—B1 bond length of **3** (2.002(4) Å) is shorter than that of **4b** (2.022(8) Å).[5e] The Si═Si double bond length is 2.1838(12) Å, which lies in the range of typical Si═Si double bonds (2.138−2.289 Å).[2a] These structural data suggest the presence of π-conjugation between the Si═Si double bond and the vacant 2p orbital on the boron atom.

In the ^{29}Si NMR spectrum of **3**, the signals of low-coordinate silicon atoms are observed at 121.7 (B—*Si*═Si) and 150.5 ppm (H—*Si*═Si); the latter ^{29}Si NMR signal is appreciably shifted downfield compared with that of **2a** (−39.3 ppm). The ^{1}H NMR spectrum of **3** also shows the characteristic signal of the Si—H unit at 6.21 ppm. The significantly downfield-shifted resonance of the Si—H unit (both ^{29}Si NMR and ^{1}H NMR), relative to those of **2a** and **2b**, can be reasonably explained in terms of the contribution of zwitterionic structure **D**, which has a cationic character on the H-substituted Si atom (Chart 2).

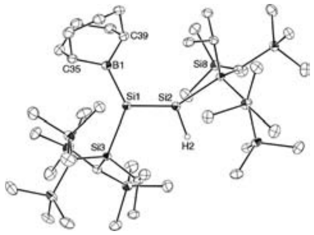
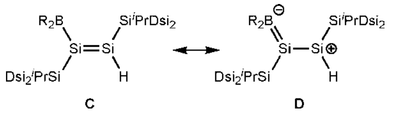


Figure 2. ORTEP drawing of **3** (30% thermal ellipsoids). Hydrogen atoms except for H2 on Si2 and the toluene molecule as a crystallization solvent are omitted for clarity. Selected bond lengths (Å): Si1−Si2 = 2.1838(12), Si1−Si3 = 2.3872(11), Si1−B1 = 2.002(4), Si2−Si8 = 2.3733(11), Si2−H2 = 1.42(3). Selected bond angles (deg): Si2−Si1−Si3 = 111.08(4), Si2−Si1−B1 = 116.89(11), Si3−Si1−B1 = 131.94(11), Si1−Si2−Si8 = 145.86(5), Si1−Si2−H2 = 111.2(13), Si8−Si2−H2 = 102.6(13), Si1−B1−C35 = 126.9(2), Si1−B1−C39 = 121.7(2), C35−B1−C39 = 111.1(3).

Chart 2



The push−pull phenomenon, discussed in the disilenes **2a** and **3**, is well-known in olefin chemistry (enamines[18a] and vinylboranes[18b]). This influences the energy levels of the HOMO and LUMO of **2a** and **3**, affecting the UV−vis absorptions (π−π^* transitions) of the Si═Si double bond (438 nm for **2a**: 469 nm for **3**; for the computational results on the model compounds **2a′** and **3′**, see Supporting Information).

Supporting Information Available: The experimental procedure of **2a**, **2b**, and **3**; computational results on the model compounds **2a′** and **3′**; tables of crystallographic data including atomic positional and thermal parameters for **2a**, **2b**, and **3** (PDF/CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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