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Reactivity of a Disilyne RSi≡SiR (R = Si^{i}Pr[CH(SiMe$_3$)$_2$]$_2$) toward π-Bonds: Stereospecific Addition and a New Route to an Isolable 1,2-Disilabenzene

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Recently, numerous multiple bond species containing heavier group 14 elements have been isolated and characterized.[1] In particular, considerable interest has been focused on the nature of alkene analogues of silicon[2] because of their unusual structures and bonding since the isolation of a stable tetramesityldisilene by West and co-workers.[3] In many cases, the π bond of the disilenes has displayed an increased reactivity toward many reagents, compared with that of alkenes and alkynes, because of the relatively small HOMO−LUMO gap and its biradical character.[4] For example, the π bond of disilenes is known to undergo smooth [2 + 2] cycloadditions toward alkenes and alkynes to give the disilacyclobutane and disilacyclobutene derivatives, respectively.[1,2] On the other hand, much less is known about the π bond nature of disilynes with a silicon−silicon triple bond, which has two distinct π bonds (π_{in} and π_{out}),[5,6] although a few papers have described the reactivity of alkyne analogues.[7] Now, a comparison of the chemical behavior of heavier group 14 element alkyne analogues with that of alkynes is of special interest. To understand the nature of the π bond of a silicon−silicon triple bond, we have examined the reaction of disilyne **1**[5a] with alkenes and alkynes. In this paper, we present the results of the stereospecific cycloadditions of **1** to 2-butenes,[8] together with those of the cycloaddition of **1** to phenylacetylene to give an isolable 1,2-disilabenzene derivative. Furthermore, we report theoretical studies on the mechanism of the reactions, showing that these reactions involve in the initial step [1 + 2] cycloaddition (the interaction between the LUMO (π_{in}*) of **1** and the HOMO of 2-butenes or acetylene), instead of a direct [2 + 2] cycloaddition.

When a hexane solution of disilyne **1** was treated with an excess of *cis*-2-butene at room temperature, *cis*-3,4-dimethyl-1,2-disilacyclobutene **2a** was obtained as the sole product in 89% yield (Scheme 1).[9] This reaction proceeded cleanly and was complete within 30 min. On the other hand, the reaction of **1** with *trans*-2-butene under the same conditions produced *trans*-3,4-dimethyl-1,2-disilacyclobutene **2b** as yellow crystals in 85% yield.[9] In contrast to the reaction with *cis*-2-butene, it took 1 day to complete this reaction. Most importantly, both reactions proceeded stereospecifically, as was determined by NMR spectra and X-ray analysis (for **2b**).[9] Although an excess of 2-butenes was used in both reactions, the subsequent cycloaddition reaction was not observed.

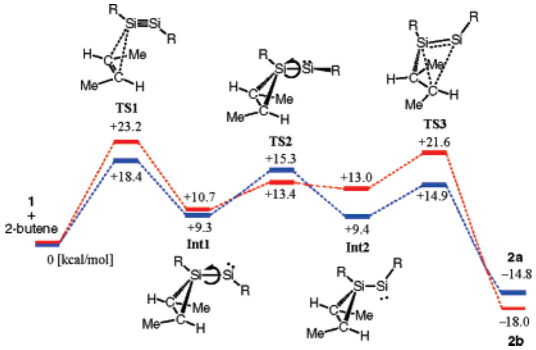
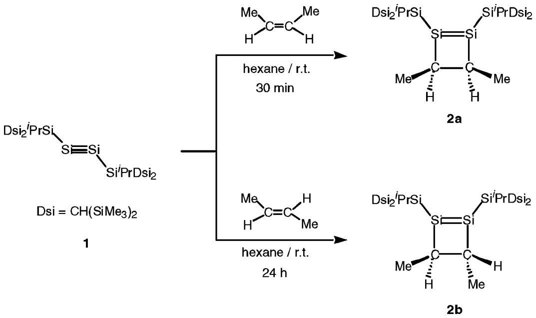


Figure 1. Energy profile for the reaction of **1** with 2-butenes (R = Si^{i}Pr[CH(SiMe$_3$)$_2$]$_2$). Transition sates and intermediates are shown for *trans*-2-butene. Red line, reaction pathway for *trans*-2-butene; blue line, reaction pathway for *cis*-2-butene.

Scheme 1



To gain a mechanistic insight, we have performed theoretical calculations of the reaction of disilyne **1** with 2-butenes. Figure 1 shows the energy profile along the reaction path calculated at the B3LYP/[Si, 6-311+G(2df); C and H, 6-31G(d)]//B3LYP/3-21G* level.[10] The interaction between the in-plane LUMO (π_{in}*) of **1** and the HOMO of 2-butene, resulting in [1 + 2] cycloaddition, is the first step in both reactions to produce the silacyclopropylsilylene intermediate (**Int1**).[11] The alternative interaction between the out-of-plane HOMO (π_{out}) of **1** and the LUMO of 2-butene is unfavorable because of the larger steric repulsion between 2-butene and the Si^{i}Pr[CH(SiMe$_3$)$_2$]$_2$ group of **1**. Because the first step is rate-determining, the reaction with *trans*-2-butene, which has a higher energy barrier ($\Delta E = +23.2$ kcal/mol), requires a longer reaction time than the reaction with *cis*-2-butene ($\Delta E = +18.4$ kcal/mol). The difference in the heights of the energy barriers is attributed to the degree of steric repulsion between the Me group of 2-butene and the Si^{i}Pr[CH(SiMe$_3$)$_2$]$_2$ group of **1**. Finally, rotation of the Si−Si bond through **TS2** followed by the intramolecular insertion of the silylene (**Int2**) into the neighboring Si−C bond with retention of the stereoconfiguration completes the formation of products **2a**,**b**.

We have also examined the reaction of **1** with an alkyne, hoping to synthesize the 1,2-disilacyclobutadiene derivative by [2 + 2] cycloaddition.[12] When a hexane solution of **1** was treated with an excess of phenylacetylene at room temperature, the 1,2-disilabenzene derivative **3** was obtained as a mixture of two regioisomers (**3a**/**3b** = 2:3), isolated as yellow crystals in 63% overall yield

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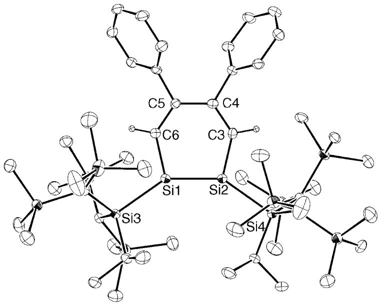
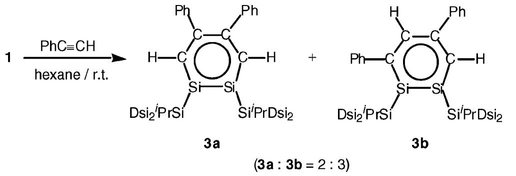


Figure 2. ORTEP drawing of **3a** (30% thermal ellipsoids). Hydrogen atoms except for the central ring are omitted for clarity. Selected bond lengths (Å): Si1−Si2 = 2.2018(18), Si2−C3 = 1.799(5), C3−C4 = 1.389(6), C4−C5 = 1.452(6), C5−C6 = 1.386(6), Si1−C6 = 1.804(4), Si1−Si3 = 2.3828(18), Si2−Si4 = 2.3730(16), Selected bond angles (deg): Si1−Si2−C3 = 103.00(15), Si2−C3−C4 = 133.2(4), C3−C4−C5 = 123.8(4), C4−C5−C6 = 124.1(4), C5−C6−Si1 = 133.2(3), C6−Si1−Si2 = 102.68(16), Si1−Si2−Si4 = 144.61(7), C3−Si2−Si4 = 112.22(15), Si2−Si1−Si3 = 144.81(7), C6−Si1−Si3 = 112.25(16).

Scheme 2



(Scheme 2).[12,13] No reaction occurred with diphenylacetylene. This is the first example of stable 1,2-disilabenzene derivatives, although the isolation of some stable monosilaaromatic compounds,[14] as well as the chemical trapping of intermediary 1,4-disilabenzene and its observation by UV/vis spectroscopy in an Ar matrix at 10 K,[15] have already been reported.

In the ^{29}Si NMR spectrum of **3**, the low-field shifted signals (99.2 ppm for **3a**, 99.4 and 106.8 ppm for **3b**) characteristic of sp^2-Si were observed. The signals of ring protons (8.47 ppm for **3a**, 8.01, 8.61 ppm for **3b**) as well as ring carbons (147.8 and 150.6 ppm for **3a**, 141.6, 146.4, 149.6, and 161.3 ppm for **3b**) were observed in a typical aromatic region.

Single crystals of **3a** were obtained by recrystallization from a mixture of pentane−toluene, and its crystal structure is shown in Figure 2. The 1,2-disilabenzene ring of **3a** is almost planar, and the sum of the bond angles around the two skeletal Si atoms is 359.74 and 359.83° for Si1 and Si2, respectively. The dihedral angle between the 1,2-disilabenzene ring and each phenyl group is ca. 54°. The length of the Si1−Si2 bond is 2.2018(18) Å, which is intermediate between the Si−Si single and double-bond lengths.[16] The lengths of Si1−C6 and Si2−C3 were found to be essentially equal to each other (1.804(4) and 1.799(5) Å, respectively), and they are intermediate between those of Si−C single and double-bond lengths.[16] Furthermore, the C3−C4 and C5−C6 bond lengths, which are also equal to each other (1.389(6) and 1.386(6) Å, respectively), are similar to the C−C bond length of the benzene ring (1.39−1.40 Å).[17] The C4−C5 bond length of 1.452(6) Å is different from that of the C−C bond length in the benzene ring, but is intermediate between those of C−C single and double-bond lengths (1.54 and 1.34 Å, respectively). Thus, it has been experimentally demonstrated that 1,2-disilabenzene has some contribution from the 6π aromatic delocalization, similar to the cases of benzene and monosilabenzene.[14,18] Indeed, NICS values, recognized as an aromaticity probe, were calculated for the model compounds **3a′** and **3b′** (Me$_3$Si groups instead of Si^{i}PrDsi$_2$) at 1 Å above the center of the ring: NICS(1) = −8.0 for **3a′** and −8.1 for **3b′** (cf. NICS(1) for benzene = −10.6).[19]

According to the theoretical calculation, the first step in the formation of 1,2-disilabenzene is the generation of a 1,2-disilacyclobutadiene-like intermediate. Then, the [2 + 4] cycloaddition reaction between this intermediate and a second acetylene molecule will take place to give 1,2-disila-Dewar benzene, followed by its valence isomerization to form the final 1,2-disilabenzene (see the Supporting Information).

Supporting Information Available: The experimental procedures of **2a**, **2b**, **3a**, and **3b**;, table of crystallographic data including atomic positional and thermal parameters for **2b** and **3a** (PDF/CIF); calculated energies of transition states and intermediates for the reaction of **1** with acetylene. This material is available free of charge via the Internet at http://pubs.acs.org.

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(10) Calculations were carried out using the Gaussian 03 program. Geometry optimization at the B3LYP/3−21G* level well reproduced the structural parameters for the disilyne **1** of the experimental values, see: Takagi, N.; Nagase, S. *J. Organomet. Chem.* **2007**, *692*, 217.
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