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Reactivity of an Aryl-Substituted Silicon−Silicon Triple Bond: Reactions of a 1,2-Diaryldisilyne with Alkenes

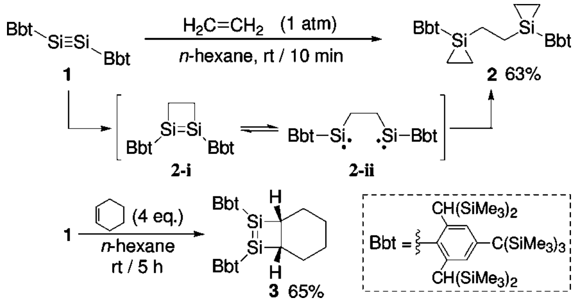
Joon Soo Han, Takahiro Sasamori, Yoshiyuki Mizuhata, and Norihiro Tokitoh*

Institute for Chemical Research, Kyoto University, Gokasho, Uji, Kyoto 611-0011, Japan

Received January 5, 2010; E-mail: tokitoh@boc.kuicr.kyoto-u.ac.jp

Since the first isolation of a disilene ($\mathrm{Mes_2Si{=}SiMes_2}$; Mes = 2,4,6-trimethylphenyl) in 1981 by West et al.,[1a] there have been many investigations of the chemistry of multiply bonded silicon compounds.[1] In 2004, Sekiguchi's and Wiberg's groups independently reported two types of disilynes ($\mathrm{RSi{\equiv}SiR}$: R = $\mathrm{SiPr^{\mathit{i}}[CH(SiMe_3)_2]_2}$,[2a] **I**; R = $\mathrm{SiMe(SiBu^{\mathit{t}}_3)_2}$,[2b] **II**), both of which are stabilized by bulky silyl substituents. As for the stabilization of the reactive Si−Si triple bond, theoretical calculations showed that significant stabilizing effects with the electropositive silyl group might be of great importance in addition to steric protection.[3] Recently, we reported the synthesis and structure of a stable 1,2-diaryldisilyne, $\mathrm{BbtSi{\equiv}SiBbt}$ (**1**, Bbt = 2,6-bis[bis(trimethylsilyl)methyl]-4-[tris(trimethylsilyl)methyl]phenyl).[4] The triple-bond character of **1** was evaluated on the basis of the experimental results with the aid of detailed theoretical calculations, and it was suggested that the Si−Si triple bond in aryl-substituted disilyne **1** is weaker than those the silyl-substituted disilynes **I** and **II**.[4] In order to understand the chemistry of the fascinating triply bonded organosilicon species, it is very important to investigate the unexplored reactivity of disilynes in detail. However, only a few reactions have been reported to date, probably because of the difficulty of synthesizing disilynes.[2b,5−7] Because **1** is the first aryl-substituted disilyne, it will provide us with valuable information about how the substituent affects the reactivity of disilynes. In this paper, we describe unique results obtained from the reactions of bulky, aryl-substituted disilyne **1** with ethylene, cyclohexene, and 2,3-dimethyl-1,3-butadiene.

Scheme 1



When a hexane solution of **1** was treated with 1 atm ethylene gas at room temperature, the dark-yellow color of **1** immediately disappeared and a colorless solid started to precipitate. An almost colorless solution with a large amount of precipitate was obtained after 10 min. Recrystallization of the precipitate using tetrahydrofuran (THF) gave **2** as colorless crystals in 63% yield. Interestingly, **1** was found to react with 3 equiv of ethylene to give an ethylene-bridged bis(silacyclopropane) product **2** (Scheme 1). A ^{29}Si NMR signal characteristic of the silacyclopropane skeletons was observed in the highly negative region at −81.9 ppm (THF-d_8).

Wiberg et al.[2b] reported that the reaction of disilyne **II** with excess ethylene afforded the corresponding 1,2-disilacyclobutene via [2 + 2] cycloaddition. Similar products were obtained in the reaction of disilyne **I** with excess 2-butene.[5c] Although they used excess alkene, no further reaction occurred. Very recently, Power and co-workers[7f] reported the reversible reactions of ethylene with distannynes ($\mathrm{ArSn{\equiv}SnAr}$, Ar = bulky *m*-terphenyl group) to give the corresponding 1,4-distannabicylo[2.2.0]butanes, which spontaneously undergo retro-cycloaddition in solution, giving the original distannynes. On the other hand, the reaction of their kinetically stabilized digermyne analogue ($\mathrm{ArGe{\equiv}GeAr}$) with ethylene was found to give the corresponding 1:2 adduct, but no retro-cyclization could be observed.[7f]

The formation of **2** is most likely interpreted in terms of initial formation of the 1,2-disilacyclobutene **2-i** via [2 + 2] cycloaddition with ethylene followed by homolytic cleavage of the Si=Si bond to give the bis(silylene) intermediate **2-ii**, which further reacts with ethylene to give **2**. We have previously shown that an extremely hindered disilene smoothly undergoes thermal dissociation into the corresponding silylenes.[8] Accordingly, if **2-i** were generated initially in this reaction, it would readily undergo dissociation into bis(silylene) **2-ii** because of the severe steric congestion of the *cis*-bis(Bbt) configuration, where the large ring strain further promotes the dissociation.

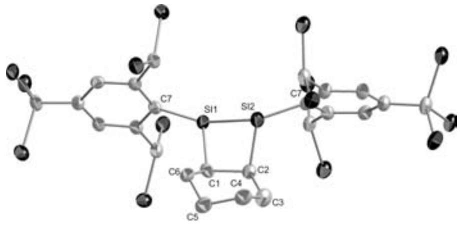


Figure 1. Thermal ellipsoid (50%) drawing of **3**. Hydrogen atoms and methyl groups on the Bbt groups have been omitted for clarity.

In order to find evidence for the formation of 1,2-disilacyclobutene species in the reaction of diaryldisilyne **1** with alkene, we examined the reaction with cyclohexene as the alkene, since the two ring Si atoms of the expected 1,2-disilacyclobutene would be held close to each other by the fused cyclohexane unit and thus keep the Si=Si bond structure. As expected, 7,8-disilabicyclo[4.2.0]oct-7-ene **3** was obtained from the reaction of **1** with 4 equiv of cyclohexene as orange-red crystals in 65% yield (Scheme 1). The reaction proceeded exclusively in syn-addition mode, and the molecular structure of **3** is shown in Figure 1. Highly crowded **3** adopts a puckered 1,2-disilacyclobutene ring, to which the cyclohexane ring was found to fuse with a chair conformation. The Si−Si bond distance is 2.213(3) Å, which is consistent with those reported for hindered disilenes.[9] The most prominent structural feature of **3** is the geometry around the Si=Si moiety, which has a twisted,

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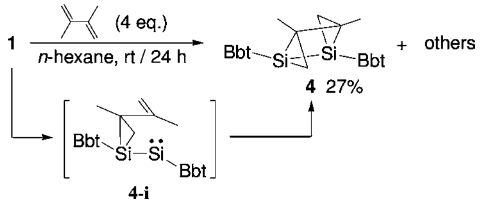
trans-bent structure with a bend angle of 26.4° and a $\mathrm{Bbt-Si{=}Si-Bbt}$ dihedral angle of 103.3(8)°.[10] Previously reported 1,2-bis(silyl)-1,2-disilacyclobutenes were reported to have an almost planar Si_2C_2 ring, and the sums of the bond angles around the skeletal Si atoms are virtually 360°.[2] A characteristically downfield-shifted ^{29}Si NMR signal at 92.3 ppm (C_6D_6) of **3** also confirms its $\mathrm{Si{=}Si}$ character. This result shows that diaryl-substituted disilyne **2** has intrinsic reactivity toward alkene similar to those of the previously reported silyl-substituted disilynes **I** and **II**.[2]

Scheme 2



On the other hand, dimetallyne species are known to show different reactivities with conjugated dienes. For example, the reaction of **II** with 1,3-butadiene gave a 1,2-disilacyclohexa-1,4-diene product, which was suggested to be a [2 + 4] cycloadduct.[2b] In the reaction of Power's diaryldigermyne with 2,3-dimethyl-1,3-butadiene, a *trans*-2,3-dimethyl-2-butene-bridged bis(3,4-dimethylgermacyclopent-3-ene) derivative was obtained.[7a] In contrast, the reaction of $\mathrm{BbtGe{\equiv}GeBbt}$ with 2,3-dimethyl-1,3-butadiene was found to give a bis(3,4-dimethylgermacyclopent-3-ene) derivative without the $\mathrm{Ge-Ge}$ bond cleavage.[7e] These differences in the reactivity of dimetallynes with dienes prompted us to investigate the same reaction with diaryl-substituted disilyne **1**.

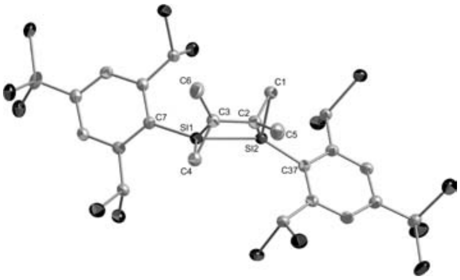


Figure 2. Thermal ellipsoid (50%) drawing of **4**. Hydrogen atoms and methyl groups on the Bbt groups have been omitted for clarity.

When a hexane solution of **1** was treated with an excess of 2,3-dimethyl-1,3-butadiene at room temperature, a light-yellow solution was obtained after 24 h. NMR analysis of the reaction mixture suggested the formation of a somewhat complex product mixture, but the most intense ^{29}Si signal was detected at −88.8 ppm, suggesting the formation of a silicon-containing three-membered-ring skeleton. When the concentrated reaction mixture was cooled, colorless crystals of **4** were obtained in 27% yield (Scheme 2). The main product **4** was finally characterized by X-ray crystallographic analysis, and the unexpected molecular structure of **4** is shown in Figure 2. The *anti*-tricyclo[3.1.0.0^{2,4}]1,2-disilahexane structure of **4** has highly distorted skeletal Si atoms, and the sums of the bond angles around the $\mathrm{Si1-C3}$ and $\mathrm{Si2-C2}$ axes are 359.6 and 359.8°, respectively.[10] In the ^{29}Si NMR spectrum of the reaction mixture, all of the signals except those of the trimethylsilyl groups were observed in the negative region, which means neither a 1,2-disilacyclohexa-1,4-diene nor a 1,2-disilacyclobutene was produced.

Sekiguchi, Nagase, and co-workers[5c] proposed that the reaction of a disilyne with an alkene involves a [1 + 2] cycloaddition between the LUMO (π_{in}^*) of the disilyne and the HOMO of the alkene as the initial step instead of a direct [2 + 2] cycloaddition. The reaction of our diaryl-substituted disilyne **1** with 2,3-dimethyl-1,3-butadiene can also be reasonably explained by the mechanism mentioned above. Thus, the initial [1 + 2] cycloaddition transforms **1** into the silacyclopropylsilylene intermediate **4-i**, and the subsequent intramolecular addition of the silylene center to the remaining $\mathrm{C-C}$ double bond gives the final product **4**. In other words, our results might be good supporting evidence for the mechanism proposed by Sekiguchi, Nagase, and co-workers.

In summary, the reactivity of 1,2-diaryldisilyne **1** was systematically compared with those of silyl-substituted disilynes. In most cases, **1** behaves as well as the silyl-substituted disilynes do, but it showed a unique reactivity toward conjugated dienes.

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Supporting Information Available: Experimental details, characterization data for new compounds, and crystallographic data for **2**, **3**, and **4** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) (a) West, R.; Fink, M. J.; Michl, J. *Science* **1981**, *214*, 1343. (b) Kira, M.; Iwamoto, T. *Adv. Organomet. Chem.* **2006**, *54*, 73. (c) Sasamori, T.; Tokitoh, N. In *Encyclopedia of Inorganic Chemistry*, 2nd ed.; King, R. B., Ed.; John Wiley & Sons: Chichester, U.K., 2005; p 1698. (d) Weidenbruch, M. In *The Chemistry of Organic Silicon Compounds*, Vol. 3; Rappoport, Z., Apeloig, Y., Eds.; John Wiley & Sons: Chichester, U.K., 2001; p 391. (e) West, R. *Polyhedron* **2002**, *21*, 467.
(2) (a) Sekiguchi, A.; Kinjo, R.; Ichinohe, M. *Science* **2004**, *305*, 1755. (b) Wiberg, N.; Vasisht, S. K.; Fischer, G.; Mayer, P. *Z. Anorg. Allg. Chem.* **2004**, *630*, 1823.
(3) (a) Kobayashi, K.; Nagase, S. *Organometallics* **1997**, *16*, 2489. (b) Nagase, S.; Kobaysahi, K.; Takagi, N. *J. Organomet. Chem.* **2000**, *611*, 264.
(4) Sasamori, T.; Hironaka, K.; Sugiyama, Y.; Takagi, N.; Nagase, S.; Hosoi, Y.; Furukawa, Y.; Tokitoh, N. *J. Am. Chem. Soc.* **2008**, *130*, 13856.
(5) (a) Sekiguchi, A.; Ichinohe, M.; Kinjo, R. *Bull. Chem. Soc. Jpn.* **2006**, *79*, 825. (b) Kinjo, R.; Ichinohe, M.; Sekiguchi, A. *J. Am. Chem. Soc.* **2007**, *129*, 26. (c) Kinjo, R.; Ichinohe, M.; Sekiguchi, A.; Takagi, N.; Sumimoto, M.; Nagase, S. *J. Am. Chem. Soc.* **2007**, *129*, 7766. (d) Takeuchi, K.; Ichinohe, M.; Sekiguchi, A. *J. Am. Chem. Soc.* **2008**, *130*, 16848. (e) Takeuchi, K.; Ichinohe, M.; Sekiguchi, A.; Guo, J.-D.; Nagase, S. *Organometallics* **2009**, *28*, 2658.
(6) For recent reviews of dimetallynes, see: (a) Power, P. P. *Appl. Organomet. Chem.* **2005**, *19*, 488. (b) Power, P. P. *Organometallics* **2007**, *26*, 4362.
(7) (a) Stender, M.; Phillips, A. D.; Power, P. P. *Chem. Commun.* **2002**, 1312. (b) Pu, L.; Philips, A. D.; Richards, A. F.; Stender, M.; Simons, R. S.; Olmstead, M. M.; Power, P. P. *J. Am. Chem. Soc.* **2003**, *125*, 11626. (c) Spikes, G. H.; Fettinger, J. C.; Power, P. P. *J. Am. Chem. Soc.* **2005**, *127*, 12232. (d) Cui, C.; Olmstead, M. M.; Fettinger, J. C.; Spikes, G. H.; Power, P. P. *J. Am. Chem. Soc.* **2005**, *127*, 17530. (e) Sugiyama, Y.; Sasamori, T.; Hosoi, Y.; Furukawa, Y.; Takagi, N.; Nagase, S.; Tokitoh, N. *J. Am. Chem. Soc.* **2006**, *128*, 1023. (f) Peng, Y.; Ellis, B. D.; Wang, X.; Fettinger, J. C.; Power, P. P. *Science* **2009**, *325*, 1668.
(8) (a) Tokitoh, N.; Suzuki, H.; Okazaki, R.; Ogawa, K. *J. Am. Chem. Soc.* **1993**, *115*, 10428. (b) Takeda, N.; Tokitoh, N. *Synlett* **2007**, 2483, and references therein.
(9) (a) Suzuki, H.; Tokitoh, N.; Okazaki, R.; Harada, J.; Ogawa, K.; Tomoda, S.; Goto, M. *Organometallics* **1995**, *14*, 1016. (b) Wiberg, N.; Auer, H.; Nöth, H.; Knizek, J.; Polborn, K *Angew. Chem., Int. Ed.* **1998**, *37*, 2869. (c) Boomgaarden, S.; Saak, W.; Marsmann, H.; Weidenbruch, M. *Z. Anorg. Allg. Chem.* **2002**, *628*, 1745.
(10) The exceptional structural features will be discussed in detail elsewhere.

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