DOI: 10.1002/asia.201100833

Evidence for LiBr-Assisted Generation of a Silylene from a 1,2-Diaryl-1,2-dibromodisilene

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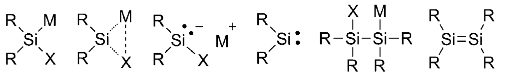
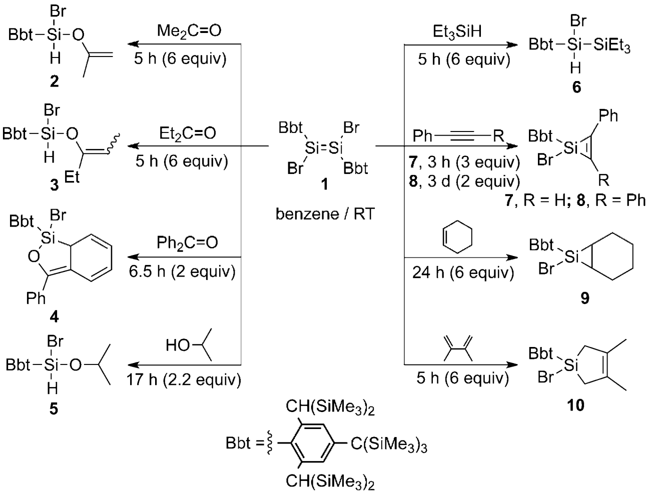
Silylenoids R_2SiMX (structures denoted as **A**–**C**) are the silicon analogues of carbenoids, where X denotes a leaving group (e.g. halogen or alkoxy) and M is a metal atom.[1] Silylenoids have comparable reactivity to silylenes (**D**) and react with both electrophiles and nucleophiles. Tamao and Kawachi showed that Ph_2tBuOSiLi underwent a self-condensation to give a product of structure type **E**.[1b] Nowadays, the synthesis of disilenes (**F**) by reduction of the corresponding halosilane is well established, and silylenoids were postulated as intermediates in this reaction.[2] The first stable silylenoid $(t\mathrm{Bu}_2\mathrm{MeSi})_2\mathrm{SiFLi}\cdot(\mathrm{THF})_3$ was reported recently, and its molecular structure was revealed as **C**.[2d] The synthesis of halosilylenoids and their silylene-like reactivity have been reported extensively.[3]



A **B** **C** **D** **E** **F**

Wiberg et al. reported the synthesis of the first stable bis(silyl)dihalodisilene and showed that the dihalodisilene has typical reactivity of a disilene, giving products with Si−Si bonds derived from Si=Si bonds.[4] Recently, we successfully synthesized a stable 1,2-dibromodisilene Bbt(Br)Si=Si(Br)Bbt (**1**, Bbt = 2,6-bis[bis(trimethylsilyl)methyl]-4-[tris(trimethylsilyl)methyl]phenyl).[5b] Disilene **1** is highly sensitive towards oxygen, both in solution and in the solid state, but stable at room temperature under the exclusion of air and moisture.

During the course of our studies using **1**, we found unexpected reactivity patterns. Disilene **1** reacted with a variety of prototypical trapping reagents for reactive intermediates (Scheme 1) to give the products **2**–**10**, which are identical to the trapping products of the corresponding aryl bromosilylene.[6] All reactions proceeded very cleanly when the respective trapping agent was added to a solution of **1** in benzene and the reaction mixture was left to stand at room temperature until the yellow color of **1** disappeared. Generally, to trap reactive silylenes, a large excess of trapping agent (about 40-fold) was required. In the case of **1**, approximately a sixfold excess was enough to complete the reaction in about 5 h (except for cyclohexene, which took 24 h). The most beneficial advantage of these reactions is the clean and quantitative conversion in all reactions shown in Scheme 1. After the completion of the reactions, excessive reagent can be removed by evaporation. However, in the case of benzophenone or diphenylacetylene, which are difficult to remove, a stoichiometric amount (2 equiv) was used, and the reactions were completed within 6.5 h and three days, respectively.



Scheme 1. Silylene-like reactivity of **1** in benzene at room temp. All reactions yield the respective products quantitatively.

At first, we believed the silylene-like reactivity of **1** to be a result of the thermal dissociation of **1** into two equivalents of the corresponding silylenes.[7] We have previously demonstrated that extremely hindered disilenes, for example, (*E*)- and (*Z*)-Mes(Tbt)Si=Si(Tbt)Mes (**12**, Mes = 2,4,6-trimethylphenyl, Tbt = 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl) un-

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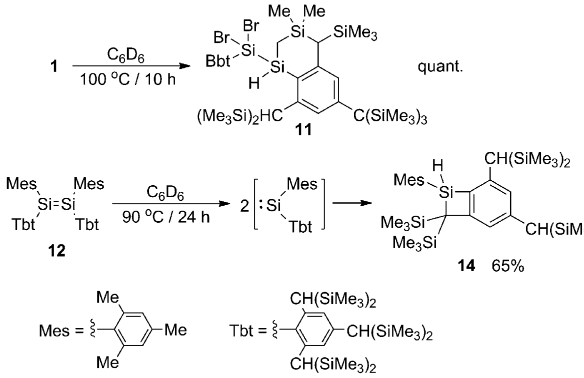
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/asia.201100833.

dergo ready thermal dissociation into the corresponding silylenes.[7b] Variable-temperature UV/Vis and NMR spectroscopy (−20 to 70 °C) suggested the thermal dissociation in the germanium analogue of **1**, Bbt(Br)Ge=Ge(Br)Bbt (**13**).[5a] In sharp contrast, we were not able to detect any changes in the variable-temperature UV/Vis and ^{1}H NMR spectra of **1** (−60 to 40 °C),[5b] suggesting that **1** does not undergo thermal dissociation into the corresponding silylenes. How can the silylene-like reactivity of **1** be otherwise explained? To explore the possibility of a photochemical dissociation process,[8] we conducted comparable control experiments under the exclusion of light and corroborated that the silylene-like reactivity is not the result of a photochemically induced dissociation process.

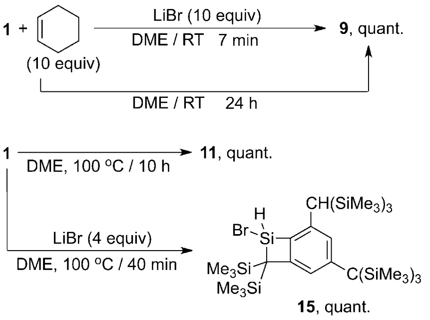
Despite the negative results from a thermal dissociation mechanism, we could not rule out the presence of undetectable amounts of dissociated BbtBrSi: in equilibrium with **1**. However, there is one crucial experimental result, which we are unable to bring into accordance with a thermal dissociation mechanism. The thermally induced decomposition of **1** results in the quantitative formation of cyclized product (**11**), which still contains a Si–Si bond.[5b] If the thermal dissociation of **1** would result in the formation of low-coordinate silylenes, why does the thermal decomposition product **11** still contain a Si–Si bond? In previous studies, we established that bulky disilene **12** can thermally dissociate into silylenes, which undergo intramolecular cyclization by C–H insertion to give **14**, which has no Si–Si bond (Scheme 2).[7a]



Scheme 2. Thermal decomposition products of disilenes **1** and **12**.

The interesting result obtained from the thermolysis of **1** prompted us to search for another mechanistic pathway in addition to thermal dissociation. Firstly, we ensured purity of **1**. Compound **1** was prepared by the reduction of $BbtSiBr_3$ with exactly two equivalents lithium naphthalenide at −78 °C in THF, followed by a general workup procedure: After removal of THF, naphthalene was separated by sublimation at 45 °C/0.01 mmHg. Trace residues of THF were removed by repeated co-evaporation with hexane, and LiBr was removed by filtration from the hexane solutions of **1**. Analytically pure, powdered samples were obtained from concentration of the hexane filtrates. No impurities could be detected spectroscopically, and acceptable values for C, H, and Br analysis were obtained.[5b] It is therefore unlikely that organic impurities are responsible for the silylene-like reactivity of **1**. Secondly, we turned our attention to the possibility of inorganic impurities, especially LiBr. Although LiBr was removed from the hexane solutions of **1** by filtration through celite, residual contamination with a trace amount of LiBr is virtually unavoidable.

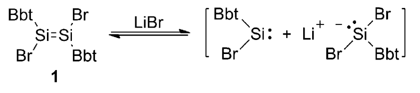
The solubility of LiBr in nonpolar solvents such as benzene is too low for equivalent amounts of LiBr and **1** to be dissolved. However, LiBr is sufficiently soluble in polar solvents such as dimethoxyethane (DME). We therefore tested the reaction between **1** and excess cyclohexene with LiBr in DME. Surprisingly, the characteristic yellow color of **1** disappeared within seven minutes, and the corresponding trapped product **9** was obtained in a quantitative yield. Without the addition of LiBr, the same reaction required 24 h for quantitative conversion (Scheme 3). Also, increased reaction rate by the addition of LiBr was observed in the reaction of **1** with excess triethylsilane in THF.[9]



Scheme 3. Effect of LiBr: Reaction rate is increased, thermolysis product **15** is obtained, which does not contain a Si–Si bond.

Furthermore, we investigated the thermolysis in the presence of LiBr. A control experiment in DME delivered the reaction times and product formation (**11**) identical to those for the reaction in benzene. However, by the addition of LiBr (4 equiv), the thermolysis reached completion after 40 min and resulted in the formation of **15** (Scheme 3).

We conclude that the silylene-like reactivity of **1** is probably the result of a trace amount of LiBr, and the most likely intermediates are the corresponding silylenoid and silylene (Scheme 4). Comparable reactions with purified **1** (obtained by passing hexane solutions of **1** through a short-path neutral silica-gel column in a glove-box) with phenylacetylene required more than twice the reaction time but resulted in the same product **7**. This result is understandable, since a complete removal of LiBr from **1** is extremely difficult. Sev-



Scheme 4. Possible equilibrium of **1** in the presence of LiBr.

eral attempts to detect intermediate species spectroscopically were unsuccessful.[10]

Our results presented herein provide evidence for the LiBr-assisted generation of a silylene from a 1,2-diaryl-1,2-dibromodisilene. Compared to disilenes, silylenes are highly reactive, and their synthesis and handling is extremely difficult due to their limited stability. This work provides the proof of concept for an alternative and complementary method for the in situ generation of silylenes from disilenes. It is noteworthy that the reaction products from this study still contain a Si−Br bond, which can be exploited in subsequent reactions. Mechanistic studies, scope, and optimization studies of this new reaction are currently in progress.

Experimental Section

General method for the synthesis of **2--10**. An NMR tube was charged with **1** (20 mg, 14 μmol), trapping agent (2–6 equiv), and C_6D_6 (0.5 mL) in an MBraun glove-box. The mixture was left to stand at room temperature until the characteristic yellow color of **1** disappeared. The resulting solution contained the reaction product in quantitative yield, as evident from ^{1}H NMR spectroscopy. Individual reaction times depended on the amount and the nature of the trapping agent and ranged from three hours to three days. An excess amount of trapping agent shortened the reaction time; however, no side product was observed, even when a stoichiometric amount of trapping agent was used. If an excess amount of trapping agent was used, removal of solvent and unreacted trapping agent gave an analytically pure product.[10]

Acknowledgements

This work was supported by a Grant-in Aid for Scientific Research (B) (No. 22350017), Young Scientist (A) (No. 23685010), and the Global COE Program B09 ("Integrated Materials Science", Kyoto University) from the Ministry of Education, Culture, Sports, Science and Technology (MEXT), Japan. J.S.H. thanks KIST for financial support (Future Key Technology Program).

Keywords: disilenes · reactive intermediates · silanes · silylenes · silylenoids

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[9] Reactions in THF gave similar results, but small amounts of by-products were observed due to the instability of the Si−Br bond in THF.

[10] For the detailed results see the Supporting Information.

Received: October 6, 2011