Synthesis of a 1-Hydrosilene Stable in Solution and Its Unique Properties[#]

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Summary: An overcrowded 1-hydrosilene bearing a 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl (denoted as Tbt) group and a xanthenyl moiety was synthesized as a compound stable in solution by dehydrofluorination reaction of the corresponding fluorosilane. The newly generated 1-hydrosilene was characterized by NMR spectroscopy to reveal its $^1J_{SiH}$ coupling constant between the sp^2-silicon atom and the attached hydrogen atom in the 1-hydrosilene skeleton. The 1-hydrosilene was found to undergo an unexpected [6+6]-dimerization during its recrystallization. In addition, the thermolysis of the isolated [6+6]-dimer in C_6D_6 at 70 °C afforded the 1-hydrosilene via retro [6+6]-cycloaddition.

Silenes, Si═C double-bond compounds, are generally difficult to isolate due to the instability caused by the small overlap between the 3p orbital of a silicon atom and the 2p orbital of a carbon atom and the extremely high reactivity toward oligomerization prompted by their polar, zwitterionic character ($Si^{\delta+}{=}C^{\delta-}$).[1] However, a number of stable silenes, the reactive Si═C moieties of which are sterically protected by bulky substituents, have been synthesized and isolated[1] since the first isolation of the stable silene $(Me_3Si)_2Si{=}C(OSiMe_3)(1\text{-Ad})$ (1-Ad = 1-adamantyl), reported by Brook and co-workers in 1981.[2]

In contrast to the chemistry of such kinetically well-stabilized silenes having two bulky substituents on the doubly bonded silicon atom, 1-hydrosilenes, i.e., silenes bearing a hydrogen atom on the sp^2-silicon atom, have been less explored so far, though they are of great interest from the viewpoints of fundamental chemistry as “a simple silene” and functionalization of the Si−H bond leading to the transformation into new silenes. Since 1-hydrosilenes should be highly reactive due to less hindrance around the sp^2-silicon atom, no stable example has been reported for 1-hydrosilenes[3] except for the generation of a 1-hydrosilene postulated on the basis of the observation of IR spectra in an Ar matrix at low temperature and the products of trapping reactions.[4]

During the course of our research on the kinetic stabilization of highly reactive species, we have developed an efficient steric protection group (Tbt) and successfully applied this group to the kinetic stabilization of a variety of novel low-coordinated compounds of heavier main group elements including doubly bonded silicon compounds.[5] As the first attempt, Tbt- and dihydroanthryl-substituted chlorosilane **3** was treated with LDA as a base in the hope of obtaining the corresponding 1-hydrosilene as a stable compound. Unexpectedly, however, this reaction resulted in the formation of not the desired 1-hydrosilene but 7-silanorbornadiene **4** in an almost quantitative yield.[6] In this paper, we present our further synthetic challenge toward 1-hydrosilene **1** as a target molecule, where the central Si═C moiety should have benefit of both kinetic stabilization by the Tbt group and thermodynamic stabilization by the π-conjugation over the xanthenyl moiety. We report here the synthesis and characterization of 1-hydrosilene **1** together with its unique reactivity.

Fluorosilane **2**, the precursor of 1-hydrosilene **1**, was synthesized as a stable crystalline compound in 80% yield by the fluorination reaction of the corresponding chlorosilane, which was prepared by the reaction of $TbtSiHCl_2$ with xanthenyllithium,[7] using an excess amount of $AgBF_4$. Then, fluorosilane **2** was treated with *t*-BuLi in Et_2O at −40 °C to afford 1-hydrosilene **1** as a main product, as judged by ^1H NMR spectroscopy. Although further purification of **1** was found to be difficult due to the small amount of inseparable and unidentified byproduct, 1-hydrosilene **1** was stable in C_6D_6 solution enough to be characterized by spectroscopic analysis under ambient conditions.[8] In addition, the generation of **1** was confirmed by the trapping reactions with methanol, diphenyl-

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[#] Dedicated to Prof. Renji Okazaki on the occasion of his 70th birthday.

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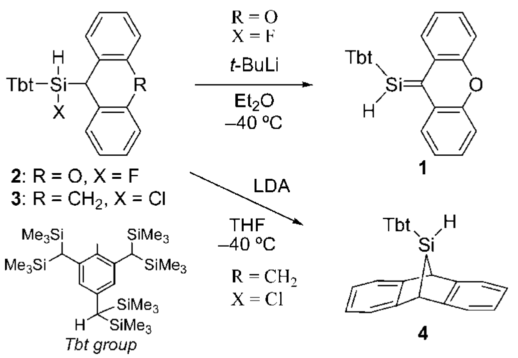
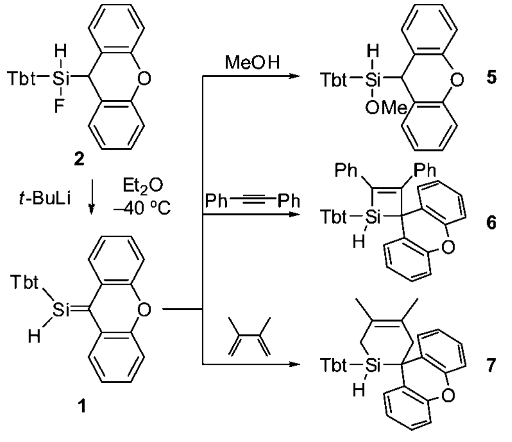
(8) All the new compounds here obtained showed satisfactory spectral data. Experimental procedures and compound data are described in the Supporting Information.

10.1021/om8001334 CCC: $40.75

Scheme 1



Scheme 2



acetylene, and 2,3-dimethyl-1,3-butadiene, leading to the formation of the corresponding adducts **5** (50%), **6** (66%), and **7** (39%), respectively (Scheme 2).[8]

The ^{29}Si NMR spectrum of **1** (C_6D_6) showed a characteristic signal at 50.2 ppm, which is similar to those of the previously reported, kinetically stabilized silenes[1] and in lower field than those of sp^3-silanes bearing an Si−H bond (e.g., $\delta_{Si} = -17.6$ for Ph_3SiH),[9,10] indicating the sp^2-hybridization of the central silicon atom. In the ^{1}H NMR spectrum (C_6D_6), the proton on the sp^2-silicon atom in **1** resonated at 6.06 ppm, the chemical shift of which is lower than those for the protons on sp^3-hybridized silicon atoms (e.g., $\delta_H = 5.71$ for Ph_3SiH)[9,10] probably due to the anisotropic effect caused by the Si=C π-electrons. The $^1J_{HSi}$ value of the (H)Si=C moiety of **1** was observed as 246 Hz, which is larger than those between sp^3-hybridized silicon and hydrogen atoms ($^1J_{HSi} = 198$ Hz for Ph_3SiH;[9] the $^1J_{HSi}$ coupling constants between sp^3-Si and H atoms are ca. 200 Hz).[10] The large $^1J_{HSi}$ value observed here reflects the high s-character of the Si−H bond of **1**, since $^1J_{HSi}$ values should correlate with the s-character of the silicon atom in the Si−H bond.[11] To the best of our knowledge, there have been only two reports on the $^1J_{HSi}$ coupling constant between the proton and the sp^2-silicon atom other than those in the hydrosilylene−transition-metal complexes ($^1J_{SiH}$ = ca. 130−180 Hz).[3] The $^1J_{HSi}$ values for hydrodisilenes, $R^*_2HSi{-}(H)Si{=}Si(H){-}SiHR^*_2$ ($R^* = Si(t\text{-}Bu)_3$)[12] and $R'(H)Si{=}Si(Li)R'$ ($R' = Si(i\text{-}Pr)[CH(SiMe_3)_2]_2$),[13] were observed as 149.8 and 155 Hz, respectively, which are smaller than that of **1**. The NBO calculations also suggested the higher s-character of the Si−H bond of **1** ($\sigma_{SiH} = 0.6436(sp^{2.38})Si + 0.7654(s)H$) than that of Ph_3SiH ($\sigma_{SiH} = 0.6402(sp^{3.17}) + 0.7682(s)H$).[14] The calculated chemical shifts and coupling constants for the optimized structures (B3LYP/6-31G(d) level) of **1** ($\delta_{Si} = 53.1$, $\delta_H = 6.15$, $^1J_{HSi} = -270$ Hz) and Ph_3SiH ($\delta_{Si} = -14.3$, $\delta_H = 5.94$, $^1J_{HSi} = -203$ Hz) are in good agreement with the observed values.[14] These results support that theoretical calculations should reflect an intrinsic nature of 1-hydrosilene **1**, where the feature of the sp^2-hybridized silicon atom appears in the bonding character of not only the Si=C bond but also the Si−H bond. On the other hand, the ^{13}C NMR chemical shift of the Si=C moiety in **1** was computed as 138.3 ppm,[14] which is similar to those of aromatic ^{13}C atoms, although the ^{13}C NMR chemical shift of the Si=C moiety in **1** has not been assigned due to the complication of spectra. In addition, the Si−H bond of **1** was characterized by IR spectroscopy in the solid state. The characteristic Si−H vibrational frequency was observed at $\nu_{SiH} = 2280$ cm^{-1}, which is in good agreement with the calculated value for **1** (2295.7 cm^{-1} at the B3LYP/6-31G(d) level). The observed ν_{SiH} value for **1** is apparently larger than those for some sp^3-hybridized silanes bearing an Si−H bond[15] (e.g., $\nu_{SiH} = 2122$ cm^{-1} (observed under the same conditions) and 2125 cm^{-1} (reported in the literature[15a]) for Ph_3SiH), also indicating the higher s-character of the hybrid orbital of the silicon atom in the Si−H bond in **1** than that of sp^3-hybridized silanes.

The crude mixture containing 1-hydrosilene **1** was subjected to slow recrystallization in a glovebox filled with argon in the expectation of obtaining single crystals for structural analysis. However, unexpected dimer **8** was obtained as orange crystals (59% from **2**) by standing of the hexane/benzene solution of the crude mixture for ca. 1 week in the dark. The structure of **8** was supported by the spectroscopic (^{1}H and ^{29}Si NMR, FAB mass, and IR spectra) and X-ray crystallographic analyses (Figure 1).[16] Dimer **8** was most likely formed by the thermal [6+6]-pericyclic self-dimerization.[17] Less hindered silenes are known to undergo [2+2]-self-dimerization, leading to the

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(9) The NMR spectral data for Ph_3SiH shown here were collected in C_6D_6 solution, and they are in good agreement with the reported data in ref 10.

(10) For examples, see: (a) Olah, G. A.; Field, L. D. *Organometallics* **1982**, *1*, 1485−1487. (b) Olah, G. A.; Hunadi, R. J. *J. Am. Chem. Soc.* **1980**, *102*, 6989–6992. (c) Sollradl, H.; Hengge, E. *J. Organomet. Chem.* **1983**, *243*, 257–269. (d) Cox, R. H.; Austin, W. K. *J. Organomet. Chem.* **1971**, *26*, 331–334. (e) Jensen, M. A. *J. Organomet. Chem.* **1968**, *11*, 423–427.

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(12) Wiberg, N.; Niedermayer, W.; Nöth, H.; Warchhold, M. *Z. Anorg. Allg. Chem.* **2001**, *627*, 1717–1722.

(13) Kinjo, R.; Ichinohe, M.; Sekiguchi, A. *J. Am. Chem. Soc.* **2007**, *129*, 26–27.

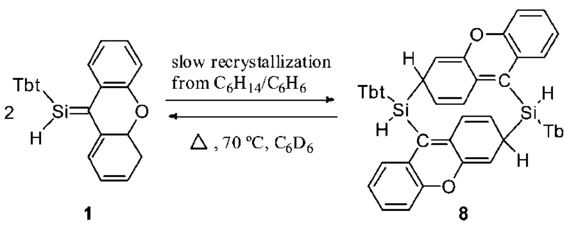
(14) The structural optimizations were performed by using the Gaussian 03 program at the B3LYP/6-31G(d) level. The calculations for the NMR chemical shifts and coupling constants were performed by using the ADF 2006 program package with TZ2Pae basis sets. The NBO calculations were performed with the NBO 5.0 program. See Supporting Information.

(15) (a) Kessler, G.; Kriegsma, H. Z. *Anorg. Allg. Chem.* **1966**, *342*, 53–62. (b) Reich, P.; Kriegsma, H. Z. *Anorg. Allg. Chem.* **1965**, *334*, 283–291.

(16) The spectral data showed that only one isomer of the [6+6]-dimer of **1** was obtained. Crystal data for **8** ($C_{80}H_{136}O_2Si_{14}$): $M = 1523.15$, $T = 103(2)$ K, triclinic, $P2/c$ (no. 13), $a = 21.0678(13)$ Å, $b = 9.8086(13)$ Å, $c = 23.437(3)$ Å, $\beta = 107.596(3)°$, $V = 4616.5(8)$ Å^3, $Z = 2$, $D_{calc} = 1.096$ g cm^{-3}, $\mu = 0.234$ mm^{-1}, $\lambda = 0.710\,69$ Å, $2\theta_{max} = 51.0$, 39 264 measured reflections, 8587 independent reflections, 437 refined parameters, GOF = 1.013, $R_1 = 0.0754$ and $wR_2 = 0.1405$ [$I > 2\sigma(I)$], $R_1 = 0.1654$ and $wR_2 = 0.1768$ [for all data], largest diff peak and hole 0.631 and−0.345 e Å^{-3}.

(17) (a) To our knowledge, no thermal [6+6]-dimerization has been reported so far, though a few reports on the photochemical [6+6]-dimerization of organic π-electron-conjugated systems have been reported. (a)Hao, N.; Sawyer, J. F.; Sayer, B. G.; Mcglinchey, M. J. *J. Am. Chem. Soc.* **1979**, *101*, 2203−2204. (b) Mukai, T.; Tezuka, T.; Akasaki, Y. *J. Am. Chem. Soc.* **1966**, *88*, 5025–5023. (c) Keil, J. M.; Massa, W.; Riedel, R.; Seitz, G.; Wocadlo, S. *Tetrahedron Lett.* **1994**, *35*, 7923–7926.

Scheme 3



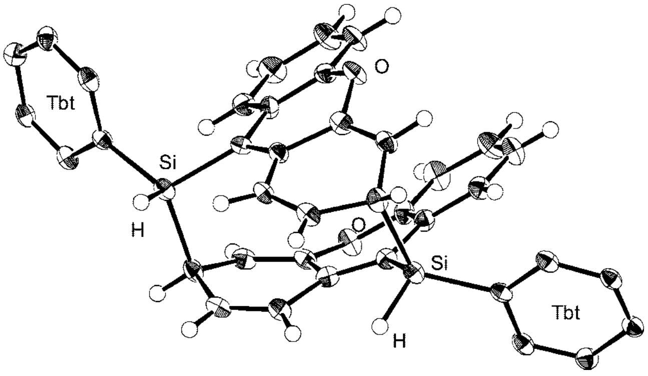


Figure 1. Molecular structure of **8**. Displacement ellipsoids are drawn at the 50% probability level. The substituents on the Tbt groups were omitted for clarity.

formation of the corresponding disilacyclobutane derivatives[1] due to the weak Si═C π-bond and the spatial extent of the 3p orbital of the silicon atom, whereas Woodward−Hoffmann rules argue that the thermal $[n+n]$-dimerization ($n = 2, 4, 6, \ldots$) should be forbidden in carbon chemistry.[18,19] Although 1-hydrosilene **1** may be prevented from its [2+2]-dimerization by the steric hindrance around the silicon atom afforded by the Tbt group, the extended π-electron conjugation between the Si═C and xanthenyl moieties should make it possible for **1** to undergo such unique thermal [6+6]-self-dimerization (Figure 2). On the other hand, the results of theoretical calculations suggested that **8** should be less stable than **1** by ca. 6.7 kcal/mol probably due to the loss of aromatic stabilization energy of the xanthenyl moiety, while the [2+2]-dimer of **1** (*trans*-configuration)[20] should be much less stable than **1** by 12.1 kcal/mol. Consequently, the [6+6]-dimerization of **1** is most likely promoted by the extremely low solubility of **8**, which forces **8** out from the equilibrium between **1** and **8** and shifts the equilibrium to the formation of **8**.

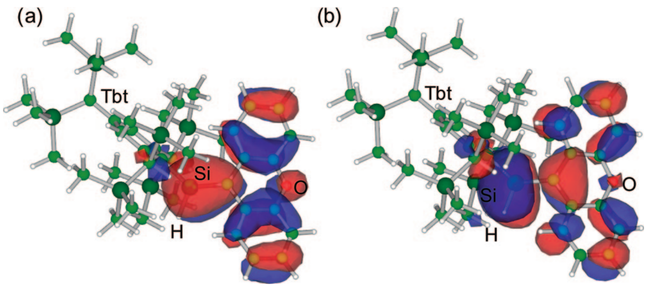


Figure 2. Depiction of (a) Kohn−Sham (KS)−HOMO and (b) KS−LUMO of **1** calculated at the B3LYP/6-31G(d) level.

Heating of the C_6D_6 suspension of isolated **8** at 70 °C for 2 h afforded hydrosilene **1** in an almost quantitative yield, as judged by the ^1H and ^{29}Si NMR spectra, probably via the retro [6+6]-pericyclic reaction. In addition, thermal reaction of **8** in the presence of trapping reagents such as methanol, diphenylacetylene, and 2,3-dimethyl-1,3-butadiene, which should not react with **8** directly, at 70 °C for 2−3 h afforded the corresponding adducts **5** (75%), **6** (40%), and **7** (62%), respectively, indicating the efficient generation of **1** on heating of the C_6D_6 suspension of **8**. At present by using this synthetic method, 1-hydrosilene **1** is difficult to isolate as a crystalline compound due to the slow dimerization of **1** during the processes of cooling and evaporation. However, it was found that 1-hydrosilene **1** can be obtained by the thermal reaction of **8** as an almost pure compound stable in C_6D_6 solution.

In conclusion, stable 1-hydrosilene **1** was successfully generated by the dehydrofluorination reaction of fluorosilane **2**, and it was reasonably characterized by ^1H and ^{29}Si NMR spectra. It should be noted that the $^1J_{HSi}$ value of **1** is larger than those between sp^3-hybridized Si and H atoms due to its high s-character of the Si−H bond. In addition, 1-hydrosilene **1** thus obtained was found to have marginal stability in solution and undergo unexpected [6+6]-dimerization on concentration to give **8**, which could be converted into monomer **1** by the thermolysis of its C_6D_6 suspension. Further investigations on the properties of 1-hydrosilene **1** and related compounds are currently in progress.

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Supporting Information Available: X-ray crystallographic data of **5**, **7**, and **8** in CIF format and experimental procedures, spectral data, ^1H NMR spectra for **1** and **8**, and optimized coordinates for **1** and **8** in PDF format. These materials are available free of charge via the Internet at http://pubs.acs.org.

OM8001334

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[18] (a) Woodward, R. B.; Hoffmann, R. *J. Am. Chem. Soc.* **1965**, *87*, 395–397. (b) Hoffmann, R. *Angew. Chem., Int. Ed.* **2004**, *43*, 6586–6590, and references therein.

[19] It is difficult to draw a conclusion whether the [6+6]-dimerization of **1** proceeded via the concerted or stepwise mechanism. It should be noted that such unusual [6+6]-dimerization of the π-conjugated system containing the Si═C unit was observed.

[20] Real molecule models were used for the theoretical calculations. The values shown here are estimated on the basis of the SCF energies calculated at the B3LYP/6-31G(d) level.