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A Stable Halosilylene at Room Temperature in THF Solution

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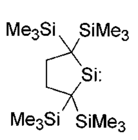
Silylenes, corresponding to carbenes in organic chemistry, are important intermediates in photochemical, thermal, and metal-reduction reactions of organosilicon compounds.[1] Among various substituted silylenes, there are several reports of halosilylenes. In most cases, halosilylenes have been generated in the gaseous state by thermolysis reactions and identified by trapping reactions[2] or observed as short-lived species by spectroscopic methods.[3] A few reports have described the existence of halosilylenes as intermediates in a condensed phase.[4] Since the first report of the stable divalent silicon species, $\mathrm{Cp^*_2Si}$: ($\mathrm{Cp^*} = \mathrm{Me_5C_5}$, silico*cene*), by Jutzi and co-workers,[5] a remarkable class of stable silylenes such as dialkyl silylene[6] **1** and cyclic silylenes **2**, **3**, and **4** has been reported recently,[7−9] but no stable halosilylene has been reported. A stable halosilylene should lead to novel silicon chemistry because of its high synthetic potential and might also be a promising precursor for disilynes and silynes.



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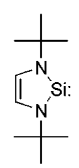

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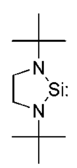

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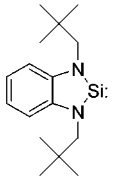

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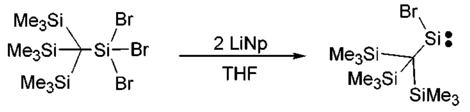
We wish to report the first stable halosilylene, bromo[tris(trimethylsilyl)methyl]silylene (**6**), in THF solution at room temperature (Scheme 1).

Scheme 1



The precursor, tribromo[tris(trimethylsilyl)methyl]silane (**5**), containing the bulky tris(trimethylsilyl)methyl group to stabilize halosilylene, **6**, kinetically[10,11] was prepared in high yield.[12] Compound **5** was reduced with 2 equiv. of LiNp(lithium naphthalenide) at −78 °C in THF. The reaction was monitored by gas chromatography. After the mixture was stirred for 24 h all the starting material was consumed, indicating the reaction was completed. To the dark orange solution an excess of MeOH cooled to −78 °C was added, whereupon the solution rapidly became light yellow. From the reaction mixture we obtained dimethoxy[tris(trimethylsilyl)methyl]silane (**7**) (93%, GC yield) and tris(trimethylsilyl)methane (5%). After the reduction of **5** was completed as described above, the reaction mixture was slowly warmed to 25 °C and kept at that temperature for 2 h. The dark orange color of the solution was preserved during this time. Alcoholysis of the dark orange colored solution with an excess of MeOH at 25 °C gave compound **7** (87%, GC yield). This result shows that bromosilylene **6** generated from the reduction of **5** was trapped by MeOH and then methanolysis of bromine took place to give **7**[13] (Scheme 2). To prevent the alcoholysis of the halosilylene-trapping compound, 2-propanol was used as a trapping agent. Using a procedure similar to that described, we obtained the corresponding halosilylene-trapping adduct, bromo(isopropoxy)[tris(trimethylsilyl)methyl]silane (**8**) in 95% yield (GC yield) at −78 °C and in 93% yield (GC yield) at room temperature. In the presence of an excess of 2,3-dimethyl-1,3-butadiene, we also obtained the bromosilylene-trapping product, **9**, in 97% yield (GC yield) at −78 °C and in 96% yield (GC yield) at room temperature. These results strongly indicate that the generated halosilylene **6** is stable in the condensed phase at room temperature (Scheme 3).

The ^{29}Si NMR of the reduction mixture containing **6** showed a gradual appearance of resonance due to **6** at 106 ppm from

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(1) For a review on silylenes, see: Gaspar, P. P.; West, R. In *the Chemistry of Organic Silicon Compounds*; Rappoport, Z., Apeloig, Y., Eds.; John Wiley & Sons: Chichester, U.K., 1998; Vol. 2, pp 2463−2567.

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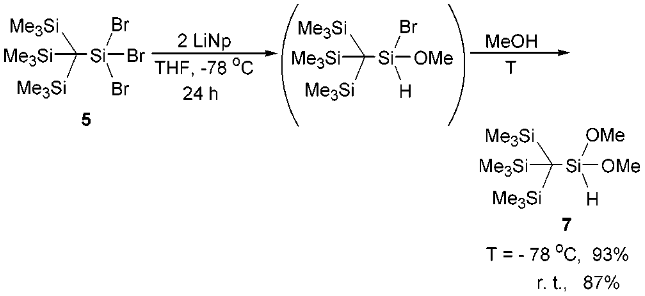
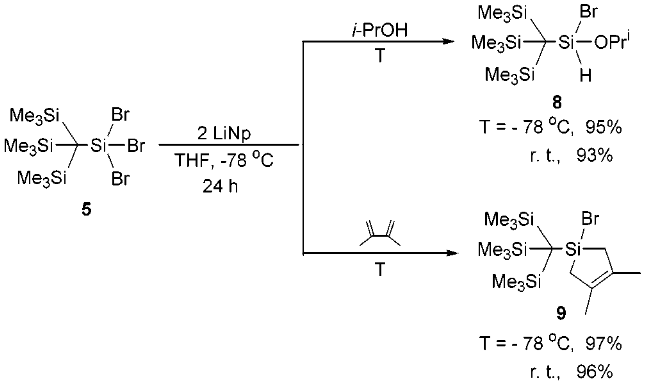
Scheme 2

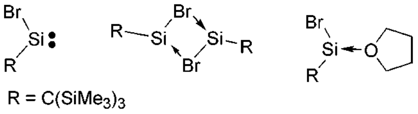


Scheme 3



−50 to −5 °C.[14] The ^{29}Si resonance for **6** is similar to those of diaminosilylenes **2**, **3**, and **4** (78, 97, and 117 ppm, respectively)[7−9] stabilized by the orbital interaction between nitrogen and silicon atoms, but very different from that of the stable dialkylsilylene,[6] **1** (567 ppm). Quite interestingly its intensity decreased as the temperature was increased. Although only 50 scans gave a distinct resonance for the divalent silicon atom at −50 °C, ca. 500 scans were required to get a distinct resonance at −5 °C. When the solution in the NMR tube was cooled from −5 to −50 °C, 50 scans again gave a distinct resonance. After the NMR experiments, the injection of an excess of 2-propanol to the mixture gave the bromosilylene-trapping adduct **8** as expected. However, in attempts to record under the condition of 4100 scans at 20 °C (about 11 h), no resonance near 100 ppm was observed and trapping-adduct **8** was not observed either in the trapping experiment with 2-propanol.

We attempted to observe the absorption band due to halosilylene **6** using UV−vis spectrometry at −78 °C, but we were unable to identify this band because of the very intense absorption arising from LiNp and naphthalene.[15]



At this moment, we are unable to state whether the generated halosilylene is free silylene, Br-bridged silylene, or THF-solvated silylene.[16] Efforts are currently underway to elucidate the structure of halosilylene.

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Supporting Information Available: Details of synthesis and spectral data for compounds **6**−**9** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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[14] Using a 5 mm inner diameter NMR tube containing about 0.16 M (4.0 mmol/25 mL of THF) halosilylene **6**, which was dipped into the solution of $CDCl_3$ and tetramethylsilane in a 10 mm outer diameter NMR tube, ^{29}Si NMR experiments were carried out (referenced to the silicon atom of tetramethylsilane being reported as δ ppm).

[15] (a) Even though a new band was found at $\lambda_{max} = 320$ nm, it is too weak and overlapped with that of LiNp to assign to **6** despite a number of experiments. (b) Apeloig, Y.; Karni, M. *J. Chem. Soc., Chem. Commun.* **1985**, 1048.

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