

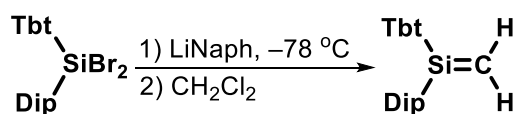
Synthesis of a Kinetically Stabilized 2,2-Dihydrosilene

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Since the successful isolation of stable silene (Me₃Si)₂Si=C(OSiMe₃)(1-Ad) (1-Ad = 1-adamantyl) in 1981 by Brook and co-workers¹, several main group-chemists were prompted to synthesize and isolate a variety of silenes by taking advantage of kinetic stabilization by using appropriate bulky substituents as steric protection groups. These Si=C doubly bonded compounds are largely difficult to isolate due to their poor 3p(Si)-2p(C) orbital overlap and their tendency to undergo facile oligomerization. Therefore, it is only imperative to discover suitable methodologies to properly synthesize, isolate, and characterize these elusive molecules.

In this work, a sterically demanding 2,2-dihydrosilene bearing 2,4,6-tris[bis-(trimethylsilyl)methyl]phenyl (Tbt) and 2,6-diisopropylphenyl (Dip) groups was synthesized by exhaustive reduction of the corresponding dibromosilane, Tbt(Dip)SiBr₂, with lithium naphthalenide at -78 °C followed by addition of CH₂Cl₂.^{2,3} ¹H-NMR signals of the dihydrosilene observed at 4.55 (dd, 1H, ²J_{H-H} = 9.8 Hz) and 4.77 (dd, 1H, ²J_{H-H} = 9.8 Hz) were assigned to the two geminal protons attached to the methylene carbon. This was established with the aid of HSQC in which a carbon atom (CH₂; 95.3 ppm) is directly bonded to two non-chemically equivalent protons. Moreover, a sharp resonance at 90.5 ppm in ²⁹Si-NMR was observed as the three-coordinate silicon atom of a silene⁴. Although establishing the purity remains a challenge due to inseparable by-product, we succeeded in the identification of the dihydrosilene by X-ray crystallographic analysis. In terms of its stability, the observed silene was found to be stable in solution at room temperature for a long period of time. The experimental data obtained in this study were further complemented with extensive DFT calculations.



1) A. G. Brook, *et al.*, *J. Chem. Soc., Chem. Commun.* **1981**, 191. 2) N. Tokitoh, K. Hatano, T. Sadahiro, R. Okazaki, *Chem. Lett.* **1999**, 28, 931. 3) M. Igarashi, M. Ichinohe, A. Sekiguchi, *the Abstract Book of the 18th Symposium on Physical Organic Chemistry*, **2006**, 18, 65. 4) G. Delpon-Lacaze, C. de Battisti, C. Couret, *J. Organomet. Chem.* **1996**, 514, 59.