

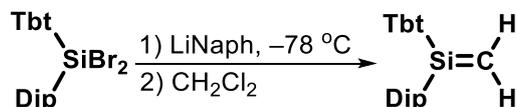
## Synthesis of a Kinetically Stabilized 2,2-Dihydrosilene

(Institute for Chemical Research, Kyoto University) ○Julius Adrie Garcia, Yuji Yasui, Mariko Yukimoto, Yoshiyuki Mizuhata, Norihiro Tokitoh

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Since the successful isolation of stable silene (Me<sub>3</sub>Si)<sub>2</sub>Si=C(OSiMe<sub>3</sub>)(1-Ad) (1-Ad = 1-adamantyl) in 1981 by Brook and co-workers<sup>1</sup>, 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)SiBr<sub>2</sub>, with lithium naphthalenide at -78 °C followed by addition of CH<sub>2</sub>Cl<sub>2</sub>.<sup>2,3</sup> <sup>1</sup>H-NMR signals of the dihydrosilene observed at 4.55 (dd, 1H, <sup>2</sup>J<sub>H-H</sub> = 9.8 Hz) and 4.77 (dd, 1H, <sup>2</sup>J<sub>H-H</sub> = 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 (CH<sub>2</sub>; 95.3 ppm) is directly bonded to two non-chemically equivalent protons. Moreover, a sharp resonance at 90.5 ppm in <sup>29</sup>Si-NMR was observed as the three-coordinate silicon atom of a silene<sup>4</sup>. 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.



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