

Note

# Facile hydroboration of (*Z*)-1-trimethylsilyl-1-alkenes with dichloroborane–dioxane complex: An easy access to *gem*-dimetalloalkanes containing boron and silicon

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## Abstract

(*Z*)-1-Trimethylsilyl-1-alkenes easily prepared by the hydroboration of the corresponding 1-trimethylsilyl-1-alkynes followed by protonolysis with acetic acid, readily react with dichloroborane–dioxane complex in dichloromethane for 6 h. The resulting solution is then treated with 1,3-propane diol in dichloromethane at 0 °C for half an hour to provide the corresponding *gem*-dimetalloalkanes containing boron and silicon. These  $\alpha$ -trimethylsilylalkylboronate esters are purified by vacuum distillation in high yields (72–84%) and the structures of these novel intermediates are further confirmed by selective oxidation with alkaline hydrogen peroxide to provide the corresponding alcohols containing  $\alpha$ -trimethylsilyl group in 78–88% isolated yields.

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## 1. Introduction

Hydroboration of 1-trimethylsilyl-1-alkynes with dicyclohexylborane [1] is well documented in literature. The protonolysis of the resulting boron intermediates with acetic acid [2] provided the corresponding (*Z*)-1-trimethylsilyl-1-alkenes in high stereochemical purities. The preparation of different *gem*-dimetallics containing aluminum and zirconium [3], zinc and zirconium [4], zinc and magnesium [5], zinc and lithium [5], zinc and boron [6], copper and boron [6], boron and lithium [7], boron and zirconium [8], boron and silicon [9,10], and boron and boron [11] and their synthetic importance are well documented in literature [3–11]. We wanted to utilize the recently discovered dichloroborane–dioxane complex [12] as an hydroborating agent to achieve a highly regioselective synthesis of *gem*-dimetalloalkanes containing boron and silicon. Conse-

quently, we undertook a methodology involving (*Z*)-1-trimethylsilyl-1-alkenes via the hydroboration–alcoholysis sequence to achieve the synthesis of *gem*-dimetalloalkanes containing boron and silicon. In this report, we reveal the results of our investigation.

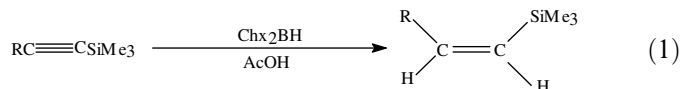
## 2. Results and discussion

We reacted terminal alkynes with *n*-butyllithium at –78 °C for 1 h followed by treatment with chlorotrimethylsilane at –78 °C for 1 h and allowed the reaction mixture to stir overnight. The resulting 1-trimethylsilyl-1-alkynes were isolated and kept in refrigerator under nitrogen atmosphere for further use. They were characterized by 300 MHz NMR spectral data.

The hydroboration of 1-trimethylsilyl-1-alkynes with dicyclohexylborane [13] (freshly prepared by mixing cyclohexene with borane–methyl sulfide complex) in tetrahydrofuran proceeded cleanly at 0 °C, for 3 h followed by stirring for 1 h at room temperature. The resulting clear solution

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was treated with acetic acid and the stirring continued for 6 h at room temperature. The solvents were removed and replaced by *n*-pentane. Monoethanolamine [14] was added to remove the boron by-product. Representative (*Z*)-1-trimethylsilyl-1-alkenes (Table 1) were prepared (Eq. (1)) and characterized by 300 MHz NMR data



The (*Z*)-1-trimethylsilyl-1-alkenes thus prepared were subjected to hydroboration with dichloroborane–dioxane complex in dichloromethane at room temperature for 6 h. The resulting solution was reacted with 1,3-propane diol in dichloromethane at 0 °C for half an hour. The solvents were pumped off and the resulting liquids were purified by high vacuum distillation. The representative selection of *gem*-dimetalloalkanes was prepared (Table 2, Eq. (2)) using the above procedure

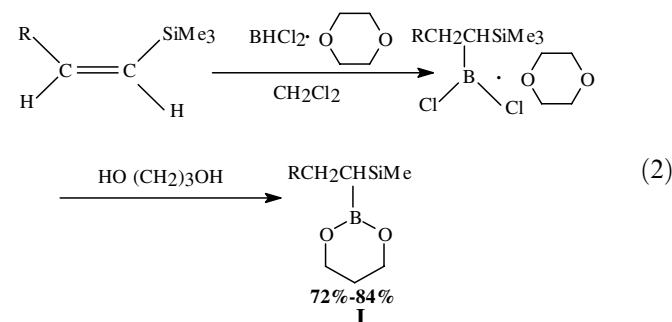


Table 1  
Synthesis of 1-trimethylsilyl-1-alkenes

No.	Eq. (1) R=	Yield <sup>a</sup> (%)
1	<i>n</i> -C <sub>4</sub> H <sub>9</sub>	82
2	<i>n</i> -C <sub>5</sub> H <sub>11</sub>	78
3	<i>n</i> -C <sub>6</sub> H <sub>13</sub>	86
4	-(CH <sub>2</sub> ) <sub>3</sub> Cl	78
6	-CH <sub>2</sub> CH <sub>2</sub> CH(CH <sub>3</sub> ) <sub>2</sub>	79
7	-CH <sub>2</sub> CH <sub>2</sub> Ph	80

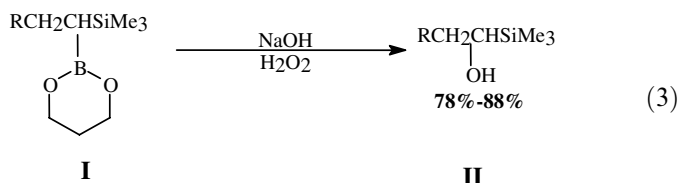
<sup>a</sup> All of the reactions were carried out on a 50 mmol scale. The compounds were purified by chromatography over alumina followed by vacuum distillation.

Table 2  
The synthesis of *gem*-dimetalloalkanes containing boron and silicon

No.	Eq. (2) R=	Yield <sup>a</sup> (%)
1	<i>n</i> -C <sub>4</sub> H <sub>9</sub>	84
2	<i>n</i> -C <sub>5</sub> H <sub>11</sub>	82
3	<i>n</i> -C <sub>6</sub> H <sub>13</sub>	80
4	-(CH <sub>2</sub> ) <sub>3</sub> Cl	74
6	-CH <sub>2</sub> CH <sub>2</sub> CH(CH <sub>3</sub> ) <sub>2</sub>	80
7	-CH <sub>2</sub> CH <sub>2</sub> Ph	72

<sup>a</sup> All of the reactions were carried out on a 10 mmol scale. The compounds were purified by vacuum distillation. The carbon skeletons present in these compounds were confirmed by selective oxidation to alcohols containing  $\alpha$ -trimethylsilyl group in >78% isolated yields (Eq. (3)).

These novel *gem*-dimetalloalkanes were reacted with alkaline hydrogen peroxide at room temperature for 3 h and the resulting alcohols containing  $\alpha$ -trimethylsilyl group (Eq. (3)) were purified by column chromatography over alumina



### 3. Experimental

The preparation of *B*-2-(1-trimethylsilyl-1-hexyl)-1,3,2-dioxaborinane and 1-trimethylsilyl-1-hexanol is representative: In an oven dried 100 mL side-arm round bottom flask equipped with a septum inlet was placed (*Z*)-1-trimethylsilyl-1-hexene (10 mmol, 1.56 g) under nitrogen atmosphere. It was cooled to 0 °C and the dichloroborane–dioxane complex (3 M solution, 10 mmol, 3.3 mL) in methylene chloride was added dropwise. The resulting mixture was stirred for 1 h at 0 °C followed by 6 h at room temperature. The reaction mixture was cooled to 0 °C. To this cooled solution was added 1,3-propane diol (10 mmol, 0.76 g) dropwise and the resulting reaction mixture was stirred at 0 °C for 0.5 h. The methylene chloride layer containing the desired product was separated and the solvent was removed to provide the *B*-2-(1-trimethylsilyl-1-hexyl)-1,3,2-dioxaborinane in 84% (2.0 g) yield. The NMR spectral data indicated that the compound was the desired product. PMR (CDCl<sub>3</sub>/without TMS):  $\delta$  0.02 (9H, s), 0.86–1.88 (14H, m), and 3.95 (4H, m), CMR (CDCl<sub>3</sub>/without TMS):  $\delta$  -0.46, 13.95, 14.21, 14.55, 22.69, 25.59, 27.79, 32.02, 33.16, and 61.59 ppm. To a solution of *B*-2-(1-trimethylsilyl-1-hexyl)-1,3,2-dioxaborinane (10 mmol, 2.42 g) in tetrahydrofuran (10 mL) was added at 0 °C the sodium hydroxide (3 M, 5 mL) followed by 30% hydrogen peroxide slowly (25 mmol, 2.5 mL). The reaction mixture was allowed to come to room temperature and the stirring was continued for 4 h at room temperature. The compound was then extracted with ether (2  $\times$  25 mL) and the ether layer was washed with water (2  $\times$  10 mL). It was then dried over anhydrous sodium sulfate. The removal of the solvent followed by chromatography over alumina provided 1-trimethylsilyl-1-hexanol in 80% (1.39 g) isolated yield. The compound was characterized by spectral data. IR (neat):  $\nu$  3398 cm<sup>-1</sup>, PMR (CDCl<sub>3</sub>/without TMS):  $\delta$  -0.20 (9H, s), 0.84 (3H, m), 1.14–1.45 (9H, m), and 03.45 (1H, s) ppm; CMR (CDCl<sub>3</sub>/without TMS):  $\delta$  -3.92, 14.03, 22.35, 25.24, 25.81, 34.15, and 65.85 ppm.

The spectral data for (1–7, Table 2) are consistent with the reported data in the literature [13].

*Product 1*, Table 2. PMR (CDCl<sub>3</sub>/without TMS):  $\delta$  -0.03 (s, 9H), 0.88 (m, 3H), 1.24–1.87 (m, 11H), and

3.95 (m, 4H) ppm. CMR (CDCl<sub>3</sub>/without TMS):  $\delta$  -0.46, 14.21, 22.70, 25.60, 27.79, 32.03, 33.16, and 61.59 ppm.

*Product 2, Table 2.* PMR (CDCl<sub>3</sub>/without TMS):  $\delta$  0.03 (s, 9H), 0.82 (m, 3H), 1.18–1.82 (m, 13H), and 3.91 (m, 4H) ppm. CMR (CDCl<sub>3</sub>/without TMS):  $\delta$  -0.58, 14.07, 22.72, 25.60, 27.78, 29.34, 29.72, 33.51, and 61.46 ppm.

*Product 3, Table 2.* PMR (CDCl<sub>3</sub>/without TMS):  $\delta$  0.04 (s, 9H), 0.82–1.86 (m, 15H), 0.84 (m, 3H), and 3.92 (m, 4H) ppm. CMR (CDCl<sub>3</sub>/without TMS):  $\delta$  -1.43, 14.15, 22.72, 25.59, 27.78, 29.73, 32.01, 33.69, and 61.54 ppm.

*Product 4, Table 2.* PMR (CDCl<sub>3</sub>/without TMS):  $\delta$  0.05 (s, 9H), 0.78–2.16 (m, 9H), and 3.41–3.90 (m, 6H) ppm. CMR (CDCl<sub>3</sub>/without TMS):  $\delta$  -0.57, 24.81, 27.70, 31.00, 32.43, 34.11, and 66.83 ppm.

*Product 5, Table 2.* PMR (CDCl<sub>3</sub>/without TMS):  $\delta$  0.05 (s, 9H), 0.83 (m, 6H), 1.11–1.85 (m, 13H), and 3.90 (m, 4H) ppm. CMR (CDCl<sub>3</sub>/without TMS):  $\delta$  -1.45, 14.07, 22.36, 22.84, 25.78, 27.87, 31.26, 39.10, and 61.49 ppm.

*Product 6, Table 2.* PMR (CDCl<sub>3</sub>/without TMS):  $\delta$  0.08 (s, 9H), 0.95–2.65 (m, 9H), 3.97 (m, 4H), and 7.20–7.29 (m, 5H) ppm. CMR (CDCl<sub>3</sub>/without TMS):  $\delta$  -1.27, 14.22, 22.49, 25.58, 26.00, 27.82, 35.47, 36.20, 61.61, 62.69, 66.90, 102.29, 125.57, 128.47, and 143.15 ppm.

*$\alpha$ -Trimethylsilyl-1-heptanol.* PMR (CDCl<sub>3</sub>/without TMS):  $\delta$  0.02 (s, 9H), 0.85 (m, 3H), 0.88–1.49 (m, 11H), and 3.30 (m, 1H) ppm. CMR (CDCl<sub>3</sub>/without TMS):  $\delta$  -3.88, 14.12, 22.72, 26.85, 29.33, 31.92, 33.59, and 66.08 ppm.

*$\alpha$ -Trimethylsilyl-1-octanol.* PMR (CDCl<sub>3</sub>/without TMS):  $\delta$  0.05 (s, 9H), 0.80 (m, 3H), 1.10–1.20 (m, 13H), and 3.41 (m, 1H) ppm. CMR (CDCl<sub>3</sub>/without TMS):  $\delta$  -3.97, 14.02, 22.64, 26.86, 27.43, 29.32, 29.57, 31.89, and 65.81 ppm.

*$\alpha$ -Trimethylsilyl-5-chloro-1-pentanol.* PMR (CDCl<sub>3</sub>/without TMS):  $\delta$  0.02 (s, 9H), 1.46–2.07 (m, 7H), and 3.21–3.49 (m, 3H) ppm. CMR (CDCl<sub>3</sub>/without TMS):  $\delta$  -3.90, 24.27, 32.57, 32.70, 45.06, and 65.70 ppm.

*$\alpha$ -Trimethylsilyl-5-methyl-1-hexanol.* PMR (CDCl<sub>3</sub>/without TMS):  $\delta$  0.03 (s, 9H), 0.86 (d, 6H), 1.15–1.47 (m, 8H), and 3.43 (m, 1H) ppm. CMR (CDCl<sub>3</sub>/without TMS):  $\delta$  -3.89, 15.29, 22.62, 24.65, 28.04, 33.84, 39.00, and 65.88 ppm.

*$\alpha$ -Trimethylsilyl-4-phenyl-1-butanol.* PMR (CDCl<sub>3</sub>/without TMS):  $\delta$  0.05 (s, 9H), 1.21–2.65 (m, 12H), 3.48 (m, 1H), and 7.20 (m, 5H) ppm. CMR (CDCl<sub>3</sub>/without TMS):  $\delta$  -3.70, 28.89, 33.34, 36.00, 66.98, 125.85, 128.46, 128.58 and 142.66 ppm.

#### 4. Conclusions

In summation, we have developed for the first time a simple, and efficient conversion of 1- trimethylsilyl-1-alkynes into the corresponding *gem*-dimetalloalkanes containing boron and silicon in high yields. These *gem*-dimetalloalkanes were isolated and characterized using 300 MHz NMR spectral data for the first time. The carbon skeletons present in these intermediates are further confirmed by selective oxidation studies with alkaline hydrogen peroxide to provide the corresponding alcohols containing  $\alpha$ -trimethylsilyl group. We are presently utilizing these valuable compounds for further synthetic transformations.

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