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# Synthesis of a *tert*-butyl substituted bis(silirane) and comparison with its methyl and phenyl analogs

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### ABSTRACT

The detailed syntheses of a series of substituted bis(silirane)s ( $Me_4C_2SiR$ )<sub>2</sub> {R = Me (1a), Ph (1b), *tert*butyl (1c)} are reported. The *tert*-butyl derivative (1c) shows steric congestion which results in conformational rigidity in solution with respect to Si–Si bond rotation. This contrasts with the methyl (1a) and phenyl (1b) analogs. The rotational barriers of all three bis(silirane)s were examined by Density Functional Theory (DFT) at the B3LYP/6-31G\* level. The calculated rotational barriers were 4.1 and 4.7 kcal/ mol for 1a and 1b, respectively, but significantly higher for 1c, 29.9 kcal/mol. The thermolysis of 1c at 145 °C in the presence of bis(trimethylsilyl)acetylene gave 1,4-di-*tert*-butyl-2,2,3,3-tetramethyl-5,6-bis (trimethylsilyl)-1,4-disilabicyclo[2.2.0]hex-5-ene (A) resulting from the [2 + 2] cycloaddition of bis(trimethylsilyl)acetylene with a 1,2-disilacyclobut-1-ene intermediate (B). The 1,2-disilacyclobut-1-ene (B) presumably originates from the rearrangement of a transient siliranylsilylene produced by loss of tetramethylethylene from 1c. Purification of the 1,4-disilabicyclo[2.2.0]hex-5-ene (A) by column chromatography resulted in its reaction with air to afford a stable 1,4-di-*tert*-butyl-2,2,3,3-tetramethyl-5,6-bis (trimethylsilyl)-7-oxa-1,4-disilabicyclo[2.2.1]hept-5-ene (C).



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### 1. Introduction

Bis(silirane)s are highly strained organosilicon compounds. Ando has reported that the pyrolysis of the bis(silirane)s **1a** and **1b** result in the extrusion of tetramethylethylene and may serve as potential precursors to disilynes (Scheme 1) [1,2].

We have reported earlier that reactive laser ablation of strained three membered ring compounds followed 2 + 1 type fragmentation yielding double bonded species in the case of carbon and heavier Group 14 elements [3–5]. We surmised that under similar laser ablation conditions, bis(silirane)s may fragment with loss of tetramethylethylene to potentially yield disilynes in the gas phase. Reactive laser ablation coupled with a molecular beam is a powerful technique to study such highly reactive species [6,7].

Bis(silirane)s, which bear methyl and phenyl substituents of the silicon atoms, are difficult to handle for laser ablation experiments since they are highly air and moisture sensitive. A bulky substituent such as *tert*-butyl group on the silicon atom might not only make the bis(silirane) less chemically reactive but also might prevent any potential disilyne from isomerizing, thereby improving its chance for direct observation.







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We report here the synthesis of an air, moisture and thermally stable *tert*-butyl substituted bis(silirane) (**1c**) and the comparison of its properties with its methyl (**1a**) and phenyl (**1b**) analogs.

### 2. Material and methods

#### 2.1. General information

Chlorosilanes and bis(trimethylsilyl)acetylene were purchased from Gelest and used without further purification. Magnesium turnings (~1/8 in, 99.95% on trace metal basis) purchased from Aldrich were used. All other reagents were purchased from Aldrich and were used without purification. Dichloromethane was dried over calcium hydride. Benzene,  $d_6$ -benzene and toluene were dried over sodium, vacuum transferred, and stored under argon. CDCl<sub>3</sub> was distilled from CaH<sub>2</sub> and stored under argon. Hexane, pentane, ether and THF were distilled directly from sodium/benzophenone. The disilane **2a** was generously provided by Prof. Peter Gaspar at Washington University in St. Louis. Phenylchlorodisilane [8] and 1,2diphenyl-1,1,2,2-tetraisopropyldisilane [9] were prepared according to literature procedures.

All NMR spectra were recorded on a Bruker Avance 300 spectrometer. <sup>29</sup>Si NMR of all compounds was recorded using inverse gated coupling technique. Preparative HPLC was performed with a Varian Prostar 210 HPLC instrument using a semi preparative column (column module C18 8U 21.4 X 250). A binary solvent delivery system was used with a combined solvent flow rate of 23 mL/min. GC–MS was performed using a Varian Saturn 2100 instrument. Mass spectroscopy (EI) and high resolution mass spectroscopy (HRMS) were recorded at the Georgia Tech mass spectrometry facility. Raman spectroscopy was recorded at the Department of Earth and Planetary Sciences of the Washington University in St. Louis. Elemental analysis was performed in Galbraith Laboratory, Schwarzopf Microanalytical Laboratory and Tulane University Coordinated Instrumentation Facility. Melting points are uncorrected.

### 2.2. Synthesis of 1,2-dimethyl 1,1,2,2-tetrakis(2-bromo-2-propyl) disilane (**3a**) [10]

1,2-Dimethyl-1,1,2,2-tetraisopropyldisilane (**2a**) (1.5 g, 5.8 mmol), *N*-bromosuccinimide (5.0 g, 28 mmol), azobisisobutyronitrile (AIBN) (0.080 g, 0.45 mmol) and 80 mL of CCl<sub>4</sub> were placed in 250 mL three neck flask and heated to reflux for 2.5 h under nitrogen. The reaction mixture was then cooled to 0 °C and the precipitated succinimide was separated from the clear solution by filtration. The filtrate was concentrated by rotary evaporation and added to 11 mL of absolute ethanol to precipitate compound **3a** as a white solid. The solid was filtered and dried under vacuum. Yield 2.4 g (72%) <sup>1</sup>H NMR ( $\delta$ , CDCl<sub>3</sub>) 0.81–0.92 (s, 6H) 2.11–2.14 (s, 6H) 2.15–2.19 (s, 6H) <sup>13</sup>C{<sup>1</sup>H} NMR ( $\delta$ , CDCl<sub>3</sub>) 1.6, 35.0, 35.2, 57.6 <sup>29</sup>Si{<sup>1</sup>H} NMR ( $\delta$ , CD<sub>2</sub>Cl<sub>2</sub>) 5.1 Elemental analysis for C<sub>14</sub>H<sub>30</sub>Br<sub>4</sub>Si<sub>4</sub>: observed (calculated): C, 29.68 (29.29) H, 5.21 (5.29). M.p. 127–135 °C with decomposition.

## 2.3. Synthesis of 3,3'-bis(3-methyl-1,1,2,2-tetramethyl-3-silacyclopropane) (1a) [10]

Magnesium turnings (99.98%, 0.75 g, 31 mmol) and 20 mL of THF were placed into a 100 mL Schlenk flask under argon. A small amount of 1,2-dibromoethane (0.70 mL) was added to the flask and the mixture stirred for 1 h in order to activate the magnesium. Compound **3a** (4.0 g 7.0 mmol), dissolved in 20 mL of THF, was added to the magnesium slurry over a of 3 h period at 0 °C. It was then stirred for an additional 5 h. The solvent was then removed under vacuum and ice-cooled hexane (25 mL) was added to the

mixture. The mixture was stirred for 10 min, and the solid was allowed to settle. The clear solution was decanted and filtered through a fritted Schlenk funnel. The solution was reduced to 3–4 mL and kept at -30 °C overnight. The colorless crystals were separated from the mother liquor by filtering through a fritted Schlenk funnel. Compound **1a** was stored in a glove box at -30 °C due to its air and thermal instability. Yield 0.35 g (20%). <sup>1</sup>H NMR ( $\delta$ , C<sub>6</sub>D<sub>6</sub>) 0.19–0.26 (s, 6H) 1.35–1.39 (s, 12H) 1.44–1.48 (s, 12H). <sup>13</sup>C{<sup>1</sup>H} NMR ( $\delta$ , C<sub>6</sub>D<sub>6</sub>) – 8.6, 21.2, 21.3, 24.0. <sup>29</sup>Si{<sup>1</sup>H} NMR ( $\delta$ , C<sub>6</sub>D<sub>6</sub>) – 82.1 EI-MS: *m/z* (relative abundance) 170 (7, M<sup>+</sup> – 84), 127 (7), 84 (90), 69 (100), 42 (73) HRMS for C<sub>8</sub>H<sub>18</sub>Si<sub>2</sub> (M<sup>+</sup> – 84 ion): observed (calculated) 170.0903 (170.0947). M.p. 50–56 °C with decomposition.

### 2.4. Synthesis of 1,2-diphenyl 1,1,2,2-tetrakis(2-bromo-2-propyl) disilane (**3b**)

Compound **2b** (1.0 g, 2.6 mmol), *N*-bromosuccinimide (2.0 g, 12 mmol), AIBN (0.050 g, 0.30 mmol) and 50 mL of CCl<sub>4</sub> were placed in a 250 mL three neck flask fitted with a condenser under nitrogen. The mixture was then heated to reflux for 2.5 h and subsequently cooled to 0 °C. The precipitated succinimide was separated from the clear solution by filtration. Rotary evaporation of the filtrate and subsequent crystallization in dichloromethane yielded **3b** as colorless crystals. Yield 1.57 g (87%) <sup>1</sup>H NMR ( $\delta$ , CDCl<sub>3</sub>) 2.06–2.17 (b, 12H) 2.21–2.31 (b, 12H), 7.33–7.53 (m, 6H) 8.05–8.17 (m, 4H), <sup>13</sup>C{<sup>1</sup>H} NMR ( $\delta$ , CDCl<sub>3</sub>) 36.1, 36.6, 57.9, 127.3, 129.4, 135.8, 137.3 <sup>29</sup>Si{<sup>1</sup>H} NMR ( $\delta$ , CDCl<sub>3</sub>) –6.5. Elemental analysis for C<sub>24</sub>H<sub>34</sub>Br<sub>4</sub>Si<sub>4</sub>; observed (calculated): C, 41.03 (41.28) H, 4.90 (4.91). M.p. 147–159 °C with decomposition.

### 2.5. Synthesis of 3,3'-bis(3-phenyl-1,1,2,2-tetramethyl-3-silacyclopropane) (1b) [1]

A 50 mL Schlenk flask was charged with 0.40 g magnesium turnings (99.98%, 16 mmol) and 10 mL of THF under argon. A small amount of 1,2-dibromoethane (0.40 mL) was added to the flask and stirred for 1 h in order to activate the magnesium. Compound **3b** (2.5 g, 3.6 mmol), dissolved in 15 mL of THF, was added to the magnesium slurry over a period of 2 h at 15 °C. The reaction mixture was then stirred for an additional 5 h at room temperature. Dioxane (5.0 mL) was added to the reaction mixture in order to precipitate the MgBr<sub>2</sub>. The resulting slurry was then filtered in a fritted Schlenk funnel. The solvent was removed from the filtrate by applying vacuum to give a yellow colored waxy substance, which upon recrystallization from a hexane:THF (3:1) mixture, yielded colorless crystals of **1b**. Bis(silirane) **1b** was stored in a glove box at  $-30^{\circ}$  due to its highly reactivity towards air and moisture and its thermal instability at room temperature. Yield 0.33 g (25%). <sup>1</sup>H NMR ( $\delta$ ,) 1.29-1.33 (s, 12), 1.36-1.41 (s, 12H), 7.07-7.37 (m, 4H), 7.54-7.8 (m, 6H)  ${}^{13}C{}^{1}H$  NMR ( $\delta$ , C<sub>6</sub>D<sub>6</sub>) 22.5, 23.8, 24.6, 128.8, 129.8, 134.0, 137.7 <sup>29</sup>Si{<sup>1</sup>H} NMR ( $\delta$ , C<sub>6</sub>D<sub>6</sub>) –82.8 EI-MS: m/z (relative abundance) 294  $(59, M^{+} - 84), 279 (4), 217 (9), 187 (34), 84 (100), 69 (90), 42 (50).$ HRMS for  $C_{18}H_{22}Si_2$  (M<sup>+</sup> – 84 ion): observed (calculated) 294.1235 (294.1260).

#### 2.6. Synthesis of bromo(tert-butyl)diisopropylsilane (6)

*Tert*-butyldiisopropylsilane (**5**) (9.1 g, 53 mmol) and dichloromethane (47 mL) were placed into a 100 mL Schlenk flask under argon and then cooled to 0 °C. Bromine (2.7 mL, 53 mmol) in 12 mL of dichloromethane was added to the flask over a span of 2 h while maintaining the temperature at 0 °C. The reaction mixture was stirred for 2 h and the solvent was subsequently removed by vacuum distillation. Compound **6** was obtained as colorless liquid. Yield 11.9 g (90%). B.p. 230–235 °C. <sup>1</sup>H NMR ( $\delta$ , CDCl<sub>3</sub>) 1.06–1.16 (s, 9H) 1.16–1.29 (two doublets, 12H, J = 1 Hz) 1.29–1.46 (m, 2H) <sup>13</sup>C {<sup>1</sup>H} NMR ( $\delta$ , CDCl<sub>3</sub>) 14.8, 18.9, 19.3, 21.9, 28.2 <sup>29</sup>Si{<sup>1</sup>H} NMR ( $\delta$ , CDCl<sub>3</sub>) 41.2. IR (NaCl, cm<sup>-1</sup>) 2946 (m), 2867 (s), 1465 (s), 1010 (s), 881(s), 815 (s). GC–MS(EI): m/z (relative abundance) 251(M<sup>+</sup>, 1), 207 (2), 194 (6), 165 (8), 131 (25), 101 (100), 75 (58), 39 (23) Elemental analysis for C<sub>10</sub>H<sub>23</sub>BrSi; observed (calculated): C, 47.97 (47.80) H, 9.86 (9.23).

### 2.7. Synthesis of 1,2-di-tert-butyl-1,1,2,2-tetraisopropyldisilane (2c)

A degassed mixture of 6 (2.0 g, 7.8 mmol) and 22 mL of THF were added to a 50 mL Schlenk flask loaded with KC<sub>8</sub> (1.3 g, 9.7 mmol). The mixture was initially stirred under argon at -30 °C. The temperature of the mixture was carefully brought to -10 °C over a 45 min period, and then to 25 °C over a 1 h period. The resulting slurry was then stirred for another 2 h and filtered through celite. The filtrate was rotary evaporated to remove THF. Recrystallization in hexane at -20 °C gave colorless crystals of **2c**. Yield 1.00 g (83%). <sup>1</sup>H NMR ( $\delta$ , CDCl<sub>3</sub>) 1.04–1.32 (m, 42H) 1.33–1.47 (m, 4H) <sup>13</sup>C{<sup>1</sup>H} NMR (δ, CDCl<sub>3</sub>) 15.0, 21.0, 22.1, 28.9, 32.0<sup>29</sup>Si{<sup>1</sup>H} NMR (δ, CDCl<sub>3</sub>) 4.1. GC–MS(EI) *m*/*z* (relative abundance) 285 (M<sup>+</sup> – *tert*-butyl, 2), 243 (23), 183 (13), 155 (15), 129 (15), 101 (100), 73 (60) Elemental analysis C<sub>20</sub>H<sub>46</sub>Si<sub>2</sub>; observed (calculated): C, 70.06 (70.17) H, 13.44 (13.45). M.p. 185–192 °C. This route is much more efficient than the two step synthesis of hexa-tert-butyldisilane from tri-tert-butylbromosilane previously reported by Wiberg [11] where the bromosilane was reduced with potassium metal, followed by an oxidation with the nitrosvl cation. A Si–Si stretching vibration at 284.5 cm<sup>-1</sup> was observed in the Raman spectrum. This value lies between the reported values for hexamethyldisilane  $(401 \text{ cm}^{-1})$  and hexa-*tert*-butyldisilane (271 cm<sup>-1</sup>) [11].

### 2.8. Synthesis of 1,2-di-tert-butyl 1,1,2,2-tetrakis(2-bromo-2-propyl)disilane (**3c**)

Finely powdered N-bromosuccinimide (2.1 g, 12 mmol), AIBN (0.40 g, 2.4 mmol), disilane **2c** (0.50 g, 1.5 mmol) and 50 mL CCl<sub>4</sub> were placed into a 100 mL Schlenk flask under nitrogen, stirred for 30 min, and then heated to 58-60 °C. The mixture was then irradiated with a 75 W incandescent bulb. The solution became a light yellow color and then to dark yellow after a few minutes. The temperature of the solution was lowered to 55 °C and maintained at this temperature for 30 min. The solution was then cooled to 0 °C, stirred for an additional 30 min, and filtered through a fritted Schlenk funnel to remove the precipitated succinimide. The solvent was removed from the filtrate by vacuum and the filtrate was dried to give 3c as a waxy substance. Recrystallization in hexane at -30 °C gave impure **3c**. The impure solid was then separated by HPLC using a CH<sub>3</sub>OH:THF eluent (93:7) to obtain analytically pure **3c.** Yield 0.35 g (37%). <sup>1</sup>H NMR ( $\delta$ , THF- $d_8$ ) 1.58–1.67 (s, 18 H) 2.38–2.58 (d, 24H, I = 15 Hz) <sup>13</sup>C{<sup>1</sup>H} NMR ( $\delta$ , THF- $d_8$ ) 30.5, 34.3, 39.1 (b) 40.8 (b) 62.0 (b)  $^{29}$ Si{<sup>1</sup>H} NMR ( $\delta$ , THF- $d_8$ ) 29.0 Elemental analysis C<sub>20</sub>H<sub>42</sub>Br<sub>4</sub>Si<sub>2</sub>; observed (calculated): C, 36.26 (36.49) H, 7.08 (6.43). M.p. 85-110 °C with decomposition. Compounds 7 and 8 were the side products obtained during the HPLC separation. Characterization for **7**. <sup>1</sup>H NMR ( $\delta$ , THF- $d_8$ ) 1.37–1.38 (s, 9H) 1.4-1.42 (s, 9H) 2.18-2.22 (d, 12H, J = 9 Hz) 4.35-4.54 (q, 2H) 7.37–7.45 (s, 1H).  $^{13}\text{C}\{^{1}\text{H}\}$  NMR ( $\delta,$  C\_6D\_6) 16.9, 22.6, 22.6, 26.1, 26.1, 32.8, 33.1, 35.0, 36.9, 37.0, 37.2, 37.3, 58.2, 58.7, 131.1, 139.7. <sup>29</sup>Si{<sup>1</sup>H} NMR (δ, C<sub>6</sub>D<sub>6</sub>) 3.2, 12.7. M.p. 102–115 °C with decomposition Elemental analysis C<sub>20</sub>H<sub>40</sub>Br<sub>4</sub>Si<sub>2</sub>; observed (calculated): C, 36.17 (36.60) H, 6.58 (6.14). Characterization for **8**. <sup>1</sup>H NMR ( $\delta$ , C<sub>6</sub>D<sub>6</sub>) 1.31-1.32 (s, 9H) 1.42-1.44 (s, 9H) 2.19-2.27 (m, 12H) 5.72-5.78 (m, 1H) 5.96–6.00 (m, 1H)  $^{13}C{^1H}$  NMR ( $\delta$ , C<sub>6</sub>D<sub>6</sub>) 16.6, 22.6, 23.1, 25.3, 26.6, 27.6, 32.9, 33.2, 37.3, 37.6, 37.9, 38.1, 59.2, 59.3, 134.5, 144.9. <sup>29</sup>Si{<sup>1</sup>H} NMR ( $\delta$ , C<sub>6</sub>D<sub>6</sub>) 3.9, 15.8. M.p. 123–135 °C with decomposition. Elemental analysis C<sub>20</sub>H<sub>42</sub>Br<sub>2</sub>Si<sub>2</sub>; observed (calculated): C, 47.33 (48.18) H, 8.11 (8.49).

### 2.9. Synthesis of 3,3'-bis(3-tert-butyl-1,1,2,2-tetramethyl-3-silacyclopropane) **1c**

Magnesium turnings (99.98%, 0.83 g, 31 mmol), 25 mL THF, and a small amount of 1,2-dibromoethane (0.70 mL) were added to a 100 mL Schlenk flask under argon and then stirred for 1 h in order to activate the magnesium. Compound 3c (6.9 g), dissolved in 15 mL of THF, was added to the magnesium slurry over a period of 4 h at 15 °C, and then stirred at room temperature for an additional 5 h. The mixture was stirred for an additional 10 min after the addition of 25 mL of hexane, and the solids were allowed to settle. The clear solution was decanted and filtered through a fritted Schlenk funnel. The solvent was removed from the filtrate by applying vacuum to give 1c as yellow color waxy substance. Analytically pure compound was obtained by reverse phase HPLC using a binary solvent system of methanol:THF in a ratio of 93:7. Yield 0.80 g (23%). <sup>1</sup>H NMR (δ, C<sub>6</sub>D<sub>6</sub>) 1.20–1.21 (s, 18H) 1.34–1.36 (d, 12H, J = 2 Hz) 1.36–1.37 (s, 6H) 1.41–1.43 (s, 6H). <sup>13</sup>C{<sup>1</sup>H} NMR ( $\delta$ , C<sub>6</sub>D<sub>6</sub>) 20.6, 21.5, 23.4, 23.9, 24.2, 26.4, 28.2, 32.5. <sup>29</sup>Si{<sup>1</sup>H} NMR ( $\delta$ , C<sub>6</sub>D<sub>6</sub>) -60.7. HRMS for C<sub>20</sub>H<sub>42</sub>Si<sub>2</sub> (M+ ion): observed (calculated) 338.28054 (338.28251). GC-MS(EI): *m*/*z* (relative abundance) 338 (M<sup>+</sup>, 4), 281 (17), 239 (2), 183 (2), 169 (7), 127 (19), 101 (100), 73 (55), 59 (49). Compound 9 was obtained as a byproduct in HPLC separation of **1c**. Characterization for **9**. <sup>1</sup>H NMR ( $\delta$ , THF- $d_8$ ) 1.16-1.17 (s, 9H), 1.17-1.18 (s, 9H), 1.12-1.14 (s, 6H), 1.25-1.26 (s, 6H), 2.01–2.03 (q, 3H), 5.46–5.51 (m, 1H), 5.76–5.81 (m, 1H) <sup>13</sup>C  ${}^{1}$ H} NMR ( $\delta$ , THF- $d_{8}$ ) 16.0, 16.2, 16.2, 21.5, 21.6, 22.2, 22.4, 22.6, 22.70, 27.1, 32.0, 32.3, 130.30,147.1 <sup>29</sup>Si{<sup>1</sup>H} NMR ( $\delta$ , C<sub>6</sub>D<sub>6</sub>) – 5.6, 1.2. GC–MS (EI): *m*/*z* (relative abundance) 340 (M<sup>+</sup>, 2), 283 (10), 241 (8), 171 (5), 127 (33), 101 (100), 73 (60), 59 (20).

### 2.10. Thermolysis of bis(silirane) **1c** with bis(trimethylsilyl) acetylene

Compound 1c (0.42 g, 1.2 mmol), bis(trimethylsilyl)acetylene (1.5 g, 9.0 mmol) and 3.0 mL of toluene were placed in a pyrolysis tube attached with a teflon stopcock. The solution was degassed under high vacuum through five freeze-pump-thaw cycles. The tube was then sealed with a torch and heated to 145-147 °C for 16 h in an oil bath. The tube was opened after cooling to room temperature and the pyrolysate was transferred to a 10 mL Schlenk flask. The solvent, as well as the excess trapping agent, were removed by vacuum to give compound **11** as a brown color waxy substance. Characterization for **11**:  ${}^{29}$ Si{ ${}^{1}$ H} NMR ( $\delta$ , C<sub>6</sub>D<sub>6</sub>) –40.5, 47.2 GC–MS(EI): *m*/*z* (relative abundance) 424 (M<sup>+</sup>, 2) 409 (5) 367 (22), 340 (5), 283 (100), 221 (22), 155 (16), 73 (67) HRMS for C<sub>22</sub>H<sub>48</sub>Si<sub>4</sub> (M<sup>+</sup> ion): calculated (observed) 424.28051 (424.28332). Further purification of compound 11 by HPLC using a methanol:THF solvent (85:15) resulted in the isolation of 12 as a colorless waxy substance. Yield 0.20 g (36%) Characterization for **12**: <sup>1</sup>H NMR (δ, C<sub>6</sub>D<sub>6</sub>) 0.3–0.4 (s, 18H), 0.89–0.95 (s, 6H), 1.13–1.17 (s, 6H), 1.28–1.33 (s, 18H)  $^{13}C{}^{1}H$  NMR ( $\delta$ , C<sub>6</sub>D<sub>6</sub>) 4.0, 19.5, 23.8, 25.2, 28.4, 29.3, 118.2 <sup>29</sup>Si{<sup>1</sup>H} NMR ( $\delta$ , C<sub>6</sub>D<sub>6</sub>) -13.1, 8.73 GC-MS(EI): m/z(relative abundance) 440 (M<sup>+</sup>, 2) 425 (7), 383 (5), 356 (19), 299 (100), 213 (7), 181 (7), 73 (33). HRMS for  $C_{22}H_{48}OSi_4$  (M<sup>+</sup> ion): observed (calculated) 440.27816 (440.27823).

### 2.11. Computational details

All of the density functional calculations reported in this paper used the GAUSSIAN03 [12] program system through the WebMo interface [13]. Geometries for model compounds **1a–1c**, **11** have been optimized using B3LYP method at 6-31G\* level. The GIAO (Gauge-Independent Atomic Orbital) nuclear magnetic shielding tensors were calculated at the B3LYP/6-31G\* level using the optimized structures at the B3LYP/6-31G\* level. The <sup>29</sup>Si NMR tensors were converted into the corresponding chemical shifts assuming  $\sigma = 386.5$  for SiMe<sub>4</sub> [14,15]. Constrained geometrical optimizations were performed by varying the dihedral angle of the attached carbon atoms of the methyl, phenyl and *tert*-butyl group of the corresponding bis(silirane)s (**1a–1c**) along the Si–Si bond. Full reference to the Quantum Chemical Software is given in the supplementary material.

### 2.12. X-ray structure determinations: general data

The solid state structures of **1a** and **2c** were determined by X-ray crystallography. ORTEP views of **1a** and **2c** are given in Figs. 1 and 2, respectively, while experimental details and relevant metrical data for both compounds are presented in Table 1. General procedures for crystal alignment, unit cell determination and refinement and collection of intensity data have been published [16].

### 3. Results and discussion

### 3.1. Synthesis of bis(silirane)s

C.5

The general synthetic approach to the bis(siliranes) 1a-1c is shown in Scheme 2. In this synthesis, 1,1,2,2-tetraisopropyldisilanes (2) are brominated to afford the 1,1,2,2-tetrakis(2-bromo-2-propyl) disilanes (3). Reaction of 3 with activated magnesium results in the formation of 1 by the Wurtz coupling of the bromoisopropyl groups in a reaction pioneered by Seyferth [17] for simple siliranes. Although the syntheses of 1a and 1b have been reported previously by Ando [1,2], detailed procedures were not provided.

A single crystal X-ray structure diffraction study was carried out on **1a**. The molecule was found to crystallize in the monoclinic C2/<sub>C</sub> space group (Fig. 1). The two silirane rings are symmetry related by a crystallographic C<sub>2</sub> axis bisecting the Si–Si bond. The silirane rings are twisted relative to each other with a C7–Si1–Si1<sup>i</sup>–C7<sup>i</sup> dihedral angle of 118.4(5)° (Si1 and C7 are symmetry related to Si1<sup>i</sup> and C7<sup>i</sup>). The central Si1–Si1<sup>i</sup> bond length is 2.310(5) Å, slightly shorter than a typical Si–Si bond length of 2.33 Å [18]. This shorter bond length is similar to the observation made for 1,1′-bi(cyclopropane) [19]. The Si–C bond distances of the silirane ring are all slightly longer than normal: Si1–C1, Si1–C2, 1.88(1) Å; compared to 1.87 Å in unstrained silicon systems [20]. Additionally, the



**Fig. 1.** Molecular structure of **1a** with atomic numbering (ORTEP, 50% probability ellipsoids; H atoms are omitted for clarity). Selected bond distances (Å) and bond angles (deg) for **1a**: Si1–Si1<sup>i</sup> = 2.3097(5), Si1–C7 = 1.876(1), Si1–C2 = 1.8817(9), Si1–C1 = 1.882(1), C7–Si1–Si1<sup>i</sup> = 117.14(3), C2–Si1–C1 = 49.34(4), C1–C2–Si1 = 65.37(5).



**Fig. 2.** Molecular structure of **2c** with atomic numbering (ORTEP, 50% probability ellipsoids; H atoms are omitted for clarity). Selected bond distances (Å) and bond angles (deg) for **2c**:  $Si-Si^i = 2.4787(6)$ , Si-C1 = 1.930(1), Si-C4 = 1.926(1), Si-C7 = 1.940(1), C4-Si-C7 = 110.95(6),  $C4-Si-Si^i = 106.11(4)$ ,  $C7-Si-Si^i = 114.33(4)$ .

endocyclic ring C1–C2 distance, 1.571(1) Å is also long as compared to the average exocyclic C–C bond length of 1.54 Å. The longer bond distances are typical for a cyclopropane structure with a high degree of p character for the endocyclic bonds [21].

The synthesis of disilane **2c** is shown in Scheme 3. *Tert*-butyldiisopropylsilane (**5**) was synthesized by the procedure reported by Wolczanski and coworkers [22]. Bromination of **5** using bromine in dichloromethane at 0 °C gave bromo(*tert*-butyl)diisopropylsilane (**6**). Reductive coupling of **6** with KC<sub>8</sub> gave **2c** in 83% yield.

A single crystal X-ray diffraction study was performed on **2c** (Fig. 2). The orthorhombic unit cell has C222<sub>1</sub> space group symmetry. Both halves of the molecule are symmetry related by a C<sub>2</sub> rotational axis bisecting the Si–Si bond. The disilane has a *gauche* conformation with the dihedral angle defined by the Si–Si bond and the *tert*-butyl groups (C7–Si–Si<sup>i</sup>–C7<sup>i</sup>) being 83.83(6)°. The Si–Si bond length of

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Experimental crystallographic data for compounds 1a and 2c.

	1a	2c
Formula	C14H30Si2	C <sub>20</sub> H <sub>46</sub> Si <sub>2</sub>
Molecular weight	254.56	342.75
Crystal dimensions (mm)	$0.24 \times 0.25 \times 0.40$	$0.25\times0.29\times0.29$
Crystal System	Monoclinic	Orthorhombic
Space group	C2/c	C222 <sub>1</sub>
Cell dimensions		
a (Å)	19.7470(8)	9.746(1)
b (Å)	6.4159(3)	14.240(1)
<i>c</i> (Å)	13.8602(6)	15.873(2)
α (°)	90	90
β(°)	113.927(1)	90
γ (°)	90	90
V (Å <sup>3</sup> )	1605.11(12)	2202.9(4)
Ζ	4	4
$\rho$ (calcd) (g/cm <sup>3</sup> )	1.053	1.033
Radiation	$(\lambda = 0.71073)$	$(\lambda = 0.71073)$
Mo Kα(mm)		
$\theta$ Range (°)	2.3-29.0	2.5-28.3
Scan type	$\omega/2\theta$	$\omega/2\theta$
Total data collected	13,701	19,490
Unique data	2112	2739
Observed data with $I_0 > 2\sigma I$	1985	2700
$\mu ({ m cm^{-1}})$	0.199	0.160
F(000)	568	776
R	0.0278	0.0314
<i>R</i> w <sup>a</sup>	0.0764	0.0860

<sup>a</sup>  $R_{\rm W} = \overline{\left\{ \left[ \sum w(F_o^2 - F_c^2) / \sum w(F_o^2)^2 \right\}^{1/2}; w = 1 / [\sigma^2 (F_o^2 + (xP)^2)], \text{ where } P = \left(F_o^2 + 2F_c^2\right) / 3. \right\}}$ 



2.4787(6) Å is 6% longer than usual Si–Si bond length (2.33 Å for hexamethyldisilane) [18] but shorter than the Si–Si bond length of 2.69 Å found in hexa-*tert*-butyldisilane [11]. The silicon to *tert*-butyl carbon bond length (Si–C7) of 1.940(1) Å is significantly longer than for a typical Si–C single bond (compared with 1.87 Å) [17]. The long Si–Si and Si–C bonds of the substituents are reflective of the sterically congestive nature of this species.

Since 3c decomposes rapidly in refluxing CCl<sub>4</sub>, a combination of white light irradiation and lower temperature (57 °C) was used in its synthesis. Even under these optimized conditions, 3c was always accompanied by small amounts of the unsaturated poly-brominated compounds 7 and 8 (Chart 1). Analytically pure compounds were obtained by reverse phase HPLC using CH<sub>3</sub>OH:THF (93:7) solvent mixtures. The  ${}^{13}C{}^{1}H$  NMR spectrum of 3c shows broad peaks for the bromoisopropyl groups which can be best understood as resulting from hindered rotation of those groups in solution. An X-ray crystal structure determination of 3c revealed a rhombohedral space group  $R\overline{3}_{C}$  with the  $\overline{3}$  axis superimposed along the molecular Si–Si axis. In part due to the superimposed  $\overline{3}$  axis, there was severe disorder arising from the positional scrambling of methyl and bromine atoms within the bromoisopropyl groups as well as disorder between the *tert*-butyl and bromoisopropyl groups. To date, a good model for the disorder has not been found. The <sup>29</sup>Si<sup>1</sup>H NMR spectrum chemical shift value of 29.0 ppm for **3c** is considerably downfield compared with the value of 5.1 ppm for **3a** and -6.5 ppm for **3b**. A similar downfield chemical shift was observed for the sterically hindered hexa-tert-butyldisilane  $(\delta = 28.7 \text{ ppm})$  [11] when compared with disilane **2c** ( $\delta = 4.1 \text{ ppm}$ ), and hexamethyldisilane ( $\delta = -4.1$  ppm).

Compounds **7** and **8** may have originated from the intermediate 1,1,2-tris(2-bromo-2-propyl)-2-isopropyldisilane during the bromination. Dehydrobromination of this compound could lead to the formation of **8** and subsequent bromination of **8** would then give **7** (Scheme in Supporting Information). The byproducts must be due to competitive reactions in the introduction of the fourth bromine in the route to **3c**. This last bromination step is relatively slow due to the increasing bulkiness of the intermediate bromination products.

Bis(silirane) **1c** was obtained from **3c** (Scheme 2) as a waxy solid with a small amount of the impurity **9** (Chart 1). In contrast to **1a** and **1b**, **1c** is air and moisture stable indefinitely in the solid state. Analytically pure **1c** was separated from compound **9** by reverse phase HPLC using methanol:THF as an eluent. The <sup>1</sup>H NMR and <sup>13</sup>C {<sup>1</sup>H} NMR spectra of **1c** are consistent with the bis(silirane) structure but show interesting differences when compared to the NMR spectra of **1a** and **1b**. Whereas the <sup>1</sup>H NMR and <sup>13</sup>C {<sup>1</sup>H} NMR spectra of **1a** and **1b**. Whereas the <sup>1</sup>H NMR and <sup>13</sup>C {<sup>1</sup>H} NMR spectra of **1a** and **1b** show only two resonances due to the two distinct pairs



of chemically equivalent *cis* ring methyl groups, compound **1c** shows four distinct methyl resonances attributable to these ring methyl groups. A variable temperature <sup>1</sup>H NMR experiment showed that the four distinct ring methyl peaks did not broaden even up to 80 °C in deuterated toluene. Only a slight upfield shift of all the peaks was observed. These observations are consistent with a significant barrier to Si–Si bond rotation which locks the molecule in a nonsymmetric conformation for **1c**. The issue of hindered rotation is computationally addressed in section 3.3 of the paper.

The <sup>29</sup>Si NMR chemical shift value for **1c** was compared experimentally with other bis(silirane)s. The observed <sup>29</sup>Si NMR chemical shift value of -60.7 ppm for 1c was found to be slightly downfield relative to -82.1 ppm and -82.8 ppm for 1a and 1b, respectively. The <sup>29</sup>Si NMR chemical shift values of compounds **1a-1c** were calculated using the GIAO (Gauge-Independent Atomic Orbital) nuclear magnetic shielding tensors corresponding to the B3LYP/6-31G\* optimized geometries. Since the most stable geometries were of C1 symmetry, the two chemical shift values were averaged to give the values found in Table 2. This approach is reasonable due to the small difference in calculated chemical shifts of the silicon atoms and the facile averaging of the silicon chemical environments in solution. In general, the calculated chemical shift values for the bis (silirane)s are close to those measured experimentally. For instance, the experimental <sup>29</sup>Si NMR chemical shift value of -60.7 was closely matched to the theoretical value of -62.9 obtained for 1c, and upfield of the chemical shifts calculated for **1b** and **1c**.

### 3.2. Thermolysis of **1c** with bis(trimethylsilyl)acetylene

The thermolysis reaction of **1c** with bis(trimethylsilyl)acetylene provided additional evidence that the product **1c** indeed

Comparison between theoretical and experimental <sup>29</sup> Si NMR values in $\delta$ (ppm)	fable 2
	Comparison between theoretical and experimental $^{29}$ Si NMR values in $\delta$ (ppm).

Bis(silirane)	$\delta$ <sup>(29</sup> Si), calculated (DFT)	$\delta(^{29}$ Si), experimental	
1a	-86.1	-82.1	
1b	-73.9	-82.8	
1c	-62.9	-60.7	



possesses the bis(silirane) structure. The thermolysis of 1c in a sealed ampule at 145 °C for 16 h yielded 1,4-di-tert-butyl-2,2,3,3tetramethyl-5,6-bis(trimethylsilyl)-1,4-disilabicyclo[2.2.0]hex-5ene (11) as the major product observed by GC-MS and <sup>29</sup>Si NMR. The observed <sup>29</sup>Si NMR chemical shift values of -40.5 and 47.2 ppm for 11 were comparable with -33.1 and 41.3 ppm from DFT calculations. However, attempts to purify 11 directly by recrystallization or sublimation failed. HPLC separation of 11 resulted the isolation of 1.4-di-tert-butyl-2.2.3.3-tetramethyl-5.6bis(trimethylsilyl)-7-oxa-1,4-disilabicyclo[2.2.1]hept-5-ene (12)which is believed to have formed from the air oxidation of 11. This type of oxygen insertion is commonly observed for strained Si–Si bonds [1,23–25]. The structure of compound **12** is strongly supported by  ${}^{1}H$ ,  ${}^{13}C{}^{1}H$ , and  ${}^{29}Si{}^{1}H$  NMR spectroscopy as well as mass spectrometry. A single crystal X-ray diffraction study performed on **12** yielded a partial structure. The peripheral substituents of 12 were highly disordered but the bicyclic backbone was clear enough to establish the atom connectivity of the core structure.

The 1,4-disilabicyclo[2.2.0]hex-5-ene (**11**) likely arises from the rearrangement of an intermediate siliranylsilylene (**A**) produced from the extrusion of tetramethylethylene from **1c**. Insertion of this silylene into a strained Si–C bond gives a transient 1,2-disilacyclobutene (**B**) which eventually traps the bis(trimethylsilyl) acetylene to give **11** (Scheme 4). Sekiguchi also proposed similar siliranylsilylenes as intermediates from the reaction of stable disilynes with alkenes [26]. These siliranylsilylenes ultimately rearrange to give **1**,2-disilacyclobutene products. Interestingly, the reported thermolysis of the less hindered bis(silirane) **1b** with bis(trimethylsilyl)acetylene gives a stable bis(silirene) [1]. The difference in reactivity may be explained by the kinetic stability of the more hindered siliranylsilylene in the case of **1c**, where rearrangement is allowed to occur before reaction with the bis(trimethylsilyl)acetylene.

#### Table 3

Comparison of the relevant bond distances (in Å) and angles (in deg) for **1a**–**1c** from DFT calculations with experimental values for **1a** reported in this paper and **1b** reported by Ando [1].

	1a		1b		1c
	DFT	X-ray	DFT	X-ray	DFT
Si—Si	2.336	2.3097(4)	2.334	2.313(19)	2.387
Si-C1	1.905	1.8828(11)	1.905	1.877(5)	1.921
Si-C2	1.906	1.8817(10)	1.906	1.879(4)	1.923
Si–C7	1.901	1.8765(11)	1.901	1.881(5)	1.970
C7–Si–Si	114.40	117.14(4)	115.22	115.15(15)	113.98
C2-Si-C1	48.69	49.34(4)	48.69	49.2(2)	48.01
C1–C2–Si	65.63	65.37(5)	65.67	65.4(2)	65.88

#### 3.3. DFT calculations and rotational barriers

Extensive studies of the rotational [27–36] and photochemical [37,38] properties of 1,1-bicyclopropanes have been made. The study of the intramolecular potential energy for rotation about the carbon-carbon bond which connects the two cyclopropyl rings in 1,1-bicyclopropane shows that the centrosymmetric trans form and a gauche conformation exist in equilibrium in the gas phase [39]. Rotational barriers for the Si-Si bond are notably smaller than those of corresponding carbon analogs. For instance, the rotational barrier of disilane is 1.2 kcal/mol [40], whereas in ethane it is 2.9 kcal/mol [41,42]. The reduced barrier in disilane comes from a relatively longer Si-Si bond length. Schlever and coworkers systematically investigated the relationship between central bond lengths and rotational barriers and found that the rotational barrier becomes smaller due to poorer orbital overlap [43]. So it will be of great interest to study the rotational behavior and conformational rigidity of bis(silirane)s.

DFT geometries of **1a**–**1c** were optimized at the B3LYP/6-31G<sup>\*</sup> level. The global minima of all three bis(silirane)s show the structures illustrated in Fig. 3. The unique C3–Si–C7 dihedral angle for **1a** is 101.31°; for **1b**, 99.40°, and for **1c**, 91.87°. Table 3 shows the relevant bond distances (in Å) and angles (in deg) for **1a**–**1c** in comparison with experimental values for **1a** reported in this paper and **1b** reported by Ando [1]. As can be seen, there is a good agreement between the experimental and calculated bond lengths and bond angles. The majority of the calculated bond lengths are slightly longer (less than 2% deviation) than those found in the crystal. The optimized structure of **1c** has Si–Si bond length of 2.387 Å and a Si–C7 bond length of 1.97 Å.

The initial structure was obtained by driving the C3–Si–C7 dihedral angle from 0 to  $180^{\circ}$  in  $10^{\circ}$  increments. The potential energy was then calculated for the fully optimized structure at each dihedral angle. Compound **1c** shows a significant barrier to rotation of 29.9 kcal/mol whereas for bis(silirane)s **1a** and **1b**, the potential energy surface is much shallower and the barriers are 4.1 kcal/mol and 4.7 kcal/mol respectively. Since the thermal potential energy at



Fig. 3. Optimized geometries of 1a-1c showing atom numbering.



Fig. 4. Potential energy of 1a-1c as a function of the dihedral angle (C3-Si-Si-C7).

298 K is 6.2 kcal/mol, bis(silirane)s **1a** and **1b** should be freely rotating about the Si–Si bond, resulting in the efficient averaging of the *cis*-methyl ring environments. The bis(silirane) **1c**, however, should be conformationally locked in respect to rotation about the Si–Si bond resulting in the inequivalence of all of the ring methyl resonances (Fig. 4).

### 4. Conclusion

The detailed synthesis and characterization of a series of substituted bis(silirane)s (**1a**–**1c**) have been reported. The structure assignment of the new hindered bis(silirane) **1c** is supported by its NMR spectra and mass spectrometry. The comparison of its <sup>29</sup>Si NMR chemical shift value of -60.7 ppm with the known bis (silirane)s **1a** and **1b**, as well as comparisons of DFT calculated values were particularly important for the verification of the bis (silirane) structure. Additionally, a chemical confirmation of the structure assignment for **1c** is provided by thermolysis of **1c** in the presence of bis(trimethylsilyl)acetylene.

Finally, the congested nature of **1c** imposes a conformational rigidity in solution not observed for **1a** and **1b**. DFT calculations suggest a high barrier to rotation along the Si–Si bond (30 kcal/mol). The generation of transient disilynes from these potential precursors using reactive laser ablation method is under progress in our lab.

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### Appendix A. Supplementary material

CCDC 796312 and 796313, for the compounds **1a** and **2c** respectively; contain the supplementary crystallographic data for

this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/ data\_request/cif.

#### Appendix. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2010.10.043.

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