

## Aromatic Benzannulated Silole Dianions. The Dilithio and Disodio Salts of a Silaindene Dianion<sup>1</sup>

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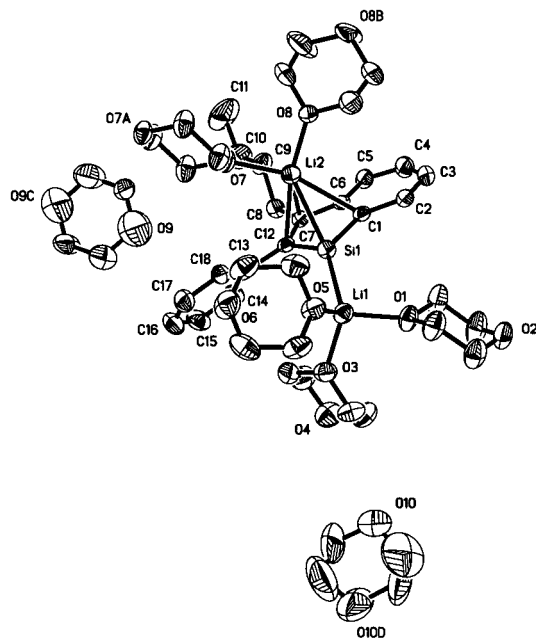
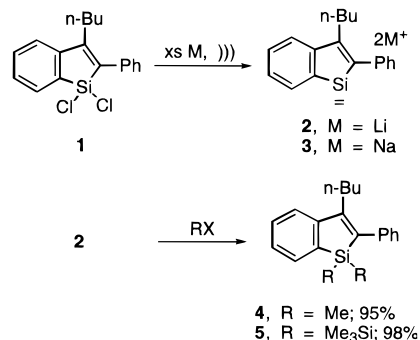
Interest in silole dianions has escalated sharply since the initial report by Joo and co-workers that stable derivatives of these species could be prepared.<sup>2</sup> The main reason for the heightened interest is the discovery that their spectroscopic and structural properties are consistent with significant  $\pi$ -delocalization.<sup>3–5</sup> These interpretations have been supported by calculations.<sup>4,6</sup>

In this communication we report the synthesis and characterization of the first benzannulated silole dianions, dilithium BPSI (**2**) (BPSI = 3-*n*-butyl-2-phenyl-1-silaindene) and disodium BPSI (**3**). To our surprise, we find that, upon formation of the dianion, the silicon containing ring becomes aromatic, apparently at the expense of the fused benzene ring, which takes on the features of a conjugated diene.

Stirring 1,1-dichloro-BPSI (**1**)<sup>7</sup> with excess lithium in THF immediately produced a dark red solution. After removal of unreacted lithium, treatment of this solution with an excess of methyl iodide or trimethylchlorosilane gave 1,1-dimethyl-BPSI (**4**)<sup>8</sup> or 1,1-bis(trimethylsilyl)-BPSI (**5**)<sup>9</sup> in high yields (Scheme 1). Compound **2**, while extremely air sensitive, is thermally stable under argon in THF for up to 1 year.

Analysis of the X-ray data for **2** shows two differently coordinated lithium ions (Figure 1).<sup>10</sup> One lithium ion is  $\eta^1$ -co-

### Scheme 1



**Figure 1.** Thermal ellipsoid diagram of structure **2**. Symmetry transformations used to generate equivalent atoms: A,  $-x, -y + 1, -z$ ; B,  $-x, y, -z + 1/2$ ; C,  $-x, y, -z - 1/2$ ; D,  $-x + 1, y, -z + 1/2$ .

ordinated to the silicon atom and also coordinated to three dioxane molecules while the other is  $\eta^5$ -coordinated with respect to the SiC<sub>4</sub> ring fragment and also coordinated to two molecules of dioxane. These two dioxane units are linked to other  $\eta^5$ -coordinated

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(7) **1** was prepared by a modification of the Rausch approach (Rausch, M. D.; Klemann, L. P. *J. Am. Chem. Soc.* **1967**, *89*, 5732). *n*-BuLi (225 mmol) was added to a stirred suspension of diphenylacetylene (21.5 g, 121 mmol) in hexane (80 mL) and TMEDA (45 mL, 300 mmol) at 0 °C and stirred for 5 h at room temperature. SiCl<sub>4</sub> (41 mL, 363 mmol) was then added at –78 °C and the mixture was stirred for 3 h while allowing the reaction mixture to warm slowly to room temperature. Filtration, followed by the removal of volatiles, afforded a viscous liquid. Crystallization of this residue in hexane at low temperature gave white crystals of **1** (27.3 g, yield 68%). Selected data for **1**: mp 64–65 °C, <sup>1</sup>H NMR (THF-*d*<sub>6</sub>, reference; THF-*d*<sub>6</sub> = 1.72 ppm), 0.85 (t, 3H), 1.34 (m, 2H), 1.57 (m, 2H), 2.64 (m, 2H), 7.27–7.71 (m, 9H); <sup>13</sup>C NMR (THF-*d*<sub>6</sub>, ref; THF-*d*<sub>6</sub> = 24.45 ppm); 14.16 (CH<sub>3</sub>), 23.72 (CH<sub>2</sub>), 28.44 (CH<sub>2</sub>), 32.09 (CH<sub>2</sub>), 158.07 (C), 146.99 (C), 137.49 (C), 134.64 (C), 130.50 (C), 133.77 (CH), 132.37 (CH), 129.70 (CH), 129.49 (CH), 128.93 (CH), 127.90 (CH), 123.89 (CH), <sup>29</sup>Si NMR (THF-*d*<sub>6</sub>, reference; ext. TMS = 0.00) 5.92. MS (M<sup>+</sup>, relative abundance), 336 (M<sup>+</sup> + 4, 6), 335 (M<sup>+</sup> + 3, 6), 334 (M<sup>+</sup> + 2, 25), 333 (M<sup>+</sup> + 1, 8), 332 (M<sup>+</sup>, 35), 290 (M<sup>+</sup> – 42, 63), 253 (M<sup>+</sup> – 79, 100), 189 (M<sup>+</sup> – 143, 75). X-ray structure determination of C<sub>18</sub>H<sub>18</sub>Cl<sub>2</sub>Si (**1**); X-ray quality crystals of **1** were grown from a concentrated hexane solution at room temperature. A single crystal of **1** was mounted in a thin-walled glass capillary tube and sealed under argon. The space group is P1, monoclinic, with unit-cell dimensions *a* = 9.4184(7) Å, *b* = 10.0417(7) Å, *c* = 10.5174(8) Å,  $\alpha$  = 66.3940(10)°,  $\beta$  = 73.0090(10)°,  $\gamma$  = 74.5340(10)°, volume = 858.88(11) Å<sup>3</sup>, *Z* = 2, fw = 333.31, *d*<sub>calc</sub> = 1.289 Mg/m<sup>3</sup>, *F*(000) = 348 and abs coeff = 0.439 mm<sup>–1</sup>. Intensity data were collected at 298(2) K on a Siemens CCD SMART diffractometer with Mo K $\alpha$  radiation and a graphite monochromator. A total of 5117 unique reflections were measured and 3690 [*R*(int) = 0.0580] having *I* > 2 $\sigma$ (*I*) were independent. The structure was solved by direct methods and refined by the full-matrix least-squares techniques on *F*<sup>2</sup> with the SHELXTL program (3679 data and 190 parameters). Final *R* = 0.0448, *R*<sub>w</sub> = 0.1242, and goodness-of-fit on *F*<sup>2</sup> = 1.064 (for all reflections, *R* = 0.0503, *R*<sub>w</sub> = 0.1232). Full details can be found in the Supporting Information.

(8) (a) Rausch, M. D.; Klemann, L. P.; Boon, W. H. *Synth. React. Inorg. Met.-Org. Chem.* **1985**, *15*, 923. (b) Stirring of **1** (1.0 g, 3 mmol) in 20 mL of THF with Li powder (130 mg, 18 mmol) for 2 h gave a dark red solution. The solution was filtered and added to a solution of MeI (1.1 mL, 18 mmol) in 10 mL of THF. The mixture was stirred for 5 h. After the volatiles were removed under reduced pressure, the residue was extracted with hexane. Evaporation of the hexane was followed by distillation of the residue under vacuum (140–150 °C, 0.05 mmHg) to give **4** as a colorless liquid. Selected data for **4**: yield 95% (by GC-MS and <sup>1</sup>H NMR for total reaction mixture); <sup>1</sup>H NMR (CDCl<sub>3</sub>, reference; CDCl<sub>3</sub> = 7.24 ppm), 0.36 (s, 6H), 0.87 (t, 3H), 1.36 (m, 2H), 1.58 (m, 2H), 2.55 (t, 2H), 7.14–7.62 (m, 9H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, reference; CDCl<sub>3</sub> = 77.23 ppm), –3.87(SiMe), 14.12 (CH<sub>3</sub>), 23.19 (CH<sub>2</sub>), 27.88 (CH<sub>2</sub>), 32.73 (CH<sub>2</sub>), 153.16 (C), 149.95 (C), 142.81 (C), 141.54 (C), 138.95 (C), 131.97 (CH), 129.95 (CH), 128.47 (CH), 127.82 (CH), 126.51 (CH), 125.70 (CH), 122.33 (CH), <sup>29</sup>Si NMR (CDCl<sub>3</sub>, reference; ext. TMS = 0.00 ppm), 3.18 (ring Si). MS (M<sup>+</sup>, relative abundance), 294 (M<sup>+</sup> + 2, 4.89), 293 (M<sup>+</sup> + 1, 19.76), 292 (M<sup>+</sup>, 74.37), 277 (M<sup>+</sup> – 15, 30.91), 250 (M<sup>+</sup> – 42, 100.00).

(9) 1,1-Bis(trimethylsilyl)-BPSI **5**: Stirring of **1** (1.0 g, 3 mmol) in 20 mL of THF with Li powder (130 mg, 18 mmol) for 2 h gave a dark red solution. The solution was filtered and added to a solution of (CH<sub>3</sub>)<sub>3</sub>SiCl (2.3 mL, 18 mmol) in 10 mL of THF. The mixture was stirred for 6 h. After the volatiles were removed under reduced pressure, the residue was extracted with hexane. Evaporation of the hexane was followed by distillation of the residue under

