Aromatic Benzannulated Silole Dianions. The Dilithio and Disodio Salts of a Silaindenyl Dianion¹ Seok-Bong Choi, Philip Boudjouk,* and Pingrong Wei

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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.² The main reason for the heightened interest is the discovery that their spectroscopic and structural properties are consistent with significant π -delocalization.³⁻⁵ These interpretations have been supported by calculations.^{4,6}

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 $(1)^7$ 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)8 or 1,1-bis(trimethylsilyl)-BPSI (5)⁹ 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).¹⁰ One lithium ion is η^1 -co-

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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. SiCl₄ (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 these articles a viscous liquid. Crystallization of this residue in nexale at low temperature gave white crystals of 1 (27.3 g, yield 68%). Selected data for 1. mp 64–65 °C, ¹H NMR (THF- d_8 , reference; THF- d_8 = 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); ¹³C NMR (THF- d_8 , ref; THF- d_8 = 24.45 ppm); 14.16 (CH₃), 23.72 (CH₂), 28.44 (CH₂), 32.09 (CH₂), 158.07 (C), 146.69 (C), 137.49 (C), 134.64 (C), 20.69 (CH₂), 20.69 (20.54 (CH2), 32.07 (CH), 132.07 (CH), 130.07 (C), 140.07 (C), 131.49 (C), 131.59 (C), 131.79 (C), 132.71 (CH), 132.87 (CH), 129.70 (CH), 129.49 (CH), 128.93 (CH), 127.90 (CH), 123.89 (CH), 2^oSi NMR (THF- d_8 , reference; ext. TMS = 0.00) 5.92. MS (M⁺, relative abundance), 336 (M⁺ + 4, 6), 335 (M⁺ + 3, 6), 334 (M⁺ + 2, 25), 333 (M⁺ + 1, 8), 332 (M⁺, 35), 290 (M⁺ - 42, 63), 253 (M⁺ - 79, 100), 189 (M⁺ - 143, 75). X-ray structure determination of C₁₈H₁₈-(M⁺ - 79, 100), 189 (M⁺ - 143, 75). X-ray structure determination of Cl₁₈H₁₈-Cl₂Si (1); X-ray quality crystals of 1 were grown from a concentrated haxane 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 PI, monoclinic, with unit-cell dimensions a = 9.4184(7) Å, b = 10.0417(7) Å, c = 10.5174(8) Å, $\alpha = 66.3940(10)^{\circ}$, $\beta = 73.0090(10)^{\circ}$, $\gamma = 74.5340(10)^{\circ}$, volume = 858.88(11) Å³, Z = 2, fw = 333.31, $d_{calc} = 1.289$ Mg/m³, F(000)= 348 and abs coeff = 0.439 mm⁻¹. Intensity data were collected at 298(2) K on a Siemens CCD SMART diffractometer with Mo Ka radiation and a graphite monochromator. A total of 5117 unique reflections were measured graphite monochromator. A total of 5117 unique reflections were measured and 3690 [R(int) = 0.0580] having $I \ge 2\sigma(I)$ were independent. The structure was solved by direct methods and refined by the full-matrix least-squares techniques on F^2 with the SHELXTL program (3679 data and 190 parameters). Final R = 0.0448, $R_w = 0.1242$, and goodness-of-fit on $F^2 = 1.064$ (for all reflections, R = 0.0503, $R_w = 0.1232$). Full details can be found in the Supporting Information.

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, $-z + \frac{1}{2}$; C, -x, y, $-z - \frac{1}{2}$; D, -x + 1, y, $-z + \frac{1}{2}$.

ordinated to the silicon atom and also coordinated to three dioxane molecules while the other is η^5 -coordinated with respect to the SiC₄ ring fragment and also coordinated to two molecules of dioxane. These two dioxane units are linked to other η^5 -coordinated

^{(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 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 ¹H NMR for total reaction mixture); ¹H NMR (CDCl₃, reference; CDCl₃ = 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); ¹³C NMR (CDCl₃, reference; CDCl₃ = 77.23 ppm), -3.87(SiMe), 14.12 (CH₃), 23.19 (CH₂), 27.88 (CH₂), 32.73 (CH₂), 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), ²⁹Si NMR (CDCl₃, reference; ext. TMS = 0.00 ppm), 3.18 (ring Si). MS (M⁺, relative abundance), 294 (M⁺ + 2, 4.89), 293 (M⁺ + 1, 19.76), 292 (M⁺, 74.37), 277 (M⁺ – 15, 30.91), 250 (M⁺ – 42, 100 00) 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 (CH₃)₃SiCl (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



Figure 2. Thermal ellipsoid diagram of structure 1.

lithium ions to give a polymeric crystal. Each unit molecule of 2 contains two half units of 1.4-dioxane in a unit cell.

Most notable among the structural changes when 1 is converted to 2 are those in the carbon-carbon bond lengths in both the silole ring and the six-membered carbon ring (Figure 2).⁷

Significant shortening of the C_6-C_7 bond to 141.8 pm from 149.7 pm in **1** and lengthening of the C_1-C_6 and C_7-C_{12} bonds to 145.5 and 142.8 pm, respectively (141.1 and 136.5 pm in 1), are observed in the silole ring. In contrast, the three nearly equal (139.2, 137.5, 138.3 pm) carbon-carbon bonds linking C₂, C₃, C_4 , and C_5 in 1, consistent with a high degree of aromaticity in the six-membered ring, undergo bond length alternation in that portion of 2 (Figure 3). The silicon-carbon bonds are lengthened slightly (0.35 pm) upon the conversion of 1 to 2. This change is similar to that observed in the analogous silole system: the Si-C bond distance in 1,1-dichloro 2,3,4,5-tetramethylsilole is 1.834 ${\rm \AA^{11}}$ and increases to 1.840 ${\rm \AA^5}$ in the aromatic dianion. The silicon carbon bonds in siloles appear to be relatively insensitive to the nature of the substituents on silicon.¹²⁻¹⁴

We attribute these changes to a fundamental alteration in the bonding of the silaindenyl system upon formation of the dianion, i.e., the SiC₄ ring becomes aromatic like other silole dianions and the six-membered ring takes on the properties of a cyclohexadiene. Consistent with this proposal is the planar geometry of the SiC₄ ring ($\sum_{\text{ring}} \angle = 540.0^{\circ}$) in **2**. By comparison, the crystal structure of [Li(THF)₂][Li(THF)₃][η^5 , η^1 -C₄Ph₄Si]⁴ shows the ring to be slightly bent with the silicon atom 11 pm out of

vacuum (85-95 °C, 0.05 mmHg) to give 5 as a colorless liquid, which solidified after a few hours at room temperature. Selected data for 5: yield 98% (by GC-MS and ¹H NMR for total reaction mixture); mp 69-70 $^{\circ}$ C; ¹H NMR (CDCl₃, reference; CDCl₃ = 7.24 ppm), 0.18 (s, 18H), 0.93 (t, 3H), 1.40 (m, 2H), 1.65 (m, 2H), 2.75 (t, 2H), 7.24–7.71 (m, 9H); ¹³C NMR (CDCl₃, reference; CDCl₃ = 77.19 ppm), -0.50 (SiMe₃), 14.12 (CH₃), 23.06 (CH₂), 28.33 (CH₂), 32.16 (CH₂), 152.61 (C), 151.43 (C), 142.93 (C), 142.60 (C), 140.48 (C), 132.49 (CH), 128.45 (CH), 128.45 (CH), 128.73 (CH), 128.17 (CH), 125.50 (CH), 125.21 (CH), 122.85 (CH), 29 Si NMR (CDCl₃, reference; ext. TMS = 0.00 ppm) -13.86 (SiMe₃), -35.01 (ring Si). MS (M⁺, relative abundance), 410 (M⁺ + 2, 0.3), 408 (M⁺, 2.4), 351 (M⁺ - 57, 1.5), 278 (M⁺ - 130, 2.4), 177 (M⁺ - 231, 2.5), 73 (M⁺ - 335, 100).

(10) X-ray structure determination of 1,1-dilithio-3-*n*-butyl-2-phenyl-1-silaindene (**2**); X-ray quality crystals of $[\text{Li}(^{1}/_{2}\text{dioxane})_{2}][\text{Li}(\text{dioxane})_{3}][\eta^{5},\eta^{1}-\eta^{1}]$ $C_{18}H_{18}Si][(^{1}_{2}dioxane)^{2}]$ (2) were grown from a concentrated 1,4-dioxane solution at room temperature. A single crystal of 2 was mounted in a thinwalled glass capillary tube and sealed under argon. The space group is C2/c, monoclinic, with unit-cell dimensions a = 29.585(2) Å, b = 16.6840(11) Å, c = 18.3095(12) Å, $\beta = 113.0690(10)^\circ$, volume = 8314.8(10) Å³, Z = 8, fw = 716.81, $d_{calc} = 1.145$ Mg/m³, F(000) = 3088, and abs coeff = 0.107 mm⁻¹. Intensity data were collected at 298(2) K on a Siemens CCD SMART diffractometer with Mo Ka radiation and a graphite monochromator. A total of 12563 unique reflections were measured and 3880 [R(int) = 0.0770] having $I > 2\sigma(I)$ were independent. The structure was solved by direct methods and refined by the full-matrix least-squares techniques on F2 with the SHELXTL program (3826 data and 460 parameters). Final R = 0.0747, $R_w = 0.2166$, and goodness-of-fit on $F^2 = 0.868$ (for all reflections, R = 0.0964, $R_w =$ (11) Bankwitz, U.; Sohn, H.; Powell, D. R.; West, R. J. Organomet. Chem.

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Figure 3. (a) Selected bond lengths (pm) of 1,1-dichloro-1-silaindene (1). b) Selected bond lengths (pm) and angles (deg) of 1,1-dilithio-1silaindene (2).

plane, and the more symmetrical complex [K(18-crown-6)]₂[η^5, η^5 - C_4Me_4Si ⁵ has a planar silole ring.

The ¹H, ¹³C, and ²⁹Si NMR spectra for 2^{15} and 3^{16} have essentially the same patterns and differ only slightly in chemical shifts for all three nuclei. It is noteworthy that the ²⁹Si chemical shifts for 2 and 3 are significantly downfield from that of 1 (5.92) and very close (29.19 and 30.44 ppm, respectively), consistent with significant π delocalization in the silicon-containing rings. The ⁷Li NMR spectra of a solution of 2 show only one peak (-0.20 ppm) over the temperature range +25 to -40 °C. These data, as in the case for NMR data obtained for the tetraphenylsilole dianions,^{3,4} do not permit unambiguous structural assignments in solution. Processes involving η^1, η^5 exchanges, possibly including LiCl, could explain the single peak in the 7Li NMR as could a static η^5 , η^5 structure. The latter seems less likely because of the location of the ⁷Li shift. Typically η^5 complexed lithium ions are found in the -4 to -9 ppm range.^{6b,17,18}

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Supporting Information Available: Details of the crystallographic analyses of 1 and 2 (13 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

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(15) NMR Study of 2: 1 (100 mg, 0.3 mmol) and Li (13 mg, 1.8 mmol) owder were placed in a 5 mm NMR tube with THF- d_8 (0.75 mL). After the NMR tube was sealed under vacuum, sonication of the NMR tube for 1 h gave a dark red solution. Selected data for 2: ¹H-NMR (THF-d₈, references; gave a dark for L^{-1} for a solution is selected data for L^{-1} . From $(111-a_8, \text{references})$, THF- $d_8 = 1.72 \text{ ppm}$ 0.99 (t, 2H), 1.91 (m, 2H), 1.73 (m, 2H), 2.99 (t, 2H), 7.85 (d, 1H), 7.45 (d, 2H), 7.37 (d, 1H), 7.03 (t, 2H), 6.77 (t, 1H), 6.42(t, 1H), 6.01 (t, 1H); ¹³C NMR (THF- $d_8, \text{reference}; \text{THF-}d_8 = 24.45 \text{ ppm}$ 13.99 (GV) 20.00 (CV) 20.00 (CV) 20.00 (CV) 11.00 (CV) 20.00 (CV) 11.00 (CV) 20.00 (C (CH₃), 23.56 (CH₂), 28.99 (CH₂), 34.86 (CH₂), 162.28 (C), 156.39 (C), 151.86 (C), 134.50 (C), 113.95 (C), 135.15 (CH), 129.29 (CH), 125.79 (CH), 120.63 (CH), 119.86 (CH), 115.07 (CH), 109.21 (CH); ²⁹Si NMR (THF-*d*₈, reference; ext. TMS = 0.00) 29.19.

(16) NMR Study of 3: 1 (60 mg, 0.18 mmol) and Na (25 mg, 1.08 mmol) were placed in a 5 mm NMR tube followed by THF- d_8 (0.75 mL). After the NMR tube was sealed under vacuum, sonication of the NMR tube for 48 h gave a dark red solution. Selected data for 3: ¹H-NMR (THF-d₈, reference; THF $d_8 = 1.72$ ppm) 0.95 (t, 3H), 1.42 (m, 2H), 1.57 (m, 2H), 2.91 (t, 2H), 8.04 (d, 1H), 7.49 (d, 2H), 7.7.29 (d, 1H), 7.01 (t, 2H), 6.71 (t, 1H), 6.37(t, 1H), 6.02 (t, 1H); ¹³C NMR (THF d_8 , reference; THF $d_8 = 24.45$ ppm) 14.80 (CH₂), 24.50 (CH₂), 30.12 (CH₂), 35.50 (CH₂), 166.80 (C), 159.61 (C), 152.85 (C), 135.61 (C), 116.63 (C), 136.54 (CH), 130.35 (CH), 126.82 (CH), 121.27 (CH), 120.56 (CH), 114.86 (CH), 109.62 (CH); ²⁹Si NMR (THF- d_8 , reference; ext. TMS = 0.00) 30.44.

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