

Supporting Information

for the Communication Entitled

Generation of Stannabenzenes and Their Properties

*Yoshiyuki Mizuhata, Naoya Noda, and Norihiro Tokitoh**

Institute for Chemical Research, Kyoto University, Gokasho, Uji, Kyoto 611-0011, Japan

General Procedure. All experiments were performed under an argon atmosphere unless otherwise noted. Solvents used for the reactions were purified by The Ultimate Solvent System (GlassContour Company).¹ ^1H NMR (300 MHz), ^{13}C NMR (76 MHz), and ^{119}Sn NMR (111 MHz) spectra were measured in CDCl_3 or C_6D_6 with a JEOL JNM-AL300 spectrometer. In ^1H NMR signals due to CHCl_3 (7.25 ppm) and $\text{C}_6\text{D}_5\text{H}$ (7.15 ppm) were used as references, and those due to CDCl_3 (77 ppm) and C_6D_6 (128 ppm) were used in ^{13}C NMR. ^{119}Sn NMR was measured with NNE technique using SnMe_4 as an external standard. Multiplicity of signals in ^{13}C NMR spectra was determined by DEPT technique. High-resolution mass spectral data were obtained on a JEOL JMS-SX102GC/MS spectrometer. WCC (wet column chromatography) was performed on Wakogel C-200. PTLC (preparative thin-layer chromatography) was performed with Merck Kieselgel 60 PF254 (Art. No. 7747). GLPC (gel permeation liquid chromatography) was performed on an LC-908 (Japan Analytical Industry Co., Ltd.) equipped with JAIGEL 1H and 2H columns (eluent: chloroform or toluene). All melting points were determined on a Yanaco micro melting point apparatus and are uncorrected. Elemental analyses were carried out at the Microanalytical Laboratory of the Institute for Chemical Research, Kyoto University. TbtSnX_3 and BbtSnX_3 were prepared according to the reported procedures of TbtSnCl_3 ² and used without sublimation. (1Z,4Z)-1,5-Diiodopenta-1,4-diene was prepared by iodination of 1,1-dibutyl-1-stannacyclohexa-2,5-diene.³

Preparation and isolation of (1Z,4Z)-1,5-dilithiopenta-1,4-diene (4). To a hexane solution (10 mL) of (1Z,4Z)-1,5-Diiodopenta-1,4-diene (245 mg, 0.766 mmol) was added *n*-butyllithium (1.49 M in hexane, 1.06 mL, 1.57 mmol) at $-50\text{ }^\circ\text{C}$. After stirring at the same temperature for 90 min, the resulting suspension was filtered with glass filter under Ar atmosphere. Filtered solid was washed with dried hexane several times, giving colorless powder of **4** (45.2 mg, 0.565 mmol, 74%). Although ^1H NMR of **4** in C_6D_6 (sealed) showed no signal due to its low solubility, exposure of its solution to air resulted in the formation of 1,4-pentadiene.

Synthesis of 5-H (detail for 5a-H). To a Et₂O solution (30 mL) of TbtSnX₃ (X = Cl or Br, 0.573 g, ca 0.737 mmol as X = Cl) was added **4** at –50 °C. After stirring for 1 h at the same temperature, the reaction mixture was warmed to room temperature. After removal of the solvent, hexane was added to the residue. The resulting suspension was filtered through Celite[®], and the solvent was removed. The residue was separated by GPLC (CHCl₃) to afford **5a-X** (111 mg, X: Cl/Br = 1/0.6). To a THF solution (15 mL) of **5a-X** (90 mg) was added lithium aluminum hydride (13 mg, 0.35 mmol) at 0 °C. After stirring for 1 h at the same temperature, ethyl acetate was added to the reaction mixture at 0 °C. After removal of the solvent, hexane was added to the residue. The resulting suspension was filtered through Celite[®], and the solvent was removed. This crude product was separated by WCC (hexane) to afford **5a-H** (74 mg, 0.10 mmol, 20% from **4**). Similarly, using BbtSnX₃ as starting materials, **5b-H** was isolated in 18% from **4**. **5a-H**: colorless crystals; m.p. 133 °C (dec.); ¹H NMR (300 MHz, C₆D₆, rt): δ 6.7-6.4 (s, 2H + m, 4H), 6.15 (t, ³J = 2.8 Hz, 1H, Sn–H), 2.88 (s, 2H), 2.16 (s, 2H), 1.44 (s, 1H), 0.19 (br s, 36H), 0.15 (s, 18H); ¹³C NMR (75 MHz, C₆D₆, rt): δ 151.45 (s×2), 144.33 (d), 143.74 (s), 144.33 (d), 133.76 (s), 126.24 (d), 126.04 (d), 35.08 (t), 32.47 (d), 30.03 (d), 0.88 (q), 0.40 (q), 0.19 (q); ¹¹⁹Sn NMR (111 MHz, C₆D₆, rt): δ –320.87; High resolution FAB-MS *m/z* calcd for C₃₂H₆₅Si₆¹²⁰Sn ([M–H]⁺): 737.2724, found: 737.2717. **5b-H**: colorless crystals; m.p. 115 °C (dec.); ¹H NMR (300 MHz, C₆D₆, rt): δ 6.7-6.2 (m, 4H), 6.46 (s, 2H), 6.17 (t, ³J = 3.2 Hz, 1H, Sn–H), 2.88 (m, 2H), 2.25 (s, 2H), 0.35 (s, 27H), 0.22 (s, 36H); ¹³C NMR (75 MHz, C₆D₆, rt): δ 151.73 (s×2), 145.94 (s), 145.04 (d), 137.82 (s), 126.95 (d), 126.35 (d), 35.63 (t), 34.05 (d), 22.27 (d), 5.71 (q), 1.42 (q); ¹¹⁹Sn NMR (111 MHz, C₆D₆, rt): δ –321.49; High resolution FAB-MS *m/z* calcd for C₃₅H₇₃Si₇¹²⁰Sn ([M–H]⁺): 809.3119, found: 809.3092. Anal. Calcd for C₃₅H₇₄Si₇Sn: C, 51.88; H, 9.21%. Found: C, 51.88; H, 9.25%.

Synthesis of 5-Br (detail for 5a-Br). A benzene (3.0 mL) solution of **5a-H** (70 mg, 0.095 mmol) and *N*-bromosuccinimide (19 mg, 0.11 mmol) was stirred for 1 h at room temperature. After removal of the solvent, hexane was added to the residue. The resulting suspension was filtered through Celite[®], and the solvent was removed to afford **5a-Br** (78 mg, 0.095 mmol, 100%). Similarly, using **5b-H** as starting materials, **5b-Br** was isolated in 88%. **5a-Br**: colorless crystals; m.p. 197 °C (dec.); ¹H NMR (300

MHz, CDCl₃, rt): δ 6.8-6.2 (s, 2H + m, 4H), 3.25 (m, 2H), 1.80 (s, 2H), 1.35 (s, 1H), 0.06 (br s, 36H), 0.04 (s, 18H); ¹³C NMR (75 MHz, CDCl₃, rt): δ 151.35 (br s), 151.19 (br s), 146.33 (d \times 2), 146.24 (s), 134.64 (s), 131.91 (d \times 2), 126.49 (d), 121.74 (d), 34.39 (t), 33.57 (d), 33.01 (d), 30.74 (d), 0.98 (q), 0.84 (q), 0.67 (q); ¹¹⁹Sn NMR (111 MHz, CDCl₃, rt): δ -179.165; High resolution FAB-MS m/z calcd for C₃₂H₆₅⁷⁹BrSi₆¹²⁰Sn ([M]⁺): 816.1900, found: 816.1907. **5b-Br**: colorless crystals; m.p. 151 °C (dec.); ¹H NMR (300 MHz, C₆D₆, rt): δ 7.00 (s, 2H), 6.69 (dt, ³ J = 13.0 Hz, ⁴ J = 1.5 Hz, 2H), 6.31 (dt, ³ J = 13.0 Hz, ³ J = 4.5 Hz, 2H), 2.72 (dt, ² J = 15.2 Hz, ³ J = 4.5 Hz, ⁴ J = 1.5 Hz, 2H), 2.19 (s, 2H), 0.34 (s, 27H), 0.27 (s, 36H); ¹³C NMR (75 MHz, C₆D₆, rt): δ 151.32 (s \times 2), 148.05 (s), 146.61 (d \times 2), 139.35 (s), 132.55 (d \times 2), 126.76 (d \times 2), 34.74 (d \times 2), 34.11 (t \times 2), 22.66 (s), 5.67 (q), 1.56 (q); ¹¹⁹Sn NMR (111 MHz, C₆D₆, rt): δ -184.38; High resolution FAB-MS m/z calcd for C₃₅H₇₃⁷⁹BrSi₆¹²⁰Sn ([M]⁺): 888.2302, found: 888.2287.

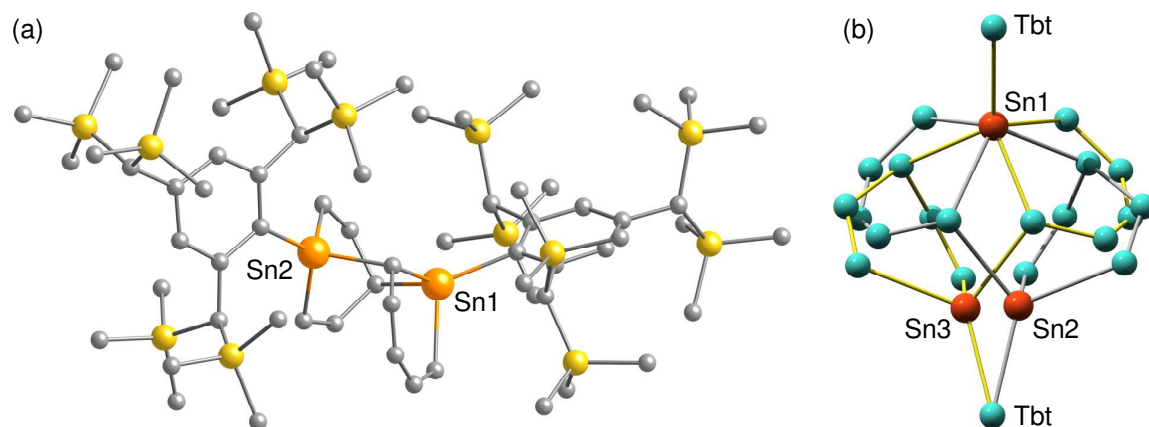
Crystal data for 5a-Br. C₃₂H₆₅BrSi₆Sn MW = 816.98; *triclinic*; space group $P\bar{1}$ (#2); a = 9.3740(2), b = 11.1189(2) Å, c = 21.3761(5) Å; α = 78.5572(9)°, β = 82.2289(16)°, γ = 76.0175(14)°; V = 2110.07(8) Å³; Z = 2; D_{calcd} = 1.286 g/cm³; μ = 1.742 mm⁻¹; $2\theta_{\text{max}}$ = 50°; T = 103 K; R_1 [$I > 2\sigma(I)$] = 0.0307; wR_2 (all data) = 0.0792; GOF = 1.091 for 17857 reflections and 379 parameters.

Generation of 3 (detail for 3a). In a glovebox filled with argon, **5a-Br** (40 mg, 0.049 mmol) was dissolved in hexane (15 mL, dried over K mirror and distilled by trap-to-trap method), and LDA (5.8 mg, 0.054 mmol) was added to the solution at -40 °C. After stirring for 0.5 h at the same temperature, the solvents were removed under reduced pressure and hexane was added to the residue. The resulting suspension was filtered through Celite®, and the solvent was removed. In the ¹H NMR of the crude mixture, almost quantitative formation of **6a** was suggested. The mixture was separated by GLPC (CHCl₃) to give **6a** (19 mg, 0.013 mmol, 53%). Similarly, using **5b-Br** as starting materials, **6b** was generated quantitatively. **6a**: colorless crystals; m.p. 165 °C (dec.); ¹H NMR (300 MHz, C₆D₆, rt): δ 7.72 (dd, J = 11.9, 6.0 Hz, 1H), 6.5-6.9 (m, 8H), 6.47 (d, J = 11.9 Hz, 1H), 6.39 (d, 6.0 Hz, 1H), 6.35 (d, 6.0 Hz, 1H), 5.65 (dd, J = 8.9, 6.0 Hz, 1H), 4.72 (dd, J = 4.9 Hz, 1H), 2.39 (s, 1H), 2.23 (s, 1H), 2.05 (s,

1H), 2.02 (s, 1H), 2.02 (d, 1H), 1.51 (s, 1H), 1.46 (s, 1H), 0.26 (s, 72H), 0.19 (s, 9H), 0.19 (s, 9H), 0.17 (s, 9H), 0.16 (s, 9H); ^{13}C NMR (75 MHz, C_6D_6 , rt): δ 152.67 (s), 152.36 (s), 151.96 (s), 151.46 (s), 148.08 (d), 146.93 (d), 145.04 (s), 144.33 (s), 142.39 (d), 140.02 (d), 138.69 (s), 133.87 (s), 132.41 (d), 130.74 (d), 128.98 (d), 127.43 (d), 126.88 (d), 122.54 (d), 122.33 (d), 122.16 (d), 43.28 (d), 33.85 (d \times 2), 32.91 (d), 32.28 (d), 30.85 (d), 30.74 (d), 15.90 (d), 1.65 (q), 1.42 (q), 1.23 (q), 1.15 (q), 1.08 (q), 1.07 (q), 0.98 (q), 0.96 (q); ^{119}Sn NMR (111 MHz, C_6D_6 , rt): δ -153, -235; High resolution TOF-MS (APPI) m/z calcd for $\text{C}_{64}\text{H}_{129}\text{Si}_{12}^{120}\text{Sn}_2$ ($[\text{M}+\text{H}]^+$): 1473.5369, found: 1473.5349. **6b**: colorless crystals; ^1H NMR (300 MHz, C_6D_6 , rt): δ 7.69 (dd, $^3J = 11.8$ Hz, $^3J = 7.4$ Hz, 1H), 7.07 (s, 2H), 7.00 (s, 2H), 6.8-7.0 (m, 2H), 6.70 (dd, $^3J = 11.6$ Hz, $^3J = 7.7$ Hz, 1H), 6.43-6.36 (m, 3H), 5.66 (dd, $^3J = 11.3$ Hz, $^3J = 6.7$ Hz, 1H), 4.75 (dd, $^3J = 7.4$ Hz, $^3J = 7.7$ Hz, 1H), 2.46 (s, 2H), 2.16 (d, $^3J = 7.4$ Hz, 1H), 2.14 (s, 2H), 0.40 (br s, 27H), 0.37 (br s, 27H), 0.32 (br s, 18H), 0.29 (br s, 54H); ^{13}C NMR (75 MHz, C_6D_6 , rt): δ 152.13 (s \times 2), 151.43 (s \times 2), 147.63 (d), 146.92 (s), 146.53 (d), 146.48 (d), 143.03 (s), 142.66 (d), 139.83 (d), 138.08 (s), 133.12 (d), 130.87 (d), 129.26 (d), 126.95 (d \times 2), 126.86 (d \times 2), 123.10 (d), 43.69 (d), 35.16 (d), 34.06 (d), 22.40 (s), 22.35 (s), 18.05 (d), 5.93 (q), 5.87 (q), 2.21 (q), 2.14 (q), 1.82 (q), 1.77 (q); ^{119}Sn NMR (111 MHz, C_6D_6 , rt): δ -159, -235; High resolution TOF-MS (APPI) m/z calcd for $\text{C}_{70}\text{H}_{145}\text{Si}_{14}^{120}\text{Sn}_2$ ($[\text{M}+\text{H}]^+$): 1617.6160, found: 1617.6268.

Crystal data for 6a. $C_{64}H_{128}Si_{12}Sn_2$ $MW = 1472.12$; *monoclinic*; space group $P2_1/a$ (#14); $a = 19.6933(10)$, $b = 12.9267(6)$ Å, $c = 33.0686(19)$ Å; $\beta = 96.509(3)^\circ$; $V = 8364.0(7)$ Å³; $Z = 4$; $D_{\text{calcd}} = 1.169$ g/cm³; $\mu = 0.801$ mm⁻¹; $2\theta_{\text{max}} = 50^\circ$; $T = 103$ K; $R_1[I > 2\sigma(I)] = 0.1464$; wR_2 (all data) = 0.3496; GOF = 1.107 for 61360 reflections and 703 parameters.

Figure S1. (a) Ball and stick model of **6a** (major part). Hydrogen atoms were omitted for clarity. (b) Disorders on the central moiety of **6a** (major:minor = 0.66:0.34).



References

- 1 Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518.
- 2 Matsubishi, Y.; Tokitoh, N.; Okazaki, R.; Goto, M.; Nagase, S. *Organometallics* **1993**, *12*, 1351.
- 3 Ashe III, A. J.; Shu, P. *J. Am. Chem. Soc.* **1971**, *93*, 1804.