

Supplementary Information for the communication entitled “Formation of the first monoanion and dianion of stannole”

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Experimental

(a) *Synthesis of Bi(1,1-stannole) 2.* To a THF (30 mL) solution of 1-bromo-4-dibromophenylstannyl-1,2,3,4-tetraphenyl-1,3-butadiene (**1**) (2030 mg, 2.56 mmol) was added *t*-butyllithium (1.60 M in pentane; 3.2 mL, 5.12 mmol) at $-100\text{ }^{\circ}\text{C}$. After warming to room temperature over 4 h, the solvent was evaporated. The residue was subjected to WCC (SiO_2 , hexane : ethyl acetate = 10 : 1) to afford bi(1,1-stannole) **2** (826 mg, 58%) together with 1-*t*-butyl-1-phenylstannole **3** (103 mg, 7%). **2**: mp $209\text{ }^{\circ}\text{C}$ (decomp)(recrystallized from methylene chloride+methanol). ^1H NMR(400 MHz, CDCl_3): 6.73-6.80(m, 8H), 6.84-6.89(m, 8H), 6.94-7.00(m, 24H), 7.13-7.20(m, 4H), 7.24-7.27(m, 6H); ^{13}C NMR(101 MHz, CDCl_3): 125.36(d), 125.88(d), 127.31(d), 127.91(d), 129.02(d), 129.55(d), 130.45(d), 137.35(d), 138.69(s), 140.51(s), 142.44(s), 145.89(s), 154.30(s); ^{119}Sn NMR(149 MHz, CDCl_3): $-99.3(^1J(^{119}\text{Sn}-^{117}\text{Sn})=2865\text{ Hz})$. Anal. Calcd for $\text{C}_{68}\text{H}_{50}\text{Sn}_2$: C, 73.94; H, 4.56. Found: C, 73.30; H, 4.31. **3**: mp $160\text{--}161\text{ }^{\circ}\text{C}$ (decomp)(recrystallized from methylene chloride+methanol). ^1H NMR(400 MHz, CDCl_3): 1.37(s, 9H), 6.79-6.80(m, 4H), 6.89-6.97(m, 12H), 7.03-7.06(m, 4H), 7.30-7.37(m, 3H), 7.48-7.61(m, 2H); ^{13}C NMR(101 MHz, CDCl_3): 31.11(q), 32.70(s), 124.98(d), 125.66(d), 127.20(d), 127.78(d), 128.77(d), 129.00(d), 129.23(d), 130.40(d), 137.18(d), 139.88(s), 140.77(s), 143.40(s), 144.61(s), 155.15(s); ^{119}Sn NMR(149 MHz, CDCl_3): -59.9 . Anal. Calcd for $\text{C}_{38}\text{H}_{34}\text{Sn}$: C, 74.90; H, 5.62. Found: C, 74.90; H, 5.58.

(b) Formation of Stannole Monoanion 5 by the Reaction of 2 with Butyllithium.

To a THF (4 mL) solution of **2** (145 mg, 0.14 mmol) was added butyllithium (1.56 M in hexane; 0.18 mL, 0.28 mmol) at $-80\text{ }^{\circ}\text{C}$. After warming to room temperature over 3h, the reaction mixture was treated with methyl iodide (0.1 mL, 1.61 mmol). After removal of volatile substances, the residue was subjected to WCC (Al_2O_3 , hexane : ethyl acetate = 10 : 1) to afford 1-methyl-1-phenylstannole **4** (32 mg, 42%). **4**: mp 139-140 $^{\circ}\text{C}$ (decomp)(recrystallized from methylene chloride+methanol). ^1H NMR(400 MHz, CDCl_3): 0.86(s, 3H), 6.79-6.88(m, 8H), 6.94-7.06(m, 12H), 7.34-7.41(m, 3H), 7.51-7.67(m, 2H); ^{13}C NMR(101 MHz, CDCl_3): $-9.06(\text{q})$, 125.19(d), 125.77(d), 127.30(d), 127.80(d), 128.76(d), 129.15(d), 129.20(d), 130.29(d), 136.45(d), 139.50(s), 140.71(s), 142.55(s), 143.62(s), 154.59(s); ^{119}Sn NMR(149 MHz, CDCl_3): -38.8 . Anal. Calcd for $\text{C}_{35}\text{H}_{28}\text{Sn}$: C, 74.10; H, 4.98. Found: C, 73.84; H, 4.96.

(c) Estimation of Generation Efficiency of 5 by ^1H NMR. After treatment of **2** (85 mg, 0.077 mmol) with *t*-butyllithium (1.50 M in hexane; 0.10 mL, 0.15 mmol) at $-100\text{ }^{\circ}\text{C}$, the reaction mixture was warmed to room temperature. To the reaction mixture was added methyl iodide (0.1 mL, 1.61 mmol) at room temperature. After warming to room temperature followed by removal of a solvent, the crude mixture (89 mg) soluble to methylene chloride was collected and evaporated. After addition of *p*-dimethoxybenzene (9 mg, 0.062 mmol) as an internal standard, the yields of **3** and **4** are estimated to be 76 and 86%, respectively, by ^1H NMR.

(d) Reduction of 2 by Lithium. To a mixture of **2** (300 mg, 0.27 mmol) and lithium (21 mg, 3.06 mmol) was added THF (10 mL) at room temperature and then the reaction mixture was stirred for 30 min. After addition of methyl iodide (0.1 mL, 1.61 mmol) to the reaction mixture, insoluble materials were filtered off. After removal of volatile substances, the residue was subjected to WCC (Al_2O_3 , hexane : ethyl acetate = 10 : 1) to afford **4** (179 mg, 58%) and **6** (16 mg, 6%).

(e) *Formation of Stannole Dianion 7 by Reduction of 2 with Lithium.* To a mixture of **2** (150 mg, 0.14 mmol) and lithium (24 mg, 3.47 mmol) was added THF (5 mL) at room temperature. After refluxing for 1.5 h, the reaction mixture was treated with methyl iodide (0.1 mL, 1.61 mmol) at room temperature. After filtration followed by removal of the solvent, the residue was recrystallized from methylene chloride and methanol to give **6** (32 mg, 23%). **7**: ^1H NMR(400 MHz, THF- C_6D_6): 6.50(t, $J=7$ Hz, 2H), 6.67-6.85(m, 14H), 7.04(d, $J=8$ Hz, 4H); ^{13}C NMR(101 MHz, THF- C_6D_6): 118.47(d), 121.56(d), 126.01(d), 126.09(d), 128.14(d), 133.12(d), 134.35(s), 147.35(s), 153.62(s), 184.58(s); ^{119}Sn NMR(149 MHz, THF- C_6D_6): 186.7.

Although $^nJ(\text{Sn}-^{13}\text{C})$ couplings were observed in ^{13}C NMR spectra as satellite signals, each $^nJ(^{119}\text{Sn}-^{13}\text{C})$ and $^nJ(^{117}\text{Sn}-^{13}\text{C})$ could not be estimated because of broadening.