Synthesis and Structures of Bi(1,1-stannole)s

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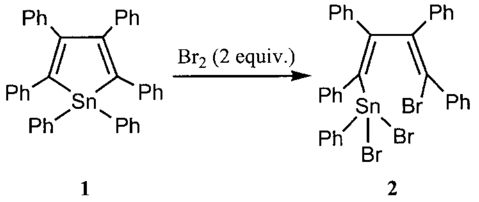
The synthesis and structures of bi(1,1-stannole)s are described. Treatment of 1-bromo-4-(dibromophenylstannyl)-1,3-butadiene with *tert*-butyllithium gives the bi(1,1-stannole) having a phenyl group on each tin atom, whereas treatment of 1-bromo-4-(tribromostannyl)-1,3-butadiene with phenyl- or bulky alkyllithiums gives the bi(1,1-stannole) having a phenyl or an alkyl group on each tin atom. The X-ray analysis of the *tert*-butyl-substituted bi(1,1-stannole) is also described. All bi(1,1-stannole)s display two shoulder absorption bands due to π–π^* and σ–π^* transitions.

Introduction

Group 14 metalloles,[1] or metallacyclopentadienes, have attracted much attention because of interest in them as a possible precursor for the preparation of conjugated polymers having unique electronic structures[2,3] as well as the potential aromaticity of their anions.[4] Since the successful synthesis of some oligo(1,1-silole)s[5,6] and poly(1,1-silole)s, they have been applied to organic electroluminescent (EL) devices.[7,8] Most recently, poly(1,1-germole) has also been reported.[9] In contrast to the silicon and germanium analogs, however, attempts to prepare oligo- and poly(1,1-stannole)s are still unknown. Although the synthesis and some simple reactions of stannoles have been reviewed,[1] even the synthesis of bi(1,1-stannole) has not yet been successful.

In the course of our studies on organotin compounds,[10] we have already reported that bromination of hexaphenylstannole (**1**) gives the ring-opened halogenated product **2** (Scheme 1).[11,12] We have also preliminarily reported that debrominative cyclization of **2** affords the bi(1,1-stannole).[13] We report herein the synthesis, structures, and physical properties of some bi(1,1-stannole)s.



Scheme 1.

Results and Discussion

Synthesis of Bi(1,1-stannole) 3

Treatment of **2** with two equivalents of *tert*-butyllithium in THF at –100 °C gave a yellow solution. After usual workup, the mixture was chromatographed to give bi(1,1-stannole) **3** as yellow crystals in 58% yield together with stannole **4** (7%) (Scheme 2). To the best of our knowledge, compound **3** is the first example of bi(1,1-stannole). Two possible mechanisms for the formation of **3** are shown in Scheme 2. The initial step of the reaction is the formation of 1-bromo-1-phenylstannole (**5**), which reacts further with *tert*-butyllithium to give the stannole anion **6** or the stannole radical **7**. The stannole anion **6** then reacts with **5** to give **3**, while the stannole radical **7** couples to itself to also give **3**. Product **4** is formed by nucleophilic substitution at the tin atom of **5** by *tert*-butyllithium. Trapping of the intermediary ionic species **6** by addition of methyl iodide or chlorotrimethylstannane, expecting to obtain a methylated or a stannylated product, failed and the bi(1,1-stannole) **3** was obtained in 71 or 77% yield, respectively. Therefore, a radical mechanism for the formation of **3** is more likely, although the ionic mechanism cannot be ruled out entirely. The yield of **3** was improved (82%) when the reaction was carried out in diethyl ether, although the reason for the solvent-dependent product yield is not clear.

Synthesis of Bi(1,1-Stannole)s Having Various Substituents on the Tin Atom

The synthesis of other bi(1,1-stannole)s having various substituents on the tin atom was achieved by the reaction of 1-bromo-4-(tribromostannyl)-1,3-butadiene (**8**) with lithium reagents.

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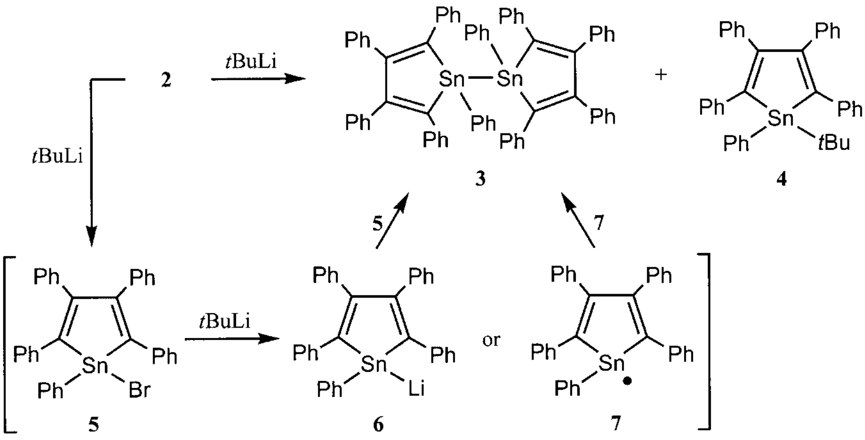
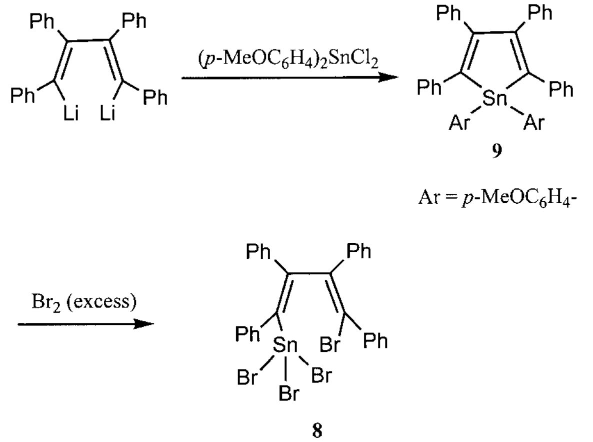


Scheme 2.

Synthesis of 1-Bromo-4-(tribromostannyl)-1,3-butadiene (8)

We attempted to synthesize **8** by the reaction of **1** or **2** with bromine. However, the reaction of **2** with bromine gave a complex mixture. Reaction of hexaphenylstannole (**1**) with excess bromine also gave a complex mixture containing 1,4-dibromo-1,2,3,4-tetraphenylbutadiene.[14]

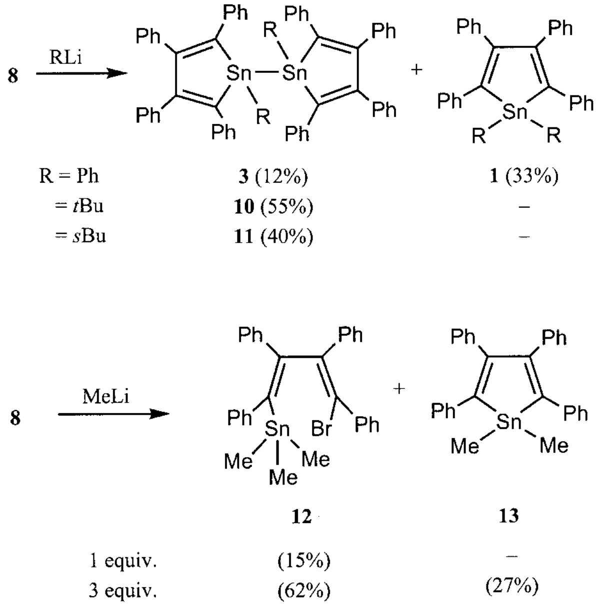
Since the *p*-methoxyphenyl group on the tin atom is known to be easily removed by halogenation,[15] the reaction of 1,1-di(*p*-methoxyphenyl)stannole (**9**) with bromine was examined. Compound **9** was prepared by the reaction of 1,4-dilithio-1,2,3,4-tetraphenylbutadiene with dichlorodi(*p*-methoxyphenyl)stannane[16] in 58% yield (Scheme 3). Reaction of **9** with bromine (1 equiv.) at –40 °C gave a complex mixture, and treatment of **9** with bromine (2 equiv.) at –20 °C afforded 1,4-dibromo-1,2,3,4-tetraphenylbutadiene (41%).[14] However, the reaction of **9** with excess bromine (10 equiv.) at room temperature gave **8** (96%). The structure of **8** was determined by NMR spectroscopy and elemental analysis (Scheme 3).



Scheme 3.

Reaction of 8 with Lithium Reagents: Synthesis of Bi(1,1-stannole)s

Treatment of **8** with phenyllithium (2 equiv.) afforded bi(1,1-stannole) **3** (12%) and hexaphenylstannole **1** (33%; Scheme 4). The preferential formation of **1** to **3** may be ascribed to the size of the lithium reagent. In fact, the reaction of **8** with bulkier *tert*-butyllithium (2 equiv.) rather than phenyllithium gave bi(1,1-stannole) **10** having a *tert*-butyl group on each tin atom as the sole product in 55% yield (Scheme 4). Reaction of **7** with *sec*-butyllithium (2 equiv.), a moderately bulky reagent, gave a bi(1,1-stannole) **11** having a *sec*-butyl group on each tin atom as a 1:1 diastereomeric mixture[17] in a relatively good yield (40%; Scheme 4). The diastereomeric ratio was estimated by signal intensities (δ = –60.59 and –60.57 ppm) in the ^{119}Sn NMR spectrum. Contrary to the bulky lithium reagent, the reaction of less bulky methyllithium (1 equiv.) with **8** gave 4-bromo-1,2,3,4-tetraphenyl-1-(trimethylstannyl)-1,3-butadiene (**12**) in 15% yield. Methyllithium would directly attack the tin to afford trimethyl derivative **12** (Scheme 4). Reaction of **8** with methyllithium (3 equiv.) gave **12** (62%) and 1,1-dimethylstannole **13** (27%; Scheme 4).



Scheme 4.

Structures of 3 and 10

Slow evaporation of the solvent from chloroform solutions of **3** and **10** gave X-ray quality crystals. The structure of **3** has been reported previously.[13] Because of the symmetrical structures of **3** and **10** with respect to the Sn–Sn bond, only a half moiety was refined. The ORTEP drawing of **10**, with selected bond lengths and angles, is shown in Figure 1. The length of the Sn–Sn bond is quite normal[18] at 2.7822(7) Å [2.7844(7) Å for **3**].[13] Each stannole ring has a nearly planar structure and is oriented in an *anti* fashion through the Sn–Sn bond probably due to steric reasons. The angle between the stannole plane and the Sn–Sn bond is 67° for **10** (74° for **3**).

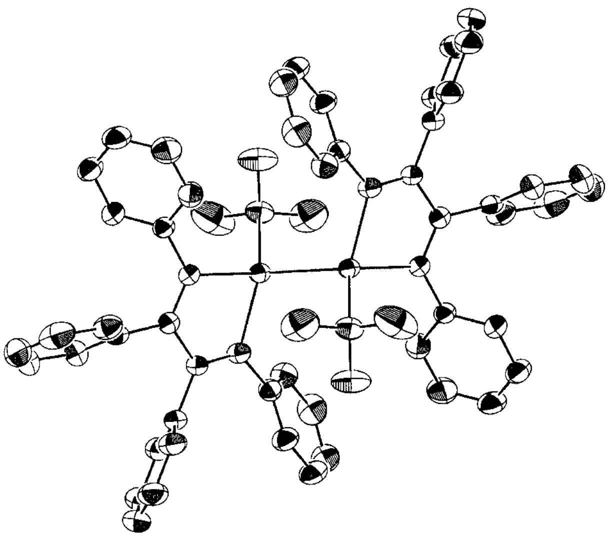


Figure 1. ORTEP drawing of **10** with thermal ellipsoid plots (40% probability for non-hydrogen atoms). Selected bond lengths [Å] and angles [°]: Sn(1)A–Sn(1)B 2.7822(7), Sn(1)A–C(1) 2.143(4), C(1)–C(2) 1.353(5), C(2)–C(3) 1.506(5), C(3)–C(4) 1.352(5), Sn(1)A–C(4) 2.157(4); C(1)–Sn(1)A–C(4) 83.28(14).

Spectroscopic Properties

In the ^{119}Sn NMR spectrum, each central tin atom of the compounds with the stannole skeleton resonates in the range from δ = –100 to –45ppm, in the same region as that of 1,1,2,3,4,5-hexaphenylstannole (δ = –88.7 ppm).[11] The tin atoms of alkyl-substituted bi(1,1-stannole)s **10** and **11** resonate to higher field than that of **3**, as is observed in normal distannanes (δ = –108.7 and –144.7 ppm for $Me_3SnSnMe_3$[19] and $Ph_3SnSnPh_3$,[20] respectively). The $^{1}J_{^{119}Sn,^{117}Sn}$ coupling constant of 2865 Hz for **3** is a normal value for distannanes (cf. 2748 Hz for $Bu_3SnSnBu_3$).[19] The UV/Vis absorption spectra for **3**, **10**, and **11** are shown in Figure 2. All bi(1,1-stannole)s display two shoulder absorption bands at around 320 and 370 nm. The latter band can be assigned to the π–π* transition of the stannole ring because a similar absorption band is found in 1,1,2,3,4,5-hexaphenylstannole (**1**; λ_{max} = 355 nm).[21] The π–π* transition of group 14 metalloles is observed in the same region, at around 360 nm, because the contributions of the diene moiety to both HOMO and LUMO are predominant rather than that of the metal moiety.[21] The shorter wavelength band can be assigned to the transition from σ(Sn–Sn) to π*(diene) because the corresponding band is absent in **1**. This absorption (320 nm) is red-shifted compared to that of a bi(1,1-silole) (300 nm)[7] because of the higher energy level of a σ(Sn–Sn) bond than that of a σ(Si–Si) bond.

Conclusions

Several bi(1,1-stannole)s combining two stannacyclopentadienyl units through an Sn–Sn bond have been synthe-

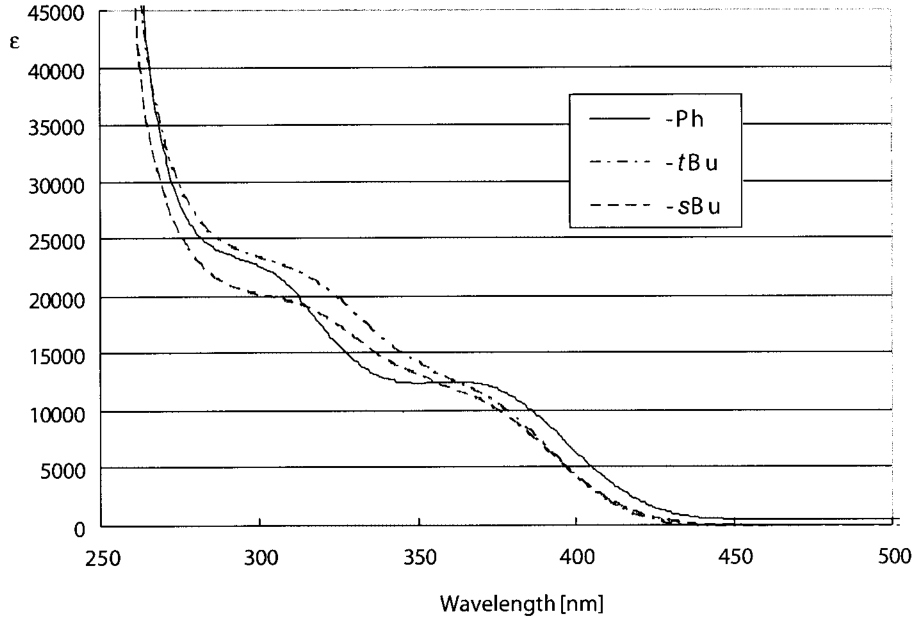


Figure 2. UV/Vis spectra of bi(1,1-stannole)s **3**, **10**, and **11**.

sized and characterized. The product yield in the formation of bi(1,1-stannole) by the reaction of 1-bromo-4-(tribromophenylstannyl)-1,3-butadiene with lithium reagent is dependent on the size of the lithium reagent used. The X-ray analysis of bi(1,1-stannole) shows a symmetrical structure with respect to the Sn–Sn bond. All bi(1,1-stannole)s display two shoulder absorption bands due to π–π^* and σ–π^* transitions.

Experimental Section

General Procedures: All reactions were carried out under argon. THF and diethyl ether used in the syntheses were distilled from sodium benzophenone ketyl under argon before use. ^{1}H (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded on a Bruker AM-400 or an ARX-400 spectrometer in $CDCl_3$ with tetramethylsilane as an internal standard. Although $^{n}J_{\mathrm{Sn},^{13}\mathrm{C}}$ couplings were observed in the ^{13}C NMR spectra as satellite signals, most of the $^{n}J_{^{119}\mathrm{Sn}\text{-}^{13}\mathrm{C}}$ and $^{n}J_{^{117}\mathrm{Sn}\text{-}^{13}\mathrm{C}}$ couplings could not be estimated separately because of line broadening. The multiplicities of the signals in the ^{13}C NMR spectra given in parentheses were deduced from DEPT spectra. ^{119}Sn NMR (149 MHz) spectra were recorded on a Bruker ARX-400 spectrometer in $CDCl_3$ with tetramethylstannane as an external standard. Column chromatography was carried out with Merck Kieselgel 60 (SiO_2). All melting points were determined on a Mitamura Riken Kogyo MEL-TEMP apparatus and are uncorrected. Electronic spectra were recorded on a JASCO V-560 UV/Vis spectrometer. Elemental analyses were carried out at the Microanalytical Laboratory of Molecular Analysis and Life Science Center, Saitama University.

Preparation of Bi(1,1-stannole) 3. (a) Method A (in THF): *tert*-Butyllithium (1.60 M in pentane; 3.2 mL, 5.12 mmol) was added at –100 °C to a THF (30 mL) solution of 1-bromo-4-(dibromophenylstannyl)-1,2,3,4-tetraphenyl-1,3-butadiene (**2**; 2030 mg, 2.56 mmol). After warming to room temperature over 4 h, the solvent was evaporated. The residue was subjected to column chromatography (hexane/ethyl acetate = 10:1) to afford bis(1,2,3,4,5-pentaphenylstannacyclopentadienyl) (**3**; 826 mg, 58 %) and 1-*tert*-butyl-1,2,3,4,5-pentaphenylstannole (**4**; 103 mg, 7 %).

3: M.p. 209 °C (decomp.) (recrystallized from dichloromethane/methanol). ^{1}H NMR: δ = 6.73–6.80 (m, 8 H), 6.84–6.89 (m, 8 H), 6.94–7.00 (m, 24 H), 7.13–7.20 (m, 4 H), 7.24–7.27 (m, 6 H) ppm. ^{13}C NMR: δ = 125.4 (d), 125.9 (d), 127.3 (d), 127.9 (d), 129.0 (d, $J_{\mathrm{Sn,C}}$ = 53 Hz), 129.6 (d, $J_{\mathrm{Sn,C}}$ = 22 Hz), 130.5 (d), 137.4 (d, $J_{\mathrm{Sn,C}}$ = 10, 46 Hz), 138.7 (s), 140.5 (s, $J_{\mathrm{Sn,C}}$ = 61 Hz), 142.4 (s, $J_{\mathrm{Sn,C}}$ = 47 Hz), 145.9 (s, $J_{\mathrm{Sn,C}}$ = 37, 334, 350 Hz), 154.3 (s, $J_{\mathrm{Sn,C}}$ = 22, 81 Hz) ppm. ^{119}Sn NMR: δ = –99.3 ppm ($^{1}J_{^{119}\mathrm{Sn},^{117}\mathrm{Sn}}$ = 2865 Hz). $C_{68}H_{50}Sn_2$ (1104.6): calcd. C 73.94, H 4.56; found C 73.30, H 4.31.

4: M.p. 160–161 °C (decomp.) (recrystallized from dichloromethane/methanol). ^{1}H NMR: δ = 1.37 (s, 9 H, $J_{\mathrm{Sn,H}}$ = 75, 78 Hz), 6.79–6.80 (m, 4 H), 6.89–6.97(m, 12 H), 7.03–7.06 (m, 4 H), 7.30–7.37 (m, 3 H), 7.48–7.61 (m, 2 H) ppm. ^{13}C NMR: δ = 31.1 (q), 32.7 (s), 125.0 (d), 125.7 (d), 127.2 (d), 127.8 (d), 128.8 (d), 129.0 (d), 129.2 (d), 130.4 (d), 137.2 (d), 139.9 (s), 140.8 (s), 143.4 (s), 144.6 (s), 155.2 (s) ppm. ^{119}Sn NMR: δ = –59.9 ppm. $C_{38}H_{34}Sn$ (609.42): calcd. C 74.90, H 5.62; found C 74.90, H 5.58.

Method B (in Diethyl Ether): *tert*-Butyllithium (1.50 M in pentane; 3.4 mL, 5.10 mmol) was added at –100 °C to a diethyl ether (40 mL) solution of **2** (1999 mg, 2.52 mmol). After warming to room temperature over 4 h, the solvent was evaporated. The residue was subjected to column chromatography (ethyl acetate) followed by recrystallization from hexane and dichloromethane to afford **3** (1141 mg, 82 %).

Attempt to Trap Intermediary Ionic Species with Methyl Iodide: *tert*-Butyllithium (1.48 M in pentane; 0.29 mL, 0.43 mmol) was added to a diethyl ether (4 mL) solution of **2** (114 mg, 0.14 mmol) at –100 °C. The color of the solution immediately turned yellow. Methyl iodide (0.05 mL, 0.80 mmol) was added to this solution. After warming to room temperature over 7 h, the solvent was evaporated. Recrystallization from hexane and dichloromethane gave **3** (56 mg, 71 %).

Attempt to Trap Intermediary Ionic Species with Chlorotrimethylstannane: *tert*-Butyllithium (1.60 M in pentane; 0.24 mL, 0.38 mmol) was added to a diethyl ether (4 mL) solution of **2** (98 mg, 0.12 mmol) at –100 °C and a diethyl ether (2 mL) solution of chlorotrimethylstannane (30 mg, 0.15 mmol) was then added. After warming to room temperature over 4 h, the solvent was evaporated. Recrystallization from hexane and dichloromethane gave **3** (53 mg, 77 %).

Preparation of 1,1-Di(*p*-methoxyphenyl)-2,3,4,5-tetraphenylstannole (9): A suspension of diphenylacetylene (4.40 g, 24.7 mmol) and lithium (171 mg, 24.7 mmol) in diethyl ether (17 mL) was stirred for 4 h at room temperature. A THF (15 mL) solution of di(*p*-methoxyphenyl)dichlorostannane[16] (4.11 g, 10.2 mmol) was added to the resulting suspension and the mixture was refluxed for 3 h. After removal of solvents, any material insoluble in dichloromethane was filtered off. After evaporation, the residue was subjected to column chromatography (hexane/ethyl acetate = 10:1) to give **9** (4.035 g, 58 %). M.p. 200 °C (decomp.) (recrystallized from dichloromethane/hexane). ^{1}H NMR: δ = 3.81 (s, 6 H), 6.80–6.86 (m, 4 H), 6.89 (d, J = 8 Hz, 4 H), 6.92–7.05 (m, 16 H), 7.50 (d, J = 8 Hz, 4 H) ppm. ^{13}C NMR: δ = 55.0 (q), 114.9 (d, $J_{\mathrm{Sn,C}}$ = 58 Hz), 125.3 (d), 125.8 (d), 127.3 (d), 127.8 (d), 128.3 (s), 129.3 (d, $J_{\mathrm{Sn,C}}$ = 22 Hz), 130.3 (d), 138.3 (d, $J_{\mathrm{Sn,C}}$ = 46 Hz), 140.7 (s, $J_{\mathrm{Sn,C}}$ = 68 Hz), 142.5 (s, $J_{\mathrm{Sn,C}}$ = 45 Hz), 143.0 (s), 154.4 (s, $J_{\mathrm{Sn,C}}$ = 89 Hz), 160.7 (s) ppm. ^{119}Sn NMR: δ = –79.9 ppm. $C_{40}H_{34}O_2Sn$ (665.44): calcd. C 72.20, H 5.15; found C 72.30, H 4.93.

Reaction of 9 with Bromine (2 equiv.): A carbon tetrachloride (8 mL) solution of bromine (0.02 mL, 0.39 mmol) at –20 °C was added to a carbon tetrachloride (7 mL) solution of **9** (134 mg, 0.19 mmol). After warming to room temperature, the solvent was evaporated. The residue was recrystallized from dichloromethane and methanol to give 1,4-dibromo-1,2,3,4-tetraphenylbutadiene (39 mg, 41 %).[14]

Reaction of 9 with Bromine (excess): A carbon tetrachloride (8 mL) solution of bromine (0.89 mL, 17.3 mmol) was added at room temperature to a dichloromethane (15 mL) solution of **9** (1200 mg, 1.74 mmol). The residue was recrystallized from dichloromethane and methanol to give 1-bromo-1,2,3,4-tetraphenyl-4-(tribromostannyl)-1,3-butadiene (**8**; 1328 mg, 96 %). M.p. 167–168 °C (decomp.) (recrystallized from dichloromethane/hexane). ^{1}H NMR: δ = 7.06–7.16 (m, 4 H), 7.20–7.39 (m, 14 H), 7.48–7.53 (m, 2 H) ppm. ^{13}C NMR: δ = 128.0 (d), 128.1 (d), 128.2 (d), 128.3 (d), 128.56 (d), 128.58 (d), 128.9 (d), 129.0 (d), 129.8 (d), 129.9 (d), 130.1 (d), 130.8 (d), 136.4 (s), 136.6 (s, $J_{\mathrm{Sn,C}}$ = 10 Hz), 136.8 (s), 138.8 (s), 141.0 (s, $J_{\mathrm{Sn,C}}$ = 67 Hz), 144.1 (s), 156.69 (s, $J_{\mathrm{Sn,C}}$ = 61 Hz) ppm. ^{119}Sn NMR: δ = –285.4 ppm. $C_{28}H_{20}Br_4Sn$ (794.78): calcd. C 42.32, H 2.54; found C 42.65, H 2.50.

Reaction of 8 with Phenyllithium: Phenyllithium (0.88 M in cyclohexane; 0.20 mL, 0.18 mmol) was added at –80 °C to a THF (3 mL) solution of **7** (70 mg, 0.09 mmol). After warming to room temperature over 3.5 h, the volatile substances were removed. After filtration of material insoluble in dichloromethane, the filtrate was subjected to column chromatography (hexane/ethyl acetate = 10:1) to afford **1** (18 mg, 33%) and **3** (6 mg, 12%).

Reaction of 8 with *tert*-Butyllithium. Formation of Bi(1,1-stannole) 10: *tert*-Butyllithium (1.43 M in pentane; 1.1 mL, 1.57 mmol) was added at –95 °C to a THF (10 mL) solution of **8** (408 mg, 0.51 mmol). After warming to room temperature over 3 h, the volatile substances were removed. After removal of material insoluble in dichloromethane by filtration, the filtrate was recrystallized from dichloromethane and methanol to give bis(1-*tert*-butyl-2,3,4,5-tetraphenylstannacyclopentadienyl) (**10**; 150 mg, 55%). M.p. 270–300 °C (decomp.) (recrystallized from dichloromethane). ^{1}H NMR: δ = 1.10 (s, 18 H, $J_{\mathrm{Sn,H}}$ = 85 Hz), 6.80–6.84 (m, 8 H), 6.87–7.04 (m, 32 H) ppm. ^{13}C NMR: δ = 31.6 (q), 35.2 (s), 124.9 (d), 125.6 (d), 127.2 (d), 127.7 (d), 129.6 (d), 130.7 (d), 140.9 (s), 143.5 (s), 148.5 (s), 154.2 (s) ppm. ^{119}Sn NMR: δ = –46.4 ppm. $C_{64}H_{58}Sn_2$ (1064.6): calcd. C 72.21, H 5.49; found C 71.54, H 5.37. The $J_{\mathrm{Sn,Sn}}$ and $J_{\mathrm{Sn,C}}$ satellites were not observed because of low solubility.

Reaction of 8 with *sec*-Butyllithium: *sec*-Butyllithium (0.96 M in pentane; 0.53 mL, 0.51 mmol) was added at –95 °C to a THF (3 mL) solution of **8** (136 mg, 0.17 mmol). After warming to room temperature over 7 h, the volatile substances were removed. After removal of material insoluble in dichloromethane by filtration, the filtrate was recrystallized from diethyl ether to give a 1:1 diastereomeric mixture of bis(1-*sec*-butyl-2,3,4,5-tetraphenylstannacyclopentadienyl) (**11**; 37 mg, 40%). M.p. 230–233 °C (decomp.) (recrystallized from dichloromethane/methanol). ^{1}H NMR: δ = 0.77 (t, J = 7 Hz, 6 H), 1.03–1.26 (m, 6 H), 1.47–1.58 (m, 4 H), 2.06–2.12 (m, 2 H), 6.76–6.78 (m, 8 H), 6.84–6.87 (m, 8 H), 6.91–6.95 (m, 16 H), 6.98–7.02 (m, 4 H) ppm. ^{13}C NMR: δ = 14.5 (q), 19.7 (q), 19.7 (q), 30.4 (t), 32.1 (d), 124.9 (d), 125.6 (d), 127.2 (d), 127.7 (d), 129.3 (d), 129.3 (d), 130.6 (d), 141.0 (s), 143.5 (s), 148.6 (s), 148.8 (s), 153.7 (s), 153.8 (s) ppm. ^{119}Sn NMR: δ = –60.59, –60.57 ppm. $C_{64}H_{58}Sn_2$ (1064.62): calcd. C 72.21, H 5.49; found C 71.58, H 5.46.

Reaction of 8 with Methyllithium (1 equiv.): Methyllithium (1.02 M in diethyl ether; 0.2 mL, 0.20 mmol) was added at –100 °C to a THF (5 mL) solution of **8** (163 mg, 0.21 mmol). After warming to room temperature, the volatile substances were removed. After removal of material insoluble in dichloromethane by filtration, the filtrate was subjected to column chromatography (hexane/ethyl acetate = 10:1) to give 4-bromo-1,2,3,4-tetraphenyl-1-(trimethylstannyl)-1,3-butadiene (**12**; 19 mg, 15%). M.p. 118 °C (decomp.) (recrystallized from dichloromethane/hexane). ^{1}H NMR: δ = 0.13 (s, 9 H, $J_{\mathrm{Sn,H}}$ = 52, 54 Hz), 6.96–7.10 (m, 9 H), 7.13–7.23 (m, 9 H), 7.36–7.40 (m, 2 H) ppm. ^{13}C NMR: δ = –7.0 (q), 124.3 (s), 124.9 (d), 126.4 (d), 127.3 (d), 127.4 (d), 127.7 (d), 127.8 (d), 127.9 (d), 128.0 (d), 128.2 (d), 130.0 (d), 130.1 (d), 130.5 (d), 138.7 (s), 139.7 (s), 140.3 (s), 144.4 (s), 145.3 (s), 148.5 (s), 152.4 (s) ppm. ^{119}Sn NMR: δ = –36.2 ppm. $C_{31}H_{29}BrSn$ (600.20): calcd. C 62.04, H 4.87; found C 62.04, H 4.79.

Reaction of 8 with Methyllithium (3 equiv.): Methyllithium (1.02 M in diethyl ether; 0.4 mL, 0.41 mmol) was added at –90 °C to a THF (4 mL) solution of **8** (101 mg, 0.13 mmol). After warming to room temperature, the volatile substances and material insoluble in dichloromethane were removed. The residue (64 mg) contained 62% of **12** and 27% of 1,1-dimethylstannole **13** by ^{1}H NMR estimation.

Crystal and Experimental Data for 10: Crystals suitable for X-ray diffraction were obtained by slow evaporation of the solvent from a chloroform solution of **10**. Data for the X-ray crystallographic analysis were collected on a Mac Science MXC18K diffractometer with Mo-K_α radiation (λ = 0.71073 Å). The structure was solved by direct methods using SIR[22] and refined by full-matrix least-squares techniques (SHELXL-97)[23] using all independent reflections (5672 reflections) for 298 parameters. The non-hydrogen atoms were refined anisotropically and all the hydrogen atoms were placed at calculated positions [d(C–H) = 0.96 Å]. R_1 = 0.042 [$I > 2\sigma(I)$, 5389 reflections], wR_2 = 0.097 (for all reflections), GOF = 1.094. The crystallographic data and details associated with data collection for **10** are given in Table 1.

Table 1. Crystallographic data for compound **10**.

Formula	$C_{64}H_{58}Sn_2$
Mol. mass	1064.52
Color	yellow
Crystal size [mm]	0.3 × 0.1 × 0.1
Temperature [K]	298
Crystal system	triclinic
Space group	$P1$ (#2)
a [Å]	12.756(2)
b [Å]	11.087(3)
c [Å]	10.685(2)
α [°]	117.650(10)
β [°]	86.180(10)
γ [°]	99.130(10)
V [Å^3]	1321.6(4)
Z	1
$D_{\mathrm{calcd.}}$ [g cm^{-3}]	1.34
μ [mm^{-1}]	0.984
Radiation	Mo-K_α
Scan type	ω-2θ
$2\theta_{\max}$ [°]	55.0
No. of reflections	5672
No. of parameters	298
R [$I > 2\sigma(I)$]	0.042
wR_2 (all data)	0.097
Goodness of fit	1.094

CCDC-260657 (for **10**) contains supplementary crystallographic data. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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