Generation and Reactions of Overcrowded Diaryldilithiostannane and Diaryldipotassiostannane

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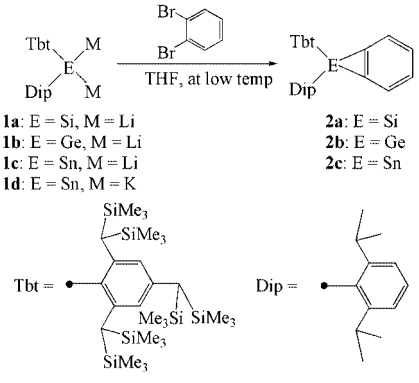
Exhaustive reduction of an overcrowded dibromostannane bearing two bulky aromatic substituents, Tbt(Dip)$SnBr_2$ {Tbt = 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl; Dip = 2,6-diisopropylphenyl}, with an excess amount of lithium naphthalenide in THF at –78 °C gave the corresponding dilithiostannane, Tbt(Dip)$SnLi_2$, the generation of which was confirmed by trapping experiments with some electrophiles together with ^{119}Sn and ^{7}Li NMR spectroscopy. The diaryldilithiostannane was found to be stable in solution under an inert gas below –25 °C. The potassium analogue, Tbt(Dip)-SnK_2, was also generated by the reduction of the dibromostannane in THF at –78 °C by the use of KC_8 as a reductant. The reactions of dilithiostannane and dipotassiostannane obtained with *o*-dibromobenzene did not give a stannacyclopropabenzene derivative but an unexpected cyclization product, a stannacyclobutabenzene derivative, in contrast to the reactions of the corresponding dilithiosilane and dilithiogermane, Tbt(Dip)ELi_2 (E = Si, Ge), with *o*-dibromobenzene leading to the formation of the corresponding metallacyclopropabenzenes as stable crystalline compounds. A preliminary result of the synthesis of a tin–tellurium double-bond compound from the dilithiostannane is also presented.

Introduction

One of the most important classes of organometallic compounds is probably that of organolithium compounds, which are now recognized as very powerful synthetic tools in organic chemistry. Among them, the chemistry of lithium compounds of heavier group 14 elements has attracted considerable interest in recent years,[1] and some dilithiosilane and dilithiogermane derivatives have been structurally characterized and successfully applied to the construction of novel bondings and/or structures of heavier group 14 elements.[2] By contrast, there are very few reports on tin dianion species. Saito and his co-workers have recently reported the spectroscopic observation of a stannole dianion.[3] Although Schmidt et al. have proposed the formation of $(C_6H_5)_2SnLi_2$ in the reaction of $(C_6H_5)_2SnCl_2$ with 4 molar amounts of Li,[4,5] the yields of the trapping reactions are not high and the generation of dilithiodiphenylstannane was not evidenced by ^{119}Sn and ^{7}Li NMR spectroscopy. More recently, Egorov et al. reported the ^{119}Sn and ^{13}C NMR studies of Et_2SnLi_2 and $(C_6H_5)_2SnLi_2$.[6] The chemistry of tin-dianion species has recently gained more and more attention.

Meanwhile, the study of three-membered ring compounds containing a heavier group 14 element is one of the most fascinating research areas in main group element chemistry.[7,8] Recently, we have also succeeded in the synthesis and isolation of the first stable sila-[9] and germacyclopropabenzenes,[10] **2a** and **2b**, by reactions of the corresponding overcrowded dilithiosilane **1a**[11] and dilithiogermane **1b**[2g,10] with *o*-dibromobenzene, respectively. Although there have been many reports on the syntheses and characterization of Si- and Ge-containing three-membered ring compounds, investigations of their tin analogues, stannacyclopropanes and stannacyclopropenes,[8] are quite rare. To the best of our knowledge, only one report has so far appeared on the synthesis of stannacyclopropenes.[8c]

In this article, we report the generation of overcrowded, diaryl-substituted dilithiostannane and dipotassiostannane together with their attempted applications to the synthesis of a hitherto unknown stannacyclopropabenzene **2c** and a tin–tellurium double-bond compound,[12] stannanetellone (Scheme 1).



Scheme 1. Synthesis of metallacyclopropabenzenes using dianion species of group 14 elements.

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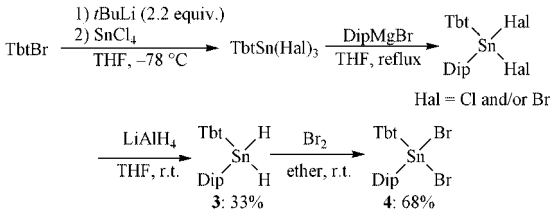
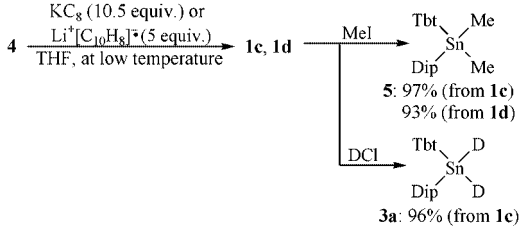
Results and Discussion

Dibromostannane **4** was prepared by a method similar to that for the synthesis of Tbt(Mes)$SnBr_2$,[13] as shown in Scheme 2. Tbt-substituted trihalostannane was synthesized by the reaction of $SnCl_4$ with TbtLi. Tbt- and Dip-substituted stannane, Tbt(Dip)SnH_2 (**3**), was prepared by the nucleophilic displacement reaction of the Tbt-substituted trihalostannane using DipMgBr, followed by reduction with $LiAlH_4$. Bromination reaction of **3** using Br_2 in ether afforded the corresponding dibromostannane **4**.



Scheme 2. Synthesis of dibromostannane **4**.

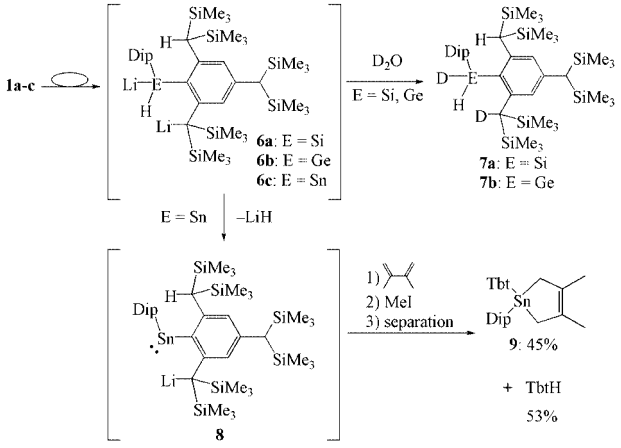
Tbt(Dip)$SnLi_2$ (**1c**) was generated by the exhaustive reduction of the overcrowded diaryldibromostannane **4** with an excess amount of lithium naphthalenide (5 equiv.) in dry THF at –78 °C under argon. The reaction mixture was stirred at the same temperature for 1 h, and then treated with an excess amount of MeI to afford Tbt(Dip)$SnMe_2$ (**5**) in 96% yield. The addition of DCl to the solution of **1c** at –78 °C resulted in the formation of Tbt(Dip)SnD_2 (**3a**) in 96% yield (D content: 93%) (Scheme 3). The formation of **3a** and **5** in the trapping experiments in high yields is most likely interpreted in terms of the almost quantitative generation of dilithiostannane **1c** as a stable compound in THF at –78 °C.



Scheme 3. Generation of overcrowded dilithiostannane **1c** and dipotassiostannane **1d**.

The ^{119}Sn NMR spectrum of **1c** in THF at –80 °C showed a broad signal at δ = –362.2 ppm, which is observed at a much higher field than that of Tbt(Dip)$SnBr_2$ (**4**: δ = –162.0 ppm in THF at –80 °C).[14] In the ^{7}Li NMR spectrum, only one singlet signal was observed at δ = 0.6 ppm, suggesting the rapid exchange of lithium cations between **1c** and LiBr. After the NMR sample was left at room temperature for a few days, the remeasurement of the ^{119}Sn NMR spectrum was performed. The ^{119}Sn NMR signal of **1c** disappeared and a new signal appeared at 1856.8 ppm, the chemical shift of which is close to those of stannylene species reported so far.[16]

Meanwhile, we have already succeeded in the generation of dilithiosilane **1a**[11] and dilithiogermane **1b**[2g,10] bearing Tbt and Dip groups on the silicon and germanium atoms, respectively. The thermal stability of **1a** and **1b** in THF solutions has been investigated by the trapping experiments using D_2O, which revealed that dilithiosilane **1a** was stable below –78 °C and dilithiogermane **1b** was stable below –25 °C. When the solutions of **1a** and **1b** were warmed above these temperatures, they underwent intramolecular proton abstraction from one of the *o*-$CH(SiMe_3)_2$ units of the Tbt group to give the corresponding lithium migration products **6a** and **6b**, respectively (Scheme 4).[10,11] Treatment of the intermediates such as **6a** and **6b** with D_2O afforded **7a** and **7b**, respectively. Similarly, thermal stability of **1c** was studied by the trapping reactions using MeI at various temperatures. The isolated yields of **5** in these reactions were 97% at –78 °C, 97% at –25 °C, and 45% at 0 °C, suggesting that dilithiostannane **1c** could be stable at least below –25 °C.

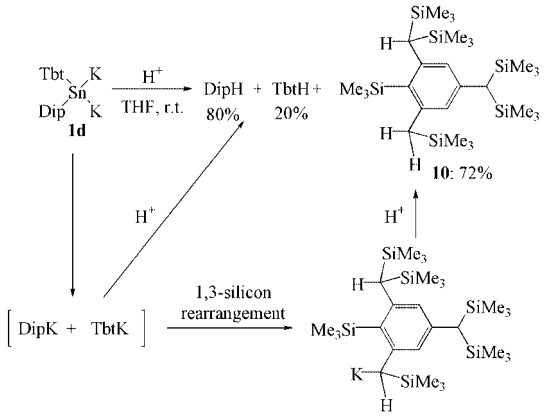


Scheme 4. Stability of **1a**, **1b**, and **1c**.

Trapping reactions of the decomposed compound from **1c** were performed. Treatment of the THF solution of **1c** with 2,3-dimethyl-1,3-butadiene at room temperature followed by the addition of MeI afforded TbtH and **9** (Scheme 4). The trapping experiment and the ^{119}Sn NMR studies suggest that dilithiostannane **1c** is initially formed and then it undergoes an intramolecular lithium migration reaction giving a lithium-migrated compound **6c** as in the case of **6a** and **6b**. However, the stability of **6c** is considered to be different from that of **6a** and **6b**. The formation of **9** strongly indicates that stannylene **8** is generated from **6c** by the elimination of LiH.

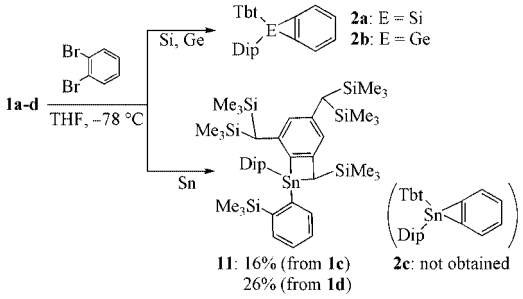
The reduction of **4** was alternatively performed with KC_8 in THF at –110 °C to give the corresponding dipotassiostannane **1d**, the generation of which was confirmed by the trapping experiment with MeI, giving **5** in 93% yield (Scheme 3). Dianion species **1d** was unstable at higher temperatures, and its purple solution in THF rapidly turned yellow at room temperature within a few minutes. The addition of H_2O to the yellow solution resulted in the formation of TbtH, DipH, and **10**[17] (Scheme 5). As this 1,3-silicon rearrangement product **10** was reportedly obtained from TbtLi above –30 °C in THF,[20] these results strongly suggest the initial formation of TbtK and DipK at low tem-

perature in this reaction. Although we attempted the reactions of **4** with other reductants (Li, K, *t*BuLi, and *n*BuLi), the generation of the corresponding dianion species (**1c** or **1d**) was not confirmed.



Scheme 5. Stability of **1d**.

With the evidence for the formation of dilithiostannane **1c** and dipotassiostannane **1d** in hand, we next attempted the synthesis of stannacyclopropabenzene **2c** by the method similar to those for the syntheses of **2a**[9] and **2b**.[10] However, the reactions of **1c** or **1d** with *o*-dibromobenzene gave an unexpected cyclic compound **11** as stable colorless crystals (16% yield from **1c** and 26% yield from **1d**) instead of the expected product **2c** (Scheme 6). The structure of the cyclic product **11** was satisfactorily confirmed by mass spectrometry, elemental analysis, and NMR spectroscopy, and the molecular structure of **11** was finally determined by X-ray crystallographic analysis. In Figure 1 the ORTEP drawing of stannacyclobutabenzene **11** is shown.[18] The deformation from the normal sp^2 configuration is larger on the C1 atom than the C6 atom, as judged by the bond angles of Sn1–C1–C6 [92.6(3)°] and C1–C6–C7 [114.4(4)°]. Additionally, the bond lengths of Sn1–C1 [2.144(4) Å] and C7–C6 [1.522(6) Å] are slightly shorter than those reported for stannabutabenzene [Sn1–C1 2.185(5) Å, C7–C6 1.588(8) Å].[18] All carbon–carbon bond lengths in the central benzene ring of **11** are almost equal.



Scheme 6. Reaction of **1a**–**d** with *o*-dibromobenzene.

Although the detailed formation mechanism for **11** is not clear at present, compound **13** might be formed as an initial intermediate by the mechanism similar to those in the reactions of **1a** and **1b**; thus, the dilithiostannane **1c** or dipotassiostannane **1d** reacts with *o*-dibromobenzene to give

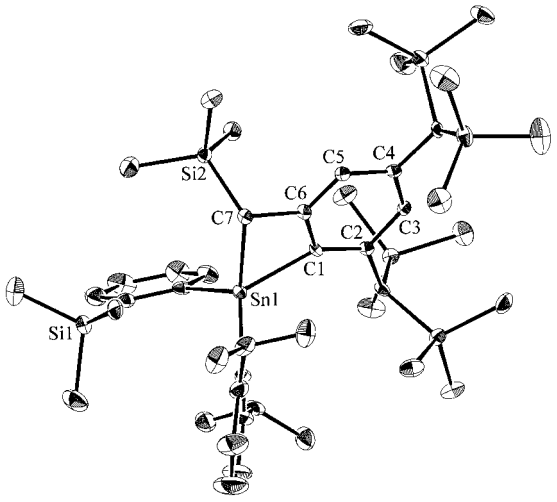
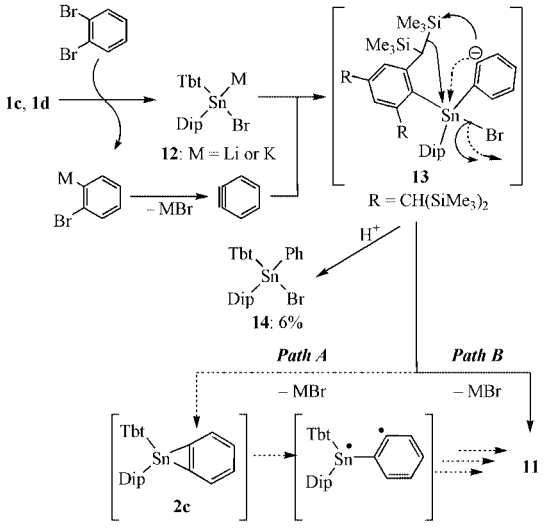


Figure 1. ORTEP drawing of **11** (50% probability). Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Sn1–C1 2.144(4), Sn1–C7 2.205(4), C7–C6 1.522(6), C1–C2 1.398(6), C2–C3 1.397(6), C3–C4 1.411(6), C4–C5 1.402(6), C5–C6 1.379(6), C6–C1 1.407(6), C1–Sn1–C7 67.62(16), Sn1–C7–C6 87.2(3), C1–C6–C7 114.4(4), Sn1–C1–C6 92.6(3), C1–C2–C3 117.8(4), C2–C3–C4 122.5(4), C3–C4–C5 118.0(4), C4–C5–C6 120.3(4), C5–C6–C1 121.0(4), C6–C1–C2 120.3(4).

Tbt(Dip)SnMBr (M = Li, K) (**12**) and 1-bromo-2-metallabenzene by the M–Br exchange reaction, and then the resulting **12** adds to benzyne generated from 1-bromo-2-metallabenzene to afford the *o*-stannylated phenyl anion **13**. The intermediacy of **13** in these reactions is strongly supported by the fact that a small amount of Tbt(Dip)SnBr(Ph) (**14**; 6%) was obtained along with **11** (7%) when the reaction mixture was quenched by the addition of water after stirring for 3 h.

For the transformation of the anionic intermediate **13** into the final product **11**, we propose here two possible mechanisms as shown in Scheme 7. In the first mechanism, the intramolecular cyclization of **13** may give stannacyclopropabenzene **2c**, and the subsequent ring-opening reaction of the three-membered ring in **2c** results in the formation of cyclic compound **11** along with the 1,6-migration of a trimethylsilyl group (path A).[19] The other is the direct nucleophilic attack of the anionic center of **13** toward one of the trimethylsilyl groups followed by the ring-closure reaction giving **11** (path B).

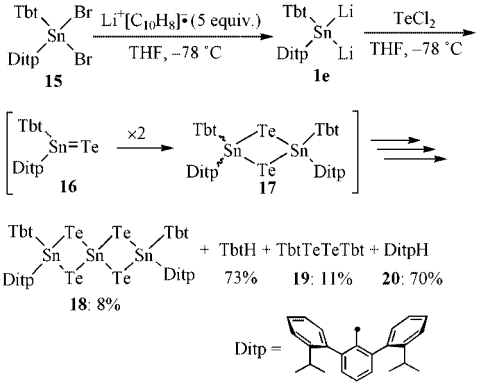
In our previous works, there was no evidence of the formation of silicon or germanium analogues of the anionic intermediate **13** under any conditions for the reactions of dilithiosilane or dilithiogermane with *o*-dibromobenzene. In fact, these anionic species were not detected by quenching reactions using D_2O.[9,10] These results suggest that these anionic species of silicon and germanium readily undergo intramolecular cyclization reactions giving metallacyclopropabenzenes, **2a** and **2b**. Thus, the different results among the reactions of **1a**, **1b**, **1c**, and **1d** with *o*-dibromobenzene are most likely interpreted in terms of much lower reactivity of **13** in the intramolecular cyclization to give **2c** than that of the silicon and/or germanium analogues or instability of the strained stannacyclopropene ring of **2c**.



Scheme 7. Possible formation mechanism for **11**.

On the other hand, it is well known that dilithiosilanes and dilithiogermanes are useful for the preparation of double-bond compounds of heavier group 14 elements.[2] Recently, we reported the synthesis of silanetellone and germanetellone by the reactions of overcrowded dilithiometallanes **1a** and **1b** with tellurium(II) dichloride, respectively.[2g,20] Taking these results into account, the dilithiostannane should be a good precursor for the synthesis of a tin–tellurium double-bond compound **16**.[12] We reported that tin–chalcogen double-bond compounds having Tbt and 2,4,6-triisopropylphenyl (Tip) groups on the tin atom easily underwent self-dimerization, giving 1,3,2,4-dichalcogenastannetanes at room temperature.[13] In order to stabilize a stannanethione and stannanesellone effectively, it was necessary to use a combination of extremely bulky ligands such as 2,2′′-diisopropylphenyl-*m*-terphenyl-2′-yl (Ditp) and the Tbt group.[21] Therefore, we tried the synthesis of stannanetellone having Tbt and Ditp groups.

Interestingly, treatment of a THF solution of Tbt(Ditp)-$SnLi_2$ (**1e**)[22] with tellurium(II) dichloride[23] at –78 °C afforded a unique cyclic compound **18** (8%) along with TbtTeTeTbt (**19**; 11%), DitpH (**20**; 70%), and TbtH (73%), (Scheme 8). Orange crystals of **18** are stable under air for at least several weeks. The ^{119}Sn NMR signals of the cyclic compound, spirobi(ditelluradistannetane) **18**, were observed at δ = –149, –384, and –387 ppm in C_6D_6. The ^{125}Te NMR chemical shift of **18** was observed at δ = 762.9, 765.0, 766.0, and 771.3 ppm in C_6D_6. The molecular structure of **18** was finally determined by X-ray crystallographic analysis (Figure 2). Both ditelluradistannetane rings were found to be nearly planar (the sums of interior bond angles are about 359.99° and 359.91°, respectively). The three tin atoms are situated in a linear alignment (angle of Sn2–Sn1–Sn3: 179.9°). All Sn–Te bond lengths [2.7445(13)–2.7661(13)] Å are in the range reported for 1,3,2,4-ditelluradistannetanes, $[(Dis)_2SnTe]_2$ [Dis = –$CH(SiMe_3)_2$] [2.756(1) and 2.771(1) Å][24a] and $(tBu_2SnTe)_2$ [2.754(1) and 2.758(1) Å].[24b]



Scheme 8. Reaction of **1e** with tellurium(II) dichloride.

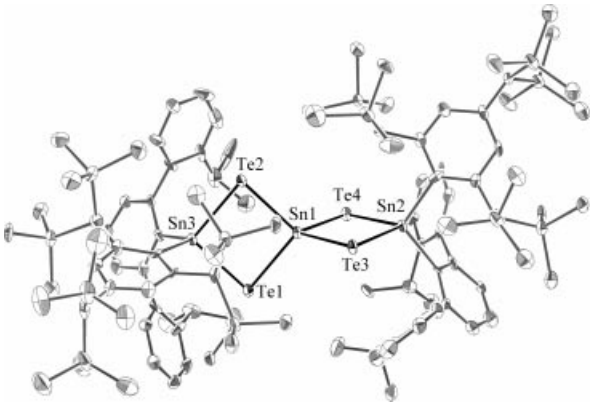


Figure 2. ORTEP drawing of **18**·1.5(toluene) (50% probability). Hydrogen atoms and solvated toluene molecules are omitted for clarity. Tbt and Ditp groups are described with gray lines for clarity. Selected bond lengths [Å] and angles [°]: Sn1–Te1 2.7445(13), Sn1–Te4 2.7526(13), Sn1–Te3 2.7536(13), Sn1–Te2 2.7574(13), Sn2–Te3 2.7577(13), Sn2–Te4 2.7657(13), Te1–Sn3 2.7661(13), Te2–Sn3 2.7627(13), Te4–Sn1–Te3 94.95(4), Te1–Sn1–Te2 95.03(4), Te3–Sn2–Te4 94.56(4), Sn1–Te1–Sn3 85.36(4), Sn1–Te2–Sn3 85.18(4), Te2–Sn3–Te1 94.42(4), Sn1–Te3–Sn2 85.27(4), Sn1–Te4–Sn2 85.13(4).

Although the formation mechanism of **18** is not clear at present, the formation of **18** can be explained in terms of a mechanism similar to the case of the formation of a spirobi(dithiasiletane) in the reaction of a silylene with S_8 through the corresponding silanethione and silanethione dimer.[25] Based on this report, the self-dimerization of stannanetellone **16**, which is generated in the reaction of dilithiostannane **1e** with tellurium(II) dichloride, afforded stannanetellone dimer **17** and the subsequent reactions of **17** result in the formation of cyclic compound **18**. The formation of **18** indicates that some amount of stannanetellone **16** might be generated in the reaction of **1e** with tellurium(II) dichloride; however, on the other hand, it suggests that stannanetellones are much less stable and much more difficult to isolate than the silicon and germanium analogues such as silanetellones and germanetellones and the lighter chalcogen analogues (e.g., stannanethiones and stannanesellones), because of the longer Sn–Te bonds and larger energy gaps between σ- and π-bond energies than those of the lighter element(s) analogues. In order to isolate a stable stannane-

tellone, it is necessary to introduce a much more crowded combination of the protection groups than that in Tbt(Ditp)Sn=Te.

Conclusions

By taking advantage of a bulky substituent, Tbt group, we succeeded in the generation of diaryldimetallastannanes **1c**, **1d**, and **1e** by the exhaustive reduction of overcrowded diaryldibromostannanes **4** and **15**. We found that the reactions of **1c** and **1d** with *o*-dibromobenzene resulted in the formation of an unexpected compound **11** instead of the expected stannacyclopropabenzene **2c**. The reaction of **1e** with tellurium(II) dichloride afforded a novel cyclic compound **18**. As **1c** and **1d** were found to have enough stability in solution at low temperature, further investigation of their synthetic application toward a variety of tin-containing new chemical species is currently in progress.

Experimental Section

General: All experiments were performed under argon unless otherwise noted. THF was dried by standard methods and freshly distilled prior to use. ^{1}H NMR (300 MHz), ^{13}C NMR (75 MHz), ^{119}Sn NMR (111 MHz), and ^{125}Te NMR (94 MHz) spectra were measured in $CDCl_3$ or C_6D_6 with a JEOL JNM AL-300 spectrometer. ^{1}H and ^{13}C NMR chemical shifts were recorded in ppm relative to tetramethylsilane (δ = 0 ppm) and were referenced internally with respect to the residual proton impurity ($CHCl_3$: δ = 7.26 ppm, benzene: δ = 7.15 ppm) and the ^{13}C resonance of the solvent ($CDCl_3$: δ = 77.2 ppm, [D_6]benzene: δ = 128.0 ppm), respectively. ^{119}Sn NMR chemical shifts were referenced with tetramethylstannane (δ = 0 ppm) as an external standard. ^{125}Te NMR chemical shifts were referenced with diphenylditelluride (δ = 450 ppm) as an external standard. Fast atom bombardment (FAB) mass spectrometric data were obtained with a JEOL JMS-700 spectrometer. Mass spectrometric data (EI) were obtained with a Shimadzu QP-5000. Preparative gel permeation liquid chromatography (GPLC) was performed with an LC-918 apparatus (Japan Analytical Industry Co., Ltd.) equipped with JAIGEL 1H and 2H columns (eluent: $CHCl_3$ or toluene). Preparative thin-layer chromatography (PTLC) was performed with Merck Kieselgel 60 PF254. All melting points were determined with a Yanaco micro melting point apparatus and are uncorrected. IR spectra were measured at room temperature with a JASCO FT/IR-460 plus. Elemental analyses were carried out at the Microanalytical Laboratory of the Institute for Chemical Research, Kyoto University. 1-Bromo-2,4,6-tris[bis(trimethylsilyl)-methyl]benzene (TbtBr),[26] 1-bromo-2,6-diisopropylbenzene (DipBr),[27] and 2′-iodo-2,2′′-diisopropyl-1,1′:3′1′′-terphenyl (DitpI)[21] were prepared according to reported procedures.

Tbt(Dip)SnH$_2$ (3): *t*BuLi (2.30 N solution in pentane, 35.2 mL, 81.0 mmol) was added to a solution of TbtBr (22.5 g, 35.6 mmol) in THF (380 mL) at –78 °C. After the reaction mixture was stirred at the same temperature for 30 min, $SnCl_4$ (5.0 mL, 42.7 mmol) and LiCl (34.4 g, 0.81 mol) were added at –78 °C. The mixture was warmed to room temperature, and then the solvents were evaporated. After removal of the insoluble inorganic salts by filtration through Celite®, the reaction mixture was concentrated to give colorless crystals. Recrystallization from CH_3CN/$CHCl_3$ afforded a mixture of TbtSn(Hal)$_3$ (Hal = Cl and/or Br) (16.4 g). A THF solution (50 mL) of DipMgBr (5.78 g, 21.8 mmol), which was prepared by the reaction of Mg (602 mg, 24.8 mmol) and DipBr (5.25 g, 21.8 mmol), was added to a THF solution (100 mL) of the mixture of TbtSn$Cl_{3-n}Br_n$ (n = 0–3) (10.1 g) at room temperature. After the solution was stirred under reflux conditions for 16 h, the reaction mixture was cooled to room temperature. $LiAlH_4$ (6.00 g, 19.5 mmol) was added to the reaction mixture at 0 °C and then the mixture was stirred for 5 h. After quenching by an ice-cold 15% NaOH solution (100 mL) and the subsequent filtration to remove the insoluble inorganic salts, the organic layer was extracted. After extraction with hexane (50 mL), the organic layers were combined, washed with H_2O, and then dried with Na_2SO_4. After the removal of the solvent, the mixture was purified by column chromatography (SiO_2/hexane) to afford Tbt(Dip)SnH_2 (**3**) as colorless crystals. Yield: 4.0 g (33%). M.p. 155.5 °C (dec.). $C_{39}H_{78}Si_6Sn$ (834.26): calcd. C 56.15, H 9.42; found C 56.06, H 9.51. FAB-MS: *m*/*z* calcd. for $C_{39}H_{78}Si_6{}^{120}Sn$ 834 [M$^+$], found 834 [M$^+$]. ^{1}H NMR (300 MHz, C_6D_6, 25 °C): δ = 0.30 (s, 9 H, $SiMe_3$), 0.32 (s, 36 H, $SiMe_3$), 0.35 (s, 9 H, $SiMe_3$), 1.34 (d, $^3J_{HH}$ = 5.5 Hz, 6 H, CH_3), 1.51 (d, $^3J_{HH}$ = 5.5 Hz, 6 H, CH_3), 1.61 (s, 1 H, *p*-BnH for Tbt), 2.15 (br. s, 1 H, *o*-BnH for Tbt), 2.45 (br. s, 1 H, *o*-BnH for Tbt), 2.91 (sept, $^3J_{HH}$ = 5.5 Hz, 2 H, BnH for Dip), 6.38 (s, $^1J_{^{117}SnH}$ = 1769.4, $^1J_{^{119}SnH}$ = 1855.2 Hz, 2 H, SnH_2), 6.73 (br. s, 1 H, *m*-PhH for Tbt), 6.87 (br. s, 1 H, *m*-PhH for Tbt), 7.14–7.50 (m, 3 H, *m*- and *p*-PhH for Dip) ppm. ^{13}C NMR (75 MHz, C_6D_6, 25 °C): δ = 0.6 (q), 1.0 (q), 1.2 (q), 25.1 (q), 30.6 (d), 33.3 (d), 37.5 (d × 2), 122.1 (d), 123.1 (d), 127.0 (d), 130.1 (d), 135.6 (s), 140.1 (s), 143.9 (s), 151.74 (s), 151.83 (s), 155.4 (s) ppm. ^{119}Sn{^{1}H} NMR (111 MHz, C_6D_6, 25 °C): δ = –345.6 ppm. IR (KBr): $\tilde{\nu}$ = 1863.9 [ν(Sn–H)] cm^{-1}.

Tbt(Dip)SnBr$_2$ (4): A solution of **3** (3.70 g, 4.43 mmol) and Br_2 (0.50 mL, 9.76 mmol) in Et_2O (130 mL) was stirred at room temperature for 2 h. The solution was washed with an aqueous solution of NaOH and then with a saturated aqueous solution of NaCl. The organic layer was dried with Na_2SO_4. After the removal of the solvent, the residue was recrystallized from $CHCl_3$ and EtOH to afford **4** as colorless crystals. Yield: 2.98 g (68%). M.p. 188.4–192.5 °C. $C_{39}H_{76}Br_2Si_6Sn$ (992.05): calcd. C 47.22, H 7.72; found C 47.24, H 7.82. FAB-MS: *m*/*z* calcd. for $C_{39}H_{76}{}^{79}Br_2Si_6{}^{120}Sn$ 992 [M$^+$], found 992 [M$^+$]. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 0.03 (s, 36 H, $SiMe_3$), 0.05 (s, 18 H, $SiMe_3$), 1.16 (s, 1 H, *p*-BnH for Tbt), 1.33 (d, $^3J_{HH}$ = 6.6 Hz, 12 H, CH_3), 2.13 (br. s, 1 H, *o*-BnH for Tbt), 2.43 (br. s, 1 H, *o*-BnH for Tbt), 3.36 (sept, $^3J_{HH}$ = 6.6 Hz, 2 H, BnH for Dip), 6.37 (br. s, 1 H, *m*-PhH for Tbt), 6.47 (br. s, 1 H, *m*-PhH for Tbt), 7.20–7.42 (m, 3 H, *m*- and *p*-PhH for Dip) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 1.2 (q), 1.8 (q), 2.0 (q), 26.4 (q), 31.1 (d), 31.8 (d), 37.4 (d × 2), 123.6 (d), 125.4 (d), 128.4 (d), 131.6 (d), 133.7 (s), 137.5 (s), 143.8 (s), 146.7 (s), 151.0 (s), 154.5 (s) ppm. ^{119}Sn NMR (111 MHz, $CDCl_3$, 25 °C): δ = –171.0 ppm.

Generation of Tbt(Dip)SnM$_2$ (M = Li, K) and Preparation of Tbt(Dip)SnMe$_2$ (5). Method A (M = Li): Lithium naphthalenide (2.33 N solution in THF, 0.14 mL, 0.33 mmol, 5 molar amounts) was added to a THF solution (1.0 mL) of **4** (62.4 mg, 62.9 μmol) at –78 °C. The reaction mixture was stirred at the same temperature for 1 h, and then an excess amount of MeI (0.1 mL, 1.6 mmol) was added to the reaction mixture. After the removal of the solvent, the residue was extracted with hexane several times. Insoluble inorganic salts were removed by filtration through Celite®. The residue was subjected to GPLC ($CHCl_3$) followed by PTLC (hexane) to afford **5** as colorless crystals. Yield: 52.7 mg (97%). **Method B (M = K):** KC_8 (98.0 mg, 0.72 mmol) was added to a THF solution (1.0 mL) of **4** (68.0 mg, 68.5 μmol) at –110 °C. The reaction mixture was stirred vigorously at the same temperature for 1 h, and

then an excess of MeI (0.1 mL, 1.6 mmol) was added to the mixture. A similar workup procedure mentioned above afforded **5** as colorless crystals. Yield: 63.5 mg (93%). M.p. 167.9–174.3 °C. $C_{41}H_{82}Si_6Sn$ (862.31): calcd. C 57.11, H 9.58; found C 56.96, H 9.59. FAB-MS: *m*/*z* calcd. for $C_{41}H_{82}Si_6{}^{120}Sn$ 863 [M$^+$], found 863 [M$^+$]. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = –0.05 (s, 18 H, $SiMe_3$), –0.01 (s, 18 H, $SiMe_3$), 0.02 (s, 18 H, $SiMe_3$), 0.64 (s, $^2J_{HSn}$ = 48.3 Hz, 6 H, SnMe), 1.23 (d, $^3J_{HH}$ = 5.5 Hz, 12 H, CH_3), 1.31 (s, 1 H, *p*-BnH for Tbt), 1.68 (br. s, 1 H, *o*-BnH for Tbt), 1.84 (br. s, 1 H, *o*-BnH for Tbt), 2.99 (sept, $^3J_{HH}$ = 5.5 Hz, 2 H, BnH for Dip), 6.25 (br. s, 1 H, *m*-PhH for Tbt), 6.38 (br. s, 1 H, *m*-PhH for Tbt), 7.18–7.40 (m, 3 H, *m*- and *p*-PhH for Dip) ppm. ^{13}C NMR (75 MHz, C_6D_6, 25 °C): δ = 0.9 (q), 1.2 (q), 1.5 (q), 3.7 (q), 26.0 (q), 30.0 (d), 30.7 (d), 30.9 (d), 36.5 (d), 122.1 (d), 123.1 (d), 127.0 (d), 128.9 (d), 131.8 (s), 137.2 (s), 143.0 (s), 143.9 (s), 151.3 (s), 155.4 (s) ppm. ^{119}Sn NMR (111 MHz, $CDCl_3$, 25 °C): δ = –126.4 ppm.

Generation of Tbt(Dip)SnLi$_2$ and the Trapping Reaction with DCl: Lithium naphthalenide (1.26 N solution in THF, 0.22 mL, 0.28 mmol, 5 molar amounts) was added to a THF solution (1.0 mL) of **4** (58.6 mg, 59.1 μmol) at –78 °C. The reaction mixture was stirred at the same temperature for 1 h. After stirring for 30 min, DCl (1.0 N solution in Et_2O, 75 μL) was added to the reaction mixture. After the removal of the solvent, the mixture was extracted with hexane several times. The extracts were combined, filtered through Celite®, and the solvents evaporated. The residue was subjected to GPLC (toluene) to give Tbt(Dip)SnD_2 (**3a**) as colorless crystals. Yield: 47.5 mg [96% (deuterium content: 93%)]. M.p. 154.8 °C (dec.). High-resolution FAB-MS: *m*/*z* calcd. for $C_{39}H_{76}D_2Si_6{}^{120}Sn$ 836.3865 [M$^+$], found 836.3894 [M$^+$]. ^{1}H NMR (300 MHz, C_6D_6, 25 °C): δ = 0.30 (s, 9 H, $SiMe_3$), 0.32 (s, 36 H, $SiMe_3$), 0.35 (s, 9 H, $SiMe_3$), 1.34 (d, $^3J_{HH}$ = 5.5 Hz, 6 H, CH_3), 1.51 (d, $^3J_{HH}$ = 5.5 Hz, 6 H, CH_3), 1.61 (s, 1 H, *p*-BnH for Tbt), 2.15 (br. s, 1 H, *o*-BnH for Tbt), 2.45 (br. s, 1 H, *o*-BnH for Tbt), 2.91 (sept, $^3J_{HH}$ = 5.5 Hz, 2 H, BnH for Dip), 6.73 (br. s, 1 H, *m*-PhH for Tbt), 6.87 (br. s, 1 H, *m*-PhH for Tbt), 7.14–7.50 (m, 3 H, *m*- and *p*-PhH for Dip) ppm. ^{13}C NMR (75 MHz, C_6D_6, 25 °C): δ = 0.6 (q), 1.0 (q), 1.2 (q), 25.1 (q), 30.6 (d), 33.3 (d), 37.5 (d × 2), 122.1 (d), 123.1 (d), 127.0 (d), 130.1 (d), 135.6 (s), 140.1 (s), 143.9 (s), 151.74 (s), 151.83 (s), 155.4 (s) ppm. ^{119}Sn NMR (111 MHz, C_6D_6, 25 °C): δ = –346.8 (quint, $^1J_{SnD}$ = 280.7 Hz) ppm. IR (KBr): $\tilde{\nu}$ = 1317.1 [ν(Sn–D)] cm^{-1}.

Generation of Tbt(Dip)SnLi$_2$ (1c) and the Trapping Reaction of the Decomposed Compounds with 2,3-Dimethyl-1,3-butadiene and MeI: Lithium naphthalenide (1.03 N solution in THF, 0.25 mL, 0.26 mmol, 5 molar amounts) was added to a THF solution (1.0 mL) of **4** (50.2 mg, 50.0 μmol) at –78 °C. The reaction mixture was stirred at the same temperature for 1 h. After additional stirring at room temperature for 30 min, 2,3-dimethyl-1,3-butadiene (0.1 mL, 82.0 μmol) was added. After stirring for 30 min, an excess of MeI (0.1 mL, 1.6 mmol) was added to the reaction mixture. After the removal of the solvent, hexane was added to the residue. Insoluble inorganic salts were removed by filtration through Celite® and the filtrate was concentrated. The residue was subjected to GPLC ($CHCl_3$) followed by PTLC (hexane) to give TbtH (14.7 mg, 53%) and **9** (20.4 mg, 45%). M.p. 164.2–166.4 °C. FAB-MS: *m*/*z* calcd. for $C_{45}H_{87}Si_6{}^{120}Sn$ 915 [M + H]$^+$, found 915 [M + H]$^+$. High-resolution FAB-MS: *m*/*z* calcd. for $C_{45}H_{87}Si_6{}^{120}Sn$ 915.4445 [M + H]$^+$, found 915.4456 [M + H]$^+$. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = –0.05 (br. s, 18 H, $SiMe_3$), –0.24 (br. s, 18 H, $SiMe_3$), 0.03 (s, 18 H, $SiMe_3$), 1.19 (d, $^3J_{HH}$ = 6.6 Hz, 9 H, CH_3 for Dip), 1.19 (br. s, 1 H, *p*-BnH for Tbt), 1.28 (d, $^3J_{HH}$ = 6.6 Hz, 3 H, CH_3 for Dip), 1.68 (s, 1 H, *o*-BnH for Tbt), 1.74 (br. s, 6 H, CH_3), 1.79 (s, 1 H, *o*-BnH for Tbt), 2.09 (d, ^2J = 17.0 Hz, 2 H, CH_2), 2.14 (d, ^4J = 17.0 Hz, 2 H, CH_2), 3.02 (sept, $^3J_{HH}$ = 6.6 Hz, 1 H, BnH for Dip), 3.12 (sept, $^3J_{HH}$ = 6.6 Hz, 1 H, BnH for Dip), 6.27 (br. s, 1 H, *m*-PhH for Tbt), 6.41 (s, 1 H, *m*-PhH for Tbt), 7.12 (d, $^3J_{HH}$ = 7.5 Hz, 2 H, *m*-PhH for Dip), 7.23 (t, $^3J_{HH}$ = 7.5 Hz, 1 H, *p*-PhH for Dip) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 0.8 (q), 1.1 (q), 1.3 (q), 21.4 (q), 24.9 (q), 25.8 (q), 30.1 (d), 31.1 (d), 31.5 (d × 2), 32.6 (t), 37.9 (d), 122.0 (d), 123.1 (d), 124.6 (d), 128.9 (d), 131.7 (s), 137.7 (s), 141.2 (s), 142.9 (s), 145.7 (s), 151.2 (s), 154.7 (s) ppm. ^{119}Sn NMR (111 MHz, $CDCl_3$, 25 °C): δ = –110.2 ppm.

Generation of Tbt(Dip)SnK$_2$ and the Trapping Reaction of the Decomposed Compounds with H$_2$O at Room Temperature: KC_8 (129 mg, 0.95 mmol) was added to a THF solution (1.5 mL) of **4** (101 mg, 0.10 mmol) at –110 °C. The reaction mixture was stirred vigorously at the same temperature for 1 h, and then warmed to room temperature. After additional stirring at the same temperature for 1 h, the reaction mixture was exposed to air. After the removal of the solvent, the mixture was extracted with hexane several times. Insoluble inorganic salts were removed by filtration through Celite® and the filtrate was concentrated. The residue was subjected to GPLC ($CHCl_3$) followed by PTLC (hexane) to give TbtH (12.1 mg, 20%), **10** (39.7 mg, 72%), and DipH (14.1 mg, 80%).[17]

Stannacyclobutabenzene (11). Method A: Lithium naphthalenide (1.56 N solution in THF, 0.67 mL, 5 molar amounts) was added to a THF solution (5.0 mL) of **4** (205 mg, 0.21 mmol) at –78 °C. After stirring at the same temperature for 1 h, *o*-dibromobenzene (25 μL, 0.21 mmol) was added to the reaction mixture. The solution was slowly warmed to room temperature over 10 h. After the removal of the solvent, hexane was added to the residue. Insoluble inorganic salts were removed by filtration through Celite® and the filtrate was concentrated. The residue was subjected to GPLC ($CHCl_3$) followed by PTLC (hexane) to give **11** as colorless crystals. Yield: 30.1 mg (16%). **Method B:** KC_8 (150 mg, 1.11 mmol) was added to a THF solution (3.0 mL) of Tbt(Dip)$SnBr_2$ (**4**) (170 mg, 0.17 mmol) at –78 °C. After stirring at the same temperature for 1 h, *o*-dibromobenzene (25 μL, 0.21 mmol) was added to the reaction mixture. The solution was slowly warmed to room temperature over 10 h, and **11** was separated and purified by a procedure similar to that described above. Yield: 40.1 mg (26%). M.p. 99.4 °C (dec.). $C_{45}H_{80}Si_6Sn$ (908.34): calcd. C 59.50, H 8.88; found C 59.53, H 8.63. FAB-MS: *m*/*z* calcd. for $C_{45}H_{80}Si_6{}^{120}Sn$ 908 [M$^+$], found 908 [M$^+$]. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = –0.26 (s, 9 H, $SiMe_3$), –0.16 (s, 9 H, $SiMe_3$), 0.02 (s, 9 H, $SiMe_3$), 0.04 (s, 9 H, $SiMe_3$), 0.15 (s, 9 H, $SiMe_3$), 0.17 (s, 9 H, $SiMe_3$), 0.86 (br. s, 6 H, Me), 1.24 (br. s, 6 H, Me), 1.34 (s, 1 H, BnH), 1.57 (s, 1 H, BnH), 2.94 (s, $^2J_{HSn}$ = 64 Hz, 1 H, BnH), 3.29 (br. s, 2 H, BnH for Dip), 6.39 (br. s, 1 H, *m*-PhH for Tbt), 6.45 (s, 1 H, *m*-PhH for Tbt), 7.07 (d, $^3J_{HH}$ = 7.2 Hz, 2 H, *m*-PhH for Dip), 7.20–7.27 (m, 2 H, PhH), 7.30 (t, $^3J_{HH}$ = 7.2 Hz, 1 H, *p*-PhH for Dip), 7.60 (dd, $^3J_{HH}$ = 7.2, $^4J_{HH}$ = 2.1 Hz, 1 H, PhH), 7.93 (dd, $^3J_{HH}$ = 7.2, $^4J_{HH}$ = 2.1 Hz, 1 H, PhH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 50 °C): δ = 0.2 (q), 0.39 (q), 0.44 (q), 0.5 (q), 0.6(q), 1.1 (q), 24.9 (br. q), 30.2 (d), 30.4 (d), 37.1 (d), 39.7 (d), 121.8 (br. d), 123.2 (d), 123.4 (d), 127.5 (d), 128.0 (d), 129.5 (d), 135.8 (d), 138.0 (d), 143.9 (s), 145.0 (s), 145.1 (s), 147.5 (s), 147.7 (s), 154.6 (s), 155.0 (s), 155.8 (s) ppm. ^{119}Sn{^{1}H} NMR (111 MHz, $CDCl_3$, 25 °C): δ = –83.4 ppm.

Tbt(Dip)Sn(Ph)Br (14): Lithium naphthalenide (1.30 N solution in THF, 1.87 mL, 5 molar amounts) was added to a THF solution (10 mL) of **4** (479 mg, 0.48 mmol) at –78 °C. After stirring at the same temperature for 1 h, *o*-dibromobenzene (65 μL, 0.54 mmol)

was added to the reaction mixture. The solution was stirred for 3 h, and then the mixture was separated by the procedure similar to that described above to afford **11** (29.0 mg, 7%) and **14** (29.6 mg, 6%). M.p. 155.8 °C (dec.). FAB-MS: *m*/*z* calcd. for $C_{45}H_{81}{}^{79}BrSi_6{}^{120}Sn$ 988 [M$^+$], found 988 [M$^+$]. High-resolution FAB-MS: *m*/*z* calcd. for $C_{45}H_{81}{}^{79}BrSi_6{}^{120}Sn$ 988.3159 [M$^+$], found 988.3193 [M$^+$]. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = –0.16 (s, 27 H, $SiMe_3$), –0.13 (s, 9 H, $SiMe_3$), –0.07 (s, 9 H, $SiMe_3$), –0.06 (s, 9 H, $SiMe_3$), 0.83 (d, $^3J_{HH}$ = 6.3 Hz, 6 H, Me), 1.20 (d, $^3J_{HH}$ = 6.3 Hz, 6 H, Me), 1.23 (s, 1 H, *p*-BnH for Tbt), 1.97 (br. s, 1 H, *o*-BnH for Tbt), 2.02 (br. s, 1 H, *o*-BnH for Tbt), 3.18 (sept, $^3J_{HH}$ = 6.3 Hz, 2 H, BnH for Dip), 6.24 (br. s, 1 H, *m*-PhH for Tbt), 6.36 (br. s, 1 H, *m*-PhH for Tbt), 7.05–7.13 (m, 2 H, PhH), 7.20–7.28 (m, 4 H, PhH), 7.59–7.82 (m, 2 H, PhH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 0.8 (q), 1.0 (q), 1.7 (q), 1.9 (q), 24.3 (q), 27.2 (q), 30.5 (d), 31.1 (d), 31.5 (d), 36.8 (d), 122.9 (d), 124.6 (d), 127.2 (d), 128.3 (d), 129.2 (d), 130.3 (d), 136.5 (d), 138.4 (s), 140.2 (s), 144.9 (s), 147.0 (s), 151.2 (s), 154.6 (s), 155.2 (s) ppm. ^{119}Sn{^{1}H} NMR (111 MHz, $CDCl_3$, 25 °C): δ = –102.2 ppm.

Synthesis of Tbt(Ditp)SnH$_2$: A THF solution (20 mL) of $TbtSn(Hal)_3$ (2.31 g) was added to a THF solution of DitpLi, prepared from DitpI (1.49 g, 3.37 mmol) and *t*BuLi (2.32 M in pentane, 3.2 mL, 7.41 mmol) at –78 °C in THF (20 mL), at –78 °C, and then the mixture was stirred at room temperature for 2 h. After the removal of the solvent, hexane was added to the residue. Insoluble inorganic salts were removed by filtration through Celite®. The filtrate was concentrated and subjected to GPLC ($CHCl_3$) to afford a mixture containing $Tbt(Ditp)Sn(Hal)_2$ (1.48 g) as colorless crystals. $LiAlH_4$ (734 mg, 19.3 mmol) was added to a THF solution (50 mL) of the mixture containing $Tbt(Ditp)Sn(Hal)_2$ (1.28 g) at 0 °C. The mixture was stirred at room temperature for 3 h. After quenching by an ice-cold 15% NaOH solution (30 mL) and subsequent filtration to remove the insoluble inorganic salts, the organic layer was extracted. After extraction with hexane (50 mL), the organic layers were combined, and washed with H_2O, and then dried with Na_2SO_4. After removal of the solvents, the mixture was purified by column chromatography (SiO_2/benzene) to afford $Tbt(Ditp)SnH_2$ as colorless crystals. Yield 962 mg (29%). M.p. 155.5 °C (dec.). FAB-MS: *m*/*z* calcd. for $C_{51}H_{87}Si_6{}^{118}Sn$ 985 [M + H]$^+$, found 985 [M + H]$^+$. ^{1}H NMR (300 MHz, C_6D_6, 25 °C): δ = 0.09 (s, 36 H, $SiMe_3$), 0.20 (s, 18 H, $SiMe_3$), 0.95 (d, $^3J_{HH}$ = 5.1 Hz, 6 H, Me), 1.40 (d, $^3J_{HH}$ = 5.1 Hz, 6 H, Me), 1.43 (s, 1 H, *p*-BnH for Tbt), 1.71 (br. s, 1 H, *o*-BnH for Tbt), 1.85 (br. s, 1 H, *o*-BnH for Tbt), 3.01 (sept, $^3J_{HH}$ = 5.1 Hz, 2 H, BnH for Ditp), 5.66 (s, $^1J_{^{117}SnH}$ = 1768.6, $^1J_{^{119}SnH}$ = 1851.7 Hz, 2 H, SnH), 6.41 (br. s, 1 H, *m*-PhH for Tbt), 6.53 (br. s, 1 H, *m*-PhH for Tbt), 7.09–7.26 (m, 9 H, ArH for Ditp), 7.52 (d, $^3J_{HH}$ = 6.6 Hz, 2 H, ArH for Ditp) ppm. ^{13}C NMR (75 MHz, C_6D_6, 25 °C): δ = 1.1 (q), 1.7 (q), 22.4 (q), 24.8 (q), 30.2 (d), 30.4 (d), 32.4 (d × 2), 122.5 (d), 125.4 (d), 125.7 (d), 126.2 (d), 128.9 (d), 129.4 (d), 129.7 (d), 135.3 (d), 139.0 (s), 141.2 (s), 143.2 (s), 143.7 (s) 147.2 (s), 149.8 (s), 151.2 (s) 151.3 (s) ppm. ^{119}Sn{^{1}H} NMR (111 MHz, C_6D_6, 25 °C): δ = –342.9 ppm. IR (KBr): $\tilde{\nu}$ = 1841.7 [ν(Sn–H)] cm^{-1}.

Synthesis of Tbt(Ditp)SnBr$_2$ (15): A solution of $Tbt(Ditp)SnH_2$ (734 mg, 0.74 mmol) and Br_2 (0.21 mL, 0.84 mmol) in Et_2O (40 mL) was stirred at room temperature for 30 min. The solution was washed with a saturated aqueous solution of Na_2SO_3 and then with a saturated aqueous solution of NaCl. The organic layer was dried with Na_2SO_4. After the removal of the solvent, the residue was recrystallized from $CHCl_3$ and EtOH to afford **15** as colorless crystals. Yield: 621 mg (73%). M.p. 278.5–279.6 °C. $C_{51}H_{84}Br_2Si_6Sn$ (1144.24): calcd. C 53.53, H 7.40; found C 53.52, H 7.46. FAB-MS: *m*/*z* calcd. for $C_{51}H_{84}{}^{79}Br_2Si_6{}^{120}Sn$ 1144 [M$^+$], found 1144 [M$^+$]. ^{1}H NMR (300 MHz, C_6D_6, 25 °C): δ = 0.19 (br. s, 36 H, $SiMe_3$), 0.21 (br. s, 18 H, $SiMe_3$), 1.03 (d, $^3J_{HH}$ = 6.3 Hz, 6 H, Me), 1.39 (d, $^3J_{HH}$ = 6.3 Hz, 6 H, Me), 1.51 (br. s, 1 H, *p*-BnH for Tbt), 1.80 (br. s, 1 H, *o*-BnH for Tbt), 2.82 (br. s, 1 H, *o*-BnH for Tbt), 2.96 (sept, $^3J_{HH}$ = 6.3 Hz, 2 H, BnH for Ditp), 6.37–6.75 (m, 2 H, *m*-PhH for Tbt), 7.01–7.35 (m, 9 H, ArH for Ditp), 7.45 (d, $^3J_{HH}$ = 7.2 Hz, 2 H, ArH for Ditp) ppm. ^{13}C NMR (75 MHz, C_6D_6, 25 °C): δ = 0.6 (q), 1.9 (q), 2.4 (q), 2.6 (q), 23.2 (q), 25.2 (q), 30.0 (d), 31.1 (d), 32.8 (d), 33.1 (d), 123.4 (d), 123.9 (d), 126.3 (d), 126.9 (d), 128.8 (d), 129.4 (d), 129.7 (d), 135.3 (d), 141.1 (s × 2), 142.9 (s), 146.1 (s), 146.4 (s) 147.7 (s), 148.8 (s), 153.5 (s) ppm. ^{119}Sn{^{1}H} NMR (111 MHz, $CDCl_3$, 25 °C): δ = –192.5 ppm.

Generation of Tbt(Ditp)SnLi$_2$ and Preparation of Tbt(Ditp)SnMe$_2$: Lithium naphthalenide (1.30 N solution in THF, 0.15 mL, 0.20 mmol, 5 molar amounts) was added to a THF solution (1.0 mL) of **15** (45.6 mg, 39.8 μmol) at –78 °C. The reaction mixture was stirred at the same temperature for 1 h, and then MeI (0.1 mL, 1.6 mmol) was added to the reaction mixture. After the removal of the solvent, hexane was added to the residue. Insoluble inorganic salts were removed by filtration through Celite®. The filtrate was concentrated and subjected to GPLC ($CHCl_3$) followed by PTLC (hexane) to afford $Tbt(Ditp)SnMe_2$ as colorless crystals. Yield: 38.1 mg (93%). M.p. 265.3–265.7 °C. $C_{53}H_{90}Si_6Sn$ (1014.50): calcd. C 62.75, H 8.94; found C 62.67, H 9.05. High-resolution FAB-MS: *m*/*z* calcd. for $C_{53}H_{90}Si_6{}^{120}Sn$ 1014.4680 [M$^+$], found 1014.4697 [M$^+$]. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = –0.45 (s, $^2J_{HSn}$ = 51.0 Hz, 6 H, SnMe), –0.04 (br. s, 36 H, $SiMe_3$), –0.09 (s, 18 H, $SiMe_3$), 1.04 (d, $^3J_{HH}$ = 6.6 Hz, 6 H, Me), 1.15 (d, $^3J_{HH}$ = 6.6 Hz, 6 H, Me), 1.27 (s, 1 H, *p*-BnH for Tbt), 1.32 (br. s, 2 H, *o*-BnH for Tbt), 2.71 (sept, $^3J_{HH}$ = 6.6 Hz, 2 H, BnH for Ditp), 6.25 (br. s, 1 H, *m*-PhH for Tbt), 6.40 (br. s, 1 H, *m*-PhH for Tbt), 6.98 (t, $^3J_{HH}$ = 7.2 Hz, 1 H, PhH for Ditp), 7.13 (d, $^3J_{HH}$ = 7.2 Hz, 2 H, PhH for Ditp), 7.21–7.39 (m, 8 H, PhH for Ditp) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = –0.4 (q, $^1J_{^{117}SnC}$ = 339.6, $^1J_{^{119}SnC}$ = 346.0 Hz), 1.0 (q), 1.9 (q), 2.2 (q), 22.8 (q), 24.9 (q), 29.2 (d × 2), 29.8 (d), 31.1 (d), 121.9 (d), 122.5 (d), 125.4 (d), 125.8 (d), 126.8 (d), 127.7 (d), 128.9 (d), 130.0 (d, $^3J_{SnC}$ = 37.7 Hz), 140.1 (s), 142.3 (s), 143.1 (s), 143.7 (s), 147.3 (s), 148.2 (s), 150.3 (s), 150.7 (s) ppm. ^{119}Sn{^{1}H} NMR (111 MHz, $CDCl_3$, 25 °C): δ = –114.9 ppm.

Reaction of Tbt(Ditp)SnLi$_2$ (1e) with Tellurium(II) Dichloride: Lithium naphthalenide (1.24 N solution in THF, 0.38 mL, 0.47 mmol, 5 molar amounts) was added to a THF solution (1.0 mL) of **15** (108 mg, 94.0 μmol) at –78 °C. After stirring at the same temperature for 1 h, tellurium(II) dichloride (20.2 mg, 101 μmol) was added to the reaction mixture. The solution was slowly warmed to room temperature over 10 h. After the removal of the solvent, hexane was added to the residue. Insoluble inorganic salts were removed by filtration through Celite® and the solvents evaporated. The residue was subjected to GPLC (toluene) to give TbtH (37.8 mg, 73%), **18** (19.6 mg, 8%), **19** (20.2 mg, 11%), and **20** (20.6 mg, 70%). **18:** Orange crystals. M.p. 129.7 °C (dec.). $C_{102}H_{168}Si_{12}Sn_3Te_4$·1.5(toluene) (2736.22): calcd. C 49.38, H 6.63; found C 49.03, H 6.85. FAB-MS: *m*/*z* calcd. for $C_{51}H_{84}Si_6{}^{120}Sn_2{}^{130}Te_3$ 1488 [{M – Tbt(Ditp)SnTe}$^+$], found 1488 [{M – Tbt(Ditp)SnTe}$^+$], $C_{51}H_{84}Si_6{}^{120}Sn{}^{130}Te$ 1115 [{M – $Tbt(Ditp)Sn_2Te_3$}$^+$], found 1115 [{M – $Tbt(Ditp)Sn_2Te_3$}$^+$]. ^{1}H NMR (300 MHz, C_6D_6, 70 °C): δ = 0.17 (br. s, 36 H, $SiMe_3$), 0.24 (s, 36 H, $SiMe_3$), 0.26 (s, 36 H, $SiMe_3$), 1.17 (d, $^3J_{HH}$ = 6.9 Hz, 6 H, Me), 1.25 (d, $^3J_{HH}$ = 6.9 Hz, 6 H, Me), 1.46 (d, $^3J_{HH}$ = 6.9 Hz, 6 H, Me), 1.55 (s, 2 H, *p*-BnH for Tbt), 1.58 (d, $^3J_{HH}$ = 6.9 Hz, 6 H, Me), 2.93 (sept, $^3J_{HH}$ = 6.9 Hz, 2 H, BnH for Ditp), 2.98 (sept, $^3J_{HH}$ = 6.9 Hz, 2 H, BnH for Ditp), 3.64 (br. s, 2 H, *o*-BnH for

Tbt), 4.31 (br. s, 2 H, *o*-BnH for Tbt), 6.67 (br. s, 4 H, *m*-ArH for Tbt), 6.88–7.11 (m, 16 H, PhH for Ditp), 7.24 (t, $^3J_{HH}$ = 7.8 Hz, 2 H, PhH for Ditp), 7.35 (d, $^3J_{HH}$ = 7.8 Hz, 2 H, PhH for Ditp), 7.43 (d, $^3J_{HH}$ = 7.8 Hz, 2 H, PhH for Ditp) ppm. ^{13}C NMR (75 MHz, C_6D_6, 70 °C): δ = 1.05 (q), 1.09 (q), 3.3 (q), 24.5 (q), 24.9 (q), 25.6 (q), 26.0 (q), 29.8 (d), 30.2 (d × 2), 30.9 (d), 31.1 (d), 125.9 (d), 126.2 (d), 126.8 (d), 127.2 (d), 127.6 (d), 128.4 (d), 128.6 (d), 128.8 (d), 128.9 (d), 129.0 (d), 131.2 (d), 131.9 (d × 2), 133.7 (s), 140.0 (s), 141.1 (s), 141.3 (s), 144.3 (s), 147.3 (s), 148.5 (s), 149.6 (s), 150.0 (s), 150.7 (s), 151.0 (s) ppm. ^{119}Sn{^{1}H} NMR (54 MHz, C_6D_6, 25 °C): δ = –384.1, –386.8, –149.0 ppm. ^{125}Te{^{1}H} NMR (94 MHz, C_6D_6, 25 °C): δ = 762.9, 765.0, 766.0, 771.3 ppm. The coupling constant between ^{119}Sn and ^{125}Te could not be determined because of low solubility of **18**. **19:** Green crystals. M.p. 253.2 °C (dec.). High-resolution FAB-MS: *m*/*z* calcd. for $C_{54}H_{118}Si_{12}{}^{128}Te_2$ 1358.4554 [M$^+$], found 1358.4556 [M$^+$]. ^{1}H NMR (300 MHz, $CDCl_3$, 60 °C): δ = 0.08 (br. s, 36 H, $SiMe_3$), 0.14 (br. s, 72 H, $SiMe_3$), 3.64 (s, 2 H, *p*-BnH for Tbt), 2.88 (br. s, 4 H, *o*-BnH for Tbt), 6.51 (br. s, 4 H, *m*-PhH for Tbt) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 60 °C): δ = 0.8 (q × 2), 1.1 (q), 30.6 (d × 2), 38.1 (d), 120.7 (d), 125.5 (d), 144.4 (s), 147.5 (s), 149.8 (s), 153.3 (s) ppm. ^{125}Te{^{1}H} NMR (94 MHz, $CDCl_3$, 60 °C): δ = 225.4 ppm. **20:** Colorless liquid. EI-MS: *m*/*z* calcd. for $C_{24}H_{26}$ 314 [M$^+$], found 314 [M$^+$]. ^{1}H NMR (300 MHz, C_6D_6, 25 °C): δ = 1.09 (d, $^2J_{HH}$ = 6.9 Hz, 12 H, Me), 3.26 (sept, $^2J_{HH}$ = 6.9 Hz, 2 H, BnH), 7.08 (t, $^3J_{HH}$ = 7.5 Hz, 1 H, ArH), 7.19 (d, $^3J_{HH}$ = 7.5 Hz, 2 H, ArH), 7.20–7.29 (m, 8 H, ArH), 7.38 (s, 1 H, ArH) ppm. ^{13}C NMR (75 MHz, C_6D_6, 25 °C): δ = 24.3 (d), 29.8 (q), 125.7 (d), 125.8 (d), 128.1 (d), 128.7 (d), 129.6 (d), 130.3 (d), 130.8 (d), 141.4 (s), 142.4 (s), 146.5 (s) ppm.

NMR Measurement of Tbt(Dip)SnLi$_2$ (1c): Lithium naphthalenide (1.33 N THF solution, 0.38 mL, 0.51 mmol) was added to a THF solution (0.5 mL) of **4** (99.2 mg, 0.1 mmol) at –78 °C in a 5-mm NMR glass tube. After it was sealed and the reaction mixture kept at –78 °C for 30 min, the ^{119}Sn NMR of this solution was measured at –80 °C.

X-ray Crystallography: Single crystals of **11** and **18**·1.5(toluene) were grown by the slow concentration of their saturated solutions in acetone and toluene, respectively, at room temperature. The sample preparation consisted of coating the crystal with hydrocarbon oil, mounting it on a glass fiber, and placing it under a cold stream of N_2 on the diffractometer. The intensity data of **11** and **18**·1.5(toluene) were collected with a Rigaku/MSC Mercury CCD diffractometer with graphite-monochromated Mo-K_α radiation (λ = 0.71071 Å) to $2\theta_{max}$ = 50° at 103 K (Table 1). All structures were solved by Patterson methods (DIRDIF)[28] and refined by full-matrix least-squares procedures on F^2 for all reflections (SHELXL-97).[29] All hydrogen atoms except for 0.5(toluene) of **18**·1.5(toluene) were placed using AFIX instructions; hydrogen atoms of 0.5(toluene) were not placed. All the other atoms were refined anisotropically. In the case of **18**·1.5(toluene), the over-

Table 1. Crystallographic data for **11** and **18**·1.5(toluene).

	11	**18**·1.5(toluene)
Empirical formula	$C_{45}H_{80}Si_6Sn$	$C_{112.50}H_{176}Si_{12}Sn_3Te_4$
Formula mass	908.32	2732.08
Crystal color	colorless	orange
Crystal dimensions [mm]	0.20 × 0.10 × 0.10	0.20 × 0.10 × 0.02
Crystal system	triclinic	triclinic
Space group	$P\bar{1}$(#2)	$P\bar{1}$(#2)
Unit cell dimensions		
a [Å]	12.395(6)	13.767(4)
b [Å]	13.847(8)	21.023(6)
c [Å]	15.867(9)	22.299(7)
α [°]	105.633(11)	95.993(7)
β [°]	90.095(9)	90.455(4)
γ [°]	91.121(8)	94.119(7)
V [Å^3]	2622(2)	6401(3)
Z	2	2
$D_{calcd.}$ [g·cm^{-3}]	1.151	1.417
μ [mm^{-1}]	0.651	1.628
F(000)	968	2754
Radiation	Mo-K_α (λ = 0.71070 Å)	Mo-K_α (λ = 0.71070 Å)
Temperature [K]	103(2)	103(2)
θ range [°]	4.82–25.00	2.36–25.00
h,*k*,*l* range	$-14 \le h \le 14$	$-12 \le h \le 16$
	$-16 \le k \le 16$	$-24 \le k \le 24$
	$-18 \le l \le 18$	$-26 \le l \le 26$
No. of reflections measured	16732	41931
No. of unique reflections	8940 (R_{int} = 0.0864)	22042 (R_{int} = 0.0689)
Completeness to θ	96.9%	97.7%
Max./min. transmission	0.9377/0.8808	0.9682/0.7367
Refinement method	full-matrix least squares on F^2	full-matrix least squares on F^2
No. of data/restraints/parameter	8940/0/469	22042/73/1210
Goodness-of-fit	1.034	1.025
Final *R* indices [$I > 2\sigma(I)$]	R_1 = 0.058	R_1 = 0.075
	wR_2 = 0.108	wR_2 = 0.170
R indices (all data)	R_1 = 0.090	R_1 = 0.121
	wR_2 = 0.117	wR_2 = 0.207
Largest diff. peak/hole [e·Å^{-3}]	0.696/–0.596	1.967/–0.822

lapped and disordered toluene molecules were restrained to be identical to each other using DFIX, SADI, SAME, and SIMU instructions. The *ipso*-carbon atom of the Ditp group was restrained using ISOR instruction. The residual electron densities of **18**·1.5(toluene) that are larger than 1.0 can be assigned to the heavy elements (Si, Sn, and Te atoms) of a minor disordered molecule (about 2%). However, the peaks for the carbon atoms of the disordered molecule could not be found. CCDC-265559 (**11**) and -276174 [**18**·1.5(toluene)] contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

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