# 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<sub>2</sub> {Tbt = 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl; Dip = 2,6-diisopropylphenyl}, with an excess amount of lithium naph-thalenide in THF at -78 °C gave the corresponding dilithiostannane, Tbt(Dip)SnLi<sub>2</sub>, the generation of which was confirmed by trapping experiments with some electrophiles together with <sup>119</sup>Sn and <sup>7</sup>Li NMR spectroscopy. The diaryldi-lithiostannane was found to be stable in solution under an inert gas below -25 °C. The potassium analogue, Tbt(Dip)SnK<sub>2</sub>, was also generated by the reduction of the dibromostannane in THF at -78 °C by the use of KC<sub>8</sub> as a reductant.

#### 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,<sup>[1]</sup> 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.<sup>[2]</sup> 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.<sup>[3]</sup> Although Schmidt et al. have proposed the formation of  $(C_6H_5)_2$ SnLi<sub>2</sub> in the reaction of  $(C_6H_5)_2$ SnCl<sub>2</sub> with 4 molar amounts of Li,<sup>[4,5]</sup> the yields of the trapping reactions are not high and the generation of dilithiodiphenylstannane was not evidenced by <sup>119</sup>Sn and <sup>7</sup>Li NMR spectroscopy. More recently, Egorov et al. reported the <sup>119</sup>Sn and <sup>13</sup>C NMR studies of Et<sub>2</sub>SnLi<sub>2</sub> and (C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>SnLi<sub>2</sub>.<sup>[6]</sup> 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.<sup>[7,8]</sup> Recently, we have also succeeded in the syn-

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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<sub>2</sub> (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. (© Wiley-VCH Verlag GmbH & Co. KGaA, 69451 Weinheim, Germany, 2005)

thesis and isolation of the first stable sila<sup>[9]</sup> and germacyclopropabenzenes,<sup>[10]</sup> **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,<sup>[8]</sup> are quite rare. To the best of our knowledge, only one report has so far appeared on the synthesis of stannacyclopropenes.<sup>[8c]</sup>

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,<sup>[12]</sup> stannanetellone (Scheme 1).



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

### **Results and Discussion**

Dibromostannane 4 was prepared by a method similar to that for the synthesis of Tbt(Mes)SnBr<sub>2</sub>,<sup>[13]</sup> as shown in Scheme 2. Tbt-substituted trihalostannane was synthesized by the reaction of SnCl<sub>4</sub> with TbtLi. Tbt- and Dip-substituted stannane, Tbt(Dip)SnH<sub>2</sub> (3), was prepared by the nucleophilic displacement reaction of the Tbt-substituted trihalostannane using DipMgBr, followed by reduction with LiAlH<sub>4</sub>. Bromination reaction of **3** using Br<sub>2</sub> in ether afforded the corresponding dibromostannane **4**.



Scheme 2. Synthesis of dibromostannane 4.

Tbt(Dip)SnLi<sub>2</sub> (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<sub>2</sub> (5) in 96% yield. The addition of DCl to the solution of 1c at -78 °C resulted in the formation of Tbt(Dip)SnD<sub>2</sub> (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 <sup>119</sup>Sn NMR spectrum of **1c** in THF at -80 °C showed a broad signal at  $\delta = -362.2$  ppm, which is observed at a much higher field than that of Tbt(Dip)SnBr<sub>2</sub> (**4**:  $\delta = -162.0$  ppm in THF at -80 °C).<sup>[14]</sup> In the <sup>7</sup>Li NMR spectrum, only one singlet signal was observed at  $\delta = 0.6$  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 <sup>119</sup>Sn NMR spectrum was performed. The <sup>119</sup>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.<sup>[16]</sup>

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<sub>3</sub>)<sub>2</sub> units of the Tbt group to give the corresponding lithium migration products 6a and 6b, respectively (Scheme 4).<sup>[10,11]</sup> Treatment of the intermediates such as **6a** and **6b** with D<sub>2</sub>O 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 <sup>119</sup>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<sub>8</sub> 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<sub>2</sub>O to the yellow solution resulted in the formation of TbtH, DipH, and **10**<sup>[17]</sup> (Scheme 5). As this 1,3-silicon rearrangement product **10** was reportedly obtained from TbtLi above -30 °C in THF,<sup>[20]</sup> these results strongly suggest the initial formation of TbtK and DipK at low temperature in this reaction. Although we attempted the reactions of 4 with other reductants (Li, K, tBuLi, and nBuLi), 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<sup>[9]</sup> and 2b.<sup>[10]</sup> 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 Xray crystallographic analysis. In Figure 1 the ORTEP drawing of stannacyclobutabenzene 11 is shown.<sup>[18]</sup> The deformation from the normal sp<sup>2</sup> 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 stannabutabenzene [Sn1–C1 2.185(5) Å, C7–C6 for 1.588(8) Å].<sup>[18]</sup> 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-2metallabenzene 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).<sup>[19]</sup> 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  $D_2O$ .<sup>[9,10]</sup> 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.

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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.<sup>[2]</sup> Recently, we reported the synthesis of silanetellone and germanetellone by the reactions of overcrowded dilithiometallanes 1a and 1b with tellurium(II) dichloride, respectively.<sup>[2g,20]</sup> Taking these results into account, the dilithiostannane should be a good precursor for the synthesis of a tin-tellurium double-bond compound 16.<sup>[12]</sup> 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.<sup>[13]</sup> 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.<sup>[21]</sup> Therefore, we tried the synthesis of stannanetellone having Tbt and Ditp groups.

Interestingly, treatment of a THF solution of Tbt(Ditp)-SnLi<sub>2</sub> (1e)<sup>[22]</sup> with tellurium(II) dichloride<sup>[23]</sup> 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 <sup>119</sup>Sn NMR signals of the cyclic compound, spirobi(ditelluradistannetane) 18, were observed at  $\delta = -149$ , -384, and -387 ppm in C<sub>6</sub>D<sub>6</sub>. The <sup>125</sup>Te NMR chemical shift of **18** was observed at  $\delta$  = 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-ditelluradistantetanes,  $[(Dis)_2SnTe]_2$  [Dis =  $-CH(SiMe_3)_2$ ] [2.756(1) and 2.771(1) Å]<sup>[24a]</sup> and  $(tBu_2SnTe)_2$  [2.754(1) and 2.758(1) Å].<sup>[24b]</sup>



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



Figure 2. ORTEP drawing of  $18\cdot1.5$ (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 S8 through the corresponding silanethione and silanethione dimer.<sup>[25]</sup> 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  $\sigma$ - and  $\pi$ -bond energies than those of the lighter element(s) analogues. In order to isolate a stable stannanetellone, 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. <sup>1</sup>H NMR (300 MHz), <sup>13</sup>C NMR (75 MHz), <sup>119</sup>Sn NMR (111 MHz), and <sup>125</sup>Te NMR (94 MHz) spectra were measured in CDCl<sub>3</sub> or C<sub>6</sub>D<sub>6</sub> with a JEOL JNM AL-300 spectrometer. <sup>1</sup>H and <sup>13</sup>C NMR chemical shifts were recorded in ppm relative to tetramethylsilane ( $\delta = 0$  ppm) and were referenced internally with respect to the residual proton impurity (CHCl<sub>3</sub>:  $\delta$  = 7.26 ppm, benzene:  $\delta = 7.15$  ppm) and the <sup>13</sup>C resonance of the solvent (CDCl<sub>3</sub>:  $\delta$  = 77.2 ppm, [D<sub>6</sub>]benzene:  $\delta$  = 128.0 ppm), respectively. <sup>119</sup>Sn NMR chemical shifts were referenced with tetramethylstannane ( $\delta = 0$  ppm) as an external standard. <sup>125</sup>Te NMR chemical shifts were referenced with diphenvlditelluride ( $\delta = 450 \text{ ppm}$ ) 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<sub>3</sub> 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)-(TbtBr),<sup>[26]</sup> 1-bromo-2,6-diisopropylbenzene methyl]benzene (DipBr),<sup>[27]</sup> and 2'-iodo-2,2''-diisopropyl-1,1':3'1''-terphenyl (DitpI)<sup>[21]</sup> were prepared according to reported procedures.

**Tbt(Dip)SnH<sub>2</sub> (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<sub>4</sub> (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<sup>®</sup>, the reaction mixture was concentrated to give colorless crystals. Recrystallization from CH<sub>3</sub>CN/CHCl<sub>3</sub> afforded a mixture of TbtSn(Hal)<sub>3</sub> (Hal = Cl and/or Br) (16.4 g). A THF solu-

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tion (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 TbtSnCl<sub>3-n</sub>Br<sub>n</sub> (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<sub>4</sub> (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<sub>2</sub>O, and then dried with Na<sub>2</sub>SO<sub>4</sub>. After the removal of the solvent, the mixture was purified by column chromatography  $(SiO_2/hexane)$  to afford Tbt(Dip)SnH<sub>2</sub> (3) as colorless crystals. Yield: 4.0 g (33%). M.p. 155.5 °C (dec.). C<sub>39</sub>H<sub>78</sub>Si<sub>6</sub>Sn (834.26): calcd. C 56.15, H 9.42; found C 56.06, H 9.51. FAB-MS: m/z calcd. for C<sub>39</sub>H<sub>78</sub>Si<sub>6</sub><sup>120</sup>Sn 834 [M<sup>+</sup>], found 834 [M<sup>+</sup>]. <sup>1</sup>H NMR (300 MHz,  $C_6D_6$ , 25 °C):  $\delta = 0.30$  (s, 9 H, SiMe<sub>3</sub>), 0.32 (s, 36 H, SiMe<sub>3</sub>), 0.35 (s, 9 H, SiMe<sub>3</sub>), 1.34 (d,  ${}^{3}J_{HH}$  = 5.5 Hz, 6 H, CH<sub>3</sub>), 1.51 (d,  ${}^{3}J_{HH}$ = 5.5 Hz, 6 H, CH<sub>3</sub>), 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,  ${}^{3}J_{\rm HH}$  = 5.5 Hz, 2 H, BnH for Dip), 6.38 (s,  ${}^{1}J_{117}{}_{\rm SnH}$  = 1769.4,  ${}^{1}J_{119}_{SnH}$  = 1855.2 Hz, 2 H, SnH<sub>2</sub>), 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. <sup>13</sup>C NMR (75 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C):  $\delta$  = 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. <sup>119</sup>Sn{<sup>1</sup>H} NMR (111 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C):  $\delta$  = -345.6 ppm. IR (KBr):  $\tilde{v}$  = 1863.9 [v(Sn-H)] cm<sup>-1</sup>.

Tbt(Dip)SnBr<sub>2</sub> (4): A solution of 3 (3.70 g, 4.43 mmol) and Br<sub>2</sub> (0.50 mL, 9.76 mmol) in Et<sub>2</sub>O (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<sub>2</sub>SO<sub>4</sub>. After the removal of the solvent, the residue was recrystallized from CHCl<sub>3</sub> and EtOH to afford 4 as colorless crystals. Yield: 2.98 g (68%). M.p. 188.4-192.5 °C. C<sub>39</sub>H<sub>76</sub>Br<sub>2</sub>Si<sub>6</sub>Sn (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<sup>+</sup>], found 992 [M<sup>+</sup>]. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$  = 0.03 (s, 36 H, SiMe<sub>3</sub>), 0.05 (s, 18 H, SiMe<sub>3</sub>), 1.16 (s, 1 H, p-BnH for Tbt), 1.33 (d,  ${}^{3}J_{HH}$  = 6.6 Hz, 12 H, CH<sub>3</sub>), 2.13 (br. s, 1 H, o-BnH for Tbt), 2.43 (br. s, 1 H, o-BnH for Tbt), 3.36 (sept,  ${}^{3}J_{HH}$  = 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. <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$  = 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. <sup>119</sup>Sn NMR (111 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$  = -171.0 ppm.

Generation of Tbt(Dip)SnM<sub>2</sub> (M = Li, K) and Preparation of Tbt(Dip)SnMe<sub>2</sub> (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<sup>®</sup>. The residue was subjected to GPLC (CHCl<sub>3</sub>) followed by PTLC (hexane) to afford 5 as colorless crystals. Yield: 52.7 mg (97%). Method B (M = K): KC<sub>8</sub> (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. C41H82Si6Sn (862.31): calcd. C 57.11, H 9.58; found C 56.96, H 9.59. FAB-MS: m/z calcd. for C41H82Si6120Sn 863 [M+], found 863 [M<sup>+</sup>]. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta = -0.05$  (s, 18 H, SiMe<sub>3</sub>), -0.01 (s, 18 H, SiMe<sub>3</sub>), 0.02 (s, 18 H, SiMe<sub>3</sub>), 0.64 (s, <sup>2</sup>J<sub>HSn</sub> = 48.3 Hz, 6 H, SnMe), 1.23 (d,  ${}^{3}J_{HH}$  = 5.5 Hz, 12 H, CH<sub>3</sub>), 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,  ${}^{3}J_{HH} = 5.5$  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. <sup>13</sup>C NMR (75 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C):  $\delta$  = 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. <sup>119</sup>Sn NMR (111 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$  = -126.4 ppm.

Generation of Tbt(Dip)SnLi<sub>2</sub> 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<sub>2</sub>O, 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<sup>®</sup>, and the solvents evaporated. The residue was subjected to GPLC (toluene) to give Tbt(Dip)SnD<sub>2</sub> (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<sub>39</sub>H<sub>76</sub>D<sub>2</sub>Si<sub>6</sub><sup>120</sup>Sn 836.3865 [M<sup>+</sup>], found 836.3894 [M<sup>+</sup>]. <sup>1</sup>H NMR (300 MHz,  $C_6D_6$ , 25 °C):  $\delta = 0.30$  (s, 9 H, SiMe<sub>3</sub>), 0.32 (s, 36 H, SiMe<sub>3</sub>), 0.35 (s, 9 H, SiMe<sub>3</sub>), 1.34 (d,  ${}^{3}J_{HH} = 5.5$  Hz, 6 H, CH<sub>3</sub>), 1.51 (d,  ${}^{3}J_{HH} = 5.5$  Hz, 6 H, CH<sub>3</sub>), 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,  ${}^{3}J_{HH} = 5.5$  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. <sup>13</sup>C NMR (75 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C):  $\delta$ = 0.6 (q), 1.0 (q), 1.2 (q), 25.1 (q), 30.6 (d), 33.3 (d), 37.5 (d  $\times$  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. <sup>119</sup>Sn NMR (111 MHz,  $C_6D_6$ , 25 °C):  $\delta = -346.8$  (quint,  ${}^1J_{SnD} = 280.7$  Hz) ppm. IR (KBr):  $\tilde{v} = 1317.1 [v(Sn-D)] \text{ cm}^{-1}.$ 

Generation of Tbt(Dip)SnLi<sub>2</sub> (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<sup>®</sup> and the filtrate was concentrated. The residue was subjected to GPLC (CHCl<sub>3</sub>) 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<sub>45</sub>H<sub>87</sub>Si<sub>6</sub><sup>120</sup>Sn 915 [M + H]<sup>+</sup>, found 915 [M + H]<sup>+</sup>. High-resolution FAB-MS: m/z calcd. for C<sub>45</sub>H<sub>87</sub>Si<sub>6</sub><sup>120</sup>Sn 915.4445 [M + H]<sup>+</sup>, found 915.4456 [M + H]<sup>+</sup>. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$  = -0.05 (br. s, 18 H, SiMe<sub>3</sub>), -0.24 (br. s, 18 H, SiMe<sub>3</sub>), 0.03 (s, 18 H, SiMe<sub>3</sub>), 1.19 (d,  ${}^{3}J_{HH} = 6.6$  Hz, 9 H, CH<sub>3</sub> for Dip), 1.19 (br. s, 1 H, *p*-BnH for Tbt), 1.28 (d,  ${}^{3}J_{HH} =$ 6.6 Hz, 3 H, CH<sub>3</sub> for Dip), 1.68 (s, 1 H, o-BnH for Tbt), 1.74 (br. s, 6 H, CH<sub>3</sub>), 1.79 (s, 1 H, *o*-BnH for Tbt), 2.09 (d,  ${}^{2}J$  = 17.0 Hz, 2 H, CH<sub>2</sub>), 2.14 (d,  ${}^{4}J$  = 17.0 Hz, 2 H, CH<sub>2</sub>), 3.02 (sept,  ${}^{3}J_{HH}$  = 6.6 Hz, 1 H, BnH for Dip), 3.12 (sept,  ${}^{3}J_{HH}$  = 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,  ${}^{3}J_{HH}$  = 7.5 Hz, 2 H, *m*-PhH for Dip), 7.23 (t,  ${}^{3}J_{HH}$ = 7.5 Hz, 1 H, *p*-PhH for Dip) ppm. <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$  = 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. <sup>119</sup>Sn NMR (111 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$  = -110.2 ppm.

Generation of Tbt(Dip)SnK<sub>2</sub> and the Trapping Reaction of the Decomposed Compounds with H<sub>2</sub>O at Room Temperature: KC<sub>8</sub> (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<sup>®</sup> and the filtrate was concentrated. The residue was subjected to GPLC (CHCl<sub>3</sub>) followed by PTLC (hexane) to give TbtH (12.1 mg, 20%), **10** (39.7 mg, 72%), and DipH (14.1 mg, 80%).<sup>[17]</sup>

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<sub>3</sub>) followed by PTLC (hexane) to give 11 as colorless crystals. Yield: 30.1 mg (16%). Method B: KC<sub>8</sub> (150 mg, 1.11 mmol) was added to a THF solution (3.0 mL) of Tbt(Dip)SnBr<sub>2</sub> (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.). C45H80Si6Sn (908.34): calcd. C 59.50, H 8.88; found C 59.53, H 8.63. FAB-MS: m/z calcd. for C<sub>45</sub>H<sub>80</sub>Si<sub>6</sub><sup>120</sup>Sn 908 [M<sup>+</sup>], found 908 [M<sup>+</sup>]. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$  = -0.26 (s, 9 H, SiMe<sub>3</sub>), -0.16 (s, 9 H, SiMe<sub>3</sub>), 0.02 (s, 9 H, SiMe<sub>3</sub>), 0.04 (s, 9 H, SiMe<sub>3</sub>), 0.15 (s, 9 H, SiMe<sub>3</sub>), 0.17 (s, 9 H, SiMe<sub>3</sub>), 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,  ${}^{2}J_{\text{HSn}}$  = 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,  ${}^{3}J_{HH} = 7.2$  Hz, 2 H, *m*-PhH for Dip), 7.20–7.27 (m, 2 H, PhH), 7.30 (t,  ${}^{3}J_{HH} = 7.2$  Hz, 1 H, *p*-PhH for Dip), 7.60 (dd,  ${}^{3}J_{HH}$ = 7.2,  ${}^{4}J_{HH}$  = 2.1 Hz, 1 H, PhH), 7.93 (dd,  ${}^{3}J_{HH}$  = 7.2,  ${}^{4}J_{HH}$  = 2.1 Hz, 1 H, PhH) ppm. <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>, 50 °C):  $\delta$  = 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. <sup>119</sup>Sn{<sup>1</sup>H} NMR (111 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$  = -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  $\mu$ L, 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 C45H8179BrSi6120Sn 988 [M<sup>+</sup>], found 988 [M<sup>+</sup>]. High-resolution FAB-MS: *m*/*z* calcd. for C<sub>45</sub>H<sub>81</sub><sup>79</sup>BrSi<sub>6</sub><sup>120</sup>Sn 988.3159 [M<sup>+</sup>], found 988.3193 [M<sup>+</sup>]. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$  = -0.16 (s, 27 H, SiMe<sub>3</sub>), -0.13 (s, 9 H, SiMe<sub>3</sub>), -0.07 (s, 9 H, SiMe<sub>3</sub>), -0.06 (s, 9 H, SiMe<sub>3</sub>), 0.83 (d,  ${}^{3}J_{HH}$  = 6.3 Hz, 6 H, Me), 1.20 (d,  ${}^{3}J_{HH}$  = 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,  ${}^{3}J_{HH} =$ 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. <sup>13</sup>C NMR (75 MHz,  $CDCl_3$ , 25 °C):  $\delta = 0.8$  (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. <sup>119</sup>Sn{<sup>1</sup>H} NMR (111 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta = -102.2$  ppm.

Synthesis of Tbt(Ditp)SnH<sub>2</sub>: A THF solution (20 mL) of TbtSn(Hal)<sub>3</sub> (2.31 g) was added to a THF solution of DitpLi, prepared from DitpI (1.49 g, 3.37 mmol) and tBuLi (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<sup>®</sup>. The filtrate was concentrated and subjected to GPLC (CHCl<sub>3</sub>) to afford a mixture containing Tbt(Ditp)Sn(Hal)<sub>2</sub> (1.48 g) as colorless crystals. LiAlH<sub>4</sub> (734 mg, 19.3 mmol) was added to a THF solution (50 mL) of the mixture containing Tbt(Ditp)Sn(Hal)<sub>2</sub> (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<sub>2</sub>O, and then dried with Na<sub>2</sub>SO<sub>4</sub>. After removal of the solvents, the mixture was purified by column chromatography (SiO<sub>2</sub>/benzene) to afford Tbt(Ditp)SnH<sub>2</sub> 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  $[M + H]^+$ . <sup>1</sup>H NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C):  $\delta = 0.09$  (s, 36 H, SiMe<sub>3</sub>), 0.20 (s, 18 H, SiMe<sub>3</sub>), 0.95 (d,  ${}^{3}J_{HH} = 5.1$  Hz, 6 H, Me), 1.40 (d,  ${}^{3}J_{HH} = 5.1$  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,  ${}^{3}J_{HH} = 5.1$  Hz, 2 H, BnH for Ditp), 5.66 (s,  ${}^{1}J_{117}_{SnH} =$ 1768.6,  ${}^{1}J_{119}_{SnH}$  = 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,  ${}^{3}J_{HH}$  = 6.6 Hz, 2 H, ArH for Ditp) ppm.  ${}^{13}C$ NMR (75 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C):  $\delta$  = 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. <sup>119</sup>Sn{<sup>1</sup>H} NMR (111 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C):  $\delta$  = -342.9 ppm. IR (KBr):  $\tilde{v} = 1841.7 [v(Sn-H)] \text{ cm}^{-1}$ .

**Synthesis of Tbt(Ditp)SnBr<sub>2</sub> (15):** A solution of Tbt(Ditp)SnH<sub>2</sub> (734 mg, 0.74 mmol) and Br<sub>2</sub> (0.21 mL, 0.84 mmol) in Et<sub>2</sub>O (40 mL) was stirred at room temperature for 30 min. The solution was washed with a saturated aqueous solution of Na<sub>2</sub>SO<sub>3</sub> and then with a saturated aqueous solution of NaCl. The organic layer was dried with Na<sub>2</sub>SO<sub>4</sub>. After the removal of the solvent, the residue was recrystallized from CHCl<sub>3</sub> and EtOH to afford **15** as colorless crystals. Yield: 621 mg (73%). M.p. 278.5–279.6 °C.  $C_{51}H_{84}Br_{2}Si_{6}Sn$  (1144.24): calcd. C 53.53, H 7.40; found C 53.52, H 7.46. FAB-MS: *m/z* calcd. for  $C_{51}H_{84}^{79}Br_{2}Si_{6}^{120}Sn$  1144 [M<sup>+</sup>],

found 1144 [M<sup>+</sup>]. <sup>1</sup>H NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C):  $\delta$  = 0.19 (br. s, 36 H, SiMe<sub>3</sub>), 0.21 (br. s, 18 H, SiMe<sub>3</sub>), 1.03 (d, <sup>3</sup>J<sub>HH</sub> = 6.3 Hz, 6 H, Me), 1.39 (d, <sup>3</sup>J<sub>HH</sub> = 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, <sup>3</sup>J<sub>HH</sub> = 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, <sup>3</sup>J<sub>HH</sub> = 7.2 Hz, 2 H, ArH for Ditp) ppm. <sup>13</sup>C NMR (75 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C):  $\delta$  = 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), 129.7 (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. <sup>119</sup>Sn{<sup>1</sup>H} NMR (111 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$  = –192.5 ppm.

Generation of Tbt(Ditp)SnLi<sub>2</sub> and Preparation of Tbt(Ditp)SnMe<sub>2</sub>: 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<sub>3</sub>) followed by PTLC (hexane) to afford Tbt(Ditp)SnMe2 as colorless crystals. Yield: 38.1 mg (93%). M.p. 265.3–265.7 °C. C<sub>53</sub>H<sub>90</sub>Si<sub>6</sub>Sn (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<sub>53</sub>H<sub>90</sub>Si<sub>6</sub><sup>120</sup>Sn 1014.4680 [M<sup>+</sup>], found 1014.4697 [M<sup>+</sup>]. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta = -0.45$  (s,  ${}^{2}J_{\text{HSn}} = 51.0 \text{ Hz}, 6 \text{ H}, \text{ SnMe}$ , -0.04 (br. s, 36 H, SiMe<sub>3</sub>), -0.09 (s, 18 H, SiMe<sub>3</sub>), 1.04 (d,  ${}^{3}J_{HH}$  = 6.6 Hz, 6 H, Me), 1.15 (d,  ${}^{3}J_{HH}$  = 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,  ${}^{3}J_{HH}$  = 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,  ${}^{3}J_{HH}$  = 7.2 Hz, 1 H, PhH for Ditp), 7.13 (d,  ${}^{3}J_{HH}$  = 7.2 Hz, 2 H, PhH for Ditp), 7.21-7.39 (m, 8 H, PhH for Ditp) ppm. <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta = -0.4$  (q,  ${}^{1}J_{117}_{SnC} = 339.6$ ,  ${}^{1}J_{119}_{SnC}$  = 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,  ${}^{3}J_{SnC} = 37.7$  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. <sup>119</sup>Sn{<sup>1</sup>H} NMR (111 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$  = -114.9 ppm.

Reaction of Tbt(Ditp)SnLi2 (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: 129.7 °C Orange crystals. M.p. (dec.).  $C_{102}H_{168}Si_{12}Sn_{3}Te_{4}$ ·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<sub>51</sub>H<sub>84</sub>Si<sub>6</sub><sup>120</sup>Sn<sub>2</sub><sup>130</sup>Te<sub>3</sub> 1488 [{M - Tbt(Ditp)SnTe}<sup>+</sup>], found 1488  $[{M - Tbt(Ditp)SnTe}^+], C_{51}H_{84}Si_6^{120}Sn^{130}Te 1115 [{M - Var}]{M}$  $Tbt(Ditp)Sn_2Te_3$ <sup>+</sup>], found 1115 [{M - Tbt(Ditp)Sn\_2Te\_3}<sup>+</sup>]. <sup>1</sup>H NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>, 70 °C):  $\delta$  = 0.17 (br. s, 36 H, SiMe<sub>3</sub>), 0.24 (s, 36 H, SiMe<sub>3</sub>), 0.26 (s, 36 H, SiMe<sub>3</sub>), 1.17 (d,  ${}^{3}J_{HH} = 6.9$  Hz, 6 H, Me), 1.25 (d,  ${}^{3}J_{HH}$  = 6.9 Hz, 6 H, Me), 1.46 (d,  ${}^{3}J_{HH}$  = 6.9 Hz, 6 H, Me), 1.55 (s, 2 H, *p*-BnH for Tbt), 1.58 (d,  ${}^{3}J_{HH} = 6.9$  Hz, 6 H, Me), 2.93 (sept,  ${}^{3}J_{HH} = 6.9$  Hz, 2 H, BnH for Ditp), 2.98 (sept,  ${}^{3}J_{\text{HH}} = 6.9 \text{ Hz}, 2 \text{ H}, \text{ BnH for Ditp}, 3.64 (br. s, 2 \text{ H}, o-\text{BnH for})$  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,  ${}^{3}J_{HH} = 7.8$  Hz, 2 H, PhH for Ditp), 7.35 (d,  ${}^{3}J_{HH} = 7.8$  Hz, 2 H, PhH for Ditp), 7.43 (d,  ${}^{3}J_{HH}$  = 7.8 Hz, 2 H, PhH for Ditp) ppm.  ${}^{13}C$  NMR  $(75 \text{ MHz}, C_6D_6, 70 \text{ °C}): \delta = 1.05 \text{ (q)}, 1.09 \text{ (q)}, 3.3 \text{ (q)}, 24.5 \text{ (q)}, 24.9 \text{ (q)})$ (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. <sup>119</sup>Sn{<sup>1</sup>H} NMR (54 MHz,  $C_6D_6$ , 25 °C):  $\delta = -384.1$ , -386.8, -149.0 ppm. <sup>125</sup>Te{<sup>1</sup>H} NMR  $(94 \text{ MHz}, C_6 D_6, 25 \text{ °C})$ :  $\delta = 762.9, 765.0, 766.0, 771.3 \text{ ppm}$ . The coupling constant between <sup>119</sup>Sn and <sup>125</sup>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<sub>54</sub>H<sub>118</sub>Si<sub>12</sub><sup>128</sup>Te<sub>2</sub> 1358.4554 [M<sup>+</sup>], found 1358.4556 [M<sup>+</sup>]. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 60 °C):  $\delta$  = 0.08 (br. s, 36 H, SiMe<sub>3</sub>), 0.14 (br. s, 72 H, SiMe<sub>3</sub>), 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. <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>, 60 °C):  $\delta = 0.8$  (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. <sup>125</sup>Te{<sup>1</sup>H} NMR (94 MHz, CDCl<sub>3</sub>, 60 °C):  $\delta$  = 225.4 ppm. **20:** Colorless liquid. EI-MS: m/z calcd. for C24H26 314 [M+], found 314 [M<sup>+</sup>]. <sup>1</sup>H NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C):  $\delta$  = 1.09 (d, <sup>2</sup>J<sub>HH</sub> = 6.9 Hz, 12 H, Me), 3.26 (sept,  ${}^{2}J_{HH}$  = 6.9 Hz, 2 H, BnH), 7.08 (t,  ${}^{3}J_{\rm HH}$  = 7.5 Hz, 1 H, ArH), 7.19 (d,  ${}^{3}J_{\rm HH}$  = 7.5 Hz, 2 H, ArH),

7.20–7.29 (m, 8 H, ArH), 7.38 (s, 1 H, ArH) ppm. <sup>13</sup>C NMR (75 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C):  $\delta$  = 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<sub>2</sub> (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 <sup>119</sup>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<sub>2</sub> 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- $K_{\alpha}$  radiation ( $\lambda = 0.71071$  Å) to  $2\theta_{max} = 50^{\circ}$  at 103 K (Table 1). All structures were solved by Patterson methods (DIRDIF)<sup>[28]</sup> and refined by full-matrix least-squares procedures on  $F^2$  for all reflections (SHELXL-97).<sup>[29]</sup> All hydrogen atoms except for 0.5(toluene) of **18**·1.5(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	<b>18</b> •1.5(toluene)
Empirical formula	$C_{45}H_{80}Si_6Sn$	C <sub>112,50</sub> H <sub>176</sub> Si <sub>12</sub> Sn <sub>3</sub> Te <sub>4</sub>
Formula mass	908.32	2732.08
Crystal color	colorless	orange
Crystal dimensions [mm]	$0.20 \times 0.10 \times 0.10$	$0.20 \times 0.10 \times 0.02$
Crystal system	triclinic	triclinic
Space group	<i>P</i> 1(#2)	<i>P</i> 1(#2)
Unit cell dimensions		
<i>a</i> [Å]	12.395(6)	13.767(4)
<i>b</i> [Å]	13.847(8)	21.023(6)
<i>c</i> [Å]	15.867(9)	22.299(7)
	105.633(11)	95.993(7)
β [°]	90.095(9)	90.455(4)
γ [°]	91.121(8)	94.119(7)
$V[A^3]$	2622(2)	6401(3)
Z	2	2
$D_{\text{calcd.}} [g \cdot \text{cm}^{-3}]$	1.151	1.417
$\mu \text{ [mm^{-1}]}$	0.651	1.628
F(000)	968	2754
Radiation	Mo- $K_{\alpha}$ ( $\lambda = 0.71070 \text{ Å}$ )	Mo- $K_{\alpha}$ ( $\lambda = 0.71070 \text{ Å}$ )
Temperature [K]	103(2)	103(2)
$\theta$ range [°]	4.82-25.00	2.36-25.00
<i>h</i> , <i>k</i> , <i>l</i> 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	$8940 \ (R_{\rm int} = 0.0864)$	22042 ( $R_{\rm int} = 0.0689$ )
Completeness to $\theta$	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 <i>R</i> indices $[I > 2\sigma(I)]$	$R_1 = 0.058$	$R_1 = 0.075$
	$wR_2 = 0.108$	$wR_2 = 0.170$
<i>R</i> 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 <sup>-3</sup> ]	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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