Synthesis and Reactions of a Stannanethione Derived from a Kinetically Stabilized Diarylstannylene

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Stannanethione Tbt(Tip)Sn=S (Tbt = 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl; Tip = 2,4,6-triisopropylphenyl), containing a novel tin−sulfur double bond, was synthesized by the reactions of the corresponding kinetically stabilized diarylstannylene Tbt(Tip)Sn: with styrene episulfide or elemental sulfur. An absorption maximum due to the n−π* transition of the tin−sulfur double bond appeared at 473 nm in hexane. It reacted with thiocumulenes such as carbon disulfide and phenyl isothiocyanate and with styrene oxide and mesitonitrile oxide to give the corresponding cycloadducts. The structure of the [2 + 2] cycloadduct of a stannanethione with carbon disulfide was determined by X-ray structural analysis. In contrast to Tbt(Tip)Sn=S, the less hindered stannanethione Tbt(Mes)Sn=S (Mes = mesityl) dimerized at room temperature to afford the corresponding 1,3,2,4-dithiadistannetane.

Introduction

For many years it was considered that compounds having double bonds between heavier main group elements would be unstable because of their weak pπ−pπ bonding (the so-called “double-bond rule”). Since the isolation of the first stable compounds with Sn=Sn,[1] P=C,[2] Si=C,[3] P=P,[4] and Si=Si[5] by taking advantage of bulky ligands which prevent them from oligomerization (kinetic stabilization), however, significant and exciting progress has been made in the chemistry of unsaturated compounds of heavier main group elements, especially of group 14 elements.[6] As for stable compounds having double bonds between group 14 and group 16 elements, the chemistry of thioketones and selenoketones has been well explored for a few decades. On the other hand, when we undertook a study of such species several years ago, there were no examples of “genuine” double-bonded compounds involving the heavier group 14 and 16 elements, heavier congeners of ketones (RR′M=X; M = Si, Ge, Sn, and Pb; X = S, Se, and Te) which we refer to as “heavy ketones”, although Corriu[7] and Veith[8ab] had reported compounds having Si=X (X = S and Se) and Ge=S bonds thermodynamically stabilized by intramolecular coordination. More recently, compounds containing Ge=X (X = S, Te)[8c] and Sn=X (X = S, Se, Te)[9] bonds of similar kinds were also isolated. Since they are strongly perturbed by electron donation from neighboring nitrogen atoms to electron-deficient group 14 metals, they do not show the intrinsic nature of such double bond species in terms of their physical properties and reactivities. The difficulty in the synthesis of kinetically stabilized “heavy ketones” consists in the fact that bulky substituents for steric protection can be introduced only on the group 14 elements and, hence, their oligomerization cannot be effectively hindered.

Recently we succeeded in the isolation and X-ray structural characterization of a kinetically stabilized silanethione,[10] germanethione,[11] and germaneselone[12] bearing a new steric protection group, 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl (Tbt) group, developed in our laboratory[13] by dechalcogenation of the corresponding tetrachalcogenametallolanes, Tbt(Tip)MX_4[14] (M = Si and Ge; X = S and Se) (Tip = 2,4,6-triisopropylphenyl), with phosphine reagents. We also reported the synthesis of tin−chalcogen double-bonded compounds[15] by dechalcogenation of 1,2,3,4,5-tetrachalcogenastan-

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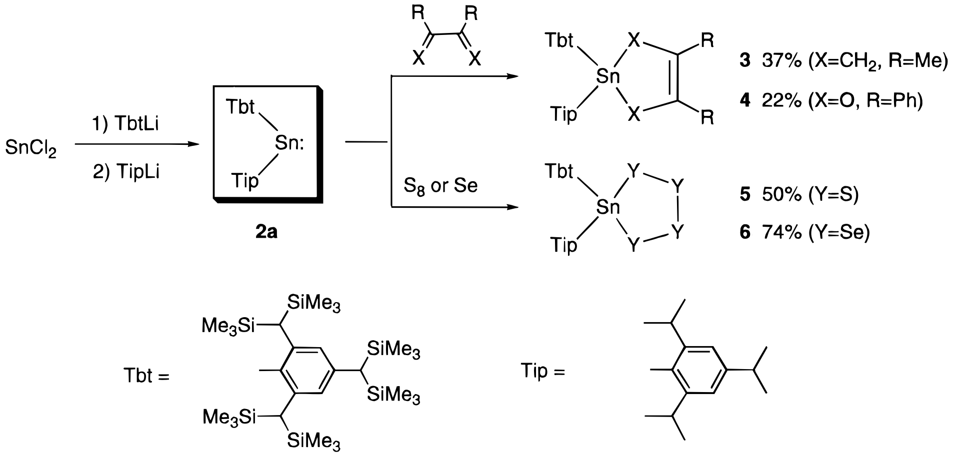
S0276-7333(96)00449-9 CCC: $12.00

Scheme 1



nolanes[16] and chalcogenation of the corresponding stannylene.[17] In this paper we report full details of the synthesis and reactions of stannanethione Tbt(Tip)Sn=S (**1a**) derived from the corresponding stannylene Tbt(Tip)Sn (**2a**).[18] The X-ray structural analysis of the newly obtained cycloadduct of stannanethione **1a** with carbon disulfide is also described.

Results and Discussion

Synthesis and Properties of Kinetically Stabilized Diarylstannylene Tbt(Tip)Sn: (2a). Stannylene **2a** was readily obtained by the treatment of a THF solution of TbtLi with an ether suspension of stannous chloride at −70 °C followed by the addition of an equimolar amount of TipLi at the same temperature. Under an inert atmosphere, stannylene **2a** was quite stable in solution even at 60 °C, and it showed a deep purple color ($\lambda_{max} = 561$ nm) after solvent exchange into hexane. On the other hand, in a mixed solvent (THF:hexane = 1:6) there appeared a new absorption at 394 nm at −40 °C assignable to a stannylene−THF complex, which was substantially blue-shifted from the absorption of the stannylene in hexane. The reasonable interpretation is that destabilization of an empty p-orbital of the stannylene upon complexation results in an increased energy gap between n- and p-orbitals, thus causing a blue shift as observed in complexations of silylenes[19] and germylenes[20] with Lewis bases such as ethers, sulfides, amines, phosphines, and alcohols. The ^{119}Sn NMR spectra of **2a** in toluene-d_8 showed only one signal at 2208 ppm, attributable to the characteristic chemical shift of a divalent organotin compound. The bandwidth and chemical shift of **2a** were almost unchanged between −30 and 60 °C, indicating the absence of a monomer−dimer equilibrium in this temperature range.[21] Recently, the X-ray structural analyses of bis[2,4,6-tris(trifluoromethyl)phenyl]stannylene[24a] and bis(2,4,6-tri-*tert*-butylphenyl)stannylene[24b] were reported.

Reactions of Diarylstannylene Tbt(Tip)Sn: (2a). The formation of **2a** was also confirmed by chemical trapping reactions with 2,3-dimethyl-1,3-butadiene and benzil which gave the expected [4 + 1] cycloadducts **3** and **4**, respectively (37 and 22%), as shown in Scheme 1. Stannylene **2a** also reacted with an excess of elemental chalcogens to furnish the corresponding tetrachalcogenastannolanes **5** and **6**.[16,17,25] The yield of the trapping products was not satisfactory probably due to low efficiency in the attack of a bulky aryllithium, TipLi, to sterically congested TbtSnCl$_3$ in the second step. The remarkable stability of stannylene **2a** prompted us to examine its sulfurization, because the reaction was expected to lead to the formation of stable stannanethione **1a**.

Synthesis and Reactions of Stannanethione Tbt(Tip)Sn=S (1a). When the deep purple solution of **1a** in hexane was treated with styrene episulfide at room temperature, the solution turned yellow, suggesting the formation of stannanethione **1a**. Monitoring of this reaction by UV/vis spectroscopy showed an appearance of a new absorption at 473 nm at the expense of the absorption of stannylene **2a** at 561 nm. The absorption at 473 nm is assignable to the n−π^* transition of the tin−sulfur double bond of stannanethione **1a**, being red-shifted compared to silanethione (396 nm)[10] and germanethione (450 nm).[11] The red shift on going from silanethione to stannanethione is theoretically supported by calculated spectra of $H_2M{=}S$ (M = Si, Ge, and Sn) at the CIS/DZ+d level using the Gaussian 92/DFT program.[10]

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[21] The first monomeric dialkylstannylene, 2,2,5,5-tetrakis(trimethylsilyl)-1-stannacyclopentane-1,1-diyl, showed a sharp singlet at 2323 ppm in ^{119}Sn NMR without any temperature dependence,[22] while bis[bis(trimethylsilyl)methyl]stannylene which exists as a monomer−dimer equilibrium mixture has been reported to show δ_{Sn} at 2315 ppm (toluene-d_8, 375 K).[23]

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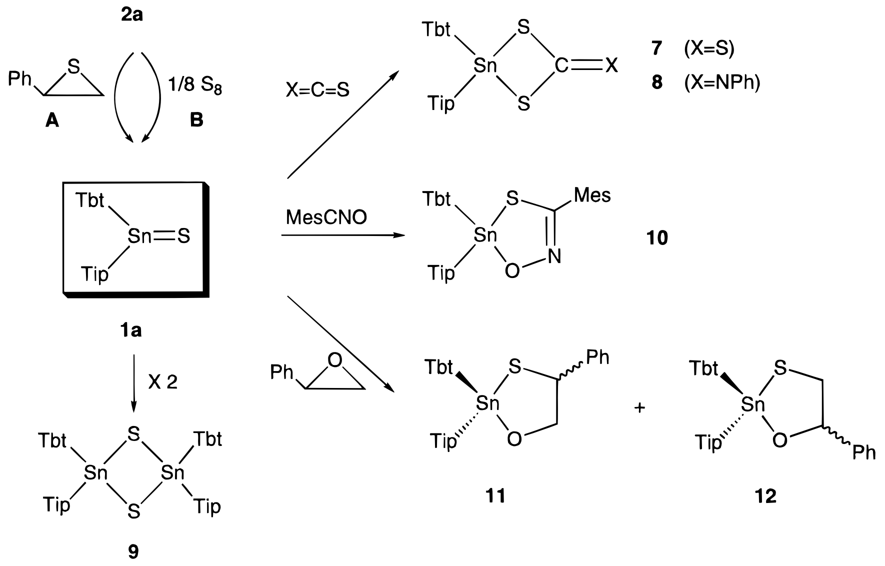
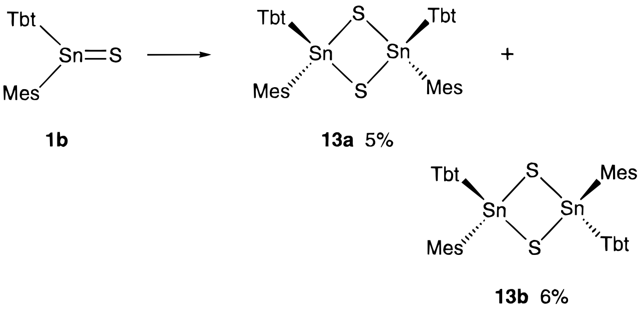
[25] For experimental details of the reaction of stannylene **2a** with elemental selenium, see ref 16b.

Scheme 2



Method	7	8	10	11	12
A	19%	38%	40%	2%	33%
B			39%	2%	28%

Scheme 3



The formation of stannanethione **1a** was chemically evidenced by trapping experiments with an excess of a thiocumulene such as carbon disulfide and phenyl isothiocyanate at room temperature which afforded 1,3,2-dithiastannetane derivatives **7** and **8** in 19 and 38% yields, respectively. The formation of adducts, **7** and **8**, is worthy of note. They are the first examples of [2 + 2] cycloaddition of a tin–sulfur double-bond compound except for self-dimerization.[26] The possibility that a chemical species involved in these cycloadditions is a dimer can be reasonably eliminated by the fact that dithiadistannetane **9**,[15] the dimer of **1a**, is inert to the thiocumulenes under the reaction conditions. The above reactions show that a stannylene is a useful, potential precursor to novel tin-containing double-bond species.

The head-to-tail coupling mode in the formation of **7** was unambiguously determined by its X-ray structural analysis (Figure 1). Selected bond lengths and angles are listed in Table 1. The angles of C(2)–Sn–C(3) and S(1)–Sn–S(2) are 123.0 and 73.6°, respectively. The SnS_2C four-membered ring is folded with an interplanar angle of 5.4° between Sn–S(1)–C(1) and S(1)–C(1)–S(2) planes.

Stannanethione **1a** was also trapped by a 1,3-dipolar cycloaddition. The reaction of **1a** with mesitonitrile oxide gave 1,3,5,2-oxathiazastannole **10**, which is of interest not only as the first example of a 1,3-dipolar cycloaddition reaction of a stannanethione but also as a novel tin-containing heterocycle. The trapping of stannanethione **1a** with styrene oxide was also carried out, since we found previously that stannanethione **1a** generated by desulfurization of **5** with triphenylphosphine reacted with styrene oxide to afford 1,3,2-oxathiastannolane.[15] Contrary to the sole formation of **11** in the reported reaction,[15] the products in the present reaction were **11** and **12**[27] as had been observed in the reaction of stannaneselone Tbt(Tip)Sn=Se generated by the reaction of **2a** with elemental selenium.[17b] The difference between these two reactions probably results

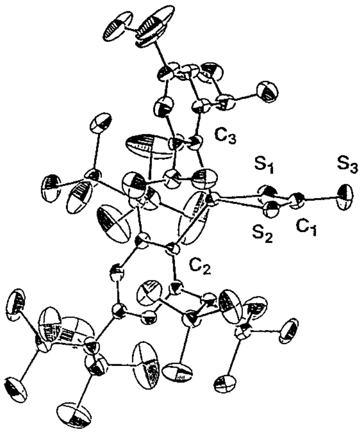


Figure 1. ORTEP drawing of $Tbt(Tip)SnS_2C{=}S$ (**7**).

Table 1. Selected Bond Lengths (Å) and Bond Angles (deg)

Sn–S(1)	2.448	S(2)–Sn	2.444
S(1)–C(1)	1.758	Sn–C(2)	2.160
C(1)–S(3)	1.626	Sn–C(3)	2.159
C(1)–S(2)	1.727		
S(2)–Sn–S(1)	73.6	C(1)–S(2)–Sn	85.4
Sn–S(1)–C(1)	86.2	C(2)–Sn–C(3)	123.0
S(1)–C(1)–S(3)	122.3	C(2)–Sn–S(2)	120.7
S(3)–C(1)–S(2)	123.3	C(3)–Sn–S(1)	115.8

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from the presence of triphenylphosphine sulfide, a nucleophilic catalyst, in the former reaction.[17b]

Since the reaction of a less encumbered diarylstannylene Tbt(Mes)Sn: (**2b**) with styrene episulfide in THF–ether at −78 °C did not give monomeric products but a mixture of *cis* and *trans* isomers of 1,3,2,4-dithiadistannetanes **13** (**13a** (*cis*, 5%); **13b** (*trans*, 6%),[15] which are the dimerization products of the intermediate stannanethione Tbt(Mes)Sn═S (**1b**), the prominent stability of the stannanethione **1a** obviously is due to the steric congestion of the combination of Tbt and Tip groups. Although **1a** is stable at room temperature, it undergoes dimerization, giving **9**[15] at 90 °C. The ^{119}Sn NMR signal of stannanethione **1a** has not been detected yet, probably due to low generation efficiency of **1a** or complexation of **1a** with THF even after solvent exchange into toluene-d_8.

Alternative Method for the Generation of a Stannanethione: Reaction of a Stannylene with Elemental Sulfur. Since Parkin's terminal sulfido complex was successfully synthesized by the reaction of a thermodynamically stabilized stannylene with elemental sulfur,[9a] we also examined the the reaction of stannylene **2a** with elemental sulfur. When sulfur (1/8 equimolar to TbtBr as S_8) was added to **2a**, the reaction solution turned yellow, suggesting the formation of stannanethione **1a**. Treatment of this reaction mixture with styrene oxide followed by column chromatography gave 1,3,2-oxathiastannolanes **11** (2%) and **12** (28%). Similar treatment of that mixture with mesitonitrile oxide afforded 1,3,5,2-oxathiazastannole **10** (39%). The formation of **10**–**12** clearly indicates the initial generation of stannanethione **1a** by the reaction of stannylene **2a** with elemental sulfur, as in the case of the reaction of **2a** with styrene episulfide. In this reaction, however, tetrathiastannolane **5** (5% based on TbtBr) was also obtained as a result of the reaction of stannanethione **1a** with an excess of elemental sulfur; the amount of sulfur used is probably still excess because of low efficiency in the generation of stannylene **2a**.

In order to isolate a stable stannanethione, further investigation on the introduction of a ligand bulkier than a Tip group on the tin is now under way.

Experimental Section

General Procedure. All reactions were carried out under argon. ^{1}H (500 MHz) and ^{13}C NMR (125 MHz) spectra were recorded on a Bruker AM-500 spectrometer with tetramethylsilane as an external standard. ^{119}Sn NMR (34 MHz) spectra were recorded on a JEOL FX-90Q spectrometer with tetramethylstannane as an external standard. High-resolution mass spectral data were obtained on a JEOL SX-102 mass spectrometer. Electronic spectra were measured on a JASCO U_{best}-50 UV/vis spectrometer. Preparative HPLC was carried out on an LC-08 or LC-908 (Japan Analytical Ind. Co., Ltd.) with JAIGEL-1H and -2H columns. Preparative thin-layer chromatography (PTLC), wet column chromatography (WCC), and dry column chromatography (DCC) were carried out with Merck Kieselgel 60 PF_{254} Art. 7747, Wako gel C-200, and ICN Silica DCC 60A, respectively. All melting points were determined on a Yanaco micro melting point apparatus and are uncorrected. Elemental analyses were carried out at the Microanalytical Laboratory of Department of Chemistry, Faculty of Science, The University of Tokyo.

Materials. 1-Bromo-2,4,6-tris[bis(trimethylsilyl)methyl]benzene (TbtBr)[13] and 1-bromo-2,4,6-triisopropylbenzene (TipBr)[28] were prepared according to procedures reported in the literature. Stannous chloride was purchased from Wako Pure Chemical Ind., Ltd. THF, ether, and hexane used in the synthesis were all distilled from benzophenone ketyl under argon atmosphere before use.

General Procedures for the Preparation of Tbt(Tip)Sn: (2a). (a) Preparation of a THF–Ether Solution of Tbt(Tip)Sn: (2a). To a THF solution (5 mL) of TbtLi, prepared from TbtBr (572 mg, 0.90 mmol) and *t*-BuLi (1.65 M in pentane; 1.20 mL, 2.2 equiv) at −70 °C was added an ether suspension (9 mL) of stannous chloride (184 mg, 0.97 mmol). After being stirred for 1.5 h at −65 °C, the reaction mixture was treated with a THF solution (5 mL) of equimolar TipLi, prepared from TipBr (253 mg, 0.89 mmol) and *t*-BuLi (2.2 equiv), to afford an orange solution of stannylene Tbt(Tip)Sn: (**2a**).

(b) Preparation of a Hexane Solution of Tbt(Tip)Sn: (2a). After a THF–ether solution of **2a**, synthesized by the above procedure a from TbtBr (572 mg, 0.90 mmol) and stannous chloride (184 mg, 0.97 mmol), was warmed to about −30 °C, the volatile substances were removed in vacuo. After drying of the dark-orange residue at room temperature, to the residue was added 7 mL of degassed dry hexane and the volatile portion was again removed at room temperature in vacuo. Several repetitions of this procedure for solvent exchange gave a deep purple hexane solution of **2a**.

Reactions of Diarylstannylene Tbt(Tip)Sn: (2a). (a) Reaction of Tbt(Tip)Sn: (2a) with 2,3-Dimethyl-1,3-butadiene. To a deep purple hexane solution (2 mL) of **2a** synthesized from TbtBr (446 mg, 0.70 mmol) and stannous chloride (142 mg, 0.75 mmol) was added 2,3-dimethyl-1,3-butadiene (1 mL, 8.84 mmol) at room temperature. After removal of volatile substances, the residue was subjected to column chromatography (Florisil/dichloromethane) followed by HPLC to yield 1-{2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}-1-(2,4,6-triisopropylphenyl)-3,4-dimethyl-2,4-dihydrostannole (**3**) (235 mg, 37%). **3**: Mp 189–190 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ −0.08 (s, 18H), −0.04 (s, 18H), 0.02 (s, 18H), 1.16 (br s, 12H), 1.20 (d, $J = 7$ Hz, 6H), 1.26 (s, 1H), 1.66 (s, 1H), 1.74 (s, 6H), 1.77 (s, 1H), 2.05 (d, $J = 16$ Hz, 2H), 2.12 (d, $J = 16$ Hz, 2H), 2.83 (sept, $J = 7$ Hz, 1H), 2.99 (sept, $J = 7$ Hz, 2H), 6.25 (s, 1H), 6.40 (s, 1H), 6.97 (s, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 0.89 (q), 1.21 (q), 1.40 (q), 21.49 (q), 24.07 (q), 25.74 (q), 30.03 (d), 30.86 (d), 31.34 (d), 32.26 (t), 34.33 (d), 37.92 (d), 121.31 (d), 121.99 (d), 127.22 (d), 131.69 (s), 137.70 (s), 142.50 (s), 142.77 (s), 149.18 (s), 151.11 (s), 151.29 (s), 154.20 (s). Anal. Calcd for $C_{48}H_{92}Si_6Sn\cdot H_2O$: C, 59.15; H, 9.74. Found: C, 59.20; H, 9.46.

Although elemental analyses were carried out twice after drying **3** at 80 °C in vacuo for 3 days, both results were consistent with a formula of monohydrate **3**·H_2O. It still contains 0.75 H_2O even after drying at 110 °C for 14 h in vacuo, as evidenced by ^{1}H NMR. Compounds having a Tbt group tend to crystallize as a hydrate probably because of the unique features of the very bulky Tbt group which leaves some space among molecules in the crystalline state. Indeed we have observed several hydrates of such type for other tin compounds bearing the Tbt group (for example, see: Matsuhashi, Y.; Tokitoh, N.; Okazaki, R.; Goto, M.; Nagase, S. *Organometallics* **1993**, *12*, 1351).

(b) Reaction of Tbt(Tip)Sn: (2a) with Benzil. To a deep purple hexane solution (10 mL) of **2a** synthesized from TbtBr (541 mg, 0.86 mmol) and stannous chloride (174 mg, 0.92 mmol) was added benzil (301 mg, 1.43 mmol) at room tem-

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(27) Both **11** and **12** were found to be *cis* and *trans* isomers. Although the stereochemistry of two ligands on the tin and a phenyl group in them was not confirmed, a less polar compound on silica gel is designated as **a** in each case.

(28) Whitesides, G. M.; Eisenhut, M.; Bunting, W. M. *J. Am. Chem. Soc.* **1974**, *96*, 5406.

perature. After removal of the solvent, the residue was subjected to DCC to afford 2-{2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}-2-(2,4,6-triisopropylphenyl)-1,3-dioxa-4,5-diphenyl-2-stannole (**4**) (210 mg, 23%). **4**: Mp 219−221 °C (dec); ^{1}H NMR (CDCl$_3$, 500 MHz) δ −0.04 (s, 18H), −0.02 (s, 18H), 0.06 (s, 18H), 1.23 (d, J = 7 Hz, 6H), 1.31 (d, J = 6 Hz, 12H), 1.37 (s, 1H), 1.87 (s, 1H), 2.11 (s, 1H), 2.88 (sept, J = 7 Hz, 1H), 3.03 (sept, J = 6 Hz, 2H), 6.37 (s, 1H), 6.51 (s, 1H), 7.05−7.06 (m, 2H), 7.07 (s, 2H), 7.09−7.12 (m, 4H), 7.35−7.37 (m, 4H); ^{13}C NMR (CDCl$_3$, 125 MHz) δ 0.53 (q), 0.78 (q), 0.79 (q), 23.95 (q), 25.74 (q), 30.79 (d), 32.42 (d), 34.47 (d), 38.81 (d), 122.01 (d), 122.54 (d), 125.49 (d), 127.21 (d), 127.38 (d), 128.34 (d), 137.40 (s), 138.48 (s), 139.27 (s), 141.39 (s), 146.33 (s), 151.01 (s), 151.38 (s), 151.90 (s), 154.34 (s). Anal. Calcd for $C_{56}H_{92}O_2Si_6Sn$: C, 62.00; H, 8.57. Found: C, 61.82; H, 8.47.

(c) Reaction of Tbt(Tip)Sn: (2a) with Elemental Sulfur. To a THF−ether solution of stannylene **2a** prepared from TbtBr (1801 mg, 2.85 mmol) and stannous chloride (586 mg, 3.09 mmol) was added elemental sulfur (1045 mg, 4.07 mmol) at −50 °C. After gradual warming to room temperature, the usual workup by DCC and HPLC afforded 5-{2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}-5-(2,4,6-triisopropylphenyl)-1,2,3,4,5-tetrathiastannolane (**5**) (1427 mg, 50%).[16]

General Procedure for the Transformation of Stannylene 2a into Stannanethione 1a. To a THF−ether or hexane solution of stannylene **2a** prepared according to the procedure described above was added styrene episulfide, during which time the solution turned yellow, suggesting the formation of stannanethione **1a**.

Reaction of Stannanethione 1a with Carbon Disulfide. Styrene episulfide (53 mg, 0.39 mmol) was added at −70 °C to a THF−ether solution of stannylene synthesized from TbtBr (231 mg, 0.36 mmol) and stannous chloride (78 mg, 0.41 mmol). After being warmed to 0 °C, the reaction solution was treated with carbon disulfide (0.20 mL, 3.32 mmol). After removal of the solvent, separation of the residue by DCC gave 2-{2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}-2-(2,4,6-triisopropylphenyl)-1,3,2,4-dithiastannetanethione (**7**) (68 mg, 19%). **7**: Mp 207−208 °C (dec); ^{1}H NMR (CDCl$_3$, 500 MHz) δ −0.02 (s, 18H), 0.05 (s, 36H), 1.23 (d, J = 7 Hz, 6H), 1.33 (d, J = 7 Hz, 12H), 1.35 (s, 1H), 2.04 (s, 1H), 2.34 (s, 1H), 2.78 (sept, J = 7 Hz, 2H), 2.89 (sept, J = 7 Hz, 1H), 6.36 (s, 1H), 6.53 (s, 1H), 7.09 (s, 2H); ^{13}C NMR (CDCl$_3$, 125 MHz) δ 0.80 (q), 0.83 (q), 1.08 (q), 23.92 (q), 28.58 (q), 30.93 (d), 32.75 (d), 32.99 (d), 34.41 (d), 40.49 (d), 122.88 (d), 123.08 (d), 128.00 (d), 135.25 (s), 140.43 (s), 146.91 (s), 151.58 (s), 151.99 (s), 152.39 (s), 153.61 (s), 228.99 (s). Anal. Calcd for $C_{43}H_{82}S_3Si_6Sn$: C, 52.55; H, 8.43; S, 9.76. Found: C, 52.31; H, 8.24; S, 10.04.

Reaction of Stannanethione 1a with Phenyl Isothiocyanate. Styrene episulfide (46 mg, 0.33 mmol) was added at −45 °C to a THF−ether solution of stannylene **2a** prepared from TbtBr (438 mg, 0.69 mmol) and stannous chloride (141 mg, 0.75 mmol). After it had been stirred for 1 h at this temperature, the reaction mixture was warmed to room temperature and then treated with phenyl isothiocyanate (1 mL, 8.36 mmol). After removal of the solvent, separation of the residue by WCC and DCC afforded 2-{2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}-2-(2,4,6-triisopropylphenyl)-4-(phenylimino)-1,3,2-dithiastannetane (**8**) (273 mg, 38%). The reaction of stannanethione **1a** synthesized from stannylene **2a** and styrene episulfide with phenyl isothiocyanate in hexane at room temperature also gave **8** (38%). **8**: Mp 145−147.5 °C; ^{1}H NMR (CDCl$_3$, 500 MHz) δ −0.03 (s, 9H), −0.01 (s, 9H), 0.03 (s, 9H), 0.04 (s, 9H), 0.05 (s, 18H), 1.23 (d, J = 7 Hz, 6H), 1.30 (d, J = 6 Hz, 6H), 1.33 (br s, 6H), 1.62 (s, 1H), 2.19 (s, 1H), 2.49 (s, 1H), 2.9 (m, 3H), 6.37 (s, 1H), 6.52 (s, 1H), 6.90 (d, J = 7 Hz, 2H), 7.02 (t, J = 7 Hz, 1H), 7.07 (s, 2H), 7.27 (dd, J = 7 Hz, 2H); ^{13}C NMR (CDCl$_3$, 125 MHz) δ 0.85 (q), 1.01 (q), 1.22 (q), 1.26 (q), 23.98 (q), 30.65 (q), 30.82 (d), 31.92 (d), 32.17 (d), 34.40 (d), 39.73 (d), 121.22 (d), 122.69 (d), 123.03 (d), 123.80 (d), 127.97 (d), 128.68 (d), 136.14 (s), 141.63 (s), 146.35 (s), 149.88 (s), 151.42 (s), 151.86 (s), 153.44 (s), 157.39 (s). Anal. Calcd for $C_{49}H_{87}NS_2Si_6Sn$: C, 56.49; H, 8.43; N, 1.21; S, 6.16. Found: C, 56.21; H, 8.51; N, 0.99; S, 5.80.

Reaction of Stannanethione 1a with Mesitonitrile Oxide. Styrene episulfide (72 mg, 0.54 mmol) was added to a hexane solution of stannylene **2a** synthesized from TbtBr (552 mg, 0.87 mmol) and stannous chloride (180 mg, 0.95 mmol) at room temperature. After the solution was stirred for 5 min, treatment with mesitonitrile oxide (224 mg, 1.39 mmol) followed by usual workup gave 2-{2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}-2-(2,4,6-triisopropylphenyl)-4-mesityl-1,3,5,2-oxathiazastannole (**10**) (373 mg, 40%). **10**: Mp 202.5−204 °C; ^{1}H NMR (CDCl$_3$, 500 MHz) δ 0.00 (s, 9H), 0.03 (s, 9H), 0.06 (s, 18H), 0.06 (s, 18H), 1.21 (d, J = 7 Hz, 6H), 1.28 (d, J = 3 Hz, 6H), 1.30 (d, J = 3 Hz, 6H), 1.36 (s, 1H), 1.90 (s, 1H), 2.10 (s, 1H), 2.13 (br s, 6H), 2.24 (s, 3H), 2.86 (sept, J = 7 Hz, 1H), 2.95 (br s, 2H), 6.41 (s, 1H), 6.54 (s, 1H), 6.80 (s, 2H), 7.03 (s, 2H); ^{13}C NMR (CDCl$_3$, 125 MHz) δ 0.87 (q), 0.89 (q), 0.92 (q), 1.06 (q), 1.10 (q), 1.35 (q), 20.34 (q), 21.02 (q), 23.84 (q), 23.91 (q), 25.73 (br q), 30.75 (d), 32.75 (d), 32.91 (d), 34.29 (d), 38.70 (d), 122.60 (d), 123.01 (d), 128.10 (d), 128.33 (d), 131.29 (s), 137.16 (s), 137.96 (s), 138.70 (s), 143.22 (s), 145.94 (s), 147.65 (s), 150.98 (s), 151.23 (s), 151.33 (s), 153.83 (s). Anal. Calcd for $C_{52}H_{93}NOSSi_6Sn$: C, 58.49; H, 8.80; N, 1.31; S, 3.00. Found: C, 58.35; H, 8.59; N, 1.57; S, 2.96.

Reaction of Stannanethione 1a with Styrene Oxide. After addition of styrene episulfide (74 mg, 0.54 mmol) to stannylene **2a** prepared from TbtBr (363 mg, 0.57 mmol) and stannous chloride (112 mg, 0.59 mmol) in THF−ether at −70 °C, the reaction solution was stirred for 1.5 h at this temperature. Styrene oxide (263 mg, 2.19 mmol) was added to the reaction solution at the same temperature. After the solution was warmed to ambient temperature, the usual workup by DCC afforded a *cis* and *trans* mixture of 2-{2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}-2-(2,4,6-triisopropylphenyl)-5-phenyl-1,3,2-oxathiastannolane (**12a**) (109 mg, 18%) and **12b** (99 mg, 15%) which contained a small amount of 2-{2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}-2-(2,4,6-triisopropylphenyl)-4-phenyl-1,3,2-oxathiastannolane (**11a**)[15] (2%), as evidenced by ^{1}H NMR. **12a**: Mp 210−212.5 °C (dec); ^{1}H NMR (CDCl$_3$, 500 MHz) δ −0.05 (s, 9H), −0.01 (s, 9H), 0.05 (s, 36H), 1.18 (br s, 6H), 1.23 (d, J = 7 Hz, 6H), 1.49 (s, 1H), 1.52 (br s, 6H), 1.85 (s, 1H), 1.96 (s, 1H), 2.71 (dd, J = 12, 12 Hz, 1H), 2.90 (sept, J = 7 Hz, 1H), 3.3 (br s, 2H), 3.39 (dd, J = 3, 12 Hz, 1H), 4.78 (dd, J = 3, 12 Hz, 1H), 6.36 (s, 1H), 6.50 (s, 1H), 7.07 (s, 2H), 7.17 (t, J = 8 Hz, 1H), 7.23 (dd, J = 7, 8 Hz, 2H), 7.36 (d, J = 7 Hz, 2H); ^{13}C NMR (CDCl$_3$, 125 MHz) δ 0.82 (q), 0.93 (q), 1.08 (q), 1.29 (q), 1.37 (q), 1.60 (q), 23.98 (q), 28 (q), 30.42 (d), 30.59 (d), 30.69 (d), 34.35 (d), 38.39 (d), 43.31 (t), 78.75 (d), 122.37 (d), 122.89 (d), 126.25 (d), 126.71 (d), 127.87 (d), 127.98 (d), 138.71 (s), 141.70 (s), 145.18 (s), 145.59 (s), 150.77 (s), 150.96 (s), 151.26 (s). Anal. Calcd for $C_{50}H_{90}OSSi_6Sn$: C, 58.49; H, 8.85; S, 3.12. Found: C, 57.85; H, 8.64; S, 3.17. **12b**: Mp 231−234 °C (dec); ^{1}H NMR (CDCl$_3$, 500 MHz) δ −0.02 (s, 9H), 0.02 (s, 9H), 0.05 (s, 18H), 0.06 (s, 18H), 1.21 (d, J = 7 Hz, 6H), 1.28 (br s, 12H), 1.34 (s, 1H), 2.15 (s, 1H), 2.40 (s, 1H), 2.73 (dd, J = 11, 11 Hz, 1H), 2.85 (sept, J = 7 Hz, 1H), 2.96 (br s, 1H), 3.34 (dd, J = 3, 11 Hz, 1H), 3.38 (br s, 1H), 4.77 (dd, J = 3, 11 Hz, 1H), 6.38 (s, 1H), 6.50 (s, 1H), 7.04 (s, 2H), 7.21 (t, J = 7 Hz, 1H), 7.28 (dd, J = 7, 8 Hz, 2H), 7.49 (d, J = 8 Hz, 2H); ^{13}C NMR (CDCl$_3$, 125 MHz) δ 0.83 (q), 0.91 (q), 1.18 (q), 1.22 (q), 1.45 (q), 1.48 (q), 23.95 (q), 28.73 (q), 28.95 (q), 30.59 (d), 31.17 (d), 31.34 (d), 34.34 (d), 36.91 (d), 38.38 (d), 40.61 (t), 80.03 (d), 122.18 (d), 122.56 (d), 122.82 (d), 126.18 (d), 126.26 (d), 126.71 (d), 137.76 (s), 142.10 (s), 144.89 (s), 145.28 (s), 150.93 (s), 151.16 (s), 151.61 (s). Anal. Calcd for $C_{50}H_{90}OSSi_6Sn$: C, 58.49; H, 8.85. Found: C, 57.75; H, 8.49.

Crystal and Experimental Data for 7: $C_{43}H_{82}S_3Si_6Sn$, M = 982.50, monoclinic, space group $C2/c$, a = 46.25(1) Å, b = 13.470(5) Å, c = 18.645(5) Å, β = 105.48(3)°, V = 11195(6) Å^3, Z = 8, D_c = 1.166 g cm^{-1}, R = 0.046 (R_w = 0.047). The intensity data ($2\theta \leq 60°$) were collected on a Rigaku AFC5R diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.710 69 Å), and the structure was solved by direct methods. The non-hydrogen atoms were refined anisotropically, and all the hydrogen atoms were located by calculation. The final cycle of full-matrix least-squares refinement was based on 6659 observed reflections [$I > 3.00(\sigma)$] and 478 variable parameters.

Reaction of Stannylene Tbt(Mes)Sn: (2b) with Styrene Episulfide. Styrene episulfide (126 mg, 0.93 mmol) was added at −70 °C to stannylene Tbt(Mes)Sn: (**2b**) prepared from TbtBr (576 mg, 0.91 mmol) and stannous chloride (175 mg, 0.92 mmol). After the mixture was warmed to ambient temperature, the usual workup of the crude reaction mixture by HPLC, DCC, and PTLC gave *cis*-2,4-bis{2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}-2,4-dimesityl-1,3,2,4-dithiastannetane (**13a**) (30 mg, 5%) and *trans*-2,4-bis{2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}-2,4-dimesityl-1,3,2,4-dithiastannetane (**13b**) (32 mg, 6%).[15]

Reaction of Stannanethione 1a, Generated by the Reaction of Stannylene 2a with Elemental Sulfur, with Styrene Oxide. Elemental sulfur (33 mg, 1.02 mmol as S) was added to a THF−ether solution of stannylene **2a** synthesized from TbtBr (552 mg, 0.87 mmol), stannous chloride (177 mg, 0.94 mmol), and TipBr (260 mg, 0.92 mmol) at −70 °C. After being stirred for 2 h at this temperature, the reaction mixture was treated with styrene oxide (0.16 mL, 1.40 mmol). After removal of the solvent at room temperature, separation of the residue by DCC gave a fraction containing oxathiastannolanes (333 mg), a part (102 mg) of which was further purified by PTLC (hexane:methylene chloride = 10:1) to afford **12a** (40 mg, 15%) and **12b** (35 mg, 13%), and 2-{2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}-2-(2,4,6-triisopropylphenyl)-4-phenyl-1,3,2-oxathiastannolane (**11b**)[15] (7 mg, 2%).

Reaction of Stannanethione 1a, Generated by the Reaction of Stannylene 2a with Elemental Sulfur, with Mesitonitrile Oxide. Elemental sulfur (29 mg, 0.90 mmol as S) was added to a THF−ether solution of stannylene **2a** synthesized from TbtBr (534 mg, 0.84 mmol), stannous chloride (173 mg, 0.91 mmol), and TipBr (218 mg, 0.77 mmol) at −70 °C. After being stirred for 1 h at this temperature, the reaction mixture was treated with mesitonitrile oxide (147 mg, 0.91 mmol). After removal of the solvent at room temperature, separation of the residue by DCC followed by HPLC gave **10** (353 mg, 39%).

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Supporting Information Available: Tables of crystallographic data, bond lengths, bond angles, and thermal and positional parameters and ORTEP diagrams for **7** (36 pages). Ordering information is given on any current masthead page.

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