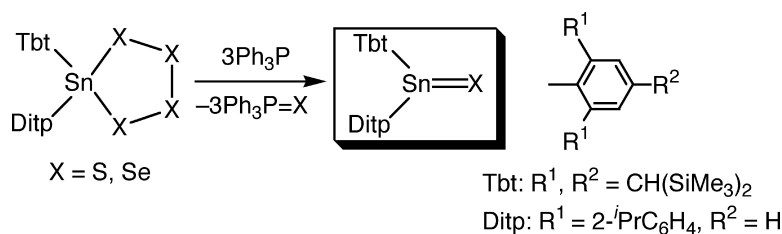# Tin–Chalcogen Double-Bond Compounds, Stannanethione and Stannaneselone: Synthesis, Structure, and Reactivities

Masaichi Saito, Norihiro Tokitoh, and Renji Okazaki

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Tin−Chalcogen Double-Bond Compounds, Stannanethione and Stannaneselone: Synthesis, Structure, and Reactivities

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Abstract: The first isolation of diarylstannanethione (tin−sulfur double-bond compound) and diarylstannaneselone (tin−selenium double-bond compound), Tbt(Ditp)Sn=X (Tbt = 2,4,6-tris[bis(trimethylsilyl)methyl]-phenyl; Ditp = 2,2″-diisopropyl-*m*-terphenyl-2′-yl; X = S and Se) was accomplished by dechalcogenation of the corresponding highly hindered tetrachalcogenastannolanes, Tbt(Ditp)SnX$_4$. The ^{119}Sn NMR of stannanethione, Tbt(Ditp)Sn=S, and stannaneselone, Tbt(Ditp)Sn=Se, showed only one low-field broad signal at 531 and 440 ppm, respectively, characteristic of a tricoordinated tin, and hence, the stannanethione and stannaneselone display an intrinsic nature of tin−chalcogen double-bond compounds. The X-ray crystallographic analysis of the isolated stannaneselone, Tbt(Ditp)Sn=Se **5a**, revealed a completely trigonal geometry around the central tin with a remarkably short Sn−Se bond length, indicative of structural similarity to a ketone.

Introduction

For many years, it was commonly accepted that compounds having double bonds between heavier main group elements would not be as stable as the corresponding second-row element compounds because of their weak pπ−pπ bonding, which was sometimes referred to as the "classical double-bond rule". Since the breakthrough of the first stable compound with P=C[1] in 1978, those with Si=C,[2] P=P,[3] and Si=Si[4] in 1981 were isolated 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 those involving group 14 elements.[5,6] Previous studies on such species, however, have centered on silicon and germanium compounds, and the chemistry of such compounds containing tin has been much less explored.

As for tin-containing double-bond compounds, some stable double-bond species with group 14 (Sn=Sn,[7−9] Sn=C,[10] Sn=C=N,[11] Sn=Si,[12] and Sn=Ge[13]) and group 15 elements (Sn=N[14] and Sn=P[15]) have been synthesized. Although tin−chalcogen double-bond compounds are very fascinating synthetic

targets as heavier congeners of a ketone which plays a key role in organic chemistry, there had been no example of the isolation using kinetic stabilization when we undertook a study of such species several years ago because bulky ligands for steric protection can be introduced only on the tin atom, and hence, their oligomerization cannot be efficiently prevented. Recently, compounds with Sn=X (X = S, Se, and Te) bonds, thermodynamically stabilized by intramolecular coordination, have been synthesized and characterized by Parkin[16] and Leung,[17] but they are highly perturbed by electron donation from neighboring

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 (6) Although the first stable compound having a formal Sn=Sn bond has been already reported by Lappert in 1976, before the breakthrough,[7] it should be described as bis(stannylene) because of its long Sn−Sn bond and its large folded angles. Recently, compounds having a remarkably short Sn= Sn bond were reported.[8]
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nitrogen atoms to electron-deficient reactive centers, as evidenced by their high-field chemical shifts in ^{119}Sn NMR (vide infra).

We previously reported the synthesis of compounds with Si=S[18] and Ge=X (X = S, Se, and Te)[19,20] bonds bearing a 2,4,6-triisopropylphenyl (Tip) group and a very efficient steric protection group, 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl (Tbt) group, developed by us.[21] Although we also described the synthesis of tin−chalcogen double-bond compounds, Tbt(Tip)-Sn=X (X = S and Se), which are stable in solution by dechalcogenation[22] of 1,2,3,4,5-tetrachalcogenastannolanes[23] and chalcogenation of the corresponding stannylene,[22b,24] they were found to exist as a dimer in the solid state. These facts clearly show that for the isolation of tin−chalcogen double-bond compounds, introduction of a ligand bulkier than a Tip group onto the tin with a Tbt group is necessary, in contrast to the cases of the silanethione and the germanium−chalcogen double-bond compounds isolated by using a Tip group together with a Tbt group.[18−20] This higher tendency of a tin−chalcogen double-bond compound to dimerize is due to (i) energy gaps between σ- and π-bonds in tin−chalcogen double-bonds being larger than those of silicon and germanium[18b] and (ii) longer bond lengths involving a tin atom. To stabilize a tin−chalcogen double-bond compound effectively, it is necessary to introduce a bulkier ligand than the Tip group. In the course of our studies on stabilization of tin−chalcogen double-bond compounds by steric protection, we found recently that the use of the combination of a Tbt group with a substituted *m*-terphenyl group[25] enabled the isolation of the first diaryl-substituted tin−selenium double-bond compound without intramolecular coordination.[26] This paper delineates a detailed account of the successful synthesis, structure, and reactivities of the first diarylstannanethione and diarylstannaneselone by using the combination of the *m*-terphenyl and Tbt groups on the tin along with the properties

of less-stable compounds having several other overcrowded ligands.

Results and Discussion

Synthesis of Highly Hindered Tetrachalcogenastannolanes by Chalcogenation of Stannylene. Highly hindered tetrathiastannolanes, Tbt(R)SnS$_4$ **1** [**1a**, R = 2,2″-diisopropyl-*m*-terphenyl-2′-yl (Ditp), 22%; **1b**, R = 2,2″-dimethyl-*m*-terphenyl-2′-yl (Dmtp), 25%; **1c**, R = 2,4,6-tricyclohexylphenyl (Tcp), 96%; **1d**, R = 2,4,6-tris[(trimethylsilyl)methyl]phenyl (Ttm), 34%; **1e**, R = bis(trimethylsilyl)methyl (Dis), 78%] and tetraselenastannolanes Tbt(R)SnSe$_4$ **2** [**2a**, 38%; **2b**, 29%; **2c**, 100%], which are useful precursors for the synthesis of tin−chalcogen double-bond compounds,[22] were easily obtained by chalcogenation of the corresponding stannylenes Tbt(R)Sn **3**, generated through two routes: successive arylation of stannous chloride and reduction of dibromostannanes (Scheme 1).[27]

Isolation of Stable Stannanethione Tbt(Ditp)Sn=S 4a and Stannaneselone Tbt(Ditp)Sn=Se 5a by Introducing a Novel Ligand, a 2,2″-Diisopropyl-*m*-terphenyl-2′-yl (Ditp) Group Having a *m*-Terphenyl Skeleton. Unsuccessful attempts at the isolation of tin−chalcogen double-bond compounds by using the combination of Tbt−Tip groups prompted us to develop a ligand bulkier than Tip. One possible strategy might be the introduction of a ligand that is longer and bulkier than an isopropyl group, such as a cyclohexyl group. Another possible approach is the introduction of a *m*-terphenyl group, which is expected to be advantageous in terms of not only synthetic facility but also steric protection.[25] Inspection of the CPK model reveals that both phenyl groups at the 2,6-positions are perpendicular to the central aromatic ring because of steric requirement when both *m*-terphenyl and Tbt groups exist on tin, and hence, the *m*-terphenyl group is expected to have a bowl-shaped conformation, which can effectively protect the reactive center in cooperation with the Tbt group. At first, introduction of a 2,2″-diisopropyl-*m*-terphenyl-2′-yl (Ditp) group onto tin was attempted.

(1) Synthesis, Isolation, and Structure of 4a and 5a (Scheme 2). When tributylphosphine was added to a toluene-d_8 solution of tetrathiastannolane **1a**, the solution turned orange (λ_{max} = 491 nm), suggesting the formation of stannanethione **4a**.[28] The ^{119}Sn NMR at room temperature showed two very broad signals at about 530 ppm, which suggested the presence of conformational isomers. At 60 °C, the ^{119}Sn NMR showed

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(28) The n−π* transition of the stannanethione, Tbt(Tip)Sn=S, has already been observed at 473 nm.[24a]

Scheme 1
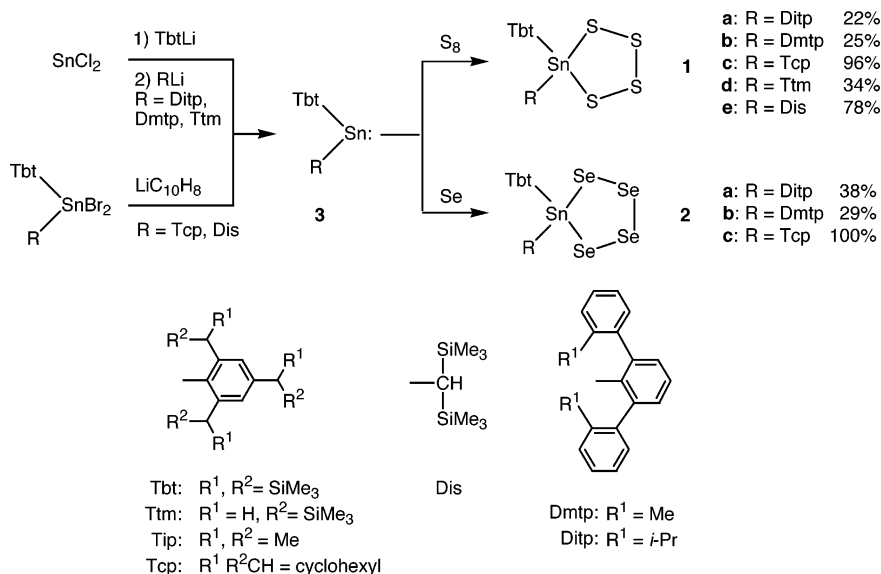
Scheme 2
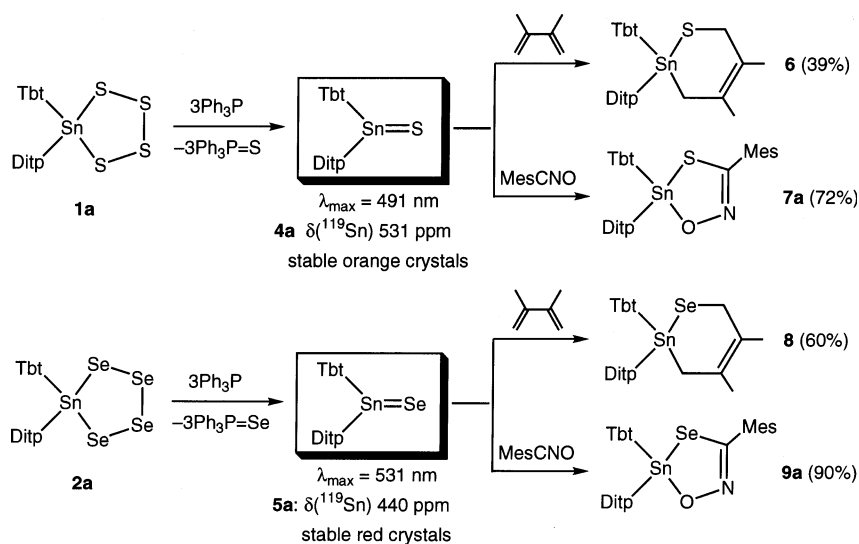
only one broad signal at 531 ppm, which could be assigned to stannanethione **4a**. Contrary to Parkin's terminal tin−sulfido complex (−303 ppm),[16] this low-field chemical shift is characteristic of a tricoordinated tin, as observed in Sn=Sn (725[7] and 427.5[8] ppm), Sn=C (835[10a] and 288[10b] ppm), Sn=Si (516.7 ppm),[12] Sn=Ge (525.1,[13a] 373.4,[13a] 268,[13b] and 360[29] ppm), and Sn=P (658.3[15a] and 499.5[15b] ppm), and hence, stannanethione **4a** displays an intrinsic nature of tin−sulfur double-bond compounds. This is the first observation of a diarylstannanethione by ^{119}Sn NMR. Even after measurement of ^{119}Sn NMR at 60 °C, the color of this solution remained orange, indicating that stannanethione **4a** was remarkably stable in solution even at 60 °C. After slow evaporation of the solvent, followed by washing with hexane in a glovebox, the first stable stannanethione **4a** was obtained as orange crystals in 26% yield.

After successful isolation of stannanethione **4a**, we examined the isolation of stannaneselone by using the same combination of ligands as that of stannanethione **4a**. When Tbt(Ditp)SnSe4

2a was allowed to react with 3 equiv of triphenylphosphine in refluxing hexane for 2 h under argon, the solution turned deep red (λ_{max} = 531 nm), indicating the formation of stannaneselone **5a**. The absorption maximum due to the n−π* transition at 531 nm is highly red-shifted compared to that of stannanethione, Tbt(R)Sn=S (R = Tip, 473 nm;[24] R = Ditp (**4a**), 491 nm), as is observed in germanium analogues.[19,20] A red shift was also found in the transition from germaneselone, Tbt(Tip)Ge=Se (519 nm),[19,20] to stannaneselone **5a** (531 nm), as is observed also in a series of the sulfur-containing double-bond systems.[18−20] In its ^{119}Sn NMR, a signal that could be assigned to **5a** was observed at 440 ppm at 60 °C. Contrary to Parkin's terminal tin−selenido complex (−444 ppm),[16] this low-field chemical shift is characteristic of a low-coordinated tin, as in the case of stannanethione **4a**, indicating that stannaneselone **5a**, again, displays an intrinsic nature of tin−selenium double-bond compounds. Although the coupling constant between [119]Sn and [77]Se is thought to be diagnostic of the degree of the multiple-bond character, it was not observed due to a low S/N ratio. Filtration of triphenylphosphine selenide, insoluble in hexane,

(29) Chaubon, M. A.; Escudie, J.; Ranaivonjatovo, H.; Satge, J. *J. Chem. Soc., Chem. Commun.* **1996**, 2621.
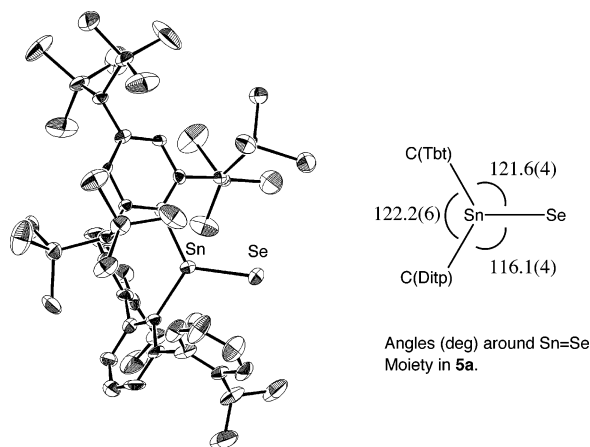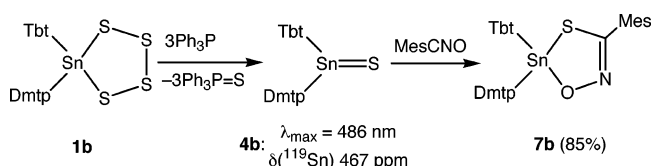
Figure 1. ORTEP drawing of stannaneselone, Tbt(Ditp)Sn═Se **5a**, with thermal ellipsoid plots (30% probability for non-hydrogen atoms). A minor disordered moiety was omitted for clarity.

followed by removal of hexane, resulted in the isolation of the stable stannaneselone **5a** as red crystals in 84% yield. The structure of this novel double-bond system was established by X-ray crystallographic analysis for single crystals obtained by recrystallization from hexane in a glovebox. The ORTEP drawing (Figure 1) shows that the stannaselenocarbonyl unit is effectively protected by one disil group in Tbt and two isopropyl groups located in a cis fashion in Ditp, which are directed toward the Sn═Se bond to avoid the steric repulsion with the Tbt group, as indicated by inspection of the CPK model. The Sn–Se distance [2.373(3) Å] is approximately 9% shorter than a Sn–Se single bond length (2.55–2.60 Å),[30] consistent with the calculated Sn═Se bond length for $H_2Sn═Se$ (2.346 Å)[18b] and slightly shorter than that of Parkin's terminal selenido complex (2.39 Å).[16] The geometry around the tin atom is trigonal planar, with the sum of the angles being 359.9°. This is indicative of structural similarity to a ketone, as in the case of silicon and germanium analogues.[18,19]

(2) Reactions of 4a and 5a (Scheme 2). Although X-ray crystallographic analysis of stannanethione **4a** has not been successful yet, the formation of **4a** was also ascertained by several trapping reactions. Stannanethione **4a** reacted with mesitonitrile oxide to give a [3 + 2] cycloadduct **7a** (72%). It is noted that the reaction of stannanethione **4a** with 2,3-dimethyl-1,3-butadiene gave a [4 + 2] cycloadduct **6** in 39% yield. This result clearly demonstrates that the stannanethione has a considerable extent of ene character, like its silicon and germanium analogues,[18,19] as well as like its carbon analogues, such as thioketones and selenoketones,[31] despite severe steric congestion around the Sn═S group.

Stannaneselone **5a** reacted with mesitonitrile oxide and 2,3-dimethyl-1,3-butadiene to afford the corresponding cycloadducts **9a** and **8** in 90 and 60%, respectively, like stannanethione **4a**. Since the [4 + 2] cycloadduct **8** could not be isolated by flash column chromatography because of its instability, the yield of **8** was estimated by NMR. These results clearly demonstrate that stannaneselone **5a** also has high ene reactivity. The

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(30) The average length of a Sn–Se single bond in X-Sn–Se-X systems (428 examples) is 2.579 Å (Cambridge Structural Database).

(31) (a) For thioketones: Duus, F. In *Comprehensive Organic Chemistry*; Barton, D. H. R., Ollis, W. D., Eds.; Pergamon Press: Oxford, 1979; Vol. 3, p 373. (b) For selenoketones: Guziec, F. S. In *The Chemistry of Organic Selenium and Tellurium Compounds*; Patai, S., Ed.; John Wiley & Sons, New York, 1987; Vol. 2, p 215 and references therein.

Scheme 3

reactivities of **4a** and **5a** indicate that there is enough space around their reactive centers to react with a small reagent by taking advantage of the intrinsic double-bond nature of their tin–chalcogen bond because the long arms of the two bulky ligands enclose each reactive center from a distance.

Synthesis of Tbt(Dmtp)Sn═X (4b, X = S; 5b, X = Se) with a Novel Ligand, a 2,2″-Dimethyl-*m*-terphenyl-2′-yl (Dmtp) Group with a *m*-Terphenyl Skeleton (Scheme 3). Next, introduction of a 2,2″-dimethyl-*m*-terphenyl-2′-yl (Dmtp) group, less bulky than a Ditp group, onto tin was attempted. Treatment of tetrathiastannolane **1b** with tributylphosphine in hexane immediately afforded a yellow-orange solution (λ_{max} = 486 nm), suggesting the formation of stannanethione **4b**. The formation of stannanethione **4b** was confirmed by a trapping reaction with mesitonitrile oxide, leading to the corresponding [3 + 2] cycloadduct **7b** in 85% yield, as well as by ^{119}Sn NMR, which showed a broad signal at 467 ppm. The color of **4b**, however, gradually disappeared at room temperature, and no identifiable product was obtained except for recovered **1b**. As in the case of stannanethione **4b**, as soon as tributylphosphine was added to a toluene solution of tetraselenastannolane **2b**, the color of the solution changed from pale orange to deep red, suggesting the formation of stannaneselone **5b**. However, the color changed to orange so rapidly (after about a minute) that the UV–vis absorption of the deep-red solution could not be measured. No identifiable product was obtained from this reaction mixture. These facts clearly show that the combination of Tbt–Dmtp groups does not provide enough bulkiness to isolate tin–chalcogen double-bond compounds.

Synthesis and Reactions of Tbt(Tcp)Sn═X (4c, X = S; 5c, X = Se): Stable Stannanethione 4c and Stannaneselone 5c, Observable by ^{119}Sn NMR. (1) Synthesis and Reactions of Tbt(Tcp)Sn═S 4c (Scheme 4). The combination of Tbt and 2,4,6-tricyclohexylphenyl (denoted as Tcp) groups was next examined. The Tcp group is potentially another ligand that is bulkier than the Tip group, where an isopropyl group in Tip is substituted by a bulkier cyclohexyl group. Treatment of Tbt-(Tcp)SnS₄ **1c** with 3 equiv of triphenylphosphine in toluene caused a change in the color of the solution to orange (λ_{max} = 488 nm), suggesting the formation of stannanethione **4c**.[32] In ^{119}Sn NMR, a signal that could be assigned to stannanethione **4c** was successfully observed at 643 ppm. Furthermore, the formation of stannanethione **4c** was evidenced by trapping experiments; treatment of the orange solution of stannanethione **4c** with phenyl isothiocyanate and mesitonitrile oxide afforded [2 + 2] and [3 + 2] cycloadducts, **10** (40%) and **7c** (35%), respectively,[24] together with an oligomeric mixture containing mainly dimeric products.[34,35] In the absence of the trapping

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(32) The absorption maximum of stannanethione **4c** in hexane is 9 nm red-shifted from that in toluene. This solvent effect observed for **4c** is nearly the same as those for thiobenzophenone.[33]

(33) (a) Lees, W. A.; Burawoy, A. *Tetrahedron* **1964**, *20*, 1527. (b) Lees, W. A.; Burawoy, A. *Tetrahedron* **1964**, *20*, 2229.

(34) Schäfer, A.; Weidenbruch, M.; Saak, W.; Pohl, S.; Marsmann, H. *Angew. Chem.*, *Int. Ed. Engl.* **1991**, *30*, 962.

Scheme 4
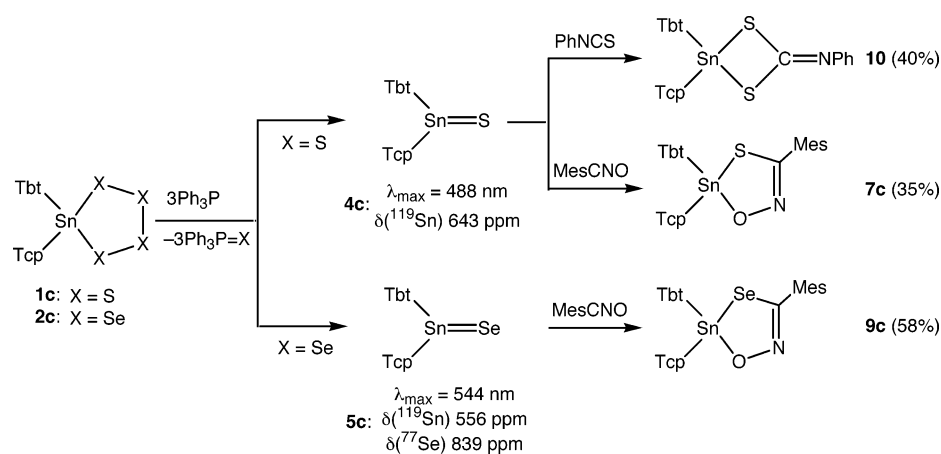
reagents, the orange color of **4c** gradually disappeared at room temperature over 1 day, suggesting the instability of stannanethione **4c**. The absence of the stannanethione in this reaction indicates that even the combination of Tbt and Tcp groups is not sufficient for the isolation of a stannanethione.

(2) Synthesis and Reactions of Tbt(Tcp)Sn=Se 5c (Scheme 4). Treatment of Tbt(Tcp)SnSe$_4$ **2c** with 3 equiv of triphenylphosphine in toluene gave a deep-red solution, suggesting the formation of stannaneselone **5c**, which is stable in solution at room temperature. Its ^{119}Sn NMR showed a signal at 556 ppm that could be assigned to stannaneselone **5c**. The ^{77}Se NMR at −10 °C shows only one singlet at 839 ppm, significantly low-field-shifted compared to the signal of α-selenium [$\delta(^{77}$Se) 321 ppm] in Tbt(Tcp)SnSe$_4$ **2c**. The ^{77}Se chemical shift of Tbt(Tip)-Ge=Se^{19b,d,20} was observed at 941 ppm, while those of most dialkyl selenoketones are in the range between 1600 and 2200 ppm. The formation of stannaneselone **5c** was also confirmed by trapping experiments. Treatment of stannaneselone **5c** thus obtained in solution with mesitonitrile oxide afforded the corresponding [3 + 2] cycloadduct **9c** (58%). Stannaneselone **5c** is less stable than stannanethione **4c**, and it gradually decomposed at ambient temperature over a few hours. After the deep-red color of the solution of **5c** completely disappeared, the ^{119}Sn NMR exhibited six signals at −294, −280, −279, −276, −119, and −111 ppm.^{34,35} No identifiable product was obtained, except triphenylphosphine selenide (91%) from this solution.

Desulfurization of Tbt(Ttm)SnS$_4$ 1d. Although it is considered best to introduce two Tbt groups onto the tin in terms of steric congestion, this attempt has not been successful yet.^{36} The combination of Tbt and Ttm, which is a less-encumbered ligand than a Tbt group, was attempted.

Treatment of Tbt(Ttm)SnS$_4$ **1d** with 3 equiv of triphenylphosphine in toluene-d_8 gave a pale-orange solution, suggesting the formation of stannanethione **4d**.^{28} In ^{119}Sn NMR,

Scheme 5
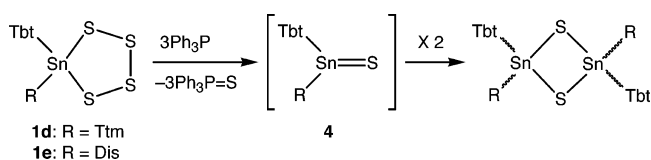
however, there appeared only one signal at 70 ppm that could be assigned to the starting material, **1d**. After 2 h, white precipitates (Ph$_3$P=S) were suddenly formed together with the colorless supernatant. The ^{119}Sn NMR of this mixture exhibited six broad signals at about −50 ppm (δ −62.1, −60.7, −57.7, −56.5, −55.5, −51.8).^{34,35} After collection of an oligomeric fraction by usual workup, its ^{1}H NMR spectrum was too complicated to assign peaks (Scheme 5).^{35}

Desulfurization of Tbt(Dis)SnS$_4$ 1e. The bis(trimethylsilyl)-methyl (Dis) group is well-known as an effective steric protection group for low-coordinated compounds of heavier group 14 elements.^{7,37} The Dis group is expected to surround the reactive center at a nearer site than other bulky aryl groups that were mentioned above.

While a toluene-d_8 solution of Tbt(Dis)SnS$_4$ **1e** and 3 equiv of triphenylphosphine in an NMR tube were degassed, considerable amounts of white precipitates were formed. The ^{31}P NMR of this mixture exhibited only one signal of Ph$_3$P=S, indicating that the reaction had completed. The supernatant was colorless, suggesting the absence of stannanethione **4e** in the solution. The absence of stannanethione **4e** in the resulting solution indicated that the combination of Tbt and Dis groups did not lead to the isolation of stannanethione **4e**, most likely because of longer bonds involving tin which make its dimerization easier (Scheme 5). In the case of the germanium congeners, Dis groups can protect the intermolecular attack of the tellurium atom onto the germanium atom, thus leading to the isolation of stable germanetellone, Tbt(Dis)Ge=Te.^{19,20}

Experimental Section

General Procedure. All of the reactions were carried out under argon. ^{1}H (500 MHz) and ^{13}C NMR (125 MHz) spectra were recorded on Bruker AM-500 and JEOL α-500 spectrometers with chloroform

(35) We tentatively assign the corresponding mixtures to oligomeric products probably containing mainly dimeric products, judging from the retention time of gel permeation chromatography. The trimerization of our double-bond compounds was probably suppressed because of the large 1,3-diaxial interactions between two bulky ligands, although the possibility that the fraction contained trimeric products is not completely excluded. The complexity in the ^{119}Sn NMR suggested the presence of conformational mixtures or trimeric products.

(36) A diarylplumbylene bearing two Tbt groups on the lead was successfully synthesized: (a) Kano, N.; Tokitoh, N.; Okazaki, R. *Organometallics* **1997**, *16*, 2748. (b) Kano, N.; Shibata, K.; Tokitoh, N.; Okazaki, R. *Organometallics* **1999**, *18*, 2999.

(37) Isolation of stable dimetallenes using disil groups has been reported. For Si=Si, see: (a) Masamune, S.; Eriyama, Y.; Kawase, T. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 584. For Ge=Ge, see: (b) Hitchcock, P. B.; Lappert, M. F.; Miles, S. J.; Thorne, A. J. *J. Chem. Soc., Chem. Commun.* **1984**, 480.

[δ(^{1}H) 7.25 ppm; δ(^{13}C) 77.00 ppm] or benzene [δ(^{1}H) 7.15 ppm; δ(^{13}C) 128.00 ppm] as an internal standard. ^{119}Sn NMR (101 MHz) and ^{77}Se NMR (51 MHz) spectra were recorded on a JEOL EX-270 spectrometer with tetramethylstannane and dimethylselenide as the external standards, respectively. 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 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 micromelting point apparatus and are uncorrected. Elemental analyses were carried out at the Microanalytical Laboratory of the Department of Chemistry, Faculty of Science, The University of Tokyo.

General Procedures for the Preparation of Tbt(Ar)Sn: 3 (Ar = Ditp, Dmtp, Ttm). To a THF solution of TbtLi, prepared from TbtBr and *t*-BuLi (1.65 M in pentane; 2.2 equiv) at −70 °C, was added an ether suspension of equimolar stannous chloride. After the mixture was stirred for 1.5 h at −65 °C, the reaction mixture was treated with a THF solution of equimolar ArLi, prepared from ArBr or ArI and *t*-BuLi (2.2 equiv), to afford an orange solution of stannylene Tbt(Ar)Sn: 3.

Preparation of 2′-Iodo-2,2″-diisopropyl-1,1′:3′,1″-terphenyl. To a solution of (2-isopropylphenyl)magnesium bromide, prepared from 1-bromo-2-isopropylbenzene[38] (3.95 g, 19.8 mmol) and magnesium (533 mg, 21.9 mmol) in 20 mL of THF by heating at reflux, was added dropwise a THF (18 mL) solution of 1,3-dichloro-2-iodobenzene[39] (1.82 g, 6.67 mmol). The resulting solution was heated at reflux for 3.5 h, cooled to 0 °C, and quenched with a THF (5 mL) solution of iodine (3.62 g, 14.3 mmol). After an aqueous solution of sodium thiosulfate was added, this mixture was extracted with ether and dried over anhydrous magnesium sulfate. After removal of the ether, the residue was separated with DCC to yield 2′-iodo-2,2″-diisopropyl-1,1′:3′,1″-terphenyl (DitpI) (2.34 g, 80%): mp 95–98 °C dec (ethanol). The ^{1}H NMR suggested the presence of two rotational isomers, two isopropyl groups of which are located in syn or anti fashion. The ratio probably depends on the populations of conformers of 2′-lithium-2,2″-diisopropyl-1,1′:3′,1″-terphenyl (DitpLi) before the reaction mixture is quenched by iodine. Inspection of the CPK models indicates that two *o*-aromatic rings in DitpI cannot rotate since iodine is much larger than lithium. For these reasons, the aromatic region of its ^{1}H and ^{13}C NMR spectrum is too complicated to be assigned. Anal. Calcd for C$_{24}$H$_{25}$I: C, 65.45; H, 5.73; I, 28.82. Found: C, 65.23; H, 5.72; I, 27.86.

Preparation of Tbt(Ditp)SnS$_4$ 1a. To a solution of Tbt(Ditp)Sn: 3a, prepared from TbtBr (994 mg, 1.57 mmol), stannous chloride (321 mg, 1.69 mmol), and DitpI (700 mg, 1.59 mmol), was added elemental sulfur (431 mg, 1.68 mmol). The solution was stirred overnight, and the solvents were removed. The resulting residue was subjected to WCC (Florisil/methylene chloride) followed by DCC to give crude Tbt(Ditp)-SnS$_4$ (456 mg), which was further purified by DCC to afford pure 5-{2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}-5-[2,6-bis(2-isopropyl-phenyl)phenyl]-1,2,3,4,5-tetrathiastannolane (**1a**) (392 mg, 22%). **1a**: mp 280–283 °C dec (recrystallized from methylene chloride/acetonitrile); ^{1}H NMR (CDCl$_3$, 500 MHz, 330 K) δ 0.01 (s, 36H), 0.13 (s, 18H), 1.07 (d, *J* = 7 Hz, 6H), 1.13 (d, *J* = 7 Hz, 6H), 1.41 (s, 1H), 1.49–1.94 (br s, 2H), 2.54 (sept, *J* = 7 Hz, 2H), 6.33–6.61 (br s, 2H), 6.97–7.01 (m, 2H), 7.26–7.35 (m, 8H), 7.39 (t, *J* = 7 Hz, 1H); ^{13}C NMR (CDCl$_3$, 125 MHz, 330 K) δ 1.12 (q), 2.35 (q), 23.44 (q), 25.14 (q), 29.78 (d), 30.93 (d), 31.96 (d), 123.75 (d), 126.26 (d), 126.71 (d), 127.76 (d), 128.42 (d), 128.86 (d), 129.04 (d), 131.11 (d), 141.37 (s), 142.29 (s), 145.45 (s), 146.44 (s), 147.55 (s), 148.45 (s), 150.6 (br s);

^{119}Sn NMR (CDCl$_3$, 101 MHz) δ 51. Anal. Calcd for C$_{51}$H$_{84}$S$_4$Si$_6$Sn: C, 55.04; H, 7.62; S, 11.53. Found: C, 54.78; H, 7.41; S, 11.69.

Preparation of Tbt(Ditp)SnSe$_4$ 2a. A solution of Tbt(Ditp)Sn: 3a, prepared from TbtBr (844 mg, 1.33 mmol), stannous chloride (274 mg, 1.44 mmol), and DitpI (591 mg, 1.34 mmol), was cooled again to −60 °C and then treated with elemental selenium (446 mg, 5.65 mmol). After the mixture was warmed to ambient temperature, the solvents were evaporated, and then the resulting residue was subjected to WCC (Florisil/methylene chloride) followed by DCC to give crude Tbt(Ditp)-SnSe$_4$ (875 mg), which was further purified by HPLC to afford pure 5-{2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}-5-[2,6-bis(2-isopropyl-phenyl)phenyl]-1,2,3,4,5-tetraselenastannolane (**2a**) (629 mg, 38%). **2a**: mp 249–251 °C dec (recrystallized from methylene chloride/acetonitrile); ^{1}H NMR (CDCl$_3$, 500 MHz, 330 K) δ 0.03 (s, 36H), 0.15 (s, 18H), 1.07 (d, *J* = 7 Hz, 6H), 1.14 (d, *J* = 7 Hz, 6H), 1.42 (s, 1H), 1.81–2.07 (br s, 2H), 2.52 (sept, *J* = 7 Hz, 2H), 6.36–6.64 (br s, 1H), 7.01–7.04 (m, 2H), 7.26 (d, *J* = 7 Hz, 2H), 7.30–7.37 (m, 7H); ^{13}C NMR (CDCl$_3$, 125 MHz, 330 K) δ 1.18 (q), 2.59 (q), 23.75 (q), 25.12 (q), 29.78 (d), 29.78 (d), 30.92 (d), 31.53 (d), 32.30 (d), 124.17 (d), 126.38 (d), 126.84 (d), 127.43 (d), 128.68 (d), 128.72 (d), 129.69 (d), 131.36 (d), 142.60 (s), 143.64 (s), 144.90 (s), 147.29 (s), 148.02 (s), 148.54 (s), 149.86 (s), 152.18 (s); ^{119}Sn NMR (CDCl$_3$, 101 MHz, 330 K) δ 2.0. Anal. Calcd for C$_{51}$H$_{84}$Se$_4$Si$_6$Sn: C, 47.10; H, 6.38; Se, 24.29. Found: C, 46.89; H, 6.38; Se, 24.38.

Preparation of Tbt(Dmtp)SnS$_4$ 1b. A solution of Tbt(Dmtp)Sn: 3b, prepared from TbtBr (669 mg, 1.05 mmol), stannous chloride (224 mg, 1.18 mmol), and DmtpI[40] (376 mg, 0.98 mmol), was cooled again to −65 °C and then treated with elemental sulfur (211 mg, 0.82 mmol). After the mixture was gradually warmed to ambient temperature, the solvents were evaporated, and then the resulting residue was subjected to WCC (Florisil/methylene chloride) followed by HPLC to give 5-{2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}-5-[2,6-bis(2-methylphen-yl)phenyl]-1,2,3,4,5-tetrathiastannolane (**1b**) (273 mg, 25%). **1b**: mp 277–280 °C dec (recrystallized from methylene chloride/ethanol); ^{1}H NMR (CDCl$_3$, 500 MHz, 330 K) δ −0.12 (br s, 36H), 0.12 (s, 18H), 1.40 (s, 1H), 1.92 (br s, 2H), 1.95 (s, 6H), 6.35–6.55 (br s, 2H), 7.00 (t, *J* = 7 Hz, 2H), 7.14–7.18 (m, 4H), 7.21 (t, *J* = 7 Hz, 2H), 7.31 (d, *J* = 7 Hz, 2H), 7.41 (t, *J* = 7 Hz, 1H); ^{13}C NMR (CDCl$_3$, 125 MHz, 330 K) δ 1.10 (q), 2.28 (q), 21.29 (q), 30.78 (d), 30.89 (d), 33.00 (d), 123.52 (d), 126.45 (d), 128.32 (d), 128.60 (d), 128.81 (d), 129.08 (d), 130.39 (d), 130.82 (d), 138.21 (s), 140.60 (s), 142.93 (s), 145.51 (s), 145.88 (s), 147.94 (s), 149.64 (s), 152.69(s); ^{119}Sn NMR (CDCl$_3$, 101 MHz, 333 K) δ 53. Anal. Calcd for C$_{47}$H$_{76}$S$_4$Si$_6$Sn: C, 53.42; H, 7.26; S, 12.14. Found: C, 51.79; H, 6.84; S, 11.48.

Preparation of Tbt(Dmtp)SnSe$_4$ 2b. A solution of Tbt(Dmtp)Sn: 3b, prepared from TbtBr (766 mg, 1.22 mmol), stannous chloride (240 mg, 1.28 mmol), and DmtpI (466 mg, 1.21 mmol), was cooled again to −50 °C and then treated with elemental selenium (533 mg, 6.74 mmol). After the mixture was gradually warmed to ambient temperature, the solvents were evaporated, and then the resulting residue was subjected to WCC (Florisil/methylene chloride) followed by DCC to give crude Tbt(Dmtp)SnSe$_4$ (581 mg), which was separated with HPLC to give 5-{2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}-5-[2,6-bis(2-methylphenyl)phenyl]-1,2,3,4,5-tetraselenastannolane (**2b**) (421 mg, 29%). **2b**: mp 267–268 °C dec (recrystallized from methylene chloride/ethanol/acetonitrile); ^{1}H NMR (CDCl$_3$, 500 MHz, 330 K) δ −0.09 (br s, 18H), 0.09 (br s, 18H), 1.40 (s, 1H), 1.93 (s, 6H), 2.01 (s, 2H), 6.35–6.55 (br s, 2H), 7.02 (t, *J* = 7 Hz, 2H), 7.11–7.15 (m, 4H), 7.21 (t, *J* = 7 Hz, 2H), 7.32 (d, *J* = 7 Hz, 2H), 7.38 (t, *J* = 7 Hz, 1H); ^{13}C NMR (CDCl$_3$, 125 MHz, 330 K) δ 1.05 (q), 2.28 (q), 21.45 (q), 30.78 (d), 32.42 (d), 123.41 (d), 126.49 (d), 128.56 (d), 128.60 (d), 128.73 (d), 129.77 (d), 130.49 (d), 130.70 (d), 138.18 (s), 142.36 (s), 143.12 (s), 144.96 (s), 147.40 (s), 147.52 (s), 149.49 (s), 152.83 (s); ^{119}Sn NMR

(38) Kiersznicki, T.; Kulicki, Z.; Troszkiewicz, C. *Zesz. Nauk. Politech. Slask.*, *Chem.* 1967, *40*, 113. See also: *Chem. Abstr.*, *69*, 51751c.
(39) Bolton, R.; Sandall, J. P. B. *J. Chem. Soc.*, *Perkin Trans. 2* 1977, 278.
(40) Wehmschulte, R. J.; Khan, M. A.; Hossain, S. I. *Inorg. Chem.* 2001, *40*, 2756.

(CDCl$_3$, 101 MHz, 333 K) δ 2.31. FAB MS [M + H] calcd for C$_{47}$H$_{77}$-^{78}Se$_2$^{80}Se$_2$Si$_6$^{120}Sn 1245.0339. Found 1245.0300. Anal. Calcd for C$_{47}$H$_{76}$-Se$_4$Si$_6$Sn: C, 45.36; H, 6.17; Se, 25.38. Found: C, 44.27; H, 5.93; Se, 23.69.

Preparation of Dibromo{2,4,6-tris[bis(trimethylsilyl)methyl]-phenyl}(2,4,6-tricyclohexylphenyl)stannane. To a solution of TbtBr (2.04 g, 3.22 mmol) in THF (20 mL) was added *t*-BuLi (4.3 mL, 1.65 M in pentane, 2.2 equiv) at −65 °C. After the reaction mixture was stirred at the same temperature for 30 min, SnCl$_4$ (0.50 mL, 4.29 mmol) was added at −65 °C. The solution was gradually warmed to room temperature. After removal of the solvent, hexane was added to the residue to precipitate inorganic salts. The residue obtained from its filtrate was dissolved in THF (30 mL). To this solution was added, at room temperature, a solution of TcpMgBr, prepared from TcpBr[41] (978 mg, 2.42 mmol) and Mg (85 mg, 3.48 mmol) in THF (4 mL) with a small amount of iodine under reflux for several hours, and the mixture was heated under reflux for 16 h. After the reaction mixture was cooled to room temperature and the solvent was evaporated, hexane was added to this residue to precipitate inorganic salts, and the resulting mixture was subjected to WCC (hexane) followed by HPLC to afford the corresponding crude dichlorostannane (1.27 g, 37%) as a white solid. The crude dichlorostannane (1.27 g, 1.19 mmol) was added to a THF (30 mL) suspension of LiAlH$_4$ (110 mg, 2.90 mmol). After the mixture was stirred for 2 h, the reaction mixture was treated with some portions of ethyl acetate and water. Volatile substances were evaporated, and then the residue was subjected to DCC to afford the corresponding dihydrostannane (872 mg, 74%). Bromine (0.1 mL, 1.94 mmol) was added to an ether (40 mL) solution of the dihydrostannane (872 mg, 0.87 mmol). After removal of the solvent, crude dibromostannane was obtained. It was recrystallized from ethanol to afford pure dibromo-stannane (800 mg, 80%) as white crystals: mp 253−255.5 °C (recrystallized from ethanol); ^{1}H NMR (CDCl$_3$, 500 MHz) δ −0.01 (s, 18H), 0.06 (s, 18H), 0.11 (s, 18H), 1.22−1.55 (m, 11H), 1.33 (s, 1H), 1.55−1.88 (m, 19H), 2.05 (br s, 2H), 2.46 (br s, 1H), 3.04−3.12 (m, 2H), 6.25 (s, 1H), 6.46 (s, 1H), 7.09 (s, 2H); ^{13}C NMR (CDCl$_3$, 125 MHz) δ 0.95 (q), 1.51 (q), 1.69 (q), 25.65 (br t), 25.88 (t), 26.11 (t), 26.84 (t), 30.64 (d), 30.76 (d), 30.76 (d), 33.26 (br t), 34.28 (t), 38.56 (br t), 44.73 (d), 46.56 (d), 123.34 (d), 125.00 (d), 128.18 (d), 138.13 (s), 140.95 (s), 146.33 (s), 150.61 (s), 151.86 (s), 152.10 (s), 153.11 (s). Anal. Calcd for C$_{51}$H$_{94}$Br$_2$Si$_6$Sn: C, 53.05; H, 8.22; Br, 13.84. Found: C, 53.30; H, 8.12; Br, 13.98.

Preparation of Tbt(Tcp)SnS$_4$ 1c. After lithium naphthalenide (0.57 M in THF, 1.84 mL, 2.5 equiv), prepared from lithium (79 mg, 11.3 mmol) and naphthalene (1.22 g, 9.50 mmol) in THF (15 mL), was added to a THF solution (10 mL) of Tbt(Tcp)SnBr$_2$ (486 mg, 0.42 mmol) at −70 °C, the reaction mixture was stirred for 30 min at this temperature. After treatment of this solution with elemental sulfur (111 mg, 0.43 mmol) at −70 °C, the resulting mixture was stirred for 3 h during which time it was warmed to room temperature. After removal of the solvent, the residue was submitted to chromatography (Florisil/methylene chloride) followed by HPLC to afford 5-(2,4,6-tricyclo-hexylphenyl)-5-{2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}-1,2,3,4,5-tetrathiastannolane (**1c**) (455 mg, 96%). **1c**: mp 262−265 °C dec (recrystallized from methylene chloride/acetonitrile); ^{1}H NMR (CDCl$_3$, 500 MHz) δ −0.08 (s, 18H), 0.04 (s, 36H), 1.12−1.39 (m, 12H), 1.32 (s, 1H), 1.56−1.95 (m, 20H), 2.42 (br s, 1H), 2.97 (br s, 2H), 6.31 (s, 1H), 6.48 (s, 1H), 7.04 (s, 2H); ^{13}C NMR (CDCl$_3$, 125 MHz) δ 0.95 (q), 1.73 (q), 2.01 (q), 25.50 (t), 25.71 (t), 25.85 (t), 26.14 (t), 26.88 (t), 30.66 (d), 31.18 (d), 31.36 (d), 33.70 (t), 34.34 (t), 38.62 (t), 44.75 (d), 49.44 (d), 123.17 (d), 124.71 (d), 128.60 (d), 137.26 (s), 143.53 (s), 145.84 (s), 149.67 (s), 151.79 (s), 152.23 (s), 152.64 (s); ^{119}Sn NMR (toluene-*d$_8$*, 101 MHz) δ 75. Anal. Calcd for C$_{51}$H$_{94}$S$_4$Si$_6$Sn: C, 54.54; H, 8.45; S, 11.42. Found: C, 55.41; H, 8.73; S, 11.67.

Preparation of Tbt(Tcp)SnSe$_4$ 2c. After lithium naphthalenide (0.53 M in THF, 1.08 mL, 2.2 equiv), prepared from lithium (86 mg, 12.3 mmol) and naphthalene (1.279 g, 9.98 mmol) in THF (15 mL), was added to a THF solution (10 mL) of Tbt(Tcp)SnBr$_2$ (305 mg, 0.26 mmol) at −65 °C, the reaction mixture was stirred for 1.5 h at this temperature. After treatment of this solution with elemental selenium (209 mg, 2.64 mmol) at −70 °C, the resulting mixture was stirred overnight during which time it was warmed to room temperature. After removal of the solvent, the residue was subjected to column chromatography (Florisil/methylene chloride) followed by HPLC to afford 5-(2,4,6-tricyclohexylphenyl)-5-{2,4,6-tris[bis(trimethylsilyl)methyl]-phenyl}-1,2,3,4,5-tetraselenastannolane (**2c**) (351 mg, 100%). **2c**: mp 224−226.5 °C dec (recrystallized from methylene chloride/acetonitrile); ^{1}H NMR (CDCl$_3$, 500 MHz) δ 0.00 (s, 18H), 0.04 (s, 18H), 0.05 (s, 18H), 1.02−1.99 (m, 32H), 1.31 (s, 1H), 2.36−2.45 (m, 1H), 3.18−3.29 (m, 2H), 6.30 (s, 1H), 6.47 (s, 1H), 7.03 (s, 2H); ^{13}C NMR (CDCl$_3$, 125 MHz) δ 0.98 (q), 2.11 (q), 2.40 (q), 25.46 (t), 25.62 (t), 25.86 (t), 26.15 (t), 26.89 (t), 30.58 (d), 30.89 (t), 31.24 (d), 34.02 (t), 34.33 (t), 38.64 (t), 44.69 (d), 48.96 (d), 123.28 (d), 124.82 (d), 128.93 (d), 138.93 (s), 144.86 (s), 145.30 (s), 149.09 (s), 152 (br s), 152.21 (s); ^{119}Sn NMR (CDCl$_3$, 101 MHz) δ 5.7 ($^1J_{Sn-Se}$ = 1337 Hz); ^{77}Se NMR (CDCl$_3$, 51 MHz) δ 321, 734. Anal. Calcd for C$_{51}$H$_{94}$Se$_4$Si$_6$Sn: C, 46.74; H, 7.24; Se, 24.10. Found: C, 46.53; H, 7.33; Se, 23.90.

Preparation of Tbt(Ttm)SnS$_4$ 1d. After addition of *t*-BuLi (1.66 M in pentane, 1.70 mL, 2.2 equiv) to an ether solution (14 mL) of TbtBr (812 mg, 1.79 mmol) at −60 °C, the solution of TbtLi thus obtained was kept at −60 °C for 45 min. It was treated with an ether (12 mL) suspension of stannous chloride (256 mg, 1.35 mmol). After the mixture was stirred for 1 h at about −60 °C, an ether (6 mL) solution of TtmLi, prepared from TtmBr[42] (541 mg, 1.30 mmol) and *t*-BuLi (1.66 M in pentane, 1.72 mL, 2.2 equiv), was added to this reaction mixture. The resulting blue-purple solution of stannylene Tbt(Ttm)Sn: **3d** was stirred for 30 min at −60 °C, and then elemental sulfur (344 mg, 1.34 mmol) was added to this solution at the same temperature. It was stirred for 1.5 h while being warmed to room temperature. After removal of the solvent, the residue was chromatographed (Florisil/methylene chloride) to give a crude mixture, from which sulfur was removed by HPLC. The crude mixture was purified again by HPLC to provide a monomeric fraction (554 mg), which was separated with DCC to give 5-{2,4,6-tris[(trimethylsilyl)methyl]phenyl}-5-{2,4,6-tris[bis-(trimethylsilyl)methyl]phenyl}-1,2,3,4,5-tetrathiastannolane (**1d**) (492 mg, 34%). **1d**: mp 176−180 °C (recrystallized from methylene chloride/ethanol/acetonitrile); ^{1}H NMR (CDCl$_3$, 500 MHz) δ −0.02 (s, 18H), 0.00 (s, 18H), 0.01 (s, 9H), 0.03 (s, 18H), 0.04 (s, 18H), 1.31 (s, 1H), 1.67 (s, 1H), 1.71 (s, 1H), 1.94 (s, 2H), 2.35−2.60 (m, 4H), 6.38 (s, 1H), 6.48 (s, 1H), 6.61 (s, 2H); ^{13}C NMR (CDCl$_3$, 125 MHz) δ −1.40 (q), −0.40 (q), 0.81 (q), 1.20 (q), 1.49 (q), 26.91 (t), 30.67 (d), 31.08 (d), 31.68 (d), 32.10 (t), 122.69 (d), 125.73 (d), 127.81 (d), 137.63 (s), 142.28 (s), 142.70 (s), 145.72 (s), 145.75 (s), 151.99 (s), 152.16 (s); ^{119}Sn NMR (toluene-*d$_8$*, 101 MHz) δ 70. Anal. Calcd for C$_{45}$H$_{94}$S$_4$Si$_9$Sn: C, 47.61; H, 8.36; S, 11.30. Found: C, 47.45; H, 8.65; S, 11.33.

Preparation of Dibromo[bis(trimethylsilyl)methyl]{2,4,6-tris[bis-(trimethylsilyl)methyl]phenyl}stannane. To a solution of TbtBr (3.25 g, 5.13 mmol) in THF (50 mL) was added *t*-BuLi (6.64 mL, 1.70 M in pentane, 2.2 equiv) at −65 °C. After the reaction mixture was stirred at the same temperature for 30 min, SnCl$_4$ (0.90 mL, 7.69 mmol) was added at −65 °C. The mixture was stirred overnight during which time it was warmed to room temperature. After removal of the solvent, hexane was added to the residue to precipitate inorganic salts. The residue obtained from its filtrate was dissolved in THF (50 mL). To this solution was added, at room temperature, a solution of DisMgCl, prepared from DisCl (1 mL, 4.58 mmol) and Mg (121 mg, 4.96 mmol) in THF (10 mL), and the mixture was heated under reflux for 26 h.

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(42) Kano, N.; Tokitoh, N.; Okazaki, R. *Chem. Lett.* **1997**, 277.

After removal of volatile substances, hexane was added to the resulting residue to precipitate inorganic salts, and this filtrate was subjected to WCC (silica gel, hexane) to provide the corresponding crude dichlorostannane (1.27 g, 37%) as a white solid. The crude dichlorostannane (623 mg, 0.67 mmol) was added to a THF (15 mL) suspension of LiAlH$_4$ (53 mg, 1.40 mmol). After the mixture was stirred for 13 h, the reaction mixture was treated with an additional amount of LiAlH$_4$ (19 mg, 0.49 mmol), and then the resulting mixture was heated under reflux for 1 h. After the mixture cooled to room temperature, the reaction was quenched by addition of some portions of ethyl acetate and water. Volatile substances were evaporated, and then the residue was purified by DCC to give the corresponding dihydrostannane (336 mg, 59%). Bromine (0.05 mL, 0.97 mmol) was added to an ether (20 mL) solution of the dihydrostannane (336 mg, 0.40 mmol). The reaction solution was kept at room temperature for 4 days. After removal of the solvent, crude dibromostannane was obtained. It was recrystallized from ethanol to afford pure dibromostannane (263 mg, 57%) as white crystals: mp 219−221.5 °C (recrystallized from ethanol); ^{1}H NMR (CDCl$_3$, 500 MHz) δ 0.05 (s, 18H), 0.12 (s, 18H), 0.14 (s, 1H), 0.32 (s, 18H), 0.96 (s, 1H), 2.10 (s, 1H), 2.45 (s, 1H), 6.32 (s, 1H), 6.45 (s, 1H); ^{13}C NMR (CDCl$_3$, 125 MHz) δ 0.84 (q), 1.42 (q), 1.56 (q), 3.75 (q), 21.23 (d), 30.63 (br d), 30.76 (d), 123.21 (d), 127.78 (d), 135.88 (s), 146.51 (s), 146.57 (s), 150.77 (s), 151.36 (s). Anal. Calcd for C$_{34}$H$_{78}$-Br$_2$Si$_8$Sn: C, 41.23; H, 7.95; Br, 16.14. Found: C, 41.31; H, 7.69; Br, 16.26.

Preparation of Tbt(Dis)SnS$_4$ 1e. After lithium naphthalenide (0.58 M in THF, 0.65 mL, 2.7 equiv), prepared from lithium (59 mg, 8.46 mmol) and naphthalene (884 mg, 6.70 mmol) in THF (10 mL), was added to a THF solution (6 mL) of the dibromostannane (141 mg, 0.14 mmol), prepared as described above at −70 °C, the reaction mixture was stirred for 1 h at this temperature. The mixture was gradually warmed to room temperature to give a THF solution of stannylene Tbt-(Dis)Sn: **3e**. After the mixture was stirred for 30 min, a THF solution of the stannylene was treated with elemental sulfur (58 mg, 0.23 mmol). After removal of the solvent, the residue was submitted to chromatography (Florisil/methylene chloride) followed by HPLC to provide 5-[bis(trimethylsilyl)methyl]-5-{2,4,6-tris[bis(trimethylsilyl)methyl]-phenyl}-1,2,3,4,5-tetrathiastannolane (**1e**) (107 mg, 78%). **1e**: mp 219−221.5 °C (recrystallized from methylene chloride/ethanol); ^{1}H NMR (CDCl$_3$, 500 MHz) δ 0.04 (s, 18H), 0.10 (s, 36H), 0.22 (s, 18H), 0.86 (s, 1H), 1.33 (s, 1H), 1.74 (s, 1H), 1.83 (s, 1H), 6.36 (s, 1H), 6.49 (s, 1H); ^{13}C NMR (CDCl$_3$, 125 MHz) δ 0.88 (q), 1.47 (q), 1.77 (q), 4.34 (q), 19.60 (d), 30.69 (d), 32.00 (d), 32.07 (d), 122.93 (d), 128.07 (d), 137.98 (s), 145.73 (s), 151.09 (s), 151.62 (s); ^{119}Sn NMR (CDCl$_3$, 101 MHz) δ 145. Anal. Calcd for C$_{34}$H$_{78}$S$_4$Si$_8$Sn: C, 42.59; H, 8.22; S, 13.38. Found: C, 42.52; H, 8.48; S, 13.31.

Isolation of Stannanethione Tbt(Ditp)Sn=S 4a. Tributylphosphine (0.12 mL, 0.46 mmol) was added to a hexane (1 mL) solution of Tbt-(Ditp)SnS$_4$ **1a** (147 mg, 0.13 mmol) at room temperature in an 8ϕ tube. After the solution was degassed and sealed, it was kept at room temperature for 12 h. The sealed tube was opened in a glovebox. After slow evaporation of the solvent over 1 day, an orange solid containing stannanethione **4a** was obtained. Removing tributylphosphine sulfide, by washing with a small portion of hexane, afforded stannanethione **4a** (35 mg, 26%) as orange crystals with a small amount of tributylphosphine sulfide as an impurity. **4a**: ^{1}H NMR (C$_6$D$_6$, 500 MHz) δ 0.13 (s, 36H), 0.18 (s, 18H), 1.00 (d, J = 7 Hz, 6H), 1.48 (s, 1H), 1.51 (d, J = 6 Hz, 6H), 3.13−3.21 (m, 2H), 6.48 (s, 1H), 6.63 (s, 1H), 7.03−7.08 (m, 3H), 7.11−7.14 (m, 2H), 7.19−7.22 (m, 2H), 7.31−7.33 (m, 2H), 7.47−7.48 (m, 2H); ^{13}C NMR (C$_6$D$_6$, 125 MHz) δ 1.21 (q), 1.84 (q), 23.26 (q), 24.91 (q), 30.23 (d), 31.51 (d), 126.40 (d), 127.34 (d), 128.30 (d), 130.02 (d), 131.27 (d), 141.79 (s), 146.09 (s), 146.70 (s), 149.32 (s); ^{119}Sn NMR (C$_6$D$_6$, 60 °C) δ 531. The signals that could be assigned to *o*-benzylic protons and carbons in the Tbt group could not be found even when CH−COSY spectra were measured at higher temperatures, which was probably due to line broadening caused by restricted rotation around the C (aromatic)−CH (SiMe$_3$)$_2$ bond. Although two *m*-aromatic carbons in a Tbt group usually resonated at about 123 and 127 ppm, their signals could not be identified due to broadening and overlapping with the signals of benzene solvent. Since one of the *m*-aromatic carbons in the Ditp group was also overlapped with carbons of the solvent, as evidenced by CH−COSY, it could not be identified. Four quaternary carbons could not be found, probably due to their broadening. The elemental analysis and measurement of the melting point of **4e** could not be carried out because of its extremely high reactivity toward water.

Isolation of Stannaneselone Tbt(Ditp)Sn=Se 5a. An orange solution of **2a** (182 mg, 0.14 mmol) and triphenylphosphine (112 mg, 0.43 mmol) in hexane (5 mL) was refluxed for 2 h in a glovebox filled with argon. The solution turned deep red, and triphenylphosphine selenide was precipitated nearly quantitatively upon the mixture being cooled to room temperature. After filtration of the selenide in a glovebox, the residual deep-red solution was concentrated in a glovebox to give pure stannaneselone **5a** (111 mg, 84% yield) as red crystals: ^{1}H NMR (C$_6$D$_6$, 500 MHz) δ 0.13 (s, 36H), 0.18 (s, 18H), 0.99 (d, J = 7 Hz, 6H), 1.48 (s, 1H), 1.49 (d, J = 7 Hz, 6H), 3.16 (br sept, J = 7 Hz, 2H), 6.47 (s, 1H), 6.63 (s, 1H), 6.96−7.08 (m, 3H), 7.10−7.13 (m, 2H), 7.18−7.21 (m, 2H), 7.30−7.32 (m, 2H), 7.47 (d, J = 7 Hz, 2H); ^{13}C NMR (C$_6$D$_6$, 500 MHz) δ 0.94 (q), 1.57 (q), 23.00 (q), 24.64 (q), 29.96 (d), 31.23 (d), 124.21 (d), 126.13 (d), 127.08 (d), 127.78 (d), 128.50 (d), 129.77 (d), 131.03 (d), 141.18 (s), 142.91 (s), 145.40 (s), 146.14 (s), 148.06 (s), 148.93 (s), 152.34 (s), 158.65 (s). The signals that could be assigned to *o*-benzylic protons and carbons in the Tbt group could not be found even when CH−COSY spectra were measured at higher temperatures, which is probably due to line broadening caused by restricted rotation around the C (aromatic)−CH (SiMe$_3$)$_2$ bond, as in the case of stannanethione **4a**. Although one of the *m*-aromatic carbons in the Tbt group usually resonates at about 127 ppm, its signal could not be identified due to overlapping with the signals of aromatic carbons in the Ditp group. The elemental analysis and measurement of the melting point of **5a** could not be carried out because of its extremely high reactivity toward water.

X-ray Data Collections of 5a. Crystals suitable for X-ray structural analysis were obtained by slow evaporation of a hexane solution of **5a** in an argon atmosphere. Crystallographic data for **5a**: C$_{51}$H$_{84}$SeSi$_6$Sn, M = 1063.39, triclinic, a = 11.939(8) Å, b = 23.478(5) Å, c = 11.471-(4) Å, α = 91.86(2)°, β = 112.61(3)°, γ = 97.45(4)°, V = 2931(2) Å^3, Z = 2, space group $P\bar{1}$. The crystal was mounted in a glass capillary. Data were collected on a Rigaku AFC5R diffractometer with Mo Kα radiation (λ = 0.71069 Å) at 296 K. The structure was solved by direct methods using SHELXS-97[43] and refined with full-matrix least-squares (SHELXL-97)[43] using all independent reflections (10 257 reflections) for 606 parameters. The non-hydrogen atoms were refined anisotropically and all of the hydrogen atoms were placed at calculated positions [d(C−H) = 0.96 Å]. Two trimethylsilyl groups at one of the *o*-positions of the Tbt group were disordered. The occupancies of the disordered trimethylsilyl groups were refined to be 0.62:0.38. U_{ij} values of disordered trimethylsilyl groups were restrained using SIMU and ISOR instructions. R1 = 0.104 (I > 2σ(I), 3427 reflections), wR2 = 0.318 (for all reflections), GOF = 1.007.

Reaction of Tbt(Ditp)Sn=S 4a with Mesitonitrile Oxide. Tributylphosphine (45 μL, 0.18 mmol) was added to a hexane (2 mL) solution of Tbt(Ditp)SnS$_4$ **1a** (65 mg, 0.059 mmol) at room temperature. After 10 min, this solution was treated with mesitonitrile oxide (18 mg, 0.11 mmol) to give 2-{2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}-2-[2,6-bis(2-isopropylphenyl)phenyl]-4-mesityl-1,3,5,2-oxathiazastannole (**7a**) (50 mg, 72%). **7a**: mp 250−253 °C dec (recrystallized from chloroform); ^{1}H NMR (CDCl$_3$, 500 MHz) δ −0.01 (s, 36H), 0.15 (s, 9H), 0.16 (s, 9H), 0.92 (d, J = 7 Hz, 3H), 1.17 (d, J = 7 Hz, 3H), 1.27 (d,

(43) Sheldrick, G. M. *SHELXL-97*, Program for Crystal Structure Refinement; Göttingen University: Göttingen, Germany, 1997.

$J = 7$ Hz, 3H), 1.30 (d, $J = 7$ Hz, 3H), 1.46 (s, 1H), 1.94 (s, 6H), 2.13 (s, 2H), 2.18 (s, 3H), 2.81−2.84 (m, 2H), 6.41 (s, 1H), 6.53 (s, 1H), 6.66 (s, 2H), 6.81−6.84 (m, 1H), 7.04−7.07 (m, 1H), 7.17−7.23 (m, 2H), 7.27−7.30 (m, 2H), 7.34−7.43 (m, 5H); ^{13}C NMR (CDCl$_3$, 125 MHz) δ 1.16 (q), 1.26 (q), 1.80 (q), 1.95 (q), 20.92 (q), 20.98 (q), 24.47 (q), 24.53 (q), 25.84 (q), 26.35 (q), 29.66 (d), 29.69 (d), 30.89 (d), 31.18 (d), 123.97 (d), 126.24 (d), 126.75 (d), 127.17 (d), 127.55 (d), 127.72 (d), 127.79 (d), 127.88 (d), 128.07 (d), 128.53 (d), 128.82 (d), 129.67 (d), 130.43 (d), 130.96 (d), 131.84 (s), 136.89 (s), 137.38 (s), 139.93 (s), 141.72 (s), 142.38 (s), 145.77 (s), 146.56 (s), 146.90 (s), 147.56 (s), 147.80 (s), 148.07 (s), 148.24 (s), 151.2 (s), 152.5 (s). FAB MS [M + H] calcd for C$_{61}$H$_{96}$NO^{32}SSi$_6$^{120}Sn 1178.4851. Found 1178.4799.

Reaction of Tbt(Ditp)Sn=S 4a with 2,3-Dimethyl-1,3-butadiene. Tributylphosphine (90 μL, 0.36 mmol) was added to a hexane (1 mL) solution of Tbt(Ditp)SnS$_4$ **1a** (105 mg, 0.095 mmol) in an 8ϕ tube at room temperature. After the solution was degassed and sealed, it was transferred into another 10ϕ Pyrex tube in a glovebox. To this solution was added 2,3-dimethyl-1,3-butadiene (0.3 mL, 2.65 mmol) at ambient temperature, and the solution was allowed to stand at room temperature for 6 h. The reaction mixture was purified by HPLC and PTLC to give a [4 + 2] cycloadduct, 2-{2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}-2-[2,6-bis(2,6-diisopropylphenyl)phenyl]-4,5-dimethyl-1-thia-2-stanna-cyclohex-4-ene (**6**) (63 mg, 61%). **6**: mp 204.5−206.5 °C dec (recrystallized from methylene chloride/ethanol); ^{1}H NMR (CDCl$_3$, 500 MHz) δ −0.10 (s, 18H), 0.03 (br s, 18H), 0.10 (s, 9H), 0.12 (s, 9H), 0.97 (d, $J = 14$ Hz, 1H), 1.05 (d, $J = 7$ Hz, 3H), 1.11−1.14 (m, 9H), 1.29 (d, $J = 14$ Hz, 1H), 1.35 (s, 1H), 1.39 (s, 3H), 1.65 (s, 3H), 1.83 (br s, 2H), 2.50 (sept, $J = 7$ Hz, 1H), 2.65 (d, $J = 14$ Hz, 1H), 2.75 (sept, $J = 7$ Hz, 1H), 2.80 (d, $J = 14$ Hz, 1H), 6.34 (s, 1H), 6.47 (s, 1H), 6.68 (br s, 1H), 6.80 (d, $J = 8$ Hz, 1H), 7.06−7.13 (m, 3H), 7.18−7.21 (m, 1H), 7.24−7.29 (m, 2H), 7.34−7.38 (m, 2H), 7.49 (d, $J = 7$ Hz, 1H); ^{13}C NMR (CDCl$_3$, 125 MHz) δ 0.98 (q), 1.05 (q), 1.25 (q), 2.14 (q), 2.18 (q), 2.31 (q), 20.31 (q), 22.70 (q), 22.96 (q), 23.31 (q), 23.56 (t), 25.07 (q), 25.14 (q), 29.66 (d), 29.75 (d), 30.28 (d), 30.83 (t), 31.61 (d), 31.92 (d), 123.30 (d), 125.55 (d), 125.68 (d), 126.19 (d), 126.61 (d), 127.19 (d), 127.27 (d), 128.06 (d), 128.13 (d), 128.44 (d), 128.81 (d), 130.69 (d), 140.52 (s), 143.27 (s), 143.29 (s), 143.72 (s), 143.96 (s), 147.14 (s), 147.66 (s), 147.80 (s), 149.51 (s), 151.54 (s). FAB MS [M] calcd for C$_{57}$H$_{94}$^{32}SSi$_6$^{120}Sn 1098.4714. Found 1098.4725.

Reaction of Tbt(Ditp)Sn=Se 5a with Mesitonitrile Oxide. Toluene (0.8 mL) was added to a mixture of Tbt(Ditp)SnSe$_4$ **2a** (80 mg, 0.061 mmol), and triphenylphosphine (48 mg, 0.19 mmol) at room temperature in an 8ϕ tube. After the solution was degassed and sealed, it was poured into mesitonitrile oxide (21 mg, 0.13 mmol) in a glovebox. The reaction mixture was subjected to HPLC to give 2-{2,4,6-tris[bis-(trimethylsilyl)methyl]phenyl}-2-[2,6-bis(2,6-diisopropylphenyl)phenyl]-4-mesityl-1,3,5,2-oxaselenazastannole (**9a**) (68 mg, 90%). **9a**: mp 267−269 °C dec (recrystallized from chloroform); ^{1}H NMR (CDCl$_3$, 500 MHz) δ −0.01 (s, 36H), 0.14 (s, 9H), 0.16 (s, 9H), 0.94 (d, $J = 7$ Hz, 3H), 1.18 (d, $J = 7$ Hz, 3H), 1.26 (d, $J = 7$ Hz, 3H), 1.30 (d, $J = 7$ Hz, 3H), 1.45 (s, 1H), 1.94 (s, 6H), 2.18−2.25 (br s, 2H), 2.18 (s, 3H), 2.78−2.84 (m, 2H), 6.39 (s, 1H), 6.51 (s, 1H), 6.67 (s, 2H), 6.75−6.77 (m, 1H), 7.08−7.11 (m, 1H), 7.14−7.19 (m, 2H), 7.26−7.32 (m, 2H), 7.36−7.42 (m, 5H); ^{13}C NMR (CDCl$_3$, 125 MHz, 330 K) δ 1.23 (q), 1.34 (q), 2.00 (q), 2.15 (q), 20.92 (q), 21.21 (q), 24.51 (q), 24.52 (q), 25.69 (q), 26.18 (q), 29.71 (d), 29.82 (d), 31.09 (d), 31.35 (d), 125.85 (d), 126.65 (d), 126.98 (d), 127.43 (d), 127.71 (d), 128.31 (d), 128.36 (d), 128.50 (d), 128.86 (d), 130.91 (d), 131.35 (s), 132.61 (s), 136.91 (s), 137.52 (s), 140.98 (s), 141.75 (s), 142.31 (s), 142.52 (s), 145.55 (s), 146.88 (s), 147.76 (s), 147.90 (s), 148.09 (s), 148.40 (s), 152.01 (s). Anal. Calcd for C$_{61}$H$_{95}$NOSeSi$_6$Sn: C, 59.82; H, 7.83; N, 1.14; Se, 6.45. Found: C, 59.74; H, 7.62; N, 1.40; Se, 5.58.

Reaction of Tbt(Ditp)Sn=Se 5a with 2,3-Dimethyl-1,3-butadiene. After toluene (0.8 mL) was added to a mixture of Tbt(Ditp)SnSe$_4$ **2a** (102 mg, 0.078 mmol), and triphenylphosphine (62 mg, 0.24 mmol) at

room temperature in an 8ϕ tube, the solution was degassed and sealed. After this tube was kept at ambient temperature for 10 h, it was opened in a glovebox. To the solution was added 2,3-dimethyl-1,3-butadiene (0.15 mL, 1.33 mmol), and the resulting mixture was kept at room temperature overnight. Volatile substances were removed, and then the residue was subjected to HPLC to give a monomeric product (58 mg). The ^{1}H NMR of the crude products showed an AB quartet that could be assigned to methylene protons next to the selenium at about 3.0 ppm. The absence of olefinic protons in the ^{1}H NMR excludes a possibility that the product was derived from an ene reaction. Mass spectrum of the crude products showed the parent peak of a [4 + 2] cycloadduct **8**. FAB MS [M − H] calcd for C$_{57}$H$_{93}$^{80}SeSi$_6$^{120}Sn 1145.4080. Found 1145.3989. Although this crude product contained a [4 + 2] cycloadduct, 2-{2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}-2-[2,6-bis(2,6-diisopropylphenyl)phenyl]-4,5-dimethyl-1-selena-2-stan-nacyclohex-4-ene (**8**), this cycloadduct decomposed during purification by flash column chromatography.

Reaction of Tbt(Dmtp)Sn=S 4b with Mesitonitrile Oxide. To a hexane (5 mL) solution of Tbt(Dmtp)SnS$_4$ **1b** (94 mg, 0.088 mmol), was added tributylphosphine (66 μL, 0.26 mmol) at −68 °C. After the mixture was warmed to ambient temperature over 10 min, the yellow-orange solution was stirred for 10 min at room temperature. Treatment of this solution with mesitonitrile oxide (18 mg, 0.11 mmol) followed by usual workup afforded 2-{2,4,6-tris[bis(trimethylsilyl)methyl]-phenyl}-2-[2,6-bis(2-methylphenyl)phenyl]-4-mesityl-1,3,5,2-oxathi-azastannole (**7b**) (86 mg, 85%). **7b**: mp 258−261 °C dec (recrystallized from chloroform/acetonitrile); ^{1}H NMR (CDCl$_3$, 500 MHz, 330 K) δ 0.00 (br s, 36H), 0.15 (s, 18H), 1.43 (s, 1H), 2.07 (br s, 12H), 2.09 (br s, 2H), 2.22 (s, 3H), 6.49 (br s, 2H), 6.73 (s, 2H), 6.96 (br s, 1H), 7.06 (br s, 1H), 7.18 (br s, 4H), 7.24−7.27 (m, 3H), 7.36 (br s, 1H), 7.40−7.45 (m, 1H); ^{13}C NMR (CDCl$_3$, 125 MHz) δ 1.26 (q), 1.30 (q), 1.81 (q), 1.98 (q), 20.73 (q), 20.91 (q), 21.06 (q), 21.34 (q), 31.13 (d), 31.38 (d), 123.93 (d), 126.44 (d), 127.55 (d), 128.20 (d), 128.46 (d), 128.60 (d), 128.74 (d), 129.46 (s), 130.76 (d), 130.88 (d), 131.66 (s), 137.01 (s), 137.62 (s), 137.94 (s), 138.21 (s), 139.06 (s), 142.21 (s), 142.81 (s), 145.85 (s), 145.90 (s), 147.00 (s), 147.44 (s), 148.30 (s), 151.98 (s). Anal. Calcd for C$_{57}$H$_{87}$NOSSi$_6$Sn: C, 61.03; H, 7.83; N, 1.25; S, 2.86. Found: C, 61.00; H, 7.84; N, 1.29; S, 2.88.

Spectral Detection of Tbt(Tcp)Sn=S 4c. Toluene-d_8 (0.5 mL) was added to a mixture of **1c** (86 mg, 0.077 mmol) and triphenylphosphine (61 mg, 0.23 mmol) in a 5ϕ NMR tube. After the solution was degassed and sealed, its ^{119}Sn NMR spectrum was measured. It showed a broad singlet at 643 ppm that could be assigned to stannanethione Tbt(Tcp)-Sn=S **4c**, together with peaks at 75 (a signal due to the starting material **1c**), −63.5, −61, −59, and −56 ppm, which were assigned to an oligomeric fraction.[34,35] This reaction solution was kept at room temperature overnight. After removal of the solvent, the residue was purified by HPLC to give mainly oligomeric (50 mg)[35] and monomeric fractions (9 mg), which contained mainly the starting material together with triphenylphosphine sulfide (77%) and triphenylphosphine (18%).

Reaction of Tbt(Tcp)Sn=S 4c with Phenyl Isothiocyanate. Hexane (3 mL) was added to a mixture of Tbt(Tcp)SnS$_4$ **1c** (52 mg, 0.046 mmol), and triphenylphosphine (42 mg, 0.16 mmol). After the mixture was refluxed for 70 min, the solution was cooled and treated with phenyl isothiocyanate (0.050 mL, 0.42 mmol) at ambient temperature. Hexane was evaporated, and then the residue was subjected to HPLC to give an oligomeric fraction[35] (12 mg), **1c** (11 mg, 23%), 2-{2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}-2-(2,4,6-tricyclohexyl-phenyl)-4-phenylimino-1,3,2-dithiastannetane (**10**) (16 mg, 31%; the conversion yield was 40%), and triphenylphosphine sulfide (10 mg, 70%), along with triphenylphosphine (11 mg, 28%). The ^{1}H NMR spectrum of the oligomeric fraction was very complicated. The ^{119}Sn NMR of this oligomeric fraction showed four signals at −70, −67, −66, and −63 ppm.[35] **10**: mp 128−131 °C dec (recrystallized from methylene chloride/acetonitrile/ethanol); ^{1}H NMR (CDCl$_3$, 500 MHz) δ −0.07 (s, 9H), 0.00 (s, 9H), 0.04 (s, 9H), 0.05 (s, 18H), 0.11 (s, 9H),

1.15−1.20 (m, 6H), 1.35 (s, 1H), 1.38−1.46 (m, 6H), 1.62−1.97 (m, 16H), 2.17−2.32 (m, 4H), 2.45−2.58 (m, 3H), 6.34 (s, 1H), 6.51 (s, 1H), 6.91 (d, *J* = 7 Hz, 2H), 7.03 (t, *J* = 7 Hz, 1H), 7.08 (s, 1H), 7.10 (s, 1H), 7.24−7.27 (m, 2H); ^{13}C NMR (CDCl$_3$, 125 MHz) δ 0.87 (q), 0.89 (q), 1.17 (q), 1.24 (q), 1.40 (q), 1.57 (q), 25.51 (t), 25.71 (t), 25.77 (t), 25.89 (t), 26.12 (t), 26.86 (t), 30.79 (d), 31.05 (br d), 32.55 (t), 33.00 (t), 34.38 (t), 38.55 (t), 39.02 (t), 44.86 (d), 49.31 (d), 50.19 (d), 121.44 (d), 123.32 (d), 123.71 (d), 124.54 (d), 128.40 (d), 128.57 (d), 134.41 (s), 142.00 (s), 146.52 (s), 149.59 (s), 150.47 (s), 152.48 (s), 152.80 (s), 152.98 (s), 157.36 (s). Anal. Calcd for C$_{58}$H$_{99}$NS$_2$Si$_6$Sn: C, 59.95; H, 8.61; N, 1.21; S, 5.52. Found: C, 59.67; H, 8.62; N, 1.47; S, 5.47.

Reaction of Tbt(Tcp)Sn=S 4c with Mesitonitrile Oxide. After hexane (1 mL) was added to a mixture of Tbt(Tcp)SnS$_4$, **1c** (82 mg, 0.073 mmol), and triphenylphosphine (59 mg, 0.22 mmol) in an 8ϕ Pyrex tube, it was degassed and sealed. The reaction mixture was kept at ambient temperature overnight. This tube was opened in a glovebox, and the resulting solution was poured into mesitonitrile oxide (14 mg, 0.089 mmol). After the reaction tube was opened in the air, the solvent was removed. The residue was purified by HPLC to yield an oligomeric fraction[35] (20 mg) and 2-{2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}-2-(2,4,6-tricyclohexylphenyl)-4-mesityl-1,3,5,2-oxathiazastannole (**7c**) (31 mg, 35%). The ^{1}H NMR spectrum of this oligomeric fraction was complicated, similarly to that of the above-mentioned oligomer. **7c**: mp 224−235 °C dec (recrystallized from methylene chloride/acetonitrile); ^{1}H NMR (CDCl$_3$, 500 MHz) δ 0.00 (s, 18H), 0.05 (s, 9H), 0.06 (s, 9H), 0.07 (s, 18H), 1.00−1.40 (m, 12H), 1.36 (s, 1H), 1.55−2.05 (m, 18H), 2.13 (br s, 6H), 2.24 (s, 3H), 2.38−2.50 (m, 3H), 6.40 (s, 1H), 6.54 (s, 1H), 6.79 (s, 2H), 7.01 (s, 1H), 7.02 (s, 1H); ^{13}C NMR (CDCl$_3$, 125 MHz) δ 1.00 (q), 1.08 (q), 1.28 (q), 1.36 (q), 1.39 (q), 1.45 (q), 20.37 (q), 21.05 (q), 25.59 (t), 25.66 (t), 25.73 (t), 25.97 (t), 26.06 (t), 26.10 (t), 26.16 (t), 26.88 (t), 30.87 (d), 31.24 (d), 31.69 (d), 32.39 (d), 32.82 (d), 34.29 (t), 34.40 (t), 38.27 (t), 39.56 (t), 44.76 (d), 48.34 (d), 49.52 (d), 123.65 (d), 124.17 (d), 124.38 (d), 128.13 (d), 128.96 (d), 131.69 (s), 136.37 (s), 136.99 (s), 137.91 (s), 142.49 (s), 146.19 (s), 148.00 (s), 149.93 (s), 152.11 (s), 152.16 (s), 152.64 (s), 152.77 (s). Anal. Calcd for C$_{61}$H$_{105}$NOSSi$_6$Sn: C, 61.67; H, 8.93; N, 1.18; S, 2.70. Found: C, 60.75; H, 9.01; N, 0.99; S, 2.81.

Spectral Detection of Tbt(Tcp)Sn=Se 5c. Toluene-d_8 (0.5 mL) was added to a mixture of Tbt(Tcp)SnSe$_4$ **2c** (88 mg, 0.067 mmol), and triphenylphosphine (54 mg, 0.21 mmol) in a 5ϕ NMR tube. After it was degassed and sealed, the ^{119}Sn NMR of this solution was measured at room temperature. The ^{119}Sn NMR of this solution showed a broad singlet at 556 ppm that could be assigned to stannaneselone Tbt(Tcp)-Sn=Se **5c**. After ^{119}Sn NMR spectra were measured overnight, the color of the solution changed from deep red to colorless. Its ^{119}Sn NMR showed two signals around −100 ppm (−111.4 and −118.8 ppm) and four signals around −300 ppm (−275.9, −278.7, −279.0, and −294.2 ppm). After removal of the solvent, the residue was subjected to HPLC to give only an oligomeric product[31] (58 mg) together with triphenylphosphine selenide (64 mg, 91%). In this case, stannaneselone **5c** dimerized slowly at room temperature before the ^{77}Se NMR spectrum was measured. The ^{77}Se NMR spectrum of Tbt(Tcp)Sn=Se **5c**, prepared in a manner similar to that described above, showed a broad signal at 839 ppm.

Reaction of Tbt(Tcp)Sn=Se 5c with Mesitonitrile Oxide. After toluene (1.5 mL) was added to a mixture of Tbt(Tcp)SnSe$_4$ **2c** (77 mg, 0.059 mmol), and triphenylphosphine (48 mg, 0.18 mmol) and placed in an 8ϕ Pyrex tube, the solution was degassed and sealed. The tube was kept at ambient temperature for 2 h and then opened in a glovebox. After this red solution was poured into mesitonitrile oxide (28 mg, 0.17 mmol), the resulting solution was exposed to the air. Chromatographic separation by DCC and HPLC afforded an oligomeric fraction[35] (24 mg) and 2-{2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}-2-(2,4,6-tricyclohexylphenyl)-4-mesityl-1,3,5,2-oxaselenazastannole (**9c**) (43 mg, 58%). **9c**: mp 225−227 °C dec (recrystallized from methylene chloride/

acetonitrile); ^{1}H NMR (CDCl$_3$, 500 MHz) δ −0.03 (s, 18H), 0.06 (s, 9H), 0.07 (s, 9H), 0.11 (s, 18H), 1.00−1.43 (m, 12H), 1.36 (s, 1H), 1.57−2.15 (m, 20H), 2.13 (br s, 6H), 2.24 (s, 3H), 2.42−2.48 (m, 2H), 2.63−2.70 (m, 1H), 6.39 (s, 1H), 6.54 (s, 1H), 6.79 (s, 2H), 7.01 (s, 2H); ^{13}C NMR (CDCl$_3$, 125 MHz) δ 0.98 (q), 1.11 (q), 1.32 (q), 1.49 (q), 1.51 (q), 1.51 (q), 20.46 (q), 21.06 (q), 25.41 (t), 25.51 (t), 25.76 (t), 25.97 (t), 26.16 (t), 26.24 (t), 26.88 (t), 30.83 (d), 30.91 (d), 31.37 (t), 32.49 (t), 32.91 (t), 34.27 (t), 34.42 (t), 37.98 (t), 39.45 (t), 44.74 (d), 48.06 (d), 48.82 (d), 123.71 (d), 124.20 (d), 124.54 (d), 128.21 (d), 129.00 (d), 132.31 (s), 136.89 (s), 136.97 (s), 138.04 (s), 142.46 (s), 143.68 (s), 145.96 (s), 149.76 (s), 152.08 (s), 152.13 (s), 152.83 (s), 158.82 (s). FAB MS [M + H] calcd for C$_{61}$H$_{106}$NO^{80}SeSi$_6$^{120}Sn 1236.5077. Found 1236.5149. Anal. Calcd for C$_{61}$H$_{105}$NOSeSi$_6$Sn: C, 59.33; H, 8.59; N, 1.13; Se, 6.39. Found: C, 59.08; H, 8.31; N, 1.30; Se, 5.38.

Desulfurization of Tbt(Ttm)SnS$_4$ 1d by Triphenylphosphine. Toluene-d_8 (0.7 mL) was added to Tbt(Ttm)SnS$_4$ **1d** (88 mg, 0.078 mmol) and triphenylphosphine (62 mg, 0.23 mmol) and placed in a 5ϕ NMR tube at room temperature. After it was degassed and sealed, the solution gradually turned pale orange. When the solution was kept at room temperature for 2 h, this solution suddenly turned colorless, and white precipitates were formed. After removal of the solvent, the residue was separated with HPLC to yield an oligomeric fraction[35] (59 mg) together with triphenylphosphine sulfide (61 mg, 88%).

Desulfurization of Tbt(Dis)SnS$_4$ 1e by Triphenylphosphine. Toluene-d_8 (0.5 mL) was added to Tbt(Dis)SnS$_4$ **1e** (73 mg, 0.076 mmol) and triphenylphosphine (60 mg, 0.23 mmol) in a 5ϕ NMR tube at room temperature. After it was degassed and sealed, the solvent was removed, and then the resulting residue was subjected to HPLC to afford an oligomeric fraction[35] (61 mg) and triphenylphosphine sulfide (61 mg, 91%).

Conclusion

Introduction of appropriately bulky ligands onto the tin led to the isolation of the first stable diaryl-substituted tin−chalcogen double-bond compounds, stannanethione Tbt(Ditp)-Sn=S and stannaneselone Tbt(Ditp)Sn=Se, without resorting to intramolecular coordination. In the ^{119}Sn NMR and ^{77}Se NMR, their tin and selenium atoms resonate at very low fields, characteristic of the doubly bonded species. X-ray structural analysis of Tbt(Ditp)Sn=Se revealed that the Sn−Se distance [2.373(3) Å] was approximately 9% shorter than a Sn−Se single bond length (2.55−2.60 Å), with trigonal planar geometry around the tin atom (sum of the angles = 359.9°), indicative of structural similarity to carbon, silicon, and germanium analogues. Their considerable double-bond character was also verified by their reactivity in the cycloaddition with 2,3-dimethyl-1,3-butadiene to afford Diels−Alder adducts, such as other group 14 element−chalcogen double-bond compounds. Despite severe steric congestion around the reactive center, they showed reactivities as double-bond compounds because long branched arms enclose the Sn=X moieties from the remote site. These facts clearly show that the chemistry of tin−chalcogen double-bond compounds is essentially similar to the chemistry of a ketone and its silicon and germanium analogues. However, they are much less stable and much more difficult to isolate even compared to silicon and germanium congeners because of longer bonds involving tin and because of energy gaps between σ- and π-bonds that are longer than those of silicon and germanium.

Supporting Information Available: Refinement, atomic coordinates, bond lengths and angles, anisotropic displacement parameters, torsion angles, for **5a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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