Formation and Reactions of Stannanethiones and Stannaneselones

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Received February 22, 1993

Two approaches for the formation of stannanethiones and stannaneselones were examined, i.e., (i) the thermal retrocycloaddition of trichalcogenastannolanes **1** and (ii) the dechalcogenation of tetrachalcogenastannolanes **2** and **3**. Novel heterocycles containing tin and chalcogen atoms, 1,2,4,3-trichalcogenastannolanes Tb(Tip)SnY_3CPh_2 [**1a,b** (Y = S, Se; Tb = 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl; Tip = 2,4,6-triisopropylphenyl)], have been synthesized by the thermal reaction of 1,2,3,4,5-tetrachalcogenastannolanes Tb(Tip)SnY_4 (**3**) with diphenyldiazomethane followed by dechalcogenation with hexamethylphosphoric triamide. Thermal decomposition of trichalcogenastannolanes **1** in the presence of dimethyl acetylenedicarboxylate (DMAD) afforded thiastannete **8** and selenastannete **14** as novel tin-containing heterocycles. The formation of **8** and **14** was explained in terms of a [2 + 2]cycloaddition of intermediary stannanethione **18a** and stannaneselone **18b** with DMAD. Dechalcogenation of tetrachalcogenastannolanes **2** and **3** with trivalent phosphorus compounds in the absence of trapping agents gave dichalcogenadistannetanes whose formation was explained in terms of dimerization of stannanethione **18a** or stannaneselone **18b**, except for the reaction of more crowded triisopropylphenyl-substituted **3a** which gave a monomeric product **28** at room temperature on account of a slower rate of dimerization. The desulfurization of **3a** with triphenylphosphine in the presence of an excess amount of 2,3-dimethyl-1,3-butadiene provided [4 + 2]cycloadduct **32** as the first example of [4 + 2]cycloaddition of a stannanethione. The structures of **26, 27, 31, 8,** and **14** were definitely determined by X-ray diffraction analysis. The central four-membered rings of *trans*-dichalcogenadistannetanes **26** and **31** were almost completely planar, while those of *cis*-**27** had unprecedentedly large fold angles due to the steric repulsion between two Tb groups. Both **8** and **14** were found to have distorted trapezoid skeletons reflecting the coexistence of long tin–chalcogen bonds and short carbon–carbon double bonds.

Introduction

For many years, it was considered that compounds featuring double bonds between heavier main-group elements would not be stable because of weak pπ-pπ bonding. From the isolation in 1981 of the first stable compounds with Si=C,[1] Si=Si,[2] and P=P[3] double bonds using sufficiently large ligands which prevented their oligomerization (kinetic stabilization), many unsaturated compounds containing group 14 and 15 elements were isolated.[4] As for stable double-bond compounds between group 14 and 16 elements, there have been relatively extensive studies on thioketones over several decades,[5] while those on selenoketones started in the 1970s[6] and those on thio- and selenoaldehydes were undertaken about 10 years ago.[7] On the other hand, very little is known for stable metallathiones and metallaselones of heavier group 14 metals (RR′M=Y; M = Si, Ge, Sn, and Pb; Y = S, Se), although there have recently been reported some examples of silanethione,[8] silaneselone,[8] and germanethione[9] stabilized by taking advantage of the intramolecular coordination of nitrogen atoms to the double bond (thermo-

(1) Brook, A. G.; Abdesaken, F.; Gutekunst, B.; Gutekunst, G.; Kallury, R. K. *J. Chem. Soc., Chem. Commun.* **1981**, 191.

(2) West, R.; Fink, M. J.; Michl, J. *Science* **1981**, *214*, 1343.

(3) Yoshifuji, M.; Shima, I.; Inamoto, N.; Hirotsu, K.; Higuchi, T. *J. Am. Chem. Soc.* **1981**, *103*, 4587.

(4) For reviews on multiple bond compounds containing group 14 and 15 elements, see the followings. Group 14: (a) Tsumuraya, T.; Batchellar, S. A.; Masamune, S. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 902. (b) Barrau, J.; Escudié, J.; Stagé, J. *Chem. Rev.* **1990**, *90*, 283. (c) Raabe, G.; Michl, J. *The Chemistry of Organosilicon Compounds*; Patai, S.; Rappoport, Z., Eds.; Wiley-Interscience: New York, 1989; Chapter 17, p 1015. (d) West, R. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 1201. (e) Brook, A. G.; Baines, K. M. *Adv. Organomet. Chem.* **1986**, *25*, 1. (f) Raabe, G.; Michl, J. *Chem. Rev.* **1985**, *85*, 419. (g) Wiberg, N. *J. Organomet. Chem.* **1984**, *273*, 141. Group 15: (h) *Multiple Bonds and Low Coordination in Phosphorus Chemistry*; Regitz, M., Scherer, O. J.; Eds.; George Thieme Verlag: New York, 1990. (i) Regitz, M.; Binger, P. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1484. (j) Cowley, A. H.; Norman, N. C. *Prog. Inorg. Chem.* **1986**, *34*, 1. (k) Lochschmidt, S.; Schmidpeter, A. *Phosphorus Sulfur* **1987**, *29*, 73.

(5) Duus, F. *Comprehensive Organic Chemistry*; Barton, D. H. R., Ollis, W. D., Eds.; Pergamon Press: Oxford, 1979; Vol. 3, p 373.

(6) (a) Magnas, P. D. *Comprehensive Organic Chemistry*; Barton, D. H. R., Ollis, W. D., Eds.; Pergamon Press: Oxford, 1979; Vol. 3, Part 12. (b) Jensen, K. A.; Kjaer, A. *The Chemistry of Organic Selenium and Tellurium Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley-Interscience: New York, 1986; Vol. 1, Chapter 1. (c) Paulmier, C. *Selenium Reagents and Intermediates in Organic Synthesis*; Pergamon Press: Oxford, 1986; Chapter 3.

(7) (a) Okazaki, R.; Ishii, A.; Fukuda, N.; Oyama, H.; Inamoto, N. *J. Chem. Soc., Chem. Commun.* **1982**, 1187. (b) Vedejs, E.; Perry, D. A.; Wilde, R. G. *J. Am. Chem. Soc.* **1986**, *108*, 2985. (c) Okazaki, R.; Ishii, A.; Inamoto, N. *J. Am. Chem. Soc.* **1987**, *109*, 279. (d) Okazaki, R.; Kumon, N.; Inamoto, N. *J. Am. Chem. Soc.* **1989**, *111*, 5949. (e) Ando, W.; Ohtaki, T.; Suzuki, T.; Kabe, Y. *J. Am. Chem. Soc.* **1991**, *113*, 7782. For reviews, see: Okazaki, R. *Yuki Gosei Kagaku Kyokai Shi* **1988**, *46*, 1149; Usov, V. A.; Timokhina, L. V.; Voronkov, M. G. *Sulfur Rep.* **1992**, *12*, 95.

(8) Arya, P.; Boyer, J.; Carré, F.; Corriu, R.; Lanneau, G.; Lapasset, J.; Perrot, M.; Priou, C. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1016.

(9) (v) Veith, M.; Becker, S.; Huch, V. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1237. (b) Veith, M.; Detemple, A.; Huch, V. *Chem. Ber.* **1991**, *124*, 1135.

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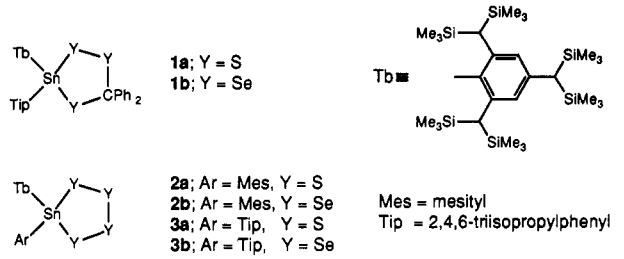
Scheme I



dynamic stabilization). Reports on tin–chalcogen double-bond compounds are even more scarce because of their lower π-bond energy (for example, the value for Sn=S is 31.8 kcal mol^{-1} while those for C=S, Si=S, and Ge=S are 56.1, 46.2, and 40.0 kcal mol^{-1}, respectively).[10] Indeed, sterically unhindered stannanethiones and stannaneselones have been known to undergo oligomerization; Ph_2SnS and Me_2SnS have the corresponding trimeric structures[11] while di-*tert*-butyltin chalcogenides t-Bu_2SnY (Y = S, Se, and Te) occur as dimers both in the solid state and in solution.[12]

In continuation of our work on thio- and selenocarbonyl compounds, we became interested in the chemistry of tin–sulfur and tin–selenium double bonds. In this paper, we report on (i) a novel mode of generation of stannanethiones and stannaneselones from trichalcogenastannolanes and tetrachalcogenastannolanes, (ii) their characteristic reactivities, and (iii) the crystallographic analyses of some reaction products with unique structures which are formed from these novel double-bond species.

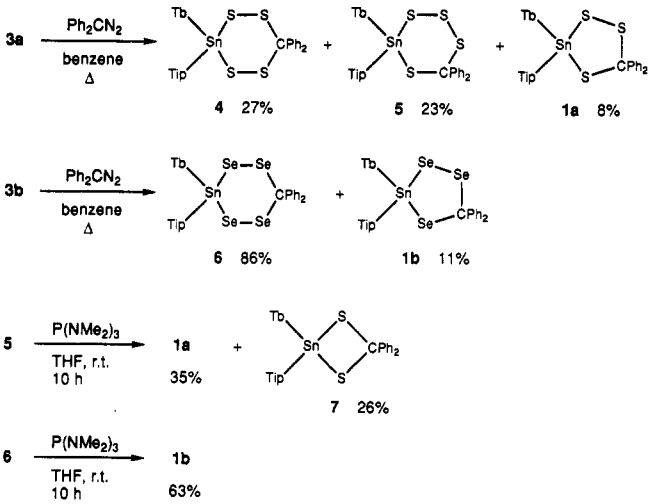
Results and Discussion

We used two approaches for the generation of stannanethiones and stannaneselones, i.e., the thermal retrocycloaddition of trichalcogenastannolanes **1** and the dechalcogenation of tetrachalcogenastannolanes **2** and **3**.

In these heterocycles **1-3**, bulky substituents such as mesityl, 2,4,6-triisopropylphenyl (Tip), and 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl (Tb) are introduced onto tin atoms in the hope of obtaining stannanethiones and stannaneselones of as high stability as possible. We have already reported the synthesis of 1,2,3,4,5-tetrachalcogenastannolanes Tb(Ar)SnY_4 **2** and **3**.[13]

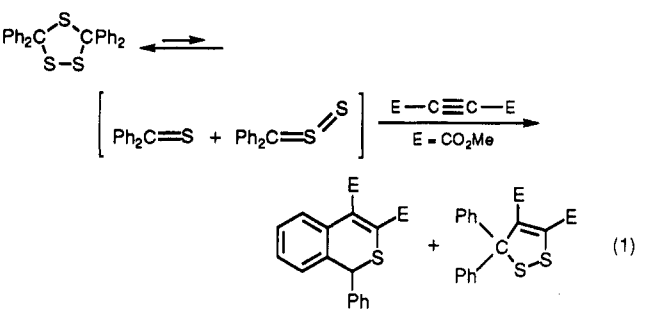
I. Thermal Decomposition of 1,2,4,3-Trichalcogenastannolanes 1.[14] **(a) Preparation of 1,2,4,3-Trichalcogenastannolanes 1.** When 1,2,3,4,5-tetrathiastannolane **3a** bearing Tb and Tip substituents was treated with an excess amount of diphenyldiazomethane in refluxing benzene for 10 h, two isomeric products, i.e., 1,2,4,5-tetrathia-3-stannacyclohexane **4** and 1,2,3,5-tetrathia-4-stannacyclohexane **5**, were isolated in 27 and 23% yields, respectively, together with 1,2,4,3-trithiastannolane **1a** (8%). Similarly, the thermal reaction of 1,2,3,4,5-tetraselenastannolane **3b** with diphenyldiazomethane resulted

Scheme II



in the formation of 1,2,4,5-tetraselena-3-stannacyclohexane **6** and 1,2,4,3-triselenastannolane **1b** in 86 and 11% yields, respectively. Tetrathiastannacyclohexane **5** was readily desulfurized by the reaction with an equimolar amount of hexamethylphosphoric triamide in THF at room temperature to afford 1,2,4,3-trithiastannolane **1a** (35%) and 1,3,2-dithiastannetane **7** (26%) along with recovered **5** (12%), while, under similar conditions, tetraselenastannacyclohexane **6** underwent deselenation more readily leading to the exclusive formation of 1,2,4,3-tetraselenastannolane **1b** in 63% yield (Scheme II).

(b) Thermal Decomposition of Trichalcogenastannolanes 1 in the Presence of Dimethyl Acetylenedicarboxylate (DMAD) and Trapping of Intermediary Stannanethione and Stannaneselone by [2 + 2]Cycloaddition Reaction. Huisgen and Rapp previously reported the thermal dissociation of 3,3,5,5-tetraphenyl-1,2,4-trithiolane into thiobenzophenone and the corresponding thiosulfine, both of which were trapped by DMAD to afford benzothiopyran and 1,2-dithiolane derivatives, respectively (eq 1).[15]



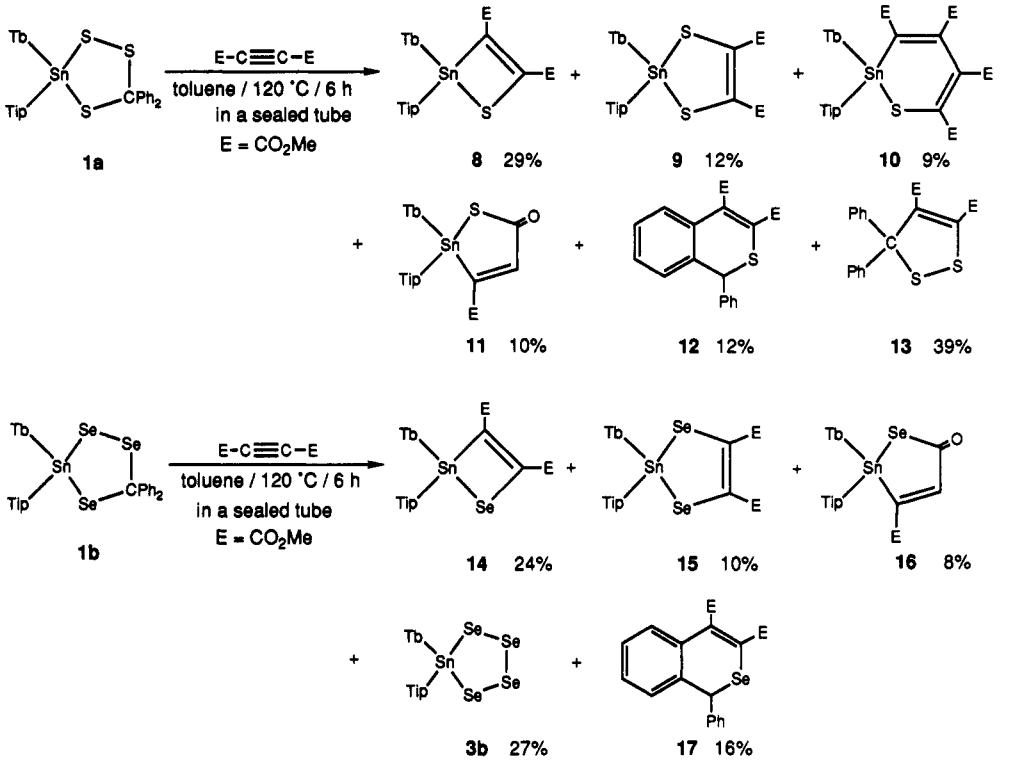
(1)

We anticipated that similar thermal retrocycloaddition of 1,2,4,3-trichalcogenastannolanes **1**, a tin analog of a trithiolane, would lead to the formation of a reactive species containing a tin–chalcogen double bond.

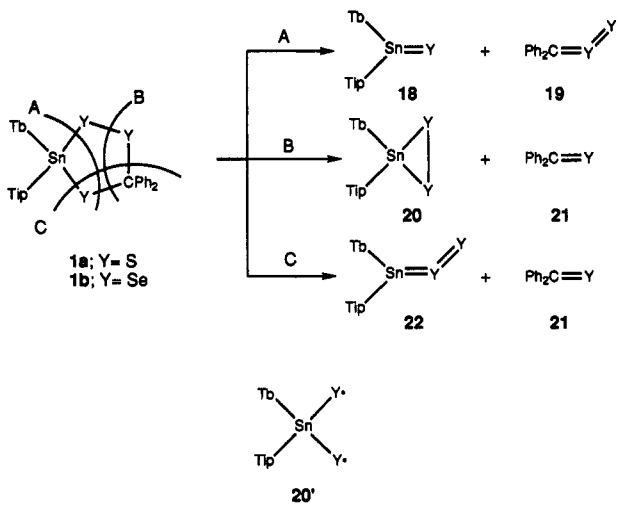
When **1a** was heated (120 °C) in toluene in the presence of DMAD in a sealed tube until **1a** was consumed (^{1}H NMR), products **8-13** were obtained after chromatographic separation in yields as shown in Scheme III. A similar reaction for **1b** gave **14-17** and **3b**. Because of their unsymmetric structures, there are three conceivable dissociation pathways (A–C) for **1** as shown in Scheme IV. The products **8** and **13** are formed by the cycloaddition of

(10) Calculated with HF/DZ (d, p). Nagase, S. Unpublished results.
(11) (a) Schumann, H. *Z. Anorg. Allg. Chem.* **1967**, *354*, 192. (b) Menzebach, B.; Bleckmann, P. *J. Organomet. Chem.* **1975**, *91*, 291.
(12) Puff, H.; Gattermayer, R.; Hundt, R.; Zimmer, R. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 547.
(13) (a) Tokitoh, N.; Suzuki, H.; Matsumoto, T.; Matsuhashi, Y.; Okazaki, R.; Goto, M. *J. Am. Chem. Soc.* **1991**, *113*, 7047. (b) Tokitoh, N.; Takahashi, M.; Matsumoto, T.; Suzuki, H.; Matsuhashi, Y.; Okazaki, R. *Phosphorus, Sulfur, Silicon* **1991**, *59*, 161. (c) Tokitoh, N.; Matsuhashi, Y.; Okazaki, R. *Tetrahedron Lett.* **1991**, *32*, 6151. (d) Matsuhashi, Y.; Tokitoh, N.; Okazaki, R.; Goto, M.; Nagase, S. *Organometallics* **1993**, *12*, 1351.
(14) Preliminary reports. (a) Tokitoh, N.; Matsuhashi, Y.; Okazaki, R. *Tetrahedron Lett.* **1992**, *33*, 5551. (b) Tokitoh, N.; Matsuhashi, Y.; Okazaki, R. *J. Chem. Soc., Chem. Commun.* **1993**, 407.
(15) (a) Huisgen, R.; Rapp, J. *J. Am. Chem. Soc.* **1987**, *109*, 902. (b) Huisgen, R. *Phosphorus, Sulfur, Silicon* **1989**, *43*, 63.

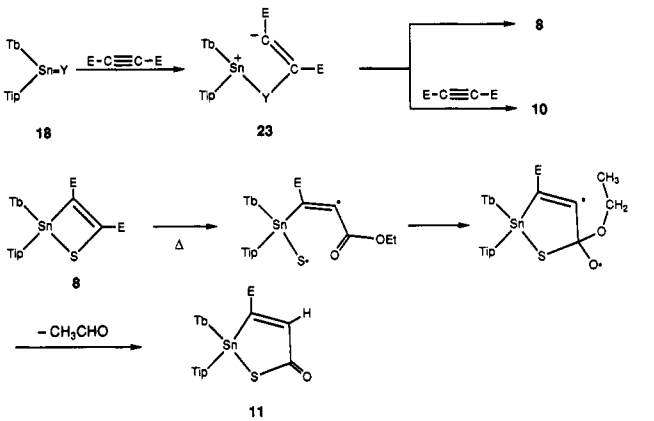
Scheme III



Scheme IV



Scheme V



DMAD with stannanethione **18a** and thioxothiobenzophenone (**19a**), respectively, generated via path A. However, the formation of 2:1 adduct **10** suggests that the reaction of stannanethione **18a** with DMAD proceeds in a stepwise fashion probably involving a zwitterionic intermediate **23** (Scheme V). The formation of thiastannolane **11** is most likely explained by homolytic cleavage of the strained C–S bond of **8** under the reaction conditions followed by loss of acetaldehyde (Scheme V).

The formation of **9** indicates the existence of path B involving **20** (or **20'**), which is in contrast with the dissociation pattern of the tetraphenyltrithiolane reported by Huisgen. Since it is known that thio- and selenobenzophenone react with DMAD to give **12** and **17**,[16] respectively, **21** formed in paths B and C is thought to result in the formation of **12** and **17**. It is reasonably considered that **22** formed in path C rearranges into **20** or loses a chalcogen atom to give **18**. The mechanism for the formation of **3b** in the reaction of **1b** is not clear, but it is probably formed by the reaction of **18**, **20**, or **22** with selenium produced in the reaction.

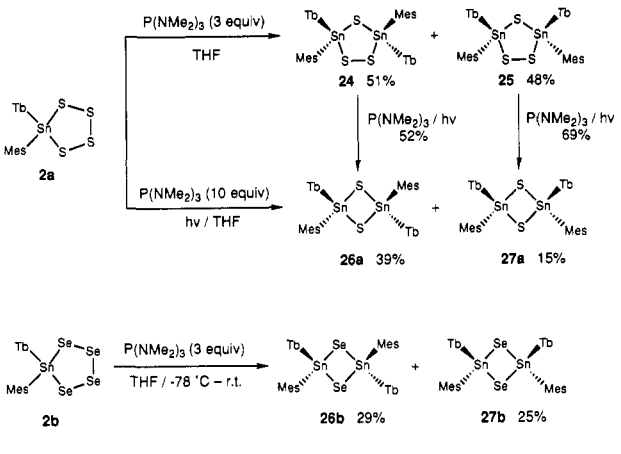
The compounds **8** and **14** are of great interest not only as the first examples of [2 + 2]cycloaddition of stannanethione and stannaneselone, respectively, but also as novel tin-containing heterocycles. The successful isolation and noticeable stability of **8** and **14** suggest that the combination of the bulky Tb and Tip groups effectively protects these highly strained molecules against their ring-opening reactions by nucleophiles.

II. Dechalcogenation of 1,2,3,4,5-Tetrachalcogenastannolanes 2 and 3 with Trivalent Phosphorus Compounds. (a) Dechalcogenation in the Absence of Trapping Agents.[17] Since the dechalcogenation of tetrachalcogenastannolanes **2** and **3** is considered to be a reasonable approach to stannanethione **18a** and stannaneselone **18b**, we first studied the reactivity of **2** and **3**

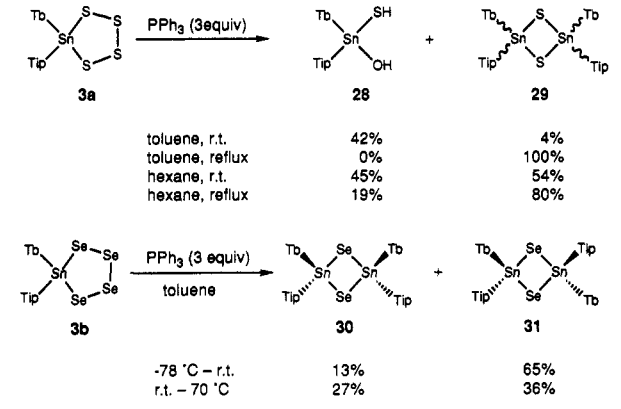
(16) (a) Ohno, A.; Koizumi, T.; Ohnishi, Y. *Bull. Chem. Soc. Jpn.* **1971**, *44*, 2511. (b) Gotthardt, H.; Nieberl, S. *Tetrahedron Lett.* **1976**, 3563. (c) Gotthardt, H.; Nieberl, S. *Liebigs Ann. Chem.* **1980**, 867. (d) Okuma, K.; Kojima, K.; Kaneko, I.; Ohta, H. *Tetrahedron Lett.* **1992**, *33*, 1333.

(17) Preliminary report: Tokitoh, N.; Matsuhashi, Y.; Goto, M.; Okazaki, R. *Chem. Lett.* **1992**, 1595.

Scheme VI



Scheme VII

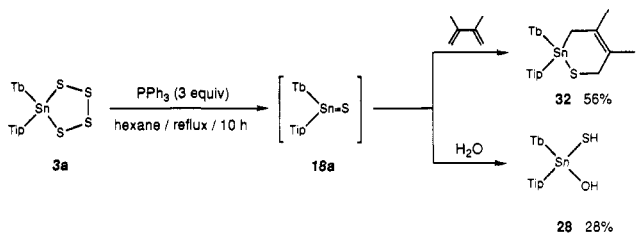


toward trivalent phosphorus compounds. The results for mesityl-substituted stannolane **2** and triisopropylphenyl-substituted stannolane **3** are shown in Schemes VI and VII, respectively.

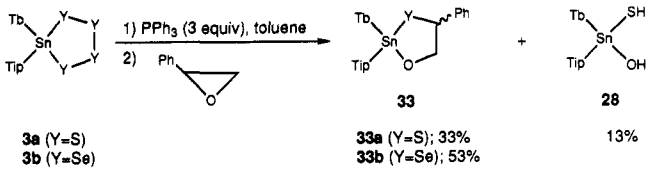
Except for the thermal reaction of **2a** with $P(NMe_2)_3$ and that of **3a** with PPh_3, there were obtained only dichalcogenadistannetanes whose formation was most likely explained in terms of dimerization of stannanethione **18a** or stannaneselone **18b** (or the corresponding mesityl derivatives). The mechanism for the formation of **24** and **25** from **2a** is not clear, but the formation of **26a** and **27a** in the photodesulfurization of **2a** is thought to proceed via **24** and **25**, respectively, because the photodesulfurization of **24** and **25** under similar conditions gave **26a** and **27a**, respectively. Although the reaction of mesityl-substituted tetrathiastannolane **2a** with 3 equiv of PPh_3 gave only dimeric products, a similar reaction of more crowded triisopropylphenyl-substituted **3a** gave a monomeric product **28**, preferentially at room temperature in particular. This suggests that the more crowded stannanethione Tb(Tip)Sn=S (**18a**) undergoes much slower dimerization than the less crowded stannanethione Tb(Mes)Sn=S, thus being capable of existing as a monomer in solution and being converted into thiol **28** by trapping with water present either adventitiously in the reaction solution or in the workup procedure.

(b) Trapping of Intermediary Stannanethione 18a by [4 + 2]Cycloaddition Reaction. In order to trap stannanethione **18a** expected to be formed by the above desulfurization reaction of **3a**, the reaction of **3a** with 3 equiv of PPh_3 was carried out in refluxing hexane in the presence of an excess amount of 2,3-dimethyl-1,3-butadiene (Scheme VIII).

Scheme VIII



Scheme IX



The reaction proceeded cleanly to give [4 + 2]cycloadduct **32** (56%) along with the thiol **28** (28%) which was considered to be formed by a mechanism similar to that described in Scheme VII. Since it is well-known that thioketones and thioaldehydes undergo facile [4 + 2]-cycloaddition with dienes,[18] the formation of a good yield of **32** provides definite evidence for the generation of stannanethione **18a** in the desulfurization of **3a**. It should be noted that this represents the first example of [4 + 2]cycloaddition of a stannanethione.

(c) Dechalcogenation of Tetrachalcogenastannolanes in the Presence of Epoxides. In view of the report that a transient germanethione can be trapped by an epoxide,[19] we became interested in the reaction of stannanethione **18a** and stannaneselone **18b** with an epoxide. When **3a** was allowed to react with PPh_3 (3 equiv) in toluene at 90 °C in the presence of styrene oxide, oxathiastannolane **33a** (33%) and thiol **28** (13%) were obtained. Similarly, **3b** gave oxaselenastannolane **33b** (53%) (Scheme IX).

The formation of **33a** and **33b** is most likely explained in terms of the reaction of stannanethione **18a** and stannaneselone **18b** with the epoxide to give **34** followed by nucleophilic attack by triphenylphosphine sulfide (or selenide), necessarily produced in the dechalcogenation step, and subsequent ring closure with loss of $Ph_3P{=}Y$ (nucleophilic assistance) (Scheme X; path A), although the possibility of direct ring opening at α-carbon to the phenyl group (Scheme X; path B) cannot be excluded. It has been known that a phosphine sulfide[20] and a phosphine selenide[21] can undergo a nucleophilic ring opening of an epoxide in the presence of an acid catalyst.

III. Structures of Dichalcogenadistannetanes (26, 27, and 31) and Chalcogenastannetes (8 and 14). The

(18) (a) Middleton, W. J. *J. Org. Chem.* **1965**, *30*, 1390. (b) Schönberg, A.; König, B. *Chem. Ber.* **1968**, *101*, 725. (c) Ohnishi, Y.; Akasaki, Y.; Ohno, A. *Bull. Chem. Soc. Jpn.* **1973**, *46*, 3307. (d) Baldwin, J. E.; Lopez, R. C. G. *Tetrahedron* **1983**, *39*, 1487. (e) Kirby, G. W.; Lochead, A. W.; Sheldrake, G. N. *J. Chem. Soc., Chem. Commun.* **1984**, 922. (f) Krafft, G. A.; Meinke, P. T. *Tetrahedron Lett.* **1985**, *26*, 1947. (g) Vedejs, E.; Eberlein, T. H.; Mazur, D. J.; McClure, C. K.; Perry, D. A.; Ruggeri, R.; Schwartz, E.; Stults, J. S.; Varie, D. L.; Wilde, R. G.; Wittenberger, S. *J. Org. Chem.* **1986**, *51*, 1556. (h) Segi, M.; Nakajima, T.; Suga, S.; Murai, S.; Ryu, I.; Ogawa, A.; Sonoda, N. *J. Am. Chem. Soc.* **1988**, *110*, 1976.

(19) Barrau, J.; Rima, G.; Lavayssiere, H.; Dousse, J.; Satgé, J. *J. Organomet. Chem.* **1983**, *246*, 227.

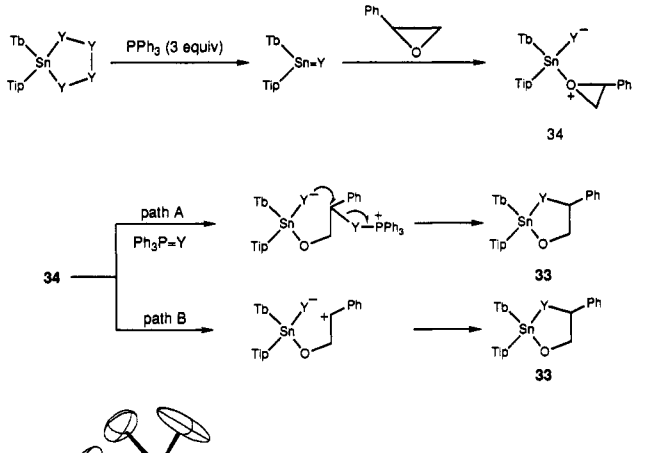
(20) Chan, T. H.; Finkenbine, J. R. *J. Am. Chem. Soc.* **1972**, *94*, 2880.

(21) Chan, T. H.; Finkenbine, J. R. *Tetrahedron Lett.* **1974**, 2091.

Table I. Crystal Data for 26, 27, 31, 8, and 14

	26a	26b	27a	27b	31	8	14
formula	$C_{72}H_{140}Sn_2Si_{12}S_2$	$C_{72}H_{140}Sn_2Si_{12}Se_2$	$C_{72}H_{140}Sn_2Si_{12}S_2$	$C_{72}H_{140}Sn_2Si_{12}Se_2$	$C_{84}H_{164}Sn_2Si_{12}Se_2$	$C_{48}H_{88}O_4SSi_6Sn$	$C_{48}H_{88}O_4SeSi_6Sn$
M	1644.52	1738.31	1644.52	1738.31	1906.55	1048.48	1095.38
crystal size, mm	0.46 × 0.4 × 0.4	0.37 × 0.16 × 0.16	0.3 × 0.2 × 0.2	0.53 × 0.3 × 0.3	0.8 × 0.6 × 0.5	0.7 × 0.75 × 0.15	0.3 × 0.4 × 0.2
crystal system	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic	triclinic	triclinic
space group	$C2/c$	$C2/c$	$C2/c$	$C2/c$	$P2_1/a$	$P\bar{1}$	$P\bar{1}$
a, Å	16.489(3)	16.416(3)	20.916(5)	20.868(7)	27.219(7)	12.401(6)	12.366(2)
b, Å	20.441(2)	20.365(2)	15.390(1)	15.402(2)	13.38(1)	22.001(7)	21.981(5)
c, Å	28.750(4)	29.241(6)	30.396(5)	30.598(8)	31.539(6)	12.359(3)	12.368(4)
α, deg						95.91(2)	100.76(2)
β, deg	102.21(1)	101.13(1)	103.82(1)	104.40(1)	110.00(1)	114.94(3)	114.86(2)
γ, deg						79.17(3)	84.08(2)
V, Å^3	9471(2)	9591.8(3)	9501.4(3)	9527(4)	10790(9)	3002(2)	2996(1)
Z	4	4	4	4	4	2	2
d_{calcd}, g cm^{-3}	1.148	1.203	1.149	1.211	1.173	1.160	1.214
μ, cm^{-1}	65.54	68.99	63.55	69.43	12.97	6.11	11.81
R	0.057	0.046	0.047	0.043	0.087	0.073	0.079
R_w	0.066	0.054	0.056	0.055	0.111	0.082	0.080

Scheme X



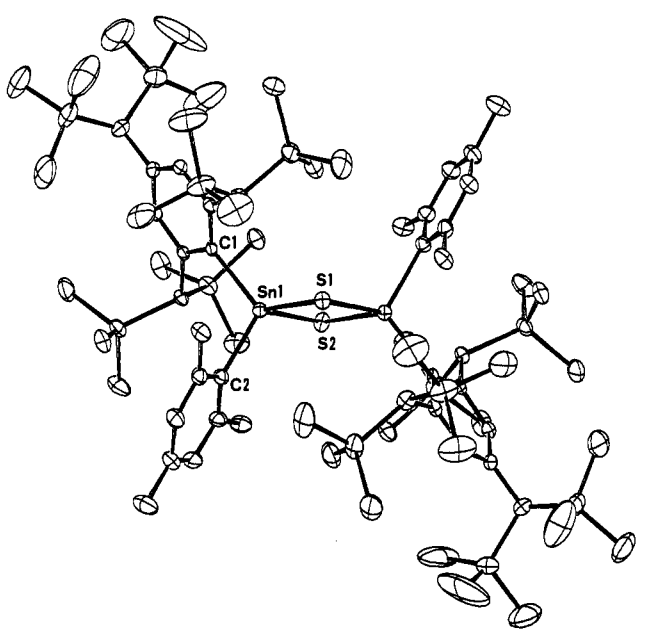


Figure 1. ORTEP drawing of *trans*-[Tb(Mes)SnS]$_2$ (**26a**) with thermal ellipsoid plot (20% probability).

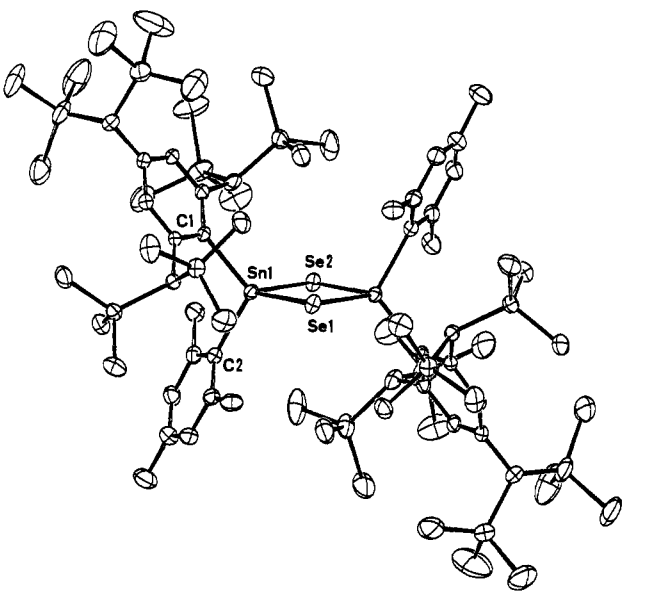


Figure 2. ORTEP drawing of *trans*-[Tb(Mes)SnSe]$_2$ (**26b**) with thermal ellipsoid plot (20% probability).

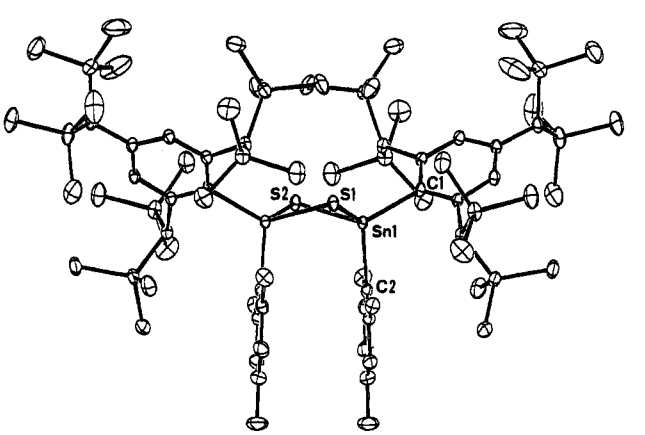


Figure 3. ORTEP drawing of *cis*-[Tb(Mes)SnS]$_2$ (**27a**) with thermal ellipsoid plot (20% probability).

newly obtained 1,3,2,4-dichalcogenadistannetanes (**26**, **27**, and **31**) and 1,2-chalcogenastannetes (**8** and **14**) showed satisfactory spectral and analytical data, and their final structures were definitely determined by X-ray crystallographic analysis. Crystal data of **8**, **14**, **26a,b**, **27a,b**, and **31** are summarized in Table I. The molecular structures of **26**, **27**, and **31** are shown in Figures 1–5, and their selected interatomic bond lengths (Å) and angles (deg) and torsion angles (deg) for the core rings are listed in Table II.

The central four-membered rings of Tb and mesityl-substituted *trans*-dichalcogenadistannolanes **26a** and **26b** were found to be completely planar as in the case of the previously reported rhombic ring systems of 2,2,4,4-tetra-*tert*-butyl-1,3,2,4-dichalcogenadistannolanes,[12] though their

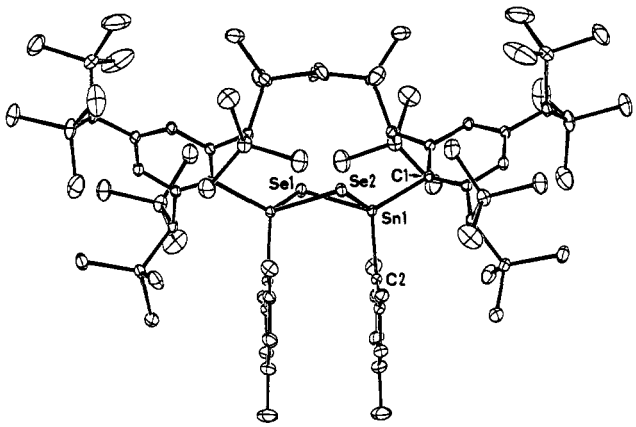


Figure 4. ORTEP drawing of *cis*-[Tb(Mes)SnSe]$_2$ (**27b**) with thermal ellipsoid plot (20% probability).

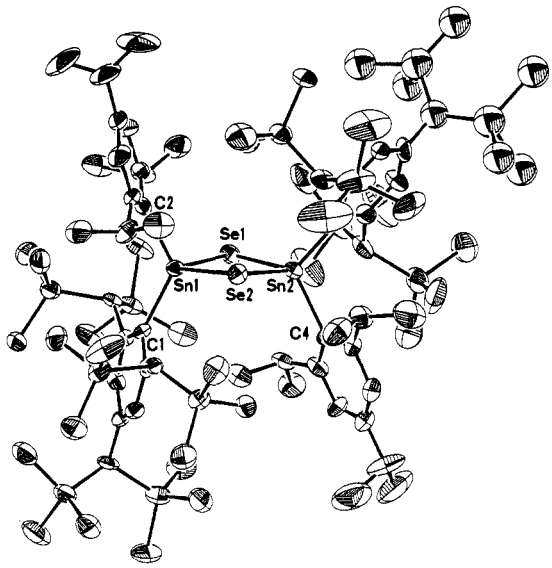


Figure 5. ORTEP drawing of *trans*-[Tb(Tip)SnSe]$_2$ (**31**) with thermal ellipsoid plot (30% probability).

ring shape becomes closer to a square. On the other hand, the crystal structure of **31** possesses an approximately square but a little puckered diselenadistannetane ring, the fold angles of which are 9.02° for Se–Se axis and 8.95° for Sn–Sn axis. The slight deviation of the core ring from planarity and the poor symmetry of the molecule of **31** are probably due to the higher steric hindrance between Tb and Tip groups than that of the mesityl analog **26b**, although R value for **31** is not so good enough to discuss its strict molecular structure. In contrast to the *trans* derivatives, *cis*-substituted dichalcogenadistannetanes **27a** and **27b** showed unprecedentedly large fold angles (**27a**: 39.8° for S–S axis and 40.9° for Sn–Sn axis; **27b**: 43.6° for Se–Se axis and 41.3° for Sn–Sn axis) probably due to the remarkable steric hindrance of the Tb groups facing each other. Since there have been no examples of unsymmetrically substituted 1,3,2,4-dichalcogenadistannetanes so far as we know, it is open to discussion whether a *cis*-substituted dichalcogenadistannetane ring system has intrinsically such a folded conformation or not.

The molecular structures of **8** and **14** are shown in Figures 6 and 7, respectively. Selected interatomic bond lengths (Å) and angles (deg) and torsion angles (deg) for the chalcogenastannete rings are listed in Table III.

Both **8** and **14** were found to have distorted trapezoid skeletons, which showed remarkably small corner angles at the tin atoms [66.5(3)° for S(1)–Sn(1)–C(1) of **8** and 74.3(7)° for Se(1)–Sn(1)–C(1) of **14**] and at the sp^2 carbons α to the tin atom [98.6(8)° and 87(2)° for Sn(1)–C(1)–

Table II. Selected Bond Lengths, Bond Angles, and Torsion Angles for 26, 27, and 31

A. Bond Lengths (Å)

26a		**26b**	
Sn(1)–S(1)	2.434(3)	Sn(1)–Se(1)	2.561(1)
Sn(1)–S(2)	2.432(3)	Sn(1)–Se(2)	2.562(1)
Sn(1)–C(1)	2.19(1)	Sn(1)–C(1)	2.192(9)
Sn(1)–C(2)	2.18(1)	Sn(1)–C(2)	2.18(1)
27a		**27b**	
Sn(1)–S(1)	2.438(2)	Sn(1)–Se(1)	2.586(1)
Sn(1)–S(2)	2.463(2)	Sn(1)–Se(2)	2.557(1)
Sn(1)–C(1)	2.192(8)	Sn(1)–C(1)	2.188(7)
Sn(1)–C(2)	2.185(9)	Sn(1)–C(2)	2.173(8)
31			
Sn(1)–Se(1)	2.559(3)	Sn(1)–C(1)	2.19(2)
Sn(1)–Se(2)	2.573(2)	Sn(1)–C(2)	2.19(2)
Sn(2)–Se(1)	2.570(2)	Sn(2)–C(3)	2.20(2)
Sn(2)–Se(2)	2.565(3)	Sn(2)–C(4)	2.22(2)

B. Bond Angles (deg)

26a		**26b**	
Sn(1)–S(1)–Sn(2)	89.1(1)	Sn(1)–Se(1)–Sn(2)	88.32(5)
Sn(1)–S(2)–Sn(2)	89.2(1)	Sn(1)–Se(2)–Sn(2)	88.28(5)
S(1)–Sn(1)–S(2)	90.84(9)	Se(1)–Sn(1)–Se(2)	91.70(4)
C(1)–Sn(1)–S(1)	118.6(3)	C(1)–Sn(1)–Se(1)	113.4(2)
C(1)–Sn(1)–S(2)	112.3(3)	C(1)–Sn(1)–Se(2)	119.2(2)
C(2)–Sn(1)–S(1)	105.2(3)	C(2)–Sn(1)–Se(1)	113.4(3)
C(2)–Sn(1)–S(2)	113.6(3)	C(2)–Sn(1)–Se(2)	104.0(3)
C(1)–Sn(1)–C(2)	114.1(4)	C(1)–Sn(1)–C(2)	113.3(3)
27a		**27b**	
Sn(1)–S(1)–Sn(2)	84.34(6)	Sn(1)–Se(1)–Sn(2)	82.88(3)
S(1)–Sn(1)–S(2)	88.33(7)	Se(1)–Sn(1)–Se(2)	89.08(3)
C(1)–Sn(1)–S(1)	116.1(2)	C(1)–Sn(1)–Se(1)	118.8(2)
C(1)–Sn(1)–S(2)	119.1(2)	C(1)–Sn(1)–Se(2)	114.9(2)
C(2)–Sn(1)–S(1)	110.6(2)	C(2)–Sn(1)–Se(1)	105.8(2)
C(2)–Sn(1)–S(2)	105.6(2)	C(2)–Sn(1)–Se(2)	111.3(2)
C(1)–Sn(1)–C(2)	114.2(3)	C(1)–Sn(1)–C(2)	114.3(3)
31			
Sn(1)–Se(1)–Sn(2)	89.47(7)	C(2)–Sn(1)–Se(2)	104.4(5)
Sn(1)–Se(2)–Sn(2)	89.26(8)	C(1)–Sn(1)–C(2)	125.8(6)
Se(1)–Sn(1)–Se(2)	90.31(8)	C(3)–Sn(2)–Se(1)	108.1(5)
Se(1)–Sn(2)–Se(2)	90.26(8)	C(3)–Sn(2)–Se(2)	122.5(7)
C(1)–Sn(1)–Se(1)	107.2(5)	C(4)–Sn(2)–Se(1)	119.4(6)
C(1)–Sn(1)–Se(2)	113.7(5)	C(4)–Sn(2)–Se(2)	104.9(5)
C(2)–Sn(1)–Se(1)	109.8(5)	C(3)–Sn(2)–C(4)	111.1(7)

C. Torsion Angles (deg)

26a		**26b**	
C(1)–Sn(1)–S(1)–Sn(2)	−116.2(3)	C(1)–Sn(1)–Se(1)–Sn(2)	−122.9(3)
C(1)–Sn(1)–S(2)–Sn(2)	121.6(3)	C(1)–Sn(1)–Se(2)–Sn(2)	118.1(3)
C(2)–Sn(1)–S(1)–Sn(2)	114.8(3)	C(2)–Sn(1)–Se(1)–Sn(2)	106.0(3)
C(2)–Sn(1)–S(2)–Sn(2)	−107.1(3)	C(2)–Sn(1)–Se(2)–Sn(2)	−114.7(3)
Sn(1)–S(1)–Sn(2)–S(2)	0.00(7)	Sn(1)–Se(1)–Sn(2)–Se(2)	−0.00(3)
S(1)–Sn(2)–S(2)–Sn(1)	−0.00(7)	Se(1)–Sn(2)–Se(2)–Sn(1)	0.00(3)
Sn(2)–S(2)–Sn(1)–S(1)	0.00(7)	Sn(2)–Se(2)–Sn(1)–Se(1)	0.00(3)
S(2)–Sn(1)–S(1)–Sn(2)	−0.00(7)	Se(2)–Sn(1)–Se(1)–Sn(2)	−0.00(3)
27a		**27b**	
C(1)–Sn(1)–S(1)–Sn(2)	150.1(2)	C(1)–Sn(1)–Se(1)–Sn(2)	−148.0(2)
C(1)–Sn(1)–S(2)–Sn(2)	−147.7(2)	C(1)–Sn(1)–Se(2)–Sn(2)	151.0(2)
C(2)–Sn(1)–S(1)–Sn(2)	−77.8(3)	C(2)–Sn(1)–Se(1)–Sn(2)	82.0(2)
C(2)–Sn(1)–S(2)–Sn(2)	82.4(3)	C(2)–Sn(1)–Se(2)–Sn(2)	−77.1(2)
Sn(1)–S(1)–Sn(2)–S(2)	−28.55(7)	Sn(1)–Se(1)–Sn(2)–Se(2)	29.49(3)
S(1)–Sn(2)–S(2)–Sn(1)	28.24(7)	Se(1)–Sn(2)–Se(2)–Sn(1)	−29.86(3)
Sn(2)–S(2)–Sn(1)–S(1)	−28.55(7)	Sn(2)–Se(2)–Sn(1)–Se(1)	29.49(3)
S(2)–Sn(1)–S(1)–Sn(2)	28.24(6)	Se(2)–Sn(1)–Se(1)–Sn(2)	−29.86(3)
31			
C(1)–Sn(1)–Se(1)–Sn(2)	−108.6(5)	C(4)–Sn(2)–Se(1)–Sn(1)	100.9(6)
C(1)–Sn(1)–Se(2)–Sn(2)	102.6(5)	C(4)–Sn(2)–Se(2)–Sn(1)	−114.3(6)
C(2)–Sn(1)–Se(1)–Sn(2)	111.7(5)	Sn(1)–Se(1)–Sn(2)–Se(2)	−6.36(7)
C(2)–Sn(1)–Se(2)–Sn(2)	−116.9(5)	Se(1)–Sn(2)–Se(2)–Sn(1)	6.33(7)
C(3)–Sn(2)–Se(1)–Sn(1)	−130.9(7)	Sn(2)–Se(2)–Sn(1)–Se(1)	−6.36(7)
C(3)–Sn(2)–Se(2)–Sn(1)	118.1(6)	Se(2)–Sn(1)–Se(1)–Sn(2)	6.34(7)

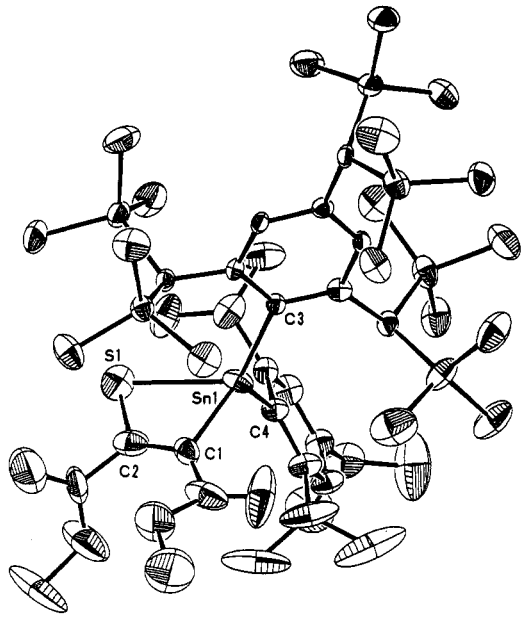


Figure 6. ORTEP drawing of 1,2-thiastannete (8) with thermal ellipsoid plot (30% probability).

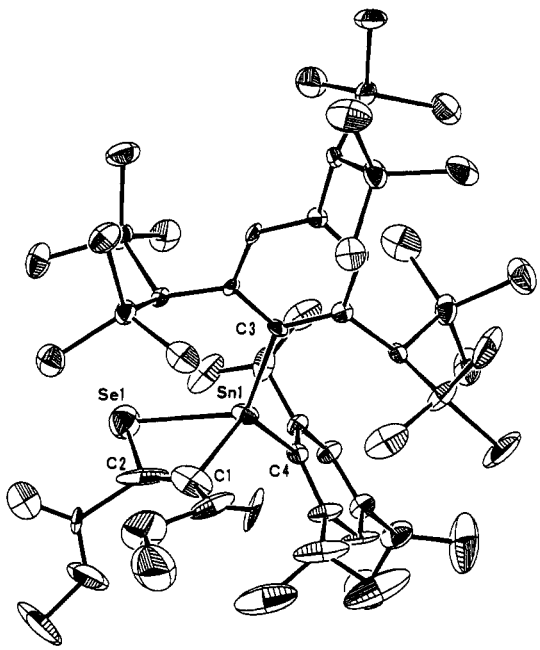


Figure 7. ORTEP drawing of 1,2-selenastannete (14) with thermal ellipsoid plot (30% probability).

C(2) of 8 and 14, respectively], reflecting the coexistence of long tin–chalcogen bonds and short carbon–carbon double bonds [Sn(1)–S(1) 2.651 Å, C(1)–C(2) 1.33 Å for 8 and Sn(1)–Se(1) 2.746 Å, C(1)–C(2) 1.33 Å for 14]. As for the bond length and angle around the chalcogen atoms, thiastannete 8 showed values [1.73(1) Å for S(1)–C(2) and 73.1(4)° for Sn(1)–S(1)–C(2)] quite similar to those of the previously reported carbon analog, i.e., thiete derivative (1.788 Å for S–C and 74.2° for C–S–C).[22] Recently, Sita et al.[23] and Weidenbruch et al.[24] have described the X-ray structure analysis of two different types of sterically congested 1,2-distannetes, where the corner angles at sp^2 carbons were reportedly between 107.6(5)° and 111.6(4)°. Furthermore, in contrast to the flat structure of the thiete ring system, the carbon analog, the four-membered rings of 8 and 14 were not planar, and the dihedral angles between the planes S(1)–C(1)–C(2) and S(1)–C(1)–Sn(1) of 8 and between the planes Se(1)–C(1)–C(2) and Se(1)–C(1)–Sn(1) of 14 are 7.3° and 10.7°, respectively.

(22) Verhoeckx, G. J.; Kroon, J.; Brouwer, A. C.; Bos, H. J. T. *Acta Crystallogr. B.* **1980**, *36*, 484.
(23) Sita, L. R.; Kinoshita, I.; Lee, S. P. *Organometallics* **1990**, *9*, 1644.
(24) Weidenbruch, M.; Schäfer, A.; Kilian, H.; Pohl, S.; Saak, W.; Marsmann, H. *Chem. Ber.* **1992**, *125*, 563.

Table III. Selected Bond Lengths, Bond Angles, and Torsion Angles for 8 and 14

8		14	
	A. Bond Lengths (Å)		
Sn(1)–S(1)	2.651(4)	Sn(1)–Se(1)	2.746(3)
Sn(1)–C(1)	2.17(1)	Sn(1)–C(1)	2.30(2)
S(1)–C(1)	1.73(1)	Se(1)–C(1)	2.00(2)
C(1)–C(2)	1.33(1)	C(1)–C(2)	1.33(3)
Sn(1)–C(3)	2.166(7)	Sn(1)–C(3)	2.17(1)
Sn(1)–C(4)	2.164(7)	Sn(1)–C(4)	2.19(1)
	B. Bond Angles (deg)		
S(1)–Sn(1)–C(1)	66.5(3)	Se(1)–Sn(1)–C(1)	74.3(7)
Sn(1)–S(1)–C(2)	73.1(4)	Sn(1)–Se(1)–C(2)	64.3(7)
S(1)–C(2)–C(1)	121(1)	Se(1)–C(2)–C(1)	134(2)
Sn(1)–C(1)–C(2)	98.6(8)	Sn(1)–C(1)–C(2)	87(2)
C(3)–Sn(1)–C(4)	122.9(3)	C(3)–Sn(1)–C(4)	121.3(5)
C(3)–Sn(1)–S(1)	119.1(2)	C(3)–Sn(1)–Se(1)	120.2(4)
C(3)–Sn(1)–C(1)	116.9(3)	C(3)–Sn(1)–C(1)	113.3(6)
C(4)–Sn(1)–S(1)	99.2(2)	C(4)–Sn(1)–Se(1)	92.2(4)
C(4)–Sn(1)–C(1)	116.4(3)	C(4)–Sn(1)–C(1)	118.4(6)
	C. Torsion Angles (deg)		
Sn(1)–C(1)–C(2)–S(1)	−6.7(9)	Sn(1)–C(1)–C(2)–Se(1)	−9(2)
C(1)–C(2)–S(1)–Sn(1)	5.7(8)	C(1)–C(2)–Se(1)–Sn(1)	9(2)
C(2)–S(1)–Sn(1)–C(1)	−3.2(4)	C(2)–Se(1)–Sn(1)–C(1)	−3.7(7)
S(1)–Sn(1)–C(1)–C(2)	4.1(6)	S(1)–Sn(1)–C(1)–C(2)	5(1)
C(3)–Sn(1)–S(1)–C(2)	−112.1(4)	C(3)–Sn(1)–Se(1)–C(2)	−111.9(7)
C(3)–Sn(1)–C(1)–C(2)	116.0(6)	C(3)–Sn(1)–C(1)–C(2)	122(1)
C(4)–Sn(1)–S(1)–C(2)	111.5(4)	C(4)–Sn(1)–Se(1)–C(2)	113.4(6)
C(4)–Sn(1)–C(1)–C(2)	−85.1(7)	C(4)–Sn(1)–C(1)–C(2)	−87(1)

Experimental Section

General Procedure. All melting points were uncorrected. All solvents used in the reactions were purified by the reported methods. THF was purified by distillation from benzophenone ketyl before use. All reactions were carried out under argon atmosphere unless otherwise noted. Preparative gel permeation liquid chromatography (GPLC) was performed by LC-908 with a JAI gel 1H and 2H columns (Japan Analytical Industry, styrene–divinylbenzene copolymer, pore size 25 Å) with chloroform as solvent. Dry column chromatography (DCC) was performed with ISN silica DCC 60A. Flash column chromatography (FCC) was carried out with Fuji Davison BW-300. Preparative thin-layer chromatography was carried out with Merck Kieselgel 60 PF254 Art. 7747. The ^{1}H NMR (500 and 400 MHz) and ^{13}C NMR spectra (125 and 100 MHz) were measured in $CDCl_3$ or $C_6D_5CD_3$ with Brucker AM-500 and JEOL GX-400 spectrometers using $CHCl_3$ or $C_6H_5CH_3$ as an internal standard.

Reaction of Tetrathiastannolane 3a with Diphenyldiazomethane. A benzene solution (15 mL) of tetrathiastannolane **3a**[13d] (468 mg, 0.47 mmol) and diphenyldiazomethane (906 mg, 4.67 mmol) was refluxed for 10 h. After removal of the solvent, the residue was separated with DCC and PTLC (hexane) to afford 3-{2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}-3-(2,4,6-triisopropylphenyl)-6,6-diphenyl-1,2,4,5-tetrathia-3-stannacyclohexane (4) (152 mg, 27%), 4-{2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}-4-(2,4,6-triisopropylphenyl)-6,6-diphenyl-1,2,3,5-tetrathia-4-stannacyclohexane (5) (129 mg, 23%), and 3-{2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}-3-(2,4,6-triisopropylphenyl)-5,5-diphenyl-1,2,4,3-trithiastannolane (1a) (44 mg, 8%), all as white crystals, which were recrystallized from ethanol–chloroform. 4: mp 183–185 °C; ^{1}H NMR ($CDCl_3$) δ −0.04 (br s, 18H), −0.02 (br s, 18H), 0.02 (s, 18H), 1.14 (br s, 6H), 1.18 (d, J = 6.9 Hz, 6H), 1.25 (br s, 6H), 1.29 (s, 1H), 1.85 (br s, 1H), 1.86 (br s, 1H), 2.81 (sept, J = 6.9 Hz, 1H), 2.99 (br s, 2H), 6.37 (s, 1H), 6.48 (s, 1H), 7.00 (s, 2H), 7.23–7.60 (m, 10H); ^{13}C NMR ($CDCl_3$) δ 0.85 (q), 1.55 (q), 1.83 (q), 23.86 (q), 25.97 (q), 30.60 (d), 32.14 (d), 32.68 (d), 34.24 (d), 38.78 (d), 77.92 (s), 122.77 (d), 122.92 (d), 127.97 (d), 128.04 (d), 128.13 (d), 128.25 (d), 140.31 (s), 140.63 (s), 141.19

(s), 141.48 (s), 144.98 (s), 150.71 (s), 150.92 (s), 151.25 (s), 154.56 (s). Anal. Calcd for $C_{55}H_{92}S_4Si_6Sn$: C, 56.52; H, 7.93; S, 10.97. Found: C, 56.76; H, 7.82; S, 10.62. **5**: mp 222 °C dec; ^{1}H NMR (toluene-d_8 at 77 °C) δ 0.10 (s, 18H), 0.13 (s, 18H), 0.19 (s, 18H), 1.01 (br s, 6H), 1.27 (d, J = 6.9 Hz, 6H), 1.41 (s, 1H), 1.42 (br s, 6H), 2.54 (br s, 2H), 2.82 (sept, J = 6.9 Hz, 1H), 2.93 (br s, 1H), 4.28 (br s, 1H), 6.56 (br s, 2H), 6.70–7.52 (m, 10H), 7.10 (br s, 2H); ^{13}C NMR ($CDCl_3$) δ 0.77 (q), 1.04 (q), 1.66 (q), 1.72 (q), 1.98 (q), 23.93 (q), 24.24 (q), 25.75 (q), 25.95 (q), 26.29 (q), 30.48 (d), 31.15 (d), 31.81 (d), 34.39 (d), 34.60 (d), 38.16 (d), 74.25 (s), 123.40 (d), 123.91 (d), 127.03 (d), 127.32 (dx2), 127.83 (d), 127.98 (d), 128.24 (dx2), 131.43 (d), 139.33 (s), 141.24 (s), 141.45 (s) 144.72 (s), 147.56 (s), 150.27 (s), 150.88 (s), 151.11 (s), 153.80 (s), 155.27 (s). Anal. Calcd for $C_{55}H_{92}S_4Si_6Sn$: C, 56.52; H, 7.93; S, 10.97. Found: C, 56.43; H, 7.86; S, 11.26. **1a**: mp 150 °C dec; ^{1}H NMR ($CDCl_3$) δ –0.09 (s, 9H), –0.07 (s, 9H), 0.04 (s, 9H), 0.05 (s, 18H), 0.07 (s, 9H), 0.89 (br s, 6H), 1.16 (br s, 6H), 1.18 (d, J = 6.9 Hz, 6H), 1.31 (s, 1H), 1.89 (s, 1H), 1.95 (s, 1H), 2.81 (sept, J = 6.9 Hz, 1H), 3.02 (br s, 2H), 6.38 (s, 1H), 6.50 (s, 1H), 6.96 (s, 2H), 7.09–7.69 (m, 10H); ^{13}C NMR ($CDCl_3$) δ 0.89 (q), 1.01 (q), 1.55 (q), 1.57 (q), 1.75 (q), 1.79 (q), 23.81 (q), 30.63 (d), 31.37 (d), 31.91 (d), 34.20 (d), 38.41 (d), 81.40 (s), 122.97 (d), 123.20 (d), 126.77 (d), 127.44 (d), 127.70 (d), 127.78 (d), 128.45 (d), 129.14 (d), 129.50 (d), 140.57 (s), 143.32 (s), 144.03 (s), 144.86 (s), 144.89 (s), 150.28 (s), 151.12 (s), 151.39 (s), 153.71 (s). Anal. Calcd for $C_{55}H_{92}S_3Si_6Sn$: C, 58.11; H, 8.16; S, 8.46. Found: C, 57.86; H, 7.94; S, 8.35.

Reaction of Tetraselenastannolane 3b with Diphenyldiazomethane. A benzene solution (30 mL) of tetraselenastannolane **3b**[13d] (271 mg, 0.23 mmol) and diphenyldiazomethane (560 mg, 2.9 mmol) was heated at reflux for 10 h. After the solvent was evaporated, the residue was chromatographed (FCC, 10% dichloromethane/hexane) to afford 3-{2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}-3-(2,4,6-triisopropylphenyl)-6,6-diphenyl-1,2,4,5-tetraselena-3-stannacyclohexane (**6**) (273 mg, 88%) and 3-{2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}-3-(2,4,6-triisopropylphenyl)-5,5-diphenyl-1,2,4,3-triselenastannolane (**1b**) (34 mg, 11%) as yellow crystals, respectively, which were recrystallized from ethanol–chloroform. **6**: mp 183–185 °C; ^{1}H NMR ($CDCl_3$ at 57 °C) δ 0.01 (s, 36H), 0.05 (s, 18H), 1.200 (br s, 6H), 1.201 (d, J = 6.9 Hz, 6H), 1.231 (br s, 6H), 1.32 (s, 1H), 1.94 (br s, 2H), 2.82 (sept, J = 6.9 Hz, 1H), 3.36 (br s, 2H), 6.40 (br s, 1H), 6.49 (br s, 1H), 7.00 (s, 2H), 7.22–7.69 (m, 10H); ^{13}C NMR ($CDCl_3$) δ 0.86 (q), 1.91 (q), 2.25 (q), 23.87 (q), 25.88 (q), 30.54 (d), 32.03 (d), 32.53 (d), 34.23 (d), 38.66 (d), 61.59 (s), 122.70 (d), 122.99 (d), 128.05 (d), 128.21 (d), 128.22 (d), 128.25 (d), 128.29 (d), 138.52 (s), 140.62 (s), 142.68 (s), 142.87 (s), 144.58 (s), 150.36 (s), 150.84 (s), 151.17 (s), 154.19 (s). Anal. Calcd for $C_{55}H_{92}Se_4Si_6Sn$: C, 48.70; H, 6.84; Se, 23.29. Found: C, 48.78; H, 6.73; Se, 23.15. **1b**: mp 209 °C dec; ^{1}H NMR ($CDCl_3$) δ –0.05 (s, 9H), –0.04 (s, 9 H), 0.06 (s, 18H), 0.08 (s, 9H), 0.11 (s, 9H), 0.86 (br s, 6H), 1.19 (d, J = 6.9 Hz, 6H), 1.20 (br s, 6H), 1.32 (s, 1H), 1.96 (s, 1H), 2.05 (s, 1H), 2.81 (sept, J = 6.9 Hz, 1H), 3.39 (br s, 2H), 6.39 (s, 1H), 6.51 (s, 1H), 6.97 (s, 2H), 7.18–7.78 (m, 10H); ^{13}C NMR ($CDCl_3$) δ 0.88 (q), 1.04 (q), 1.80 (q), 1.84 (q), 2.03 (q), 23.79 (q), 23.93 (q), 30.57 (d), 31.39 (d), 32.01 (d), 34.18 (d), 38.02 (d), 70.49 (s), 123.07 (d), 123.19 (d), 126.89 (d), 127.41 (d), 127.74 (d), 127.84 (d), 128.52 (d), 129.53 (d), 130.46 (d), 140.83 (s), 143.99 (s), 144.54 (s), 144.88 (s), 145.23 (s), 149.88 (s), 150.97 (s), 151.29 (s), 153.53 (s). Anal. Calcd for $C_{55}H_{92}Se_3Si_5Sn$: C, 51.71; H, 7.26; Se, 18.54. Found: C, 51.30; H, 7.01; Se, 18.01.

Desulfurization of 1,2,3,5-Tetrathia-4-stannacyclohexane 5 with Hexamethylphosphoric Triamide (HMPT). To a THF solution (5 mL) of **5** (100 mg, 0.86 mmol) was added HMPT (85% purity, 18 μL, 0.86 mmol) at room temperature, and the mixture was stirred at ambient temperature for 10 h. After removal of the solvent, the residue was separated with GPLC to afford a monomeric fraction containing Tb and Tip substituents (80 mg) (by NMR) which was further purified by PTLC (hexane) to afford trithiastannolane (**1a**) (34 mg, 35%) and 2-{2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}-2-(2,4,6-triisopropylphenyl)-4,4-diphenyl-1,3,2-dithiastannetane (**7**) (25 mg, 26%) as white crystals. **5** (12 mg, 12%) was recovered, **7** was recrystallized from ethanol–chloroform. **7**: mp 215–217 °C; ^{1}H NMR ($CDCl_3$) δ –0.069 (s, 18H), –0.066 (s, 18H), 0.03 (s, 18H), 1.06 (br s, 12H), 1.24 (d, J = 6.9 Hz, 6H), 1.31 (s, 1H), 2.55 (s, 1H), 2.66 (s, 1H), 2.89 (sept, J = 6.9 Hz, 1H), 2.90 (br s, 2H), 6.36 (s, 1H), 6.47 (s, 1H), 6.97 (s, 2H), 6.95–7.70 (m, 10H); ^{13}C NMR ($CDCl_3$) δ 0.94 (q), 1.06 (q), 1.29 (q), 23.95 (q), 25.20 (q), 30.42 (q), 30.72 (d), 30.80 (d), 34.29 (d), 38.50 (d), 61.92 (s), 122.73 (d), 123.42 (d), 125.45 (d), 125.76 (d), 126.16 (d), 127.08 (d), 127.35 (d), 127.44 (d), 128.61 (d), 137.15 (s), 142.62 (s), 145.29 (s), 150.70 (s), 151.70 (s), 151.78 (s), 151.82 (s), 152.25 (s), 153.58 (s). Anal. Calcd for $C_{55}H_{92}S_2Si_6Sn$: C, 59.80; H, 8.39; S, 5.81. Found: C, 59.62; H, 8.32; S, 5.99.

Deselenation of 1,2,4,5-Tetraselena-3-stannacyclohexane 6 with HMPT. A THF solution (10 mL) of **6** (180 mg, 0.13 mmol) and HMPT (85% purity, 84 μL, 0.39 mmol) was stirred at room temperature for 10 h. After removal of the solvent, the residue was chromatographed (DCC, hexane) to afford **1b** (108 mg, 63%).

Thermolysis of Trichalcogenastannolanes 1a,b in the Presence of Dimethyl Acetylenedicarboxylate (DMAD). (a) A toluene solution (3 mL) of **1a** (286 mg, 0.25 mmol) and DMAD (310 μL, 2.5 mmol) was heated at 120 °C for 6 h in a degassed sealed tube. After removal of the solvent, the residue was chromatographed (GPLC) to afford a fraction containing a Tb substituent (328 mg) and a fraction containing a diphenyl moiety (73 mg). The former fraction was purified was FCC followed by PTLC (20% ether/hexane) to afford 2-{2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}-2-(2,4,6-triisopropylphenyl)-3,4-bis(methoxycarbonyl)-1,2-thiastannete (**8**) (78 mg, 29%), 2-{2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}-2-(2,4,6-triisopropylphenyl)-4,5-bis(methoxycarbonyl)-1,3,2-dithiastannolene (**9**) (33 mg, 12%), 2-{2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}-2-(2,4,6-triisopropylphenyl)-3,4,5,6-tetrakis(methoxycarbonyl)-1,2-thiastannanacyclohexa-3,5-diene (**10**) (26 mg, 9%), and 2-{2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}-2-(2,4,6-triisopropylphenyl)-3-(methoxycarbonyl)-1,2-thiastannolen-5-one (**11**) (27 mg, 10%). The latter fraction was purified with PTLC (10% ethyl acetate/hexane) to provide dimethyl 1-phenyl-1*H*-2-benzothiopyran-3,4-dicarboxylate (**12**) (11 mg, 12%) and dimethyl 3,3-diphenyl-3*H*-1,2-dithiole-4,5-dicarboxylate (**13**) (36 mg, 39%). **8** and **9** were recyrstallized from ethanol–chloroform, and **10** and **11** from acetonitrile–dichloromethane. **8**: slightly yellow crystals; mp 173–175 °C; ^{1}H NMR ($CDCl_3$ at 57 °C) δ –0.04 (br s, 18H), 0.058 (s, 9H), 0.062 (s, 9H), 0.08 (br s, 18H), 1.22 (d, J = 6.3 Hz, 6H), 1.23 (d, J = 6.9 Hz, 6H), 1.31 (d, J = 6.1 Hz, 6H), 1.36 (s, 1H), 1.96 (br s, 1H), 2.21 (br s, 1H), 2.862 (br s, 2H), 2.868 (sept, J = 6.9 Hz, 1H), 3.62 (s, 3H), 3.76 (s, 3H), 6.41 (br s, 1H), 6.53 (br s, 1H), 7.06 (s, 2H); ^{13}C NMR ($CDCl_3$ at 57 °C) δ 0.90 (q), 1.02 (br q), 1.24 (q), 23.91 (q), 25.69 (br q), 30.98 (d), 32.72 (br d), 32.95 (br d), 34.44 (d), 39.90 (d), 51.21 (q), 52.25 (q), 122.64 (d), 123.02 (br d), 128.12 (br d), 132.64 (s), 137.42 (s), 141.37 (s), 146.03 (s), 151.68 (s), 151.89 (s), 152.23 (br s), 154.23 (s), 159.35 (s), 163.24 (s), 166.25 (s). Anal. Calcd for $C_{48}H_{88}O_4SSi_6Sn$: C, 54.98; H, 8.46; S, 3.06. Found: C, 54.69; H, 8.21; S, 3.49. **9**: slightly yellow crystals; mp 157–159 °C; ^{1}H NMR ($CDCl_3$) δ –0.02 (s, 18H), 0.02 (s, 18H), 0.03 (s, 18H), 1.20 (d, J = 6.8 Hz, 6H), 1.27 (d, J = 6.4 Hz, 12H), 1.32 (s, 1H), 1.96 (s, 1H), 2.19 (s, 1H), 2.84 (sept, J = 6.4 Hz, 1H), 2.91 (sept, J = 6.4 Hz, 2H), 3.76 (s, 6H), 6.33 (s, 1H), 6.48 (s, 1H), 7.01 (s, 2H); ^{13}C NMR ($CDCl_3$) δ 0.83 (q), 1.20 (q), 1.39 (q), 23.91 (q), 26.35 (q), 30.68 (d), 31.86 (d), 32.30 (d), 34.35 (d), 39.31 (d), 52.84 (q), 122.61 (d), 122.90 (d), 127.95 (d), 133.87 (s), 138.28 (s), 143.74 (s), 145.96 (s), 150.96 (s), 151.32 (s), 151.47 (s), 152.76 (s), 166.12 (s). Anal. Calcd for $C_{48}H_{88}O_4S_2Si_6Sn$: C, 53.35; H, 8.21; S, 5.93. Found: C, 53.18; H, 7.92; S, 6.18. **10**: yellow crystals; mp 195–197 °C; ^{1}H NMR ($CDCl_3$) δ –0.19 (s, 9H), –0.16 (s, 9H), 0.01 (s, 9H), 0.02 (s, 9H), 0.05 (s, 9H), 0.06 (s, 9H), 1.15 (d, J = 6.4 Hz, 3H), 1.22 (d, J = 6.9 Hz, 6H), 1.29 (d, J = 6.4 Hz, 3H), 1.31 (s, 1H), 1.43 (d, J = 6.4 Hz, 3H), 1.46 (d, J = 6.4 Hz, 3H), 1.69 (br s, 1H), 1.85 (br s, 1H), 2.56 (sept, J = 6.4 Hz, 1H), 2.857 (s, 3H), 2.867 (sept, J = 6.9 Hz, 1H), 3.19 (sept, J = 6.4 Hz, 1H), 3.65 (s, 3H), 3.77 (s, 3H), 3.90 (s, 3H), 6.33 (s, 1H), 6.45 (s, 1H), 7.03 (s, 1H), 7.09 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 0.75 (q), 0.84 (q), 0.90 (q), 1.02 (q), 1.14 (q), 23.22 (q), 23.24 (q), 23.85 (q), 23.98 (q), 27.63 (q), 27.78 (q), 30.35

(d), 30.84 (d), 38.77 (d), 40.47 (d), 111.98 (s), 121.22 (s), 122.67(d), 122.82 (d), 123.26 (d), 128.30 (d), 129.00 (s), 138.67 (s), 143.61 (s), 146.35 (s), 148.77 (s), 151.16 (s), 151.55 (s), 151.60 (s), 152.64 (s), 153.33 (s), 161.62 (s), 162.43 (s), 166.05 (s), 175.22 (s). Anal. Calcd for $C_{54}H_{94}O_8SSi_6Sn\cdot H_2O$: C, 53.66; H, 8.01; S, 2.65. Found: C, 53.60; H, 7.57; S, 2.88. **11**: white crystals; mp 190–192 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ –0.05 (s, 9H), –0.02 (s, 9H), 0.01 (s, 9H), 0.04 (s, 27H), 1.20 (d, J = 7.0 Hz, 6H), 1.26 (br s, 6H), 1.29 (d, J = 6.7 Hz, 6H), 1.35 (s, 1H), 1.63 (s, 1H), 1.81 (s, 1H), 2.85 (sept, J = 7.0 Hz, 1H), 2.81 (br s, 2H), 2.86 (sept, J = 7.0 Hz, 1H), 3.75 (s, 3H), 6.37 (s, 1H), 6.51 (s, 1H), 7.06 (s, 2H), 7.25 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 0.52 (q), 0.71 (q), 0.82 (q), 0.99 (q), 1.22 (q), 23.83 (q), 23.87 (q), 25.80 (br q), 30.95 (d), 33.04 (d), 33.15 (d), 34.37 (d), 39.42 (d), 51.49 (q), 122.48 (d), 122.75 (d), 123.18 (d), 127.59 (s), 136.05 (s), 140.36 (s), 146.83 (s), 147.31 (s), 151.23 (s), 151.59 (s), 152.54 (s), 153.83 (s), 166.64 (s), 166.98 (s). Anal. Calcd for $C_{47}H_{86}O_3SSi_6Sn\cdot H_2O$: C, 54.46; H, 8.56; S, 3.09. Found: C, 54.43; H, 8.24; S, 3.17. (b) A toluene solution (3 mL) of **1b** (300 mg, 0.24 mmol) and DMAD (289 μL, 2.4 mmol) was heated at 120 °C for 6 h in a degassed sealed tube. After removal of the solvent, the residue was chromatographed (GPLC) to afford a fraction containing a Tb substituent (460 mg) and a fraction containing a diphenyl moiety (39 mg). The former fraction was purified with PTLC (20% ether/hexane) to afford 2-{2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}-2-(2,4,6-triisopropylphenyl)-3,4-bis(methoxycarbonyl)-1,2-selenastannete (**14**) (62 mg, 24%), 2-{2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}-2-(2,4,6-triisopropylphenyl)-4,5-bis(methoxycarbonyl)-1,3,2-diselenastannolene (**15**) (28 mg, 10%), 2-{2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}-2-(2,4,6-triisopropylphenyl)-3-(methoxycarbonyl)-1,2-selenastannolen-5-one (**16**) (20 mg, 8%), and **3b** (76 mg, 27%). The latter fraction was purified with PTLC (30% ethyl acetate/hexane) to provide dimethyl 1-phenyl-1*H*-2-benzoselenopyran-3,4-dicarboxylate (**17**) (14 mg, 16%). **14** and **15** were recrystallized from ethanol–chloroform and **16** from acetonitrile–dichloromethane. **14**: slightly orange crystals; mp 165–167 °C; ^{1}H NMR ($CDCl_3$ at 57 °C) δ –0.01 (br s, 18H), 0.058 (s, 9H), 0.062 (s, 9H), 0.08 (br s, 18H), 1.22 (d, J = 6.4 Hz, 6H), 1.23 (d, J = 6.9 Hz, 6H), 1.29 (d, J = 6.2 Hz, 6H), 1.35 (s, 1H), 2.08 (br s, 1H), 2.36 (br s, 1H), 2.87 (sept, J = 6.9 Hz, 1H), 2.92 (br s, 2H), 3.61 (s, 3H), 3.74 (s, 3H), 6.40 (br s, 1H), 6.53 (br s, 1H), 7.05 (s, 2H); ^{13}C NMR ($CDCl_3$ at 57 °C) δ 0.90 (q), 1.11 (br q), 1.31 (q), 23.91 (q), 25.68 (br q), 30.91 (d), 32.62 (br d), 32.93 (br d), 34.39 (d), 39.85 (d), 51.34 (q), 52.26 (q), 122.55 (d), 123.03 (br d), 128.11 (br d), 136.06 (s), 141.28 (s), 141.92 (s), 145.72 (s), 150.19 (s), 151.46 (s), 151.86 (br s), 152.28 (s), 154.10 (s), 164.41 (s), 165.73 (s). Anal. Calcd for $C_{48}H_{88}O_4SeSi_6Sn$: C, 52.63; H, 8.10; Se, 7.21. Found: C, 52.42; H, 7.97; Se, 7.22. **15**: slightly orange crystals; mp 202–205 °C; ^{1}H NMR ($CDCl_3$) δ –0.02 (s, 18H), 0.03 (s, 36H), 1.20 (d, J = 6.9 Hz, 6H), 1.25 (d, J = 6.5 Hz, 12H), 1.31 (s, 1H), 2.06 (s, 1H), 2.31 (s, 1H), 2.84 (sept, J = 6.4 Hz, 1H), 2.96 (sept, J = 6.5 Hz, 2H), 3.75 (s, 6H), 6.31 (s, 1H), 6.47 (s, 1H), 7.00 (s, 2H); ^{13}C NMR ($CDCl_3$ at 57 °C, 400 MHz) δ 0.91 (q), 1.63 (br q), 23.87 (q), 26.11 (br q), 30.88 (d), 32.05 (d), 32.51 (d), 34.35 (d), 39.53 (d), 52.77 (q), 122.74 (d), 123.05 (d), 128.33 (d), 136.10 (s), 137.59 (s), 143.55 (s), 145.67 (s), 151.21 (s), 151.22 (br s), 152.82 (s), 166.88 (s). Anal. Calcd for $C_{48}H_{88}O_4Se_2Si_6Sn$: C, 49.09; H, 7.55; Se, 13.45. Found: C, 48.83; H, 7.47; Se, 13.39. **16**: white crystals; mp 177–180 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ –0.05 (s, 9H), –0.014 (s, 9H), –0.008 (s, 9H), 0.03 (s, 9H), 0.04 (s, 18H), 1.20 (d, J = 7 Hz, 6H), 1.261 (d, J = 6.4 Hz, 6H), 1.262 (br s, 6 H), 1.35 (s, 1H), 1.71 (s, 1H), 1.88 (s, 1H), 2.85 (sept, J = 7 Hz, 1H), 2.88 (br s, 2H), 3.77 (s, 3H), 6.35 (s, 1H), 6.49 (s, 1H), 7.05 (s, 2H), 7.57 (s, 1H); ^{13}C NMR ($CDCl_3$, 400 MHz) δ 0.67 (q), 0.83 (q), 0.86 (q), 0.93 (q), 1.18 (q), 1.41 (q), 23.94 (q), 24.00 (q), 25.93 (br q), 30.96 (d), 32.60 (d), 32.77 (d), 34.47 (d), 38.70 (d), 51.89 (q), 122.77 (d), 122.90 (d), 122.91 (s), 126.78 (d), 127.75 (d), 135.70 (s), 140.47 (s), 146.34 (s), 147.06 (s), 151.24 (s), 151.59 (s), 152.37 (s), 167.36 (s), 167.97 (s). Anal. Calcd for $C_{47}H_{86}O_3SeSi_6Sn$: C, 52.02; H, 7.99. Found: C, 52.30; H, 7.71. **17**: yellow oil; ^{1}H NMR ($CDCl_3$) δ 3.76 (s, 3H), 3.95 (s, 3H), 5.28 (s, 1H), 7.06–7.48 (m, 9H); ^{13}C NMR ($CDCl_3$) δ 41.94 (d), 52.82 (q), 52.91 (q), 123.83 (s), 127.33 (d), 127.47 (d), 127.67 (d), 127.80 (d), 128.12 (d), 128.70 (d), 131.05 (d), 132.11 (s), 133.20 (s), 138.98 (s), 139.93 (s), 165.10 (s), 168.36 (s); high-resolution MS m/z 388.0240, $C_{16}H_{14}O_4$ ^{80}Se requires 388.0213.

Desulfurization of 1,2,3,4,5-Tetrathiastannolane 2a with HMPT. To a THF solution (30 mL) of **2a** (504 mg, 0.55 mmol) was added HMPT (85% purity, 352 μL, 1.65 mmol) at room temperature, and the solution was stirred at room temperature for 10 h. After the solvent was evaporated, the residue was separated with DCC (hexane) to afford *trans*-3,5-dimesityl-3,5-bis{2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}-1,2,4,3,5-trithiadistannolane (**24**) (236 mg, 51%) and *cis*-3,5-dimesityl-3,5-bis{2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}-1,2,4,3,5-trithiadistannolane (**25**) (220 mg, 48%) as white crystals, both of which were recrystallized from ethanol–chloroform. **24**: mp >300 °C; ^{1}H NMR ($CDCl_3$ at 57 °C) δ –0.36 (s, 36H), 0.01 (s, 18H), 0.02 (s, 18H), 0.14 (s, 36H), 1.28 (s, 2H), 2.17 (s, 6H), 2.38 (br s, 2H), 2.51 (br s, 2H), 2.62 (br s, 12H), 6.29 (s, 2H), 6.40 (s, 2H), 6.71 (s, 4H); ^{13}C NMR ($CDCl_3$) δ 0.02 (q), 0.70 (q), 0.92 (q), 1.65 (q), 1.89 (q), 20.87 (q), 29.70 (q), 30.29 (d), 31.72 (d), 32.05 (d), 122.57 (d), 127.43 (d), 128.98 (d), 138.84 (s), 139.91 (s), 143.56 (s), 143.63 (s), 144.51 (s), 151.08 (s), 151.28 (s). Anal. Calcd for $C_{72}H_{140}S_3Si_{12}Sn_2\cdot 2H_2O$: C, 50.49; H, 8.48; S, 5.62. Found: C, 50.34; H, 8.12; S, 5.76. **25**: mp >300 °C; ^{1}H NMR ($CDCl_3$) δ –0.04 (s, 36H), –0.01 (s, 18H), 0.00 (s, 18H), 0.02 (s, 36H), 1.29 (s, 2H), 2.13 (s, 6H), 2.18 (s, 2H), 2.33 (s, 12H), 2.35 (s, 2H), 6.32 (s, 2H), 6.40 (br s, 4H), 6.44 (s, 2H); ^{13}C NMR ($CDCl_3$) δ 0.80 (q), 0.85 (q), 1.02 (q), 1.27 (q), 1.36 (q), 1.56 (q), 20.90 (q), 24.99 (q), 26.31 (q), 30.29 (d), 31.86 (d), 32.14 (d), 122.61 (d), 127.58 (d), 128.25 (d), 138.30 (s), 139.41 (s), 142.44 (s), 143.02 (s), 144.75 (s), 151.38 (s), 151.60 (s). Anal. Calcd for $C_{72}H_{140}S_3Si_{12}Sn_2$: C, 51.58; H, 8.41; S, 5.73. Found: C, 51.28; H, 8.34; S, 5.82.

Desulfurization of 2a with HMPT under Irradiation. A benzene solution (1 mL) of **2a** (100 mg, 0.11 mmol) and HMPT (85% purity, 200 μL, 1.10 mmol) in a Pyrex glass tube was irradiated by a high-pressure mercury lamp for 1.5 h under ice cooling. After removal of the solvent, the residue was separated with PTLC (hexane) to afford *trans*-2,4-dimesityl-2,4-bis{2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}-1,3,2,4-dithiadistannetane (**26a**) (35 mg, 39%) and *cis*-2,4-dimesityl-2,4-bis{2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}-1,3,2,4-dithiadistannetane (**27a**) (14 mg, 15%) as white crystals, both of which were recrystallized with ethanol–chloroform. **26a**: mp >300 °C; ^{1}H NMR ($CDCl_3$ at 57 °C) δ –0.06 (br s, 72H), 0.03 (s, 36H), 1.29 (s, 2H), 2.09 (br s, 2H), 2.20 (s, 6H), 2.29 (br s, 2H), 2.62 (s, 12H), 6.26 (br s, 2H), 6.37 (br s, 2H), 6.71 (s, 4H); ^{13}C NMR ($CDCl_3$ at 57 °C) δ 0.92 (q), 1.02 (q), 1.30 (q), 20.89 (q), 26.56 (q), 30.54 (d), 30.98 (br d × 2), 122.74 (br d), 127.64 (br d), 128.89 (d), 138.96 (d), 139.37 (s), 143.06 (s), 143.84 (s), 144.64 (s), 151.45 (br s), 151.82 (br s). Anal. Calcd for $C_{72}H_{140}S_2Si_{12}Sn_2$: C, 52.59; H, 8.58; S, 3.90. Found: C, 52.29; H, 8.46; S, 4.31. **27a**: mp >300 °C; ^{1}H NMR ($CDCl_3$) δ –0.03 (br s, 72H), 0.02 (s, 36H), 1.28 (s, 2H), 2.01 (br s, 2H), 2.09 (s, 2H), 2.17 (s, 6H), 2.33 (s, 12H), 6.24 (s, 2H), 6.38 (s, 2H), 6.48 (s, 4H); ^{13}C NMR ($CDCl_3$) δ 0.83 (q), 1.14 (q), 1.49 (q), 20.96 (q), 26.16 (q), 30.34 (d), 30.75 (d), 30.98 (d), 122.43 (d), 127.41 (d), 128.50 (d), 138.33 (s), 138.54 (s), 141.81 (s), 143.99 (s), 144.77 (s), 151.11 (s), 151.38 (s). Anal. Calcd for $C_{72}H_{140}S_2Si_{12}Sn_2$: C, 52.59; H, 8.58; S, 3.90. Found: C, 52.30; H, 8.42; S, 3.97.

Desulfurization of 1,2,4,3,5-Trithiadistannolanes 24 and 25 with HMPT under Irradiation. In the same procedure as above, **24** (44 mg, 0.026 mmol) and **25** (42 mg, 0.025 mmol) gave **26a** (22 mg, 52%) and **27a** (28 mg, 69%), respectively.

Deselenation of 1,2,3,4,5-Tetraselenastannolane 2b with HMPT. HMPT (85% purity, 29 μL, 0.14 mmol) was added to a THF solution (5 mL) of **2b** (50 mg, 0.045 mmol) at –78 °C, and the reaction mixture was stirred for 10 h, during which time it was warmed to room temperature. After removal of the solvent, the residue was chromatographed (DCC, hexane) to afford *trans*-2,4-dimesityl-2,4-bis{2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}-1,3,2,4-diselenadistannetane (**26b**) (11 mg, 29%) and *cis*-2,4-dimesityl-2,4-bis{2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}-1,3,2,4-diselenadistannetane (**27b**) (10 mg, 25%) as white crystals, both of which were recrystallized with ethanol–chloroform. **26b**: mp >300 °C; ^{1}H NMR ($CDCl_3$) δ –0.09 (br s, 36H), –0.06

(s, 36H), 0.01 (s, 36H), 1.26 (s, 2H), 2.08 (br s, 2H), 2.21 (s, 6H), 2.39 (br s, 2H), 2.62 (s, 12H), 6.20 (s, 2H), 6.32 (s, 2H), 6.70 (s, 4H); ^{13}C NMR ($CDCl_3$) δ 0.85 (q), 0.94 (q), 1.25 (q), 20.96 (q), 26.62 (q), 30.21 (q), 30.58 (d), 30.69 (d), 122.48 (d), 127.24 (d), 128.76 (d), 135.35 (s), 138.71 (s), 139.70 (s), 143.65 (s), 144.36 (s), 151.10 (s), 151.51 (s). Anal. Calcd for $C_{72}H_{140}Se_2Si_{12}Sn_2$: C, 49.75; H, 8.12; Se, 9.08. Found: C, 49.51; H, 7.88; Se, 9.35. **27b**: mp >300 °C; ^{1}H NMR ($CDCl_3$ at 57 °C) δ −0.017 (br s, 72H), 0.04 (s, 36H), 1.27 (s, 2H), 2.06 (br s, 2H), 2.14 (br s, 2H), 2.23 (br, 6H), 2.36 (s, 12H), 6.25 (br s, 2H), 6.37 (br s, 2H), 6.50 (s, 4H); ^{13}C NMR ($CDCl_3$ at 57 °C) δ 0.91 (q), 1.31 (q), 1.60 (q), 20.91 (q), 26.27 (q), 30.63 (d), 31.27 (d), 31.39 (d), 122.70 (d), 127.61 (d), 128.90 (d), 135.73 (d), 138.42 (s), 139.95 (s), 144.28 (s), 144.74 (s), 151.24 (s), 151.38 (s). Anal. Calcd for $C_{72}H_{140}Se_2Si_{12}Sn_2$: C, 49.75; H, 8.12; Se, 9.08. Found: C, 49.48; H, 7.88; Se, 9.39.

Desulfurization of 1,2,3,4,5-Tetrathiastannolane 2a with Triphenylphosphine. To a toluene solution (1 mL) of **2a** (50 mg, 0.055 mmol) was added triphenylphosphine (43 mmg, 0.16 mmol) at room temperature, and the reaction mixture was stirred at room temperature for 10 h. After removal of the solvent, the residue was separated by GPLC to afford *cis*-1,3,2,4-dithiadistannetane **27a** (37.1 mg, 83%) and triphenylphosphine sulfide (37 mg, 76%).

Deselenation of 1,2,3,4,5-Tetraselenastannolane 2b with Triphenylphosphine. A toluene solution (2 mL) of triphenylphosphine (36 mg, 0.14 mmol) was added to a toluene solution (5 mL) of **2b** (50 mg, 0.045 mmol) at −78 °C, and the reaction mixture was stirred for 10 h, during which time the temperature was raised to room temperature. After the solvent was evaporated, the residue was chromatographed (GPLC) to afford a dimeric fraction (37 mg) and triphenylphosphine selenide (40 mg, 86%). The dimeric fraction was further purified by PTLC to afford *cis*-1,3,2,4-diselenadistannetane **27b** (15 mg, 38%) and *trans*-1,3,2,4-diselenadistannetane **26b** (1 mg, 3%).

Desulfurization of 1,2,3,4,5-Tetrathiastannolane 3a with Triphenylphosphine. (a) To a toluene solution (10 mL) of **3a** (95 mg, 0.094 mmol) was added triphenylphosphine (74 mg, 0.28 mmol) at room temperature, and the reaction mixture was stirred at the same temperature for 10 h. After removal of the solvent, the residue was separated with GPLC to afford 2,4-bis(2,4,6-triisopropylphenyl)-2,4-bis{2,4,6-tris[bis(trimethylsilyl)methyl]-phenyl}-1,3,2,4-dithiadistannetane (**29**) (4.6 mg, 4%, the ratio of *cis*- and *trans*-isomer = 1:1 determined by ^{1}H NMR) and {2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}hydroxy(2,4,6-triisopropylphenyl)mercaptostannane (**28**) (35 mg, 42%), both as white crystals, which were recrystallized from ethanol–chloroform. (b) By the same procedure as above except that the reaction was carried out in refluxing toluene, **3a** (50 mg, 0.05 mmol) and PPh_3 (39 mg, 0.15 mmol) gave exclusively **29** (44 mg, 100%, the ratio of *cis*- and *trans*-isomer = 1:1 determined by ^{1}H NMR). (c) In a manner similar to procedure a except for use of hexane as a solvent, **3a** (50 mg, 0.05 mmol) and PPh_3 (39 mg, 0.15 mmol) gave **28** (21 mg, 45%) and **29** (25 mg, 54%, *trans*-isomer as a main product). (d) By the same procedure as procedure b except for use of hexane as a solvent, **3a** (50 mg, 0.05 mmol) and PPh_3 (39 mg, 0.15 mmol) afforded **28** (9 mg, 19%) and **29** (36 mg, 80%, the ratio of *cis*- and *trans*-isomer = 1:1 determined by ^{1}H NMR). *trans*- and *cis*-**29** were separated by PTLC (hexane) and recrystallized from ethanol–chloroform. *trans*-**29**: mp >300 °C; ^{1}H NMR ($CDCl_3$ at 67 °C) δ −0.27 (s, 18H), −0.12 (s, 18H), 0.07 (s, 18H), 0.08 (s, 36H), 0.25 (s, 18H), 1.05 (d, J = 6.0 Hz, 6H), 1.16 (br s, 6H), 1.22 (d, J = 6.9 Hz, 12H), 1.27 (d, J = 6.6 Hz, 6H), 1.33 (s, 2H), 1.42 (br s, 2H), 1.48 (br s, 6H), 2.53 (sept, J = 6.6 Hz, 4H), 2.82 (sept, J = 6.9 Hz, 2H), 3.78 (br s, 2H), 6.38 (br s, 4H), 6.92 (s, 2H), 6.96 (s, 2H); ^{13}C NMR ($C_2D_2Cl_4$ at 140 °C) δ 1.49 (qx2), 2.13 (q), 2.73 (q), 2.90 (q), 3.02 (q), 23.63 (q), 23.91 (q), 25.38 (q), 26.94(q), 27.12(q), 30.27 (q), 30.97 (d), 31.54 (d), 32.90 (d), 34.24 (d), 34.55 (d), 38.75 (d), 123.50 (br d), 127.22 (br d), 143.63 (s), 144.53 (s), 146.33 (s), 150.08 (s), 150.40 (s), 152.26 (s), 154.15 (s), 155.41 (s). Anal. Calcd for $C_{84}H_{164}S_2Si_{12}Sn_2$: C, 55.66; H, 9.12; S, 3.54. Found: C, 55.39; H, 8.87; S, 3.59. *cis*-**28**: mp >300 °C; ^{1}H NMR ($CDCl_3$ at 67 °C) δ −0.31 (s, 18H), 0.06 (s, 18H), 0.08 (s, 18H), 0.12 (s, 18H), 0.22 (s, 18H), 0.24 (d, J = 6.6 Hz, 6H), 0.27 (s, 18H), 0.85 (br s, 6H), 1.15 (d, J = 6.9 Hz, 6H), 1.16 (d, J = 6.9 Hz, 6H), 1.23 (d, J = 6.6 Hz, 6H), 1.33 (br s, 6H), 1.34 (s, 2H), 2.59 (br s, 2H), 2.75 (sept, J = 6.9 Hz, 2H), 3.28 (br s, 4H), 4.61 (sept, J = 6.6 Hz, 2H), 6.37 (br s, 2H), 6.41 (br s, 2H), 6.90 (s, 2H), 6.91 (s, 2H); ^{13}C NMR ($C_2D_2Cl_4$ at 140 °C) δ 1.49 (q), 1.57 (q), 2.51 (q), 2.61 (q), 3.41 (q), 3.57 (q), 23.39 (q), 23.69 (q), 23.77 (q), 25.86 (q), 27.29 (q), 28.55 (q), 30.05 (d), 31.07 (d), 32.36 (d), 32.83 (d), 34.27 (d), 38.70 (d), 123.50 (d), 123.65 (d), 124.51 (d), 127.22 (d), 143.64 (s), 143.79 (s), 143.85 (s), 149.91 (s), 150.56 (s), 152.69 (s), 154.31 (s), 156.79 (s). Anal. Calcd for $C_{84}H_{164}S_2Si_{12}Sn_2$: C, 55.66; H, 9.12; S, 3.54. Found: C, 55.78; H, 8.89; S, 3.46. **28**: mp 160–162 °C; ^{1}H NMR ($CDCl_3$) δ −0.09 (s, 9H), −0.03 (s, 9H), 0.03 (s, 9H), 0.04 (s, 9H), 0.07 (s, 9H), 0.10 (s, 9H), 0.91 (s, 1H), 1.21 (d, J = 6.9 Hz, 6H), 1.24 (d, J = 6.5 Hz, 6H), 1.31 (s, 1H), 1.33 (d, J = 6.5 Hz, 6H), 1.96 (br s, 1H), 2.18 (br s, 1H), 2.84 (sept, J = 6.9 Hz, 1H), 3.27 (br s, 2H), 6.31 (s, 1H), 6.45 (s, 1H), 7.03 (s, 2H); ^{13}C NMR ($CDCl_3$) δ 0.71 (q), 0.77 (q), 0.88 (q), 0.99 (q), 1.20 (q), 1.46 (q), 23.86 (q), 23.94 (q), 25.30 (br q), 26.20 (br q), 30.51 (d), 31.32 (d), 31.57 (d), 34.33 (d), 36.27 (d), 122.15 (d), 122.53 (d), 127.36 (d), 137.83 (s), 141.08 (s), 145.33 (s), 150.77 (s), 150.99 (s), 151.23 (s), 154.48 (s). Anal. Calcd for $C_{42}H_{84}OSSi_6Sn$: C, 54.57; H, 9.16; S, 3.47. Found: C, 54.32; H, 8.86; S, 3.38.

Deselenation of 1,2,3,4,5-Tetraselenastannolane 3b with Triphenylphosphine. (a) To a toluene solution (5 mL) of **3b** (50 mg, 0.042 mmol) was added a toluene solution (2 mL) of PPh_3 (33 mg, 0.13 mmol) at −78 °C, and the reaction mixture was stirred for 10 h while being warmed to room temperature. After the solvent was evaporated, the residue was separated with PTLC (hexane) to afford *cis*-2,4-bis(2,4,6-triisopropylphenyl)-2,4-bis-{2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}-1,3,2,4-diselenadistannetane (**30**) (5 mg, 13%) and *trans*-2,4-bis(2,4,6-triisopropylphenyl)-2,4-bis{2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}-1,3,2,4-diselenadistannetane (**31**) (26 mg, 65%), both as white crystals, which were recrystallized from ethanol–chloroform. (b) In a manner similar to the above except that the reaction was carried out at 70 °C, **3b** (100 mg, 0.084 mmol) and PPh_3 (66 mg, 0.25 mmol) gave **30** (21 mg, 27%) and **31** (29 mg, 36%). **30**: mp >300 °C; ^{1}H NMR ($CDCl_3$ at 67 °C) δ −0.30 (s, 18H), 0.07 (s, 18H), 0.06 (s, 18H), 0.08 (s, 18H), 0.26 (s, 18H), 0.27 (s, 18H), 0.83 (d, J = 6.0 Hz, 6H), 1.155 (d, J = 6.9 Hz, 6H), 1.16 (d, J = 6.9 Hz, 6H), 1.22 (d, J = 6.7 Hz, 6H), 1.28 (s, 2H), 1.33 (d, J = 6.4 Hz, 6H), 1.39 (s, 2H), 1.48 (br s, 6H), 2.58 (br s, 2H), 2.75 (sept, J = 6.9 Hz, 2H), 3.39 (s, 2H), 4.79 (br s, 2H), 6.33 (br s, 2H), 6.36 (br s, 2H), 6.88 (s, 2H), 6.89 (s, 2H); ^{13}C NMR ($C_2D_2Cl_4$ at 140 °C) δ 1.49 (q), 1.53 (q), 2.54 (q), 2.61 (q), 3.27 (q), 3.47 (q), 23.61 (q), 23.70 (q), 23.76 (q), 25.93 (q), 27.22 (q), 28.68 (q), 30.52 (d), 31.03 (d), 32.17 (d), 32.81 (d), 34.27 (d), 38.70 (d), 123.68 (d), 124.47 (d), 126.55 (d), 128.51 (d), 139.78 (s), 140.94 (s), 143.66 (s), 149.85 (s), 150.33 (s), 152.74 (s), 154.28 (s), 156.58 (s). Anal. Calcd for $C_{84}H_{164}Se_2Si_{12}Sn_2 \cdot 2H_2O$: C, 51.93; H, 8.72; Se, 8.13. Found: C, 51.45; H, 8.21; Se, 7.94. **31**: mp 288–299 °C dec; ^{1}H NMR ($CDCl_3$ at 67 °C) δ −0.25 (s, 18H), −0.06 (s, 18H), 0.06 (s, 18H), 0.08 (s, 36H), 0.26 (s, 18H), 1.06 (d, J = 6.1 Hz, 6H), 1.23 (d, J = 6.9 Hz, 12H), 1.26 (d, J = 6.5 Hz, 12H), 1.33 (s, 2H), 1.36 (br s, 2H), 1.49 (br s, 6H), 2.47 (sept, J = 6.1 Hz, 2H), 2.58 (br s, 2H), 2.83 (sept, J = 6.9 Hz, 2H), 3.79 (br s, 2H), 6.34 (br s, 4H), 6.90 (s, 2H), 6.94 (s, 2H); ^{13}C NMR ($C_2D_2Cl_4$ at 140 °C) δ 1.50 (q), 2.06 (br q), 2.89 (q), 23.77 (qx2), 25.83 (q), 26.75 (q), 27.47 (q), 29.99 (q), 30.95 (d), 31.71 (d), 33.16 (d), 34.21 (d), 34.69 (d), 39.08 (d), 123.44 (d), 126.93 (d), 141.08 (s), 143.40 (s), 143.59 (s), 149.98 (s), 150.33 (s), 152.30 (s), 154.14 (s), 155.26 (s). Anal. Calcd for $C_{84}H_{164}Se_2Si_{12}Sn_2$: C, 52.91; H, 8.67; Se, 8.28. Found: C, 52.63; H, 8.49; Se, 8.64.

Desulfurization of 1,2,3,4,5-Tetrathiastannolane 3a with Triphenylphosphine in the Presence of 2,3-Dimethyl-1,3-butadiene. A hexane solution (3 mL) of tetrathiastannolane **3a** (50 mg, 0.05 mmol), triphenylphosphine (39 mg, 0.15 mmol), and 2,3-dimethyl-1,3-butadiene (0.3 mL) was refluxed for 10 h. After removal of the solvent, the residue was separated with GPLC to afford a monomeric fraction containing Tb and Tip substituents (40 mg), which was further purified by FCC (hexane) to provide **28** (13 mg, 28%) and 2-{2,4,6-tris[bis(trimethylsilyl)methyl]-

phenyl}-2-(2,4,6-triisopropylphenyl)-1,2-thiastannacyclohex-4-ene (**32**) (27 mg, 56%), both as white solids, which were recrystallized from ethanol–chloroform. **32**: mp 148–150 °C dec; ^{1}H NMR ($CDCl_3$) δ −0.12 (s, 9H), −0.06 (s, 9H), 0.03 (s, 9H), 0.04 (s, 9H), 0.10 (s, 9H), 0.13 (s, 9H), 1.02 (br s, 6H), 1.17 (d, J = 6.9 Hz, 6H), 1.28 (br s, 6H), 1.29 (s, 1H), 1.45 (s, 3H), 1.56 (s, 1H), 1.65 (s, 1H), 1.78 (s, 3H), 2.18 (d, J = 10 Hz, 1H), 2.44 (d, J = 10 Hz, 1H), 2.79 (sept, J = 6.9 Hz, 1H), 3.22 (d, J = 13 Hz, 1H), 3.33 (d, J = 13 Hz, 1H), 3.79 (br s, 2H), 6.29 (s, 1H), 6.43 (s, 1H), 6.92 (br s, 2H); ^{13}C NMR ($CDCl_3$) δ 0.74 (q), 1.01 (q), 1.29 (q), 1.55 (q), 1.83 (q), 2.08 (q), 19.91 (q), 20.64 (q), 23.88 (q), 23.93 (q), 25.09 (br q), 27.16 (br q), 27.79 (br q), 30.15 (t), 30.32 (d), 31.82 (d), 32.22 (d), 32.92 (d), 34.12 (t), 34.34 (d), 37.89 (d), 122.07 (d), 122.17 (d), 127.42 (d), 128.45 (s), 129.73 (s), 139.30 (s), 140.14 (s), 143.64 (s), 149.53 (s), 150.79 (s), 150.86 (s), 154.05 (br s), 155.94 (br s). Anal. Calcd for $C_{48}H_{92}SSi_6Sn$: C, 58.32; H, 9.38; S, 3.24. Found: C, 58.14; H, 9.13; S, 2.96.

Dechalcogenation of 1,2,3,4,5-Tetrachalcogenastannolanes 3a,b with Triphenylphosphine in the Presence of Styrene Oxide. (a) PPh_3 (74 mg, 0.28 mmol) was added to a toluene solution of **3a** (94 mg, 0.094 mmol) at room temperature. After the mixture was stirred for 1 h at ambient temperature, styrene oxide (100 μL) was added to the solution. Then the reaction mixture was heated to 90 °C and stirred at the same temperature for 10 h. After evaporation of the solvent, the residue was chromatographed (GPLC) to afford a monomeric fraction (79 mg), which was further purified with PTLC (20% dichloromethane/hexane) to give two isomers of 2-{2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}-2-(2,4,6-triisopropylphenyl)-4-phenyl-1,3,2-oxathiastannolane (**33a**) (isomer I, 12 mg and isomer II, 20 mg, 33%) as white crystals and **28** (11 mg, 13%). Both isomers of **33a** were recrystallized from ethanol–chloroform. The stereochemical configuration of the two isomers was not determined. **33a-I**: mp 188–192 °C; ^{1}H NMR ($CDCl_3$ at 57 °C) δ 0.03 (br s, 18H), 0.07 (br s, 36H), 1.24 (d, J = 6.9 Hz, 6H), 1.30 (d, J = 6.5 Hz, 6H), 1.31 (d, J = 6.5 Hz, 6H), 1.35 (s, 1H), 2.13 (br s, 1H), 2.35 (br s, 1H), 2.88 (sept, J = 6.9 Hz, 1H), 3.10 (sept, J = 6.5 Hz, 2H), 3.56 (dd, J = 11 and 11 Hz, 1H), 4.44 (dd, J = 4 and 11 Hz, 1H), 4.66 (dd, J = 4 and 11 Hz, 1H), 6.39 (br s, 1H), 6.50 (br s, 1H), 7.06 (s, 2H), 7.18–7.41 (m, 5H); ^{13}C NMR ($CDCl_3$ at 57 °C) δ 0.91 (q), 0.98 (q), 1.33 (q), 23.93 (q), 26.12 (br q), 30.88 (d), 31.41 (d), 34.42 (d), 38.31 (d), 55.72 (d), 73.94 (t), 122.44 (d), 123.10 (d), 127.23 (d), 128.20 (d), 128.27 (d), 128.39 (d), 138.92 (s), 140.78 (s), 142.39 (s), 145.37 (s), 151.14 (s), 151.63 (br s), 154.61 (s). Anal. Calcd for $C_{50}H_{90}OSSi_6Sn$: C, 58.50; H, 8.84; S, 3.12. Found: C, 58.44; H, 8.58; S, 3.52. **33a-II**: mp 192–194 °C; ^{1}H NMR ($CDCl_3$ at 57 °C) δ 0.00 (br s, 18 H), 0.07 (br s, 18H), 0.11 (br s, 18H), 1.25 (d, J = 6.0 Hz, 6H), 1.27 (br s, 6H), 1.35 (d, J = 6.5 Hz, 6H), 1.36 (s, 1H), 1.92 (br s, 1H), 2.09 (br s, 1H), 2.88 (sept, J = 6.9 Hz, 1H), 3.26 (br s, 2H), 3.57 (dd, J = 11 and 11 Hz, 1H), 4.32 (dd, J = 4 and 11 Hz, 1H), 4.54 (dd, J = 4 and 11 Hz, 1H), 6.40 (br s, 1H), 6.52 (br s, 1H), 7.07 (s, 2H), 7.20–7.42 (m, 5H); ^{13}C NMR ($CDCl_3$ at 57 °C) δ 0.89 (q), 1.01 (q), 1.21 (br q), 1.47 (br q), 23.90 (q), 23.93 (q), 25.99 (br q), 30.89 (d), 31.09 (d), 34.39 (d), 38.25 (d), 57.21 (d), 72.41 (t), 122.58 (d), 123.24 (d), 127.34 (d), 128.07 (d), 128.26 (d), 128.45 (d), 138.83 (s), 140.24 (s), 141.81 (s), 145.40 (s), 150.95 (s), 151.32 (s), 151.58 (s), 154.89 (s). Anal. Calcd for $C_{50}H_{90}OSSi_6Sn$: C, 58.50; H, 8.84; S, 3.12. Found: C, 57.94; H, 8.44; S, 3.48. (b) To a THF solution (3 mL) of **3b** (100 mg, 0.084 mmol) was added a THF solution (3 mL) of PPh_3 (66 mg, 0.25 mmol) at −78 °C, and the solution was stirred at −78 °C for 30 min. After styrene oxide (100 μL) was added to the mixture, it was stirred for 10 h, during which time it was warmed to room temperature. After evaporation of the solvent, the residue was chromatographed (GPLC) to afford a monomeric fraction (61 mg) which was further purified by PTLC (hexane) to provide two isomers of 2-{2,4,6-tris[bis(trimethylsilyl)-methyl]phenyl}-2-(2,4,6-triisopropylphenyl)-4-phenyl-1,3,2-oxaselenastannolane (**33b**) (isomer I, 15 mg and isomer II, 33 mg, 53%) as white crystals. The sterechemical configuration of the two isomers was not determined. Both isomers of **33b** were recrystallized from ethanol–chloroform. **33b-I**: mp 218–220 °C; ^{1}H NMR ($CDCl_3$) δ −0.35 (s, 9H), 0.02 (s, 9H), 0.03 (s, 9H), 0.04 (s, 18H), 0.09 (s, 9H), 1.22 (d, J = 6.9 Hz, 6H), 1.28 (br s, 12H), 1.32 (s, 1H), 2.07 (s, 1H), 2.31 (s, 1H), 2.86 (sept, J = 6.9 Hz, 1H), 3.13 (br s, 2H), 3.71 (dd, J = 18 and 18 Hz, 1H), 4.62 (dd, J = 18 and 9 Hz, 1H), 4.67 (dd, J = 18 and 9 Hz, 1H), 6.33 (s, 1H), 6.47 (s, 1H), 7.04 (s, 2H), 7.15–7.38 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 0.81 (q), 0.93 (q), 1.09 (q), 1.25 (q), 1.31 (q), 1.47 (q), 23.97 (q), 29.13 (br q), 30.58 (d), 30.79 (d), 34.36 (d), 38.01 (d), 52.79 (d), 73.39 (t), 122.38 (d), 122.88 (d), 127.10 (d), 127.86 (d), 128.33 (d), 128.41 (d), 138.37 (s), 140.63 (s), 141.62 (s), 145.13 (s), 150.89 (s), 151.03 (s), 151.42 (s), 154.44 (s). Anal. Calcd for $C_{50}H_{90}OSeSi_6Sn$: C, 55.95; H, 8.45; Se, 7.36. Found: C, 55.65; H, 8.15; Se, 7.63. **33b-II**: mp 193–195 °C; ^{1}H NMR ($CDCl_3$ at 57 °C, 400 MHz) δ 0.01 (br s, 18H), 0.09 (br s, 18H), 0.11 (br s, 18H), 1.25 (d, J = 6.9 Hz, 6H), 1.258 (br s, 6H), 1.35 (d, J = 6.4 Hz, 6H), 1.36 (s, 1H), 1.95 (br s, 1H), 2.09 (br s, 1H), 2.88 (sept, J = 6.9 Hz, 1H), 3.41 (br s, 2H), 3.77 (dd, J = 11 and 11 Hz, 1H), 4.54 (dd, J = 4 and 11 Hz, 1H), 4.60 (dd, J = 4 and 11 Hz, 1H), 6.40 (br s, 1H), 6.52 (br s, 1H), 7.07 (s, 2H), 7.19–7.41 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 0.61 (q), 0.95 (q), 1.06 (q), 1.27 (q), 1.36 (q), 1.83 (q), 23.26 (br q), 23.98 (q), 30.34 (d), 30.45 (d), 30.58 (d), 34.35 (d), 37.99 (d), 54.06 (d), 72.13 (t), 122.51 (d), 123.00 (d), 127.23 (d), 127.79 (d), 128.09 (d), 128.52 (d), 138.79 (s), 140.00 (s), 141.45 (s), 145.10 (s), 150.68 (s), 150.99 (s), 151.32 (s), 154.60 (s). Anal. Calcd for $C_{50}H_{90}OSeSi_6Sn$: C, 55.95; H, 8.45; Se, 7.36. Found: C, 55.39; H, 8.25; Se, 7.85.

Crystal and Experimental Data for 26a,b, 27a,b, 31, 8, and 14.[25] (a) **26a,b** and **27a,b**: Data were collected through a capillary glass tube with Cu Kα radiation (λ = 1.5418 Å) on Enraf-Nonius CAD-4 diffractometer. Unique reflactions ($|F_o| > 3\sigma|F_o|$, 6742 for **26a**; 6538 for **26b**; 6986 for **27a**; 7380 for **27b**) were observed ($4° < 2\theta < 130°$). Empirical absorption correction was applied and structure was solved by direct methods (MULTAN 78) using an SDP package and program systems Molen and/or UNICS III. The non-hydrogen atoms were refined anisotropically, and the hydrogen atoms were refined isotropically. Some hydrogen atoms were found in D-fourier map and the others were located by calculation. Refinement was performed by the full-matrix least-squares method with 398 (for **26a** and **26b**) and 397 (for **27a** and **27b**) variable parameters (anisotropic thermal parameters for non-hydrogen atoms, where the positions and thermal parameters for hydrogen atoms were not refined). (b) **31**, **8**, and **14**: The intensity data ($2\theta \leq 55°$) 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. All calculations were perfomed using TEXSAN crystallographic software package of Molecular Structure Corporation. The non-hydrogen atoms were refined anisotropically, and all hydrogen atoms were located by calculation. The final cycle of full-matrix least-squares refinement was based on 8262 (for **31**), 6588 (for **8**), and 3701 (for **14**) observed reflections ($I > 3\sigma(I)$ for **31** and **14**, $I > 4\sigma(I)$ for **8**) and 828 (for **31**) and 541 (for **8** and **14**) variable parameters respectively. In the case of **31**, non-hydrogen atoms of the *p*-[bis(trimethylsilyl)methyl] group of the Tb group bound to Sn2 atom (C17, C73–C78, Si9, and Si10) were refined isotropically with the thermal parameters for carbon atoms being fixed (U_{11} = 0.1267) because of their severe disorder.

Acknowledgment. This work was partially supported by Grand-in-Aid for Scientific Research on Priority Area (No. 03215101) from the Ministry of Education, Science and Culture, Japan. We are grateful to Shin-etsu Chemical and Toso Akzo Co. Ltd. for chlorosilanes and alkyllithiums, respectively.

Supplementary Material Available: Crystallographic data and tables listing atomic coordinates, temperature factors, bond lengths and angles, and torsional angles for **26a**, **26b**, **27a**, **27b**, **31**, **8**, and **14** (211 pages). Ordering information is given on any current masthead page.

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(25) Atomic coordinates, bond lengths and angles, and thermal parameters for **8** and **14** have been deposited at the Cambridge Data Centre.[14b]