Synthesis and Structure of 1,2,3,4,5-Tetrachalcogenastannolanes

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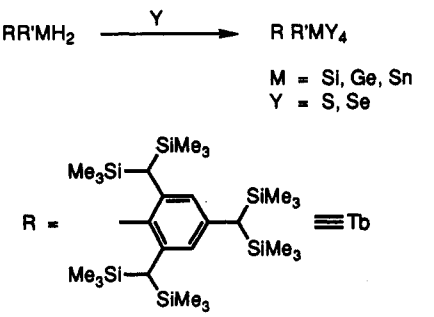
Novel cyclic polychalcogenides, 1,2,3,4,5-tetrathia- and tetraselenastannolanes [Tb(R)SnY_4 (Y = S, Se; Tb = 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl; R = mesityl or 2,4,6-triisopropylphenyl)], have been synthesized by two routes, i.e., (a) the reaction of dihydrostannanes Tb(R)SnH_2 with sulfur or selenium and (b) the lithiation of dihydrostannanes Tb(R)SnH_2 or dichlorostannanes Tb(R)$SnCl_2$ with t-BuLi followed by reaction with sulfur or selenium. All the tetrachalcogenastannolanes have been characterized by ^1H and ^{13}C NMR and elemental analysis. In addition, Tb(Mes)SnS_4 (**7b**) and Tb(Mes)$SnSe_4$ (**8b**) have been subjected to single-crystal X-ray diffraction analysis. Both five-membered **7b** and **8b** have distorted envelope conformation, the former of which is slightly more distorted. The reason for the exclusive formation of five-membered polychalcogenides has been discussed on the basis of the X-ray structural analysis and ab initio calculations for the model ring system H_2SiS_n (n = 2–6).

Introduction

Over the past decades, much attention has been paid to the chemistry of polychalcogenides, particularly that of metal-containing cyclic polychalcogenides from the viewpoints of not only their unique structures but also their synthetic and biological utilities. Among them are known some metal complexes with polysulfido ligands which are suspected to play an important role either in the bioorganic chemistry of Fe–Mo–S systems or in catalysis (particularly in hydrosulfurization).[1] For transition-metal compounds there have been several reports on the successful construction and thorough characterization of cyclic polysulfides such as Cp_2TiS_5,[2] Cp_2VS_5,[3] Cp_2MoS_4,[4] and Cp_2WS_4[5] (Cp = η^5-C_5H_5), which can be used as versatile sources to prepare the sulfur rings of predetermined size.[2a,4a,6] On the other hand, very little interest has been focused on the metal-containing cyclic polyselenides on account of their instability and the limitation of synthetic methods, though there have been a few examples such as Cp_2VSe_5[3b] and Cp_2TiSe_5[2a] so far. Recently, a new type of zinc polychalcogenides, (N-MeIm)$_2$$ZnS_6$ and (N-MeIm)$_2$$ZnSe_4$, have been successfully synthesized by direct chalcogenation of zinc dust in N-methylimidazole (N-MeIm).[7] It should be noted here that the number of chalcogen atoms in the polychalcogenido ligands of these metal complexes seems to vary with the kinds of transition metals and chalcogen atoms, the reasons for which being not clear. Meanwhile, as for the main-group element counterpart, there had been no stable examples of metal-containing cyclic polychalcogenides until we recently described some preliminary reports on the synthesis of novel 1,2,3,4,5-tetrachalcogenamet-

Scheme I



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(4) (a) Köpf, H. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 375. (b) Köpf, H.; Hazari, S. K. S. *Z. Anorg. Allg. Chem.* **1976**, *426*, 49.

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(6) (a) Schmidt, M. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 445. (b) Steudel, R. *Top. Curr. Chem.* **1982**, *102*, 149.

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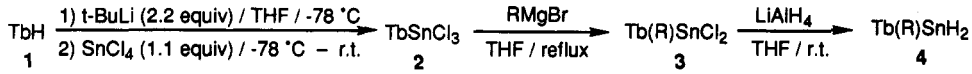
Scheme II



a: R = Ph; b: R = Mes (2,4,6-trimethylphenyl); c: R = Tip (2,4,6-triisopropylphenyl)

Scheme III

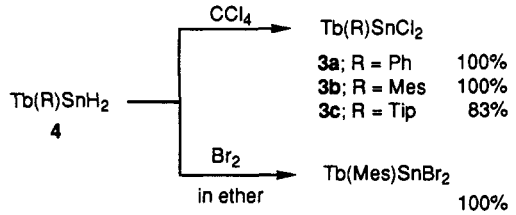


Table I. Synthesis of 3 and 4 from Trichlorostannane 2

R	RMgBr	Tb(R)$SnCl_2$ (3)	Tb(R)SnH_2 (4)	Tb(R)$_2$SnH
Ph	1 equiv		39% (**4a**)	1%
	2 equiv		0%	30%
Mes	1 equiv		57% (**4b**)	0%
	2 equiv		9%	23%
Tip	2 equiv	47% (**3c**)	77% (**4c**)	

allolanes of group 14 metals such as RR'MY_4 (M = Si, Ge, Sn; Y = S, Se)[8] by taking advantage of a new and efficient steric protection group, 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl (denoted as Tb in this paper) which was developed in the course of our study on the sterically congested molecules.[9] The present paper delineates detailed accounts of the synthesis and characterization of 1,2,3,4,5-tetrachalcogenastannolanes, Tb(R)SnY_4 (Y = S, Se; R = mesityl or 2,4,6-triisopropylphenyl) together with a discussion on the reasons for the exclusive formation of five-membered cyclic polychalcogenides.

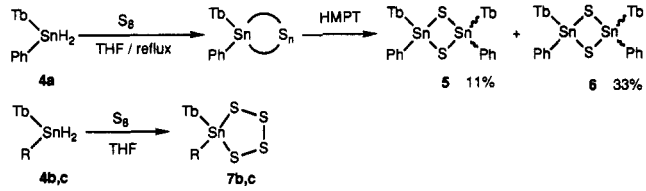
Results and Discussion

Synthesis of Dichlorostannanes 3 and Dihydrostannanes 4. Tin trichloride **2** bearing a Tb group was synthesized in a moderate yield by the reaction of tin tetrachloride with TbLi prepared from TbBr and t-BuLi in THF. Further functionalization of **2** leading to key substances **3** and **4** was readily performed by nucleophilic substitution using Grignard reagents, followed by $LiAlH_4$ reduction (Scheme II and Table I). Phenyl- and mesityl-substituted dichlorostannanes **3a** and **3b** were decomposed during chromatographic purification, while Tip-substituted dichlorostannane **3c** was isolated by silica gel column chromatography. Two Tip groups could not be introduced onto **2** even by the treatment of **2** with an excess amount of TipMgBr in refluxing THF, probably for a steric reason.

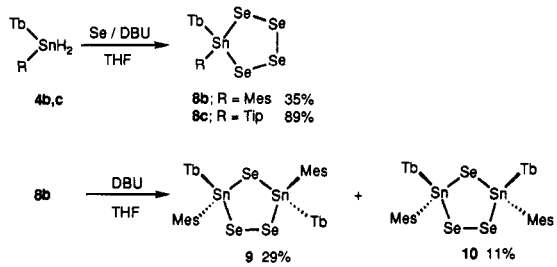
The dihydrostannanes **4** were easily chlorinated just by stirring in CCl_4 and brominated with bromine in ether (Scheme III). This fact suggests that the hydrogen attached to the tin atom has remarkable reducing power.

Synthesis of Tetrathiastannolanes 7 and Tetraselenastannolanes 8 by Direct Chalcogenation of 4. With **4** in hand we first attempted the reaction of **4** with sulfur and selenium. In the case of mesityl-substituted dihydrostannane **4b**, tetrathiastannolane **7b** was readily obtained in 92% by treatment of dihydrostannane **4b** with sulfur (5 equiv mol as S_8) in refluxing THF for 18 h. This is in sharp contrast to the fact that the formation of the corresponding tetrathiasilolane and tetrathiagermolane demanded much higher temperatures (230 and 180 °C in molten sulfur, respectively). It is also noteworthy that the sulfurization of **4b** proceeded in THF even at room temperature to give **7b** (21%, 37 h). The reaction with more hindered dihydrostannane **4c** proceeded under similar conditions (24 h in refluxing THF), though more slowly, to give **7c** (61%). In contrast to the case of **4b** and **4c**, treatment of phenyl-substituted dihydrostannane **4a** with S_8 (5 equiv) under reflux in THF gave an inseparable mixture of two cyclic polysulfides,[10] which reacted with HMPT (hexamethylphosphorous triamide) to afford two types of cyclic sulfides having two tin atoms (**5**, 11% and **6**, 33%) (Scheme IV). When **4a** was treated with molten sulfur at 120–130 °C, **5** (23%) and **6** (18%) were directly obtained.

Scheme IV



Scheme V



Similar treatment of dihydrostannane **4b** with elemental selenium in refluxing THF led to tetraselenastannolane **8b** in poor yield (5%), probably because of insolubility of selenium in the solvent. Addition of DBU known to activate selenium,[11] however, raised the yield of **8b** to 35%, although cyclic polyselenides **9** and **10** were also formed (Scheme V). Reaction for prolonged reaction time resulted in the sole formation of **9** and **10**, suggesting the conversion of **8** to **9** and **10** during the reaction. This was demonstrated in a separate experiment (Scheme V). In contrast to the reaction of **4b**, Tip-substituted dihydrostannane **4c** gave tetraselenastannolane **8c** in high yield, although the reaction proceeded more slowly because of steric congestion around the tin atom.

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(10) The ^{119}Sn NMR measurement of the mixture showed two signals (192 and 206 ppm, Me_4Sn as internal standard) considered to be assigned to cyclic polysulfides containing a tin atom in the light of δ_{Sn} 182 for **7c**.

(11) Activation of elemental selenium with DBU has been demonstrated in several reports. (a) Tokitoh, N.; Hayakawa, H.; Goto, M.; Ando, W. *Tetrahedron Lett.* **1988**, *29*, 1935. (b) Chenard, B. L.; Miller, T. J. *J. Org. Chem.* **1988**, *49*, 1221. (c) Yoshida, H.; Kabe, Y.; Ando, W. *Organometallics* **1991**, *10*, 27.

Scheme VI

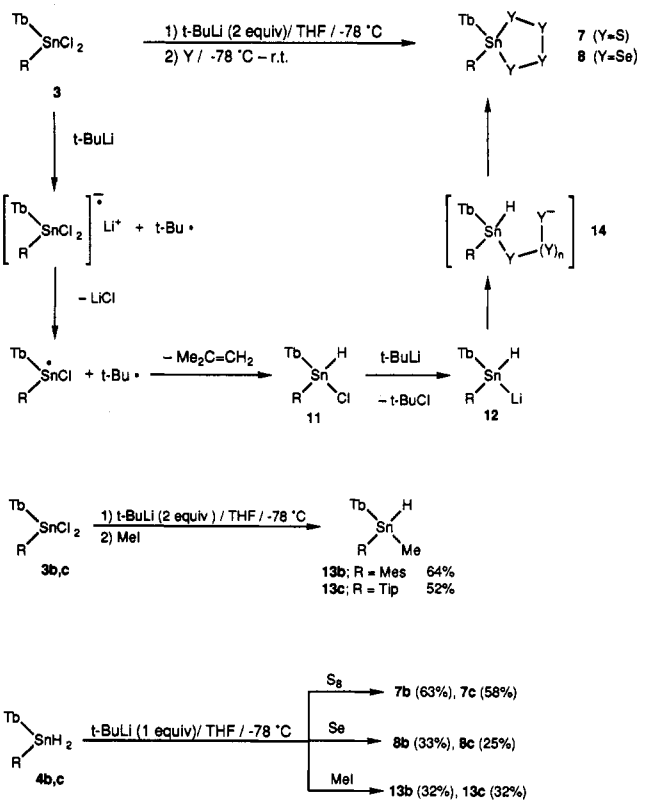


Table II. Synthesis of 7 and 8 via Lithiation of 3 and 4

$$\underset{\textbf{3b,c, 4b,c}}{Tb(R)SnX_2} \xrightarrow[(2)\ Y/-78\ °C\text{–rt}]{(1)\ t\text{-BuLi}/-78\ °C} \underset{\textbf{7b,c, 8b,c}}{Tb(R)SnY_4}$$

R	X	Y	yield/% 7, 8	yield/% 9
Mes	Cl	S	60	
	H	S	63	
	Cl	Se	27	11
	H	Se	33	9
Tip	Cl	S	72	
	H	S	58	
	Cl	Se	78	
	H	Se	25	

Alternative Synthetic Method of Tetrachalcogenastannolanes 7 and 8 via Lithiation of 3 and 4. The alternative preparation of 7 and 8 was accomplished by the lithiation of the corresponding diaryldichlorostannanes 3 with 2 equiv mol of t-BuLi in THF at −78 °C, followed by addition of elemental sulfur or selenium (Scheme VI and Table II). The formation of 7 and 8 is most likely explained in terms of the intermediacy of hydrostannyllithium 12 which was formed by the initial reduction of sterically hindered dichlorostannane 3 with t-BuLi via single-electron transfer followed by halogen–lithium exchange of the resulting chlorostannane 11 with a second t-BuLi. The intermediacy of 12 is reasonably supported by the fact that the reaction of **3b** and **3c** with t-BuLi (2 equiv) followed by treatment with an excess amount of methyl iodide gave the corresponding methylated hydrostannanes **13b** (64%) and **13c** (52%), respectively (Scheme VI). Furthermore, the hydrostannyllithium 12 independently derived from the dihydrostannanes **4b,c** with t-BuLi (1 equiv) in THF also reacted with sulfur, selenium, and methyl iodide to yield **7b,c** (63%, 58%), **8b,c** (33%, 25%), and methylstannane **13b,c** (32%, 32%),

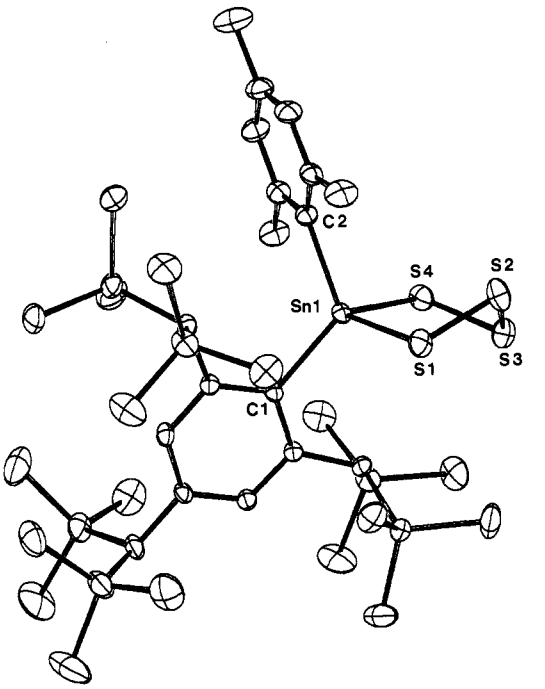


Figure 1. ORTEP drawing of **7b**. Selected bond lengths (Å) and angles (deg): Sn(1)–S(1), 2.438(3); S(1)–S(2), 2.050(4); S(2)–S(3), 2.036(5); S(3)–S(4), 2.048(3); S(4)–Sn(1), 2.481(2); Sn(1)–C(1), 2.164(6); Sn(1)–C(2), 2.160(7); S(1)–Sn(1)–S(4), 95.4(1); Sn(1)–S(1)–S(2), 98.5(1); S(1)–S(2)–S(3), 100.6(2); S(2)–S(3)–S(4), 102.6(2); S(3)–S(4)–Sn(1), 100.9(2); C(1)–Sn(1)–S(1), 106.2(2); C(1)–Sn(1)–S(4), 119.2(2); C(2)–Sn(1)–S(1), 117.2(2); C(2)–Sn(1)–S(4), 96.2(2); C(1)–Sn(1)–C(2), 120.3(2).

respectively. The reaction of 12 with chalcogen most likely proceeds via formation of acyclic stannapolychalcogenide 14, followed by reductive cleavage of the chalcogen chain with hydride attached to the tin atom. In the reaction of mesityl-substituted **3b** and **4b**, cyclic selenides **9** and **10** (inseparable from unidentified cyclic polyselenides) were also formed probably via reaction between two molecules of 14 (R = Mes, Y = Se).

Structures of 7 and 8. 1,2,3,4,5-Tetrachalcogenastannolanes **7b,c** and **8b,c** showed satisfactory spectral and analytical data, and the final molecular structures for **7b** and **8b** were determined by X-ray crystallographic analysis (Figures 1–3 and Table III). As can be seen in Table III, there is hardly any difference between the two tetrachalcogenastannolane rings; the five-membered rings in **7b** and **8b** have a similar envelope conformation, though **7b** is slightly more distorted. Of particular note is that the crystal of **7b** was solvated with chloroform as shown in Figure 3. However, there are no close contacts within 3.65 Å between the molecules of **7b** and chloroform. In both cases the Y_4 units (Y = chalcogen atom) are asymmetrically bound with two unequal tin–chalcogen bond lengths, and there is almost no alternation in the S–S bonds of the sulfur chain of **7b** in contrast to the previously reported Cp_2MS_4 systems (M = Mo, W) which show distinct alternation in S–S bonds with no asymmetry in the bonding of the S_4 unit.[12] Although it can be seen that there is a little alternation in the Se–Se bonds of the selenium chain of **8b** in contrast to the reported $(N\text{-MeIm})_2ZnSe_5$,[7] which shows almost no alternation in the Se–Se bonds, this is

(12) (a) Block, H. D.; Allmann, R. *Crystal. Struct. Commun.* **1975**, *4*, 53. (b) Davis, B. R.; Bernal, I.; Köpf, H. *Angew. Chem., Int. Ed. Engl.* **1971**, *10*, 921.

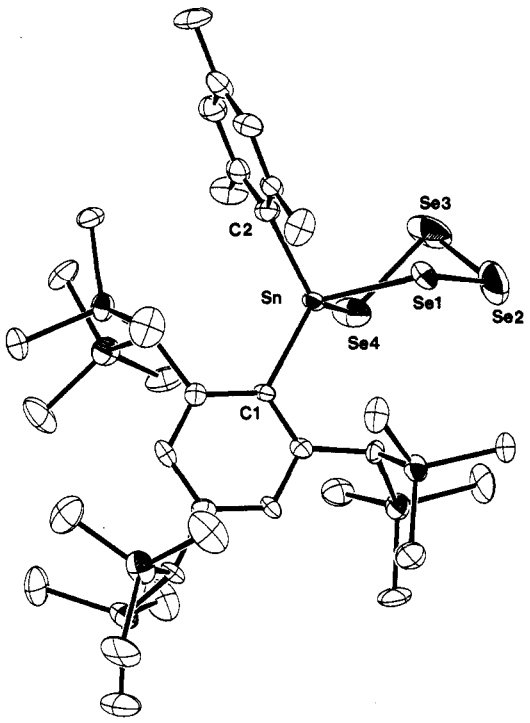
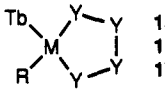


Figure 2. ORTEP drawing of **8b**. Selected bond lengths (Å) and angles (deg): Sn(1)–Se(1), 2.603(2); Se(1)–Se(2), 2.294(3); Se(2)–Se(3), 2.338(4); Se(3)–Se(4), 2.311(3); Se(4)–Sn(1), 2.549(2); Sn(1)–C(1), 2.18(1); Sn(1)–C(2), 2.16(1); Se(1)–Sn(1)–Se(4), 99.1(1); Se(1)–Sn(1)–C(1), 118.2(3); Se(1)–Sn(1)–C(2), 96.7(3); Se(4)–Sn(1)–C(1), 106.4(3); Se(4)–Sn(1)–C(2), 115.0(3); Sn(1)–Se(1)–Se(2), 101.3(1); Se(1)–Se(2)–Se(3), 99.0(1); Se(2)–Se(3)–Se(4), 96.5(1); Se(3)–Se(4)–Sn(1), 95.3(1); C(1)–Sn(1)–C(2), 119.7(4).

probably due to the effect of a slight disorder of Se2 and Se3 atoms from a view onto their higher temperature coefficients than for all carbons.

Neither pure pentathiolane (S_5) nor tetrathiolane (R_2CS_4) has been synthesized yet, probably due to their unfavorable bond geometry. By contrast, the corresponding higher homologs, i.e., tetrathiasilolane **15**,[8a] tetrathiagermolane **16**,[8a] and tetraselenagemolane **17**,[8c] have been synthesized as stable species in our laboratory, in addition to **7** and **8** reported here.



15; M = Si Y = S
16; M = Ge Y = S
17; M = Ge Y = Se

The polychalcogenides **15–17** were synthesized by the reaction of the corresponding hydrides or the lithiated species derived from dihydrides or dichlorides with chalcogen molecules as in the case of the present tin analogs **7** and **8**. The successful isolation of these higher homologs suggests that the introduction of a heavier atom (M) with tetrahedral environment and the longer M–S bonds compared to the S–S bond (2.060 Å, orthorhombic sulfur)[13] and the C–S bond (1.80 Å in CH_3SCH_3)[14] eases the ring strain of these tetrachalcogenametallolane ring systems.

It should be noted that all these reactions result in the isolation of only the five-membered polychalcogenides. In order to clarify reasons for this interesting phenomenon,

(13) Caron, A.; Donohue, J. *Acta Crystallogr.* **1965**, *18*, 562.
(14) Pierce, L.; Hayashi, M. *J. Chem. Phys.* **1961**, *35*, 479.

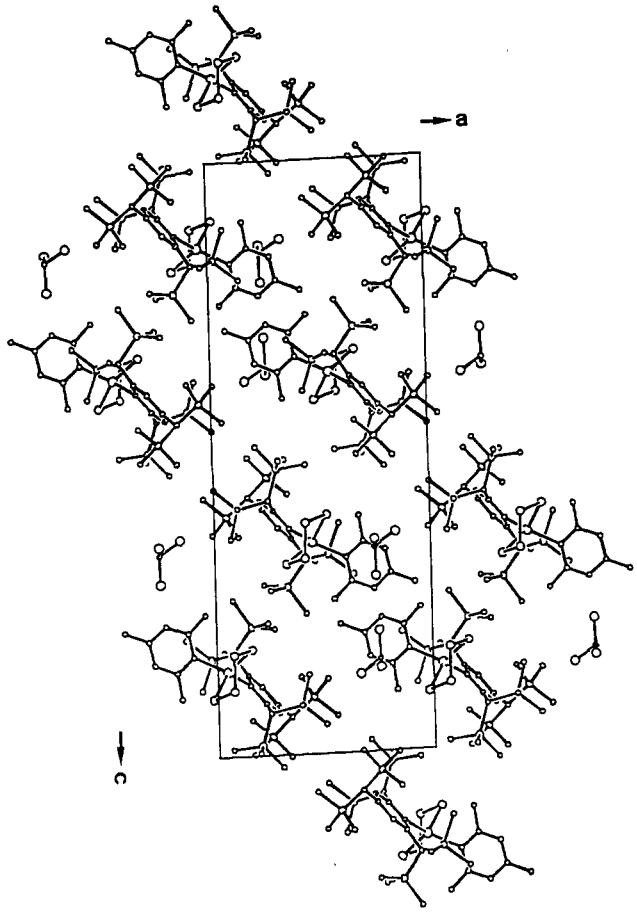


Figure 3. Packing diagram of **7b** solvated with chloroform (from *b* axis).

we have carried out ab initio calculations for the heat of reaction of the following two reactions (eqs 1 and 2) with

$$H_2Si + S_n \rightarrow H_2SiS_n \quad (1)$$

$$H_2Si + nS \rightarrow H_2SiS_n \quad (2)$$

a silicon analog H_2SiS_n as a model (Table IV).[15] As can be seen from Table IV, the values of the heat of reaction for the both reactions gradually increase as n increases, indicating that $n = 4$ (five-membered ring) is not a magic number for special thermodynamic stabilization. The reason for the isolation of the five-membered polychalcogenides, therefore, is probably that the steric repulsion between the two bulky aryl groups widens the angles C(1)–Sn(1)–C(2) (120.3° for **7b** and 119.7° for **8b**) and hence narrows the angles Y(1)–Sn(1)–Y(4) (Y = S or Se; 95.4° for **7b** and 99.1° for **8b**) (see Table III), thus making a five-membered ring preferable to the other rings from the conformational point of view.

(15) Geometries were fully optimized at the Hartree–Fock (HF) level with the 3-21G* basis set using the GAUSSIAN 90 program. Energies were calculated with the larger 6-31G* basis set using the Møller–Plesset perturbation method up to second order (MP2). 3-21G*: Pietro, W. J.; Francl, M. M.; Hehre, W. J.; DeFrees, D. J.; Pople, J. A.; Binkley, J. S. *J. Am. Chem. Soc.* **1982**, *104*, 5039. 6-31G*: Francl, M. M.; Pietro, W. J.; Hehre, W. J.; Binkley, J. S.; Gordon, M. S.; DeFrees, D. J.; Pople, J. A. *J. Chem. Phys.* **1982**, *77*, 3654. MP2: Pople, J. A.; Binkley, J. S.; Seeger, R. *Int. J. Quantum Chem. Symp.* **1976**, *10*, 1. GAUSSIAN 90: Frisch, M. J.; Head-Gordon, M.; Trucks, G. W.; Foresman, J. B.; Schlegel, H. B.; Raghavachari, K.; Robb, M.; Binkley, J. S.; Gonzalez, C.; DeFrees, D. J.; Fox, D. J.; Whiteside, R. A.; Seeger, R.; Melius, C. F.; Baker, J.; Martin, R. L.; Kahn, L. R.; Stewart, J. J. P.; Topiol, S.; Pople, J. A. Gaussian, Inc., Pittsburgh, USA.

Table III. Selected Bond Lengths, Bond Angles, and Torsion Angles for 7b and 8b[a]

7b		8b	
	A. Bond Lengths (Å)		
Sn(1)–S(1)	2.438(3)	Sn(1)–Se(4)	2.549(2)
S(1)–S(2)	2.050(4)	Se(4)–Se(3)	2.311(3)
S(2)–S(3)	2.036(5)	Se(3)–Se(2)	2.338(4)
S(3)–S(4)	2.048(3)	Se(2)–Se(1)	2.294(3)
S(4)–Sn(1)	2.481(2)	Se(1)–Sn(1)	2.603(2)
Sn(1)–C(1)	2.164(6)	Sn(1)–C(1)	2.18(1)
Sn(1)–C(2)	2.160(7)	Sn(1)–C(2)	2.16(1)
	B. Bond Angles (deg)		
S(1)–Sn(1)–S(4)	95.4(1)	Se(1)–Sn(1)–Se(4)	99.1(1)
Sn(1)–S(1)–S(2)	98.5(1)	Sn(1)–Se(4)–Se(3)	95.3(1)
S(1)–S(2)–S(3)	100.6(2)	Se(4)–Se(3)–Se(2)	96.5(1)
S(2)–S(3)–S(4)	102.6(2)	Se(3)–Se(2)–Se(1)	99.0(1)
S(3)–S(4)–Sn(1)	100.9(2)	Se(2)–Se(1)–Sn(1)	101.3(1)
C(1)–Sn(1)–S(1)	106.2(2)	C(1)–Sn(1)–Se(4)	106.4(3)
C(1)–Sn(1)–S(4)	119.2(2)	C(1)–Sn(1)–Se(1)	118.2(3)
C(2)–Sn(1)–S(1)	117.2(2)	C(2)–Sn(1)–Se(4)	115.0(3)
C(2)–Sn(1)–S(4)	96.2(2)	C(2)–Sn(1)–Se(1)	96.7(3)
C(1)–Sn(1)–C(2)	120.3(2)	C(1)–Sn(1)–C(2)	119.7(4)
	C. Torsion Angles[b] (deg)		
Sn(1)–S(1)–S(2)–S(3)	–56.7(2)	Sn(1)–Se(4)–Se(3)–Se(2)	63.0(1)
S(1)–S(2)–S(3)–S(4)	68.1(2)	Se(4)–Se(3)–Se(2)–Se(1)	–68.6(1)
S(2)–S(3)–S(4)–Sn(1)	–43.4(2)	Se(3)–Se(2)–Se(1)–Sn(1)	40.4(1)
S(3)–S(4)–Sn(1)–S(1)	8.9(1)	Se(4)–Sn(1)–Se(1)–Se(2)	–2.7(1)
S(4)–Sn(1)–S(1)–S(2)	27.3(1)	Se(3)–Se(4)–Sn(1)–Se(1)	–36.0(1)
C(1)–Sn(1)–S(1)–S(2)	149.8(2)	C(1)–Sn(1)–Se(4)–Se(3)	–159.2(3)
C(2)–Sn(1)–S(1)–S(2)	–72.5(2)	C(2)–Sn(1)–Se(4)–Se(3)	65.8(4)
C(1)–Sn(1)–S(4)–S(3)	–103.1(2)	C(1)–Sn(1)–Se(1)–Se(2)	111.5(3)
C(2)–Sn(1)–S(4)–S(3)	127.0(2)	C(2)–Sn(1)–Se(1)–Se(2)	–119.5(3)

[a] Atom numbering of the chalcogen atoms for **8b** is reversed from that of **7b**. [b] Clockwise rotation based on the atom numbering sequence is given as a positive value.

Conclusion

The first cyclic polychalcogenides of typical metal elements, $Tb(R)SnY_4$ (Y = S, Se), were synthesized in the present work by direct chalcogenation of hydrides $Tb(R)SnH_2$ or by lithiation of hydrides $Tb(R)SnH_2$ or dichlorides $Tb(R)SnCl_2$ with t-BuLi followed by reactions with S_8 or Se. In previous preliminary papers we have also reported the synthesis of the corresponding silicon and germanium analogs $Tb(R)SiS_4$,[8a] $Tb(R)GeS_4$,[8a] and $Tb(R)GeSe_4$.[8c] Very recently, Steudel et al. also described the synthesis of Ph_2SiS_4 and Ph_2GeS_4 by the reaction of Cp_2TiS_2M (M = Si, Ge) with S_2Cl_2.[16] The tin chalcogenides described in the present paper as well as the corresponding Si and Ge analogs are thermally quite stable, whereas the Steudel's tetrasulfides are reportedly thermally unstable to decompose above –20 °C. The much higher stability of our chalcogenides is clearly due to the presence of a very bulky substituent, the Tb group, on the central metal which efficiently protects the metal–chalcogen bonds which are highly susceptible to hydrolysis. Although Steudel's methodology necessarily leads to the preparation of the tetrasulfides, our methodology should, in principle, produce polychalcogenides of various sizes. The formation of only tetrachalcogenides in our experiments and the ab initio calculations with H_2SiS_n as a model suggest that the two bulky substituents on the central metal play an important role in determining the ring size of the cyclic polychalcogenides probably by enlarging the bond angle of Tb–M–R (M = Si, Ge, Sn) and hence by narrowing the bond angle of Y–M–Y (Y = S, Se) so as to make a five-membered ring more preferable to rings of other sizes. Work toward the synthesis of the remaining group 14 tetrachalcogenides like $Tb(R)SiSe_4$ as well as $Tb(R)CY_4$ (Y = S, Se) is currently in progress.

(16) (a) Albertsen, J.; Steudel, R. *Phosphorus, Sulfur, and Silicon* **1992**, *65*, 165. (b) Steudel, R. *The Chemistry of Inorganic Ring Systems*; Steudel, R., Ed.; Elsevier: Amsterdam, 1992; p 233.

Table IV. Heat of Reaction (kcal mol^{-1}) for Reactions 1 and 2 (MP2/6-31G*//HF/3-21G*)

n	2	3	4	5	6
reaction 1	78.8	83.3	83.1	89.5	90.3
reaction 2	162.2	209.0	273.9	314.9	375.7

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 JAI gel 1H, and 2H, columns (Japan Analytical Industry) with chloroform as solvent. Dry column chromatography (DCC) was performed with ISN silica DCC 60A. Preparative thin-layer chromatography was carried out with Merck Kieselgel 60 PF254 Art. 7747. The ^{1}H NMR (500 MHz) and ^{13}C NMR spectra (125 MHz) were measured in $CDCl_3$ and C_6D_6 with a Brucker AM-500 spectrometer using $CHCl_3$ or C_6H_6 as an internal standard.

Preparation of Trichloro{2,4,6-tris[bis(trimethylsilyl)-methyl]phenyl}stannane (2). To a solution of 1-bromo-2,4,6-tris[bis(trimethylsilyl)methyl]benzene[9a] (TbBr) (5.0 g, 7.52 mmol) in THF (80 mL) was added t-BuLi (8.7 mL, 2 M in pentane, 17.4 mmol) at –78 °C. After the solution was stirred at the same temperature for 10 min, $SnCl_4$ (1.1 mL, 9.5 mmol) was added at –78 °C. The solution was stirred for 10 h, during which time it was warmed to room temperature. After removal of the solvent, hexane was added to the residue to precipitate inorganic salts, and the filtrate, after evaporation of hexane, was purified by sublimation (200 °C, 0.04 mmHg) to afford **2** (3.3 g, 54%) as a white solid: ^{1}H NMR ($CDCl_3$) δ 0.04 (s, 18 H), 0.07 (br s, 36 H), 1.35 (s, 1 H), 2.02 (br s, 1 H), 2.05 (br s, 1 H), 6.38 (br s, 1 H), 6.49 (br s, 1 H); ^{13}C NMR ($CDCl_3$) δ 0.73 (q), 0.90 (q), 1.18 (br q), 30.67 (d), 33.50 (br d), 33.89 (br d), 121.84 (d), 126.70 (d), 134.67 (s), 146.51 (s), 151.59 (br s), 151.77 (br s).

Preparation of Dihydro(mesityl){2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}stannane (4b). (a) To a solution of **2** (1.0 g, 1.29 mmol) in THF (20 mL) was added a THF solution (2 mL) of MesMgBr (Mes = mesityl) prepared from MesBr (0.17 mL, 1.0 mmol) and Mg (25 mg, 1.0 mmol) at room temperature, and the mixture was heated under reflux for 10 h. After the reaction solution was cooled to room temperature, $LiAlH_4$ (150 mg, 3.89 mmol) was added and the mixture was stirred for 3 h. The reaction was quenched with ethyl acetate, and after removal of the solvent, hexane was added to the residue to precipitate inorganic salts. The resulting filtrate was subjected to DCC (hexane) to afford **4b** (585 mg, 57%) as a white solid. (b) Similarly, the reaction of **2** (1.0 g, 1.29 mmol) with MesMgBr (4.4 mL, 0.62 M in THF, 2.71 mmol) gave **4b** (88 mg, 9%) and hydrodimesityl{2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}stannane (273 mg, 23%) as white crystals. $Tb(Mes)_2SnH$ was recrystallized from ethanol. **4b**: mp 146–148 °C dec; ^{1}H NMR (C_6D_6) δ 0.13 (br s, 18 H), 0.14 (br s, 18 H), 0.15 (s, 18 H), 1.44 (s, 1 H), 2.00 (br s, 1 H), 2.12 (s, 1 H), 2.19 (s, 3 H), 2.51 (s, 6 H), 6.07 (s, 2 H), 6.54 (br s, 1 H), 6.68 (s, 1 H), 6.79 (s, 2 H); ^{13}C NMR (C_6D_6) δ 0.59 (q), 0.96 (q), 1.13 (q), 21.08 (q), 27.15 (q), 30.61 (d), 32.84 (d × 2), 122.10 (d), 126.86 (d), 128.32 (d), 134.32 (s), 137.15 (s), 138.87 (s), 143.98 (s), 144.45 (s), 152.02 (s), 152.07 (s).

Hydrodimesityl{2,4,6-tris[bis(trimethylsilyl)-methyl]phenyl}stannane: mp 190–195 °C dec; ^{1}H NMR ($CDCl_3$) δ –0.11 (s, 18 H), –0.08 (s, 18 H), 0.06 (s, 18 H), 1.31 (s, 1 H), 1.75 (br s, 1 H), 1.77 (br s, 1 H), 2.23 (s, 6 H), 2.40 (s, 12 H), 6.32 (s, 1 H), 6.45 (s, 1 H), 6.80 (s, 1 H), 6.81 (s, 4 H); ^{13}C NMR ($CDCl_3$) δ 0.78 (q), 1.10 (q), 1.50 (q), 20.93 (q), 27.38 (q), 30.11

(d × 2), 30.78 (d), 122.13 (d), 127.01 (d), 128.15 (d), 136.63 (s), 138.16 (s), 139.55 (s), 143.41 (s), 144.61 (s), 151.79 (s), 151.95 (s). Anal. Calcd for $C_{45}H_{82}Si_6Sn \cdot {}^1/_2H_2O$: C, 58.79; H, 9.10. Found: C, 58.67; H, 8.68.

Preparation of Dihydro(phenyl){2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}stannane (4a). By using the same procedure as above, the reaction of **2** (2.0 g, 2.58 mmol) with PhMgBr (3.2 mL, 0.8 M in THF, 2.58 mmol) gave **4a** (757 mg, 39%) and hydrodiphenyl{2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}stannane (21 mg, 1%) as white crystals. $TbPh_2SnH$ was recrystallized from ethanol. **4a**: mp 112–114 °C; ^{1}H NMR (C_6D_6) δ 0.14 (br s, 36 H), 0.15 (s, 18 H), 1.45 (s, 1 H), 2.11 (s, 2 H), 6.29 (s, 2 H), 6.57 (br s, 1 H), 6.68 (br s, 1 H), 7.15 (m, 3 H), 7.71 (m, 2 H); ^{13}C NMR (C_6D_6) δ 0.66 (q), 0.86 (q), 0.98 (q), 30.62 (d), 33.29 (d), 33.69 (d), 121.78 (d), 126.53 (d), 129.07 (d), 129.09 (d), 133.85 (s), 138.17 (d), 139.14 (s), 144.59 (s), 152.08 (s), 152.21 (s). **Hydrodiphenyl{2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}stannane**: mp 140–142 °C; ^{1}H NMR ($CDCl_3$) δ −0.12 (br s, 18 H), −0.10 (br s, 18 H), 0.04 (s, 18 H), 1.31 (s, 1 H), 1.91 (br s, 1 H), 1.92 (br s, 1 H), 6.32 (s, 1 H), 6.45 (s, 1 H), 6.79 (s, 1 H), 7.30 (m, 6 H), 7.63 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 0.46 (q), 0.70 (q), 0.84 (q), 30.25 (d), 31.55 (d), 31.99 (d), 121.68 (d), 126.55 (d), 128.55 (d), 128.63 (d), 133.55 (s), 137.65 (d), 142.10 (s), 144.27 (s), 151.95 (s), 152.07 (s). Anal. Calcd for $C_{39}H_{70}Si_6Sn \cdot H_2O$: C, 55.48; H, 8.60. Found: C, 55.05; H, 8.33.

Preparation of Dihydro(2,4,6-triisopropylphenyl){2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}stannane (4c). To a solution of TbBr (5.0 g, 7.52 mmol) in THF (80 mL) was added t-BuLi (9.6 mL, 1.81 M in pentane, 17.4 mmol) at −78 °C. After the reaction mixture was stirred at the same temperature for 10 min, $SnCl_4$ (1.1 mL, 9.5 mmol) was added at −78 °C. The solution was stirred for 10 h, 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 (80 mL). To this solution was added at room temperature a solution of TipMgBr (Tip = 2,4,6-triisopropylphenyl) prepared from TipBr (1.8 g, 6.4 mmol) and Mg (0.16 g, 6.7 mmol) in THF (12.5 mL), and the mixture was heated under reflux for 10 h. After the reaction mixture was cooled to room temperature, hexane was added to precipitate inorganic salts, and the resulting mixture was chromatographed (silica gel, hexane) to afford dichlorostannane **3c** (2.7 g, 30%) as a white solid. **3c** (500 mg, 0.54 mmol) was added to the suspension of $LiAlH_4$ (50 mg, 1.32 mmol) in THF (10 mL) and the mixture was stirred for 3 h at room temperature and worked up as above to afford **4c** (357 mg, 77%) as a white solid. **3c**: mp 190–193 °C; ^{1}H NMR ($CDCl_3$) δ 0.01 (s, 18 H), 0.05 (s, 18 H), 0.06 (s, 18 H), 1.22 (d, J = 6.9 Hz, 6 H), 1.32 (d, J = 6.5 Hz, 12 H), 1.35 (s, 1 H), 2.00 (s, 1 H), 2.25 (s, 1 H), 2.87 (sept, J = 6.9 Hz, 1 H), 3.21 (sept, J = 6.5 Hz, 2 H), 6.33 (s, 1 H), 6.48 (s, 1 H), 7.08 (s, 2 H); ^{13}C NMR ($CDCl_3$) δ 0.81 (q), 1.04 (q), 1.27 (q), 23.83 (q), 25.89 (q), 29.71 (d), 30.71 (d), 31.46 (d), 34.29 (d), 37.16 (d), 122.90 (d), 123.01 (d), 127.75 (d), 138.12 (s), 140.87 (s), 146.46 (s), 150.71 (s), 151.07 (s), 152.11 (s), 154.19 (s). Anal. Calcd for $C_{42}H_{82}Cl_2Si_6Sn \cdot H_2O$: C, 52.37; H, 8.79; Cl, 7.36. Found: C, 52.60; H, 8.99; Cl, 7.31. **4c**: mp 146–148 °C; ^{1}H NMR (C_6D_6) δ 0.13 (s, 18 H), 0.16 (s, 18 H), 0.19 (s, 18 H), 1.23 (d, J = 6.9 Hz, 6 H), 1.40 (d, J = 6.6 Hz, 12 H), 1.44 (s, 1 H), 2.01 (s, 1 H), 2.29 (s, 1 H), 2.80 (sept, J = 6.9 Hz, 1 H), 3.31 (sept, J = 6.6 Hz, 2 H), 6.20 (s, 2 H), 6.55 (s, 1 H), 6.70 (s, 1 H), 7.16 (s, 2 H); ^{13}C NMR (C_6D_6) δ 1.00 (q), 1.21 (q), 1.27 (q) 24.29 (q), 25.22 (q), 30.64 (d), 33.13 (d × 2), 34.84 (d), 37.45 (d), 121.16 (d), 122.16 (d), 127.00 (d), 135.68 (s), 137.14 (s), 143.83 (s), 150.55 (s), 151.76 (s), 151.88 (s), 155.45 (s).

Preparation of Dichloro(mesityl){2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}stannane (3b). **4b** (200 mg, 0.25 mmol) was dissolved in CCl_4 (20 mL) and the solution was stirred at room temperature for 10 h. Removal of the solvent afforded **3b** (218 mg, 100%) as a white solid, which was recrystallized from ethanol: mp 213–216 °C; ^{1}H NMR ($CDCl_3$) δ 0.00 (s, 18 H), 0.03 (s, 18 H), 0.05 (s, 18 H), 1.36 (s, 1 H), 2.03 (s, 1 H), 2.20 (s, 1 H), 2.27 (s, 3 H), 2.61 (s, 6 H), 6.36 (s, 1 H), 6.49 (s, 1 H), 6.90 (s, 2 H); ^{13}C NMR ($CDCl_3$) δ 0.67 (q), 0.75 (q), 0.95 (q), 21.03 (q), 26.25 (q), 30.87 (d), 31.18 (d), 31.43 (d), 122.77 (d), 127.45 (d), 129.70 (d), 136.77 (s), 141.05 (s), 141.60 (s), 142.84 (s), 147.15 (s), 151.46 (s), 151.70 (s). Anal. Calcd for $C_{36}H_{70}Cl_2Si_6Sn \cdot H_2O$: C, 49.18; H, 8.26; Cl, 8.07. Found: C, 49.37; H, 7.98; Cl, 8.20.

Preparation of Dichloro(phenyl){2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}stannane (3a). By using the same procedure as for **3b**, **4a** (50 mg, 0.067 mmol) gave **3a** (54 mg, 100%) as white crystals, which were recrystallized from ethanol: mp 204–206 °C; ^{1}H NMR ($CDCl_3$) δ −0.03 (s, 18 H), 0.03 (s, 18 H), 0.05 (s, 18 H), 1.92 (s, 1 H), 2.00 (s, 1 H), 6.38 (s, 1 H), 6.52 (s, 1 H), 7.49 (m, 3 H), 7.78 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 0.39 (q), 0.58 (q), 0.67 (q), 31.04 (d), 32.46 (d), 32.98 (d), 122.42 (d), 127.11 (d), 129.59 (d), 130.73 (d), 134.62 (d), 135.22 (s), 146.43 (s), 147.90 (s), 151.38 (s), 151.96 (s). Anal. Calcd for $C_{33}H_{64}Cl_2Si_6Sn \cdot H_2O$: C, 47.35; H, 7.94; Cl, 8.47. Found: C, 47.24; H, 8.29; Cl, 8.04.

Preparation of Dichloro(2,4,6-triisopropylphenyl){2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}stannane (3c). In a manner similar to that for **3b**, **4c** (200 mg, 0.23 mmol) gave **3c** (179 mg, 83%), which was recrystallized from ethanol.

Preparation of Dibromo(mesityl){2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}stannane. To an ether solution (20 mL) of **4b** (200 mg, 0.25 mmol) was added bromine (81 mg, 0.51 mmol) at room temperature, and the solution was stirred for 10 h. Removal of the solvent afforded the dibromostannane (240 mg, 100%) as white crystals, which were recrystallized from ethanol: mp 209–210 °C; ^{1}H NMR ($CDCl_3$) δ 0.01 (s, 18 H), 0.05 (s, 18 H), 0.06 (s, 18 H), 1.36 (s, 1 H), 2.18 (s, 1 H), 2.27 (s, 3 H), 2.36 (s, 1 H), 2.66 (s, 6 H), 6.34 (s, 1 H), 6.47 (s, 1 H), 6.88 (s, 2 H); ^{13}C NMR ($CDCl_3$) δ 0.77 (q), 0.87 (q), 1.14 (q), 21.00 (q), 26.63 (q), 30.81 (d), 30.97 (d), 31.25 (d), 122.87 (d), 127.57 (d), 135.82 (s), 140.84 (s), 141.34 (s), 142.63 (s), 146.87 (s), 151.22 (s), 151.49 (s). Anal. Calcd for $C_{36}H_{70}Br_2Si_6Sn \cdot H_2O$: C, 44.67; H, 7.50; Br, 16.51. Found: C, 44.89; H, 7.37; Br, 16.09.

Reaction of Dihydrostannane 4a with Sulfur. (a) A solution of **4a** (200 mg, 0.27 mmol) and sulfur (343 mg, 1.34 mmol) in THF (20 mL) was heated under reflux for 10 h. After removal of the solvent, the crude reaction products were chromatographed (GPLC) to afford an inseparable mixture of cyclic stannapolysulfides (166 mg) as a pale yellow solid. To a THF solution of this mixture was added hexamethylphosphorous triamide (HMPT) (0.10 mL, 0.57 mmol) at −78 °C, and the mixture was warmed to room temperature. The reaction products were subjected to DCC (hexane) to afford 2,4-diphenyl-2,4-bis{2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}-1,3,2,4-dithiadistannetane (**5**) (22 mg, 11%) and 2,4-diphenyl-2,4-bis{2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}-1,3,2,4-dithiadistannetane (**6**) (69 mg, 33%). (b) A mixture of **4a** (100 mg, 0.13 mmol) and sulfur (1 g) was heated at 120–130 °C for 3 h under a stream of N_2. The mixture was cooled to room temperature and recrystallized from benzene several times to remove excess sulfur, and the residue was chromatographed (GPLC) to afford a fraction (63.5 mg) considered to contain two Tb(Ph)Sn units, which was further purified with preparative thin layer chromatography to afford **5** (25 mg, 23%) and **6** (20 mg, 18%) as white crystals. The configuration (cis vs trans) of **5** and **6** could not be determined by spectroscopic data. **5**: mp >300 °C; ^{1}H NMR ($CDCl_3$) δ −0.07 (s, 72 H), 0.00 (s, 36 H), 1.28 (s, 2 H), 2.05 (s, 2 H), 2.09 (s, 2 H), 6.24 (s, 2 H), 6.36 (s, 2 H), 7.30 (m, 6 H), 7.79 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 0.57 (q), 0.67 (q), 0.86 (q), 30.39 (d), 31.82 (d), 32.26 (d), 122.07 (d), 126.82 (d), 128.38 (d), 128.97 (d), 135.48 (d), 135.66 (s), 145.33 (s), 147.10 (s), 151.45 (s), 151.35 (s). Anal. Calcd for $C_{66}H_{128}S_2Si_{12}Sn_2 \cdot 2H_2O$: C, 49.65; H, 8.33; S, 4.02. Found: C, 49.08; H, 8.44; S, 4.32. **6**: mp >300 °C; ^{1}H NMR ($CDCl_3$) δ 0.00 (s, 72 H), 0.01 (s, 36 H), 1.30 (s, 2 H), 1.85 (s, 2 H), 1.96 (s, 2 H), 6.27 (s, 2 H), 6.38 (s, 2 H), 6.98 (m, 6 H), 7.08 (m, 2 H), 7.46 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 0.70 (q), 0.76 (q), 1.04 (q), 30.47 (d), 31.91 (d), 32.66 (d), 122.07 (d), 126.92 (d), 127.92 (d), 128.47 (d), 135.23 (d), 135.49 (s), 145.49 (s), 146.05 (s), 151.46 (s × 2). Anal.

Calcd for $C_{66}H_{128}S_2Si_{12}Sn_2 \cdot 2H_2O$: C, 49.65; H, 8.33; S, 4.02. Found: C, 49.39; H, 8.01; S, 4.54.

Preparation of 5-Mesityl-5-{2,4,6-tris[bis(trimethylsilyl)-methyl]phenyl}-1,2,3,4,5-tetrathiastannolane (7b). (a) A THF (30 mL) solution of dihydrostannane **4b** (200 mg, 0.25 mmol) and sulfur (325 mg, 1.27 mmol) was heated under reflux for 18 h and then cooled to room temperature. After removal of the solvent, the residue was chromatographed (GPLC) to afford **7b** (213 mg, 92%), which was recrystallized from ethanol–chloroform to give pale yellow crystals. (b) To a THF solution (5 mL) of dichlorostannane **3b** (50 mg, 0.058 mmol) was added t-BuLi (0.08 mL, 1.68 M in pentane, 0.128 mmol) at −78 °C and the solution was stirred at −78 °C for 30 min. Then sulfur (74 mg, 0.29 mmol) was added at −78 °C in one portion. The solution was stirred for 10 h while the temperature was raised to room temperature. After removal of the solvent, the residue was chromatographed (DCC, hexane) to afford **7b** (32 mg, 60%). (c) By using the same procedure as b, the reaction of **4b** (100 mg, 0.13 mmol) with t-BuLi (0.07 mL, 1.70 M in pentane, 0.13 mmol) and sulfur (100 mg, 0.39 mmol) afforded **7b** (70 mg, 63%): mp 209–211 °C; ^{1}H NMR ($CDCl_3$) δ −0.02 (s, 36 H), 0.04 (s, 18 H), 1.34 (s, 1 H), 1.73 (s, 1 H), 1.83 (s, 1 H), 2.22 (s, 3 H), 2.52 (s, 6 H), 6.39 (s, 1 H), 6.50 (s, 1 H), 6.85 (s, 2 H); ^{13}C NMR ($CDCl_3$) δ 0.74 (q), 0.93 (q), 1.16 (q), 20.93 (q), 26.95 (q), 30.79 (q), 32.05 (d), 32.56 (d), 122.64 (d), 127.53 (d), 129.29 (d), 136.62 (s), 140.10 (s), 142.05 (s), 144.24 (s), 146.36 (s), 152.03 (s × 2). Anal. Calcd for $C_{36}H_{70}S_4Si_6Sn$: C, 47.08; H, 7.68; S, 13.97. Found: C, 46.78; H, 7.56; S, 14.13.

Preparation of 5-(2,4,6-Triisopropylphenyl)-5-{2,4,6-tris-[bis(trimethylsilyl)methyl]phenyl}-1,2,3,4,5-tetrathiastannolane (7c). In a manner similar to that for **7b**, the reaction of **4c** (100 mg, 0.11 mmol) with sulfur (150 mg, 0.57 mmol) (procedure a), that of **3c** (1 g, 1.1 mmol) with t-BuLi (1.43 mL, 1.48 M in pentane, 2.12 mmol) and sulfur (960 mg, 3.8 mmol) (procedure b), and that of **4c** (60 mg, 0.069 mmol) with t-BuLi (0.04 mL, 1.70 M in pentane, 0.069 mmol) and sulfur (90 mg, 0.34 mmol) (procedure c) gave **7c** ((a) 70 mg, 61%; (b) 881 mg, 83%; (c) 40 mg, 58%) as pale yellow crystals: mp 246–248 °C; ^{1}H NMR ($CDCl_3$) δ −0.01 (s, 18 H), 0.01 (s, 18 H), 0.03 (s, 18 H), 1.18 (br s, 12 H), 1.19 (d, J = 6.9 Hz, 6 H), 1.32 (s, 1 H), 1.68 (s, 1 H), 1.72 (s, 1 H), 2.83 (sept, J = 6.9 Hz, 1 H), 3.31 (br s, 2 H), 6.36 (s, 1 H), 6.50 (s, 1 H), 7.04 (s, 2 H); ^{13}C NMR ($CDCl_3$) δ 0.83 (q), 1.57 (q), 1.63 (q), 23.69 (q × 2), 30.70 (d), 31.58 (d), 32.25 (d), 34.30 (d), 39.98 (d), 122.84 (d × 2), 128.15 (d), 138.51 (s), 143.33 (s), 146.66 (s), 151.01 (s), 151.37 (s), 151.70 (s), 153.43 (s). Anal. Calcd for $C_{42}H_{82}S_4Si_6Sn \cdot H_2O$: C, 49.42; H, 8.30; S, 12.57. Found: C, 49.37; H, 8.19; S, 12.97.

Preparation of 5-Mesityl-5-{2,4,6-tris[bis(trimethylsilyl)-methyl]phenyl}-1,2,3,4,5-tetraselenastannolane (8b). (a) Immediately after THF (10 mL) was added to a mixture of dihydrostannane **4b** (100 mg, 0.13 mmol) and selenium metal (100 mg, 1.3 mmol), 1,8-diazabicyclo[5.4.0]-7-undecene (DBU) (19 μL, 0.13 mmol) was added at room temperature in one portion. The suspension was stirred for 30 min, and the residue, obtained by filtration of excess selenium, was chromatographed (DCC, hexane) to afford a main fraction (67 mg), which was further purified by GPLC to afford **8b** (49 mg, 35%) as orange crystals. **8b** was recrystallized from ethanol–chloroform. (b) To a THF (10 mL) solution of dichlorostannane **3b** (100 mg, 0.12 mmol) was added t-BuLi (0.14 mL, 1.80 M in pentane, 0.26 mmol) at −78 °C, and the solution was stirred at −78 °C for 30 min. Then elemental selenium (100 mg, 1.2 mnol) was added at −78 °C in one portion and the solution was stirred for 10 h, during which time it was warmed to room temperature. After removal of excess selenium and the solvent, the residue was chromatographed (DCC, hexane) to afford the first fraction (**9**, 12 mg, 11%) as orange crystals and the second fraction (57 mg), which was further chromatographed (GPLC) to afford **8b** (34 mg, 27%), as orange crystals. **8b** and **9** were recrystallized from ethanol–chloroform. Similarly, the reaction of **4b** (100 mg, 0.13 mmol) with t-BuLi (0.07 mL, 1.76 M in pentane, 0.12 mmol) and selenium (100 mg, 1.3 mmol) afforded **8b** (46 mg, 33%) and **9** (11 mg, 9%). **8b**: mp 238–240 °C; ^{1}H NMR ($CDCl_3$) δ −0.01 (s, 36 H), 0.05 (s, 18 H), 1.33 (s, 1 H), 1.91 (s, 1 H), 2.01 (s, 1 H), 2.21 (s, 3 H), 2.56 (s, 6 H), 6.39 (s, 1 H), 6.50 (s, 1 H), 6.62 (s, 2 H); ^{13}C NMR ($CDCl_3$) δ 0.77 (q), 1.28 (q), 1.54 (q), 20.98 (q), 27.35 (q), 30.77 (d), 32.18 (d), 32.67 (d), 122.83 (d), 127.75 (d), 129.42 (d), 138.86 (s), 139.69 (s), 142.05 (s), 145.83 (s), 145.88 (s), 151.91 (s), 151.95 (s). Anal. Calcd for $C_{42}H_{82}Se_4Si_6Sn$: C, 39.09; H, 6.38; Se, 28.56. Found: C, 39.20; H, 6.29; Se, 28.85.

Preparation of 5-(2,4,6-Triisopropylphenyl)-5-{2,4,6-tris-[bis(trimethylsilyl)methyl]phenyl}-1,2,3,4,5-tetraselenastannolane (8c). By using the same procedure as that for **8b** (procedure a) except that the reaction time was changed to 10 h, the reaction of **4c** (100 mg, 0.11 mmol) with selenium (90 mg, 1.1 mmol) and DBU (17 μL, 0.11 mmol) gave **8c** (122 mg, 89%) as orange crystals. Similarly, **8c** (procedure b, 644 mg, 73%; procedure c, 34 mg, 25%) was obtained from **3c** (699 mg, 0.74 mmol), t-BuLi (1.1 mL, 1.50 M in pentane, 1.63 mmol), and selenium (600 mg, 7.4 mmol) (procedure b) and from **4c** (100 mg, 0.11 mmol), t-BuLi (0.07 mL, 1.70 M in pentane, 0.12 mmol), and selenium (90 mg, 1.1 mmol) (procedure c): mp 220–222 °C; ^{1}H NMR ($CDCl_3$) δ −0.003 (s, 18 H), 0.009 (s, 18 H), 0.019 (s, 18 H), 1.16 (br d, J = 5 Hz, 12 H), 1.18 (d, J = 7 Hz, 6 H), 1.30 (s, 1 H), 1.80 (s, 1 H), 1.83 (s, 1 H), 2.81 (sept, J = 7 Hz, 1 H), 3.52 (br sept, J = 5 Hz, 2 H), 6.36 (s, 1 H), 6.46 (s, 1 H), 7.01 (s, 2 H); ^{13}C NMR ($CDCl_3$) δ 0.86 (q), 1.92 (q), 2.21 (q), 23.91 (q), 28.60 (br q), 30.61 (d), 31.48 (d), 32.30 (d), 34.25 (d), 39.63 (d), 122.82 (d), 122.89 (d), 128.28 (d), 140.17 (s), 144.75 (s), 145.11 (s), 150.46 (s), 151.54 (s), 153.30 (s). Anal. Calcd for $C_{42}H_{82}Se_4Si_6Sn$: C, 42.39; H, 6.94; Se, 26.54. Found: C, 42.19; H, 6.77; Se, 26.41.

Reaction of Tetraselenastannolane 8b with DBU. A THF solution (5 mL) of **8b** (40 mg, 0.036 mmol) and DBU (5 μL, 0.036 mmol) was stirred at room temperature for 10 h. After filtration of precipitated selenium and removal of the solvent, the residue was chromatographed (PTLC, hexane) to afford **9** (9.8 mg, 29%) and **10** (3.7 mg, 11%), both being orange crystals. The configuration (cis vs trans) of **9** and **10** was determined by their ^{1}H NMR spectra. **9**: mp >300 °C; ^{1}H NMR ($CDCl_3$) δ −0.39 (s, 18 H), −0.37 (s, 18 H), 0.00 (s, 36 H), 0.12 (s, 18 H), 0.14 (s, 18 H), 1.25 (s, 2 H), 2.17 (s, 6 H), 2.41 (br s, 4 H), 2.66 (s, 12 H), 6.26 (s, 2 H), 6.38 (s, 2 H), 6.68 (s 4 H); ^{13}C NMR ($CDCl_3$) δ 0.14 (q), 0.42 (q), 0.69 (q), 0.94 (q), 1.82 (q), 2.02 (q), 20.86 (q), 25.32 (q), 30.28 (d), 31.86 (d), 32.20 (d), 122.72 (d), 127.51 (d), 128.97 (d), 138.62 (s), 140.20 (s), 143.10 (s), 143.23 (s), 144.29 (s), 150.99 (s), 151.20 (s). Anal. Calcd for $C_{72}H_{140}Se_3Si_{12}Sn_2$: C, 47.59; H, 7.77; Se, 13.03. Found: C, 47.08; H, 7.38; Se, 13.16. **10**: mp >300 °C; ^{1}H NMR ($CDCl_3$) δ −0.03 (s, 18 H), −0.02 (s, 18 H), 0.00 (s, 18 H), 0.02 (s, 18 H), 0.027 (s, 36 H), 1.29 (s, 2 H), 2.14 (s, 6 H), 2.26 (s, 2 H), 2.35 (br s, 12 H), 2.42 (s, 2 H), 6.32 (s, 2 H), 6.44 (s, 4 H), 6.46 (s, 4 H); ^{13}C NMR ($CDCl_3$) δ 0.82 (q), 0.85 (q), 1.02 (q), 1.21 (q), 1.41 (q), 1.53 (q), 1.70 (q), 20.88 (q), 25.74 (q), 26.08 (q), 30.35 (d), 32.04 (d), 32.40 (d), 122.66 (d), 127.63 (d), 128.40 (d), 138.24 (s), 139.32 (s), 141.94 (s), 142.95 (s), 144.51 (s), 151.27 (s), 151.48 (s). Anal. Calcd for $C_{72}H_{140}Se_3Si_{12}Sn_2$: C, 47.59; H, 7.77; Se, 13.03. Found: C, 47.85; H, 7.50; Se, 12.99.

Trapping of Intermediary Hydrostannyllithium 12. (a) To a THF solution (5 mL) of dichlorostannane **3c** (100 mg, 0.11 mmol) was added t-BuLi (0.14 mL, 1.46 M in pentane, 0.23 mmol) at −78 °C, and the mixture was stirred at −78 °C for 30 min. Then methyl iodide (60 μL, 1.1 mmol) was added at −78 °C to the reaction mixture, which was stirred for 10 h while being warmed to room temperature. After removal of the solvent, the residue was chromatographed (DCC, hexane) to afford **13c** (49 mg, 52%) as white crystals. Similarly, the reaction of **3b** (50 mg, 0.06 mmol), t-BuLi (0.07 mL, 1.76 M in pentane, 0.12 mmol), and methyl iodide (36 μL, 0.6 mmol) gave **13b** (30 mg, 64%) as white crystals. (b) In a similar manner except for use of equimolar t-BuLi, dihydrostannane **4b** (50 mg, 0.063 mmol) and **4c** (200 mg, 0.23 mmol) gave **13b** (16 mg, 32%) and **13c** (66 mg, 32%) as white crystals, respectively. **13c** was recrystallized from ethanol. **13c**: mp 166–168 °C; ^{1}H NMR (C_6D_6) δ 0.05 (s, 9 H), 0.13 (s, 9 H), 0.16 (s, 9 H), 0.17 (s, 9 H), 0.23 (s, 9 H), 0.26 (s, 9 H), 0.91 (d, J = 2.9 Hz, 3 H), 1.24 (d, J = 6.9 Hz, 3 H), 1.25 (d, J = 6.9 Hz, 3 H), 1.35

(d, J = 6.5 Hz, 6 H), 1.39 (d, J = 6.5 Hz, 6 H), 1.45 (s, 1 H), 1.95 (s, 1 H), 2.11 (s, 1 H), 2.81 (sept, J = 6.9 Hz, 1 H), 3.31 (br s, 2 H), 6.39 (q, J = 2.9 Hz, 1 H), 6.53 (s, 1 H), 6.66 (s, 1 H), 7.16 (s, 2 H); ^{13}C NMR (C_6D_6) δ 0.59 (q), 0.98 (q), 1.08 (q), 1.23 (q), 1.42 (q), 1.72 (q), 24.23 (q), 24.34 (q), 25.59 (br q), 26.12 (br q), 30.55 (d), 31.47 (d), 31.71 (d), 34.80 (d), 37.39 (d), 121.34 (d), 122.37 (d), 127.39 (d), 136.32 (s), 140.07 (s), 143.66 (s), 150.05 (s), 151.84 (s × 2), 155.36 (s). Anal. Calcd for $C_{43}H_{86}Si_6Sn$: C, 58.00; H, 9.86. Found: C, 58.30; H, 9.86. **13b**: mp 170–172 °C; ^{1}H NMR (C_6D_6) δ 0.12 (br s, 9 H), 0.16 (br s, 9 H), 0.17 (s, 18 H), 0.18 (br s, 18 H), 0.76 (d, J = 2.7 Hz, 3 H), 1.45 (s, 1 H), 1.98 (s, 1 H), 2.10 (s, 1 H), 2.13 (s, 3 H), 2.52 (s, 6 H), 6.29 (q, J = 2.7 Hz, 1 H), 6.54 (s, 1 H), 6.67 (s, 1 H), 6.80 (s, 2 H); ^{13}C NMR (C_6D_6) δ −1.89 (q), 0.79 (q), 0.95 (q), 0.99 (q), 1.06 (q), 1.36 (q), 21.02 (q), 27.12 (q), 30.55 (d), 31.64 (d), 31.91 (d), 122.20 (d), 127.08 (d), 127.54 (d), 135.63 (s), 138.65 (s), 139.86 (s), 143.83 (s), 144.29 (s), 152.02 (s), 152.11 (s).

Crystal and Experimental Data for 7b and 8b.[17] **7b**: $C_{36}H_{70}SnS_4Si_6{\cdot}CHCl_3$, FW = 1037.9, crystal size (mm) 0.5 × 0.4 × 0.13, monoclinic space group $P2_1/n$, a = 12.305(3) Å, b = 13.187(1) Å, c = 33.739(8) Å, β = 91.39(1)°, V = 5473(2) Å^3, Z = 4, D_c = 1.260 g/cm^3, R = 0.059 (R_w = 0.067), $w = 1/(A|F_o|^2 + B|F_o| + C)$, A = 0.005 55, B = −0.492, C = 19.85. Data were collected through a capillary glass tube with Cu Kα radiation (λ = 1.5418 Å) on Enraf-Nonius CAD-4, μ = 79.46 cm^{-1}. 6370 unique reflections ($|F_o| > 3.0\sigma|F_o|$) were observed ($4° < 2\theta < 120°$). Empirical absorption correction was applied, and the structure was solved by direct methods (MULTAN 78)[18] using an SDP package and a program system UNICS III.[19] All hydrogen atoms were located by calculation. Refinement was performed by a full-matrix least-square method with 460 variable parameters (anisotropic thermal parameters for non-hydrogen atoms, where the positions and thermal parameters for hydrogen atoms were not refined). **8b**: $C_{36}H_{70}SnSe_4Si_6$, FW = 1105.99, crystal size (mm) 0.1 × 0.3 × 0.7, triclinic, space group $P\bar{1}$, a = 12.229(6) Å, b = 19.465(4) Å, c = 11.819(4) Å, α = 99.96(3)°, β = 114.07(3)°, γ = 80.49(3)°, V = 2516(2) Å^3, Z = 2, D_c = 2.920 g/cm^3, μ = 70.73 cm^{-1}. The intensity data ($2° \le \theta \le 60°$) were collected on a Rigaku AFC5R diffractometer with graphite-monochromated Mo Kα radiation (γ = 0.710 69 Å), and the structure was solved by direct methods.[20] All calculations were performed using TEXSAN[21] crystallographic software package of Molecular Structure Corporation. The non-hydrogen atoms were refined anisotropically, and all the hydrogen atoms were located by calculation. The final cycle of full-matrix least-squares refinement was based on 4029 observed reflections ($I > 3.00\sigma(I)$) and 424 variable parameters with R (R_w) = 0.064 (0.058).

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Supplementary Material Available: Tables listing atomic coordinates, temperature factors, bond lengths and angles, and torsion angles for **7b** and **8b** (45 pages). Ordering information is given on any current masthead page.

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(17) All the crystallographic data with tables of thermal and positional parameters for tetrathiastannolane **7b** have already been deposited as the supplementary material of the preliminary paper (ref 8a), while those for tetraselenastannolane **8b** have also been deposited at the Cambridge Crystallographic Data Centre (ref 8b).

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