

Synthesis and structures of polychalcogenadistannabicyclo[*k.l.m*]alkanes

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Abstract

Reaction of steric encumbered trichlorostannane with disodium sulfide or dilithium selenide gave 2,4-dimercapto-1,3,2,4-dithiadistannetane or tetraselenadistannabicyclo[2.1.1]hexane, respectively. Reactions of steric encumbered trihydrostannane with elemental chalcogens gave pentachalcogenadistannabicyclo[*k.l.m*]heptanes (*k* = 2 and 3). The two bridgehead tin atoms of the first polychalcogenadistannabicyclo[*k.l.m*]alkanes are concluded to have no significant bonding interaction, judging from the longer bond distances than those of the normal tin–tin single bonds.

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1. Introduction

Over the past decade much attention has been paid to the chemistry of cage-like compounds containing heavier Groups 14 and 16 elements from the standpoints of their unique structure and reactivity [1,2]. Some cage compounds such as double decker- and adamantane-type compounds of heavier Groups 14 and 16 elements have been synthesized and characterized [3–8]. Among cage-like compounds, the nature of the bridgehead bond of bicyclo[1.1.1]pentanes has been of considerable interest. According to theoretical studies, the type of H₂M₂Ch₃ [1.1.1]propellanes **1** (R = H; M = Si, Ge, Sn; Ch = O) is predicted to have a short non-bonded distance between the two bridgehead Group 14 atoms [9,10]. Although no reports on the synthesis of trioxadimetallabicyclo[1.1.1]pentanes of heavier Group 14 elements have so far appeared, trithia- and triselenad derivatives have been relatively well-investigated. Ando et al. reported the synthesis of trithia- and triselenadimetalbicyclo[1.1.1]pentanes **1** (R = tris(trimethylsilyl)methyl;

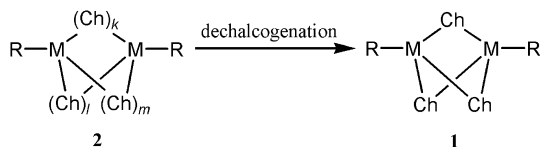
M = Si, Ge; Ch = S, Se) by the dechalcogenation of the corresponding polythia- and polyselena-dimetallabicyclo[*k.l.m*]alkanes **2** (R = tris(trimethylsilyl)methyl; M = Si, Ge; Ch = S, Se) (Scheme 1) [11]. As for tin analogues, however, neither trichalcogenadistannabicyclo[1.1.1]pentane derivative **1** (M = Sn) nor polychalcogenadistannabicyclo[*k.l.m*]alkanes **2** (M = Sn) has been reported [12]. We report herein the synthesis of novel tin-containing cage-like polychalcogenides, polythia- and polyselena-distannabicyclo[*k.l.m*]alkanes **2** and their structural properties.

2. Results and discussion

2.1. Synthesis of aryltrichloro- **4** and aryltrihydrostannanes **3**

Since some silicon derivatives of polythiabicyclo[1.1.1]pentane are moisture-sensitive even by the introduction of a bulky tris(trimethylsilyl)methyl group on the silicon atom [11], we chose a bulky *m*-terphenyl ligand, 2,6-bis(2,4,6-triisopropylphenyl)phenyl (denoted as Ar hereafter) group as an efficient steric protection group, which has been utilized for the kinetic stabilization of highly reactive species having a heavier Group 14 elements

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Scheme 1.

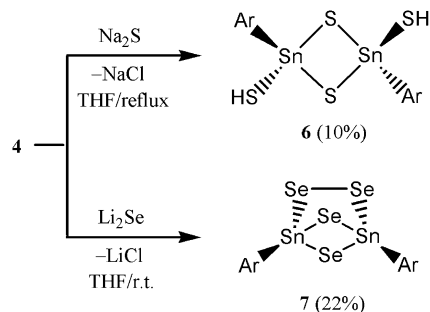
[13,14]. The starting compound, aryltrichlorostannane **4**, was prepared by the reaction of in situ-generated chlorostannylylene **5** [15] with carbon tetrachloride [16] (Scheme 2) in 45% yield. Reduction of aryltrichlorostannane **4** with LiAlH_4 in THF gave aryltrihydrostannane **3** in 83% yield.

2.2. Reactions of aryltrichlorostannane **4** with alkali chalcogenide

The most straightforward strategy for the synthesis of trichalcogenadistannabicyclo[1.1.1]pentanes is the reaction of trichlorostannane with alkali chalcogenide. Reaction of trichlorostannane **4** with disodium sulfide, however, gave dimercapto derivative **6** in 10% yield and the *trans* stereochemistry of **6** in the solid state was confirmed by X-ray diffraction analysis (Scheme 3). Thus, the third sulfur bridge could not arch between the two tin atoms. Although a main fraction contained monomeric products, judging from the retention time of gel permeation chromatography, no identifiable products were obtained from the monomeric fraction. On the contrary, reaction of **4** with dilithium selenide gave a novel cage compound, tetraselenadistannabicyclo[2.1.1]hexane **7**, in 22% yield (Scheme 3). The ^{77}Se NMR spectrum of **7** showed two signals at 174.2 and 275.7 ppm with an equal intensity, suggesting that the three selenium bridges should have one, one, and two selenium atoms, respectively, and the structure of **7** was finally established by X-ray diffraction analysis.

2.3. Reactions of aryltrihydrostannane **3** with elemental chalcogen

Reaction of trihydrometallanes of Group 14 elements with elemental chalcogen [17] is also one of the most promising methods for the synthesis of chalcogen-containing cage compounds. Treatment of **3** with an excess amount of elemental sulfur in toluene at 110 °C gave a complex mixture, containing a novel cage compound, 2,4,5,6,7-pentathia-1,3-distannabicyclo[3.1.1]heptane **8** (vide infra). After purification by gel permeation chromatography, the



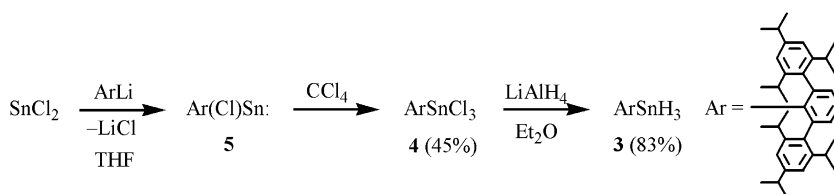
Scheme 3.

main fraction consisted of dimeric products, judging from its retention time of gel permeation chromatography. The ^{119}Sn NMR spectrum of the dimeric fraction in CDCl_3 showed signals at -31.7 (**6**), -30.0 , -9.6 , -9.2 , -7.2 , 29.8 (**8**), 49.2 and 110.0 ppm. Although the mixture might contain some polysulfides, their separation could not be achieved by column chromatography and preparative gel permeation chromatography. On the other hand, the reaction of **3** with elemental sulfur (3.8 equiv. as S) in the presence of triethylamine afforded **8** as yellow crystals stable under air in 71% yield (Scheme 4) [18]. Thus, the presence of a base remarkably affects the product distribution. The structure of **8** was determined by elemental analysis, NMR spectroscopy and X-ray diffraction analysis.

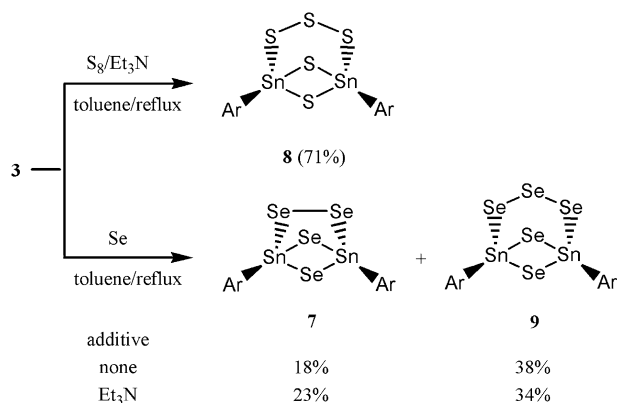
Reaction of trihydrostannane with selenium was also examined. Heating at reflux of a mixture of **3** and elemental selenium in toluene overnight gave two selenium-containing cage compounds, **7** and **9** in 18% and 38% yields, respectively, estimated by NMR spectroscopy. Recrystallization of the mixture from methanol gave **9**, the structure of which was determined by NMR spectroscopy, elemental analysis and X-ray diffraction analysis. Treatment of **3** with elemental selenium in the presence of triethylamine also gave **7** and **9** in 23% and 34% yields, respectively. Although the product distribution is slightly different from that in the absence of triethylamine, the presence of a base does not have a strong effect on the product distribution.

2.4. NMR spectroscopy

The ^{119}Sn chemical shifts of **6–9** (**6**: -31.7 [19], **7**: 240.5, **8**: 29.7, **9**: 262.0 ppm) are in the normal range for the compounds having a 1,3,2,4-dichalcogenadistannetane ring. The resonances due to the selenium atoms attached to the tin atom range from 174 to 276 ppm. The ^{119}Sn



Scheme 2.



Scheme 4.

NMR spectra of newly obtained chalcogen-containing compounds, **6–9**, showed signals accompanied with $J(\text{Sn}–\text{Sn})$ coupling constants, the largest of which is 779 Hz, suggesting no significant bonding interaction between the two tin atoms [20]. The $^1J(\text{Sn}–\text{Se})$ coupling constants of **7** and **9** range from 1060 to 1316 Hz, which are in the normal range for the compounds having a tin–selenium bond [21].

2.5. Molecular structures of the newly obtained chalcogen-containing compounds

All the molecular structures of the newly obtained chalcogen-containing cage compounds were confirmed by X-ray diffraction analysis. The dithiadistannetane ring of **6** is almost planar (see Fig. 1). The average angle between the four-membered ring and the Sn–C vectors is 144° , preventing steric repulsion of the two bulky aryl groups, while that between the four-membered ring and the out-of-plane Sn–S vectors is much narrower to be 113° . The average bond angle around the sulfur atoms in the four-membered ring is 85° , which is comparable to those of 1,3,2,4-dithiadistannetanes [22]. The non-bonded distances between the two tin atoms are longer than those of the corresponding single bonds (2.81 Å) [2].

The structures of **8** and **9** are similar (see Figs. 3 and 4). Although disorder around the trichalcogenide chains of **8** and **9** was found, appropriate refinement was achieved with the occupancies of the disordered chalcogenide chains of 60:40 for **8** and 50:50 for **9**. The 1,3,2,4-dichalcogenadistannetane ring of **8**, **7** and **9** is each found to be folded (see Figs. 2–4). The dihedral angle between the Sn1–S1–Sn2 and Sn1–S2–Sn2 planes in **8** is 148° , while those between the Sn1–Se1–Sn2 and Sn1–Se2–Sn2 and between Sn1–Se1–Sn1# and Sn1–Se1#–Sn1# in **7** and **9** are 155° and 149° , respectively. All the lengths of the Sn–Ch (Ch = S or Se) bonds in the four-membered rings of **7–9** are in the range of those reported for 1,3,2,4-dichalcogenadistannetane rings [2.38–2.49 and 2.55–2.59 Å for Ch = S and Se, respectively] [22]. The six-membered rings of **8** and **9** (Sn1–S3–S4–S5–Sn2–S1 and Sn1–Se2–Se3–Se4–Sn1#–Se1, respectively) have chair conformation, while

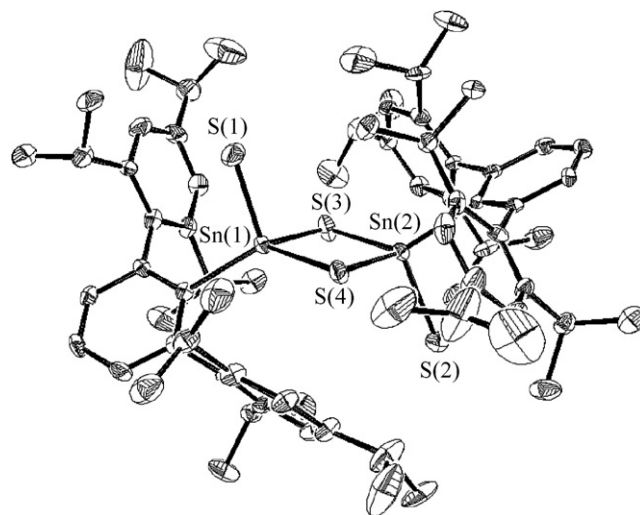


Fig. 1. ORTEP drawing of **6** with the thermal ellipsoids plots (40% probability for non-hydrogen atoms). All hydrogens and a solvent molecule were omitted for clarity. Selected bond lengths (Å) and angles ($^\circ$): Sn(1)–S(1), 2.331(2); Sn(2)–S(2), 2.373(2); Sn(1)–S(3), 2.413(2); Sn(1)–S(4), 2.511(2); Sn(2)–S(3), 2.392(2); Sn(2)–S(4), 2.381(2) S(3)–Sn(1)–S(4), $93.99(8)$; S(3)–Sn(2)–S(4), $95.31(8)$.

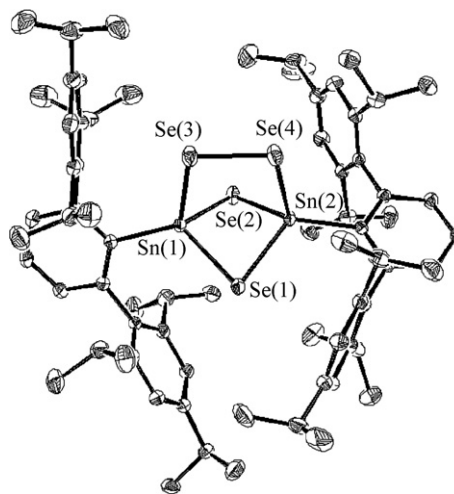


Fig. 2. ORTEP drawing of **7** with the thermal ellipsoids plots (40% probability for non-hydrogen atoms). All hydrogens were omitted for clarity. Selected bond lengths (Å) and angles ($^\circ$): Sn(1)–Se(1), 2.5605(4); Sn(1)–Se(2), 2.5341(4); Sn(1)–Se(3), 2.5688(4); Sn(2)–Se(1), 2.5445(4); Sn(2)–Se(2), 2.5529(5); Sn(2)–Se(4), 2.5581(4) Se(3)–Se(4), 2.3737(5); Sn(1)–Sn(2), 3.1453(4); Se(1)–Sn(1)–Se(2), $93.752(13)$; Se(1)–Sn(2)–Se(2), $93.685(8)$.

the others (Sn1–S3–S4–S5–Sn2–S2 and Sn1–Se2–Se3–Se4–Sn1#–Se1#, respectively) have boat conformation. The average values of 2.062 and 2.333 Å for the S–S and Se–Se bonds in **8** and **9**, respectively, are in the normal range. The length of the Se–Se bond in **7** (2.3737(5) Å) is slightly longer than those in **9**. The lengths of Sn1–Ch bonds in five- or six-membered rings [2.482(7) and 2.453(5) Å for **8**, 2.5688(4) and 2.5581(4) Å for **7** and 2.5433(17) and 2.6098(17) Å for **9**] are slightly longer than those of Sn–Ch bonds in the four-membered rings.

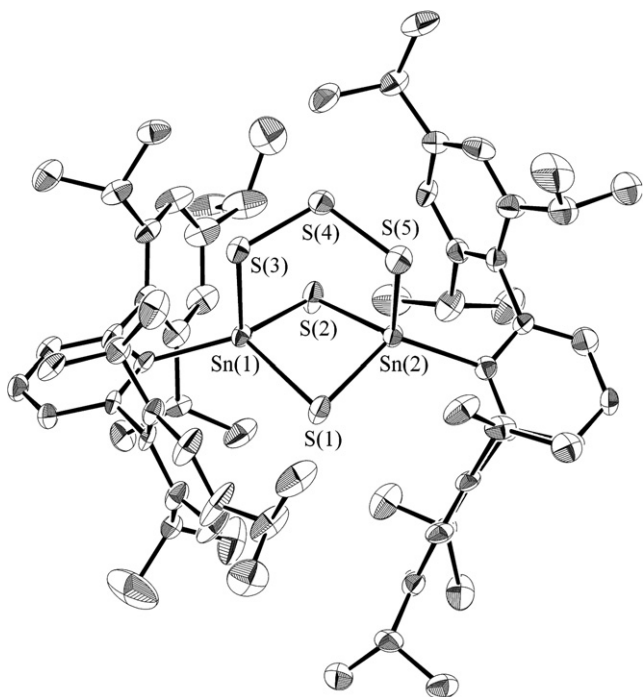


Fig. 3. ORTEP drawing of **8** with the thermal ellipsoids plots (40% probability for non-hydrogen atoms). All hydrogens were omitted for clarity. Selected bond lengths (Å) and angles (°): Sn(1)–S(1), 2.394(2); Sn(1)–S(2), 2.411(2); Sn(1)–S(3), 2.482(7); Sn(2)–S(1), 2.403(2); Sn(2)–S(2), 2.421(2); Sn(2)–S(5), 2.453(5); S(3)–S(4), 2.057(9); S(4)–S(5), 2.067(8); Sn(1)–Sn(2), 3.1736(8); S(1)–Sn(1)–S(2), 92.81(8); S(1)–Sn(2)–S(2), 92.36(8).

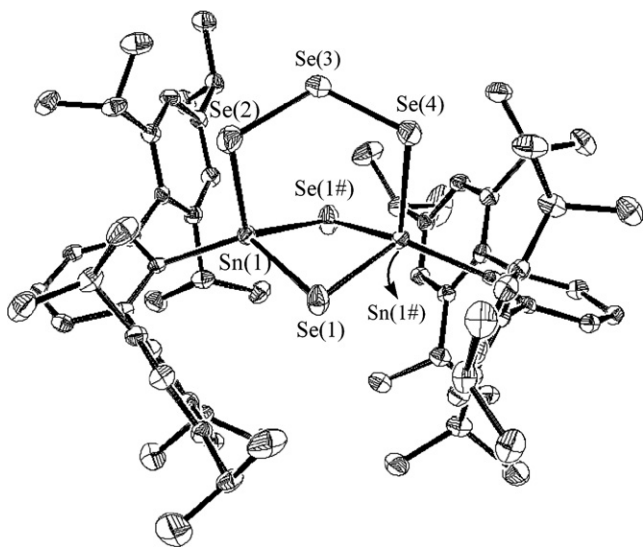


Fig. 4. ORTEP drawing of **9** with the thermal ellipsoids plots (40% probability for non-hydrogen atoms). All hydrogens were omitted for clarity. Selected bond lengths (Å) and angles (°): Sn(1)–Se(1), 2.5378(6); Sn(1)–Se(2), 2.5433(17); Sn(1#)–Se(4), 2.6098(17); Se(2)–Se(3), 2.339(2); Se(3)–Se(4), 2.327(2); Sn(1)–Se(1#), 3.3082(6); Se(1)–Sn(1)–Se(1#), 94.129(19).

The non-bonding distances between the two bridgehead tin atoms of **8**, **7** and **9** of 3.1736(8), 3.1453(4) and 3.3082(6) Å, respectively, are longer than the normal tin–tin single bond

(2.81 Å) [2], suggesting no significant bonding interaction, as was suggested by the ^{119}Sn NMR spectroscopy.

3. Conclusion

The first polychalcogenadistannabicyclo[*k.l.m*]alkanes have been successfully synthesized by the chalcogenation of trichloro- and trihydro-stannanes. The X-ray analysis reveals the longer non-bonded distances between the two bridgehead tin atoms than those of the normal single bonds, suggesting no significant bonding interaction between the two tin atoms. Further investigation on dechalcogenation of the newly obtained polychalcogen derivatives to synthesize trichalcogenadistannabicyclo[1.1.1]pentanes is currently in progress.

4. Experimental

4.1. General procedures

THF and diethyl ether were distilled over sodium/benzophenone. ^1H NMR (400 MHz), ^{13}C NMR (101 MHz), ^{119}Sn NMR (149 MHz) and ^{77}Se NMR (76 MHz) spectra were recorded on a Bruker DRX-400 or a Bruker DPX-400 spectrometer in CDCl_3 . The $^nJ(\text{Sn}-^{13}\text{C})$ couplings were observed in the ^{13}C NMR spectra as satellite signals. Wet column chromatography (WCC) was carried out with Kanto silica gel 60N. Preparative thin-layer chromatography (PTLC) was carried out with Merck silica gel 60 PF₂₅₄. Preparative gel permeation chromatography (GPC) was carried out on an LC-918 (Japan Analytical Ind. Co., Ltd.) with JAIGEL-1H and -2H columns with CHCl_3 as the eluant. FAB mass spectra were recorded on a JEOL JMS-700AM. IR spectrum was recorded on a JASCO FT/IR-660 Plus at room temperature. Data for the X-ray crystallographic analyses were collected on Bruker SMART APEX diffractometer with Mo $K\alpha$ radiation ($\lambda = 0.71073$ Å) and the structures were solved by direct methods. All melting points were determined on a Mitamura Riken Kogyo MEL-TEMP apparatus and were uncorrected. Elemental analyses were carried out at the Microanalytical Laboratory of Molecular Analysis and Life Science Center, Saitama University.

4.2. Preparation of aryltrichlorostannane **4**

After treatment of a THF (40 mL) solution of 2,6-bis(2,4,6-triisopropylphenyl)iodobenzene (ArI) [23] (2.229 g, 3.66 mmol) with *t*-butyllithium (1.40 N in pentane; 5.2 mL, 7.28 mmol) at -78 °C, the mixture was stirred at below -50 °C for 2 h. The resulting THF solution of ArLi was treated with stannous chloride (741 mg, 3.91 mmol) to give a solution of arylchlorostannylenes **5**. After being stirred at below -30 °C for 1 h, to a solution of **5** was added carbon tetrachloride (5 mL, 51.6 mmol) and the resulting mixture was warmed to room temperature. After removal

of materials insoluble in dichloromethane, the residue was subjected to column chromatography (hexane followed by ethyl acetate) to afford trichloro[2,6-bis(2,4,6-triisopropylphenyl)phenyl]stannane (**4**) (984 mg, 45%). Compound **4**: mp 211–215 °C (dichloromethane + methanol). ¹H NMR: δ 1.07 (d, *J* = 7 Hz, 12H), 1.28 (d, *J* = 7 Hz, 24H), 2.60 (sept, *J* = 7 Hz, 4H), 2.93 (sept, *J* = 7 Hz, 2H), 7.07 (s, 4H), 7.31–7.48 (m, 2H), 7.62 (t, *J* = 7 Hz, 1H); ¹³C NMR: δ 22.83 (q), 23.89 (q), 25.85 (q), 30.86 (d), 34.51 (d), 121.67 (d), 130.88 (d), 131.19 (d, *J*(Sn–C) = 117, 121 Hz), 134.12 (s, *J*(Sn–C) = 40 Hz), 140.72(s), 147.12 (s, *J*(Sn–C) = 78 Hz), 147.28(s), 150.52(s); ¹¹⁹Sn NMR: δ –116.8. Anal. Calc. for C₃₆H₄₉Cl₃Sn: C, 61.17; H, 6.99. Found: C, 61.50; H, 7.10%.

4.3. Preparation of aryltrihydrostannane 3

To a mixture of aryltrichlorostannane **4** (125 mg, 0.18 mmol) and LiAlH₄ (24 mg, 0.62 mmol) was added ether (8 mL) and the resulting mixture was stirred for 3 h at 0 °C. After removal of insoluble materials, the residue was subjected to column chromatography (hexane:ethyl acetate = 4:1) to afford trihydro[2,6-bis(2,4,6-triisopropylphenyl)phenyl]stannane (**3**) (92 mg, 83%). Compound **3**: mp 199 °C (dec.)(dichloromethane + methanol). ¹H NMR: δ 1.07 (d, *J* = 7 Hz, 12H), 1.10 (d, *J* = 7 Hz, 12H), 1.29 (d, *J* = 7 Hz, 12H), 2.62 (sept, *J* = 7 Hz, 4H), 2.93 (sept, *J* = 7 Hz, 2H), 3.86 (s, *J*(Sn–H) = 1848, 1934 Hz, 3H), 7.01 (s, 4H), 7.18–7.25 (m, 2H), 7.39 (t, *J* = 8 Hz, 1H); ¹³C NMR: δ 22.93 (q), 24.21 (q), 25.42 (q), 30.48 (d), 34.33 (d), 120.57 (d), 127.57 (d, *J*(Sn–C) = 42 Hz), 127.97 (d), 139.64 (s, *J*(Sn–C) = 25 Hz), 140.57 (s), 146.00 (s), 148.66 (s), 148.85 (s, *J*(Sn–C) = 37 Hz); ¹¹⁹Sn NMR: δ –384.7. IR(KBr): ν(Sn–H) 1875 cm⁻¹. Anal. Calc. for C₃₆H₅₂Sn: C, 71.65; H, 8.68. Found: C, 71.46; H, 8.71%.

4.4. Reaction of aryltrichlorostannane 4 with disodium sulfide

To a mixture of aryltrichlorostannane **4** (161 mg, 0.23 mmol) and disodium sulfide (29 mg, 0.37 mmol) was added THF (10 mL) and then the mixture was refluxed for 21 h. After removal of insoluble materials, the residue was subjected to GPC to afford *trans*-2,4-bis[2,6-bis(2,4,6-triisopropylphenyl)phenyl]-2,4-dimercapto-1, 3,2,4-dithia-distannane (**6**) (17 mg, 10%). Compound **6**: mp 219 °C (dec.)(dichloromethane + methanol). ¹H NMR: δ 0.94 (d, *J* = 7 Hz, 24H), 1.19 (d, *J* = 7 Hz, 24H), 1.31 (d, *J* = 7 Hz, 24H), 2.54 (sept, *J* = 7 Hz, 8H), 2.88 (sept, *J* = 7 Hz, 4H), 6.92 (s, 8H), 7.15 (d, *J* = 7 Hz, 4H), 7.38 (t, *J* = 7 Hz, 2H); ¹³C NMR: δ 23.07 (q, *J*(Sn–C) = 66 Hz), 24.18 (q), 25.79 (q), 30.64 (d, *J*(Sn–C) = 48 Hz), 34.29 (d), 121.05 (d), 129.11 (d), 130.70 (d), 134.75 (s, *J*(Sn–C) = 35 Hz), 144.76 (s), 145.95 (s), 147.00 (s), 149.16 (s); ¹¹⁹Sn NMR: δ –31.7 (*J*(Sn–Sn) = 666 Hz). Anal. Calc. for C₇₂H₁₀₀S₄Sn₂: C, 64.96; H, 7.57. Found: C, 63.96; H, 7.40%.

4.5. Reaction of aryltrichlorostannane 4 with dilithium selenide

To a THF (3 mL) solution of dilithium selenide prepared from elemental selenium (25 mg, 0.32 mmol) and Super hydride® (1 M LiEt₃BH in THF; 0.65 mL, 0.65 mmol) was added a THF (3 mL) solution of aryltrichlorostannane **4** (148 mg, 0.21 mmol) and the resulting mixture was stirred for 17 h at room temperature. After removal of volatile substances, insoluble materials in chloroform were filtered off. The residue was subjected to GPC followed by PTLC (hexane:ethyl acetate = 30:1) to give 1,3-bis[2,6-bis(2,4,6-triisopropylphenyl)phenyl]-2,3,4,5-tetraselena-1,3-distannabicyclo[2.1.1]hexane (**7**) (35 mg, 22%). Compound **7**: mp 243–244 °C (dichloromethane + chloroform). ¹H NMR: δ 0.98 (d, *J* = 7 Hz, 24H), 1.21 (d, *J* = 7 Hz, 24H), 1.25 (d, *J* = 7 Hz, 24H), 2.55 (sept, *J* = 7 Hz, 8H), 2.85 (sept, *J* = 7 Hz, 4H), 6.93 (s, 8H), 7.17 (d, *J* = 8 Hz, 4H), 7.39 (t, *J* = 8 Hz, 2H); ¹³C NMR: δ 23.46 (q), 23.95 (q), 25.87 (q), 30.77 (d, *J*(Sn–C) = 34 Hz), 34.28 (d), 121.38 (d), 128.90 (d), 130.30 (d, *J*(Sn–C) = 62 Hz), 135.83 (s, *J*(Sn–C) = 28 Hz), 140.73 (s, *J*(Sn–C) = 26 Hz), 146.75 (s), 147.23 (s, *J*(Sn–C) = 59 Hz), 149.05(s); ¹¹⁹Sn NMR: δ –240.5 (*J*(Sn–Sn) = 779 Hz, *J*(Sn–Se) = 1040, 1316 Hz); ⁷⁷Se NMR: δ 174.2, 275.7. FAB MS, [M]⁺: 1516. Found: 1516.

4.6. Reaction of aryltrihydrostannane 3 with elemental sulfur

To a mixture of aryltrihydrostannane **3** (120 mg, 0.20 mmol) and elemental sulfur (21 mg, 0.64 mmol as S) was added toluene (6 mL) and then the mixture was refluxed for 4 h. After removal of volatile substances, the residue was subjected to GPC to give a dimeric fraction (80 mg). The ¹¹⁹Sn NMR spectrum of the dimeric fraction showed signals at –31.7 (**6**), –30.0, –9.6, –9.2, –7.2, 29.8 (**8**), 49.2 and 110.0 ppm.

4.7. Reaction of aryltrihydrostannane 3 with elemental sulfur in the presence of triethylamine

To a mixture of aryltrihydrostannane **3** (65 mg, 0.11 mmol) and elemental sulfur (13 mg, 0.42 mmol as S) in the presence of triethylamine (0.08 mL, 0.58 mmol) was added toluene (5 mL) and then the mixture was refluxed for 16 h. After removal of volatile substances, the residue was subjected to GPC to give 1,3-bis[2,6-bis(2,4,6-triisopropylphenyl)phenyl]-2,4,5,6,7-pentathia-1,3-distannabicyclo[3.1.1]heptane (**8**) (53 mg, 71%). Compound **8**: mp 250–251 °C (dichloromethane + methanol). ¹H NMR: δ 0.94 (d, *J* = 7 Hz, 12H), 0.98 (d, *J* = 7 Hz, 12H), 1.13 (d, *J* = 7 Hz, 12H), 1.26 (d, *J* = 7 Hz, 12H), 1.34 (d, *J* = 7 Hz, 24H), 2.41 (sept, *J* = 7 Hz, 4H), 2.43 (sept, *J* = 7 Hz, 4H), 2.94 (sept, *J* = 7 Hz, 4H), 6.90 (br s, 4H), 6.96 (br s, 4H), 7.11 (d, *J* = 8 Hz, 4H), 7.34 (t, *J* = 8 Hz, 2H); ¹³C NMR: δ 23.00 (q), 23.32 (q), 24.04 (q), 25.77 (q), 30.68 (d), 34.20 (d), 120.97 (d), 121.10 (d),

128.93 (d), 130.45 (d, $J(\text{Sn}-\text{C}) = 68$ Hz), 134.89 (s, $J(\text{Sn}-\text{C}) = 31$ Hz), 144.62 (s, $J(\text{Sn}-\text{C}) = 12$ Hz), 146.16 (s, $J(\text{Sn}-\text{C}) = 61$ Hz), 146.52 (s), 146.72 (s), 148.83 (s); ^{119}Sn NMR: δ 29.7 ($J(\text{Sn}-\text{Sn}) = 32, 64$ Hz). Anal. Calc. for $\text{C}_{72}\text{H}_{98}\text{S}_5\text{Sn}_2$: C, 63.53; H, 7.26. Found: C, 63.66; H, 7.20%.

4.8. Reaction of aryltrihydrostannane **3** with elemental selenium

To a mixture of aryltrihydrostannane **3** (80 mg, 0.13 mmol) and elemental selenium (31 mg, 0.40 mmol) was added toluene (6 mL) and then the mixture was refluxed for 14 h. After removal of volatile substances, the residue was subjected to GPC to give a dimeric fraction (57 mg) containing **7** (18 mg, 18%) and 1,3-bis[2,6-bis(2,4,6-triisopropylphenyl)phenyl]-2,3,4,5,6-pentaseleena-1, 3-distannabicyclo[3.1.1]heptane (**9**) (39 mg, 38%), estimated by ^1H NMR spectroscopy. Compound **9**: mp 243–244 °C (dichloromethane + methanol). ^1H NMR: δ 0.94 (d, $J = 7$ Hz, 24H), 1.17–1.30 (br m, 24H), 1.33 (d, $J = 7$ Hz, 24H), 2.47 (sept, $J = 7$ Hz, 8H), 2.92 (sept, $J = 7$ Hz, 4H), 6.91 (s, 8H), 7.03 (d, $J = 7$ Hz, 4H), 7.29 (t, $J = 7$ Hz, 2H); ^{13}C NMR: δ 23.47 (q), 24.06 (q), 25.87 (q), 30.75 (d), 34.23 (d), 120.96 (d), 128.47 (d), 130.48 (d, $J(\text{Sn}-\text{C}) = 57$ Hz), 134.78 (s), 139.99 (s) 145.71 (s), 146.80 (s), 148.68 (s); ^{119}Sn NMR: δ -262.0 ($J(\text{Sn}-\text{Sn}) = 394$ Hz, $J(\text{Sn}-\text{Se}) = 1002, 1288$ Hz); ^{77}Se NMR: δ 255.2, 630.3. Anal. Calc. for $\text{C}_{72}\text{H}_{98}\text{Se}_5\text{Sn}_2$: C, 54.19; H, 6.19. Found: C, 54.09; H, 6.22%.

4.9. Reaction of aryltrihydrostannane **3** with elemental selenium in the presence of triethylamine

To a mixture of aryltrihydrostannane **3** (93 mg, 0.15 mmol) and elemental selenium (49 mg, 0.62 mmol) in the presence of triethylamine (0.1 mL, 0.72 mmol) was added toluene (7 mL) and then the mixture was refluxed for 18 h. After removal of volatile substances, the residue was subjected to GPC to give a dimeric fraction (67 mg) containing **7** (26 mg, 23%) and **9** (41 mg, 34%), estimated by ^1H NMR spectroscopy.

4.10. Crystallographic data for **6**

0.40 × 0.10 × 0.10 mm, orthorhombic, $a = 44.746(3)$ Å, $b = 52.011(4)$ Å, $c = 12.2152(8)$ Å, $V = 28428(4)$ Å³, $T = 123$ K, $\rho_{\text{calc}} = 1.271$ g cm⁻³, $Z = 16$, space group $Fdd2$, $R_1 = 0.074$ ($I > 2\sigma(I)$), 10614 reflections, $wR_2 = 0.167$ (for all reflections) for 14579 reflections and 745 parameters. GOF = 1.036.

4.11. Crystallographic data for **7**

0.50 × 0.40 × 0.04 mm, monoclinic, $a = 17.485(3)$ Å, $b = 17.990(3)$ Å, $c = 22.314(3)$ Å, $\beta = 94.763(3)^\circ$, $V = 6994.6(17)$ Å³, $T = 123$ K, $\rho_{\text{calc}} = 1.440$ g cm⁻³, $Z = 4$, space group $P2_1/n$, $R_1 = 0.034$ ($I > 2\sigma(I)$), 13624 reflec-

tions), $wR_2 = 0.088$ (for all reflections) for 16777 reflections and 727 parameters. GOF = 1.041.

4.12. Crystallographic data for **8**

0.40 × 0.20 × 0.10 mm, monoclinic, $a = 27.506(2)$ Å, $b = 11.2077(9)$ Å, $c = 25.658(2)$ Å, $\beta = 114.756(2)^\circ$, $V = 7182.9(10)$ Å³, $T = 123$ K, $\rho_{\text{calc}} = 1.259$ g cm⁻³, $Z = 4$, space group $P2_1/c$, $R_1 = 0.073$ ($I > 2\sigma(I)$), 8899 reflections, $wR_2 = 0.207$ (for all reflections) for 14078 reflections and 796 parameters. GOF = 1.042. Disorder around the trisulfide chain of **8** was found. The occupancies of the disordered trisulfide chains were refined to be 0.60:0.40.

4.13. Crystallographic data for **9**

0.50 × 0.20 × 0.05 mm, monoclinic, $a = 24.1691(17)$ Å, $b = 10.9409(6)$ Å, $c = 26.3617(16)$ Å, $\beta = 95.926(2)^\circ$, $V = 6933.6(7)$ Å³, $T = 103$ K, $\rho_{\text{calc}} = 1.529$ g cm⁻³, $Z = 4$, space group $C2/c$, $R_1 = 0.042$ ($I > 2\sigma(I)$), 5218 reflections, $wR_2 = 0.112$ (for all reflections) for 6271 reflections and 382 parameters. GOF = 1.095. Disorder around the triselenide chain of **9** was found. The occupancies of the disordered triselenide chains were refined to be 0.50:0.50.

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Appendix A. Supplementary material

CCDC 627566, 625924, 607160 and 625925 contain the supplementary crystallographic data for **6**, **7**, **8** and **9**. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2007.02.004.

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