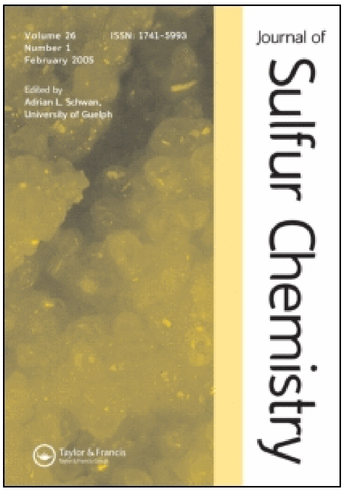

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Reactions of a kinetically stabilized 2-stannanaphthalene with elemental sulfur and selenium: synthesis of novel cyclic chalcogenides containing a tin atom

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Reactions of a kinetically stabilized 2-stannanaphthalene with elemental sulfur and selenium: synthesis of novel cyclic chalcogenides containing a tin atom

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This paper is dedicated to Professor Juzo Nakayama on the occasion of his 65th birthday and retirement.

Novel five-membered cyclic trisulfide and 1,3-dihydrobenzo[*c*]selenophene derivatives containing a tin atom were synthesized by the reaction of a kinetically stabilized 2-stannanaphthalene with elemental sulfur and selenium, and their molecular structures were determined by X-ray crystallographic analysis. In addition, the results obtained for 2-stannanaphthalene were systematically compared with those obtained for germanium and silicon analogs.

Keywords: metallaaromatic compounds; 1,2,3,4-trithiastannolane; 1,2,3,4-trithiagermolane; thiagermirane; 1,3-dihydrobenzo[*c*][1,2]selenastannole

1. Introduction

We have already succeeded in the synthesis of stable and neutral metallaaromatic systems containing a silicon or a germanium atom (*1–3*), *i.e.* the heavier analogs of benzene, naphthalene, anthracene, and phenanthrene, by taking advantage of an efficient steric protection group, 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl (Tbt). The reactions of 2-sila- and 2-germanaphthalenes and germabenzene with elemental sulfur or selenium afforded the novel cyclic chalcogenides (*4–6*). Very recently, 2-stannanaphthalene **1a** bearing a Tbt group, the first example of a stable neutral stannaaromatic compound, was synthesized and fully characterized (*7, 8*) (Chart 1). Herein, we present the reactions of **1a** with elemental sulfur and selenium leading to the formation of a novel Sn-containing cyclic chalcogenide. In addition, we performed similar chalcogenation reactions of recently reported *t*-Bu-substituted 2-germanaphthalene **2a** (*8*) for comparison.

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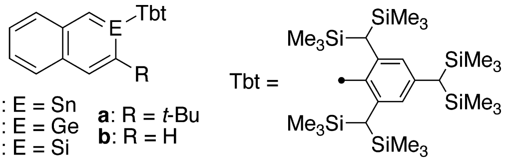


Chart 1.

2. Results and discussion

2.1. *The reactions of (1a) and (2a) with elemental sulfur*

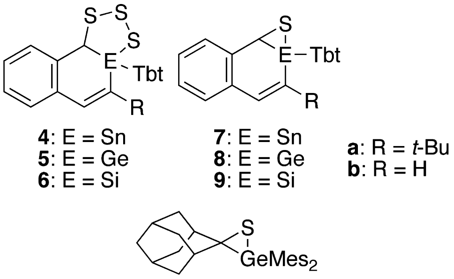
At first, we performed the reactions of **1a** and **2a** with elemental sulfur. To the benzene solutions of **1a** or **2a** was added an excess amount of sulfur at room temperature, and the crude products were separated by gel permeation liquid chromatography (GPLC) and subsequent preparative thin-layer chromatography (PTLC) (Scheme 1). In the case of **1a**, a novel Sn-containing cyclic trisulfide, 1,2,3,4-trithiastannolane **4a**, was obtained exclusively in 50% yield. On the other hand, the sulfurization of the germanium analog **2a** afforded 1,2,3,4-trithiagermolane **5a** (26%) and a three-membered ring compound, thiagermirane **8a** (35%). The relatively low total yields were due to the decomposition of the products during separations.

The molecular structures of **4a**, **5a**, and **8a** were confirmed by the NMR and mass spectral data together with elemental analysis, and finally established by an X-ray crystallographic analysis (Figures 1 and 2). Trisulfides **4a** and **5a** have geometries similar to each other, and the structural parameters of **5a** were in the same range of those of 1,2,3,4-trithiagermolane reported previously (*5*, *6*). As for **8a**, the bond lengths of Ge1–C1 (Ge2–C46) bonds [1.929(6) and 1.930(6) Å] were measurably shorter than that of **5a** [2.000(2) Å] and the Ge–C bond lengths in the three-membered ring of **10** (*9*), the only example of thiagermirane structurally determined by X-ray crystallographic analysis [1.973(5) and 1.970(5) Å, two independent molecules]. On the other hand, the bond lengths in **8a** of Ge1–S1 (Ge2–S2) [2.2154(17) and 2.2185(18) Å] and S1–C1 (S2–C46) [1.875(7) and 1.871(7) Å] were close to those in **10** [2.222(1) Å (Ge–S), 1.880(5) and 1.877(5) Å (Ge–C)]. These results suggested the increase of the π-complex character in **8a**.

As previously reported, the reaction of 2-germanaphthalene **2b**, which does not have a 3-t-Bu group, with an excess amount or 1 molar equiv. (as S atom) of elemental sulfur afforded only

$$\mathbf{1\text{–}3} \xrightarrow[\text{Benzene, rt}]{S_8} \mathbf{4\text{–}6} + \mathbf{7\text{–}9}$$

1–3	S_8	Yield (%) 4–6	7–9
1a (this work)	Excess	50 (**4a**)	–
2a (this work)	Excess	26 (**5a**)	35 (**8a**)
2b(*5*)	Excess	55 (**5b**)	–
2b(*5*)	1.0 equiv.	12 (**5b**)	–
3b(*4*)	Excess	20 (**6b**)	–
3b(*4*)	1.0 equiv.	n.d. (**6b**)	n.d. (**9b**)



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Scheme 1. The reactions of 2-metallanaphthalenes **1–3** with elemental sulfur. Although the yields of **6b** and **9b** were not determined, their generation was suggested by their ^{29}Si NMR signals [$\delta_{\mathrm{Si}} = 15.78$ (**6b**) and -67.72 (**9b**)].

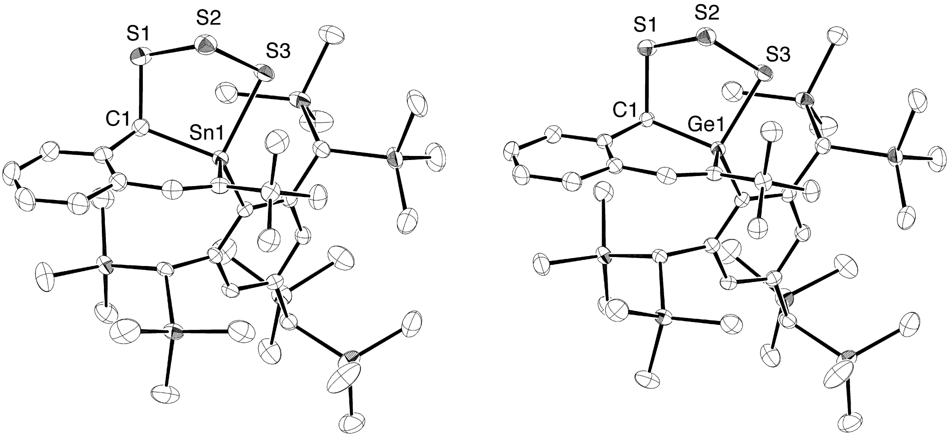


Figure 1. Thermal ellipsoid plots of [**4a**·benzene] (left) and [**5a**·benzene] (right) were drawn at the 50% probability level. Hydrogen atoms and benzene molecules are omitted for clarity. Selected bond lengths (Å) and angles (deg) for [**4a**·benzene]: Sn1–S3 2.4461(7), Sn1–C1 2.180(2), S1–C1 1.822(3), S1–S2 2.0452(10), S2–S3 2.0713(10), S3–Sn1–C1 95.76(7), Sn1–C1–S1 110.57(12), C1–S1–S2 103.00(9), S1–S2–S3 100.15(4), S2–S3–Sn1 90.87(3); for [**5a**·benzene]: Ge1–S3 2.2754(7), Ge1–C1 2.000(2), S1–C1 1.835(2), S1–S2 2.0408(10), S2–S3 2.0593(10), S3–Ge1–C1 98.64(7), Ge1–C1–S1 111.63(12), C1–S1–S2 100.73(9), S1–S2–S3 97.12(4), S2–S3–Ge1 92.23(3).

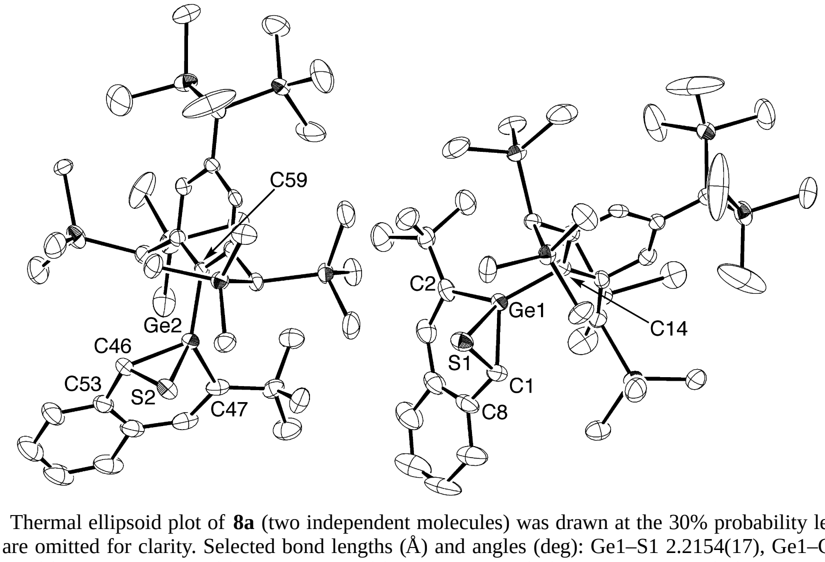
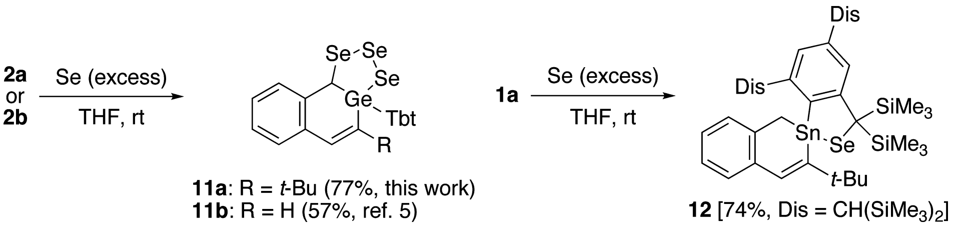


Figure 2. Thermal ellipsoid plot of **8a** (two independent molecules) was drawn at the 30% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ge1–S1 2.2154(17), Ge1–C1 1.929(6), Ge1–C2 1.952(6), Ge1–C14 1.959(5), S1–C1 1.875(7), C1–C8 1.490(10), Ge2–S2 2.2185(18), Ge2–C46 1.930(6), Ge2–C47 1.936(6), Ge2–C59 1.952(5), S2–C46 1.871(7), C46–C53 1.477(9), Ge1–S1–C1 55.52(19), Ge1–C1–S1 71.2(2), S1–Ge1–C1 53.3(2), Ge2–S2–C46 55.54(19), Ge2–C46–S2 71.4(2), S2–Ge2–C46 53.1(2).

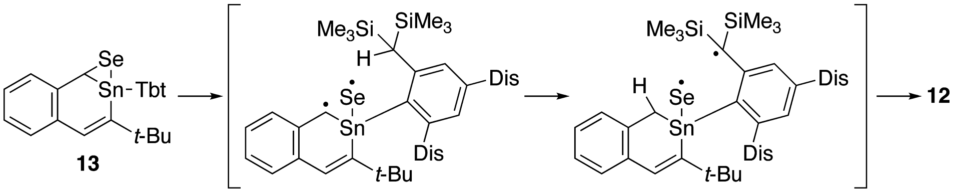
trisulfide **5b** (55 and 12%, respectively), and the generation of thiagermirane **8b** was not observed in either case (*5*). In the case of silicon analog **3b** (*4*), trisulfide **6b** was obtained (20%) when using an excess amount of elemental sulfur. Although the generation of thiasilirane **9b** was suggested by the characteristic signal of the ^{29}Si NMR when using 1 molar equiv. (as S atom) of elemental sulfur, the isolation of **9b** was not successful due to its instability in the air. Taking these results into consideration, the numbers of the sulfur atoms in the products were related to the steric congestion derived from the sizes of the center element and substituent.

2.2. *The reactions of (1a) and (2a) with elemental selenium*

Next, the reactions with elemental selenium were performed (Scheme 2). 2-Germanaphthalenes **2a** and **2b** reacted with an excess amount of elemental selenium to give only the cyclic triselenides **11a** and **11b** (*5*), respectively, in both cases with and without the *t*-Bu group. On the other hand, the reaction of 2-stannanaphthalene **1a** with elemental selenium afforded the five-membered ring compound **12**, in which the selenium atom bonded to the *ortho*-benzyl carbon atom of the Tbt group. Compound **12** was probably generated via the three-membered ring compound, selenastannirane **13**, in which the Se–C bond cleavage, hydrogen abstraction, and recombination of radicals could occur to afford **12** (Scheme 3). These are very interesting results, indicating the difference between the tin and germanium systems.



Scheme 2. Reactions of **1a**, **2a**, and **2b** with elemental selenium.



Scheme 3. Possible mechanism for the generation of **12**.

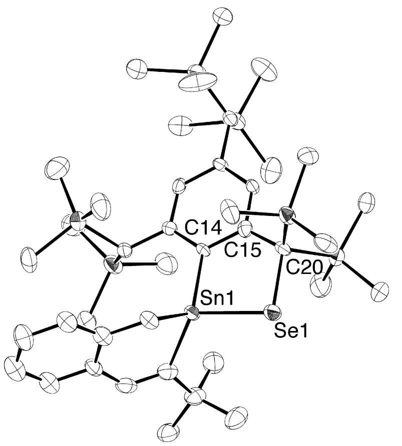


Figure 3. Thermal ellipsoid plot of **12** was drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Sn1–Se1 2.5049(7), Sn1–C14 2.128(5), Se1–C20 2.033(5), C14–C15 1.411(7), C15–C20 1.532(7), C14–Sn1–Se1 89.08(13), C20–Se1–Sn1 93.23(14), C15–C14–Sn1 117.4(4), C14–C15–C20 124.4(4), C15–C20–Se1 114.9(3).

The molecular structures of **11a** and **12** were confirmed by the NMR and mass spectral data together with elemental analysis, and that of **12** was finally determined by the X-ray crystallographic analysis (Figure 3). It should be noted that compound **12** has the first 1,3-dihydrobenzo[*c*][1,2]selenastannole skeleton. Although the bond lengths in **12** are typical, the geometry around the tin atom is quite deviated from the ideal tetrahedral structure, especially in the bond angle of C14–Sn1–Se1 [89.08(13)°].

3. Conclusion

We have performed the reactions of 2-stanna- and 2-germanahthalenes, **1a** and **2a**, with elemental sulfur or selenium, and revealed the similarity and differences in the reactivities between the tin and germanium cases.

4. Experimental

All experiments were performed under an argon atmosphere. Benzene and THF used for the reactions were purified by The Ultimate Solvent System (GlassContour Company) (*10*), dried over K mirror, and distilled by trap-to-trap method. ^{1}H NMR (300 MHz), ^{13}C NMR (76 MHz), ^{77}Se NMR (57 MHz), and ^{119}Sn NMR (111 MHz) spectra were measured in C_6D_6 with a JEOL JNM-AL300 spectrometer. In ^{1}H NMR, signal due to C_6D_5H (7.15 ppm) was used as a reference, and that due to C_6D_6 (128 ppm) was used in ^{13}C NMR. ^{119}Sn NMR was measured with the NNE technique using $SnMe_4$ as an external standard. Multiplicity of signals in ^{13}C NMR spectra was determined by the DEPT technique. ^{77}Se NMR was measured using diphenyl diselenide (460 ppm) as an external standard. High-resolution mass spectral data were obtained on a JEOL JMS-SX102GC/MS spectrometer. Wet column chromatography (WCC) was performed on Wakogel C-200. PTLC was performed with Merck Kieselgel 60 PF254 (Art. No. 7747). GPLC was performed on an LC-918 (Japan Analytical Industry Co., Ltd.) equipped with JAIGEL 1H and 2H columns (eluent:toluene). All melting points were determined on a Yanaco micro-melting point apparatus and were uncorrected. Elemental analyses were carried out at the Microanalytical Laboratory of the Institute for Chemical Research, Kyoto University.

4.1. *The reaction of 2-stannanaphthalene (1a) with elemental sulfur*

In a glovebox filled with argon, to a mixture of **1a** (45.8 mg, 0.0544 mmol) and elemental sulfur (17.7 mg, 0.533 mmol as S) in a 5 mm ø NMR tube was added benzene-d_6 (0.5 mL) at room temperature, and the tube was sealed. After standing at this temperature for 2 h, the signals of **1a** in the ^{1}H NMR completely disappeared. Then, the tube was opened to air and the solvent was removed under reduced pressure. The mixture was separated by PTLC (hexane) to give **4a** (25.3 mg, 0.0274 mmol, 50%). **4a**: colorless crystals; m.p. 209–211 °C; ^{1}H NMR (300 MHz, rt, C_6D_6): δ 0.06 (s, 9H), 0.11 (s, 9H), 0.14 (s, 18H), 0.19 (s, 9H), 0.23 (s, 9H), 1.35 (s, 9H), 1.45 (s, 1H), 1.96 (br s, 2H), 4.51 (s, 1H), 6.56 (br s, 1H), 6.71 (br s, 1H), 6.83–6.97 (m, 3H + s, 1H), 7.20–7.25 (m, 1H); ^{13}C NMR (75 MHz, rt, C_6D_6): δ 0.91 (q), 0.95 (q), 1.04 (q), 1.13 (q), 1.61 (q), 30.87 (d), 33.02 (q), 34.33 (d), 35.13 (d), 38.47 (s), 45.80 (d), 122.93 (d), 127.54 (d), 127.84 (d), 128.54 (d), 134.51 (d), 136.09 (s), 136.51 (d), 137.41 (s), 138.14 (s), 143.22 (d), 145.47 (s), 151.10 (s), 151.66 (s), 155.53 (s); ^{119}Sn NMR (111 MHz, 323 K, C_6D_6): δ 7.1; High resolution FAB-MS m/z calcd for $C_{40}H_{75}S_3Si_6{}^{120}Sn$: 939.2668 ($[M + H]^+$), found: 939.2690 ($[M + H]^+$). Anal. calcd for $C_{40}H_{74}S_3Si_6Sn$: C, 51.20; H, 7.95. Found: C, 51.11; H, 7.99.

4.2. *The reaction of 2-germanaphthalene (2a) with elemental sulfur*

In a glovebox filled with argon, to a mixture of **2a** (45.3 mg, 0.0569 mmol) and elemental sulfur (33.0 mg, 1.03 mmol as S) in a 5 mm ø NMR tube was added benzene-d_6 (0.5 mL) at room temperature, and the tube was sealed. After standing at this temperature for 1 h, the signals of **2a** in the ^{1}H NMR completely disappeared. Then, the tube was opened to air and the solvent was removed under reduced pressure. The mixture was separated by GPLC and PTLC (hexane) to give **5a** (13.6 mg, 0.0152 mmol, 26%) and **8a** (16.3 mg, 0.0197 mmol, 35%). **5a**: colorless crystals; m.p. 209–211 °C; ^{1}H NMR (300 MHz, rt, C_6D_6): δ –0.07 (s, 9H), 0.04 (s, 9H), 0.15 (s, 18H), 0.33 (s, 18H), 1.40 (s, 9H), 1.57 (s, 1H), 2.55 (br s, 2H), 4.68 (s, 1H), 6.51 (br s, 1H), 6.67 (br s, 1H), 6.84–6.95 (m, 3H), 7.14 (s, 1H), 7.25–7.29 (m, 1H); ^{13}C NMR (75 MHz, rt, C_6D_6): δ 0.94 (q), 1.10 (q), 1.31 (q), 2.10 (q), 2.19 (q), 29.56 (d), 30.78 (d), 32.41 (d), 32.78 (q), 38.26 (s), 45.85 (d), 123.15 (d), 123.97 (d), 127.64 (d), 127.80 (d), 131.38 (s), 133.22 (d), 134.67 (s), 135.59 (d), 137.68 (s), 142.16 (d), 145.03 (s), 148.07 (s), 150.55 (s), 151.34 (s); High resolution FAB-MS m/z calcd for $C_{40}H_{75}{}^{74}GeS_3Si_6$: 892.2780 ($M^+$), found: 892.2767 ($M^+$). Anal. calcd for $C_{40}H_{74}GeS_3Si_6$: C, 53.84; H, 8.36. Found: C, 53.71; H, 8.59. **8a**: colorless crystals; m.p. 180°C (decomp.); ^{1}H NMR (300 MHz, 323 K, C_6D_6): δ 0.01 (s, 9H), 0.06 (s, 9H), 0.14 (s, 18H), 0.32 (s, 9H), 0.33 (s, 9H), 1.38 (s, 9H), 1.47 (s, 1H), 1.94 (s, 1H), 3.11 (s, 1H), 4.01 (s, 1H), 6.50 (br s, 1H), 6.66 (br s, 1H), 6.88 (s, 1H), 6.97–7.04 (m, 2H), 7.09–7.12 (m, 1H), 7.36–7.39 (m, 1H); ^{13}C NMR (75 MHz, 323 K, C_6D_6): δ 0.96 (q), 1.41 (q), 1.54 (q), 2.34 (q), 2.39 (q), 28.89 (d), 31.21 (d), 32.55 (d + q), 32.84 (d), 38.87 (s), 126.48 (d), 127.77 (d), 129.98 (s), 131.96 (d), 133.11 (s), 133.66 (d), 133.95 (d), 140.18 (s), 146.36 (s), 151.37 (s), 151.43 (s), 158.78 (s). Two CH signals assigned to those for the Tbt ring were not observed, probably due to their broadening or overlap. High resolution FAB-MS m/z calcd for $C_{40}H_{75}{}^{74}GeSSi_6$: 829.3417 ($[M + H]^+$), found: 829.3408 ($[M + H]^+$). Anal. calcd for $C_{40}H_{74}GeSSi_6$: C, 58.01; H, 9.01. Found: C, 57.82; H, 8.97.

4.3. *The reaction of 2-stannanaphthalene (1a) with elemental selenium*

In a glovebox filled with argon, to a THF solution (2 mL) of **1a** (57.9 mg, 0.0687 mmol) was added elemental selenium (55.9 mg, 0.708 mmol) at room temperature. After stirring at this temperature for 1 h, the solvent was removed under reduced pressure. The mixture was separated by GPLC to give **12** (46.0 mg, 0.0506 mmol, 74%). **12**: colorless crystals; m.p. 241–243 °C; ^{1}H NMR (300 MHz, rt, C_6D_6): δ -0.12 (s, 9H), 0.11 (s, 9H), 0.13 (s, 9H), 0.14 (s, 9H), 0.33 (s, 9H), 0.44 (s, 9H), 0.96 (s, 1H), 1.37 (s, 9H), 1.50 (s, 1H), 2.75 (d, $^2J = 14.6$ Hz, 1H), 2.94 (d, $^2J = 14.6$ Hz, 1H), 6.59 (s, 1H), 6.88–7.05 (m, 4H + s, 2H); ^{13}C NMR (75 MHz, rt, C_6D_6): δ 0.47 (q), 0.66 (q), 1.20 (q), 1.57 (q), 2.06 (q), 23.46 (t), 30.73 (d), 31.60 (q), 38.62 (d), 39.22 (s), 39.59 (s), 121.58 (d), 126.18 (d), 126.30 (d), 127.28 (d), 132.35 (d), 133.21 (d), 135.75 (s), 137.24 (s), 140.61 (d), 141.17 (s), 144.25 (s), 150.55 (s), 152.79 (s), 158.78 (s); ^{119}Sn NMR (111 MHz, rt, C_6D_6): δ 11.4; ^{77}Se NMR (57 MHz, rt, C_6D_6): δ -227.6; high resolution FAB-MS m/z calcd for $C_{40}H_{74}{}^{80}SeSi_6{}^{120}Sn$: 922.2593 ($[M]^+$), found: 922.2596 ($[M]^+$). Anal. calcd for $C_{40}H_{74}SeSi_6Sn$: C, 52.15; H, 8.10. Found: C, 52.24; H, 8.21.

4.4. *The reaction of 2-germanaphthalene (2a) with elemental selenium*

In a glovebox filled with argon, to a THF solution (3 mL) of **2a** (60.6 mg, 0.0761 mmol) was added elemental selenium (48.0 mg, 0.608 mmol) at room temperature. After stirring at this temperature for 2 days, the solvent was removed under reduced pressure. The mixture was separated by WCC to give **11a** (60.7 mg, 0.0588 mmol, 77%). **11a**: yellow crystals; m.p. 196°C (decomp.); ^{1}H NMR

Table 1. Crystal data for [**4a**·benzene], [**5a**·benzene], **8a**, and **12**.

	[**4a**·benzene]	[**5a**·benzene]	**8a**	**12**
Formula	$C_{40}H_{74}S_3Si_6Sn{\cdot}C_6H_6$	$C_{40}H_{74}GeS_3Si_6{\cdot}C_6H_6$	$C_{40}H_{74}GeSSi_6$	$C_{40}H_{74}SnSeSi_6$
Mw	1016.51	970.41	828.18	921.18
Crystal color, habit	Colorless, prism	Colorless, prism	Colorless, prism	Colorless, prism
Crystal system	Triclinic	Triclinic	Triclinic	Triclinic
Space group	P-1 (#2)	P-1 (#2)	P-1 (#2)	P-1 (#2)
a (Å)	11.3766(2)	11.3206(4)	12.0997(4)	12.1784(4)
b (Å)	12.8602(2)	12.6633(5)	17.7032(6)	12.8279(5)
c (Å)	18.9954(4)	19.0292(8)	23.0304(9)	17.1052(7)
α (°)	88.5313(12)	87.7653(16)	78.9047(14)	113.3945(13)
β (°)	88.7050(9)	89.3036(17)	86.8394(16)	95.2302(13)
γ (°)	88.0643(10)	88.152(3)	90.132(3)	95.1583(12)
V (Å^3)	2775.97(9)	2724.30(18)	4833.2(3)	2418.98(16)
Z	2	2	4	2
T (K)	103(2)	103(2)	103(2)	103(2)
ρ_{calcd} (g cm^{-1})	1.216	1.183	1.138	1.265
μ (mm^{-1})	0.731	0.838	0.851	1.454
Independent reflections	9744	9411	16998	8415
R_{int}	0.0322	0.0312	0.0759	0.0696
Number of parameters	526	526	1004	455
Goodness-of-fit on F^2	1.021	1.024	1.076	1.027
R_1 [$I > 2\sigma(I)$]	0.0293	0.0359	0.0744	0.0481
wR_2 (all data)	0.0730	0.0861	0.1960	0.1075

(300 MHz, 323 K, C_6D_6): δ 0.04 (s, 9H), 0.13 (s, 9H), 0.14 (s, 18H), 0.21 (s, 9H), 0.24 (s, 9H), 1.60 (s, 1H), 1.95 (br s, 1H), 2.28 (br s, 1H), 5.28 (s, 1H), 6.51 (br s, 1H), 6.63 (br s, 1H), 6.83–6.94 (m, 3H), 7.10 (s, 1H), 7.38–7.41 (m, 1H); ^{13}C NMR (75 MHz, rt, C_6D_6): δ 1.11 (q), 1.58 (q), 1.79 (q), 1.92 (q), 2.09 (q), 30.71 (d), 32.62 (d), 32.77 (d), 33.30 (q), 38.36 (s), 44.95 (d), 122.89 (d), 127.33 (d), 127.59 (d), 129.10 (d), 132.23 (s), 133.06 (d), 134.27 (s), 135.68 (d), 138.61 (s), 140.81 (d), 144.64 (s), 150.10 (s), 150.96 (s), 151.38 (s); ^{77}Se NMR (57 MHz, rt, C_6D_6): δ 410.5, 508.0, 840.4; Anal. calcd for $C_{40}H_{74}GeSe_3Si_6$: C, 46.51; H, 7.22. Found: C, 46.37; H, 7.27.

4.5. *X-ray crystallography*

Single crystals of [**4a**·benzene], [**5a**·benzene], **8a**, and **12** were grown by the slow evaporation of the saturated benzene solution. Their intensity data were collected on a Rigaku/MSC Mercury CCD diffractometer with graphite monochromated MoKα radiation ($l = 0.71069$ Å) to $2\theta_{\max} = 50°$ at 103 K. Their structures were solved by the direct method (SHELXS-97) and refined by a full-matrix least-squares procedure on F^2 for all reflections (SHELXL-97) (*11*). All non-hydrogen atoms were refined anisotropically and all hydrogen atoms were placed using AFIX instructions. The coordinates for the methyl H atoms at C91 in **8a** are not reliable. All crystallographic data are summarized in Table 1 and have been deposited with the Cambridge Crystallographic Data Centre, as CCDC Nos. 717682 ([**4a**·benzene]), 717680 ([**5a**·benzene]), 717679 (**8a**), and 717683 (**12**).[1]

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Note

1. A copy of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK. Fax. (int. code) +44 1223 336 033 or email: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk.

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