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Synthesis and reactions of stannaneselone ☆

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Abstract

Stannaneselone Tbt(Tip)Sn=Se (Tbt = 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl; Tip = 2,4,6-triisopropylphenyl), a novel compound containing a tin–selenium double bond was synthesized by the reaction of the corresponding stannylene Tbt(Tip)Sn with elemental selenium. It reacted with phenyl isothiocyanate, mesitonitrile oxide and styrene oxide to afford cycloadducts. In the reaction with phenyl isothiocyanate, 1,3,2-dithia- and diselenastannetanes were obtained instead of the expected 1,3,2-thiaselenastannetane. Another approach to the stannaneselone by deselenation of the corresponding 1,2,3,4,5-tetraselenastannolane with triphenylphosphine is also described.

Keywords: Tin; Selenium; Bulky ligand; Stannylene; Cycloaddition; Stannaneselone

1. Introduction

For many years it was considered that compounds having double bonds between heavier Main Group elements would be unstable because of their weak $p\pi$–$p\pi$ bonding. Since the isolation of the first stable compounds with Si=C [1], P=P [2] and Si=Si [3] by taking advantage of bulky ligands which prevent them from oligomerizing (kinetic stabilization), however, many unsaturated compounds containing Group 14 and 15 elements have been synthesized and characterized [4]. For stable compounds containing double bonds between Group 14 and 16 elements, the chemistry of thioketones and selenoketones has been well explored. When we undertook to synthesize such species some years ago, however, there were no examples of "genuine" compounds containing double bonds between heavier Group 14 and 16 elements, heavier element analogues of ketones (RR'M=Y; M = Si, Ge, Sn or Pb; Y = S, Se), which we refer to as "heavy ketones", although recently some examples of silanethione [5], silaneselone [5] and germanethione [6] compounds, stabilized by the intramolecular coordination of nitrogen atoms to the double bond (thermodynamic stabilization), have been reported.

Very recently we have succeeded in the synthesis and X-ray structural characterization of kinetically stabilized silanethione [7], germanethione [8] and germaneselone [9] by taking advantage of a new steric protection group, 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl [10] (Tbt), developed in this laboratory. We have also successfully synthesized and studied by UV–vis spectroscopy stannanethione Tbt(Tip)Sn=S (Tip 2,4,6-triisopropylphenyl) which is stable in solution at room temperature, by sulfurization of the corresponding stannylene [11], although ab initio calculations for $H_2M{=}X$ (M = Si, Ge or Sn; X = S or Se) indicate that the π-bond energy of the tin–sulfur double bond (31.8 kcal mol^{-1}) is lower than those of the silicon–sulfur (46.2 kcal mol^{-1}), germanium–sulfur (40.0 kcal mol^{-1}), and even germanium–selenium (35.0 kcal mol^{-1}) [12]. In addition, we reported earlier an alternative method for the synthesis of compounds containing the tin–chalcogen double-bonds by dechalcogenation of 1,2,3,4,5-tetrachalcogenastannolanes [13]. In the course of our studies on the "heavy ketones" we became interested in the chemistry of compounds containing the tin–selenium double bond. In this paper we report on two new aspects of stannaneselone chemistry; (1) a new approach to species containing a tin–selenium double bond, i.e. the selenation of a stannylene; and (2) new

☆ Dedicated to Professor Hideki Sakurai on the occasion of his retirement from Tohoku University.

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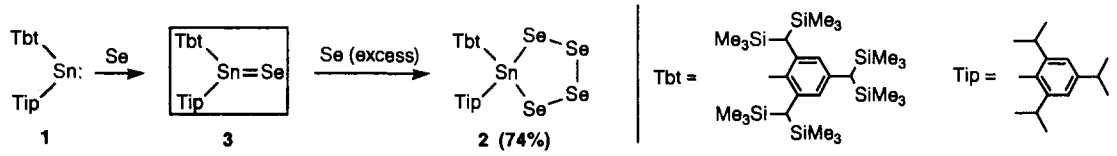
trapping reactions of a stannaneselone generated by the deselenation of a tetraselenastannolane.

2. Results and discussion

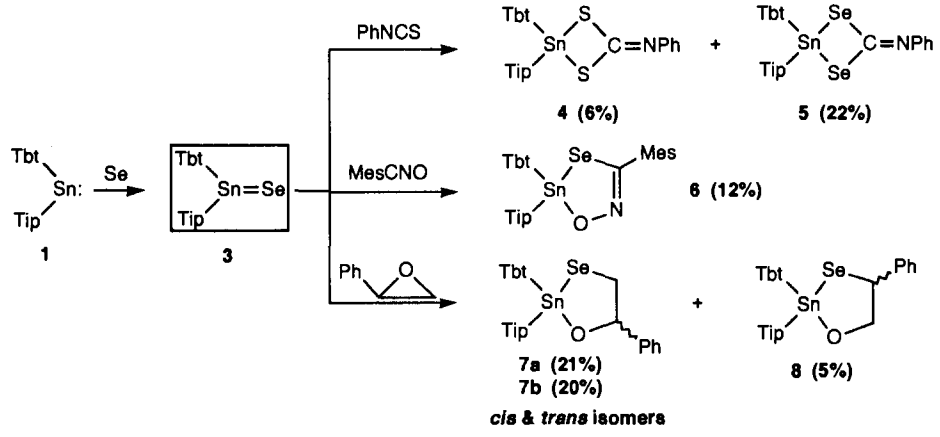
We used two approaches for the synthesis of a stannaneselone, i.e. the selenation of stannylene Tbt (Tip) Sn **1** and the deselenation of tetraselenastannolane Tbt (Tip) $SnSe_4$ **2**.

2.1. Selenation of stannylene 1

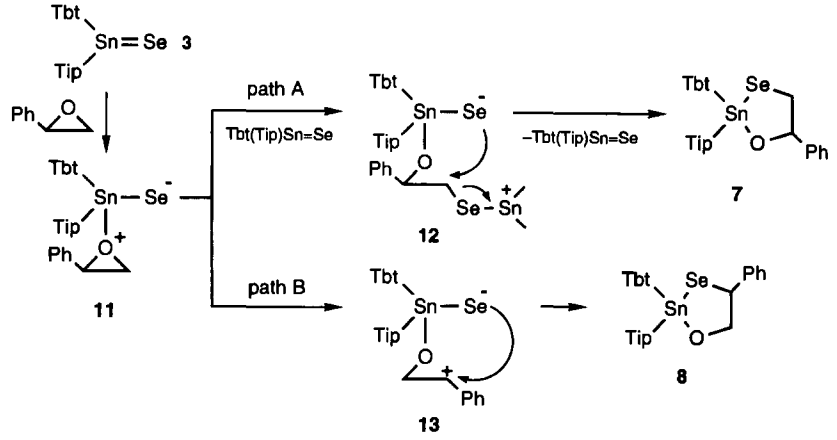
We have previously reported that an orange solution of stannylene **1** is readily obtained by treatment of a THF solution of TbtLi with an ether suspension of stannous chloride at −78°C, followed by the addition of a THF solution of an equimolar amount of TipLi at the same temperature [11]. Addition of excess elemental selenium to the solution of **1** at −70°C resulted in a color change of the solution from orange to yellow, suggesting the formation of stannaneselone Tbt (Tip) Sn=Se **3**. When this reaction mixture was gradually warmed to room temperature, however, the solution turned deep orange, and after purification 1,2,3,4,5-tetraselenastannolane **2** was obtained in 74% yield as the sole product (Scheme 1). Since the formation of **2** could be reasonably interpreted in terms of the selenation of initially formed stannaneselone **3** by excess elemental selenium, we examined chemical trapping reactions of



Scheme 1.



Scheme 2.



Scheme 3.

stannaneselone **3** using a THF–ether solution of stannaneselone **3** synthesized from **1** and an equimolar amount of elemental selenium at −70°C.

First, we attempted a trapping reaction with phenyl isothiocyanate (Scheme 2), since we had found previously that stannanethione Tbt(Tip)Sn=S reacts with phenyl isothiocyanate to give a [2 + 2]cycloadduct [11]. Interestingly, 1,3,2-dithia- **4** (6%) and 1,3,2-di-selenastannetane **5** (22%) were obtained instead of the expected [2 + 2]cycloadduct 1,3,2-thiaselenastannetane **9**.

Stannaneselone **3** from **1** was also trapped by a 1,3-dipolar cycloaddition. The reaction of **3** with mesitonitrile oxide afforded 1,3,5,2-oxaselenastannole **6**. Compound **6** is of interest not only as the first example of the [3 + 2]cycloaddition of a stannaneselone but also as a novel tin-containing heterocycle. It is thermally very stable and does not decompose even at 200°C in toluene.

The trapping of stannaneselone **3** with styrene oxide was also carried out, since we had found previously that the reaction of styrene oxide with stannaneselone **3** generated by deselenation of **2** with triphenylphosphine gives a 1,3,2-oxaselenastannolane [13]. The products in the present reaction were **7** and **8**. In the case of **7**, the *cis*- and *trans*-isomers were found in approximately equal amounts and could be seperated by chromatography. It has been reported that diethylgermanethione generated by the thermolysis (100°C) of $(Et_2GeS)_3$ reacts with ethylene oxide to give 1,3,2-oxathiagermolane [14]. A plausible mechanism for the formation of **7** and **8** is shown in Scheme 3. The first step is coordination of styrene oxide to **3**, leading to the formation of a zwitterionic intermediate **11**. Since the selenium of **3** is a good but bulky nucleophile, it will attack a less substituted carbon to give **12**, which then cyclizes with elimination of **3** to afford the final product **7**. Since the positive charge on the methine carbon next to the phenyl group is stabilized, a unimolecular process giving **13** could also take place to afford 4-phenyl-1,3,2-oxaselenastannolane **8** as a minor product. We reported previously that only **8** was formed in the reaction with stannaneselone **3** generated from deselenation of the tetraselenastannolane **2** [13]. The difference between these two reactions probably results from the presence of triphenylphosphine selenide, a nucleophilic catalyst, in the latter reaction. Since the phosphine selenide is smaller and less nucleophilic than **3**, cyclization at the carbon bearing a phenyl substituent is more favorable. However, in the present reaction, the bulky nucleophilic catalyst **3** attacks the less hindered carbon leading to the formation of **7** as the major product.

2.2. Deselenation of 1,2,3,4,5-tetraselenastannolane 2

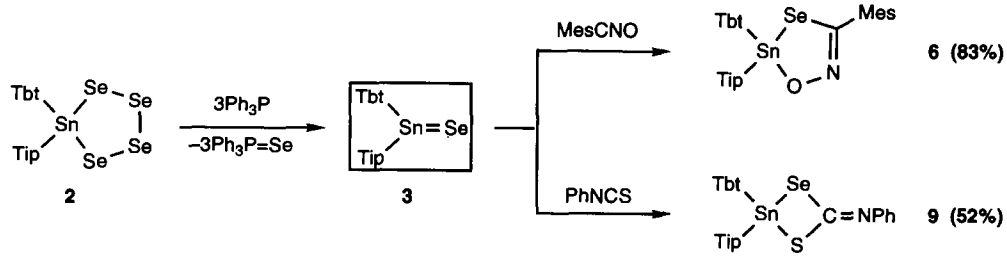
Although we reported previously the generation of stannaneselone **3** by the deselenation of **2** with triphenylphosphine [13], we trapped **3** with styrene oxide only. In the present work we also attempted to trap **3** with mesitonitrile oxide and phenyl isothiocyanate.

The stannaneselone **3**, generated by addition of triphenylphosphine to a THF solution of **2** at −70°C, was allowed to react with mesitonitrile oxide to give the corresponding adduct **6** in 83% yield. A similar reaction with phenyl isothiocyanate afforded 1,3,2-thiaselenastannetane **9** in 52% yield, unlike the reaction shown in Scheme 2. The difference between the results shown in Schemes 2 and 4 is unclear at present.

3. Experimental details

3.1. General procedure

All reactions were carried out under argon. ^1H and ^{13}C NMR spectra were recorded on a Bruker AM-500 spectrometer with tetramethylsilane as internal standard. Preparative HPLC was carried out on an LC-08 or LC-908 (Japan Analytical Ind. Co., Ltd.) with JAIGEL-1H and -2H columns. Preparative thin-layer chromatography (PTLC) was done with Merck Kieselgel 60 PF_{254} Art. 7747. Dry column chromatography (DCC) was carried out with ICN Silica DCC 60A. All melting points were determined on a Yanaco micro melting point apparatus and are uncorrected. Elemental analyses were carried out at the Microanalytical Laboratory of Department of Chemistry, Faculty of Science, The University of Tokyo.



Scheme 4.

3.2. Materials

1-Bromo-2,4,6-tris[bis(trimethylsilyl)methyl]benzene (TbtBr) [10] and 1-bromo-2,4,6-triisopropylbenzene (TipBr) [15] were prepared according to procedures reported in the literature. Stannous chloride was purchased from Wako Pure Chemical Ind. Ltd. THF, ether and hexane used in synthesis were all distilled from benzophenone ketyl under argon before use.

3.3. General procedure for the preparation of a THF–ether solution of Tbt(Tip)Sn: 1

To a THF solution (5 ml) of TbtLi, prepared from TbtBr (572 mg, 0.90 mmol) and Bu^{t}Li (1.65 M in pentane; 1.20 ml, 2.2 equiv.) at −70°C was added an ether suspension (9 ml) of stannous chloride (184 mg, 0.97 mmol). After stirring for 1.5 h at −65°C, the reaction mixture was treated with a THF solution (5 ml) of equimolar TipLi, prepared from TipBr (253 mg, 0.89 mmol) and Bu^{t}Li (2.2 equiv.), to afford an orange solution of stannylene Tbt(Tip)Sn: **1**.

3.4. Reaction of stannylene 1 with excess elemental selenium

Elemental selenium (531 mg, 6.72 mmol) was added to a THF–ether solution of stannylene **1** synthesized from TbtBr (1.01 g, 1.59 mmol), stannous chloride (334 mg, 1.76 mmol) and TipBr (495 mg, 1.75 mmol) at −70°C. After warming to room temperature, the solvents were evaporated and the residue was subjected to DCC and HPLC to give 2-tris[bis(trimethylsilyl)-methyl]phenyl-2-(2,4,6-triisopropylphenyl)-1,2,3,4,5-tetraselenastannolane **2** (1.34 g, 74%).

3.5. Reaction of stannaneselone 3 with mesitonitrile oxide

Elemental selenium (111 mg, 1.41 mmol) was added to a THF–ether solution of stannylene **1** synthesized from TbtBr (931 mg, 1.47 mmol), stannous chloride (299 mg, 1.58 mmol) and TipBr (432 mg, 1.53 mmol) at −70°C. After stirring for 2.5 h at this temperature, the reaction mixture was treated with a THF solution of mesitonitrile oxide (294 mg, 1.82 mmol). After removal of the solvent at room temperature, the residue was subjected to HPLC followed by PTLC to afford 2-tris[bis(trimethylsilyl)methyl]phenyl-2-(2,4,6-triisopropylphenyl)-4-mesityl-1,3,5,2-oxaselenazastannole **6** (144 mg, 12%) **6**: m.p. 197–200°C (decomp.) (methylene chloride–ethanol). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.02 (s, 9H), 0.05 (s, 27H), 0.06 (s, 9H), 0.07 (s, 9H), 1.23 (d, $J = 6$ Hz, 6H), 1.27 (d, $J = 6$ Hz, 6H), 1.29 (d, $J = 7$ Hz, 6H), 1.37 (s, 1H), 2.01 (s, 1H), 2.14 (s, 1H), 2.18 (brs, 6H), 2.26 (s, 3H), 2.87 (sept, $J = 6$ Hz, 1H), 3.05 (brsept, 2H), 6.41 (s, 1H), 6.54 (s, 1H), 6.82 (s, 2H), 7.04 (s, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 0.91 (q), 0.93 (q), 0.99 (q), 1.23 (q), 1.50 (q), 20.70 (q), 21.03 (q), 23.63 (q), 23.94 (q), 25.86 (brq), 30.74 (d), 31.95 (d), 32.29 (d), 34.30 (d), 38.42 (d), 122.57 (d), 123.16 (d), 128.28 (d), 128.34 (d), 131.83 (s), 137.05 (s), 138.09 (s), 139.04 (s), 143.52 (s), 143.61 (s), 145.71 (s), 151.08 (s), 151.17 (s), 151.25 (s), 153.86 (s). Anal. Calc. for $C_{52}H_{93}NOSeSi_6Sn$: C, 56.03; H, 8.43; N, 1.26; Se, 7.08%. Found: C, 55.74; H, 8.70; N, 1.36; Se, 6.75%.

3.6. Reaction of stannaneselone 3 with phenyl isothiocyanate

Elemental selenium (60 mg, 0.76 mmol) was added to a THF–ether solution of stannylene **1** synthesized from TbtBr (489 mg, 0.77 mmol), stannous chloride (157 mg, 0.83 mmol) and TipBr (238 mg, 0.84 mmol) at −70°C. After stirring for 1 h at this temperature, phenyl isothiocyanate (0.15 ml, 1.25 mmol) was added to the reaction mixture. After warming to room temperature and removal of the solvent, the residue was subjected to HPLC followed by DCC to afford 2-tris[bis(trimethylsilyl)methyl]phenyl-2-(2,4,6-triisopropylphenyl)-4-phenylimino-1,3,2-dithiastannetane **4** (48 mg, 6%) and 2-tris[bis(trimethylsilyl)methyl]phenyl-2-(2,4,6-triisopropylphenyl)-4-phenylimino-1,3,2-diselenastannetane **5** (166 mg, 22%). **4**: m.p. 145–147.5°C (methylene chloride–ethanol). ^{1}H NMR ($CDCl_3$, 500 MHz) δ −0.03 (s, 9H), −0.01 (s, 9H), 0.03 (s, 9H), 0.04 (s, 9H), 0.05 (s, 18H), 1.23 (d, $J = 7$ Hz, 6H), 1.30 (d, $J = 6$ Hz, 6H), 1.33 (brs, 6H), 1.62 (s, 1H), 2.19 (s, 1H), 2.49 (s, 1H), 2.9 (m, 3H), 6.37 (s, 1H), 6.52 (s, 1H), 6.90 (d, $J = 7$ Hz, 2H), 7.02 (t, $J = 7$ Hz, 1H), 7.07 (s, 2H), 7.27 (dd, $J = 7$ Hz, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 0.85 (q), 1.01 (q), 1.22 (q), 1.26 (q), 23.98 (q), 30.65 (q), 30.82 (d), 31.92 (d), 32.17 (d), 34.40 (d), 39.73 (d), 121.22 (d), 122.69 (d), 123.03 (d), 123.80 (d), 127.97 (d), 128.68 (d), 136.14 (s), 141.63 (s), 146.35 (s), 149.88 (s), 151.42 (s), 151.86 (s), 153.44 (s), 157.39 (s). Anal. Calc. for $C_{49}H_{87}NS_2Si_6Sn$: C, 56.49; H, 8.43; N, 1.21; S, 6.16%. Found: C, 56.21; H, 8.51; N, 0.99; S, 5.80%. **5**: m.p. 154–156°C (decomp.) (methylene chloride–ethanol). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.01 (s, 18H), 0.06 (s, 36H), 1.24 (d, $J = 7$ Hz, 6H), 1.31 (brs, 12H), 1.36 (s, 1H), 2.40 (s, 1H), 2.68 (s, 1H), 2.89 (sept, $J = 7$ Hz, 1H), 3.10 (brs, 2H), 6.37 (s, 1H), 6.52 (s, 1H), 6.91 (d, $J = 8$ Hz, 2H), 7.06 (s, 2H), 7.10 (t, $J = 7$ Hz, 1H), 7.31 (dd, $J = 7$, 8 Hz, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 0.81 (q), 1.13 (q), 1.35 (q), 22.95 (q), 23.96 (q), 28.74 (q), 30.66 (d), 31.29 (d), 31.67 (d), 34.35 (d), 39.49 (d), 120.39 (d), 122.60 (d), 123.00 (d), 124.40 (d), 128.00 (d), 128.89 (d), 132.66 (s), 134.33 (s), 141.06 (s), 145.77 (s), 150.62 (s), 151.33 (s), 151.76 (s), 153.20 (s); Anal.

Calc. for $C_{49}H_{87}NSe_2Si_6Sn$: C, 51.83; H, 7.74; N, 1.23; Se, 13.91%. Found: C, 51.58; H, 7.87; N, 1.29; Se, 13.78%.

3.7. Reaction of stannaneselone 3, generated by selenation of stannylene 1, with styrene oxide

Elemental selenium (77 mg, 0.97 mmol) was added to a THF-ether solution of stannylene **1** synthesized from TbtBr (572 mg, 0.90 mmol), stannous chloride (184 mg, 0.97 mmol) and TipBr (253 mg, 0.89 mmol) at −70°C. After stirring for 30 min at this temperature, the reaction mixture was treated with styrene oxide (0.1 ml, 0.88 mmol). After removal of the solvent at room temperature, separation of the residue by HPLC gave a fraction containing oxaselenastannolanes (485 mg), a part (158 mg) of which was further purified by PTLC to afford 2-tris[bis(trimethylsilyl)methyl]phenyl-2-(2,4,6-triisopropylphenyl)-5-phenyl-1,3,2-oxaselenastannolanes **7a** (62 mg, 21%) and **7b** (61 mg, 20%), and 2-tris[bis(trimethylsilyl)methyl]phenyl-2-(2,4,6-triisopropylphenyl)-4-phenyl-1,3,2-oxaselenastannolane **8** (13 mg, 5%). **7a**: m.p. 209–211°C (methylene chloride–ethanol). ^{1}H NMR ($CDCl_3$, 500 MHz) δ −0.08 (s, 18H), −0.03 (s, 18H), 0.04 (s, 18H), 1.14 (brs, 6H), 1.24 (d, J = 7 Hz, 6H), 1.31 (brs, 6H), 1.43 (s, 1H), 1.86 (s, 1H), 1.95 (s, 1H), 2.79 (dd, J = 11, 11 Hz, 1H), 2.87 (sept, J = 7 Hz, 1H), 3.1 (brs, 2H), 3.38 (dd, J = 3, 11 Hz, 1H), 4.80 (dd, J = 3, 11 Hz, 1H), 6.34 (s, 1H), 6.47 (s, 1H), 7.05 (s, 2H), 7.13 (t, J = 7 Hz, 1H), 7.23 (dd, J = 7, 7 Hz, 2H), 7.36 (d, J = 7 Hz, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 0.82 (q), 0.90 (q), 1.18 (q), 1.40 (q), 1.47 (q), 1.70 (q), 23.94 (q), 24 (brq), 30.16 (d), 30.55 (d), 34.34 (d), 37.16 (t), 37.95 (d), 79.20 (d), 122.40 (d), 122.92 (d), 126.28 (d), 126.67 (d), 127.85 (d), 128.02 (d), 138.78 (s), 141.42 (s), 144.99 (s), 145.79 (s), 150.59 (s), 150.87 (s), 151.16 (s), 154.47 (s). Anal. Calc. for $C_{50}H_{90}OSeSi_6Sn$: C, 55.95; H, 8.45; Se, 7.36%. Found: C, 55.90; H, 8.23; Se, 7.62%. **7b**: m.p. 231–234°C (decomp.) (methylene chloride–ethanol). ^{1}H NMR ($CDCl_3$, 500 MHz) δ −0.01 (s, 18H), 0.02 (s, 9H), 0.03 (s, 9H), 0.04 (s, 9H), 0.05 (s, 9H), 1.20 (d, J = 7 Hz, 6H), 1.2 (brs, 12H), 1.33 (s, 1H), 2.20 (s, 1H), 2.41 (s, 1H), 2.8 (m, 2H), 3.14 (brs, 1H), 3.3 (m, 2H), 4.76 (dd, J = 3, 11 Hz, 1H), 6.36 (s, 1H), 6.48 (s, 1H), 7.01 (s, 2H), 7.20 (t, J = 7 Hz, 1H), 7.27 (dd, J = 7, 8 Hz, 2H), 7.48 (d, J = 8 Hz, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 0.82 (q), 0.90 (q), 1.28 (q), 1.53 (q), 1.54 (q), 22.89 (q), 23.42 (q), 23.93 (q), 29.05 (brq), 30.55 (d), 30.91 (d), 31.19 (d), 34.31 (d), 34.96 (t), 36.72 (d), 37.90 (d), 80.15 (d), 122.18 (d), 122.51 (d), 122.82 (d), 126.30 (d), 126.69 (d), 127.79 (d), 127.91 (d), 137.39 (s), 141.82 (s), 145.07 (s), 145.10 (s), 150.81 (s), 151.09 (s), 151.49 (s), 154.21 (s), 154.44 (s). Anal. Calc. for $C_{50}H_{90}OSeSi_6Sn$: C, 55.95; H, 8.45; Se, 7.36%. Found: C, 55.74; H, 8.34; Se, 7.15%. **8**: m.p. 218–221°C (decomp.) (methylene chloride–ethanol). ^{1}H NMR ($CDCl_3$, 500 MHz, 330 K) δ 0.00 (s, 18H), 0.07 (s, 18H), 0.11 (s, 18H), 1.19–1.29 (m, 12H), 1.34 (d, J = 6 Hz, 6H), 1.36 (s, 1H), 1.97 (s, 1H), 2.08 (s, 1H), 2.88 (sept, J = 7 Hz, 1H), 3.18–3.48 (brsept, 2H), 3.77 (dd, J = 10, 11 Hz, 1H), 4.53 (dd, J = 4, 11 Hz, 1H), 4.55 (dd, J = 4, 10 Hz, 1H), 6.26–6.64 (brs, 2H), 7.06 (s, 2H), 7.19–7.21 (m, 1H), 7.25–7.28 (m, 2H), 7.39–7.40 (m, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 0.80 (q), 0.94 (q), 1.05 (q), 1.26 (q), 1.35 (q), 1.62 (q), 23.96 (q), 23.98 (q), 30.32 (d), 30.44 (d), 30.57 (d), 34.35 (d), 38 (brd), 54.04 (d), 72.13 (t), 122.50 (d), 122.99 (d), 127.22 (d), 128.08 (d), 128.52 (d), 138.75 (s), 139.99 (s), 141.44 (s), 145.09 (s), 150.67 (s), 150.95 (s), 151.30 (s), 154.56 (s). Anal. Calc. for $C_{50}H_{90}OSeSi_6Sn$: C, 55.95; H, 8.45; Se, 7.36%. Found: C, 55.70; H, 8.51; Se, 7.08%.

3.8. Reaction of stannaneselone 3, generated by deselenation of 2, with mesitonitrile oxide

Triphenylphosphine (54 mg, 0.21 mmol) was added to a THF solution of 1,2,3,4,5-tetraselenastannolane **2** (82.0 mg, 0.069 mmol) at −70°C. After stirring for 2.5 h at this temperature, the reaction mixture was treated with a THF solution of mesitonitrile oxide (68 mg, 0.42 mmol). After removal of the solvent at room temperature, the residue was subjected to HPLC to afford oxaselenazastannole **6** (64 mg, 83%).

3.9. Reaction of stannaneselone 3, generated by deselenation of 2, with phenyl isothiocyanate

Triphenylphosphine (68.1 mg, 0.26 mmol) was added to a THF solution of 1,2,3,4,5-tetraselenastannolane **2** (100 mg, 0.084 mmol) at −70°C. After stirring for 2 h at this temperature, the reaction mixture was treated with phenyl isothiocyanate (60 μl, 0.50 mmol). After removal of the solvent at room temperature, the residue was subjected to HPLC to afford 2-tris[bis(trimethylsilyl)methyl]phenyl-2-(2,4,6-triisopropylphenyl)-4-phenylimino-1,3,2-thiaselenastannetane **9** (49 mg, 52%). **9**: ^{1}H NMR ($CDCl_3$, 500 MHz) δ −0.02 (s, 9H), −0.01 (s, 9H), 0.02 (s, 9H), 0.04 (s, 18H), 0.05 (s, 9H), 1.23 (d, J = 7 Hz, 6H), 1.28 (d, J = 6 Hz, 6H), 1.32 (brs, 6H), 1.34 (s, 1H), 2.27 (s, 1H), 2.56 (s, 1H), 2.88 (sept, J = 7 Hz, 1H), 2.96 (brs, 2H), 6.35 (s, 1H), 6.50 (s, 1H), 6.87–6.89 (m, 2H), 7.05 (s, 2H), 7.05–7.08 (m, 1H), 7.27–7.30 (m, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 0.82 (q), 1.02 (q), 1.11 (q), 1.26 (q), 1.34 (q), 23.04 (brq), 23.96 (q), 23.97 (q), 28.72 (brq), 30.73 (d), 31.64 (d), 31.95 (d), 34.40 (d), 39.56 (d), 120.76 (d), 122.64 (d), 123.01 (d), 124.32 (d), 127.97 (d), 128.86 (d), 135.36 (s), 141.44 (s), 146.06 (s), 146.52 (s), 150.98 (s), 151.33 (s), 151.60 (s), 151.79 (s), 153.36 (s). FAB

MS [M + H], Calc. for $C_{49}H_{88}NSi_6S^{80}Se^{118}Sn$: 1088.3435. Found: 1088.3451.

4. Conclusion

We have successfully generated a kinetically stabilized stannaneselone **3** by both the reaction of the corresponding stannylene **1** with elemental selenium or by the deselenation of 1,2,3,4,5-tetraselenastannolane **2**, which can be synthesized by the reaction of stannylene **1** with excess elemental selenium. The former route represents the first example of the formation of a stannaneselone from a stannylene. Stannaneselone **3** reacted with phenyl isothiocyanate, mesitonitrile oxide and styrene oxide to afford the corresponding cycloadducts.

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