

# The First Kinetically Stabilized Stannaneselone and Diselenastannirane: Synthesis by Deselenation of a Tetraselenastannolane and Structures

Masaichi Saito,<sup>†</sup> Norihiro Tokitoh, and Renji Okazaki\*

Department of Chemistry, Graduate School of Science  
The University of Tokyo, 7-3-1, Hongo, Bunkyo-ku  
Tokyo 113 Japan

Received July 7, 1997

Recently, significant progress has been made in the chemistry of low-coordinated and strained compounds of heavier main group elements, especially those involving group 14 elements.<sup>1</sup> Previous studies on such species, however, have centered on silicon and germanium compounds, and the chemistry of such compounds containing tin has been much less explored.

As for low-coordinated tin compounds, some stable double-bond species with group 14 (Sn=Sn,<sup>2</sup> Sn=C,<sup>3</sup> and Sn=C=N<sup>4</sup>) and group 15 elements (Sn=N<sup>5</sup> and Sn=P<sup>6</sup>) have been synthesized, but tin–chalcogen double-bond compounds so far reported are restricted to those thermodynamically stabilized by intramolecular coordination,<sup>7</sup> which are highly perturbed by electron donation from neighboring nitrogen atoms to an electron-deficient tin center as evidenced by their high-field chemical shifts in <sup>119</sup>Sn NMR (vide infra). We previously reported the synthesis of heavier element analogues of a ketone with Si=S<sup>8</sup> and Ge=X (X = S, Se, Te)<sup>9</sup> kinetically stabilized by a very efficient steric protection group, 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl (Tbt) group, developed by us. Although we also described the synthetic approach to tin–chalcogen double-bond compounds, Tbt(Tip)Sn=X (Tip = 2,4,6-triisopropylphenyl; X = S, Se), by dechalcogenation of 1,2,3,4,5-tetrachalcogenastannolanes<sup>10</sup> and chalcogenation of the corresponding stannylenes,<sup>11</sup> they were found to be stable only in solution and dimerize in the solid state. With regard to three-membered ring compounds of heavier group 14 elements, a relatively large number of examples have been described<sup>1</sup>

<sup>†</sup> Present address: Department of Chemistry, Faculty of Science, Saitama University, Japan.

(1) For reviews, see: (a) West, R. *Pure Appl. Chem.* **1984**, *56*, 163. (b) Satgé, J. *Pure Appl. Chem.* **1984**, *56*, 137. (c) Raabe, G.; Michl, J. *Chem. Rev.* **1985**, *85*, 419. (d) West, R. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 1201. (e) Barrau, J.; Escudié, J.; Satgé, J. *Chem. Rev.* **1990**, *90*, 283. (f) Satgé, J. *J. Organomet. Chem.* **1990**, *400*, 121. (g) Neumann, W. P. *Chem. Rev.* **1991**, *91*, 311. (h) Tsumuraya, T.; Batcheller, S. A.; Masamune, S. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 902. (i) Brook, A. G.; Brook, M. A. *Adv. Organomet. Chem.* **1996**, *39*, 71. (j) Okazaki, R.; West, R. *Adv. Organomet. Chem.* **1996**, *39*, 232. (k) Baines, K. M.; Stibbs, W. G. *Adv. Organomet. Chem.* **1996**, *39*, 275.

(2) (a) Goldberg, D. E.; Harris, D. H.; Lappert, M. F.; Thomas, K. M. *J. Chem. Soc., Chem. Commun.* **1976**, 261. (b) Masamune, S.; Sita, L. R. *J. Am. Chem. Soc.* **1985**, *107*, 6390.

(3) (a) Meyer, H.; Baum, G.; Massa, W.; Berger, S.; Berndt, A. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 546. (b) Anselme, G.; Ranaivonjatovo, H.; Escudié, J.; Couret, C.; Satgé, J. *Organometallics* **1992**, *11*, 2748.

(4) Grützmacher, H.; Freitag, S.; Herbst-Irmer, R.; Sheldrick, G. S. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 437.

(5) Ossig, G.; Meller, A.; Freitag, S.; Herbst-Irmer, R. *J. Chem. Soc., Chem. Commun.* **1993**, 497.

(6) (a) Couret, C.; Escudié, J.; Satgé, J.; Raharinirina, A.; Andriamizaka, J. D. *J. Am. Chem. Soc.* **1985**, *107*, 8280. (b) Ranaivonjatovo, H.; Escudié, J.; Couret, C.; Satgé, J. *J. Chem. Soc., Chem. Commun.* **1992**, 1047.

(7) (a) Kuchta, M. C.; Parkin, G. *J. Am. Chem. Soc.* **1994**, *116*, 8372. (b) Leung, W.-P.; Kwok, W.-H.; Law, L. T. C.; Zhou, Z.-Y.; Mak, T. C. W. *J. Chem. Soc., Chem. Commun.* **1996**, 505.

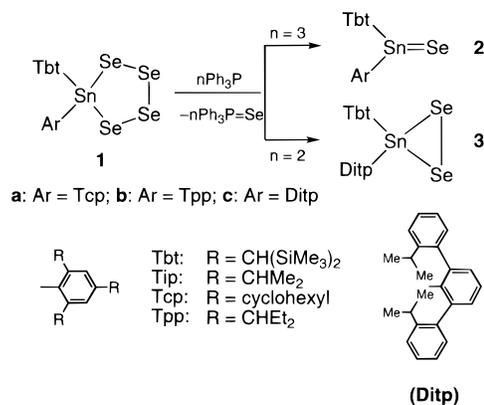
(8) Suzuki, H.; Tokitoh, N.; Nagase, S.; Okazaki, R. *J. Am. Chem. Soc.* **1994**, *116*, 11578.

(9) (a) Tokitoh, N.; Matsumoto, T.; Manmaru, K.; Okazaki, R. *J. Am. Chem. Soc.* **1993**, *115*, 8855. (b) Matsumoto, T.; Tokitoh, N.; Okazaki, R. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 2316. (c) Tokitoh, N.; Matsumoto, T.; Okazaki, R. *J. Am. Chem. Soc.* **1997**, *119*, 2337.

(10) (a) Matsushashi, Y.; Tokitoh, N.; Okazaki, R. *Organometallics* **1993**, *12*, 2573. (b) Saito, M.; Tokitoh, N.; Okazaki, R. *J. Organomet. Chem.* **1995**, *499*, 43.

(11) (a) Tokitoh, N.; Saito, M.; Okazaki, R. *J. Am. Chem. Soc.* **1993**, *115*, 2065. (b) Saito, M.; Tokitoh, N.; Okazaki, R. *Organometallics* **1996**, *15*, 4531.

## Scheme 1



including those containing one chalcogen atom,<sup>12</sup> but there is no precedent which contains two chalcogen atoms in the ring.<sup>13</sup>

We report here that the deselenation of a tetraselenastannolane by a phosphine reagent affords a stannaneselone without intramolecular coordination or a diselenastannirane, depending on the equivalence of the phosphine reagent used. Each of them represents the first isolation of such a species.

Tetraselenastannolanes Tbt(Ar)SnSe<sub>4</sub> (**1a**, Ar = 2,4,6-tricyclohexylphenyl (Tcpc), 22%; **1b**, Ar = 2,4,6-tris(1-ethylpropyl)phenyl (Tpp), 22%; **1c**, Ar = 2,2''-diisopropyl-*m*-terphenyl-2'-yl (Ditp), 38%), precursors for the synthesis of tin–selenium double-bond compounds,<sup>15</sup> were easily obtained by the reactions of the corresponding stannylenes Tbt(Ar)Sn: with excess of elemental selenium. Our previous observation that Tbt(Tip)Sn=Se readily dimerized at ambient temperature so that its <sup>119</sup>Sn NMR was unable to be measured<sup>11</sup> led us to use a bulkier Tcpc or Tpp group instead of Tip group. Treatment of Tbt(Tcpc)SnSe<sub>4</sub> **1a** with 3 equiv of triphenylphosphine in toluene gave a deep red solution, whose <sup>119</sup>Sn signal showed a signal at 556 ppm assignable to stannaneselone **2a**. This low-field chemical shift is characteristic of low-coordinated tin, e.g., R<sub>2</sub>Sn=SnR<sub>2</sub> (725,<sup>2a</sup> 427.5<sup>2b</sup> ppm), R<sub>2</sub>Sn=CR'<sub>2</sub> (835,<sup>3a</sup> 288<sup>3b</sup> ppm), and R<sub>2</sub>Sn=PR' (658.3,<sup>6a</sup> 499.5<sup>6b</sup> ppm), indicating that stannaneselone **2a** displays an intrinsic nature of tin–selenium double-bond compounds, in sharp contrast to the Parkin's terminal selenido complex whose <sup>119</sup>Sn NMR appears at a much higher field (−444 ppm).<sup>7a</sup> Similarly, the reaction of Tbt(Tpp)SnSe<sub>4</sub> **1b** with 3 equiv of triphenylphosphine also gave stannaneselone **2b** (δ<sub>Sn</sub>: 547 ppm). Although stannaneselones **2a** and **2b** were stable in solution for a short time at room temperature, the deep red color of the solution gradually disappeared over a few hours.

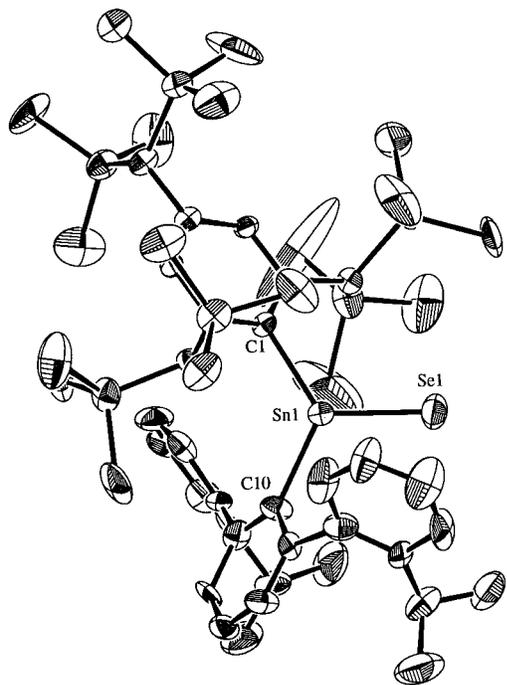
The unsuccessful attempts at the isolation of a stable stannaneselone by using the combination of Tbt-Tcpc and Tbt-Tpp groups prompted us to develop a ligand even bulkier than Tcpc and Tpp. We have introduced a new efficient steric

(12) (a) Tan, R. P.-K.; Gillette, G. R.; Powell, D. R.; West, R. *Organometallics* **1991**, *10*, 546. (b) Tsumuraya, T.; Saito, S.; Ando, W. *Organometallics* **1988**, *7*, 2015. (c) Schäfer, A.; Weidenbruch, M.; Saak, W.; Pohl, S.; Marsmann, H. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 962.

(13) The isolation of stable dithiirane and its oxide has recently been reported. (a) Ishii, A.; Akazawa, T.; Ding, M.-X.; Honjo, T.; Nakayama, J.; Hoshino, M.; Shiro, M. *J. Am. Chem. Soc.* **1993**, *115*, 4914. (b) Ishii, A.; Akazawa, T.; Maruta, T.; Nakayama, J.; Hoshino, M.; Shiro, M. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 777.

(14) For some recent reports on the synthesis of main group element compounds with unique structures using *m*-terphenyl ligands, see: (a) Schiemenz, B.; Power, P. P. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2150. (b) Grigsby, W. J.; Power, P. P. *J. Am. Chem. Soc.* **1996**, *118*, 7981. (c) Simons, R. S.; Power, P. P. *J. Am. Chem. Soc.* **1996**, *118*, 11966. We also developed a new type of bowl-shaped *m*-terphenyl ligand. (d) Goto, K.; Holler, M.; Okazaki, R. *Tetrahedron Lett.* **1996**, *37*, 3141. (e) Goto, K.; Holler, M.; Okazaki, R. *J. Am. Chem. Soc.* **1997**, *119*, 1460.

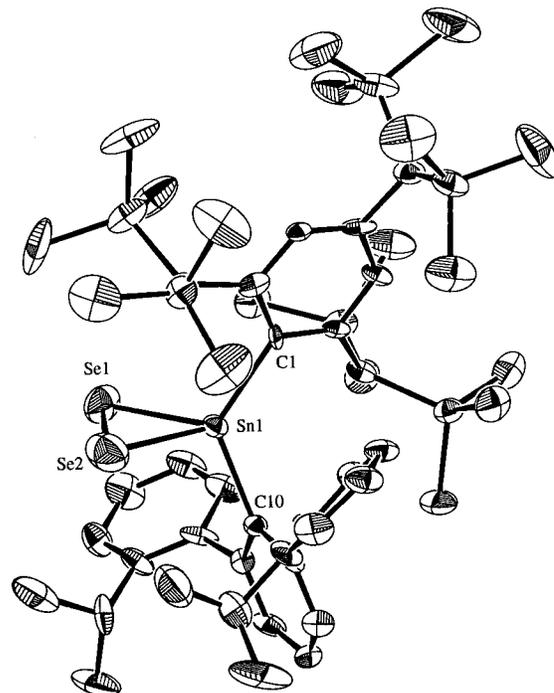
(15) For the details of the spectral data, see Supporting Information.



**Figure 1.** ORTEP drawing of Tbt(Ditp)Sn=Se (**2c**). Selected bond lengths (Å) and angles (deg): Sn(1)–Se(1), 2.375(3); Sn(1)–C(1), 2.23(2); Sn(1)–C(10), 2.20(2); C(1)–Sn(1)–Se(1), 121.6(5); C(10)–Sn(1)–Se(1), 115.8(6); C(1)–Sn(1)–C(10), 122.5(7).

protection group having a *m*-terphenyl skeleton, Ditp (2,2'-diisopropyl-*m*-terphenyl-2'-yl).<sup>14</sup> When Tbt(Ditp)SnSe<sub>4</sub> **1c** was allowed to react with 3 equiv of triphenylphosphine in refluxing hexane for 2 h under argon, the solution turned deep red, and a <sup>119</sup>Sn NMR signal was observed at 440 ppm, indicating the formation of stannaneselone **2c**. Filtration of triphenylphosphine selenide insoluble in hexane, followed by removal of hexane, resulted in the isolation of the stable stannaneselone **2c** as red crystals in 84% yield.<sup>15</sup> The molecular structure of **2c** was determined by X-ray crystallographic analysis.<sup>16</sup> The ORTEP drawing (Figure 1) shows that the stannaneselenocarbonyl unit is effectively protected by one disil group in Tbt and two isopropyl groups in Ditp which are directed toward the Sn=Se bond in order to avoid the steric repulsion with the Tbt group. The Sn–Se distance (2.375(3) Å) is approximately 9% shorter than a Sn–Se single bond length (2.55–2.60 Å)<sup>17</sup> and slightly shorter than that of the Parkin's terminal selenido complex (2.39 Å).<sup>7a</sup> The geometry around the tin atom is trigonal planar, the sum of the angles being 359.9°, indicative of structural similarity to a ketone.

Interestingly, treatment of **1c** with 2 equiv of triphenylphosphine in hexane at room temperature, followed by removal of triphenylphosphine selenide gave orange-red crystals of diselenastannirane **3** (56%).<sup>15</sup> In <sup>119</sup>Sn NMR a broad signal was



**Figure 2.** ORTEP drawing of Tbt(Ditp)SnSe<sub>2</sub> (**3**). Selected bond lengths (Å) and angles (deg): Sn(1)–Se(1), 2.528(2); Sn(1)–Se(2), 2.532(3); Se(1)–Se(2), 2.524(4); Se(1)–Sn(1)–Se(2), 59.84(9); Sn(1)–Se(1)–Se(2), 60.17(9); Sn(1)–Se(2)–Se(1), 59.99(9); C(1)–Sn(1)–C(10), 124.0(6).

observed at –406 ppm assignable to **3**. This high-field signal is characteristic of tin-containing three-membered compounds (Sn–C=C, –537 ppm;<sup>18</sup> Sn–C–S, –365 ppm;<sup>19</sup> Sn–Sn–S, –309 ppm;<sup>12c</sup> Sn–Sn–Se, –393 ppm;<sup>12c</sup> Sn–Sn–Te, –594 ppm<sup>20</sup>). The <sup>77</sup>Se NMR also showed a characteristic high-field signal at –193 ppm as have been similarly observed for Si–Si–Se (–287 ppm)<sup>12a</sup> and Sn–Sn–Se (–378 ppm) ring systems.<sup>12c</sup>

These spectral data were consistent with the diselenastannirane structure, but the molecular structure of **3** was finally established by X-ray crystallographic analysis (Figure 2).<sup>21</sup> The diselenastannirane ring system of **3** forms an equilateral triangle. It is noted that the Se–Se bond is very long (2.524(4) Å), about 0.2 Å longer than the typical Se–Se single bond<sup>22</sup> although the Sn–Se bond lengths (2.528(2), 2.532(3) Å) are almost equal to typical Sn–Se bond lengths (2.58 Å).<sup>17</sup>

In summary, deselenation of tetraselenastannolane **1c** bearing Tbt and Ditp groups gave two novel types of organotin compounds, *i.e.*, the first kinetically stabilized stannaneselone **2c** and first diselenirane derivative, diselenastannirane **3**, and their molecular structures were determined. This successful deselenation indicates that the dechalcogenation of a tetrachalcogenometalolane with appropriate ligands may constitute a useful synthetic method for compounds with unique structure.

**Acknowledgment.** This work was partially supported by a Grant-in-Aid for Scientific Research No. 05236102 from the Ministry of Education, Science, Sports and Culture, Japan. M.S. thanks Research Fellowships of the Japan Society for the Promotion of Science for Young Scientists. We are also grateful to Shin-etsu Chemical Co., Ltd. and Tosoh Akzo Co., Ltd. for the generous gift of chlorosilanes and alkyllithiums, respectively.

**Supporting Information Available:** Experimental procedures for the synthesis and physical properties of **1c**, **2c**, and **3** and crystallographic data with complete tables of bond lengths, bond angles, and thermal and positional parameters for **2c** and **3** (37 pages). See any current masthead page for ordering and Internet access instructions.

(16) Crystallographic data for **2c**: C<sub>51</sub>H<sub>84</sub>SeSi<sub>6</sub>Sn, *M* = 1063.39, triclinic, *a* = 11.939(8) Å, *b* = 23.478(5) Å, *c* = 11.471(4) Å, α = 91.86(2)°, β = 112.61(3)°, γ = 97.45(4)°, *V* = 2931(2) Å<sup>3</sup>, *Z* = 2, space group *P*1. *R*(*R*<sub>w</sub>) = 0.074 (0.086). Full details for the crystallographic analysis of **2c** are described in the Supporting Information.

(17) The average of a Sn–Se single bond in X–Sn–Se–X systems (428 examples) is 2.579 Å (Cambridge Structural Database).

(18) Sita, L. R.; Bickerstaff, R. D. *J. Am. Chem. Soc.* **1988**, *110*, 5208.

(19) Ohtaki, T.; Kabe, Y.; Ando, W. *Organometallics* **1993**, *12*, 4.

(20) Schäfer, A.; Weidenbruch, M.; Saak, W.; Pohl, S.; Marsmann, H. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 834.

(21) Crystals suitable for X-ray structural analysis were obtained by slow evaporation of a hexane solution of **3** in an argon atmosphere. Crystal data for **3**: C<sub>54</sub>H<sub>91</sub>Se<sub>2</sub>Si<sub>6</sub>Sn, *M* = 1185.44, triclinic, *a* = 12.97(1) Å, *b* = 22.36(1) Å, *c* = 12.91(2) Å, α = 104.54(7)°, β = 115.86(7)°, γ = 74.29(6)°, *V* = 3205(6) Å<sup>3</sup>, space group: *P*1, *Z* = 2, *D*<sub>c</sub> = 1.228 g cm<sup>-3</sup>. *R*(*R*<sub>w</sub>) = 0.072 (0.056). Full details for the crystallographic analysis of **3** are described in the Supporting Information.

(22) The average of 115 examples of a Se–Se bond in the C–Se–Se–C systems is 2.324 Å (Cambridge Structural Database).