Synthesis of a Thiastannirane by the Reaction of a Stannylene with a Thiocarbonyl Compound

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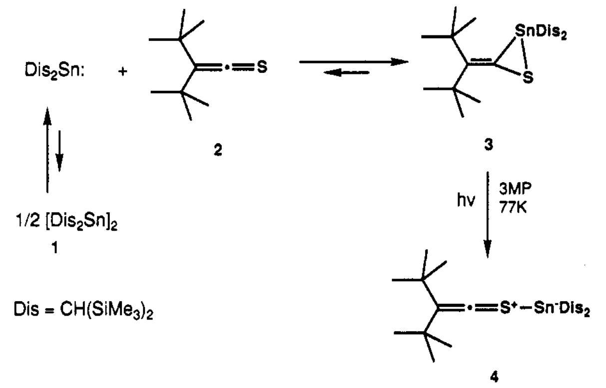
*Summary: The reaction of stannylene **1** with di-tert-butylthioketene (**2**) gave first thiastannirane **3** as air- and moisture-sensitive crystals. X-ray analysis showed that **3** contains an acute C–Sn–S angle (45.7°) and a short C–S bond (1.79 Å) responsible for the weakness of the Sn–C and Sn–S bonds. The reaction of **1** with thioketones **5a,b** furnished thiastannolanes **8a,b** via stannathiocarbonyl ylides **6** or thiastannirane **7** intermediates. Crystal data for **3**: space group $P2_12_12_1$, $Z = 4$, $a = 12.308$ (2) Å, $b = 14.725$ (2) Å, $c = 18.947$ (2) Å, $V = 3433.8$ Å^3, $R = 0.050$, $R_w = 0.064$ based on 2505 reflections with $|F_o^2| \geq 3\sigma|F_o^2|$.*

The addition reactions of main group divalent (R_2M)[1] and double-bond ($R_2M{=}MR_2$) (M = Si, Ge, Sn)[2] species with unsaturated substrates give a variety of three- and four-membered ring compound containing one and/or two metal atoms. Recently, we demonstrated that germylene undergoes cycloaddition reaction with thiocarbonyl compounds to afford a novel thiagermirane (GeCS) ring system.[1k,l] Herein we describe the corresponding tin chemistry, i.e., the reaction of a stannylene/distannene mixture (**1**)[3] with thiocarbonyl compounds to provide the first example of a thiastannirane (SnCS) ring compound.

Scheme I



The treatment of a deep red solution of **1** with 1.0 equiv of di-*tert*-butylthioketene (**2**) in benzene results in rapid decolorization of the solution. Removal of the solvent under reduced pressure gave air- and moisture-sensitive colorless crystals of **3**, which were purified by flash chromatography on Florisil under an argon atmosphere (67% yield). Crystals suitable for X-ray structural analysis were obtained by slow evaporation of a hexane solution of **3** in an argon atmosphere (Scheme I). The thiastannirane ring system of **3** forms an acute triangle with a C–Sn–S bond angle of 45.7 (4)° and three bond lengths of 2.438 (4) (Sn–S), 1.79 (1) (C–S), and 2.12 (1) Å (Sn–C), respectively, shown in Figure 1. For comparison, in the thiasilirane[1e] and thiagermirane systems,[1k], the C–Si–S and C–Ge–S bond angles are 56.7 and 52.9°, whereas the two sets of bond lengths are 2.09 (Si–S), 1.90 (C–S), 1.90 Å (Si–C) and 2.22 (Ge–S), 1.88 (C–S), 1.97 Å (Ge–C). The colorless crystals of **3** were redissolved in toluene to yield a pale red solution, which reveals that dissociation of **3** to **1** and **2** takes place. Actually, the ^{1}H and ^{119}Sn NMR spectra showed resonances corresponding to three compounds (**1**–**3**). A high-field ^{119}Sn resonance at −365 ppm (relative to Me_4Sn) assigned to **3** fell in the region related to other three-membered ring containing tin atoms (values in ppm): stannirene[1m] (SnC=C, −536.8) and distannirane (Sn_2N, −194;[2m] Sn_2S, −309;[2i] Sn_2Se, −393;[2l] Sn_2Te, −594[2i]). The ^{1}H NMR integrations of **2** and **3** at temperature intervals between −10 and 90 °C were reproducible to allow the determination of dissociation enthalpy the ($\Delta H° =$ 19.5 kcal mol^{-1}) and entropy ($\Delta S° = 47$ cal K^{-1} mol^{-1}).[5] Because of the large $\Delta H°$ value for dissociation, the coalescence of resonances among **1**–**3** was not well defined and the chemical shifts of these resonances were not

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(1) Papers on ring systems from metallylenes (R_2M) are as follows. M = Si: (a) Ando, W.; Hamada, Y.; Sekiguchi, A.; Ueno, K. *Tetrahedron Lett.* **1982**, *23*, 5232. (b) Conlin, R. T.; Gaspar, P. P. *J. Am. Chem. Soc.* **1976**, *98*, 3715. (c) Seyferth, D.; Annarelli, D. C.; Vick, S. C. *J. Am. Chem. Soc.* **1976**, *98*, 6382. (d) Schäfer, A.; Weidenbruch, M.; Saak, W.; Pohl, S. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 776. (e) Ando, W.; Hamada, Y.; Sekiguchi, A.; Ueno, K. *Tetrahedron Lett.* **1983**, *24*, 4033. (f) Ando, W.; Fujita, M.; Yoshida, H.; Sekiguchi, A. *J. Am. Chem. Soc.* **1988**, *110*, 3310. (g) Saso, H.; Ando, W.; Ueno, K. *Tetrahedron* **1989**, *45*, 1929. M = Ge: (h) Krebs, A.; Berndt, J. *Tetrahedron Lett.* **1983**, *24*, 4083. (i) Egorov, M. P.; Kolesnikov, S. P.; Struchkov, Y. T.; Antipin, M. Y.; Sereda, S. V.; Nefedov, O. M. *J. Organomet. Chem.* **1985**, *290*, C27. (j) Cowley, A. H.; Hall, S. W.; Nunn, C. M.; Power, J. M. *J. Chem. Soc., Chem. Commun.* **1988**, 753. (k) Tsumuraya, T.; Sato, S.; Ando, W. *Organometallics* **1989**, *8*, 161. (l) Ando, W.; Tsumuraya, T. *Organometallics* **1989**, *8*, 1467. M = Sn: (m) Sita, L. R.; Bickerstaff, R. D. *J. Am. Chem. Soc.* **1988**, *110*, 5208.

(2) Papers on three- and four-membered ring systems from dimetallenes ($R_2M{=}MR_2$) are as follows: M = Si: (a) West, R. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 1201. (b) West, R.; Gillette, G. R.; Yokelson, H. B.; Millevolte, A. J. *Phosphorus, Sulfur, Silicon* **1989**, *41*, 3. M = Si: (c) Weidenbruch, M.; Flintjer, B.; Pohl, S.; Saak, W. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 95. M = Si, Ge, and Sn: (d) Tsumuraya, T.; Batcheller, S. A.; Masamune, S. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 902. M = Ge: (e) Tsumuraya, T.; Sato, S.; Ando, W. *Organometallics* **1988**, *7*, 2015. (f) Tsumuraya, T.; Sato, S.; Ando, W. *Organometallics* **1990**, *9*, 2061. (g) Ando, W.; Tsumuraya, T. *J. Chem. Soc., Chem. Commun.* **1989**, 770. M = Sn: (h) Cowley, A. H.; Hall, S. W.; Nunn, C. M.; Power, J. M. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 838. (i) Schäfer, A.; Weidenbruch, M.; Saak, W.; Pohl, S.; Marsmann, H. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 834. (j) Krebs, A.; Jacobsen-Bauer, A.; Haupt, E.; Veith, M.; Huch, V. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 603. (k) Sita, L. R.; Kinoshita, I.; Lee, S. P. *Organometallics* **1990**, *9*, 1644. (l) Schäfer, A.; Weidenbruch, M.; Saak, W.; Pohl, S.; Marsmann, H. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 962. (m) Grützmacher, H.; Pritzkow, H. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1017.

(3) (a) Goldberg, D. E.; Hitchcock, P. B.; Lappert, M. F.; Thomas, K. M.; Thorne, A. J.; Fjeldberg, T.; Haaland, A.; Schilling, B. E. R. *J. Chem. Soc., Dalton Trans.* **1986**, 2387. (b) Zilm, K. W.; Lawless, G. A.; Merrill, R. M.; Millar, J. M.; Webb, G. G. *J. Am. Chem. Soc.* **1987**, *109*, 7236.

(4) Crystal of **3** suitable for X-ray crystallography were obtained by recrystallization from hexane in a glovebox. Data for **3**: orthorhombic, space group $P2_12_12_1$, $a = 12.308$ (2) Å, $b = 14.725$ (2) Å, $c = 18.947$ (2) Å, $V = 3433.8$ Å^3, $\rho_{calcd} = 1.18$ g/cm^3, $\mu = 9.5$ cm^{-1}, and $Z = 4$. The structure was solved from 2505 collected independent reflections [$2\theta \leq 50°$, $|F_o^2| > 3\sigma|F_o^2|$] measured on an Enraf-Nonius CAD4 diffractometer using Mo Kα irradiation and an ω–2θ scan. The structure was solved by direct methods, and all non-hydrogen atoms were refined anisotropically to $R = 0.050$ and $R_w = 0.064$.

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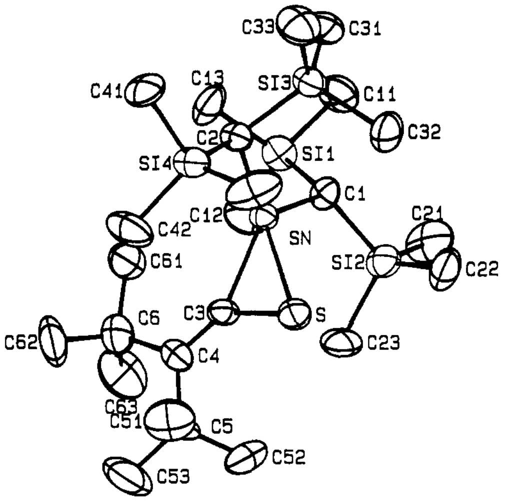
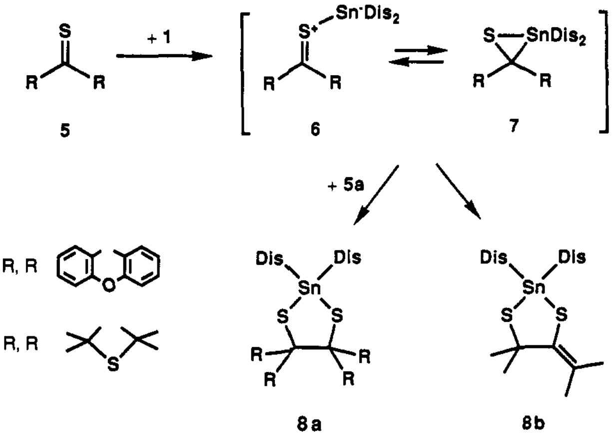


Figure 1. Perspective ORTEP drawing of 3 showing 50% thermal ellipsoids for the non-hydrogen atoms. Selected bond distances (Å) and angles (deg): Sn–S = 2.438 (4), Sn–Cl = 2.15 (1), Sn–C2 = 2.19 (1), Sn–C3 = 2.12 (1), S–C3 = 1.79 (1), C3–C4 = 1.34 (2), Cl–Sn–C2 = 116.1 (5); S–Sn–C3 = 45.7 (4), Sn–S–C3 = 57.8 (4), Sn–C3–S = 76.5 (5), Sn–C3–C4 = 149 (1), S–C3–C4 = 134 (1).

temperature dependent except for a transient line broadening.[5]

In contrast, on treatment of **1** with 1.0 equiv of thioketones **5a,b** in benzene followed by Florisil chromatography, dithiastannolanes **8a,b** were isolated (Scheme II) in 90% and 30% yield, respectively. The construction of both ring systems was established by spectroscopic data[6] and X-ray crystallographic analysis.[7]

Scheme II



The most reasonable first step of the pathway by which the **8a,b** are formed is the formation of a stannathiocarbonyl ylide or a thiastannirane. Assuming these intermediates, **8a** can be seen to arise from [2 + 3] cycloaddition of **5a** with **6** or insertion of **5a** into the Sn–C bond of **7**, while intramolecular rearrangement from both **6** and **7** might produce **8b**. The isolation of stannathiocarbonyl ylide **4** was tried in a 3-methylpentane (3-MP) matrix at 77 K upon irradiation of **3** with a low-pressure Hg lamp. A new band appeared at 600 nm and was assigned to **4** on the basis of our experience in sila-[8] and germathiocarbonyl ylides[1k,l] (485 and 580-690 nm).

Thus, the course of the reaction is highly dependent upon a fine balance between steric and electronic factors of thiocarbonyl compounds. Work along these lines is in progress.

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Supplementary Material Available: Text describing crystallographic procedures, tables of crystallographic data, atomic coordinates and thermal parameters, and bond lengths and angles for **3** and **8a,b**, figures showing ORTEP structures, and figures showing variable-temperature ^{1}H and ^{119}Sn NMR spectra of **3** (43 pages). Ordering information is given on any current masthead page.

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(5) The ^{1}H, ^{13}C, and ^{119}Sn NMR chemical shifts cited in ref 1m and the following reference were obtained at the slow-exchange limit (ca. −70 °C) for the thermal equilibrium of stannylene and adducts: Grützmacher, H.; Freitag, S.; Herbst-Irmer, R.; Sheldrick, G. S. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 437. However, the chemical shifts of **3** are not temperature dependent, and variable-temperature ^{1}H and ^{119}Sn NMR spectra are available in the supplementary material. Data for **3**: decomp pt 70 °C; ^{1}H NMR (C_6D_6, δ) 0.22 (s, 18 H), 0.28 (s, 2 H), 0.29 (s, 18 H), 1.36 (s, 9 H), 1.70 (s, 9 H); ^{13}C NMR (C_6D_6, δ) 3.29 (q), 3.57 (q), 9.85 (d), 31.07 (q), 33.16 (q), 38.21 (s), 40.91 (s), 137.42 (s), 149.35 (s); ^{119}Sn NMR (C_6D_6, δ) −365. Anal. Calcd for $C_{24}H_{56}SSi_4Sn$: C, 47.43; H, 9.29. Found: C, 46.67; H, 9.00.

(6) Data for **8a**: decomp pt 155 °C; ^{1}H NMR (C_6D_6, δ) 0.44 (s, 2 H), 0.46 (s, 18 H), 0.54 (s, 18 H), 6.80–7.08 (m, 12 H), 7.84–7.97 (m, 4 H); ^{13}C NMR (C_6D_6, δ) 1.75 (d), 5.04 (q), 5.24 (q), 72.79 (s), 116.65 (d), 122.20 (d), 124.90 (s), 129.29 (d), 132.20 (d), 152.68 (s). Anal. Calcd for $C_{40}H_{56}O_2S_2Si_4Sn$: C, 55.73; H, 6.31. Found: C, 55.39; H, 6.12. Data for **8b**: mp 101–103 °C; ^{1}H NMR (C_6D_6, δ) 0.14 (s, 2 H), 0.34 (s, 18 H), 0.37 (s, 18 H), 1.62 (s, 3 H), 1.95 (s, 6 H), 2.23 (s, 3 H); ^{13}C NMR (C_6D_6, δ) 3.85 (q), 3.89 (q), 14.97 (d), 22.88 (q), 30.50 (q), 36.01 (q), 61.08 (s), 131.20 (s), 136.55 (s); ^{119}Sn NMR (C_6D_6, δ) 99. Anal. Calcd for $C_{21}H_{50}S_2Si_4Sn$: C, 42.19; H, 8.43. Found: C, 41.83; H, 8.13.

(7) The X-ray analyses of **8a,b** were carried out in a fashion similar to cited in ref 4. The poor crystal qualities caused large standard deviations in the cell constants, but the strongly diffracting Sn and S enabled a satisfactory solution of the Sn frameworks. Data for **8a**: monoclinic, space group Pc, $a = 11.908$ (121) Å, $b = 24.510$ (40) Å, $c = 21.947$ (66) Å, $\beta = 136.39$ (70)°, $V = 4418.2$ Å^3, $\rho_{calcd} = 1.30$ g/cm^3, $\mu = 8.1$ cm^{-1}, 5386 collected reflections, and $R = 0.060$ ($R_w = 0.062$). Data for **8b**: monoclinic, space group $P2_1/n$, $a = 18.303$ (14) Å, $b = 9.031$ (4) Å, $c = 21.137$ (17) Å, $\beta = 112.67$ (30)°, $V = 3223.8$ Å^3, $\rho_{calcd} = 1.23$ g/cm^3, $\mu = 10.7$ cm^{-1}, $Z = 4$, 1584 collected reflections, and $R = 0.084$ ($R_w = 0.105$).

(8) Ando, W.; Hagiwara, K.; Sekiguchi, A. *Organometallics* **1987**, *6*, 2270.