Synthesis and Structure of a Kinetically Stabilized Stannanethione

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The X-ray crystallographic analysis of a stable stannanethione, Bbt(Titp)Sn=S, reveals that the tin–sulfur bond distance [2.221(3) Å] is ca. 10% shorter than the normal tin–sulfur single bonds and the tin atom of the stannanethione has a trigonal planar geometry, as do as the carbonyl carbon atoms.

The chemistry of compounds with double bonds between group 14 metals and heavier chalcogen atoms has continued to attract the attention of chemists in various fields.[1–6] We have already reported the synthesis of a series of stable heavy ketones, Tbt(Ar)M=Ch (M = Si, Ge, and Sn; Ch = S, Se, and Te), by taking advantage of the kinetic stabilization afforded by an extremely bulky Tbt group (Tbt = 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl).[1a–d] In most cases, the heavy ketones (Si=S, Ge=S, Ge=Se, Ge=Te, and Sn=Se) have been isolated as stable crystalline compounds and characterized by X-ray crystallographic analysis. Recently, Kira et al. have also reported the synthesis and structures of dialkyl-substituted silaneselone (Si=Se) and silanetellone (Si=Te).[4] Furthermore, we have succeeded in the first synthesis of a stable stannanetellone, Bbt(Titp)Sn=Te[5c] (Bbt = 2,6-bis[bis(trimethylsilyl)methyl]-4-[tris(trimethylsilyl)methyl]phenyl; Titp = 2,2″,4,4″-tetraisopropyl-*m*-terphenyl-2′-yl). Although stannanethione Tbt(Ditp)Sn=S[5b] (**2a**, Ditp = 2,2″-diisopropyl-*m*-terphenyl-2′-yl) has already been isolated as a stable compound, the crystallographic structural analysis of a stannanethione has not been achieved due to its low crystallinity. On the other hand, some compounds with Sn=Ch (Ch = S, Se, and Te) bonds thermodynamically stabilized by intramolecular coordination have been synthesized and isolated.[3] However, they are highly perturbed by electron donation from the neighboring nitrogen atoms to the central Sn=Ch moiety, as evidenced by their high-field chemical shifts in ^{119}Sn NMR spectra. We present here the structure of a new type of stannanethione **2b**, which is kinetically stabilized by the combination of Bbt and Titp groups.

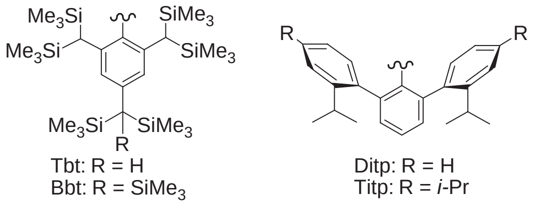
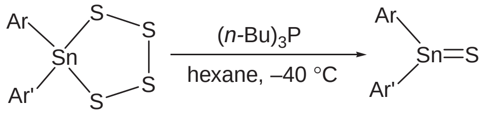


Chart 1.



1a: Ar = Tbt, Ar' = Ditp
1b: Ar = Bbt, Ar' = Titp

2a: Ar = Tbt, Ar' = Ditp 26%
2b: Ar = Bbt, Ar' = Titp 56%

Scheme 1.

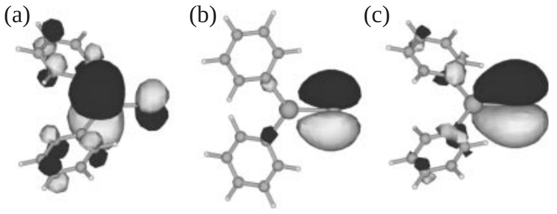


Fig. 1. Depiction of the KS molecular orbitals of $Ph_2Sn{=}S$ at B3LYP/6-31+G(d) [TZ(2d) for Sn] level. a) LUMO, b) HOMO, c) HOMO−1.

Similar to the synthesis of **2a**,[5b] treatment of **1b** with 3 equiv of tributylphosphine in hexane at −40 °C, followed by removal of tributylphosphine sulfide gave orange crystals of Bbt(Titp)Sn=S **2b** (Scheme 1). Although stannanethione **2b** was highly moisture-sensitive, it was stable in a benzene solution without any decomposition even after heating at 60 °C for 3 h in a sealed tube.

The UV–vis spectrum of **2b** in benzene showed an absorption maximum at 475 nm ($\varepsilon = 40\,M^{-1}\,cm^{-1}$), which can be assigned to the n–π^* transition for the Sn=S chromophore. The absorption maximum lies between those of the previously reported stannanethiones, **2a** (491 nm) and Tbt(Tip)Sn=S (473 nm).[5b] Assignments of the observed absorption maxima for **2b** is reasonably supported by the TDDFT calculations for the excited state of $Ph_2Sn{=}S$ [463 nm (n–π^*, HOMO–LUMO)]. The Kohn–Sham (KS)-LUMO, KS-HOMO, and KS-HOMO−1 orbitals of $Ph_2Sn{=}S$ were assigned to π^*(Sn=S), n(S), and π(Sn=S) orbitals, respectively (Fig. 1). In the ^{119}Sn NMR spectrum, a broad signal was observed at 532 ppm, which is characteristic of a low-coordinated tin compound. The signal is almost the same as that of **2a** (531 ppm). Contrary to the terminal tin–sulfido complexes (−54.7,[3e] −236.2,[3c] and −303 ppm[3a]), this low-field signal is characteristic of that for an sp^2-hybridized tin atom.

The molecular structure of **2b** was confirmed by using X-ray crystallographic analysis, and an ORTEP drawing of **2b** is shown in Fig. 2. The stannathiocarbonyl unit is effectively

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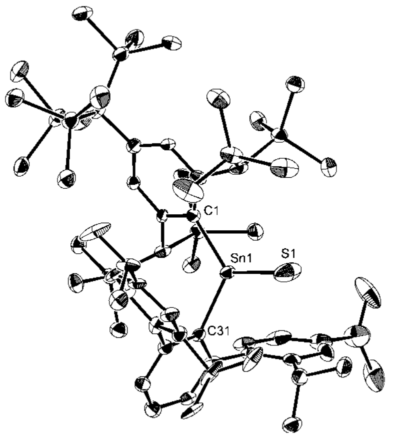

Fig. 2. ORTEP drawing of Bbt(Titp)Sn=S (30% probability). A hexane molecule, hydrogen atoms, and a minor disordered moiety of the Titp group was omitted for clarity. Selected bond lengths (Å) and angle (°): Sn1–S1 2.221(3), Sn1–C1 2.154(7), Sn1–C31 2.192(8), C1–Sn1–S1 124.2(2), C1–Sn1–C31 119.1(3), C31–Sn1–S1 116.2(2).

protected by the *o*-CH$(SiMe_3)_2$ units of the Bbt group and the isopropyl units of the Titp group, and no intermolecular interaction was observed in the crystalline state. The shortest intermolecular distance between Sn and S atoms for **2b** was found to be 7.066 Å, which is considerably longer than the sum of the van der Waals radii of Sn (2.17 Å) and S (1.85 Å) atoms. The Sn1–S1 bond distance [2.221(3) Å] is shorter by about 10% than those of normal tin–sulfur single bonds, similar to the previously reported Sn=Ch compounds (Ch = Se, Te)[5,7] and in good agreement with the calculated Sn=S bond length of $Ph_2Sn{=}S$ (2.254 Å). The bond length of the observed Sn=S unit is shorter than those of Tbt(Ditp)Sn=Se [2.373(3) Å][5b] and Bbt(Titp)Sn=Te [2.5705(6) Å].[5c] Interestingly, the tin atom of **2b** has a trigonal planar geometry as evidenced by the sum of the angles of 359.4°, which shows a structural similarity to the carbonyl carbon atoms of ketones. The calculated natural atomic Mulliken charges on the sp^2 tin and sulfur atoms in the model system, $Ph_2Sn{=}S$, were +0.741 and −0.430, respectively (at B3LYP/6-31+G(d) [TZ(2d) for Sn] level). These results demonstrate that stannanethiones have a highly polarized $Sn^{\delta+}{=}S^{\delta-}$ double-bond character.

Experimental

General. All experiments were performed under an argon atmosphere unless otherwise noted. THF was dried by the standard method and freshly distilled prior to use. ^{1}H NMR (300 MHz), ^{13}C NMR (75 MHz), and ^{119}Sn NMR (111 MHz) spectra were measured in $CDCl_3$ or C_6D_6 on a JEOL JNM AL-300 spectrometer. ^{1}H and ^{13}C NMR chemical shifts were recorded in ppm relative to tetramethylsilane ($\delta = 0$) and were referenced internally with respect to the residual proton impurity ($CDCl_3$: $\delta = 7.26$, benzene-d_6: $\delta = 7.15$) and the ^{13}C resonance of the solvent ($CDCl_3$: $\delta = 77.2$, benzene-d_6: $\delta = 128.0$), respectively. ^{119}Sn NMR chemical shifts were referenced with tetramethylstannane ($\delta = 0$) as an external standard. Fast atom bombardment (FAB) mass spectral data were obtained on a JEOL JMS-700 spectrometer. Gel permeation liquid chromatography (GPLC) was performed on an LC-918 apparatus (Japan Analytical Industry Co., Ltd.) equipped with JAIGEL 1H and 2H columns (eluent: $CHCl_3$). 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. Bbt(Titp)$SnBr_2$[5c] was prepared according to the reported procedure.

Tetrathiastannolane (1b). Lithium naphthalenide (0.25 M solution in THF, 5.8 mL, 1.45 mmol, 3.0 molar amounts) was added to a THF solution (20 mL) of Bbt(Titp)$SnBr_2$ (621 mg, 478 µmol) at −78 °C. The reaction mixture was stirred for 20 min at the same temperature, and then the mixture was gradually warmed to room temperature to give a THF solution of stannylene [Bbt(Titp)-Sn:].[5c,8] After the mixture was stirred for 1 h, elemental sulfur (S_8, 161 mg, 629 µmol) was added to the reaction mixture. After the removal of the solvent, hexane was added to the residue. Insoluble inorganic salts were removed by filtration through Celite®. The residue was subjected to GPLC ($CHCl_3$) followed by recrystallization (hexane/EtOH) to afford **1b** (341 mg, 269 µmol, 56%) as colorless crystals. mp 220.1–221.5 °C; ^{1}H NMR ($CDCl_3$) δ −0.09 (s, 18H), 0.09 (s, 18H), 0.32 (s, 27H), 1.08 (d, $J = 6.9$ Hz, 6H), 1.14 (d, $J = 6.9$ Hz, 6H), 1.25 (d, $J = 6.9$ Hz, 6H), 1.27 (d, $J = 6.9$ Hz, 6H), 1.43 (s, 1H), 2.01 (s, 1H), 2.48 (sept, $J = 6.9$ Hz, 2H), 2.87 (sept, $J = 6.9$ Hz, 2H), 6.73–6.90 (m, 4H), 7.10 (d, $J = 7.7$ Hz, 2H), 7.17 (s, 2H), 7.20 (d, $J = 7.7$ Hz, 2H), 7.33 (t, $J = 7.7$ Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 2.7 (q), 3.1 (q), 5.8 (q), 23.4 (q), 23.8 (q), 24.1 (s), 24.4 (q), 25.6 (q), 29.8 (d), 30.2 (d), 32.2 (d), 33.9 (d), 120.8 (d), 122.2 (d), 124.0 (d), 124.7 (d), 127.4 (d), 128.1 (d), 128.3 (d), 128.4 (d), 129.4 (d), 131.2 (d×2), 139.6 (s), 145.1 (s), 146.3 (s), 147.4 (s), 147.6 (s), 148.1 (s), 148.7 (s), 149.2 (s), 151.8 (s), 152.5 (s), 153.5 (s); ^{119}Sn NMR ($CDCl_3$) δ 53.0; HRMS(FAB), *m*/*z*: calcd for $C_{60}H_{104}S_4Si_7{}^{120}Sn$ 1268.4428 [M^+], found 1268.4454 [M^+]. Anal. Calcd for $C_{60}H_{104}S_4Si_7Sn$: C, 56.79; H, 8.26%. Found: C, 56.83; H, 8.15%.

Stannanethione (2b). A hexane solution of tributylphosphine (0.93 M, 80 µL, 74.4 µmol) was added to a hexane (2.0 mL) solution of **1b** (41.9 mg, 33.0 µmol) at −40 °C. After removal of the solvent under reduced pressure, hexane was added to the residue to precipitate insoluble phosphinesulfide. After removal of phosphinesulfide by filtration, the residue was recrystallized at −40 °C to afford stannanethione **2b** (24.1 mg, 20.5 µmol, 62% yield) as orange crystals. mp 220 °C (decomp); ^{1}H NMR (C_6D_6) δ 0.12 (s, 18H), 0.20 (s, 18H), 0.37 (s, 27H), 1.06 (d, $J = 6.9$ Hz, 6H), 1.21 (d, $J = 6.9$ Hz, 12H), 1.60 (d, $J = 6.9$ Hz, 6H), 2.07 (br s, 1H), 2.79 (sept, $J = 6.9$ Hz, 2H), 3.35 (sept, $J = 6.9$ Hz, 2H), 5.40 (br s, 1H), 6.94 (br s, 2H), 7.00 (t, $J = 7.8$ Hz, 1H), 7.05 (d, $J = 7.8$ Hz, 2H), 7.09 (d, $J = 7.8$ Hz, 2H), 7.37 (s, 2H), 7.45 (d, $J = 7.8$ Hz, 2H); ^{13}C NMR (C_6D_6) δ 2.3 (q×2), 5.8 (q), 23.0 (s), 23.2 (q), 24.0 (q), 24.1 (q), 25.0 (q), 27.7 (d), 30.4 (d), 34.4 (d), 35.1 (d), 124.3 (d), 125.5 (d), 127.1 (d), 128.4 (d), 128.7 (d), 130.1 (d), 131.3 (d), 139.6 (s), 146.2 (s), 148.3 (s), 148.8 (s), 149.4 (s), 150.2 (s), 153.6 (s), 154.5 (s), 157.2 (s); ^{119}Sn NMR (C_6D_6) δ 532.2; UV–vis (benzene) 474.5 nm ($\varepsilon = 40\,M^{-1}\,cm^{-1}$); HRMS(FAB), *m*/*z*: calcd for $C_{60}H_{105}SSi_7{}^{120}Sn$ 1173.5344 $[M + H]^+$, found 1173.5363 $[M + H]^+$.

X-ray Data Collections of [2b•C_6H_{14}]. Single crystals of [**2b**•C_6H_{14}] were grown by the slow evaporation of its saturated solution in hexane at −40 °C. Sample preparation consisted of coating the crystal with hydrocarbon oil, mounting it on a glass fiber, and placing it under a cold stream of N_2 on the diffractometer. The intensity data of [**2b**•C_6H_{14}] were collected on a Rigaku/MSC Mercury CCD diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.71071$ Å) to $2\theta_{max} = 50°$ at

103 K. The structure was solved by Patterson methods (DIRDIF)[9] and refined by full-matrix least-squares procedures on F^2 for all reflections (SHELXL-97).[10] $C_{66}H_{118}SSi_7Sn$, MW: 1163.74, monoclinic, space group $P2_1/n$ (#19), $a = 19.0166(4)$ Å, $b = 16.6509(5)$ Å, $c = 21.3779(8)$ Å, $\beta = 99.889(9)^\circ$, $V = 6668.6(3)$ Å^3, $Z = 4$, $D_{\text{calcd}} = 1.168\,\text{g}\,\text{cm}^{-3}$, $\mu = 0.574\,\text{mm}^{-1}$, $R_1(I > 2\sigma(I)) = 0.0791$, $wR_2(\text{all data}) = 0.2355$, $T = 103(2)$ K, GOF = 1.203. All hydrogen atoms were placed using AFIX instructions. All other atoms were refined anisotropically. The disordered Titp groups were restrained to be identical to each other using DFIX, ISOR, and SIMU instructions. CCDC-628079 ([**2b**$\cdot C_6H_{14}$]) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; Fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

Theoretical Calculations. All calculations were carried out using the Gaussian 03W package program[11] with density functional theory at the B3LYP level. It was confirmed by frequency calculations that the optimized structures have minimum energies. The 6-31G+(d) basis sets were used for C, H, and S. The Lanl2DZ basis sets were used with effective core potential for Sn.

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