Notizen / Notes

Investigation on the Product from Monobutyltin(IV) Compounds and Benzoyl(thiobenzoyl)methane: a 1,3,2λ^5,4λ^5-Dithiadistannetane

Neena Seth[a], **Vishnu D. Gupta***[a], **Gerald Linti**[b], **and Heinrich Nöth***[b]

Department of Chemistry, Faculty of Science, Banares Hindu University[a],
Varanasi, 221005, India

Institut für Anorganische Chemie der Universität München[b],
Meiserstraße 1, D-8000 München 2

Received May 25, 1990

Key Words: 1,3,2λ^5,4λ^5-Dithiadistannetane, 2,4-bis[benzoyl(thiobenzoyl)methanato-*O*,*S*]-2,4-dibutyl- / Anisobidentate ligands

Butyltin triisopropoxide reacts with benzoyl(thiobenzoyl)methane (LH) to yield BuSn(S)L and an organic sulfide **2** instead of the expected $BuSnL_3$. The use of other butyltin(IV) starting materials invariably leads to the same products. From an X-ray structure determination the tin sulfido complex is found to be a centrosymmetric dimer, $[BuSn(S)L]_2$ (**1**) with a planar four-membered Sn_2S_2 ring containing pentacoordinated tin atoms.

We are currently interested in structural aspects of asymmetrical bidentate sulfur ligands such as thiocarbamates[1)] and thio-β-diketonates[2-5)] of main group elements. Competitive electronic and steric factors are well reflected in the crystal and molecular structures of tin *N*-pyrrolylthiocarbamates of type $R_{4-n}Sn[S(O)CNC_4H_4]_n$[1)] where *n* changes from 1 to 4. The chemistry of monoorganotin(IV) compounds has been explored only recently[6,7)] and found to give new and unusual structural forms with oxygen donor ligands. The present report summarizes results on the reaction products of monoorganotin(IV) compounds with the anisobidentate benzoyl(thiobenzoyl)methanato ligand.

Results and Discussion

The reaction of butyltin triisopropoxide, $BuSn(OiPr)_3$, with benzoyl(thiobenzoyl)methane, LH, in benzene has been investigated in a search for a new synthetic method to produce $BuSnL_3$ according to equation (1). However, it did not turn out to be as simple an exchange reaction as expected. Two major products were obtained, the dimeric [benzoyl(thiobenzoyl)methanato]butyltin sulfide (**1**) and 3,3′-thiobis(1,3-diphenyl-2-propen-1-one) (**2**), which turns out to be a *Z*,*Z*′-isomer. The course of the reaction described by eq. (2) is followed irrespective of the stoichiometry applied.

$$\begin{aligned}&BuSn(OiPr)_3 + 3\ S{=}(Ph)C{-}CH_2{-}C(Ph){=}O \rightarrow\\&BuSn[S{=}(Ph)C{-}CH{-}C(Ph){=}O]_3 + 3\ HOiPr\end{aligned}\qquad(1)$$

$$\begin{aligned}&BuSn(OiPr)_3 + 3\ S{=}(Ph)C{-}CH_2{-}C(Ph){=}O \rightarrow\\&\qquad\underset{\mathbf{1}}{BuSn(S)[S{=}(Ph)C{-}CH{-}C(Ph){=}O]}\\&\qquad+ \underset{\mathbf{2}}{S[C(Ph){=}CH{-}C(Ph){=}O]_2}\end{aligned}\qquad(2)$$

It has been observed earlier[2)] that $AsCl_3$ catalyzes the conversion of benzoyl(thiobenzoyl)methane into **2**. Neither **1** nor $BuSn(OiPr)_3$ has this effect on benzoyl(thiobenzoyl)methane since an excess of LH remains unaffected. Therefore, the formation of **2** must result from an intramolecular elimination of **2** from either $BuSnL_3$ or $BuSnL_2OiPr$. **2** has been found to have identical physical constants, IR as well as NMR data to that of the earlier reported *Z*,*Z*′ isomer, whose molecular structure has been established by X-ray diffraction analysis[2)].

1 is a yellow crystalline solid soluble in common organic solvents. The IR spectrum of the compound exhibits a strong band at 1590 cm^{-1} due to $\nu(C{=}O)$, indicating weak interaction between tin and oxygen consistent with an anisobidentate bonding pattern[8,9)] of the thio-β-diketone. In addition to the carbonyl absorption, the intense band at 1565 cm^{-1} is due to a C=C stretching vibration. $\nu(C{=}S)$ is observed as a strong band at 1265 cm^{-1}, the latter being coupled with CH deformation frequencies[9)]. The absorptions at 575, 510, and 362 cm^{-1} are assignable to Sn–C, Sn–O-, and Sn–S-stretching vibrations, respectively.

The proton NMR spectrum of **1** is consistent with the proposed structure, and the same holds for the ^{13}C-NMR spectrum which shows a total of eleven signals for the benzoyl(thiobenzoyl)methanato group. δ values are given in the experimental section. $\delta^{13}C$ = 174.7 provides additional evidence for the anisobidentate behaviour of the ligand. The value of the ^{119}Sn chemical shift ($\delta = -287.8$) is consistent with pentacoordination at the Sn center.

In order to establish the nature of the complex **1**, its crystal and molecular structure has been determined by X-ray methods. Figure 1 shows the molecular structure of the molecule which crystallizes in the triclinic system. The principal feature of **1** is that it is present as a BuSn(S)L dimer rather than a monomer in accord with the ^{119}Sn-NMR result. The central part of the molecule consists of a crystallographically imposed planar 1,3,2λ^4,4λ^4dithiadistannetane ring system. The benzoyl(thiobenzoyl)methanato ligand shows anisobidentate bonding to the thione atom as also observed for Me_2SnL_2 and Cl_2SnL_2[3)]. However, the SnS bond in **1** to the ligand L is approximately 0.1 Å shorter than the SnS bond to the hexacoordinated Sn in Me_2SnL_2. We attribute this to the pentacoordinated tin atom in **1**. However, the SnS bond length in **1** matches

0009–2940/91/0101–0083 \$ 3.50+.25/0

that in Cl_2SnL_2. The SnS bonds of the dithiadistannetane unit in **1** differ significantly, and the SnS bond length to the ligand L is intermediate to the SnS bond lengths of the four-membered ring.

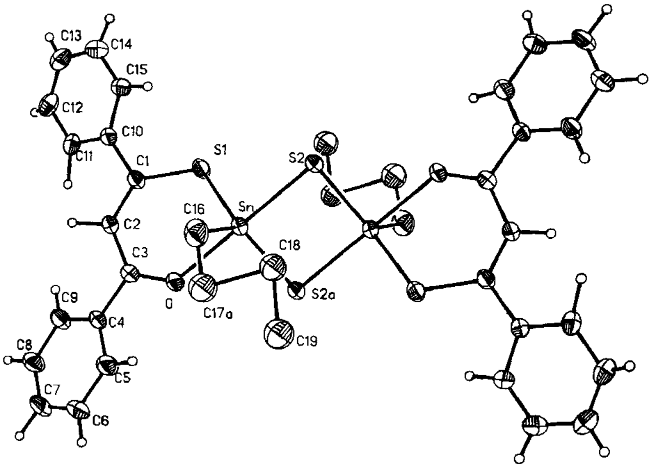

Figure 1. ORTEP plot of dimeric **1**. Thermal ellipsoids are drawn for the 25% probability limit. Selected bond lenghts (in Å): Sn–S2 2.480(2), Sn–S2a, 2.373(2), Sn–S1 2.444(2), S1–C1, 1.743(8), Sn–O 2.309(6), C3–O 1.249(10), Sn–C16 2.154(8). Selected bond angles (in °): S2–Sn–S2a 92.1(1), Sn–S2–Sna 87.9(1), S1–Sn–O 82.4(1), S1–Sn–S2 90.6(1), S1–Sn–Sn2a 115.6(1), S1–Sn–C16 115.3(2), S2–Sn–C16 104.9(3), O–Sn–C16 85.6(4), O–Sn–S2 169.1(1), O–Sn–S2a 83.6(1), Sn–S1–Cl 109.2(2), Sn–O–C3 133.1(4). Normals between planes (in °): S_2Sn_2/OSnS1 64.5, S_2Sn_2/S1C16S2a 82.4. The Sn atom lies 0.184 Å above the best plane through Sn, S1, S2a, and C16, and the atoms S1, S2a, and C16 0.05, 0.06, and 0.07 Å below this plane. S2 and O are 2.64 and 2.12 Å apart from the best plane through SnS1S2aC16

The tin atom is pentacoordinated and is the central part of a distorted trigonal bipyramid. The atoms C16, S1, and S2a are to be considered equatorial atoms, and S2 and O the axial ones. This is not only in accord with the rules for apicophilicity, but also the SnS bond lengths are compatible with the geometry at Sn. The SnO distance in **1** lies between those found for Me_2SnL_2 (2.49, 2.51 Å) and Cl_2SnL_2 (2.12 Å). Considering the axial position of the oxygen atom in **1** the observed bond length would be compatible with comparatively strong SnO bonding[3].

The butyl group in **1** is disordered, and the CC distances deviate from the CC single bond length. Consequently, well defined difference Fourier peaks for hydrogen atoms were not reliably revealed, and the final refinement of the structure was carried out without the hydrogen atoms for the butyl group.

In view of the unusual products described above we have examined the reactions of LH with other tin compounds such as butyltin trichloride and butylstannoic acid. **1** and **2** invariably form irrespective of the starting materials. However, in these reactions a small quantity of intractable material was always generated which could not yet be characterized.

The results presented here indicate a thermal instability of $BuSnL_3$, which obviously decomposes by elimination of **2**. So far this is unprecedented in the tin chemistry of the ligand LH[3]. It may well be that there is steric overcrowding for $RSnL_3$ compounds which is relieved by expulsion of **2**. We shall, therefore, investigate the influence of various groups R on the stability of $RSnL_3$ compounds and will include the as yet unknown SnL_4, which in the light of the present result should also be unstable.

N. S. is grateful to U.G.C., New Dehli (India), for the award of J.R.F.

Experimental

All experimental manipulations were carried out under anhydrous conditions. Solvents were purified by standard methods. $BuSnCl_3$, b.p. 93°C/10 Torr, was distilled before use. $BuSn(O\textit{i}Pr)_3$ was prepared by the literature method[8], and benzoyl(thiobenzoyl)methane synthesized by the Claisen condensation method[9]. – IR: Perkin-Elmer 783 spectrometer, range 4000–200 cm^{-1}, Nujol mulls, CsI plates. – NMR (^1H, ^{13}C and ^{119}Sn): JEOL FX 90Q spectrometer, at 25°C in $CDCl_3$ and TMS as internal reference for ^1H and ^{13}C, and Me_4Sn in a sealed capillary for ^{119}Sn as an external reference. – Elemental analyses: Perkin-Elmer 240 elemental analyzer.

Reaction of BuSn(OiPr)₃ with Benzoyl(thiobenzoyl)methane: A solution of benzoyl(thiobenzoyl)methane (1.98 g, 8.2 mmol) in benzene (10 ml) was added dropwise to $BuSn(O\textit{i}Pr)_3$ (0.97 g, 2.7 mmol) dissolved in benzene (10 ml) with continuous stirring at ambient temp. (32°C). The solution was stirred for 5 h. The yellow insoluble solid which had been formed was removed by filtration, then dried and crystallized form dichloromethane/hexane (1:3) to give yellow crystals of *2,4-bis[benzoyl(thiobenzoyl)methanato-O,S]-2,4-dibutyl-1,3,$2\lambda^5$,$4\lambda^5$-dithiadistannetane* (**1**), yield 1.13 g (94%), m.p. 180 to 182°C. – IR (cm^{-1}): $\tilde{\nu}$ = 1590 [s, ν(C=O)], 1565 [s, ν(C=C], 1265 [m, ν(C=S)], 510 [s, ν(SnO)], 362 [s, ν(SnS)], 575 [m, ν(SnC)]. – ^1H NMR: δ = 7.0–7.8 (m, CH and C_6H_5), 0.7–2.06 (m, C_4H_9). – ^{13}C NMR: δ = 190.3 (CS), 174.6 (CO), 115.6 CH, 31.9, 27.8, 15.8, 13.7 (C_4H_9). – ^{119}Sn NMR: δ = −287.8.

$C_{19}H_{20}OS_2Sn$ (447.2)	Calcd.	C 51.03	H 4.51	S 14.3	Sn 26.5
	Found	C 50.59	H 4.54	S 14.6	Sn 28.3

On reducing the volume of the filtrate crystals of *3,3′-thiobis(1,3-diphenyl-2-propen-1-one* (**2**)[2], separated. Yield: 2.27 g (94%), m.p. 178–179°C. – IR (cm^{-1}): $\tilde{\nu}$ = 1640 [s, ν(C=O)] and 1530 [m, ν(C=C)]. – ^1H NMR: δ = 6.6–8.0 (CH, C_6H_5). – ^{13}C NMR: δ = 188.5 (CS), 155.5 (CO), 124.8 (methine-C).

$C_{30}H_{22}O_2S$ (446.5)	Calcd.	C 80.69	H 4.97	S 7.1
	Found	C 80.66	H 4.52	S 7.7

Reaction of BuSn(OiPr)₃ with Benzoyl(thiobenzoyl)methane in a 1:10 Molar Ratio: To the solution of $BuSn(O\textit{i}Pr)_3$ (0.30 g, 0.85 mmol) in benzene (10 ml) was added the solution of benzoyl(thiobenzoyl)methane (2.0 g, 8.3 mmol) in benzene (30 ml). This mixture was refluxed for approximately 4 h. Isopropyl alcohol was removed azeotropically, and then the solvent was evaporated. The pasty residue was treated with 5 ml of acetone to separate out the sulfide complex **1** (yield: 79%). The remaining portion was extracted with 15 ml of *n*-hexane to separate **2** (yield: 89%) leaving behind unreacted ligand (92%). Analytical and spectral data for **1** and **2** corresponded with those described above.

Reaction of Butylstannoic Acid with Benzoyl(thiobenzoyl)methane: To the suspension of butylstannoic acid BuSn(O)OH (0.75 g, 3.5 mmol) in benzene (15 ml) was added the solution of benzoyl(thiobenzoyl)methane (2.58 g, 10.7 mmol) in the same solvent (50 ml). This mixture was refluxed for 4 h. The water formed in the reaction was removed azeotropically as soon as it formed. The solvent was evaporated and the remaining pasty product was treated with 10 ml of acetone to separate **1** from the organic sulfide **2**. Yield: 1.41 g of **1** (90%), m.p. 180–182°C.

X-Ray Structure Determination of **1**: A single crystal of **1** (0.3 × 0.25 × 0.41 mm), obtained from dichloromethane/hexane (1:3), was sealed in a glass capillary and centered on a NICOLET R3m four-circle diffractometer. Graphite-monochromated Mo-K_α radiation was used. The dimensions of the unit cell were calculated from the setting angles of 24 centered reflexions. Intensity data were recorded using ω scans, variable scan speed (3.3–29.3°/min), and a scan widths of 1.0°. Two check reflections were monitored after every 48 intensity measurements. Data reduction included absorption correction (ψ scans, max./min. transmission: 0.875/0.681). The structure was solved by Patterson and Fourier methods applying the SHELXTL PLUS software programs. Nonhydrogen atoms were refined anisotropically, and hydrogen atoms were included in the final refinement with fixed isotropic U_i values except for the hydrogen atoms of the disordered butyl group. Table 1 contains the atom coordinates of the nonhydrogen atoms. Further details on the structure determination may be obtained from Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, 7514 Eggenstein-Leopoldshafen 2, quoting the depository number CSD-54847, the authors and the reference.

Table 1. Atom coordinates ($\times 10^4$) of the nonhydrogen atoms of **1**. Estimated standard deviations in parentheses. Equivalent U (Å^2 $\times$ 10^3) is defined as one third of the trace of the orthogonalized U_{ij} tensors

	x	y	z	U(eq)
Sn	1417(1)	4217(1)	4467(1)	45(1)
S(1)	1178(3)	1918(2)	5974(2)	61(1)
S(2)	1262(2)	4794(2)	6203(2)	52(1)
O	1099(7)	3432(5)	3061(4)	60(2)
C(1)	2118(8)	1033(6)	5261(6)	47(3)
C(2)	2274(8)	1343(6)	4018(6)	47(3)
C(3)	1612(9)	2444(6)	3001(6)	49(3)
C(4)	1452(9)	2407(6)	1824(6)	52(3)
C(5)	1444(12)	3553(8)	719(7)	68(4)
C(6)	1238(13)	3554(10)	-404(8)	79(4)
C(7)	1146(13)	2436(10)	-462(8)	82(5)
C(8)	1065(13)	1262(9)	634(7)	73(4)
C(9)	1273(11)	1260(8)	1754(7)	62(3)
C(10)	2725(8)	-226(6)	6166(6)	49(3)
C(11)	2498(9)	-1311(7)	5999(7)	55(3)
C(12)	3008(11)	-2506(7)	6886(9)	67(4)
C(13)	3686(11)	-2640(8)	7929(9)	73(4)
C(14)	3877(16)	-1595(12)	8085(8)	79(5)
C(15)	3428(11)	-393(8)	7238(7)	62(3)
C(16)	3971(11)	4919(9)	3473(9)	77(4)
C(17A)	3920(30)	6015(22)	2239(22)	98(6)
C(17B)	3973(54)	7412(40)	2785(39)	171(14)
C(18)	3366(33)	7158(25)	1982(24)	211(9)
C(19)	3928(33)	8486(24)	1332(24)	106(7)

$C_{19}H_{20}OS_2Sn$, M_r = 447.2, triclinic system, space group *P*1*bar* (No. 2), a = 7.683(2), b = 11.690(4), c = 12.102(3) Å, α = 62.31(2), β = 84.66(2), γ = 89.54(3)°, V = 957.5(5) Å^3, Z = 2, $d_{calcd.}$ = 1.551 g/cm^3, μ = 15.5 cm^{-1}. Data collection: 2Θ-range 2–50°C in $+/-h$, $+/-k$, $+/-l$, 6036 intensity data recorded, 3288 unique reflections and 2988 considered observed [$I > 3\sigma(I)$]. 227 variables refined, R = 0.0527, R_w = 0.0578, $w^{-1} = \sigma^2(F) + 0.01128(F)^2$, GOOF 1.712, largest residual electron density 1.41 e/Å^3.

CAS Registry Numbers

1: 128243-41-4 / **2**: 53246-46-1 / BuSn(O*i*Pr)$_3$: 40542-28-7 / PhC(S)CH$_2$C(O)Ph: 1215-43-6 / BuSn(O)OH: 2273-43-0

---

[1] D. K. Srivastava, V. D. Gupta, W. Rattay, H. Nöth, *J. Chem. Soc., Dalton Trans.* **1988**, 1533.

[2] R. P. Singh, V. D. Gupta, E. N. Duesler, C. K. Narula, *J. Chem. Soc., Dalton Trans.* **1988**, 1269.

[3] C. Sreelatha, D. K. Srivastava, V. D. Gupta, H. Nöth, *J. Chem. Soc., Dalton Trans.* **1988**, 407.

[4] D. K. Srivastava, R. P. Singh, V. D. Gupta, *Polyhedron* 7 (1988) 483.

[5] V. D. Gupta, A. K. Mishra, H. Nöth, K. Polborn, *Z. Naturforsch., Part B,* **44** (1989) 149.

[6] R. R. Holmes, *Acc. Chem. Res.* **22** (1989) 190.

[7] K. C. Kumara Swamy, C. G. Schmid, R. O. Day, R. R. Holmes, *J. Am. Chem. Soc.* **112** (1990) 223.

[8] S. E. Livingstone, *Coord. Chem. Rev.* 7 (1971) 59.

[9] M. Cox, J. Darken, *Coord. Chem. Rev.* 7 (1971) 21.

[10] D. P. Gaur, G. Srivastava, R. C. Mehrotra, *J. Organomet. Chem.* **63** (1973) 221.

[180/90]