

Molecular Structures of the Free and η^1 -Coordinated Triphenylstannane Dithiobenzylester, $(C_6H_5)_3SnCS_2CH_2C_6H_5^*$

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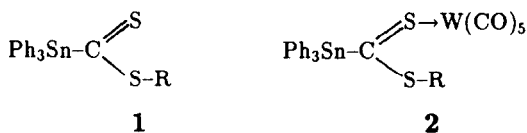
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Abstract

The crystal structures of the free and η^1 -coordinated benzylester of triphenylstannane dithiocarboxylic acid were determined by X-ray analysis. Both compounds crystallize in the triclinic space group $P\bar{1}$ ($Z = 2$) with $R = 0.043$ (ester **1b**, -80°C) and $R = 0.027$ (complex **2b**, 20°C). Tin adopts a tetrahedral environment with a Sn–C1 distance of 218–219 pm similar to other tin–alkyl bond lengths. The planar $SnCS_2$ unit contains C–S distances of 163–164 pm (S1–C1) and 169–171 pm (S2–C1) as well as S1–C1–S2 angles of 125.7° (**1b**) and 119.6° (**2b**). The main structural difference is a *cisoid* (*s-cis*) arrangement of S1–C1 and S2–C2 in **1b** but a *transoid* (*s-trans*) conformation in the complex **2b** (W–S1 = 250.2 pm) which causes a considerable steric repulsion of the benzyl group and one of the tin–phenyl rings.

Introduction

Some years ago we reported the synthesis of novel stannanedithiocarboxylic esters [3] and stannanedithiocarboxylato complexes [4] by nucleophilic addition of appropriate organotin anions to carbon disulfide. The topic has been reviewed in ref. 2. These compounds represent the first (and still only) metallodithiocarboxylates for a heavy main group element [5–8].



1,2: R=alkyl
1a,2a: R=methyl
1b,2b: R=benzyl

*Part VIII of 'Nucleophilic Addition of Triorganotin Anions to Carbon Disulfide'; Part VII is ref. 1 (cf. also ref. 2).

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The alkyl esters (**1**) were isolated as air-stable, purple crystals after chromatographical purification. They form the neutral-ligand complexes (**2**) by reaction with irradiated metal carbonyls [9]. Surprisingly, the methyl ester (**1a**) [3] crystallizes in the same tetragonal space group ($P4_2/c$, $Z = 2$) as tetraphenyltin [10] with almost identical lattice constants. However, the exact determination of the molecular geometry was prevented by disorder problems which resulted mainly in a reduced reliability of the calculated bond distances and angles. To avoid these faults, we repeated the X-ray structural analysis with the analogous benzyl ester (**1b**) [11, 12] and its pentacarbonyltungsten complex (**2b**) [12].

Experimental

Dithioester (**1b**)

The benzyl dithioester (**1b**) was prepared according to the 'dioxane method' [4] in 64% yield and recrystallized from acetone; melting point (m.p.) 96°C (ref. 11: 65°C). A red-violet single crystal of the size $0.4 \times 0.2 \times 0.2$ mm was mounted on a glass fiber. For all structural investigations, an automated four-circle diffractometer (CAD4, ENRAF-NONIUS) with graphite-monochromated Mo K α radiation was used. The cell dimensions (Table I) were obtained from a least-squares refinement of the setting angles of 25 reflections in the range of $12^\circ < \theta < 28^\circ$. For 5186 intensity data collected by the ω/θ scan mode ($3^\circ < \theta < 27^\circ$), Lorentz and polarization corrections and empirical absorption corrections (azimuthal scans) [13] were applied. Averaging equivalent reflections gave 4971 unique reflections. The structure was solved by direct methods [14]. A full matrix refinement [15] (3843 reflections with $I > 3\sigma(I)$) with anisotropic thermal parameters for all atoms (non-H) was carried out. Hydrogen positions of the methylene group were found by a difference Fourier synthesis and refined with isotropic thermal parameters; the phenyl H-atoms calculated in idealized positions with $d(C-H) = 95$ pm were included in the structure factor calculations only. A secondary

TABLE I. Crystal Data of $\text{Ph}_3\text{SnC(S)SCH}_2\text{Ph}$ (**1b**) and $\text{Ph}_3\text{SnC(S)SCH}_2\text{Ph}\cdot\text{W(CO)}_5$ (**2b**)

	1b	2b
Formula	$\text{C}_{26}\text{H}_{22}\text{S}_2\text{Sn}$	$\text{C}_{31}\text{H}_{22}\text{O}_5\text{S}_2\text{SnW}$
Molar mass	517.28	841.19
Space group	$P\bar{1}$, triclinic	$P\bar{1}$, triclinic
Temperature ($^\circ\text{C}$)	-80	20
Lattice constants		
a (pm)	925.0(3)	1278.0(4)
b (pm)	1003.6(3)	1303.4(4)
c (pm)	1343.8(4)	1068.1(3)
α ($^\circ$)	101.02(4)	102.43(4)
β ($^\circ$)	101.08(4)	93.18(4)
γ ($^\circ$)	104.92(4)	115.05(4)
Cell volume, V (pm^3)	1144.2×10^6	1552.4×10^6
Formula units, Z	2	2
Density, ρ_x (g cm^{-3})	1.501	1.799
$F(000)$	520	808
Absorption coefficient, $\mu(\text{Mo K}\alpha)$ (cm^{-1})	13.042	47.549
Secondary extinction value	1.662×10^{-7}	5.542×10^{-8}
No. reflections with $I \geq 3\sigma(I)$	3843	3766
Parameters refined	271	370
R values		
R	0.043	0.027
R_w	0.048	0.029

extinction coefficient [16] was refined in least-squares. Final refinement converged to $R = 0.043$ and $R_w = 0.048$. The positional parameters are given in Table II. Atomic scattering factors were taken from International Tables for X-ray Crystallography [17]. Calculations were performed on a VAX 11/750 (Zentrum für Datenverarbeitung der Universität Tübingen).

Tungsten Complex (**2b**)

The $\text{W(CO)}_5\cdot\text{THF}$ adduct (from irradiated W(CO)_6 in THF; mercury lamp Hanau TQ 150) and **1b** were stirred under exclusion of light for 2 h. **2b** was isolated by reducing the volume of the solution and recrystallization from n-hexane [3, 9, 12] (yield 48%, m.p. 124°C with decomposition). A red crystal of approximate dimensions $0.3 \times 0.2 \times 0.2$ mm was chosen for structural investigation as described for **1b**. 5101 data were measured in the range $3^\circ < \theta < 24^\circ$. For the structure determination Patterson search methods [18] with the fragment W(CO)_5 were applied. The subsequent tangens expansion [14] revealed all other non-H atoms. Isotropic refinement converged at 0.075 for all 4605 unique reflections. An empirical absorption correction was undertaken using DIFABS [19], whereupon R dropped to 0.048. The subsequent difference Fourier synthesis showed the positions of the methylene H-atoms. Final refinement based on F by full-matrix least-squares tech-

TABLE II. Positional Parameters and Equivalent Isotropic Thermal Parameters of Compound **1b**

Atom	x	y	z	B_{eq}^a
Sn	0.06088(4)	0.03792(4)	0.29387(3)	2.441(6)
S1	0.1753(2)	0.0331(2)	0.0736(1)	4.18(3)
S2	0.1456(5)	0.2610(5)	0.1597(1)	4.37(3)
C1	0.1456(5)	0.0873(5)	0.1604(4)	2.4(1)
C2	0.2562(7)	0.2839(7)	0.0487(5)	4.2(1)
C11	0.0174(6)	-0.1822(5)	0.2825(4)	2.6(1)
C12	-0.1084(6)	-0.2598(6)	0.3113(4)	3.3(1)
C13	-0.1304(7)	-0.4027(6)	0.3108(5)	3.9(1)
C14	-0.0273(7)	-0.4701(6)	0.2821(5)	3.6(1)
C15	0.0981(7)	-0.3941(6)	0.2528(5)	3.5(1)
C16	0.1201(6)	-0.2538(6)	0.2543(5)	3.2(1)
C21	0.2455(6)	0.1504(6)	0.4299(4)	2.8(1)
C22	0.2971(7)	0.2978(6)	0.4635(5)	3.7(1)
C23	0.4177(8)	0.3651(8)	0.5536(5)	4.7(2)
C24	0.4837(7)	0.2862(9)	0.6087(5)	4.8(2)
C25	0.4333(7)	0.1411(8)	0.5772(5)	4.8(2)
C26	0.3143(7)	0.0725(6)	0.4885(5)	3.5(1)
C31	-0.1327(6)	0.1135(5)	0.2998(4)	2.7(1)
C32	-0.2527(7)	0.0860(6)	0.2122(5)	3.7(1)
C33	-0.3779(7)	0.1355(7)	0.2181(6)	5.0(2)
C34	-0.3863(7)	0.2126(7)	0.3118(6)	5.1(2)
C35	-0.2674(7)	0.2441(7)	0.3995(5)	4.8(2)
C36	-0.1402(7)	0.1950(6)	0.3945(5)	3.5(1)
C41	0.3037(6)	0.4382(6)	0.0524(4)	3.2(1)
C42	0.2107(7)	0.4941(7)	-0.0101(5)	3.8(1)
C43	0.2555(8)	0.6360(7)	-0.0082(5)	4.4(2)
C44	0.3953(8)	0.7250(7)	0.0553(5)	4.2(1)
C45	0.4884(7)	0.6725(7)	0.1175(5)	4.1(1)
C46	0.4452(7)	0.5306(7)	0.1161(4)	3.8(1)

$$^a B_{\text{eq}} = \frac{4}{3}(B_{11}a^2 + B_{22}b^2 + B_{33}c^2 + B_{12}ab \cos \gamma + B_{13}ac \cos \beta + B_{23}bc \cos \alpha).$$

niques using 3766 reflections with intensities $I > 3\sigma(I)$ and anisotropic thermal parameters for all non-H atoms (H atoms similar to **1b**) converged to $R = 0.027$ and $R_w = 0.029$ (Table III).

Description of the Structures

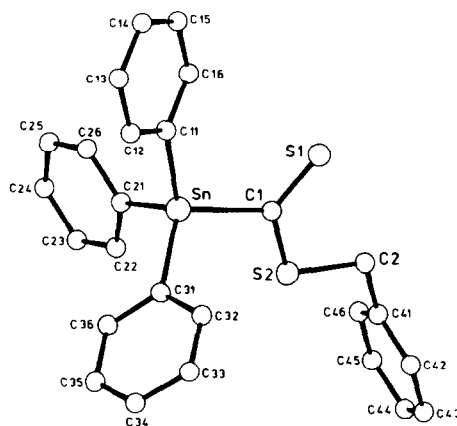
The molecular structure of the benzyl stannane-dithioester (**1b**) (Fig. 1, Table IV) reveals some characteristic differences compared to the previously found bond lengths and angles of the methyl ester (**1a**) [3]. The Sn—Cl distance of **1b** is significantly increased to 218 pm. This value lies in the order of aliphatic Sn—C bond lengths in tetrahedral tin compounds like $(\text{C}_6\text{H}_5\text{CH}_2)_4\text{Sn}$ [20, 21], $(\text{C}_6\text{H}_5\text{CH}_2)_3\text{SnO}_2\text{CCH}_3$, $(\text{C}_6\text{H}_{11})_3\text{SnO}_2\text{CCH}_3$ and $(\text{CH}_3)_3\text{SnMn(CO)}_5$ [22], namely 215–219 pm, corresponding to the sum of covalent radii (217 pm [23]). Similar Sn—C distances were reported for tetramethyltin and methyltin chlorides recorded by electron diffraction in the gas phase [22, 23]. Apart from the different

TABLE III. Positional Parameters and Equivalent Isotropic Thermal Parameters of Compound **2b**

Atom	x	y	z	B_{eq}^a
W	0.12255(2)	0.34905(2)	0.11002(3)	3.559(6)
Sn	0.34578(3)	0.23838(3)	0.49166(4)	3.004(9)
S1	0.2286(1)	0.3479(1)	0.3134(2)	3.34(3)
S2	0.2705(1)	0.1621(1)	0.1584(2)	3.95(4)
O3	-0.0255(5)	0.3665(5)	-0.1208(6)	7.7(2)
O4	0.2983(5)	0.6169(4)	0.1483(6)	6.9(2)
O5	-0.0547(5)	0.0784(5)	0.0578(7)	7.6(2)
O6	-0.0282(5)	0.4253(5)	0.2993(6)	7.8(2)
O7	0.2583(5)	0.2717(5)	-0.1012(5)	7.1(2)
C1	0.2833(5)	0.2539(4)	0.3053(6)	2.9(1)
C2	0.3611(6)	0.0903(6)	0.1861(7)	4.8(2)
C3	0.0292(6)	0.3601(6)	-0.0347(7)	4.9(2)
C4	0.2369(6)	0.5220(6)	0.1378(7)	4.6(2)
C5	0.0094(6)	0.1761(6)	0.0781(8)	4.9(2)
C6	0.0271(5)	0.3972(6)	0.2301(8)	4.9(2)
C7	0.2140(6)	0.3020(5)	-0.0191(7)	4.5(2)
C11	0.3553(5)	0.3810(5)	0.6415(6)	3.1(1)
C12	0.4601(5)	0.4518(6)	0.7264(7)	4.3(2)
C13	0.4692(7)	0.5429(6)	0.8285(7)	5.5(2)
C14	0.3761(6)	0.5649(6)	0.8477(7)	5.2(2)
C15	0.2713(6)	0.4956(6)	0.7653(7)	4.7(2)
C16	0.2604(5)	0.4035(5)	0.6629(6)	4.0(2)
C21	0.2179(5)	0.0721(5)	0.5062(6)	3.7(2)
C22	0.1323(6)	-0.0085(6)	0.4017(7)	4.7(2)
C23	0.0494(7)	-0.1150(6)	0.4161(9)	5.8(2)
C24	0.0528(6)	-0.1410(6)	0.5315(9)	6.4(2)
C25	0.1360(7)	-0.0626(7)	0.6350(8)	6.4(2)
C26	0.2191(6)	0.0453(6)	0.6228(7)	4.9(2)
C31	0.5164(5)	0.2474(5)	0.5040(6)	3.2(1)
C32	0.6101(5)	0.3447(5)	0.4831(6)	3.9(2)
C33	0.7221(6)	0.3568(6)	0.5000(7)	4.9(2)
C34	0.7434(6)	0.2739(7)	0.5396(8)	5.8(2)
C35	0.6528(6)	0.1769(6)	0.5590(9)	6.0(2)
C36	0.5410(6)	0.1659(5)	0.5436(7)	4.7(2)
C41	0.3443(5)	0.0007(5)	0.0629(7)	4.2(2)
C42	0.3859(6)	0.0336(6)	-0.0440(7)	5.5(2)
C43	0.3689(7)	-0.0540(7)	-0.1576(8)	6.6(2)
C44	0.3098(7)	-0.1693(7)	-0.1566(8)	6.9(2)
C45	0.2695(7)	-0.2021(7)	-0.050(1)	7.1(3)
C46	0.2863(6)	-0.1170(6)	0.0596(8)	5.5(2)

$$^a B_{eq} = \frac{4}{3}(B_{11}a^2 + B_{22}b^2 + B_{33}c^2 + B_{12}ab \cos \gamma + B_{13}ac \cos \beta + B_{23}bc \cos \alpha).$$

physical state, much shorter bond lengths were published by other authors [22] so that there is less reliability. On the other hand, the solid iodomethyl compound $(C_6H_5)_3SnCH_2I$ shows a reduced Sn–C distance of 214 pm which approaches the range of aromatic Sn–C bonds with 212–215 pm [21, 22]. The mean distance of 213 pm takes account of the bond shortening by linking tin with an sp^2 hybridized carbon. The Sn–C distance of aromatic organotin is much less affected by substituent influences as the comparison of $(C_6H_5)_4Sn$ [10] and $(C_6F_5)_4Sn$ [24] shows.

Fig. 1. Molecular structure of $(C_6H_5)_3SnCS_2CH_2C_6H_5$ (**1b**).TABLE IV. Selected Bond Distances (pm) and Bond Angles ($^\circ$) of **1b** (e.s.d.s in parentheses)

Distances		Angles	
Sn–C1	218.1(4)	Sn–C1–S1	122.0(2)
S1–C1	162.9(4)	Sn–C1–S2	112.3(2)
S2–C1	169.5(4)	S1–C1–S2	125.7(3)
S2–C2	182.0(5)	C1–S2–C2	105.9(2)
C2–C41	148.4(7)	S2–C2–C41	108.2(4)
Sn–C11	211.1(4)	C1–Sn–C11	109.0(2)
Sn–C21	213.3(4)	C1–Sn–C21	106.2(2)
Sn–C31	212.5(4)	C1–Sn–C31	108.5(2)

A slight distortion of the tetrahedral geometry around the tin atom of **1b** is observed which is expressed in an increase of C11–Sn–C31 and decrease of C21–Sn–C1 probably due to packing effects.

The *s-cis* conformation of the planar $SnCS_2$ unit (with respect to C1–S2) is analogous to **1a**, but differs in the enlarged Sn–C1–S2 angle. The non-equivalence of the C–S distances with a difference of 6.5 pm is more obvious than in **1a** but still indicates a considerable extent of π -electron delocalization when compared to the S2–C2 single bond. In anionic [25] and zwitterionic dithiocarboxylates [26], both C–S distances lie in the order of 168 pm although coordinated ligands may show a larger inequality [27]. The observed bond distances and angles of **1b** agree fairly well with those of the few known structures of organic dithioesters [28, 29].

The X-ray structural analysis of the tungsten complex (**2b**) confirms the η^1 -coordination of the dithioester ligand through the thion sulfur previously suggested by spectroscopic data [3, 9] (Fig. 2, Table V). It is to our knowledge the first documented molecular structure of this coordination type [30]. In an earlier reported platinum complex, the methyl ester (**1a**) [11] adopts a side-on η^2 -

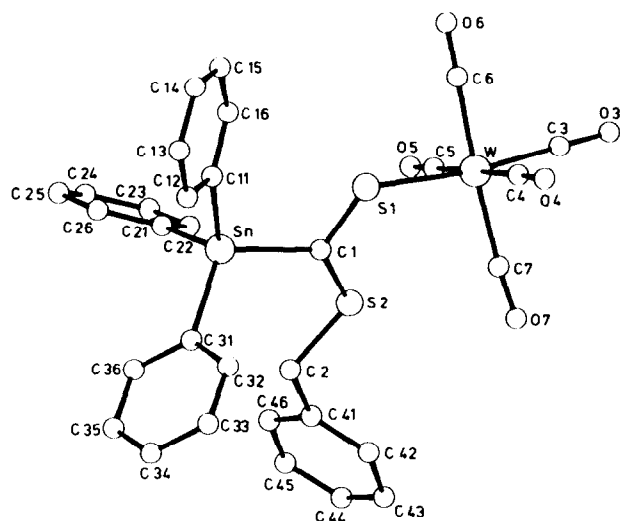


Fig. 2. Molecular structure of $(\text{C}_6\text{H}_5)_3\text{SnCS}_2\text{CH}_2\text{C}_6\text{H}_5 \cdot \text{W}(\text{CO})_5$ (**2b**).

TABLE V. Selected Bond Distances (pm) and Bond Angles ($^\circ$) of **2b** (e.s.d.s in parentheses)

Distances		Angles	
Sn—C1	218.5(5)	Sn—C1—S1	115.7(2)
S1—C1	163.8(5)	Sn—C1—S2	124.1(3)
S2—C1	170.8(5)	S1—C1—S2	119.6(3)
S2—C2	181.9(6)	C1—S2—C2	105.9(3)
C2—C41	149.6(8)	S2—C2—C41	108.0(4)
Sn—C11	213.0(6)	C1—Sn—C11	108.5(2)
Sn—C21	213.7(5)	C1—Sn—C21	104.2(2)
Sn—C31	212.9(6)	C1—Sn—C31	113.3(2)
W—S1	250.2(1)	W—S1—C1	118.9(2)
W—C3	196.6(5)	S1—W—C3	172.4(1)
C3—O3	116.4(7)	S1—W—C4	89.4(2)
W—C4	204.4(5)	S1—W—C5	91.5(2)
C4—O4	112.6(7)	S1—W—C6	84.1(2)
W—C5	203.6(6)	S1—W—C7	99.1(2)
C5—O5	114.8(8)	C4—W—C5	178.7(2)
W—C6	200.1(6)	C6—W—C7	176.8(3)
C6—O6	115.8(7)		
W—C7	201.6(7)		
C7—O7	115.8(9)		

coordination of the C=S group. The structural parameters of the ester (**1b**) show only minor alterations in its coordinated form **2b**, mainly a decrease of the S1—C1—S2 angle. The most striking difference consists in the change to a *s-trans* arrangement of S1—C1 and S2—C2. The CS_2 unit is slightly distorted with an out-of-plane deviation of the C1 atom of 8.3 pm. The methylene carbon C2 lies 39.6 pm above and the tungsten atom 31.8 pm below the averaged SnCS_2 plane. A considerable steric hindrance between the benzyl group (C2, C41) and the neighbored phenyl ring (Sn, C31) is responsible for the increase

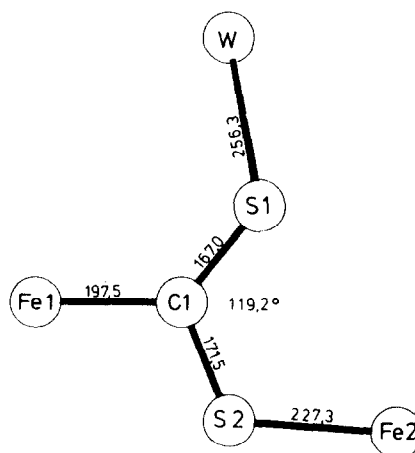


Fig. 3. Partial structure of Busetto's complex [31].

of Sn—C1—S2 from 112.3 $^\circ$ to 124.1 $^\circ$ and the enlarged tetrahedral angle C31—Sn—C1.

The two substituents at S1 and S2 adopt just the opposite position as in the comparable, threefold metal-substituted, dithiocarboxylato complex $(\text{CO})_2\text{-CpFeC}(\text{S})\text{SFeCp}(\text{CO})_2\text{W}(\text{CO})_5$ (Fig. 3) of Busetto [31]. The size of the S1—C1—S2 angle is quite similar but the C—S bond lengths vary less than in **2b**. No structural data are available of the metallodithioester complexes germane to **2b**, e.g. $(\text{CO})_2\text{CpFeC}(\text{S})\text{SMeM}(\text{CO})_5$ (M = Cr, Mo, W) [32].

In Busetto's complex, the strong steric repulsion of the $\text{W}(\text{CO})_5$ and the neighbored $\text{CpFe}(\text{CO})_2$ group (Fe1) leads to an expanded W—S1—C1 angle of 125.9 $^\circ$ and a considerable deviation of S1—W— $(\text{CO})_{\text{trans}}$ from linearity (165.9 $^\circ$). The steric effect may also contribute to the increase of the W—S1 distance compared to **2b**. In both complexes, the bond length of W—C *trans* to W—S1 is slightly reduced and the C—O distance increased due to the good σ donor properties of the dithiocarboxylic ligand.

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