Chinese Journal of Chemistry, **2004**, *22*, 348—353 **Article**

Synthesis, Characterization and Crystal Structure of (*Z*)-1-[2-(Triarylstannyl)vinyl]-1-indanols and Their Arylhalostannyl Derivatives

ZHU, Dong-Sheng[a,b](朱东升) LÜ, Chun-Sheng[a](吕春胜) MEI, Ze-Min[a](梅泽民)
GAO, Wei[a](高伟) ZHANG, Yue-Tao[a](张越涛) MU, Ying*[,a](母瀛)
WANG, Zong-Mu[a](王宗睦)

[a] *School of Chemistry, Jilin University, Changchun, Jilin 130023, China*
[b] *School of Chemistry, Northeast Normal University, Changchun, Jilin 130024, China*

(*Z*)-1-[2-(Tri-*o*-tolylstannyl)vinyl]-1-indanol (**1**) and (*Z*)-1-[2-(tri-*p*-tolylstannyl)vinyl]-1-indanol (**2**) were synthesized by the addition reaction of 1-ethynylindanol with tri-*o*-tolyltin and tri-*p*-tolyltin hydride. The aryl groups in compound **1** and **2** were substituted by Br_2 or I_2 to yield monohalide derivatives (**3**—**6**). The compounds **1**—**6** were characterized by elemental analysis, ^{1}H NMR and FT-IR spectroscopy. The crystal structures of **1**, **2** and **4** have been determined by single crystal X-ray diffraction analysis. The Sn atom in **1** and **2** exhibits a tetrahedral geometry distorted towards trigonal bipyramid due to a weak intramolecular interaction between Sn and the hydroxyl O atoms [0.2839(4) nm and 0.2744(5) nm], while the Sn atom in **4** adopts a trigonal bipyramidal geometry with a significant O→Sn(1) interaction [0.2552(5) nm].

Keywords organotin compounds, aryltin compounds, FT-IR spectroscopy, NMR spectroscopy, X-ray crystal structure

Introduction

Organotin compounds, being important organometallic chemicals, have shown a variety of technical applications as insecticides, fungicides, bactericides, acaricides, wood preservatives, plastic stabilizers and antifouling agents.[1] In recent years there has been increasing interest in study of the antitumour medicines. Some organotin compounds have displayed obvious effect to prevent many tumour cells from upgrowth.[2-4] As a result, their antitumour activity is over the 100 times as great as that of the *cis*-platinum complexes.[5] Moreover, the influence of the structural features of organotin compounds on the antitumour activity has received considerable attention.

Recently, the synthesis and antitumour activity of organotin compounds of the type (*Z*)-$(Ar_3Sn)CH=CHC(OH)R^1R^2$ (Ar = phenyl and *p*-tolyl) and their arylhalostannyl derivatives have been actively studied.[6-13] The solid-state structures of (*Z*)-$(Ar_3Sn)CH=CHC(OH)R^1R^2$ exhibit a weak intramolecular HO→Sn interaction. The Sn atom in these compounds is located in a distorted tetrahedral environment, while the Sn atom adopts a trigonal bipyramidal geometry in the diarylhalostannyl and aryldihalostannyl derivatives of (*Z*)-$(Ar_{3-n}X_nSn)CH=CHC(OH)R^1R^2$ due to strong HO→Sn interaction. It has been reported that the antitumor activity of these compounds is related to the strength of the HO→Sn interaction, which is determined by the number and nature of the aryl groups and the Lewis acidity of the central tin atom.[7-9] In this paper, the synthesis and structure of (*Z*)-1-[2-(tri-*o*-tolylstannyl)-vinyl]-1-indanol (**1**) and (*Z*)-1-[2-(tri-*p*-tolylstannyl)-vinyl]-1-indanol (**2**) and their *o*-tolylhalostannyl and *p*-tolylhalostannyl derivatives are reported. Their structural features, particularly the HO→Sn coordination interaction, are discussed. These compounds are possible to serve as new models for further investigation on the structure-antitumour activity relationship.

Experimental

General procedures

Elemental analyses were carried out on a Perkin-Elmer PE 2400 CHN instrument. ^{1}H NMR spectra were recorded in $CDCl_3$ on a Varian Mercury 300 MHz spectrometer. Infrared spectra (KBr pellets) were recorded on an Alpha Centauri FI/IR spectrometer (400—4000 cm^{-1} range).

Indanone, tri-*o*-tolyltin chloride, tri-*p*-tolyltin chloride, $LiAlH_4$, bromine and iodine were obtained from commercial sources and used without further purification. 1-Ethynylindanol was prepared by a modified re-

* E-mail: ymu@mail.jlu.edu.cn (Y. Mu); Tel.: +80-431-8499136; Fax: +86-431-8949334
Received August 7, 2003; revised and accepted December 20, 2003.
Project supported by the National Natural Science Foundation of China (Nos. 29734143, 29672013).

ported method.[14] Tri-*o*-tolyltin and tri-*p*-tolyltin hydride were obtained from reaction of tri-*o*-tolyltin or tri-*p*-tolyltin chloride with $LiAlH_4$ in anhydrous diethyl ether respectively.[15,16] Diethyl ether was dried and distilled from Na-K alloy under nitrogen. Other solvents were used without further purification.

Synthesis of (*Z*)-1-[2-(tri-*o*-tolylstannyl)vinyl]-1-indanol (1)

Tri-*o*-tolyltin hydride (39.31 g, 100 mmol), 1-ethynylindanol (15.82 g, 100 mmol) and dibenzoyl peroxide (100 mg) were dissolved in 100 mL of dry diethyl ether under a nitrogen atmosphere. The mixture was stirred for 30 h at room temperature, and the solvent was evaporated off. The residue was recrystallized from ethanol to yield 46.40 g of **1** as white crystalline solid. Single crystals suitable for X-ray analysis were obtained by slow evaporation of ethanol solution at room temperature over one week. Yield 84.16%, m.p. 143.2—144.7 ℃, ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 1.28 (s, 1H, OH), 6.43 (d, J_{HH}=12.6 Hz, 1H, =CH—Sn), 6.92 (d, J_{HH}=12.6 Hz, 1H, CH=), 2.35 (s, 9H, CH_3, Ph—CH_3), 7.49, 7.58 (d, J_{HH}=7.2 Hz, J_{HH}=8.1 Hz, 3H, *o*-H, Ph), 7.11—7.30 (m, 13H, Ph), 1.98—2.06, 2.85—2.99 (m, 4H, CH_2CH_2); IR (KBr) ν_{CO}: 1070, ν_{OH}: 3549 cm^{-1}. Anal. calcd for $C_{32}H_{32}OSn$: C 69.72, H 5.85, Sn 21.53; found C 69.83, H 5.76, Sn 21.62.

Synthesis of (*Z*)-1-[2-(tri-*p*-tolylstannyl)vinyl]-1-indanol (2)

1-Ethynylindanol (15.82 g, 100 mmol) and dibenzoyl peroxide (200 mg) were added to a solution of tri-*p*-tolyltin hydride in diethyl ether prepared from the reaction of tri-*p*-tolyltin chloride (53.43 g, 125 mmol) with $LiAlH_4$ (4.74 g, 125 mmol). The mixture was stirred for 35 h at room temperature under nitrogen, and the solvent was evaporated off. The residue was recrystallized from ethanol to yield 42.48 g of **2** as white crystalline solid. Single crystals suitable for X-ray analysis were obtained by slow evaporation of ethanol solution at room temperature over one week. Yield 76.64%, m.p. 118.2—118.7 ℃, ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 1.25 (s, 1H, OH), 6.38 (d, J_{HH}=12.3 Hz, 1H, =CH—Sn), 6.87 (d, J_{HH}=12.3 Hz, 1H, CH=), 2.33 (s, 9H, CH_3, $PhCH_3$), 7.43, 7.53 (d, J_{HH}=7.8 Hz, J_{HH}=7.8 Hz, 6H, *o*-H, Ph), 7.14—7.26 (m, 10H, Ph); 2.06—2.14, 2.82—3.09 (m, 4H, CH_2CH_2); IR (KBr) ν_{CO}: 1069, ν_{OH}: 3548 cm^{-1}. Anal. calcd for $C_{32}H_{32}OSn$: C 69.72, H 5.85, Sn 21.53; found C 69.80, H 5.91, Sn 21.47.

Syntheses of (*Z*)-1-[2-(bromodi-*o*-tolylstannyl)vinyl]-1-indanol (3) and (*Z*)-1-[2-(bromodi-*p*-tolylstannyl)-vinyl]-1-indanol (4)

Bromine (0.48 g, 3.0 mmol) in 15 mL of CCl_4 was added slowly with stirring to a solution of **1** (1.65 g, 3.0 mmol) in 20 mL of CCl_4 at −5 ℃. The colour of bromine disappeared immediately. The mixture was allowed to warm to room temperature and stirred for 1 h. The solvent was evaporated off and the residue was recrystallized from cyclohexane to give 1.41 g of compound **3** as white crystals. Yield 87.04%, m.p. 170.8—171.6 ℃, ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 2.78 (s, 1H, OH), 6.55 (d, J_{HH}=11.4 Hz, 1H, =CH—Sn), 6.77 (d, J_{HH}=11.4 Hz, 1H, CH=), 2.30 (s, 6H, CH_3, $PhCH_3$), 7.49, 7.63 (d, J_{HH}=7.2 Hz, J_{HH}=7.2 Hz, 2H, *o*-H, Ph), 7.12—7.33 (m, 10H, Ph), 2.11—2.19, 2.88—3.10 (m, 4H, CH_2CH_2); IR (KBr) ν_{CO}: 1034, ν_{OH}: 3388 cm^{-1}. Anal. calcd for $C_{25}H_{25}BrOSn$: C 55.60, H 4.67, Sn 21.98; found C 55.71, H 4.60, Sn 21.87.

The compound **2** reacted with one equivalent of bromine to form **4** by similar operation, Yield 78.50 %, m.p. 139.8—140.5 ℃, ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 2.63 (s, 1H, OH), 6.56 (d, J_{HH}=11.1 Hz, 1H, =CH—Sn), 6.78 (d, J_{HH}=11.1 Hz, 1H, CH=), 2.31 (s, 6H, CH_3, $PhCH_3$), 7.57, 7.70 (d, J_{HH}=7.5 Hz, J_{HH}=7.5 Hz, 4H, *o*-H, Ph), 7.06—7.30 (m, 8H, Ph), 2.12—2.20, 2.89—3.14 (m, 4H, CH_2CH_2); IR (KBr) ν_{CO}: 1071, ν_{OH}: 3385 cm^{-1}. Anal. calcd for $C_{25}H_{25}BrOSn$: C 55.60, H 4.67, Sn 21.98; found C 55.64, H 4.71, Sn 21.84. The structure was determined by the single-crystal X-ray diffraction analysis.

Syntheses of (*Z*)-1-[2-(iododi-*o*-tolylstannyl)vinyl]-1-indanol (5) and (*Z*)-1-[2-(iododi-*p*-tolylstannyl)vinyl]-1-indanol (6)

Iodine (0.76 g, 3.0 mmol) dissolved in 60 mL of CCl_4 was added dropwise with stirring to a solution of **1** (1.65 g, 3.0 mmol) in 20 mL of CCl_4 at room temperature. The color of iodine disappeared immediately. The mixture was stirred for 1.5 h, and the solvent was evaporated off. The residue was recrystallized from cyclohexane to yield 1.31 g of compound **5** as white crystals. Yield 74.43%, m.p. 156.5—157.8 ℃, ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 2.65 (s, 1H, OH), 6.66 (d, J_{HH}=11.8 Hz, 1H, =CH—Sn), 6.97 (d, J_{HH}=11.8 Hz, 1H, CH=), 2.37 (s, 6H, CH_3, $PhCH_3$), 7.51, 7.65 (d, J_{HH}=7.6 Hz, J_{HH}=7.6 Hz, 2H, *o*-H, Ph), 7.03—7.28 (m, 10H, Ph), 2.11—2.19, 2.85—3.10 (m, 4H, CH_2CH_2); IR (KBr) ν_{CO}: 1034, ν_{OH}: 3514 cm^{-1}. Anal. calcd for $C_{25}H_{25}IOSn$: C 51.15, H 4.29, Sn 20.22; found C 51.22, H 4.37, Sn 20.13.

The compound **2** reacted with one equivalent of iodine to form **6** by similar operation, Yield 63.41 %, m.p. 143.0—143.7 ℃, ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 2.50 (s, 1H, OH), 6.62 (d, J_{HH}=11.4 Hz, 1H, =CH—Sn), 6.71 (d, J_{HH}=11.4 Hz, 1H, CH=), 2.38 (s, 6H, CH_3, $PhCH_3$), 7.56, 7.69 (d, J_{HH}=7.5 Hz, J_{HH}=7.5 Hz, 2H *o*-H, Ph), 7.04—7.28 (m, 10H, Ph), 2.09—2.17, 2.84—3.08 (m, 4H, CH_2CH_2); IR (KBr) ν_{CO}: 1069, ν_{OH}: 3523 cm^{-1}. Anal. calcd for $C_{25}H_{25}IOSn$: C 51.15, H 4.29, Sn 20.22; found C 51.24, H 4.71, Sn 23.24.

Crystal structure determination of compounds 1, 2 and 4

Diffraction data were collected on a Rigaku RAXIS-RAPID diffractometer for compound **1** and on a Siemens P4 diffractometer for compounds **2** and **4** with graphite monochromated Mo Kα (λ=0.071073 nm) at

ambient temperature. The structures were solved by the heavy-atom method (SHELXS 97), and were refined by full-matrix least squares techniques (SHELXL 97).[17] Non-hydrogen atoms were refined anisotropically.

Results and discussion

Synthesis

Compounds **1**—**6** were synthesized according to Scheme 1. Reactions of compounds **1** and **2** with halogens in a 1∶1 molar ratio yield the corresponding monohalides **3**—**6**, respectively. Compounds **1**—**6** were all characterized by IR, ^{1}H NMR and elemental analysis.

^{1}H NMR and IR spectra

The solution ^{1}H NMR spectra of compounds **1**—**6** are consistent with their structures. All spectra show characteristic ethylenic proton signals of a doublet of doublets with $^3J_{(HC—CH)}$=11.1—12.6 Hz in the regions of δ 6.38—6.66 and δ 6.71—6.97. The $^3J_{(HC—CH)}$ coupling constant of 12.6 and 12.3 Hz observed for **1** and **2** is quite large since the cis coupling constant in similar compounds with a five-membered ring substituent usually amounts to 8 Hz or even less.[18] In regard to the stannyl group, the $^3J_{(HC—CH)}$ coupling constant decreases in the order $Sn(aryl)_3 > Sn(aryl)_2I > Sn(aryl)_2Br$, $Sn(o\text{-tolyl})_3 > Sn(p\text{-tolyl})_3$ and $Sn(o\text{-tolyl})_2X > Sn(p\text{-tolyl})_2X$. The chemical shift of OH shifts to high field following the same order, which indicates that the strength of the HO→Sn interaction increases with the decrease in the steric hindrance of the stannyl group.

The infrared spectra of all compounds **1**—**6** show the presence of strong absorptions in the regions of 1034—1071 and 3385—3549 cm^{-1}, which can be assigned to $\nu_{(C—O)}$ and $\nu_{(O—H)}$ stretching vibrations, respectively.

Crystal structure discussion of compounds 1, 2 and 4

The molecular structures of compounds **1**, **2** and **4** are shown in Figures 1, 2 and 3. The crystal parameters and procedure information corresponding to data collection and structure refinement are given in Table 1. The selected bond distances and angles are listed in Table 2. The Sn atom in **1**, bonded to three *o*-tolyl groups and the C(1) atom of the vinyl residue, adopts a distorted tetrahedral geometry with C-Sn-C angles ranging from 104.63(10)° to 114.09(11)°. The C(1)-Sn(1)-C(21) angle (114.09(11)°) is significantly larger than other C-Sn-C angles due to weak coordination of the O(1) atom of the cyclopentanol hydroxyl group. The distance between the O(1) and the Sn(1) atoms is 0.2839(4) nm, which is

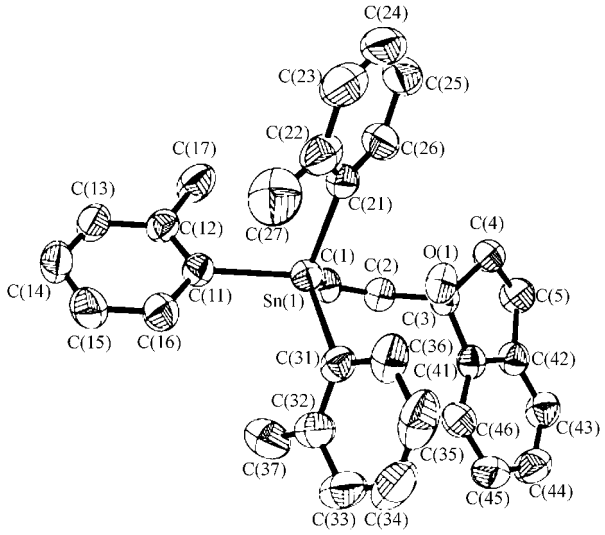
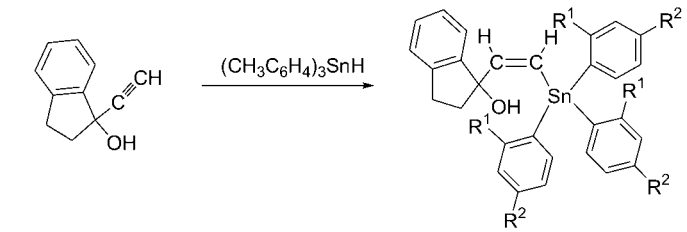
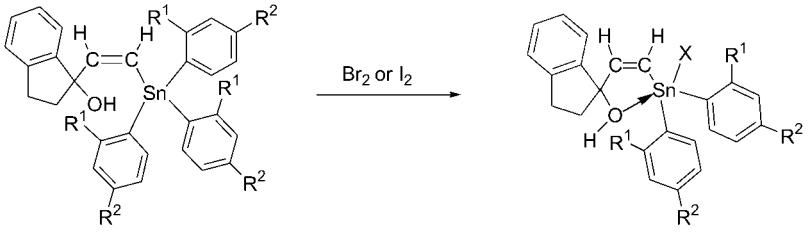


Figure 1 The molecular structure and crystallographic numbering scheme for compound **1**.

Scheme 1



1: $R^1 = CH_3$, $R^2 = H$; **2**: $R^1 = H$, $R^2 = CH_3$.



3: $R^1 = CH_3$, $R^2 = H$, X = Br. **4**: $R^1 = H$, $R^2 = CH_3$, X = Br.
5: $R^1 = CH_3$, $R^2 = H$, X = I. **6**: $R^1 = H$, $R^2 = CH_3$, X = I.

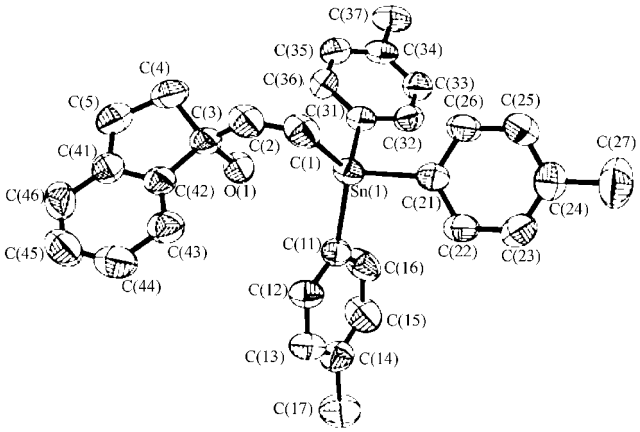


Figure 2 The molecular structure and crystallographic numbering scheme for compound **2**.

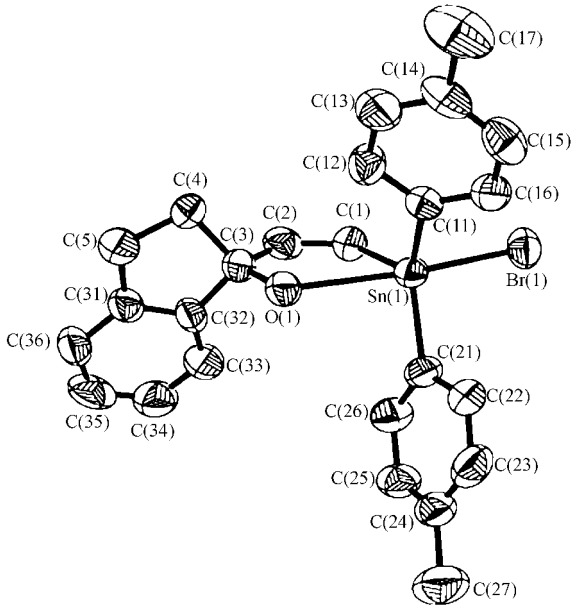


Figure 3 The molecular structure and crystallographic numbering scheme for compound **4**.

significantly shorter than the sum of their van der Waals radii [0.370 nm]).[19] The weak coordination of the O(1) atom also influences the strength of the Sn(1)—C(*o*-tolyl).

Table 1 Crystal data and details of structure refinement parameters for compounds **1**, **2** and **4**

Compound	**1**	**2**	**4**
Formula	$C_{32}H_{32}OSn$	$C_{32}H_{32}OSn$	$C_{25}H_{25}BrOSn$
Molecular weight	551.27	551.27	540.05
Temperature/K	293(2)	293(2)	293(2)
Crystal size/mm	0.73×0.44×0.29	0.50×0.42×0.32	0.52×0.32×0.28
Wavelength/nm	0.071073	0.071073	0.071073
Crystal system	Triclinic	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P2_1/n$
Cell constants			
a/nm	0.9805(2)	0.9632(3)	1.1936(3)
b/nm	1.0514(2)	1.2234(2)	1.2756(4)
c/nm	1.3255(3)	1.30893(16)	1.5834(5)
α/(°)	97.99(3)	106.293(16)	
β/(°)	90.23(3)	104.955(18)	105.86(2)
γ/(°)	94.30(3)	101.67(2)	
V/nm^3	1.3491(5)	1.3660(5)	2.3192(11)
Z	2	2	4
D_{calc}/(g•cm^{-3})	1.357	1.340	1.547
F(000)	564	564	1072
Scan mode	*ω*	*ω*	*ω*
$2\theta_{max}$/(°)	54.86	52.02	52.00
Total reflections collected	5938	5275	4560
Absorption coefficient *μ*(Mo K*α*)/mm^{-1}	0.968	0.956	2.836
R_1 (on *F* for reflections with $I>2\sigma(I)$)	0.0300 (for 5327 reflections)	0.0322 (for 4274 reflections)	0.0575 (for 2785 reflections)
wR_2 (on F^2 for all reflections)	0.0897 (for 5938 reflections)	0.0759 (for 5275 reflections)	0.1363 (for 4560 reflections)
Goodness of fit	1.142	0.941	0.937

Table 2 Selected bond distances (nm) and angles (°) in **1**, **2** and **4**

Parameter	**1**	Parameter	**2**	Parameter	**4**
Sn(1)—C(1)	0.2126(3)	Sn(1)—C(1)	0.2125(3)	Sn(1)—C(1)	0.2101(7)
Sn(1)—C(11)	0.2161(3)	Sn(1)—C(11)	0.2139(3)	Sn(1)—C(11)	0.2145(7)
Sn(1)—C(21)	0.2151(3)	Sn(1)—C(21)	0.2160(3)	Sn(1)—C(21)	0.2113(7)
Sn(1)—C(31)	0.2137(3)	Sn(1)—C(31)	0.2145(3)	Sn(1)—Br(1)	0.25985(11)
Sn(1)—O(1)	0.2839(4)	Sn(1)—O(1)	0.2744(5)	Sn(1)—O(1)	0.2552(5)
O(1)—C(3)	0.1420(3)	O(1)—C(3)	0.1442(4)	O(1)—C(3)	0.1468(8)
C(1)—C(2)	0.1318(4)	C(1)—C(2)	0.1307(5)	C(1)—C(2)	0.1352(10)
C(2)—C(3)	0.1498(4)	C(2)—C(3)	0.1487(5)	C(2)—C(3)	0.1478(11)
C(3)—C(4)	0.1551(4)	C(3)—C(4)	0.1545(5)	C(3)—C(4)	0.1587(10)
C(3)—C(41)	0.1504(4)	C(3)—C(42)	0.1516(4)	C(3)—C(32)	0.1497(10)
C(1)-Sn(1)-C(11)	106.33(10)	C(1)-Sn(1)-C(11)	124.69(12)	C(1)-Sn(1)-C(11)	116.7(3)
C(1)-Sn(1)-C(21)	114.09(11)	C(1)-Sn(1)-C(21)	102.70(13)	C(1)-Sn(1)-C(21)	120.3(3)
C(1)-Sn(1)-C(31)	111.85(11)	C(1)-Sn(1)-C(31)	111.35(13)	C(21)-Sn(1)-C(11)	117.4(3)
C(21)-Sn(1)-C(11)	104.63(10)	C(21)-Sn(1)-C(11)	101.62(11)	C(1)-Sn(1)-Br(1)	96.5(2)
C(21)-Sn(1)-C(31)	112.70(11)	C(21)-Sn(1)-C(31)	101.16(11)	C(11)-Sn(1)-Br(1)	96.7(2)
C(31)-Sn(1)-C(11)	106.46(10)	C(31)-Sn(1)-C(11)	111.46(11)	C(21)-Sn(1)-Br(1)	100.6(2)
C(1)-Sn(1)-O(1)	65.2(3)	C(1)-Sn(1)-O(1)	66.4(4)	C(1)-Sn(1)-O(1)	70.7(2)
C(11)-Sn(1)-O(1)	171.6(3)	C(11)-Sn(1)-O(1)	80.4(4)	C(11)-Sn(1)-O(1)	90.0(2)
C(21)-Sn(1)-O(1)	79.5(2)	C(21)-Sn(1)-O(1)	166.9(4)	C(21)-Sn(1)-O(1)	85.8(2)
C(31)-Sn(1)-O(1)	78.1(3)	C(31)-Sn(1)-O(1)	89.9(4)	Br(1)-Sn(1)-O(1)	167.19(11)
Sn(1)-C(1)-C(2)	128.9(2)	Sn(1)-C(1)-C(2)	127.8(3)	Sn(1)-C(1)-C(2)	123.2(6)
O(1)-C(3)-C(2)	107.2(2)	O(1)-C(3)-C(2)	106.5(3)	O(1)-C(3)-C(2)	107.4(6)
O(1)-C(3)-C(4)	112.4(2)	O(1)-C(3)-C(4)	111.3(3)	O(1)-C(3)-C(4)	110.0(6)
O(1)-C(3)-C(41)	113.1(2)	O(1)-C(3)-C(42)	111.1(2)	O(1)-C(3)-C(32)	111.2(6)
C(1)-C(2)-C(3)	127.1(2)	C(1)-C(2)-C(3)	127.2(3)	C(1)-C(2)-C(3)	125.4(7)
C(2)-C(3)-C(4)	111.7(2)	C(2)-C(3)-C(4)	113.8(3)	C(2)-C(3)-C(4)	112.6(6)
C(2)-C(3)-C(41)	110.2(2)	C(2)-C(3)-C(42)	112.7(3)	C(2)-C(3)-C(32)	113.7(7)
C(4)-C(3)-C(41)	102.3(2)	C(4)-C(3)-C(42)	101.5(3)	C(4)-C(3)-C(32)	101.9(6)

As a result, the Sn(1)—C(11) is longer by 0.001 nm than the other two Sn(1)—C(*o*-tolyl) bonds. The fact that the *Z* isomer rather than the *E* isomer was obtained from this type of reactions might be attributed to the weak intra molecular O→Sn coordination.[6] The geometry about the Sn atom in **2** is essentially the same as that for **1** with the C-Sn-C angles ranging from 101.16(11)º to 124.69(12)º. The C(1)-Sn(1)-C(11) angle of 124.69(12)° is much larger than the corresponding angle in **1** due to stronger interaction between the O(1) atom and the Sn atom in **2**, which can be clearly seen from the relatively short Sn···O(1) distance (0.2744(5) nm). These results also reflect greater Lewis acidity of the Sn atom in **2** than in **1**.

The Sn atom in **4** is five coordinated and the molecule has a distorted trigonal bipyramid geometry with the trigonal plane defined by C(1), C(11) and C(21) atoms and the axial positions occupied by the Br(1) and O(1) atoms, which is similar to the analogue (Z)-1-[2-(chlorodi-*p*-tolylstannyl)vinyl]-1-cycloheptanol.[8] The Sn···O(1) distance of 0.2552(5) nm is in the range of a normal Sn—O coordination bond length,[6,8-10] indicating that the Sn atom in **4** is formally coordinated by the O(1) atom of the hydroxyl group and the Lewis acidity of the Sn atom in the $(p\text{-tolyl})_2SnBr$ moiety is greater than in the $(p\text{-tolyl})_3Sn$ moiety. On the other hand, the O(1)—C(3) bond (0.1468(8) nm) in **4** is weaker than the corresponding bond (0.1442(4) nm) in **2** due to the strong coordination interaction between the O(1) and the Sn atoms. The Sn(1)-C(1)-C(2) angle (123.2(6)º) in **4** is considerably smaller than the equivalent angle ((127.8(3)º) in **2** and the C(1)—C(2) bond (0.1352(10) nm) in **4** is longer than the corresponding one (0.1307(5) nm) in **2**, which is apparently resulted from the strain of the five-membered ring.

References

1 Blunden, S. J.; Evans, C. J. In *The Handbook of Environmental Chemistry*, Hutzinger, O., Ed.; Springer-Verlag: Heidelberg, **1990**, Vol. 3 Part E., pp. 1—44.

2 Barbieri, R.; Pellerito, L.; Ruisi, G.; Lo Giudice, M. J. *Inorg. Chim. Acta* **1982**, *66*, 39.

3 Huber, F.; Roger, G.; Carl, L.; Atassi, G.; Spreafico, F. *J. Chem. Soc., Dalton. Trans.* **1985**, 523.

4 Gielen, M.; Vanbellinghen, C.; Felan, J.; Willem, R. *Bull. Soc. Chim. Belg.* **1988**, *97*, 873.

5 Crow, A. J.; Smith, P. J.; Atassi, G. *Chem. Biol. Intact.* **1980**, *32*, 171.

6 Pan, H.; Willem, R.; Meunier-Piret, J.; Gielen, M. *Organometallics* **1990**, *9*, 2199.

7 Gielen, M.; Lelieveld, P.; De Vos, D.; Pan, H.; Willem, R.; Biesemans, M.; Fiebig, H. H. *Inorg. Chim. Acta* **1992**, *196*, 115.

8 Fu, F.; Li, H.; Zhu. D.; Fang, Q.; Pan, H.; Tiekink, E. R. T.; Kayser, F.; Biesemans, M.; Verbruggen, I.; Willem, R.; Gielen, M. *J. Organomet. Chem.* **1995**, *490*, 163.

9 Dai, H. C.; Ying, Q. H.; Wang, X. H.; Yue, S. M.; Pan, H. D.; Chen, X. *Polyhedron* **1998**, *17*, 2503.

10 Zhu, D.-S.; Dai, H.-C.; Shan, X.-L.; Tian, L.-J.; Fu, F.-X.; Pan, H.-D.; Xin, Y.; Lin, Y.-H. *Chin. J. Org. Chem.* **1998**, *18*, 162 (in Chinese).

11 Fu, F.-X.; Fu, Y.-J.; Zhu, D.-S.; Fang, Q.-X.; Pan, H.-D. *Chin. J. Chem.* **1994**, *12*, 365 (in Chinese).

12 Ren, Y.-J.; Fu, F.-X.; Zhu, D.-S.; Pan, H.-D.; Jing, F.-Y. *Acta Chim. Sinica* **1996**, *54*, 929 (in Chinese).

13 Zhu, D.-S.; Dai, H.-C.; Shan, X.-L.; Fu, F.-X.; Pan, H.-D. *Chin. J. Org. Chem.* **1998**, *18*, 447 (in Chinese).

14 Vercruijsse, H. D.; De Graaf, W.; Brandsma, L. *Synth. Commun.* **1988**, *18*, 131.

15 kuivila, H. D.; Jr Beumel, O. F. *J. Am. Chem. Soc.* **1961**, *83*, 1246.

16 Lorenz, D. H.; Shapiro, P.; Stern, A.; Becker, E. I. *J. Org. Chem.* **1964**, *28*, 2335.

17 Sheldrick, G. M. SHELXL-97, *A Program for Structure Refinement*, University of Göttingen, Göttingen, Germany, **1997.**

18 Silverstein, R. M.; Bassler, C. G.; Morrill, T. C. *Spectrometric Identification of Organic Compounds*, 4th Edn., John Wiley Sons., New York, **1981**, pp. 235—253.

19 Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441.

(E0308077 ZHAO, X. J.)