Synthesis and crystal structure of (*Z*)-1-(triphenylstannyl)-3-*p*-chlorophenyl-1-butene-3-ol

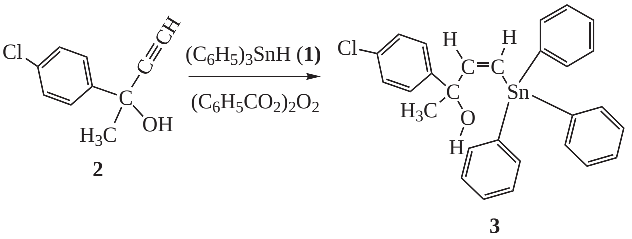
Xing-Qi Li, Dong-Sheng Zhu*, Xi-Guang Du, Kui-Zhan Shao and Xing-Hua Yang

School of Chemistry, Northeast Normal University, Changchun 130024, P.R. China

(*Z*)-1-(Triphenylstannyl)-3-*p*-chlorophenyl-1-butene-3-ol was synthesised and its structure was determined by X-ray diffraction analysis.

Keywords: organotin compound, phenyltin compound, crystal structure

Since Crowe *et al*. reported that organotin compounds are anti-tumour active and hypotoxic compounds,[1] great attention has been paid to the synthesis, structure and antitumour activity of such compounds. It has been reported that the antitumour activity of organotin compounds with intramolecular O→Sn coordination 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. [2–4] It is of considerable interest to prepare more organotin compounds with various novel structures in view of this potential application related to antitumour activity. Therefore, we have synthesised a new organotin compound, (*Z*)-1-(triphenylstannyl)-3-*p*-chlorophenyl-1-butene-3-ol, and its structure has been determined by single crystal X-ray diffraction.



Scheme 1

The title compound **3** was obtained from the reactions shown in Scheme 1. Under a nitrogen atmosphere, the reaction of triphenyltin hydride **1** with 3-(*p*-chlorophenyl)-1- butyn-3-ol **2** in a 1:1 molar ratio in dried diethyl ether at room temperature for 30 h gave compound **3**.

Some selected distances and bond angles of compound **3** are listed in Table 1. The molecular structure of compound **3** is shown in Fig. 1 and there are two molecules in the crystallographic unit, labelled A and B, with only slight conformational differences between them and no intermolecular contact occurs. The central tin atom is bonded to four carbon atoms, one (C1) from the ethylene residue and three (C11, C21, C31) from the phenyl groups, appearing in a four-coordinated environment with a tetrahedral geometry distorted towards trigonal bipyramidal. The Sn–C distances are in the range from 2.126(2) to 2.159(2) Å for part A and 2.119(2) to 2.163(2) Å for part B, and the angles of C–Sn–C bond are in the range from 101.15(8) to 120.92(9)° for part A and 102.35(9) to 121.45(8)° for part B. The Sn(1)–C(31) bond distance is longer than the Sn(1)–C(11) and Sn(1)–C(21) bond distances. In addition, the angle of C(11)–Sn(1)–C(21) bond is rather larger than that of C(11)–Sn(1)–C(31) and C(31)–Sn(1)–C(21) bonds. The distorted geometry is due to the close proximity between the O(1)

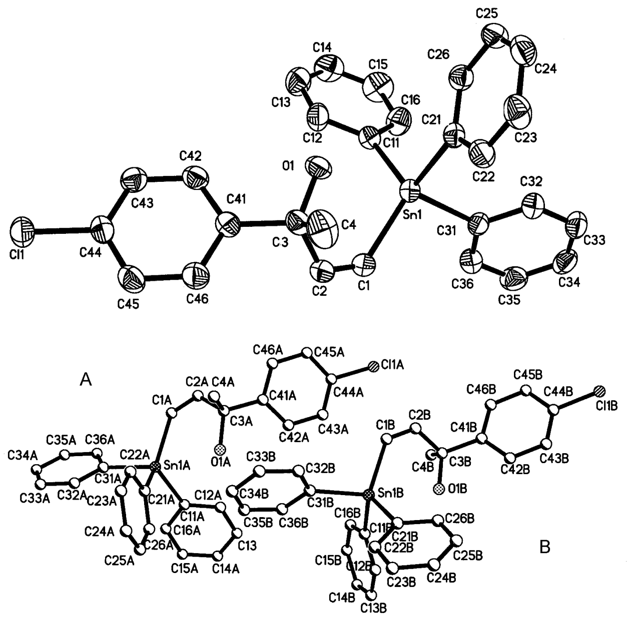


Fig. 1 Molecular structure and crystallographic numbering scheme for compound **3**.

Table 1 Selected bond lengths (/Å) and bond angles (/°) of compound **3**

Sn(1A)–C(1A)	2.126(2)	Sn(1B)–C(1B)	2.119(2)
Sn(1A)–C(21A)	2.143(2)	Sn(1B)–C(11B)	2.139(2)
Sn(1A)–C(11A)	2.145(2)	Sn(1B)–C(21B)	2.148(2)
Sn(1A)–C(31A)	2.159(2)	Sn(1B)–C(31B)	2.163(2)
Sn(1A)...O(1A)	2.812	Sn(1B)...O(1B)	2.833
O(1A)–C(3A)	1.435(3)	O(1B)–C(3B)	1.431(3)
C(1A)–C(2A)	1.323(3)	C(1B)–C(2B)	1.329(3)
C(2A)–C(3A)	1.504(3)	C(2B)–C(3B)	1.512(3)
C(1A)–Sn(1A)–C(21A)	120.92(9)	C(1B)–Sn(1B)–C(11B)	121.45(8)
C(1A)–Sn(1A)–C(11A)	117.14(9)	C(1B)–Sn(1B)–C(21B)	114.44(9)
C(21A)–Sn(1A)–C(11A)	106.09(8)	C(11B)–Sn(1B)–C(21B)	107.60(8)
C(1A)–Sn(1A)–C(31A)	103.60(9)	C(1B)–Sn(1B)–C(31B)	105.43(9)
C(21A)–Sn(1A)–C(31A)	101.15(8)	C(11B)–Sn(1B)–C(31B)	102.35(9)
C(11A)–Sn(1A)–C(31A)	105.32(9)	C(21B)–Sn(1B)–C(31B)	103.06(8)
O(31A)–Sn(1A)–C(1A)	165.8°	O(31B)–Sn(1B)–C(1B)	168.6°

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* Correspondence. E-mail: zhuds206@nenu.edu.cn

atom (O1A from part A or O1B from part B) and the tin atom, with a distance of 2.812 Å or 2.833 Å which reveals the presence of a weak interaction between Sn and O atoms.[5] The O(1) atom may make an influence on both the Sn–C bond distances and the C–Sn–C bond angles, so that the distortion of the tetrahedral geometry towards trigonal bipyramid occurs. The axial sites being occupied by the O(1) and C(31) atoms, and the angles of O(31)–Sn(1)–C(1) in the structure are 165.8° and 168.6° for parts A and B, respectively.

Experimental

Melting points were determined on a Yanaco melting point apparatus and are uncorrected. ^{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 (400–4000cm^{-1} range). Elemental analyses were carried out on a Perkin-Elmer PE 2400 CHN instrument and Sn was analysed gravimetrically.

Preparation of (Z)-1-(triphenylstannyl)-3-p-chlorophenyl-1-butene-3-ol (**3**): Triphenyltin hydride (1) and 3-(*p*-chlorophenyl)-1-butyn-3-ol (2) were prepared according to the literature.[6,7]

To the diethyl ether solution of triphenyltin hydride (**1**), which was prepared by reaction of triphenyltin chloride (48.18 g, 125 mmol) and $LiAlH_4$ (4.81 g, 125 mmol) was added 3-(*p*-chlorophenyl)-1-butyn-3-ol (1805 mg, 100mmol) (**2**) and dibenzoyl peroxide (300 mg). Then the reaction mixture was stirred for 30 h at room temperature under a nitrogen atmosphere. Ether was removed by evaporation and the residue was recrystallised from ethanol. Product (**3**) was obtained in 57% yield (30.29 g) and also the by-product of hexaphenylditin (10.59 g) in 30% yield (m.p. 233–234 °C.[5]). (*Z*)-1-(Triphenylstannyl)-3-*p*-chlorophenyl-1-butene-3-ol (**3**): Colourless crystal, m.p. 105–106 °C, Elemental analysis: Found (Calc) $C_{28}H_{25}ClOSn$: C, 63.5(63.2), H, 4.7(4.7), Sn, 22.4(22.5)%. IR: $\nu_{O\text{-}H}$: 3529 cm^{-1}, $\nu_{C\text{-}O}$: 1072 cm^{-1}. ^{1}H NMR ($CDCl_3$, δ): 6.30 (d, 1H, $^3J_{H\text{-}C=C\text{-}H}$ = 12.3 Hz), 7.02 (d, 1H, $^3J_{H\text{-}C=C\text{-}H}$ = 12.3 Hz), 1.78 (s, 1H, OH), 1.61 (s, 3H, CH_3), 7.16-7.62 (m, 19H, Ph).

Crystal data (**3**): $C_{28}H_{25}OSnCl$, Mr = 531.61, triclinic, $P\bar{1}$, a = 10.941 (2) Å, b = 13.818(3) Å, c = 16.274(3) Å, α = 85.28(3)°, β = 88.62(3)°, γ = 79.63(3)°, V = 2411.9(8) Å^3, Z = 4, D_x = 1.464 g cm^{-3}, μ = 1.187 cm^{-1}, T = 298 K. The colourless block crystals for X-ray determination were obtained by evaporating an ethanol solution slowly at room temperature over one week. The data were collected at room temperature using a Rigaku R-AXISRAPID diffractometer with graphite monochromatized Mo–Kα radiation (λ = 0.7107 Å) by the ω scan mode. Empirical absorption corrections (multi-scan) were applied in each case. The data were collected in the ω scan mode and were corrected for Lorentz and polarisation effects.[8] The structures were solved by the heavy-atom method (SHELXS 97),[9] and were refined by full-matrix least squares techniques (SHELXL 97).[10] Non-hydrogen atoms were refined anisotropically. The hydrogen atoms were generated geometrically. A total of 16998 reflections were collected. The final cycle of full-matrix least-squares refinement was based on 10591 observed reflections ($I > 2\sigma(I)$) and 559 variable parameters and converged with R_1 = 0.0277 and wR_2 = 0.0680. Full crystallographic details have been deposited at the Cambridge Crystallographic Data Centre, CDDC NO. 211795.

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