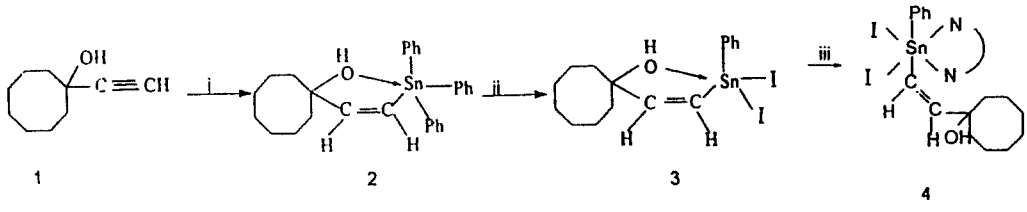
Synthesis and Characterization of a Novel Intramolecular O→Sn Coordinated (Z)-1-[2-(triphenylstannyl)vinyl]-cyclooctanol

Ren Yu-Jie, Yang Xue-Feng
Department of Chemistry, Dalian University of Technology, Dalian 116024, China
Chen Hui-lin
Dalian Institute of chemical physics, The Chinese Academy of science, Dalian 116023, China

Abstract: Intramolecular O→Sn coordinated (Z)-1-[2-(triphenylstannyl) vinyl]-cyclooctanol (2) was synthesized and characterized by X-ray diffraction analysis, iododemetallation and substitutive coordination.
Keywords: (Z)-1-[2-(triphenylstannyl)vinyl]-cyclooctanol, Synthesis, Characterization

In recent years, there has been much effort in the development of new organotin compounds and its analogues for antitumor agents.[1] Of particular interest have been the intramolecular O→Sn coordination structures[2] and their anticancer activity.[3] The moderate stability of the organotin compounds would be required to exhibit the expected antitumour characteristics in the form of the inhibition of DNA synthesis in the cancer cells.[4] The predissociation of intramolecular O→Sn coordination bond with N-containing bientate ligand may be a crucial step in the formation of a tin-DNA complex.[3,4,5] Although several intramolecular O→Sn coordination organotin compounds have been previously prepared, characterized[2,6,7] and tested against various tumor cells,[3] nevertheless, more appropriate organotin compounds are still being expected to be exploited, more analogue compounds to octahedral *cis*-platin[4,5] are to be found. There was no report on their further adduct with N-containing bientate ligand yet. A new organotin compound (Z)-1-[2-(triphenylstannyl)vinyl]-cyclooctanol (2) and its iodinated (3) and chelated(4) derivatives are thus synthesized as follows:



1 2 3 4

Scheme *Reagents and conditions*: i, Ph_3SnH (1 equiv.), $(PhCOO)_2$ (0.018 equiv.), diethyl ether, N_2, 25℃, 30h. ii, I_2(2 equiv.),CCl_4, 25℃, 20h. iii, bipyridyl (1 equiv.), EtOH, reflux, 3h

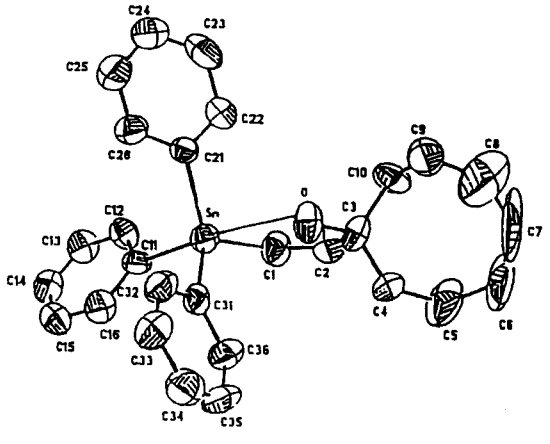


Fig. 1 X-ray structure of 2. Selected bond length (Å) and angles (°): Sn-O 2.729, Sn-C(1) 2.132 (8), Sn-C(11) 2.174 (8)., Sn-C(21) 2.143 (7) , Sn-C(31) 2.146 (7) , C (1)-C (2) 1.313 (13) , C (2)-C (3) 1.498 (11) , C (3)-O 1, 423 (9). O-Sn-C (11) 169.5 , C (1)-Sn-C (11) 105.6 (3) , O-Sn-C (21) 86.9 , C (1)-Sn-C (21) 114.6 (3) , O-Sn-C (31) 76.7 , C (1)-Sn-C (31) 116.1 (3) , O-Sn-C (1) 66.2, C(3)-O-Sn 113.7 , Sn-C(1)-C(2) 126.7 , C (1)-C (2)- C (3) 128.0 (7) , C (2)-C (3)-O 105.2 (7).

The X-ray diffraction analysis of compound 2 illuminates that tin atom exists in a tetrahedral geometry distorted towards a trigonal bipyramidal one , with a distortion due to the close approach of the OH group . Hydrostannation[8] of this alkyne with triphenyltin hydride would yield a mixture of Z and E olefins.[9] However, it would be reasonable to get more Z isomers from the mixture in the type reaction attributed by the intramolecular O→Sn coordination. The C(11)-Sn-O angle (169.5°) is considerably close to 180°, and the order of C-Sn length in compound 2 would be Sn-C(11) > Sn-C(21) > Sn-C(31) > Sn-C(1) , thus the phenyl group with C(11) , probably the apical one ,would likely be the most active one[2] in the oxidative cleavage with iodine. The other phenyl groups also might be demetallated more easily than the vinyl substituent.[6]

The IR data show that intramolecular O→Sn coordination. The addition of triphenyltin hydride to the triple bond in compound would have taken place and the broad and strong OH absorption peaks have become slightly shorter and sharper. The iododematallation of compound 2 to compound 3 would further shorten the sharp OH absorption peaks. However , on the substitutive coordination of compound 3 with bipyridyl, the broad and strong OH absorption peaks resumed. These phenomena would clearly provide new evidences and counterevidence for the existence of the intramolecular O→Sn coordination and stimulate further studies aimed at the understanding for the mechanism of anticancer activity and drug action.

The proton NMR data are also illustrative for the intramolecular O→Sn coordination. The coordination of hydroxyl group to the tin atom would naturally and probably fix the oxygen atom to the apical one of the distorted trigonal bipyramidal geometry. As if the inhibition association of hydroxy group in compound 2 by the hindrance of its configuration would get the chemical shift value of proton increased. However, the hydroxy group might be in the screen region of the phenyl ring , that is , it might be just above the phenyl ring ,[10] then the resonance of proton in the hydroxyl group should be suffered with a large scale upfield shift. The O-Sn-C(31) angle (76.7°) is much smaller than right angle (90°) , and the O-Sn bond (2.729Å) is much longer than Sn-C(31) (2.146(7) Å) , the proton in hydroxyl group still tends to form hydrogen bond with another same molecule , thus , the proton would be likely to lie above phenyl ring containing C(31).[10, 7] The substitution of compound 2 with iodo atom would not only enhance acidity of tin atom , and to have the chemical shift value of proton incerased, but shorten the length of O→Sn bond, [2] extend the O-Sn-C angle, [2] the proton at hydroxyl group might partially shift from the screen region of the phenyl ring to the deshielding region., and have the chemical shift value of proton increased. When the coordination of O→Sn in compound 3 was displaced by a bipyridyl , the acidity of central tin atom is likely to be weakened and the resonance of proton in hydroxy group would be upfield. The acidity of tin atom in the compounds could also be employed to interpret the changes of δ (=CH—Sn) and δ (CH=—Sn).

Table 1 Selected IR(KBr) data (υ/cm^{-1})

Compound	υ(OH)	υ(C—O)	υ(Sn—O)
1	3307-3598	1062	—
2	3569	1071	525
3	3566	1068	—
4	3373-3500	1090	—

Table 2 Selected proton NMR data ($CDCl_3$, ppm)

Compound	δ (OH)	δ (=CH—Sn)	δ (CH=—Sn)	δ (HC≡C—)
1	2.05	—	—	2.38
2	1.11	6.18	7.03	—
3	2.79	6.64	6.69	—
4	2.38	6.45	6.82	—

Footnotes

1. All new compounds were identified with satisfactory elemental analysis.
2. Crystal data for compound 2:Nicolet R 3M/E automatic diffractioneter. $C_{28}H_{32}OSn$, M=502.69, monoclinic, space group $C_{2/c}$. a=23.195(10), b=11.675(5), c=18.653(4) Å , β =105.40(3), V=4869.9(5) $Å^3$, Z=8, Dc=1.35g cm^{-3} F(0 0 0)=1504, μ (Mo μ_α) =10.48cm^{-1}, specimen 0.14×0.42×0.28mm^3, 4768 unique reflection for 2° <2θ <29.32°, of which 2686 with I>3σ(I) were used in the refinement. R=0.0436, Rw=0.0424. S=0.4522.

References

1 C. J. Cardin and A.Roy, Inorg. Chim. Acta 1985, **107**,57.

2 F. Kayser, M.Biesemans, A. Delmotte, I. Verbruggen, I. De Borger, M. Gielen and R. Willen,Organometallics 1994,**13**, 4026

3 M. Gielen, P.Leieveld,D.de Vos, H. D. Pan, R.Willem,M.Biesemans and H. H. Fiebig , Inorg. Chim. Acta 1992,**196**,115

4 A .J.Crowe and P .J.Smith,Inrog. Chim. Acta 1984, **93**,179

5 J .Wan, J.Huang, L.Huang, D.Shi and S.Hu, Inrog. Chim. Acta 1988, **152**, 67

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

7 F . -X. Fu, Y.-J. Fu, D.-S. Zhu, Q.-X. Fang and H. -D. Pan, Chin. J. Chem. 1994, **12**, 365.

8 G. J. M. Van der Kerd , J. G. Nolts and J. G. A. Luijten , J. Appl . Chem . 1959 , **9** , 106.

9 A. J. Leusink and H. A. Budding , J. Organomet. Chem. 1968 , **11** , 533.

10 R. Willem , A. Delmotte , I. De Borger , M. Biesemans , M. Gielen , F. Kayser and E. R. T. Tiekink, J.Organomet . Chem . 1994 ,**480** , 255.