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Synthesis, X-ray Diffraction Analysis, and Multinuclear NMR Study of (*Z*)-3,4,4-Trimethyl-1-(triphenylstannyl)-1-penten-3-ol and Its Monoiodinated Derivative

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The syntheses of (*Z*)-3,4,4-trimethyl-1-(triphenylstannyl)-1-pentene-3-ol (**1**) and (*Z*)-3,4,4-trimethyl-1-(iododiphenylstannyl)-1-penten-3-ol (**2**) are reported. The solid-state structures of these tetra- and triorganotin compounds were determined by X-ray diffraction methods. The tin atom in **1** exists in a tetrahedral geometry distorted toward a trigonal bipyramidal one, with the distortion due to the close approach of the OH atom, i.e. 2.772(5) Å. A trigonal bipyramidal geometry is found in **2** where the oxygen atom, which forms significant O→Sn interactions of 2.498(4) and 2.550(4) Å for the two independent molecules, respectively, is in an apical position as is the iodine atom. The different strengths of the HO→Sn interactions are related to the Lewis acidities of the respective tin centers. Crystals of **1** are triclinic, space group $P\bar{1}$, with $a = 11.120(6)$ Å, $b = 11.652(6)$ Å, $c = 9.998(5)$ Å, $\alpha = 110.15(5)°$, $\beta = 106.39(4)°$, $\gamma = 87.74(6)°$, $V = 1164(1)$ Å^3, and $Z = 2$. Crystals of **2** are triclinic, space group $P\bar{1}$, with $a = 12.631(4)$ Å, $b = 13.887(1)$ Å, $c = 12.252(4)$ Å, $\alpha = 95.91(2)°$, $\beta = 107.00(3)°$, $\gamma = 74.67(2)°$, $V = 1981(1)$ Å^3, and $Z = 2$. The structures were refined to final $R = 0.048$ for **1** and R = 0.038 for **2**. These compounds were characterized in solution by ^{1}H, ^{13}C, and ^{119}Sn NMR spectroscopy. The existence of an intramolecular HO→Sn coordination in solution was assessed by ^{13}C and ^{119}Sn secondary isotope multiplet of partially labeled entities (SIMPLE-NMR) experiments.

Introduction

Organotin compounds and analogue derivatives containing donor moieties causing the tin atom to extend its coordination sphere through intramolecular coordination have been the subject of much interest.[1] In this context, compounds of the type (*Z*)-(Ph_3Sn)CH=CH-C(OH)RR′ as well as their mono- and diiodinated derivatives, (*Z*)-(Ph_2ISn)CH=CHC(OH)RR′ and (*Z*)-(PhI_2Sn)CH=CHC(OH)RR′, have been recently investigated in our group.[2−7] The tetraorganotin compounds present some interesting structural features. It has been shown by X-ray diffraction analysis for (*Z*)-17-[2-(triphenylstannyl)vinyl]-4-estren-17β-ol[7] that such compounds can exhibit a pentacoordinated tin atom resulting from a weak intramolecular HO→Sn interaction. Strong evidence was recently found that this weak coordinative bond exists likewise in solution for 3-methoxy-(*Z*)-17-[2-(triphenylstannyl)vinyl]estran-1,3,5(10)-trien-17β-ol[2,3] and related compounds.[4,5,8] Owing to their very low Lewis acidity, pentacoordinated tin atoms in tetraorganotin derivatives are not common even if some compounds presenting such a coordination are known.[1,7,8] The common feature of these compounds is that the coordinating group is in a favorable position with respect to the tin atom and can thus be "locked" in a very weak potential hole by the coordinative bond.

The present paper compares the structural features of such HO→Sn interactions in a tetraorganotin compound, (*Z*)-3,4,4-trimethyl-1-(triphenylstannyl)-1-penten-

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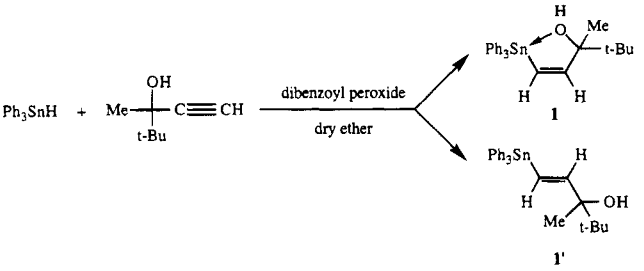
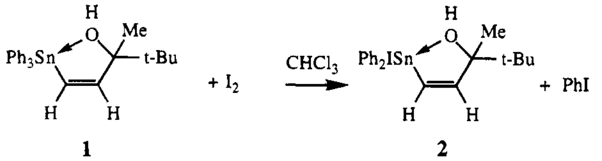
Scheme 1



Scheme 2



1 2

3-ol (**1**), and its iododiphenylstannyl analog (**2**) using X-ray diffraction methods. A multinuclear NMR study provides evidence for the existence of such an intramolecular interaction in solution in noncoordinating solvents.

Results and Discussion

Syntheses. The addition of ethyne to 3,3-dimethyl-2-butanone in the presence of *t*-BuOK according to Verkruijsse[9] yielded 3,4,4-trimethyl-1-pentyn-3-ol racemate in good yield (75%). Hydrostannation[10] of this alkyne with triphenyltin hydride using dibenzoyl peroxide as a catalyst yielded a mixture of *Z* and *E* olefins[11] (Scheme 1). The *Z* compound, **1**, was purified by crystallization from hexane. The *E* isomer, **1′**, could not be entirely separated as a pure compound from **1**.

The reaction of **1** with iodine in 1:1 molar ratio yielded **2** quantitatively (Scheme 2). Hence, the phenyl–tin bond is cleaved regiospecifically. Such regiospecific cleavages have been observed previously in organotin compounds containing donor groups.[1a,6,7,12]

Pan et al. interpreted[7] this preferred cleavage in the case of (*Z*)-(Ph_3Sn)CH=CHC(OH)RR′ compounds[6,7] by a weak intramolecular HO→Sn interaction in the tetraorganotin compound observed in both the crystalline and solution states.[2,3] Such a weak coordination results in a tetrahedral geometry distorted toward a trigonal bipyramid with a pentacoordinated tin atom; the coordinating oxygen and one phenyl group are in the axial positions, and the remaining two phenyl and the vinyl moieties are in equatorial positions. The axial C–Sn bond, being weaker, is more reactive toward iodine so that the phenyl group in this position solely is cleaved.

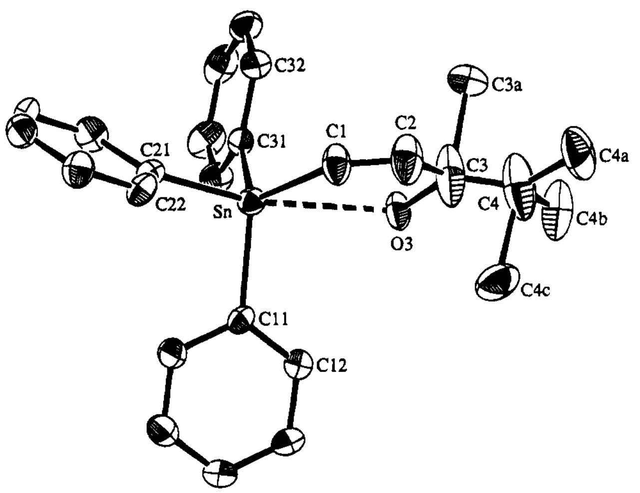


Figure 1. Molecular structure and crystallographic numbering scheme for compound **1**.

Table 1. Selected Bond Distances (Å) and Angles (deg) for 1

Sn–C(1)	2.107(8)	Sn–C(11)	2.121(7)
Sn–C(21)	2.135(7)	Sn–C(31)	2.122(7)
Sn••O(3)	2.772(5)	O(3)–C(3)	1.43(1)
C(1)–C(2)	1.26(1)	C(2)–C(3)	1.49(1)
C(1)–Sn–C(11)	118.4(3)	C(1)–Sn–C(21)	101.6(3)
C(1)–Sn–C(31)	117.3(3)	C(11)–Sn–C(21)	104.2(3)
C(11)–Sn–C(31)	109.4(3)	C(21)–Sn–C(31)	103.5(3)
Sn–C(1)–C(2)	127.9(7)	C(1)–C(2)–C(3)	128.6(9)
C(2)–C(3)–O(3)	107.0(9)		

X-ray Crystallography. The molecular structure of **1** is shown in Figure 1, and selected interatomic parameters are listed in Table 1. The structure is molecular, there being no intermolecular contacts in the lattice; the closest non-hydrogen contact of 3.51(1) Å occurs between the C(14) and C(24)′ atoms (symmetry operation: $-x$, $1 - y$, $1 - z$). The tin atom is bonded to the C(1) atom, derived from the ethylene residue, and three phenyl groups. The geometry is distorted tetrahedral with the range of angles about the tin atom being 101.6(3)–118.4(3)°. The distortion in the coordination geometry is due to the close proximity of the O(3) atom, which is separated by 2.772(5) Å from the tin atom; this separation, though long, reveals a weak bonding interaction. The presence of the O(3) atom has the effect of opening up the C(1)–Sn–C(11) and C(1)–Sn–C(31) angles and therefore clearly exerts a stereochemical influence in the molecule. If the O(3) atom is considered to occupy a coordination site, the geometry about the tin atom is distorted trigonal bipyramidal with the axial sites being occupied by the O(3) and C(21) atoms; the angle O(3)••Sn–C(21) in this description is 166.4(2)°. Support for the existence of some HO→Sn interaction is found in the elongation of the Sn–C(21) bond by 0.01 Å over the other two Sn–C(phenyl) bonds; the relatively high errors associated with these parameters are noted, however. The C(1), C(2), C(3), and O(3) atoms of the 3,4,4-trimethyl-1-penten-3-ol molecule are nearly coplanar as evidenced by their torsion angle of −10(2)°; the same holds for the atoms Sn, C(1), C(2), and C(3), the torsion angle being 2(2)°. Substitution of one of the phenyl groups in **1** by an iodine atom gave rise to **2** in which a major structural change is evident.

The two molecular structures of **2** are shown in Figure 2, and selected interatomic parameters are listed in Table 2; there are two molecules in the crystallographic unit, labeled a and b, with only minor conformational

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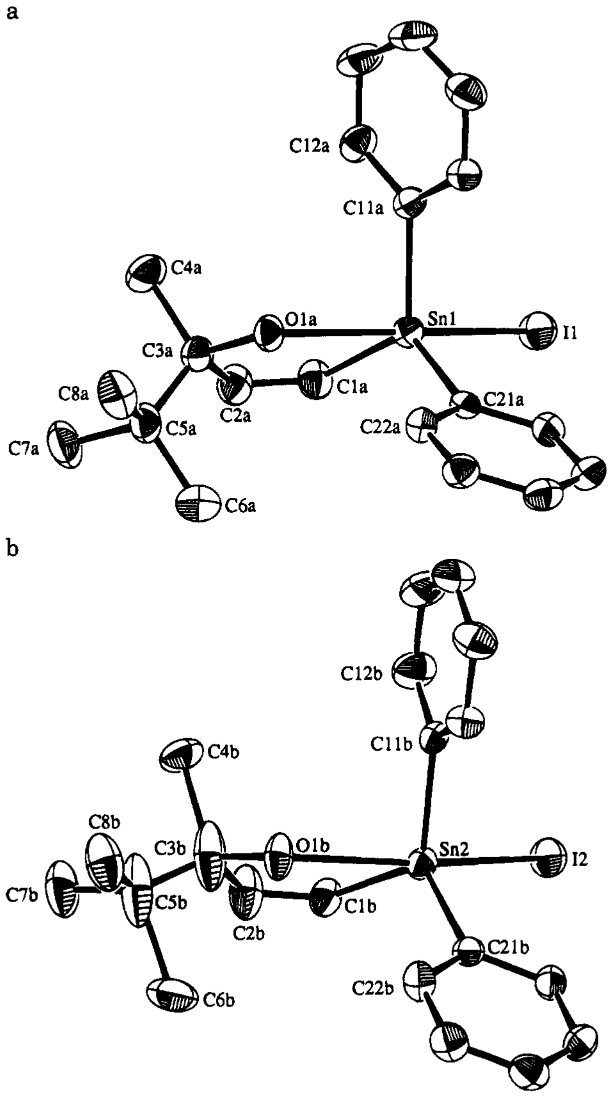


Figure 2. Molecular structure and crystallographic numbering scheme for molecules a and b of compound **2**.

Table 2. Selected Bond Distances (Å) and Angles (deg) for 2

params	molecule a	molecule b
Sn—I	2.7710(8)	2.763(1)
Sn—O(1)	2.498(4)	2.550(4)
Sn—C(1)	2.074(6)	2.077(6)
Sn—C(11)	2.103(5)	2.104(5)
Sn—C(21)	2.131(5)	2.118(5)
O(1)—C(3)	1.453(6)	1.462(7)
C(1)—C(2)	1.307(8)	1.289(7)
C(2)—C(3)	1.489(8)	1.493(8)
I—Sn—O(1)	165.92(8)	163.28(8)
I—Sn—C(1)	96.3(2)	95.1(1)
I—Sn—C(11)	98.8(1)	98.0(1)
I—Sn—C(21)	100.9(1)	103.6(1)
O(1)—Sn—C(1)	70.5(2)	70.4(2)
O(1)—Sn—C(11)	84.2(2)	83.3(2)
O(1)—Sn—C(21)	90.8(2)	91.2(2)
C(1)—Sn—C(11)	120.3(2)	121.2(2)
C(1)—Sn—C(21)	123.1(2)	120.4(2)
C(11)—Sn—C(21)	109.9(2)	111.6(2)
Sn—O(1)—C(3)	113.7(3)	110.3(3)
Sn—C(1)—C(2)	123.9(4)	123.7(4)
C(1)—C(2)—C(3)	125.0(5)	125.5(6)
O(1)—C(3)—C(2)	105.7(5)	105.9(5)

differences between them. The structure of **2** is molecular with the closest non-hydrogen intermolecular contact being 3.294(7) Å for O(1a)···C(23a)′ (symmetry operation: $-x, 1-y, 1-z$). The tin atom is coordinated by the C(1) and O(1) atoms of the 3,4,4-trimethyl-1-penten-3-ol ligand, the iodine atom, and two phenyl groups. The Sn···O(1) separations of 2.498(4) and 2.550(4) Å for molecules a and b, respectively, clearly represent significant bonding interactions. The geometry about the tin atom is thus best described as being based on a trigonal bipyramid with the axial positions occupied by the iodine and O(1) atoms; I(1)—Sn(1)—O(1a) = 165.92(8)°, and I(2)—Sn(2)—O(1b) = 163.28(8)°. The equatorial plane being defined by the carbon atoms, the Sn(1) atom lies 0.3149(4) Å out of the trigonal plane toward the I(1) atom; the comparable value for the Sn(2) atom of molecule b is 0.3204(4) Å. The small differences in the Sn—O(1) bond distances are reflected in the Sn—I distances since the shorter Sn—O(1) bond is associated with the longer Sn—I(1) bond. The five-membered Sn/C(1)/C(2)/C(3)/O(1) rings that are formed are planar to ±0.046(6) and ±0.09(1) Å for molecules a and b, respectively. The stronger Sn—O interactions in **2** result in some systematic variations in the geometric parameters describing the 3,4,4-trimethyl-1-penten-3-ol moiety compared with the molecule of **1**.

The relatively high values of the estimated standard deviations for the derived geometric parameters describing the 3,4,4-trimethyl-1-penten-3-ol moiety preclude a comparison of individual pairs of parameters. However, it is possible to ascertain trends which may be related to the strength of the Sn—O interaction. Thus, in **2** where the Sn—O interactions are strongest, the O(1)—C(3) bonds are weaker than the comparable bond in **1**. Further, although the Sn—C(1) bond lengths are equal in the three molecules, the C(1)—C(2) bonds are longer in **2** compared with **1**. In addition, there has been a small contraction in the O(1)—C(3)—C(2) angles in **2**. These results suggest that there is a significantly greater transfer of electron density from the 3,4,4-trimethyl-1-penten-3-ol moiety to tin in **2** compared with that in **1**. This is consistent with the enhanced Lewis acidity of the tin atom in the Ph$_2$SnI moiety compared with the Ph$_3$Sn moiety.

Mössbauer Spectroscopy. The Mössbauer spectrum of compound **1** exhibits an isomer shift (IS) of 1.23 mm/s relative to Ca^{119m}SnO$_3$ and a quadrupole splitting (QS) of 0.58 mm/s. The small quadrupole splitting indicates a deviation from the symmetry of the electron cloud of the tin atom in triphenylvinyltin compounds without the HO→Sn interaction, where QS = 0; thus, the nonzero QS in **1** is in agreement with an intramolecular HO→Sn coordination in the solid state as observed previously for related compounds.[3,4,5,8] For **2** an IS of 1.40 mm/s and a large QS of 3.03 mm/s is found. This larger QS, as compared to **1**, is in agreement with the trigonal bipyramidal geometry of the iododiphenylstannyl compound found from X-ray data.

NMR Spectroscopy. The ^{1}H and ^{13}C resonance assignments and coupling data obtained for compounds **1** and **2** are given in Table 3.

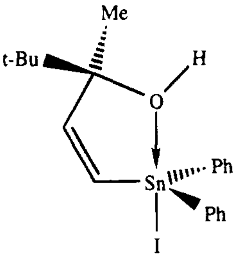
The phenyl groups of the monoiodinated compound **2** are diastereotopic as evidenced by the pairwise splitting of their resonances. This indicates pseudorotation or, more likely, dissociation—recombination of the intramo-

Table 3. ^{1}H and ^{13}C Resonance Assignments and Coupling Data for Compounds 1 and 2[a]

	^{1}H		^{13}C	
	1	**2**	**1**	**2**
=CH−Sn	6.35 (d, 12) [95/99]	6.51 (d, 11) [125/131]	122.9 [568/595]	127.9 [671/702]
CH=−Sn	7.06 (d, 12) [180/189]	6.82 (dd, 11, 1) [239/250]	152.7 [5]*	149.3 [5]*
COH	1.31 (s)	2.23 (d, 1)	79.4 [28]*	82.3 [33/35]
ipso			142.4 [516/540]	140.4 [669/696] 141.6 [645/675]
ortho	7.6−7.8 (m)	7.6−7.8 (m)	136.9 [37]*	135.6 [48/50] 136.0 [48/50]
meta	7.3−7.5 (m)	7.3−7.5 (m)	128.2 [49/51]	128.4 [64/67] 128.7 [66/69]
para	7.3−7.5 (m)	7.3−7.5 (m)	128.3 [11]*	129.2 [15]* 129.3 [14]*
CH_3	1.21 (s)	1.26 (s)	24.0 [10]*	24.0 [12]*
t-Bu CH_3	0.86 (s)	0.81 (s)	25.3	25.2
t-Bu C			37.3 [7]*	37.4 [9]*

[a] Chemical shifts in ppm. Proton multiplicities and $^nJ(^1H-^1H)$ coupling constants in Hz between parentheses: s = singlet; d = doublet; dd = doublet of doublets; m = complex pattern. $^nJ(^1H-^{117/119}Sn)$ and $^nJ(^{13}C-^{117/119}Sn)$ coupling constants are between brackets. An asterisk indicates unresolved $^nJ(^{13}C-^{117/119}Sn)$ coupling satellites.

lecular coordination[1a,13] in the trigonal bipyramid, if any, to be slow on the NMR time scale:



These observations are in agreement with the structures in the crystalline state.

For compound **1**, the $^1J(^{13}C-^{119}Sn)$ coupling constant of the olefinic carbon resonance of 595 Hz is significantly larger than that of the aromatic ipso carbon resonances of 540 Hz. In order to assess the significance of these different $^1J(^{13}C-^{119}Sn)$ coupling constants, we determined likewise those of **1′**, the *E*-analogue of the *Z*-compound **1** and of triphenylvinyltin, $CH_2{=}CHSnPh_3$. These two compounds are functionally similar to **1** around the tin atom, except that they cannot undergo intramolecular coordination extension by a HO→Sn interaction. The $^1J(^{13}C-^{119}Sn)$ coupling constants of **1′**, as determined by ^{119}Sn NMR from a solution of a mixture of **1** and **1′**, were found to be 523 Hz for the olefinic carbon and 533 Hz for the ipso carbon. The values found for $CH_2{=}CHSnPh_3$ are comparable, 511 Hz for the olefinic carbon and again 533 Hz for the ipso carbon. The dramatically higher $^1J(^{13}C-^{119}Sn)$ olefinic coupling of **1** with respect to **1′** and to $CH_2{=}CHSnPh_3$ (595 Hz versus 523 and 511 Hz, respectively) provides evidence to the existence of a HO→Sn coordination for compound **1** in solution. Thus, this larger value can be assigned to the increased "s" character of the olefinic carbon−tin bond[14] in the equatorial position of the trigonal bipyramidal geometry of **1**. The only slightly higher value of the $^1J(^{13}C-^{119}Sn)$ ipso couplings in **1** (540 Hz) with respect to **1′** and to $CH_2{=}CHSnPh_3$ can also be understood in this context. Thus, in compound **1**, which appears to be fluxional on the NMR time scales, the $^1J(^{13}C-^{119}Sn)$ ipso coupling results from two equatorial $C_{ipso}-Sn$ coupling contributions, being expected to be larger, and from one axial $C_{ipso}-Sn$ coupling contribution, being expected to be smaller than in "pure" four-coordinate triphenylvinyltin compounds like **1′** and $CH_2{=}CHSnPh_3$.

Comparison of the $^1J(^{13}C-^{119}Sn)$ couplings of compounds **1** and **2** provides an additional argument in favor of a HO→Sn interaction to exist in the former. The $^1J(^{13}C-^{119}Sn)$ coupling values of the olefinic and the aromatic ipso carbon resonances increase in **2** with respect to **1**. This indicates that the more marked trigonal bipyramidal geometry observed in the solid state for **2** with respect to **1**, with the two phenyl groups in equatorial positions in the former, likewise holds in solution. This lies in line with the higher Lewis acidity of the tin atom in **2** as compared to **1**.

The ^{119}Sn NMR spectra of compounds **1**, **1′**, and **2** exhibit a single resonance at −156.7, −130.9, and −164.5 ppm, respectively. The low-frequency shift of the ^{119}Sn resonance of 25.8 ppm of the *Z*-compound **1** with respect to the *E*-one **1′** is not an unambiguous argument in favor of an intramolecular HO→Sn coordination in solution. Indeed, analogous compounds where the HO group is substituted for either an H atom or a CH_3 group exhibit only slightly smaller chemical shift differences between the *Z* and *E* isomers.[5] In addition, low-frequency shifts of ^{119}Sn resonances in *Z*-isomers of triorganovinyltin compounds with respect to *E*-isomers are well-known.[15]

Consequently, the existence of an intramolecular HO→Sn coordination in solution for **1** and **2** was assessed by ^{13}C and ^{119}Sn secondary isotope multiplet of partially labeled entities (SIMPLE-NMR) experiments[3,8,16] (Figure 3). For compound **1** there are secondary isotopic effects on the ^{13}C chemical shift, $\delta(^{13}C^2H) - \delta(^{13}C^1H)$, of −0.123, −0.022, −0.065, and −0.016 ppm for the COH, *t*-Bu C, CH_3, and ipso carbon of the triphenyltin moiety, respectively. For **2** the secondary isotopic effects observed are −0.138, −0.017, and −0.061 ppm for the carbon resonances of the COH, *t*-Bu C, and CH_3 and −0.039 ppm for both diastereotopic ipso carbon atoms.

The isotope shift observed for the ipso carbon resonances can reasonably only result from a three bond effect through the D−O→Sn−C ipso pathway and hence provides evidence for HO→Sn coordination in the triphenylstannyl compound as well as its iododiphenylstannyl analog. The pathway D−O−C−C=C−Sn is far less probable especially because isotopic effects over more than three bonds are generally not observed.[17] Furthermore, comparison of the ^{13}C SIMPLE NMR results of compound **1** with those of **2** confirmed this view. The secondary isotopic effects on the aliphatic ^{13}C resonances

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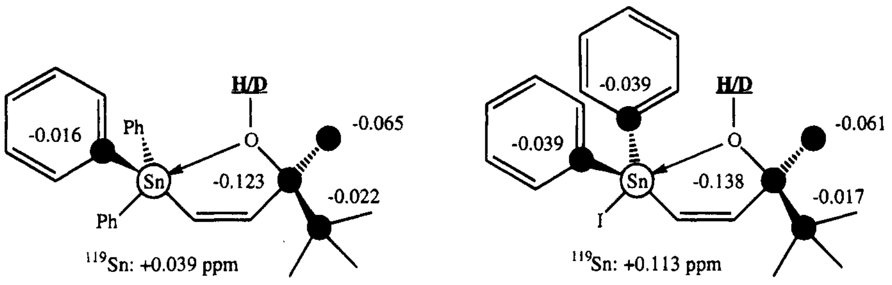

1 **2**

Figure 3. Secondary isotopic effects on the ^{13}C and ^{119}Sn chemical shifts observed for compounds **1** and **2** in SIMPLE-NMR experiments. Digital resolution: ^{13}C, 0.006 ppm/pt; ^{119}Sn, 0.002 ppm/pt.

Table 4. Crystallographic Data for 1 and 2

	compd	
	1	**2**
formula	$C_{26}H_{30}OSn$	$C_{20}H_{25}IOSn$
fw	477.2	527.0
space group	triclinic, $P\bar{1}$	triclinic, $P\bar{1}$
a, Å	11.120(6)	12.631(4)
b, Å	11.652(6)	13.887(1)
c, Å	9.998(5)	12.252(4)
α, deg	110.15(5)	95.91(2)
β, deg	106.39(4)	107.00(3)
γ, deg	87.74(6)	74.67(2)
V, Å^3	1164(1)	1981(1)
Z	2	2
D_{calcd}, g·cm^{-3}	1.361	1.767
μ, cm^{-1}	11.10	28.51
cryst size, mm	0.16 × 0.16 × 0.24	0.24 × 0.48 × 0.65
no. of unique rflns collcd	5855	9893
no. of rflns in refinement with $I \geq 3.5\sigma(I)$	2851	6961
no. of params refined	253	415
R, R_w	0.048, 0.047	0.038, 0.039
ϱ_{max}, e Å^{-3}	0.49	1.18

Table 5. Fractional Atomic Coordinates and Their Estimated Standard Deviations for 1

atom	*x*	*y*	*z*
Sn	0.35120(5)	0.27688(5)	0.60580(6)
O(3)	0.5919(4)	0.3392(5)	0.7986(5)
C(1)	0.4941(8)	0.2276(8)	0.4998(9)
C(2)	0.6109(10)	0.2401(11)	0.5590(12)
C(3a)	0.7266(11)	0.1501(9)	0.7683(13)
C(3)	0.6811(11)	0.2884(15)	0.7195(13)
C(4)	0.7921(12)	0.3243(18)	0.7701(14)
C(4a)	0.8923(10)	0.2777(13)	0.6936(15)
C(4b)	0.8527(10)	0.3831(14)	0.9340(16)
C(4c)	0.7396(12)	0.4626(9)	0.7155(14)
C(11)	0.3155(7)	0.4648(6)	0.6872(7)
C(12)	0.4028(7)	0.5544(7)	0.7858(9)
C(13)	0.3738(9)	0.6755(7)	0.8360(11)
C(14)	0.2563(10)	0.7060(7)	0.7822(11)
C(15)	0.1684(8)	0.6192(8)	0.6873(10)
C(16)	0.1963(7)	0.4983(7)	0.6391(8)
C(21)	0.1874(7)	0.1960(6)	0.4259(7)
C(22)	0.1683(7)	0.2085(7)	0.2931(8)
C(23)	0.0662(9)	0.1533(8)	0.1737(9)
C(24)	−0.0192(8)	0.0834(8)	0.1863(9)
C(25)	−0.0069(8)	0.0689(7)	0.3148(12)
C(26)	0.0975(8)	0.1244(8)	0.4347(9)
C(31)	0.3457(6)	0.1953(6)	0.7640(7)
C(32)	0.3836(8)	0.0794(7)	0.7508(9)
C(33)	0.3756(9)	0.0283(8)	0.8549(13)
C(34)	0.3305(10)	0.0914(11)	0.9666(11)
C(35)	0.2937(9)	0.2047(9)	0.9810(9)
C(36)	0.3020(8)	0.2569(7)	0.8799(8)

vary only slightly from **1** to **2**. In contrast, the magnitude of the secondary isotopic effect on the ipso carbon resonance is twice as large, in agreement with the coordinative bond being stronger in **2** than in **1**.

The secondary isotopic effect on the ^{119}Sn chemical shift, $\delta(^{119}Sn^{2}H) - \delta(^{119}Sn^{1}H)$, of +0.039 and +0.113 ppm observed for **1** and **2**, respectively, can reasonably only result from a two bond effect through the D—O→Sn pathway and confirms the HO→Sn coordination to exist.

Significantly, the *E*-compound **1′** did not display any secondary isotopic effect, either in the ^{13}C or in the ^{119}Sn spectrum.

Conclusion

The X-ray analysis on **1** and **2** reveals the presence of significant intramolecular HO→Sn interactions of 2.772(5) and 2.498(4) Å (2.550(4) Å for molecule b), respectively. The magnitudes of the interactions are related to the increased Lewis acidity of the tin atom in Ph_2SnI compared with Ph_3Sn. The ^{13}C and ^{119}Sn SIMPLE NMR experiments show the existence of a HO→Sn interaction in the tetraorganotin as well as in the triorganotin compounds, in agreement with the solid-state results. While for the latter type of compounds such intramolecular HO→Sn interactions in solution are well-known, there are not much literature data supporting the existence of such coordinations in tetraorganotin compounds in solution.

Experimental Section

Synthesis. 3,4,4-Trimethyl-1-pentyn-3-ol was prepared according to Verkruijsse.[9] An emulsion of 4.26 g (38 mmol) of *t*-BuOK in 40 mL of THF was saturated with purified[18] acetylene during 15 min (1 L/min) under vigorous stirring at 0 °C. A 3.8 g amount (38 mmol) of 3,3-dimethyl-2-butanone was added to the white viscous gel over a period of 25 min at −10 to −15 °C while the acetylene flow was maintained at 400 mL/min. The acetylene stream was maintained an additional 5 min until the reaction mixture became clear. The mixture was then hydrolyzed with 40 mL of an aqueous NH_4Cl solution and extracted three times with ether. The collected organic layers were dried over $MgSO_4$, and the ether was evaporated under reduced pressure. 3,4,4-Trimethyl-1-pentyn-3-ol was further purified by vacuum distillation (bp 33−46 °C, 16.5 Torr; yield 75%).

Triphenyltin hydride was prepared according to Kuivila[19] by the reaction of triphenyltin chloride and $LiAlH_4$ in dry

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Table 6. Fractional Atomic Coordinates and Their Estimated Standard Deviations for 2

atom	*x*	*y*	*z*	atom	*x*	*y*	*z*
Sn(1)	0.02865(3)	0.23727(3)	0.44286(3)	Sn(2)	0.38440(3)	0.26131(3)	0.03510(3)
I(1)	0.17521(4)	0.05837(3)	0.40340(4)	I(2)	0.40928(4)	0.45256(3)	0.09894(4)
O(1a)	−0.1377(3)	0.3726(3)	0.4693(3)	O(1b)	0.3030(3)	0.1079(3)	−0.0186(4)
C(1a)	−0.0883(5)	0.1747(4)	0.4801(5)	C(1b)	0.2105(5)	0.3055(4)	−0.0452(5)
C(2a)	−0.1867(5)	0.2262(4)	0.4935(5)	C(2b)	0.1442(5)	0.2452(5)	−0.0723(7)
C(3a)	−0.2319(5)	0.3360(4)	0.4797(5)	C(3b)	0.1785(6)	0.1372(5)	−0.0444(8)
C(4a)	−0.3288(5)	0.3577(5)	0.3698(5)	C(4b)	0.1452(6)	0.1206(5)	0.0730(5)
C(5a)	−0.2681(5)	0.3865(5)	0.5834(5)	C(5b)	0.1252(6)	0.0758(6)	−0.1195(9)
C(6a)	−0.1698(6)	0.3583(6)	0.6907(6)	C(6b)	0.1640(7)	0.0979(6)	−0.2385(6)
C(7a)	−0.3723(6)	0.3574(6)	0.5960(6)	C(7b)	−0.0048(6)	0.1019(6)	−0.1464(7)
C(8a)	−0.2997(6)	0.4994(5)	0.5744(6)	C(8b)	0.1678(6)	−0.0355(5)	−0.1005(7)
C(11a)	−0.0093(5)	0.3021(4)	0.2839(4)	C(11b)	0.4451(5)	0.2005(4)	0.1987(4)
C(12a)	−0.1026(5)	0.2956(4)	0.1951(5)	C(12b)	0.3876(6)	0.2312(6)	0.2795(6)
C(13a)	−0.1262(6)	0.3423(5)	0.0938(5)	C(13b)	0.4280(7)	0.1929(7)	0.3861(7)
C(14a)	−0.0555(7)	0.3949(5)	0.0811(5)	C(14b)	0.5283(7)	0.1235(6)	0.4125(6)
C(15a)	0.0383(6)	0.4020(5)	0.1665(6)	C(15b)	0.5880(6)	0.0930(5)	0.3368(6)
C(16a)	0.0612(5)	0.3557(4)	0.2664(5)	C(16b)	0.5470(5)	0.1310(4)	0.2293(5)
C(21a)	0.1435(4)	0.3064(4)	0.5692(4)	C(21b)	0.5024(4)	0.2057(4)	−0.0624(4)
C(22a)	0.1065(5)	0.3975(4)	0.6190(5)	C(22b)	0.5062(5)	0.1170(4)	−0.1229(5)
C(23a)	0.1835(5)	0.4412(4)	0.6984(5)	C(23b)	0.5795(5)	0.0841(4)	−0.1899(5)
C(24a)	0.2967(5)	0.3968(4)	0.7267(5)	C(24b)	0.6516(5)	0.1386(5)	−0.1951(5)
C(25a)	0.3355(5)	0.3074(5)	0.6762(5)	C(25b)	0.6515(5)	0.2270(5)	−0.1338(5)
C(26a)	0.2582(5)	0.2616(4)	0.5988(5)	C(26b)	0.5782(5)	0.2603(4)	−0.0678(5)

diethyl ether. The obtained reaction mixture was purified[8] by column chromatography on silica gel using benzene/petroleum ether (1/4) as eluent to yield (89%) the pure hydride.

Dibenzoyl peroxide (60 mg) was added under nitrogen atmosphere to a solution of 3,4,4-trimethyl-1-pentyn-3-ol (3.79 g; 30 mmol) and triphenyltin hydride (10.53 g; 30 mmol) in dry ether (150 mL) at room temperature.[6,7] After 20 h of magnetic stirring at room temperature under nitrogen atmosphere the ether was evaporated under reduced pressure. A mixture of *Z* and *E* isomers in the ratio 36/64 was observed in the ^{1}H NMR spectrum. Crystallization from hexane yielded a mixture of large crystals (2.83 g) of **1** and a white powder (0.24 g). The latter undesired byproduct was not further analyzed. The crystals were manually selected and recrystallized from hexane to yield 20% of pure **1** (mp 89–91 °C). Elemental analysis (Redox SNC, Cologno, Italy) is as follows. Found (calcd): C, 65.5 (65.4); H, 6.3 (6.4); Sn, 24.8 (24.9). IR (KBr): ν(O–H) = 3582 cm^{-1} (medium, sharp), ν(C–O) = 1075 cm^{-1} (strong, sharp). IR (CCl$_4$): ν(O–H) = 3605 (weak, broad), 3579 cm^{-1} (shoulder), ν(C–O) = 1074 cm^{-1} (strong, sharp). The single crystal of **1** studied by X-ray diffraction was obtained by slow evaporation of a cyclohexane solution.

A 67.8 mL volume of a 14.9 mM solution of iodine (1.01 mmol) in CHCl$_3$ was added dropwise to a solution of 480 mg (1.01 mmol) of compound **1** dissolved in 15 mL of chloroform. The violet color disappeared nearly instantaneously. The solvent was evaporated under vacuum and the compound **2** was obtained after recrystallization from cyclohexane (yield 79%; mp 133–135 °C). Anal. Found (calcd): C, 45.8 (45.6); H, 4.8 (4.8); Sn, 22.4 (22.5). IR (KBr): ν(O–H) = 3529 cm^{-1} (medium, broad with two weak high-frequency shoulders), ν(C–O) = 1075 cm^{-1} (strong, broad with low-frequency shoulder). IR (CCl$_4$): ν(O–H) = 3600 cm^{-1} (medium, sharp), ν(C–O) = 1074 cm^{-1} (strong, sharp). The single crystal studied by X-ray diffraction was obtained by slow evaporation of a cyclohexane solution of **2**. NMR data of **1′** in the mixture of **1′** and **1** are as follows. ^{1}H NMR data: olefinic protons, AB spectrum, 6.51 and 6.48 ppm (J = 19 Hz) [$^nJ(^1H-^{117/119}\mathrm{Sn})$ = 83/86 and 87/91]; ortho, 7.5–7.8 (m); meta + para, 7.3–7.5 (m); COH, 1.33 (bs); CH$_3$, 1.32 (s); *t*-Bu CH$_3$, 0.99 (s). ^{13}C NMR data, (chemical shifts in ppm, $^nJ(^{13}\mathrm{C}-^{117/119}\mathrm{Sn})$ between brackets): =CH–Sn, 120.7 [500/523]; CH=–Sn, 156.8 [5]*; COH, 79.0 [64/67]; ipso, 138.5 [509/533]; ortho, 137.1 [37]*; meta, 128.6 [50/52]; para, 129.1 [11]*; CH$_3$, 23.4 [7]*; *t*-Bu CH$_3$, 37.3 [5]* (asterisk indicates unresolved $^nJ(^{13}\mathrm{C}-^{117/119}\mathrm{Sn})$ couplings). IR (CCl$_4$) of the mixture of **1′** and **1**: ν(O–H) = 3608 (weak, broad), 3578 cm^{-1} (shoulder) (**1**), 3481 cm^{-1} (**1′**), ν(C–O) = 1075 cm^{-1} (strong, sharp) (**1**), 1099 cm^{-1} (medium, broad) (**1′**).

All IR data were obtained from a Perkin-Elmer FT-IR 2000 instrument.

X-ray Diffraction Analysis of 1 and 2. Intensity data for the colorless crystals were measured at room temperature on a Rigaku AFC6R diffractometer fitted with graphite-monochromatized Mo Kα radiation, λ = 0.710 73 Å; the $2\theta-\omega$ scan technique was used, and $\theta_{\max}$ was 27.5° in each case. For **1**, the net intensity values for three standard reflections remeasured after every 400 reflections decreased to *ca.* 80% of their initial values. The data set was corrected for this variation, and both sets were corrected for Lorentz and polarization effects[20] and for absorption.[21] Crystal data are listed in Table 4.

The structures were solved by direct methods[22] and refined by a full-matrix least-squares procedure based on F.[20] Non-hydrogen atoms were refined with anisotropic thermal parameters, and hydrogen atoms were included in the model at their calculated positions (C–H = 0.97 Å); no evidence was found for the O*H* atoms. High thermal motion associated with some of the atoms of the 3,4,4-trimethyl-1-penten-3-ol ligand was found leading to less than optimal interatomic parameters. Final refinement details are listed in Table 4. Fractional atomic coordinates are listed in Tables 5 and 6, and the numbering schemes employed are shown in Figures 1 and 2, which were drawn with ORTEP[23] at 30% probability ellipsoids. Calculations were performed with the teXsan[20] program installed on an Iris Indigo work station.

NMR Experiments. Solutions of *ca.* 100 mg of compounds **1** and **2** in 0.5 mL of CDCl$_3$ were used. Standard spectra were recorded on a Bruker AC250 NMR spectrometer at 250.13 MHz proton resonance frequency interfaced with an Aspect-3000 computer and equipped with a 5 mm QNP (^{1}H, ^{19}F, ^{119}Sn, ^{13}C) probe. ^{13}C and ^{119}Sn SIMPLE NMR experiments were run on a Bruker AMX500 spectrometer equipped with a 5 mm inverse detection triple resonance (^{1}H, ^{13}C, ^{15}N) probe head tuned at 125.76 MHz ^{13}C frequency and a 5 mm ^{119}Sn{^{1}H} probe head tuned at 186.50 MHz ^{119}Sn frequency. Chemical shifts were referenced to the residual solvent peak and converted to the standard TMS scale by adding 7.24 and 77.0 ppm for ^{1}H and ^{13}C nuclei, respectively. The ^{119}Sn chemical shift is given with respect to 10% Me$_4$^{119}Sn in CDCl$_3$.

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[20] teXsan: Structure Analysis Software. Molecular Structure Corp., The Woodlands, TX.

[21] Walker, N.; Stuart, D. *Acta Crystallogr., Sect. A* **1983**, *39*, 158.

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Totally deuterated samples were prepared by dissolving the compounds in CD_3OD and subsequently evaporating the methanol under reduced pressure. The HO/DO ratio for the ^{13}C and ^{119}Sn SIMPLE-NMR experiments was adjusted to 60/40 by adding 40 mg of the totally deuterated sample to a 0.5 mL of $CDCl_3$ solution of 60 mg of the totally protonated one.

Mössbauer Spectroscopy. The Mössbauer spectra were recorded as previously described.[8]

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Supplementary Material Available: Tables of anisotropic thermal parameters, hydrogen atom parameters, all bond distances, and all bond angles for compounds **1** and **2** (10 pages). Ordering information is given on any current masthead page.

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