Quest for Organotin(IV) Cations Containing O,C,O-Chelating Ligands

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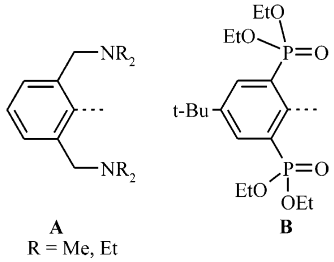
A set of triorganotin(IV) compounds Ph_2L^1SnX and Ph_2L^2SnX (**1**−**9**) with O,C,O-chelating ligands L^1 and L^2 (L^1 = 2,6-$(MeOCH_2)_2C_6H_3$ and L^2 = 2,6-(t-$BuOCH_2)_2C_6H_3$) containing different electronegative substituents X (X = I, CF_3COO, CF_3SO_3, PF_6, and HgI_3) was prepared. These compounds have been characterized by elemental analysis, ESI-MS, and ^1H, ^{13}C, and ^{119}Sn NMR spectroscopy. X-ray diffraction analysis showed that the decrease of the nucleophilicity of X resulted in the formation of organotin cations stabilized by two strong Sn−O intramolecular interactions. In this transformation the ligand geometry about the tin atom changed from tetrahedral to trigonal bipyramidal with the OR groups in *trans* arrangement. Solution NMR studies indicated that the coordination geometry of these compounds is the same in the solid state and solution.

Introduction

Despite the long history of the development of organotin(IV) cations,[1] which are belived to play an important role in the cytotoxic activity of organotin compounds[2] or in catalytic applications involving organic reactions such as esterification,[3] only a limited number of cationic compounds stabilized by donor atoms[4] or free stannylium cations[5] have been isolated. The use of Y,C,Y-chelating ligands in organotin compounds (Chart 1) is one of the possible entrees to the preparation of organotin cations. Jastrzebski et al. reported the use of N,C,N-chelating ligand in the synthesis of air-stable triorganotin cations[6] (some of which were insoluble in organic solvents)[7] involving two strong Sn−N intramolecular interactions. Jurkschat and co-workers prepared triorganotin cations stabilized by two strong Sn−O intramolecular interactions.[8] Recently, we have prepared organotin derivatives of O,C,O-chelating ligands. However, triorganotin chlorides containing such O,C,O-chelating ligands did not form organotin cations containing two strong Sn−O interactions. The dissociation of the tin−chloride bond was not observed in this case, in contrast to analogous triorganotin compounds containing N,C,N-chelating ligands.[9]

Chart 1



This paper describes the synthesis of sets of triorganotin compounds containing O,C,O-chelating ligands L^1 and L^2 (where L^1 = 2,6-$(MeOCH_2)_2C_6H_3$ and L^2 = 2,6-(t-$BuOCH_2)_2C_6H_3$; see Scheme 1). As the nucleophilic character of the electronegative substituent X decreased (Scheme 1), organotin cations stabilized by two Sn−O intramolecular interactions were formed. Prepared compounds enable us to study the effect of moderation of

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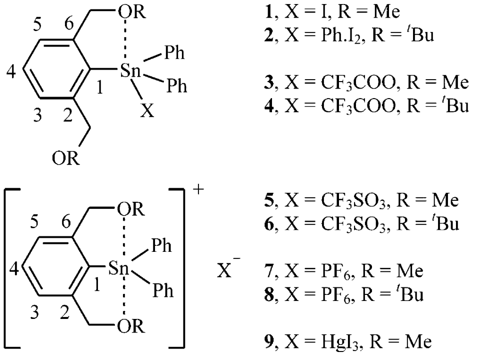
10.1021/om049636f CCC: $27.50

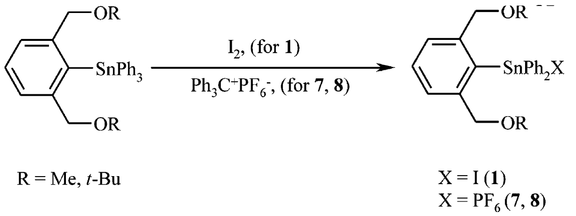
Scheme 1: Numbering of Prepared Compounds and Labeling of Atoms (for NMR solution only)



the Lewis acidity of the tin center on the magnitude of the intramolecular tin–oxygen interactions and its influence on the shape of tin coordination polyhedron. The dependence of the Sn–O interaction strength on increasing ligand spatial hindrance can be studied as well.

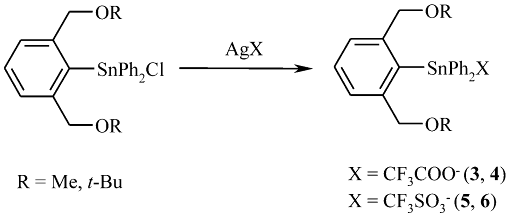
Results and Discussion

Synthetic Aspects. Three synthetic methods were used for preparation of the compounds studied. The reaction of organotin compounds of type Ph_3L^1Sn with I_2 or Ph_3L^1Sn and Ph_3L^2Sn with $Ph_3C^+PF_6^-$ gave the corresponding organotin derivatives **1**, **7**, and **8** (eq 1). However, the reaction of Ph_3L^2Sn with I_2 under various reaction conditions (elevated temperatures, different solvents, and reaction time) did not lead to the expected product, Ph_2L^2SnI. The product of this reaction was identified as an adduct of Ph_3L^2Sn and I_2 (**2**) (based on ^1H, ^{13}C, ^{119}Sn NMR spectroscopy, electrospray ionization mass spectrometry (ESI-MS), and elemental analysis; see Experimental Section), a type of organotin compounds for which, to the best of our knowledge, there is no precedent.



(1)

The conversion of triorganotin chlorides Ph_2L^1SnCl and Ph_2L^2SnCl by reaction with the appropriate silver salt, AgX, was the second procedure used for the preparation of **3**–**6** (eq 2).



(2)

In both procedures, the reaction of organotin compounds with the sterically more hindered ligand L^2 required the use of longer reaction times and higher temperatures than were needed in the case of the L^1-containing compounds.

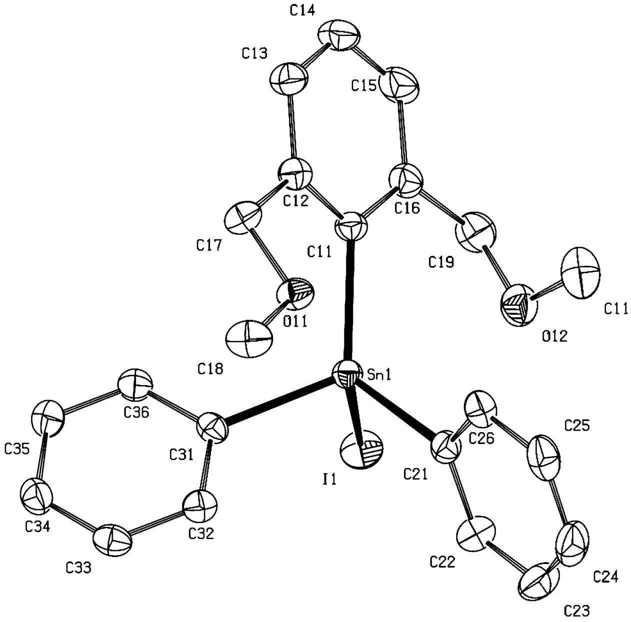
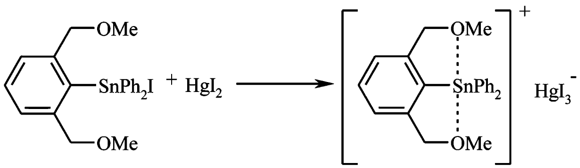


Figure 1. General view (ORTEP) of a molecule of **1** showing 50% probability displacement ellipsoids and the atom-numbering scheme. Only one molecule from the crystal lattice of **1** without hydrogen atoms has been chosen for clarity.

The attempted use of the strong Lewis acid $AlCl_3$ to induce ionization of the Sn–Cl bond in the Ph_2L^1SnCl and Ph_2L^2SnCl compounds was unsuccessful.[11] However, the weaker Lewis acid (HgI_2) did induce ionization of the Sn–I bond of **1** to ionize, giving the organotin cation with the triiodomercurate counterion (eq 3).



1 **9**

(3)

Molecular Structures of 1, 3, 5, and 6. The molecular structures of **1**, **3**, **5**, and **6** are depicted in Figures 1–4 (unit cells of compounds **1** and **6** consist of two independent molecules). The crystallographic data, selected bond lengths, and angles are given in Tables 1 and 2.

The shape of the tin coordination polyhedron is the so-called "bicapped" tetrahedron in **1**, and this compound is an example of [4+2]-coordination, where a C_3-ISn tetrahedron is *cis*-attacked by two oxygen donor atoms. The range of Sn–O bond lengths in **1** (Sn–O = 2.592(2)–2.991(2) Å) is substantially smaller than the sum of the van der Waals radii of oxygen and tin atoms (3.70 Å),[12] but larger than the sum of the covalent radii (2.066 Å),[12] thus representing both weak and medium-strong Sn–O interactions. The values of O(11)–Sn(1)–O(12) bonding angles (117.50(6)° and 109.60(6)°) show

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(10) Kost, D.; Kingston, V.; Gostevskii, B.; Ellern, A.; Stalke D.; Walfort, B.; Kalikhman, I. *Organomettalics* **2002**, *21*, 2293.

(11) Similar results have been observed during the reaction of $AlCl_3$ with organolithium compounds L^1Li and L^2Li.

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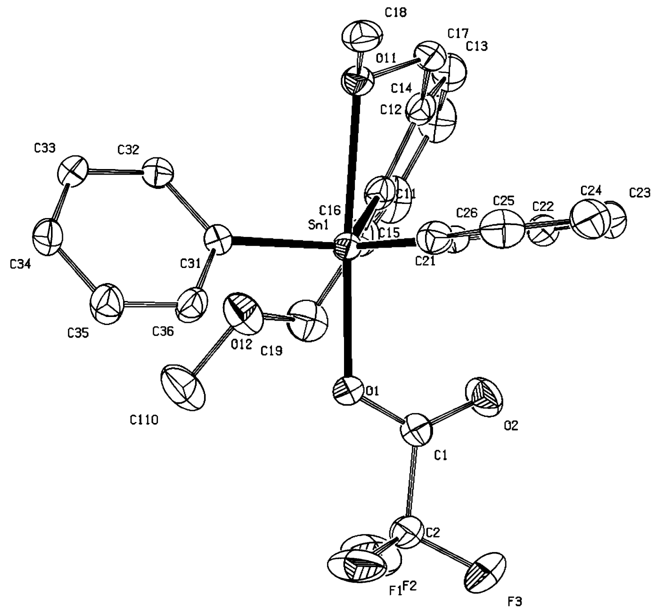

Figure 2. General view (ORTEP) of a molecule of **3** showing 50% probability displacement ellipsoids and the atom-numbering scheme. The hydrogen atoms are omitted for clarity.

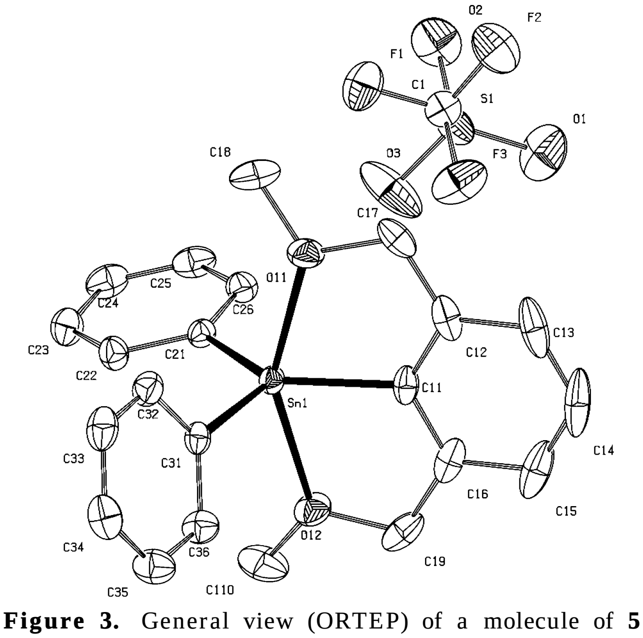

Figure 3. General view (ORTEP) of a molecule of **5** showing 50% probability displacement ellipsoids and the atom-numbering scheme. The hydrogen atoms are omitted for clarity.

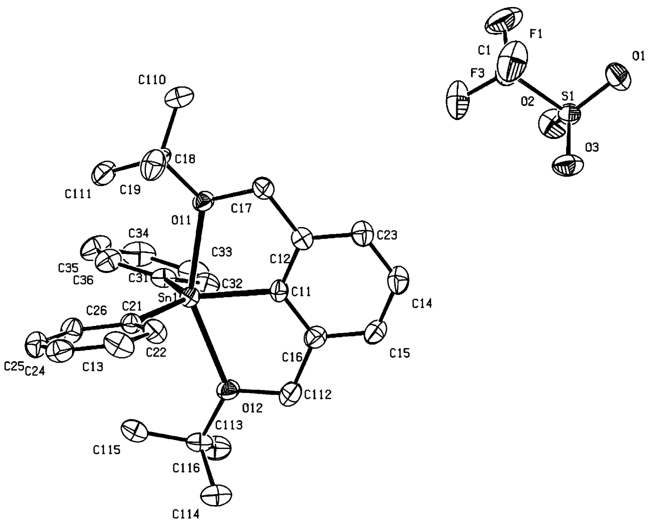

Figure 4. General view (ORTEP) of a molecule of **6** showing 50% probability displacement ellipsoids and the atom-numbering scheme. Only one molecule from the crystal lattice of **6** without hydrogen atoms has been chosen for clarity.

the *cis* coordination of both oxygen donor atoms of the O,C,O-chelating ligand. These oxygen atoms are bound in pseudo-*trans* positions to I(1) and C(31) atoms, resulting in the values of the C(31)−Sn(1)−I(1) bonding angles of 93.81(7)° and 93.47(7)°, thus representing the greatest deviations from the ideal tetrahedral shape.

The value of the Sn(1)−O(11) (2.4990(13) Å) bond length indicates that the presence of the CF_3COO^- group results in an increase of the Sn−O bond strength in **3** in comparison to **1**. The shape of the coordination polyhedron is different: a *trans*-trigonal bipyramid formed by three C atoms in the equatorial plane and two oxygen donor atoms in axial positions (bonding angle O(11)−Sn(1)−O(1) is 174.53(5)°). One oxygen atom O(11) originates from the O,C,O-pincer ligand, while the second one, O(1), is from the CF_3COO^- group. The different values of the Sn(1)−O(1) (2.1546(13) Å) and Sn(1)−O(2) (3.2096(15) Å) bond lengths clearly indicate a monodentate bonding fashion of the CF_3COO^- group to the central tin atom. The value of C(1)−O(2) (1.215(2) Å) typical for the carbonyl part in the monodentate carboxylic groups also proves this coordination mode of the CF_3COO^- group.[13] While the value of the Sn(1)−O(11) bond length indicates a medium strength interaction, the second oxygen donor atom from the O,C,O-pincer ligand is bound weakly (Sn(1)−O(12) = 2.7940(15) Å).[14] The value of the O(11)−Sn(1)−O(12) bonding angle (117.24(4)°) shows that both oxygen donor atoms of the O,C,O-chelating ligand are mutually in *cis* positions.

Compounds **5** and **6** contain an organotin cation, while the trifluoromethanesulfonate anion is out of the primary tin coordination sphere (the nearest Sn(1)−O(3) distance is 5.7446(18) Å for **5** and Sn(2)−O(6) is 6.978(3) Å for **6**). The central tin atom is coordinated by a carbon atom and two oxygen atoms from the ligand L^1 for **5** and L^2 for **6** in a tridentate fashion and by two carbon atoms from phenyl groups. The resulting geometry is pseudo-*trans*-trigonal bipyramidal formed by three carbon atoms in the equatorial plane and two *trans*-oxygen atoms. The C_3Sn girdle is almost planar (ΣC−Sn−C = 359.79(7)° for **5** and 359.97(12)° for **6**; for comparison, the same parameter is 351.71(7)° for **3**). Nearly equivalent Sn−O bond distances (Sn(1)−O(11) 2.2724(14) Å, Sn(1)−O(12) 2.3013(15) Å in **5** and in the range 2.3591(19)−2.391(2) Å in **6**) indicate strong Sn−O interactions in the cations and are comparable with those found in diorganotin compounds (the range of

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[13] Allen, F. H.; Kennard, O.; Watson, D. G.; Brammer, L.; Orpen G.; Taylor, R. *J. Chem. Soc., Perkin. Trans. 2* **1987**, *12*, S1

[14] However, if this weak bond of Sn(1)−O(12) is taken in account, then the geometry of **3** is an example of [5+1]-coordination where the C_3O_2Sn trigonal bipyramid is attacked by the second oxygen donor atom from the pincer ligand.

Table 1. Crystal Data and Structure Refinement 1, 3, 5, and 6

	1	**3**	**5**	**6**
empirical formula	$C_{22}H_{23}IO_2Sn$	$C_{24}H_{23}F_3O_4Sn$	$C_{22}H_{23}O_2Sn{\cdot}CF_3O_3S$	$C_{28}H_{35}O_2Sn{\cdot}CF_3O_3S$
color	yellow	colorless	colorless	colorless
cryst syst	orthorhombic	monoclinic	triclinic	orthorhombic
space group	*Pccn* (No. 56)	$P2_1/n$ (No. 14)	$P\bar{1}$ (No. 2)	$Pna2_1$ (No. 33)
a [Å]	25.1170(1)	10.4900(1)	8.6530(1)	20.8400(1)
b [Å]	25.6710(2)	11.5600(1)	10.7140(2)	18.0680(1)
C [Å]	13.0740(2)	18.8060(3)	13.0900(2)	15.9170(2)
α [deg]			94.9900(8)	
β [deg]		90.4990(6)	99.4120(9)	
γ [deg]			101.1630(7)	
Z	16	4	2	8
μ [mm^{-1}]	2.690	1.173	1.242	0.976
D_x [Mg m^{-3}]	1.781	1.605	1.673	1.488
cryst size [mm]	0.3 × 0.17 × 0.13	0.35 × 0.2 × 0.2	0.50 × 0.0.3 × 0.2	0.38 × 0.2 × 0.15
cryst shape	bulk	prism	prism	prism
θ range, deg	1.0−27.5	1.0−27.5	1.0−27.5	1. 0−27.5
T_{min}, T_{max}	0.600, 0.717[a]	0.683, 0.727[b]	0.797, 0.855[b]	0.806, 0.864[a]
no. of reflns measd	141 938	42 162	18 305	76 586
no. of unique reflns; R_{int}	9672, 0.048	5237,0.037	5310, 0.036	13 631; 0.044
no. of obsd reflns [$I > 2\sigma(I)$]	8744	4655	5014	12 487
no. of params	473	292	301	715
S^c all data	1.080	1.077	1.042	0.995
final R^a indices [$I > 2\sigma(I)$]	0.027	0.023	0.022	0.028
wR2[a] indices (all data)	0.069	0.053	0.055	0.067
$w_1/w_2{}^d$	0.0295/17.5166	0.0161/1.7470	0.0244/0.6254	0.0404/1.1718
absolute struct param				−0.033(10)
$\Delta\rho$, max., min. [e Å−3]	1.494, −1.313	0.816,−0.629	0.694,−0.714	0.471, − 0.774

[a] Correction by SORTAV program. [b] Correction by PLATON program. [c] Definitions: $R(F) = \sum||F_o| - ||F_c||/\sum|F_o|$, $wR2 = [\sum(w(F_o^2 - F_c^2)^2)/\sum(w(F_o^2)^2]^{1/2}$, $S = [\sum(w(F_o^2 - F_c^2)^2)/(N_{reflns} - N_{params})]^{1/2}$. [d] Weighting scheme $w = [\sigma^2(F_o^2) + (w_1P) + w_2P]^{-1}$. $P = [\max(F_o^2,0) + 2F_c^2]/3$. $R_{int} = \sum|F_o^2 - F_o^2(\text{mean})\ |/\sum F_o^2$ (summation is carried out only where more than one symmetry equivalent is averaged).

Table 2. Selected Values of Bonding Lengths (Å) and Angles (deg) for Compounds 1, 3, 5, and 6[a]

	1(A)	**1**(B)	**3**	**5**	**6**(A)	**6**(B)
Sn1−C11	2.148(3)	2.139(3)	2.1302(19)	2,0871(18)	2.088(3)	2.091(2)
Sn1−C21	2.136(3)	2.129(3)	2.1384(18)	2.1030(17)	2.110(2)	2.111(2)
Sn1−C31	2.148(3)	2.151(3)	2.1196(17)	2.1246(17)	2.112(3)	2.115(3)
Sn1−O11	2.641(2)	2.592(2)	2.4990(13)	2.2724(14)	2.3590(18)	2.3704(19)
Sn1−O12	2.991(2)	2.906(2)	2.7940(15)	2.3013(15)	2.3764(19)	2.391(2)
C11−Sn1−C21	121.92(10)	124.24(10)	113.49(7)	127.61(7)	121.10(11)	119.24(11)
C11−Sn1−C31	113.66(10)	114.14(10)	124.18(7)	116.26(7)	115.39(12)	117.52(10)
C21−Sn1−C31	110.62(11)	110.87(11)	114.05(7)	115.93(7)	123.48(12)	123.15(11)
C11−Sn1−O11	69.68(8)	69.72(9)	71.67(6)	75.79(7)	75.30(9)	74.47(8)
C21−Sn1−O11	86.83(8)	89.79(8)	81.05(6)	100.47(6)	96.45(8)	95.36(10)
C31−Sn1−O11	76.29(8)	77.97(8)	88.58(6)	98.97(6)	98.99(9)	102.24(9)
C11−Sn1−O12	66.76(9)	64.21(9)	65.90(5)	74.89(7)	74.98(9)	74.47(8)
C21−Sn1−O12	80.58(9)	76.48(9)	158.30(6)	96.65(6)	98.59(8)	98.30(10)
C31−Sn1−O12	163.46(9)	169.90(9)	79.79(6)	94.66(6)	93.85(9)	93.41(9)
O11−Sn1−O12	117.50(6)	109.60(6)	117.24(4)	150.67(5)	150.28(7)	148.90(6)

[a] Two independent molecules (A, B) have been found in the unit cells of **1** and **6**.

Sn−O is 2.203−2.278 Å)[15] and in organotin cations (Sn−O distances 2.249(2) and 2.241(3) Å)[8] containing different types of O,C,O-chelating ligands (aryldiphosphonic ester $C_6H_2[P(O)(OEt)_2]_2$-1,3-*t*-Bu-5). Since both oxygen atoms are part of one tridentate O,C,O-chelating ligand, the main deformation from the ideal trigonal bipyramidal geometry is seen for the O(11)−Sn(1)−O(12) angle (150.67(5)° for **5** and 150.28(7)° for **6**). Comparable deviations in pseudo-*trans*-trigonal bipyramidal structures have also been found in other triorganotin cations bearing both N,C,N- (C_6H_3-$(CH_2NMe_2)_2{}^-$, range of N−Sn−N bonding angles is 150.7−152.7°)[6,7,16] and O,C,O-chelating ligands (C_6H_2-$[P(O)(OEt)_2]_2$-1,3-*t*-Bu-5, O−Sn−O = 159.01(9)°).[8] Comparison of compounds **5** and **6** shows that the Sn−O donor−acceptor bond is somewhat weaker in **6** than in **5**, as the result of steric hindrance of ligand L^2.

The shapes of coordination polyhedra of **1**, **3**, and **5** form a natural transformation from tetrahedron to trigonal bipyramid going from **1** to **5**. The strength of the Sn−O intramolecular interaction seems to be a particular factor for establishing the shape of the tin coordination geometry in these compounds. The forcing of the Sn−O bond thus leads to a shift toward trigonal bipyramid, and one of the possible indicators of this transformation is the sum of all bonding angles C−Sn−C (328.5° in an ideal tetrahedron and 360° in an ideal trigonal bipyramid). The value of this parameter being 349° in **1** indicates that the shape of the tin coordination polyhedron is shifted to tetrahedron in **1**, while the value 359.8° establishes the trigonal bipyramidal geometry in **5**. The values of the bonding angle O(11)−

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Table 3. Selected ^{1}H, ^{13}C, and ^{119}Sn NMR Data[a] for 1−8

compound	$\delta(^{119}\text{Sn})_{\text{iso}}$ [ppm][b]	$\delta(^{119}\text{Sn})$ [ppm]	$\delta(^1\text{H}(\text{CH}_2))$ [ppm]	$\delta(^{13}\text{C}(1))$ [ppm] ($^nJ(^{119}\text{Sn}, ^{13}\text{C})$[Hz])	$\delta(^{13}\text{C}(1'))$ [ppm] ($^nJ(^{119}\text{Sn}, ^{13}\text{C})$[Hz])
1		−204.7	4.5	133.8 (555.7)	136.3 (535.2)
2		−113.3	4.4	134.7[c]	136.5 (565.9)
3	−199.2	−179.8	4.5	134.6 (786.4)	140.6 (774.5)
4	−172.5	−152.7	4.6	132.6 (738.8)	141.6 (776.2)
5	−25.7	−33.5	5.1	123.6 (776.2)	134.4 (752.9)
6	−17.5	−25.8	4.9	119.7 (760.1)	139.9 (742.6)
7	−26.8	*c*	*c*	*c*	*c*
8	−19.5	*c*	*c*	*c*	*c*

[a] Measured in CDCl$_3$. [b] ^{119}Sn CP/MAS was measured only for compounds **3**−**8**. [c] Not found.

Table 4. Temperature Dependence of Selected ^{1}H NMR Parameters [ppm] (range 170−300 K for toluene-d_8 and methanol-d_4 and 190−300 K for chloroform-d_1)

		toluene-d_8 (for **3**, **4**) or chloroform-d_1 (for **5**, **6**, **9**)[b]		methanol-d_4	
compound	T[a] [K]	CH_3	CH_2OR	CH_3	CH_2OR
3	300	2.57	4.07	2.96	4.55
	170	2.83/1.99	4.24/3.43	2.93/2.77	4.45/4.40
4	300	0.76	4.49	0.99	4.75
	170	1.01/0.98	4.87/4.03	1.01	4.67
5	300	3.65	5.08	3.35	4.90
	190	3.35	4.95	2.87	4.67
6	300	1.05	4.87	1.16	4.87
	190	1.00	4.75	1.14;1.02/1.00[c,d]	5.11;4.59/4.57[c,d]
9	300	3.56	5.02		
	190	3.60	5.03		

[a] The temperature range 300−190 K has been measured in chloroform-d_1. [b] Explained in text. [c] New signal observed at 230 K. [d] Decoalescence at 190 K.

Sn(1)−O(12) of 117.50(6)° for **1**, 117.24(4)° for **3**, and 150.67(5) for **5** indicate a transformation of both oxygen donor atoms' coordination mode from *cis* to *trans*.

Solution and CP/MAS NMR Studies. It is well known that the ^{119}Sn NMR shifts and $^1J(^{119}\text{Sn}, ^{13}\text{C})$ coupling constants are sensitive indicators for elucidation of the coordination numbers and geometries of organotin compounds, but ^{1}H NMR shifts of methylene protons also gave suitable information about the Sn−O interaction strength (downfield shift going from covalent to ionic species). None of the studied compounds exhibit any concentration dependences of the ^{119}Sn NMR shifts, and the values of $\delta(^{119}\text{Sn})_{\text{iso}}$ are similar to the values of the ^{119}Sn NMR shifts in solution (see Table 3), indicating no intermolecular interactions are present in solution and in the solid state.

The value of $\delta(^{119}\text{Sn}) = -204.7$ ppm in **1** (see Table 3) does not correspond to a stronger Sn−O interaction and a higher coordination number of the tin atom than in analogous triorganotin chloride Ph$_2$L^{1}SnCl ($\delta(^{119}\text{Sn}) = -144.4$ ppm), but it can be the result of the different halide present (compare the values of $\delta(^{119}\text{Sn})$ in Ph$_3$SnCl (−44.7 ppm) and Ph$_3$SnI (−112.8 ppm)).[17] The other NMR parameters ($^1J(^{119}\text{Sn}, ^{13}\text{C}(1))$, $^1J(^{119}\text{Sn}, ^{13}\text{C}(1'))$) and magnitudes of the calculated bond angles C(1)−Sn−C(1′) and C(1′)−Sn−C(1′)[18] (108.2°, 106.9°) established a similar shape of tin atom coordination polyhedra in **1** going from the solid state to solution.

In compounds **3** and **4**, the values of $\delta(^{119}\text{Sn})$ (see Table 3) are shifted upfield compared to the corresponding chlorides Ph$_2$L^{1}SnCl (−144.4 ppm) and Ph$_2$L^{2}SnCl (−121.7 ppm), reflecting, together with an increase of the $^1J(^{119}\text{Sn}, ^{13}\text{C}(1))$ and $^1J(^{119}\text{Sn}, ^{13}\text{C}(1'))$ coupling constant values, the increased strength of the Sn−O interaction in **3** and **4**. The magnitudes of the calculated bond angles C(1)−Sn−C(1′) and C(1′)−Sn−C(1′) (122.6°, 121.8° for **3** and 119.7°, 121.9° for **4**) indicate *trans*-trigonal bipyramidal geometry similar to the molecular structure of **3**. To prove the nonequivalence of both *ortho*-CH$_2$OR substituents and to see if the ionic species is not formed at a lower temperature or in a polar solvent, the dynamic behavior of **3** and **4** was studied by ^{1}H NMR spectroscopy at various temperatures (range 300−170 K) in both toluene-d_8 and methanol-d_4 solution.[10,19]

At room temperature, the ^{1}H NMR spectrum displays one set of sharp signals for all the protons. As the temperature decreased, first a broadening of the CH_2 and CH_3 protons was observed, followed by decoalescence of all the protons at 260 K for **3**, 200 K for **4** in toluene-d_8, and 185 K for **3** in methanol-d_4 (no decoalescence was observed for **4** in methanol-d_4; see Table 4). This indicates the well-known dissociation/association dynamic procedure[20] resulting in nonequivalence of both CH$_2$OR "arms" in **3** and **4**, similar to the molecular structure of **3**. The energy barriers ($\Delta G^{\ddagger}$)[21] of the fluxional processes are 47.8 kJ mol^{-1} (**3**) and 36.1 kJ mol^{-1} (**4**) in toluene and 37.6 kJ mol^{-1} (**3**) in methanol-d_4, respectively. This clearly shows the different strength of the Sn−O bond both in **3** and **4** (steric factor of L^2) and in nonpolar and polar solvents.

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(21) Eyring equation: $\Delta G^{\ddagger} = -RT_c \ln [2\pi h(\Delta v)/kT_c\sqrt{3}]$ with $\Delta G^{\ddagger}$ = free energy of activation (J), T_c = coalescence temperature (K), and Δv = chemical shift difference (Hz); the other symbols have their usual meanings.

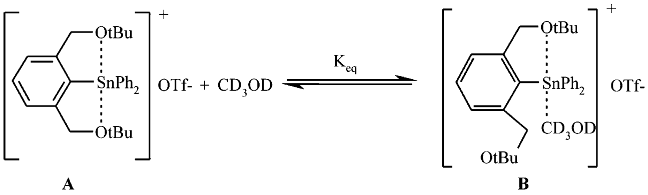

Figure 5. Equilibrium between the noncoordinated (A) and coordinated (B) form of organotin cation **6**.

One narrow signal ($\delta(^{119}Sn) = -33.5$ ppm for **5** and -25.8 ppm for **6**) was observed in the ^{119}Sn NMR spectra of **5** and **6**. These significant downfield shifts of $\delta(^{119}Sn)$ ($\Delta\delta(^{119}Sn) = -110.9$ ppm for **5** and -95.9 ppm for **6**) going from Ph_2L^1SnCl and Ph_2L^2SnCl to **5** and **6** indicate their coordination mode and the presence of organotin cations.[22] Other NMR parameters ($^1J(^{119}Sn,^{13}C)$ and the downfield shift of $\delta(^1H(CH_2))$ of about 0.5 ppm (see Table 3)) established an important increase of Sn−O bond strength in **5** and **6** compared to Ph_2L^1SnCl and Ph_2L^2SnCl. The values of the C(1)−Sn−C(1′) and C(1′)−Sn−C(1′) bonding angles (122°, 121° for **5** and 120°, 121° for **6**) define the *trans*-trigonal bipyramidal geometry of these organotin cation containing O,C,O-chelating ligands, similar to those found in the solid state for **5** and **6**.

The various temperatures of ^{1}H NMR spectroscopy both in chloroform-d_1 (range 300-190 K) and in methanol-d_4 (range 300−170 K, **5** and **6** are insoluble in toluene) solution of **5** and **6** also proved the equivalence of both CH_2OR groups, being strongly coordinated to the tin atom through the Sn−O bond, and no decoalescence of any protons has been observed in chloroform-d_1 (**5** and **6**) and in methanol-d_4 (**5**).

However, in methanol-d_4 solution of **6**, the second set of aliphatic signals (in addition to the previous one observed at 300 K, see Table 4) was observed on decreasing the temperature to 230 K (approximately 5% of main peaks' intensity), and these signal intensities were increased with the decrease of temperature. Other temperature lowering resulted in the broadening of these new CH_2 and CH_3 protons followed by decoalescence of these proton signals at 190 K (see Table 4, nonequivalence of both CH_2OR groups in this new species $\Delta G^‡$ of the dissociation/association dynamic procedure is 40.2 kJ mol^{-1}). The coordination of methanol to the central tin atom seems to be the best explanation for this observation.

The methanol molecules probably start to coordinate the organotin cation resulting in the new species at 230 K, and its concentration is increased during the temperature decrease (see Figure 5, equilibrium of noncoordinated (A) and coordinated (B) form of organotin cation **6**). The equilibrium constants $K = [B]/[A]$ were evaluated directly from ^{1}H NMR spectra of **6** below 230 K, when the signals for both species were observed. The K values for A ↔ B equilibrium have been evaluated at a number of temperatures and used for a ln K vs T^{-1} plot (Figure 6), and from the linear relation the reaction enthalpy and entropy have been extracted: $\Delta H° = -17.5$ kJ mol^{-1}, $\Delta S° = -89.7$ J mol^{-1} K^{-1}.

Compounds **7** and **8** are insoluble in common organic solvents and could not be investigated by NMR spectroscopy. IR study of these compounds has shown the presence of characteristic bands ν(P−F) at 878, 341 cm^{-1} for **7** and 878, 342 cm^{-1} for **8**, which are typical for inorganic ionic compounds containing the PF_6^- group.[23] Also ^{119}Sn CP/MAS NMR study has proved the ionic character of **7** and **8**, because the obtained values of $\delta(^{119}Sn)_{iso}$ are comparable with **5** and **6** (see Table 3). Also **9** is poorly soluble in common organic solvents, but ^{1}H NMR spectroscopy in chloroform-d_1 (range 300−190 K) gives information about the ionic character of **9** (the downfield shift of $\delta(^1H(CH_2))$ and no decoalescence of any protons at low temperate was observed similarly to **6**; see Table 4).

Experimental Section

General Methods. Solvents were dried by standard methods and distilled prior to use. All moisture- and air-sensitive reactions were carried out in an argon atmosphere using standard Schlenk techniques. The reactions with silver salts were protected from light. The ^{1}H,^{13}C, and^{119}Sn NMR spectra were acquired on Bruker AMX360 or Avance500 spectrometers at 300 K in $CDCl_3$ or in toluene-d_8 and methanol-d_4 for temperatures in the range 300−170 K. Appropriate chemical shifts were calibrated on the ^{1}H residual peak of $CHCl_3$ ($\delta =$

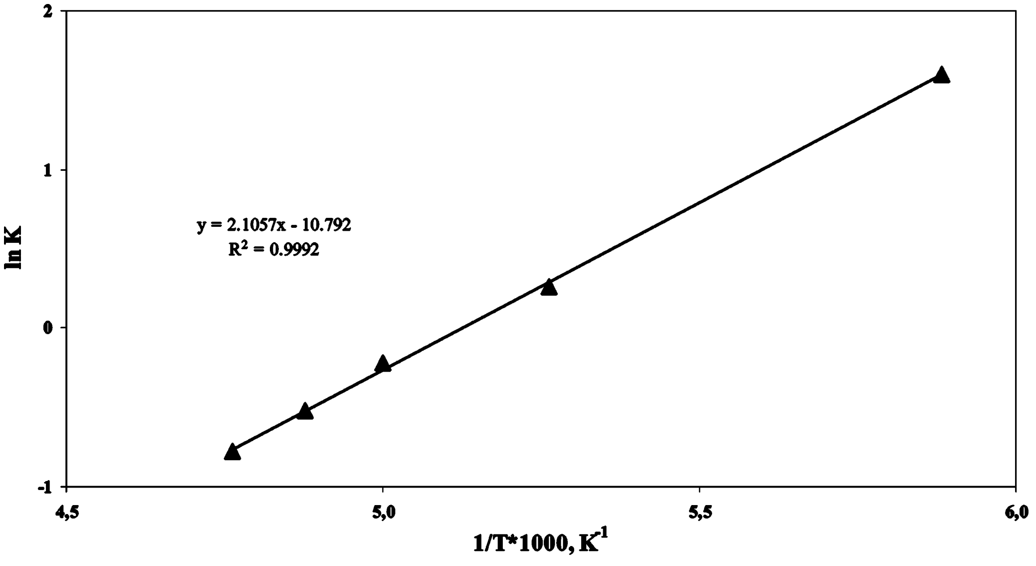

Figure 6. Plot of ln K vs $1/T$ for the equilibrium reaction of **6** with CD_3OD.

7.25 ppm), toluene ($\delta = 2.09$ ppm), and methanol ($\delta = 3.31$ ppm), the ^{13}C residual peak of $CHCl_3$ ($\delta = 77.00$ ppm), and ^{119}Sn external tetramethylstannane ($\delta = 0.00$ ppm). Chemical shift data are provided in ppm, with coupling constants in Hz. Abbreviations used are as follows: s = singlet; q = quartet; m = complex multiplet. Solid-state ^{119}Sn spectra were recorded on a Bruker DSX 200 spectrometer equipped with a double-bearing CP/MAS probe at room temperature. The ^{119}Sn Hartman−Hahn cross-polarization match was set with tetracyclohexyl tin using a ^{1}H 90° pulse of 4 μs. RAMP/CP/MAS (ramped/cross-polarization/magic angle spinning) experiments were used with a repetition delay of 10 s, and the contact time was set at 2 ms. In each case, at least two spinning rates (4.5−10 kHz) were used to identify the isotropic chemical shift. The number of scans varied between 500 and 1024. The ^{119}Sn chemical shifts were calibrated indirectly using tetracyclohexyl tin (δ −97.35 ppm). The ^{119}Sn NMR chemical shift was allocated approximately to the center of gravity of the signal. Electrospray mass spectra (ESI/MS) were recorded in positive mode on an Esquire3000 ion trap analyzer (Bruker Daltonics) in the range 100−600 *m/z* and in the negative mode on the Platform quadrupole analyzer in the range 100−800 *m/z*. The samples were dissolved in acetonitrile and analyzed by direct infusion at a flow rate of 1−10 μL/min. The IR spectra (cm^{-1}) were recorded on Perkin-Elmer 684 equipment as Nujol suspensions or $CHCl_3$ solutions (except **7** and **8**). Starting compounds Ph_3L^1Sn, Ph_3L^2Sn, Ph_2L^1SnCl, and Ph_2L^2SnCl were prepared according to the literature.[9]

Synthesis of [2,6-Bis(methoxymethyl)phenyl]diphenyltin iodide [1]. Iodine (0.1 g, 0.4 mmol) in CH_2Cl_2 (10 mL) was added dropwise to a stirred solution of Ph_3L^1Sn (0.2 g, 0.4 mmol) in CH_2Cl_2 (10 mL). The mixture was stirred for 2 days at 25 °C. The solvent was evaporated in vacuo, and the residue was washed with pentane to give **1** as a yellow solid. Yield: 0.15 g (70%); mp 115−118 °C. Anal. Calcd for $C_{22}H_{23}IO_2Sn$ (MW 565.02): C, 46.77; H, 4.10. Found: C, 46.67; H, 4.11. MS: *m/z* 127, 100%, $[I]^-$; *m/z* 439, 100%, $[M - I]^+$. ^{1}H NMR ($CDCl_3$, 360 MHz): δ (ppm) 2.86 (s, 6H, CH_3), 4.47 (s, 4H, CH_2, $^{n}J(^{119}Sn,^{1}H) = 7.6$ Hz), 7.30−7.80 (complex pattern, 13H, $SnPh_2$, SnC_6H_3). ^{13}C NMR ($CDCl_3$, 90 MHz): 57.4 (CH_3), 73.6 (CH_2, $^{n}J(^{119}Sn,^{13}C) = 23.8$ Hz), SnC_6H_3, 133.8 (C(1), $^{1}J(^{119}Sn,^{13}C) = 555.7$ Hz), 125.5, 127.5, 144.8; $SnPh_2$, 141.5 (C(1′), $^{1}J(^{119}Sn,^{13}C) = 535.2$ Hz), 126.9, 133.9, 127.5.

Synthesis of the Adduct of [2,6-Bis(*tert*-butoxymethyl)phenyl]triphenyltin with Iodine [2]. Iodine (0.09 g, 0.4 mmol) in CH_2Cl_2 (10 mL) was added dropwise to a stirred solution of Ph_3L^2Sn (0.2 g, 0.4 mmol) in CH_2Cl_2 (10 mL). The mixture was stirred for 2 days at 25 °C, and the solvent was evaporated in vacuo. The residue was washed with pentane to provide a yellow solid. Recrystallization of the residue from CH_2Cl_2/pentane led to **2**. Yield: 0.28 g (85%); mp 99−102 °C. Anal. Calcd for $C_{34}H_{40}I_2O_2Sn$ (MW 837.15): C, 47.80; H, 4.73. Found: C, 46.80; H, 4.48. MS: *m/z* 127, 100%, $[I]^-$; *m/z* 380, 12%, $[I_3]^-$; *m/z* 411, 100%, $[M - I - 2 \times \text{isobutene}]^+$; *m/z* 467, 65%, $[M - I - \text{isobutene}]^+$; *m/z* 523, 53%, $[M - I_2 - C_6H_6]^+$; 351, 5%, $[M - I - 2 \times \text{isobutene} - C_6H_6 + H_2O]^+$. ^{1}H NMR ($CDCl_3$, 360 MHz): δ (ppm) 1.31 (s, 18H, CH_3), 4.44 (s, 4H, CH_2), 7.40−7.75 (complex pattern, 18H, $SnPh_2$, SnC_6H_3). ^{13}C NMR ($CDCl_3$, 90 MHz): 27.7 (CH_3), 65.8 (CH_2), 73.7 ($OCMe_3$); SnC_6H_3, 134.7 (C(1)), 127.2, 128.8, 141.8; $SnPh_2$, 136.5 (C(1′), $^{1}J(^{119}Sn,^{13}C) = 565.9$ Hz), 129.0, 136.3, 130.2.

Synthesis of [2,6-Bis(methoxymethyl)phenyl]diphenyltin Trifluoroacetate [3]. CF_3COOAg (0.04 g, 0.2 mmol) was added to a stirred solution of Ph_2L^1SnCl (0.06 g, 0.1 mmol) in CH_2Cl_2 (10 mL). The suspension was stirred for 5 days at 25 °C, the solid residue was filtered off, and the solvent was evaporated in vacuo. The residue was washed with pentane. Recrystallization of the residue from a $CHCl_3$/pentane solution (1:1) led to **3** as a white solid. Yield: 0.052 g (78%); mp 120−123 °C. Anal. Calcd for $C_{24}H_{23}F_3O_4Sn$ (MW 551.13): C, 52.30; H, 4.21. Found: C, 52.15; H, 4.19. MS: *m/z* 385, 33%, $[3 \times CF_3COO + 2 \times Na]^-$; *m/z* 249, 73%, $[2 \times CF_3COO + Na]^-$; *m/z* 113, 100%, $[CF_3COO]^-$; *m/z* 439, 100%, $[M - CF_3COO]^+$. ^{1}H NMR ($CDCl_3$, 360 MHz): δ (ppm) 2.97 (s, 6H, CH_3), 4.52 (s, 4H, CH_2, $^{n}J(^{119}Sn,^{1}H) = 7.9$ Hz), 7.20−7.90 (complex pattern, 13H, $SnPh_2$, SnC_6H_3). ^{13}C NMR ($CDCl_3$, 90 MHz): 57.8 (CH_3), 74.5 (CH_2, $^{n}J(^{119}Sn,^{13}C) = 22.2$ Hz), 114.4 (q-CF_3, $^{n}J(^{19}F,^{13}C) = 289.2$ Hz), 160.3 (COO); SnC_6H_3, 134.6 (C(1), $^{1}J(^{119}Sn,^{13}C) = 786.4$ Hz), 145.8, 126.4, 136.2; $SnPh_2$, 140.6 (C(1′), $^{1}J(^{119}Sn,^{13}C) = 774.5$ Hz), 136.1, 128.6, 129.5. IR (suspension in Nujol): $\nu_{as}(CO)$ 1699 cm^{-1}, $\nu_s(CO)$ 1456 cm^{-1}; (solution in $CHCl_3$) $\nu_{as}(CO)$ 1709 cm^{-1}, $\nu_s(CO)$ 1455 cm^{-1}.

Synthesis of [2,6-Bis(*tert*-butoxymethyl)phenyl]diphenyltin Trifluoroacetate [4]. CF_3COOAg (0.03 g, 0.12 mmol) was added to a stirred solution of Ph_2L^2SnCl (0.06 g, 0.1 mmol) in CH_2Cl_2 (10 mL). The suspension was stirred for 7 days at 25 °C, the solid was filtered off, and the solvent was evaporated in vacuo. The residue was washed with pentane to provide **4** as a brownish solid. Yield: 0.052 g (75%); mp 161−164 °C. Anal. Calcd for $C_{30}H_{35}F_3O_4Sn$ (MW 635.30): C, 56.72; H, 5.55. Found: C, 56.70; H, 5.56. MS: *m/z* 749, 100%, $[M + CF_3COO]^-$; *m/z* 521, 70%, $[4 \times CF_3COO + 3 \times Na]^-$; *m/z* 385, 51%, $[3 \times CF_3COO + 2 \times Na]^-$; *m/z* 249, 33%, $[2 \times CF_3COO + Na]^-$; *m/z* 113, 15%, $[CF_3COO]^-$; *m/z* 523, 100%, $[M - CF_3COO]^+$. ^{1}H NMR ($CDCl_3$, 360 MHz): δ (ppm) 0.91 (s, 18H, CH_3), 4.64 (s, 4H, CH_2, $^{n}J(^{119}Sn,^{1}H) = 7.2$ Hz)), 7.41−7.95 (complex pattern, 13H, $SnPh_2$, SnC_6H_3). ^{13}C NMR ($CDCl_3$, 90 MHz): δ (ppm) 27.1 (CH_3), 65.3 (CH_2, $^{n}J(^{119}Sn,^{13}C) = 23.3$ Hz), 76.5 ($OCMe_3$), 119.0 (q-CF_3, $^{n}J(^{19}F,^{13}C) = 289.2$ Hz) 160.3 (COO); SnC_6H_3, 132.6 (C(1), $^{1}J(^{119}Sn,^{13}C) = 738.8$ Hz), 147.4, 126.3, 130.0; $SnPh_2$, 141.6 (C(1′), $^{1}J(^{119}Sn,^{13}C) = 776.2$ Hz), 136.2, 128.6, 129.8. IR (suspension in Nujol): $\nu_{as}(CO)$ 1705 cm^{-1}, $\nu_s(CO)$ 1456 cm^{-1}; (solution in $CHCl_3$) $\nu_{as}(CO)$ 1709 cm^{-1}, $\nu_s(CO)$ 1455 cm^{-1}.

Synthesis of [2,6-Bis(methoxymethyl)phenyl]diphenyltin Trifluoromethansulfonate [5]. A procedure similar to that for **3** was used. Reaction of Ph_2L^1SnCl (0.1 g, 0.2 mmol) and CF_3SO_3Ag (0.06 g, 0.3 mmol) resulted in **5**. Yield: 0.095 g (70%); mp 164−170 °C. Anal. Calcd for $C_{23}H_{23}F_3O_5SSn$ (MW 587.19): C, 47.05; H, 3.95. Found: C, 46.71; H, 3.90. MS: *m/z* 321, 46%, $[2\ (0.06\ g,\ 0.3\ mmol)\ CF_3SO_3 + Na]^-$; *m/z* 149, 100%, $[CF_3SO_3]^-$; *m/z* 439, 100%, $[M - CF_3COO]^+$. ^{1}H NMR ($CDCl_3$, 360 MHz): δ (ppm) 3.65 (s, 6H, CH_3), 5.08 (s, 4H, CH_2, $^{n}J(^{119}Sn,^{1}H) = 8.5$ Hz), 7.35−7.70 (complex pattern, 13H, $SnPh_2$, SnC_6H_3). ^{13}C NMR ($CDCl_3$, 90 MHz): δ (ppm) 60.4 (CH_3), 74.9 (CH_2, $^{n}J(^{119}Sn,^{13}C) = 21.8$ Hz), 120.48 (q-CF_3, $^{n}J(^{19}F,^{13}C) = 320.4$ Hz), SnC_6H_3, 123.6 (C(1), $^{1}J(^{119}Sn,^{13}C) = 738.8$ Hz), 142.5, 124.2, 134.7; $SnPh_2$, 134.4 (C(1′), $^{1}J(^{119}Sn,^{13}C) = 752.9$ Hz), 136.0, 130.1, 132.1. IR (suspension in Nujol): $\nu_{as}(SO_3)$ 1260 cm^{-1}; (solution in $CHCl_3$) $\nu_{as}(SO_3)$ 1262 cm^{-1}.

Synthesis of [2,6-Bis(*tert*-butoxymethyl)phenyl]diphenyltin Trifluoromethansulfonate [6]. A procedure similar to that for **4** was used. Reaction of Ph_2L^2SnCl (0.1 g, 0.2 mmol) and CF_3SO_3Ag (0.06 g, 0.2 mmol) resulted in **6**. Yield: 0.099 g (70%); mp 146−150 °C. Anal. Calcd for $C_{29}H_{35}F_3O_5SSn$ (MW 671.35): C, 51.08, H 5.25. Found: C, 50.99, H 5.15. MS: *m/z* 321, 46%, $[2 \times CF_3SO_3 + Na]^-$, *m/z* 149, 100%, $[CF_3SO_3]^-$, *m/z* 523, 100%, $[M - CF_3SO_3]^+$. ^{1}H NMR ($CDCl_3$, 360 MHz): δ (ppm) 1.05 (s, 18H, CH_3), 4.87 (s, 4H, CH_2, $^{n}J(^{119}Sn,^{1}H) = 8.7$ Hz), 7.30−7.75 (complex pattern, 13H, $SnPh_2$, SnC_6H_3). ^{13}C NMR ($CDCl_3$, 90 MHz): δ (ppm) 27.8 (CH_3), 65.0 (CH_2, $^{n}J(^{119}Sn,^{13}C) = 19.4$ Hz), 84.5 ($OCMe_3$), 122.5 (CF_3, $^{n}J(^{19}F,^{13}C) = 320.2$ Hz), SnC_6H_3, 119.7 (C(1), $^{1}J(^{119}Sn,^{13}C) = 760.1$ Hz),), 143.7, 124.3, 132.0, $SnPh_2$: 139.9 (C(1′),

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[22] These values of tin chemical shift are typical for pentacoordinated organotin(IV) C_3Sn^+ cations with *trans*-trigonal bipyramidal geometry (carbon atoms form an equatorial plane and two donor atoms are in axial position) found in triorganotin compounds containing N,C,N-chelating ligands.

[23] Sokrates, G. *Infrared Characteristic Group Frequencies*; 1980.

$^1J(^{119}Sn,^{13}C) = 742.6$ Hz), 136.1, 130.2, 132.1. IR (suspension in Nujol): $\nu_{as}(SO_3)$ 1267 cm^{-1}; (solution in CHCl$_3$) $\nu_{as}(SO_3) =$ 1262 cm^{-1}.

Synthesis of [2,6-Bis(methoxymethyl)phenyl]diphenyltin Hexafluorophosphate [7]. Ph$_3$CPF$_6$ (0.03 g, 0.1 mmol) was added to a stirred solution of Ph$_3$L^{1}Sn (0.06 g, 0.1 mmol) in toluene (20 mL). The suspension was stirred for 2 days at 25 °C, and the solid was filtered off and washed with two portions of chloroform (20 mL) to provide **7** as a brownish solid. Yield: 0.18 g (80%); mp 340 °C (dec). Anal. Calcd for $C_{22}H_{23}F_6O_2PSn$ (MW 583.08): C, 45.32; H, 3.98. Found: C, 45.45; H, 4.03. MS: *m*/*z* 145, 100%, [PF$_6$]$^-$, *m*/*z* 439, 100%, [M − PF$_6$]$^+$. IR (suspension in Nujol): $\nu(PF_6)$ 878, 343 cm^{-1}.

Synthesis of [2,6-Bis(*tert*-butoxymethyl)phenyl]diphenyltin Hexafluorophosphate [8]. Ph$_3$CPF$_6$ (0.09 g, 0.2 mmol) was added to a stirred solution of Ph$_3$L^{2}Sn (0.1 g, 0.2 mmol) in toluene (10 mL). The suspension was stirred for 4 days at 55 °C. The solid was filtered off and washed with two portions of chloroform (20 mL) to provide **8** as a brownish solid. Yield: 0.098 g (70%); mp 355°C (dec). Anal. Calcd for $C_{28}H_{35}F_6O_2PSn$ (MW 667.24): C, 50.40; H, 5.29. Found: C, 50.25; H 5.33. MS: *m*/*z* 145, 100%, [PF$_6$]$^-$, *m*/*z* 523, 100%, [M − PF$_6$]$^+$. IR (suspension in Nujol): $\nu(PF_6)$ 878, 342 cm^{-1}.

Synthesis of [2,6-Bis(methoxymethyl)phenyl]diphenyltin Triiodomercurate [9]. HgI$_2$ (0.08 g, 0.2 mmol) was added to a stirred solution of **1** (0.1 g, 0.2 mmol) in CH$_2$Cl$_2$ (10 mL). The suspension was stirred for 30 min at 25 °C, and the solvent was evaporated in vacuo to provide **9** as an orange solid. Yield: 0.105 g (75%); mp 142°C (dec). Anal. Calcd for $C_{22}H_{23}HgIO_2Sn$ (MW 1019.42): C, 25.92, H, 2.27. Found: C, 25.75, H, 2.19. MS: *m*/*z* 127, 17%, [I]$^-$, *m*/*z* 582, 100%, [HgI$_3$]$^-$, *m*/*z* 439, 100%, [M − HgI$_3$]$^+$. ^{1}H NMR (CDCl$_3$, 360 MHz): δ (ppm) 3.56 (s, 6H, CH$_3$), 5.02 (s, 4H, CH$_2$), 7.30−7.70 (complex pattern, 13H, SnPh$_2$, SnC$_6$H$_3$).

Crystallography Studies. Colorless crystals were obtained from layering of *n*-hexane onto a dichloromethane solution of the compound. Crystals of compounds of **1**, **3**, **5**, and **6** were mounted on a glass fiber with epoxy cement and measured on a KappaCCD four-circle diffractometer with a CCD area detector by monochromatized Mo Kα radiation ($\lambda = 0.71073$ Å) at 150(2) K. The crystallographic details are summarized in Table 1, and empirical absorption corrections[24] were applied (multiscan from symmetry-related measurements). The structures were solved by the direct method (SIR97[25]) and refined by a full-matrix least-squares procedure based on F^2 (SHELXL97[26]). Hydrogen atoms were fixed into idealized positions (riding model) and assigned temperature factors $H_{iso}(H) = 1.2U_{eq}$(pivot atom); for the methyl moiety a multiple of 1.5 was chosen. The final difference maps displayed no peaks of chemical significance. Crystallographic data for structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 237988, 237989, 237990, and 237991 for **1**, **3**, **5**, and **6**, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EY, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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Supporting Information Available: Tables of all crystal data and structure refinement, atomic coordinates, anisotropic displacement parameters, and geometric data for compounds **1**, **3**, **5**, and **6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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