The O,C,O-Coordinating Pincer-Type Ligand $\{2,6\text{-}[P(O)(OEt)_2]_2\text{-}4\text{-}t\text{-}Bu\text{-}C_6H_2\}^-$ in Organotin Chemistry. Halide Exchange, Cyclization, and Novel Coordination Mode†

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Reactions in solution of the hypercoordinated organotin chlorides $\{2,6\text{-}[P(O)(OEt)_2]_2\text{-}4\text{-}t\text{-}Bu\text{-}C_6H_2\}SnCl_2X$ (X = Ph, Cl) with fluoride ions have been studied using temperature-dependent ^{119}Sn and ^{31}P NMR spectroscopy and electrospray mass spectrometry. The syntheses and molecular structures of the novel intramolecularly coordinated diorganotin difluoride $\{2,6\text{-}[P(O)(OEt)_2]_2\text{-}4\text{-}t\text{-}Bu\text{-}C_6H_2\}SnF_2Ph\cdot 0.5H_2O$ (**1**), the heterocyclic compound $\{[1(Sn),3(P)\text{-}PhClSnOP(O)(OEt)\text{-}5\text{-}t\text{-}Bu\text{-}7\text{-}P(O)(OEt)_2]C_6H_2\}_2$ (**3**), and the monoorganotin difluoride hydroxide $\{\{2,6\text{-}[P(O)(OEt)_2]_2\text{-}4\text{-}t\text{-}Bu\text{-}C_6H_2\}SnF_2OH\}_2$ (**6**) are reported. In the crystal lattice, compound **1** forms an adduct composed of two tin moieties and a water molecule which are linked via F···H−O−H···F hydrogen bridges. The intramolecularly coordinated benzoxaphosphastannole derivative **3** is formed by intramolecular cyclization of $\{2,6\text{-}[P(O)(OEt)_2]_2\text{-}4\text{-}t\text{-}Bu\text{-}C_6H_2\}SnCl_2Ph$ with elimination of ethyl chloride and dimerization. The organotin difluoride hydroxide derivative **6** is a dimer in the solid state as a result of intermolecular hydroxide bridges. Also present are intramolecular Sn−O−H···O═P hydrogen bonds. The configuration at tin is best described as a monocapped octahedron.

Introduction

Organofluorostannanes usually form strong intermolecular tin−fluorine bonds which often give poorly soluble polymeric compounds.[1−5] Higher solubility of this type of compounds is achieved by the introduction of bulky organic substituents and/or intramolecular or intermolecular coordination with additional Lewis bases, making it possible to study the structure of organotin fluorides in solution.[6−17] Nevertheless, X-ray crystal structure analyses of organofluorostannanes containing more than one covalent Sn−F bond are still scarce.[18] To date only one monoorganotin trifluoride[19] and two diorganotin difluorides[2,7] have been structurally characterized.

For some time we have been interested in the synthesis and structural characterization, including dynamic stereochemistry, of intramolecularly coordinated organotin fluorides such as $N(CH_2CH_2CH_2)_3SnF$[6] and $[Me_2N(CH_2)_3]_2SnF_2$.[7] Recently, we have reported the synthesis of a series of organotin and organosilicon compounds containing the O,C,O-coordinating pincer-type ligand $\{2,6\text{-}[P(O)(OEt)_2]_2\text{-}4\text{-}t\text{-}Bu\text{-}C_6H_2\}^-$,[20−23] and in continuation of these studies we now report our attempts to prepare novel intramolecularly coordinated organofluorostannanes containing this ligand. The single-crystal structure analyses of the novel organotin difluorides $\{2,6\text{-}[P(O)(OEt)_2]_2\text{-}4\text{-}t\text{-}Bu\text{-}C_6H_2\}SnF_2Ph$ (**1**) and $\{\{2,6\text{-}[P(O)(OEt)_2]_2\text{-}4\text{-}t\text{-}Bu\text{-}C_6H_2\}SnF_2OH\}_2$ (**6**) and of the intramolecularly coordinated benzoxaphosphastan-

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† This work includes parts of the Ph.D. thesis of M.M., Dortmund University, 1998, and of the Diploma thesis of I.V., Dortmund University, 1997.

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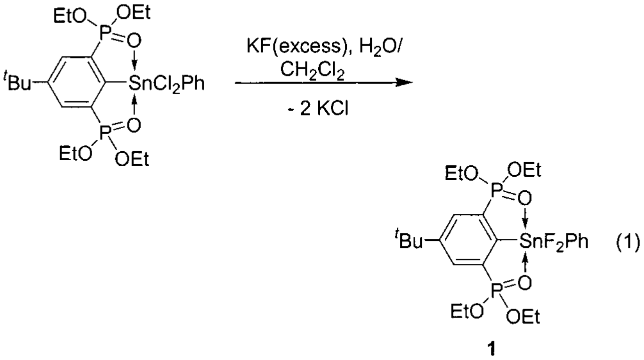
Table 1. Crystal Data and Structure Refinement for 1, 3 and 6

	1	3	6
formula	$C_{24}H_{36}F_2O_6P_2Sn{\cdot}0.5H_2O$	$C_{44}H_{62}Cl_2O_{12}P_4Sn_2$	$C_{36}H_{64}F_4O_{14}P_4Sn_2{\cdot}2CH_2Cl_2$
fw	648.17	1215.10	1327.98
cryst syst	triclinic	triclinic	triclinic
cryst size, mm	0.15 × 0.10 × 0.10	0.20 × 0.15 × 0.10	0.29 × 0.13 × 0.10
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a, Å	9.298(1)	9.751(1)	9.884(1)
b, Å	11.247(1)	11.361(1)	11.346(1)
c, Å	14.978(1)	24.075(1)	14.043(1)
α, deg	73.516(1)	101.414(1)	73.849(1)
β, deg	81.568(1)	97.153(1)	79.668(1)
γ, deg	87.871(1)	95.182(1)	74.396(1)
V, Å^3	1485.7(2)	2575.7(2)	1447.6(2)
Z	2	2	1
ρ_{calcd}, Mg/m^3	1.449	1.567	1.528
μ, mm^{-1}	1.015	1.254	1.226
$F(000)$	662	1232	672
θ range, deg	2.92−25.66	2.94−27.45	3.04−25.67
index ranges	$-9 \le h \le 9$ $-13 \le k \le 13$ $-17 \le l \le 18$	$-12 \le h \le 12$ $-14 \le k \le 14$ $-31 \le l \le 0$	$-10 \le h \le 10$ $-12 \le k \le 13$ $-16 \le l \le 17$
no. of rflns collcd	20 538	27 963	16 257
completeness to θ_{max}	92.8	97.2	90.9
no. of indep rflns/R_{int}	5232/0.027	11 442/0.048	4977/0.041
no. of reflns obsd with ($I > 2\sigma(I)$)	3668	5245	3090
no. of refined params	389	586	362
GOF (F^2)	0.953	0.826	0.947
R1(F) ($I > 2\sigma(I)$)	0.0335	0.0415	0.0485
wR2(F^2) (all data)	0.0872	0.0737	0.1239
$(\Delta/\sigma)_{max}$	0.001	0.001	0.001
largest diff peak/hole, e/Å^3	0.488 / −0.349	0.649 / −0.672	0.384 / −0.512

nole derivative {[1(*Sn*),3(*P*)-PhClSnOP(O)(OEt)-5-*t*-Bu-7-P(O)(OEt)$_2$]C$_6$H$_2$}$_2$ (**3**) are discussed.

Results and Discussion

Compound **1** was synthesized by treatment of a CH_2Cl_2 solution of the corresponding dichloride with aqueous potassium fluoride (eq 1) and isolated in 80% yield as colorless crystals.



1

The molecular structure of the diorganotin difluoride **1** is shown in Figure 1, relevant crystallographic parameters are listed in Table 1, and selected bond lengths and angles are given in Table 2. Compound **1** crystallizes with 0.5 mol of water, i.e., two molecules of **1** are connected via unsymmetrical hydrogen bonds of the type F···H−O−H···F (F(1)−O(3) = 2.589(15) Å, F(1a)−O(3) = 2.668(14) Å). The tin atom in **1** adopts a distorted-octahedral configuration with the carbon, fluorine, and oxygen atoms, respectively, mutually trans. The distortion from the ideal octahedral geometry is reflected especially in the O(1)−Sn(1)−O(2) angle of 159.8(1)° and is the result of the ligand constraint. The intramolecular Sn(1)−O(1) and Sn(1)−O(2) distances of 2.244(2) and 2.243(2) Å are comparable to those of the corresponding dichloro-substituted derivative. The Sn(1)−F(1) and Sn(1)−F(2) bond lengths of 2.017(2) and 2.012(2) Å are shorter as compared to those of six-coordinate $[Me_2N(CH_2)_3]_2SnF_2{\cdot}2H_2O$ (Sn−F = 2.084(6) Å),[7] Me_2SnF_2 (Sn−F = 2.12(1) Å),[2] and $(NH_4)_2(Me_2SnF_4)$ (Sn−F = 2.121(5), 2.126(3), 2.135(4) Å).[24]

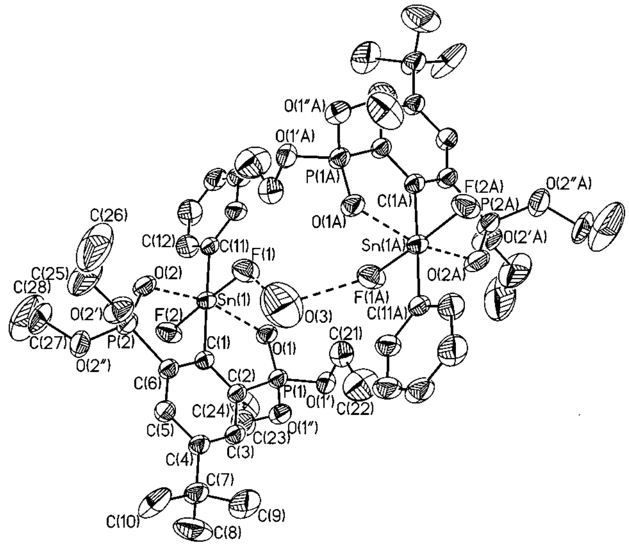


Figure 1. General view (SHELXTL-PLUS) of **1** showing 30% probability displacement ellipsoids and the atom-numbering scheme (symmetry transformations used to generate equivalent atoms: (A) $1 - x$, $-y$, $1 - z$).

The octahedral coordination geometry at tin in the diorganotin difluoride **1** is retained in its toluene solution, as is evidenced by observation of a triplet of triplets ^{119}Sn NMR resonance. The Sn−F bonds in **1** are kinetically inert on the ^{119}Sn NMR time scale to about 70 °C. Above this temperature loss of $^1J(^{119}Sn-^{19}F)$ coupling is observed. The electrospray mass spectrum (ESMS)

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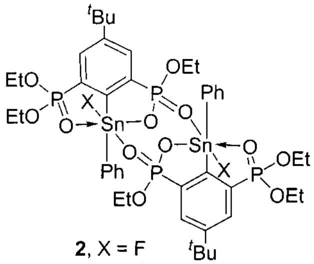
[24] Tudela, D. *J. Organomet. Chem.* **1994**, *471*, 63.

Table 2. Selected Interatomic Distances (Å) and Angles (deg) for 1 and 6[a]

	1: X = C(11)	**6**: X = O(3), Y = O(3a)
Sn(1)−C(1)	2.135(3)	2.192(5)
Sn(1)−F(1)	2.017(2)	1.951(3)
Sn(1)−F(2)	2.012(2)	1.947(4)
Sn(1)−X	2.116(3)	2.157(4)
Sn(1)−Y		2.069(4)
Sn(1)−O(1)	2.244(2)	2.186(3)
Sn(1)−O(2)	2.243(2)	3.364(3)
P(1)−O(1)	1.489(2)	1.480(4)
P(2)−O(2)	1.489(3)	1.450(4)
F(1)−O(3)	2.589(15)	
F(1a)−O(3)	2.668(14)	
O(2)−Y		2.592(5)
C(1)−Sn(1)−F(1)	89.1(1)	96.7(2)
C(1)−Sn(1)−F(2)	86.9(1)	165.8(2)
C(1)−Sn(1)−X	177.2(1)	90.3(2)
C(1)−Sn(1)−Y		105.6(2)
X−Sn(1)−Y		78.2(2)
F(1)−Sn(1)−F(2)	176.0(1)	88.5(2)
F(1)−Sn(1)−X	92.4(1)	172.9(1)
F(2)−Sn(1)−X	91.6(1)	85.1(2)
F(1)−Sn(1)−Y		98.5(1)
F(2)−Sn(1)−Y		86.6(2)
C(1)−Sn(1)−O(1)	80.0(1)	84.2(2)
C(1)−Sn(1)−O(2)	80.0(1)	
X−Sn(1)−O(1)	79.7(1)	86.5(1)
Y−Sn(1)−O(1)		161.6(1)
X−Sn(1)−O(2)	102.4(1)	
F(1)−Sn(1)−O(1)	88.0(1)	95.6(1)
F(1)−Sn(1)−O(2)	89.8(1)	
F(2)−Sn(1)−O(1)	91.5(1)	82.0(1)
F(2)−Sn(1)−O(2)	89.4(1)	
O(1)−Sn(1)−O(2)	159.8(1)	
C(2)−P(1)−O(1)	107.5(1)	108.8(2)
C(6)−P(2)−O(2)	108.8(2)	114.7(2)
P(1)−O(1)−Sn(1)	117.7(1)	115.9(2)
P(2)−O(2)−Sn(1)	116.4(1)	
F(1)−O(3)−F(1a)	111.1(5)	
Sn(1)−O(3)−Sn(1a)		101.8(2)

[a] Symmetry transformations used to generate equivalent atoms: (a) $1 - x, -y, 1 - z$.

Chart 1



2, X = F
3, X = Cl

of **1** in acetonitrile/CH_2Cl_2 reveals formation of $\{\{2,6\text{-}[P(O)(OEt)_2]_2\text{-}4\text{-}t\text{-}Bu\text{-}C_6H_2\}SnFPh\}^+$ (*m*/*z* 621.4).

Heating of a solution of **1** in toluene at 110 °C for 2 weeks gave a reaction mixture, the ^{31}P NMR spectrum of which showed resonances at δ 27.7 ($\nu_{1/2} = 30$ Hz, integral 48), δ 20.1 (t, $\nu_{1/2} = 22$ Hz, $J(^{31}P-^{117/119}Sn) = 60$ Hz, signal **a**), and several overlapping resonances centered at δ 15.5 (signals **b**) and at δ 13.6 ($\nu_{1/2} = 25$ Hz, $J(^{31}P-^{117/119}Sn) = 60$ Hz, signal **c**) with the total integral of the signals **a**−**c** adding up to 52. The ^{119}Sn NMR spectrum of the same solution showed a doublet of doublet of doublet of doublets resonance at δ −521 ($^1J(^{119}Sn-^{19}F) = 2920$ Hz, $J(^{119}Sn-^{31}P) = 100, 103, 162$, integral 70) and broad resonances of minor but equal intensity at −503 ($\nu_{1/2} = 330$ Hz), −517 ($\nu_{1/2} = 310$ Hz), −523 ($\nu_{1/2} = 250$ Hz), and −535 ($\nu_{1/2} = 300$ Hz). The major ^{31}P and ^{119}Sn resonances are assigned with caution to the dimeric fluorine-substituted benzoxaphosphole **2** (Chart 1), whereas the low intense signals might belong to structural isomers of **2**. Compound **2** was not isolated, but its monocation was detected as the most prominent species ($[\mathbf{2} - F]^+$ *m*/*z* 1163.5) in the ESMS of an NMR sample of **2** from which the solvent was stripped off in vacuo. Interestingly, the monomeric fluoride adduct of compound **2** was detected as the most prominent species ($[^1/_2\ \mathbf{2} + F]^-$ *m*/*z* 611.1) of a solution of the diorganotin difluoride **1** to which had been added an excess of $Bu_4NF{\cdot}3H_2O$. The interpretation of the aforementioned NMR spectra is further supported by the results obtained from the chlorine-substituted analogue of compound **1** (see below).

In analogy to compound **1**, the ESMS of $\{2,6\text{-}[P(O)(OEt)_2]_2\text{-}4\text{-}t\text{-}Bu\text{-}C_6H_2\}SnCl_2Ph$ in acetonitrile/CH_2Cl_2 reveals formation of the diorganotin halide cation $\{\{2,6\text{-}[P(O)(OEt)_2]_2\text{-}4\text{-}t\text{-}Bu\text{-}C_6H_2\}SnClPh\}^+$ (*m*/*z* 637.3). Heating of the diorganotin dichloride in toluene/xylene at 110 °C for 2 weeks (Scheme 1) provided a crude reaction mixture, the ^{31}P NMR spectrum of which displayed two major resonances at δ 15.0 ($^4J(^{31}P-^{31}P) = 5$ Hz, $J(^{31}P-^{119}Sn) = 176$ Hz, $J(^{31}P-^{119}Sn) = 96$ Hz, integral 43%) and δ 27.7 ($^4J(^{31}P-^{31}P) = 5$ Hz, $J(^{31}P-^{119}Sn) = 100$ Hz, integral 43%), which are assigned to the benzoxaphosphole derivative **3**. In addition, there are 10 minor resonances at δ 11.3 (integral 0.5%), δ 12.3 ($J(^{31}P-^{31}P) = 5$ Hz, integral 0.5%), δ 15.3 (integral 3%), δ 16.2 (integral 3%), δ 16.8 ($J(^{31}P-^{31}P) = 5$ Hz, integral 0.5%), δ 19.0 (integral 1%), δ 25.4 ($^4J(^{31}P-^{31}P) = 5$ Hz, integral 0.5%), δ 27.8 (integral 3%), and δ 28.0 (integral 2%). The benzoxaphosphole derivative **3** was isolated from the reaction mixture in 80% yield as a colorless crystalline solid. The resonance at δ 19.0 is assigned to $1,3\text{-}[P(O)(OEt)_2]_2\text{-}5\text{-}t\text{-}Bu\text{-}C_6H_3$. The remaining signals could not be assigned but might belong to other isomers of **3**.

The ^{119}Sn NMR spectrum of pure **3** shows a doublet of doublets of doublets at δ −474 ($J(^{119}Sn-^{31}P) = 98$ Hz, $J(^{119}Sn-^{31}P) = 100$ Hz, $J(^{119}Sn-^{31}P) = 176$ Hz). The ESMS of a CH_3CN/CH_2Cl_2 solution of **3** displays mass clusters centered at *m*/*z* 1179.3 and 609.1, which are assigned to the dimeric organotin cation $[\mathbf{3} - Cl]^+$ and the monomeric cation $[^1/_2\ \mathbf{3} + H]^+$, respectively.

The monoorganotin trichloride $\{2,6\text{-}[P(O)(OEt)_2]_2\text{-}4\text{-}t\text{-}Bu\text{-}C_6H_2\}SnCl_3$ undergoes an analogous cyclization to give the dichloro-substituted 2,3,1-benzoxaphosphastannole $\{[1(Sn),3(P)\text{-}Cl_2SnOP(O)(OEt)\text{-}5\text{-}t\text{-}Bu\text{-}7\text{-}P(O)(OEt)_2]C_6H_2\}_2$ (**A**).[21] Remarkably and in contrast to the diorganotin dichloride $\{2,6\text{-}[P(O)(OEt)_2]_2\text{-}4\text{-}t\text{-}Bu\text{-}C_6H_2\}SnCl_2Ph$, the reaction time required to give **A** by heating at reflux a toluene solution of the organotin trichloride is only several hours.

The formation of the monomeric diphenyl-substituted 2,3,1-benzoxaphaphastannole derivative $[1(Sn),3(P)\text{-}Ph_2SnOP(O)(OEt)\text{-}5\text{-}t\text{-}Bu\text{-}7\text{-}P(O)(OEt)_2]C_6H_2$ (**B**) by reaction of the intramolecularly coordinated tetraorganotin compound $\{2,6\text{-}[P(O)(OEt)_2]_2\text{-}4\text{-}t\text{-}Bu\text{-}C_6H_2\}SnPh_3$ with HCl proceeds even faster and to the extent that the intermediate triorganotin chloride $\{2,6\text{-}[P(O)(OEt)_2]_2\text{-}4\text{-}t\text{-}Bu\text{-}C_6H_2\}SnPh_2Cl$ could not be isolated under the reaction conditions applied.[21] As suggested in a previous paper[21] and proven in the meantime[25] by isolation, as its PF_6^- salt, of the intramolecularly coordinated cation $[\{2,6\text{-}[P(O)(O\text{-}i\text{-}Pr)_2]_2\text{-}4\text{-}t\text{-}Bu\text{-}C_6H_2\}SnPh_2]^+$, the first step in the cyclization process involves heterolytic cleavage of a tin−halogen bond. This is likely being followed by

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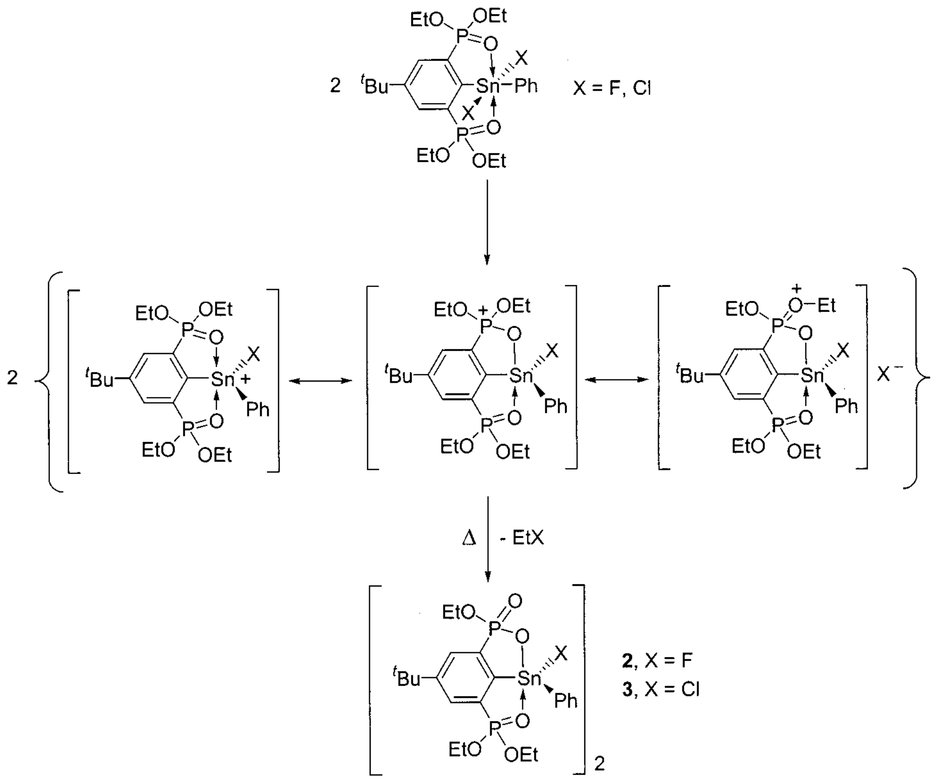
[25] Mehring, M.; Löw, C.; Jurkschat, K. Unpublished results.

Scheme 1



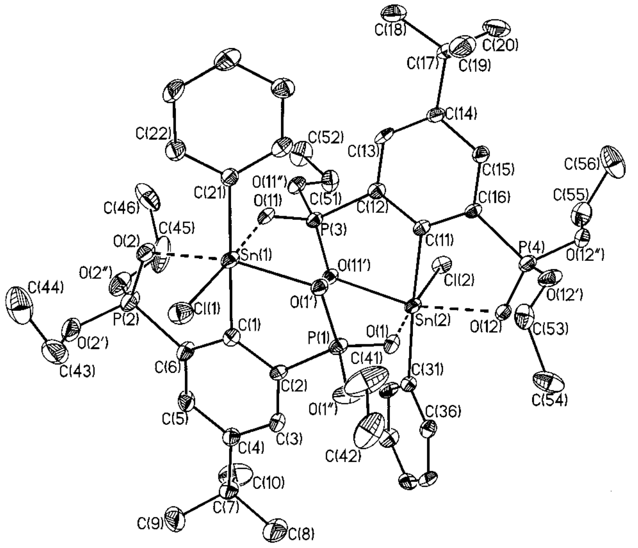


Figure 2. General view (SHELXTL-PLUS) of **3** showing 30% probability displacement ellipsoids and the atom-numbering scheme.

nucleophilic attack of the halide ion at the methylene carbon of the ethoxy group and release of ethyl halide (Scheme 1). The very different rates at which the cyclization reactions take place suggest the tendency of intramolecularly coordinated organotin chlorides to undergo Sn−Cl dissociation to follow the sequence $RSnPh_2Cl > RSnCl_3 > RSnPhCl_2$ (R = {2,6-[P(O)-$(OEt)_2]_2$-4-*t*-Bu-C_6H_2}), provided that the rate of the subsequent attack of the halide ion is not or only little influenced by the substituent pattern at tin.

The molecular structure of **3** is shown in Figure 2, relevant crystallographic parameters are listed in Table 1, and selected bond lengths and angles are given in Table 3. The structure of compound **3** resembles that of previously reported {[1(*Sn*),3(*P*)-$Cl_2SnOP(O)(OEt)$-5-*t*-Bu-7-$P(O)(OEt)_2]C_6H_2\}_2$ (**A**),[21] and both compounds are characterized by intermolecular and intramolecular O−Sn interactions resulting in formation of dimers. The tin centers in **3** adopt distorted-octahedral coordination geometries, with cis angles ranging from 80.03(13) to 102.43(13)° and trans angles ranging from 161.35(9) to 177.11(7)°. The intramolecular O(2)−Sn(1) and O(12)−Sn(2) distances amount to 2.251(3) and 2.274(3) Å, respectively, and lie between the values for the corresponding dative bonds in **A** (2.204(3) Å) and **B** (2.396(4) Å). These interatomic distances reflect the increasing Lewis acidity of the tin fragments in the order $Ph_2Sn < PhClSn < Cl_2Sn$. The intermolecular dative bonds O(1)−Sn(2) (2.219(3) Å) and O(11)−Sn(1) (2.222(3) Å) in **3** are longer than the corresponding interatomic distances in **A** (O−Sn = 2.140(3) Å), the latter being comparable with typical O−Sn single-bond lengths (2.15 Å).[26] The shortest O−Sn distances in **3** are found for O(1′)−Sn(1) and O(11′)−Sn(2), which amount to 2.175(3) and 2.177(2) Å, respectively.

The ^{119}Sn NMR spectrum at −40 °C of a freshly prepared CD_2Cl_2 solution of {2,6-$[P(O)(OEt)_2]_2$-4-*t*-Bu-$C_6H_2\}SnCl_3$ to which had been added 3 mol equiv of $Bu_4NF \cdot 3H_2O$ displays a triplet of triplets at δ −596 ($^1J(^{119}Sn-^{19}F) = 2250$ Hz, $J(^{119}Sn-^{31}P) = 194$ Hz) and a doublet of triplets of triplets at δ −638 ($^1J(^{119}Sn-^{19}F) = 2098$ Hz, $^1J(^{119}Sn-^{19}F) = 2398$ Hz, $J(^{119}Sn-^{31}P) = 200$ Hz) with an integral ratio of approximately 1:2.5. The triplet of triplets resonance is assigned to {2,6-$[P(O)(OEt)_2]_2$-4-*t*-Bu-$C_6H_2\}SnClF_2$ (**4**), and the doublet of triplets of triplets is assigned to the organotin trifluoride {2,6-$[P(O)(OEt)_2]_2$-4-*t*-Bu-$C_6H_2\}SnF_3$ (**5**). On

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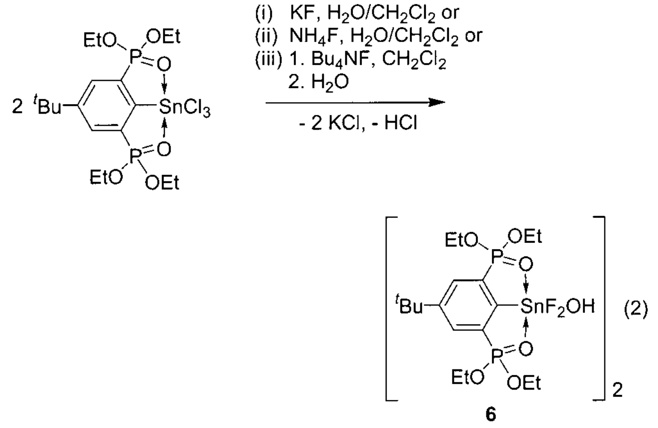
Table 3. Selected Interatomic Distances (Å) and Angles (deg) for 3

Sn(1)−C(1)	2.122(4)	Sn(2)−C(11)	2.117(4)
Sn(1)−Cl(1)	2.4802(12)	Sn(2)−Cl(2)	2.4967(12)
Sn(1)−C(21)	2.097(4)	Sn(2)−C(31)	2.116(4)
Sn(1)−O(11)	2.222(3)	Sn(2)−O(1)	2.219(3)
Sn(1)−O(1′)	2.175(3)	Sn(2)−O(11′)	2.177(2)
Sn(1)−O(2)	2.251(3)	Sn(2)−O(12)	2.274(3)
P(1)−O(1)	1.493(3)	P(3)−O(11)	1.501(3)
P(1)−O(1′)	1.524(3)	P(3)−O(11′)	1.523(3)
P(1)−O(1″)	1.582(3)	P(3)−O(11″)	1.578(3)
P(2)−O(2)	1.505(3)	P(4)−O(12)	1.497(3)
P(2)−O(2′)	1.558(3)	P(4)−O(12′)	1.550(3)
P(2)−O(2″)	1.557(3)	P(4)−O(12″)	1.558(3)
P(1)−C(2)	1.799(4)	P(3)−C(12)	1.793(4)
P(2)−C(6)	1.786(4)	P(4)−C(16)	1.783(4)
C(1)−Sn(1)−Cl(1)	90.74(11)	C(11)−Sn(2)−Cl(2)	89.80(11)
C(1)−Sn(1)−C(21)	176.75(17)	C(11)−Sn(2)−C(31)	174.42(16)
C(1)−Sn(1)−O(1′)	82.14(13)	C(11)−Sn(2)−O(11′)	81.56(13)
C(1)−Sn(1)−O(2)	80.41(13)	C(11)−Sn(2)−O(12)	80.03(13)
C(1)−Sn(1)−O(11)	89.02(13)	C(11)−Sn(2)−O(1)	88.18(13)
Cl(1)−Sn(1)−C(21)	92.39(12)	Cl(2)−Sn(2)−C(31)	93.86(11)
Cl(1)−Sn(1)−O(1′)	95.22(8)	Cl(2)−Sn(2)-O(11′)	92.92(7)
Cl(1)−Sn(1)−O(2)	91.45(8)	Cl(2)−Sn(2)−O(12)	89.99(7)
Cl(1)−Sn(1)−O(11)	177.11(7)	Cl(2)−Sn(2)−O(1)	175.44(7)
C(21)−Sn(1)−O(1′)	98.44(13)	C(31)−Sn(2)−O(11′)	102.43(13)
C(21)−Sn(1)−O(2)	98.62(14)	C(31)−Sn(2)−O(12)	95.74(13)
C(21)−Sn(1)−O(11)	87.81(13)	C(31)−Sn(2)−O(1)	87.87(13)
O(1′)-Sn(1)−O(2)	161.38(9)	O(11′)−Sn(2)−O(12)	161.35(9)
O(1′)-Sn(1)−O(11)	87.60(9)	O(1)−Sn(2)−O(11′)	90.82(9)
O(2)−Sn(1)−O(11)	85.67(10)	O(1)−Sn(2)−O(12)	85.64(9)
O(1)−P(1)−O(1′)	114.93(16)	O(11)−P(3)−O(11′)	116.45(16)
O(1)−P(1)−O(1″)	107.78(17)	O(11)−P(3)−O(11″)	104.13(15)
O(1′)−P(1)−O(1″)	110.21(16)	O(11′)−P(3)−O(11″)	110.24(15)
O(1)−P(1)−C(2)	112.27(17)	O(11)−P(3)−C(12)	111.86(17)
O(1′)−P(1)−C(2)	106.39(17)	O(11′)−P(3)−C(12)	105.12(17)
O(1″)−P(1)−C(2)	104.80(18)	O(11″)−P(3)−C(12)	108.97(18)
O(2)−P(2)−O(2′)	115.31(17)	O(12)−P(4)−O(12′)	114.22(18)
O(2)−P(2)−O(2″)	114.49(19)	O(12)−P(4)-O(12″)	115.25(16)
O(2′)−P(2)−O(2″)	98.6(2)	O(12′)−P(4)−O(12″)	100.17(18)
O(2)−P(2)−C(6)	107.07(18)	O(12)−P(4)−C(16)	107.56(18)
O(2′)−P(2)−C(6)	110.9(2)	O(12′)−P(4)−C(16)	108.88(18)
O(2″)−P(2)−C(6)	110.42(19)	O(12″)−P(4)−C(16)	110.55(18)
P(1)−O(1′)−Sn(1)	117.33(14)	P(3)−O(11′)−Sn(2)	118.82(14)
P(1)−O(1)−Sn(2)	135.03(16)	P(3)−O(11)−Sn(1)	139.47(17)
P(2)−O(2)−Sn(1)	117.05(16)	P(4)−O(12)−Sn(2)	116.33(15)

the basis of the $^1J(^{119}Sn-^{19}F)$ couplings being indicative of terminal Sn−F bonds,[17] both compounds are suggested to be monomeric in solution. Under the reaction conditions employed, attempts at isolating the intramolecularly coordinated monorganotin trifluoride **5** failed, and regardless of the synthetic procedure (eq 2) the monoorganotin hydroxide difluoride $\{\{2,6\text{-}[P(O)(OEt)_2]_2\text{-}4\text{-}t\text{-}Bu\text{-}C_6H_2\}SnF_2OH\}_2$ (**6**) was isolated instead.



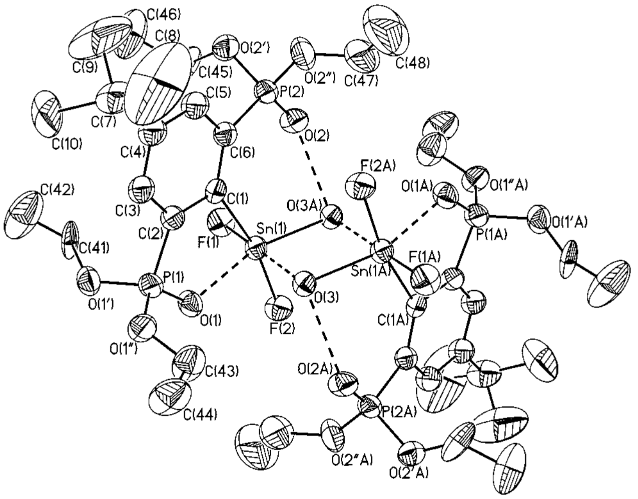


Figure 3. General view (SHELXTL-PLUS) of **6** showing 30% probability displacement ellipsoids and the atom-numbering scheme (symmetry transformations used to generate equivalent atoms: (A) 1 − *x*, −*y*, 1 − *z*).

The molecular structure of **6** (Figure 3) shows a centrosymmetric dimer in which two, at first approximation, octahedrally configurated tin atoms are connected by two asymmetric oxygen bridges of 2.157(4) and 2.069(4) Å. Similar structural motifs were reported for $[EtSn(OH)Cl_2(H_2O)]_2$,[27] $[Me_2Sn(OH)(NO_3)]_2$,[28] and $[t\text{-}Bu_2Sn(OH)X]_2$,[29] with Sn−O distances ranging from 2.012(5) to 2.237(9) Å.[29] The octahedral configuration at tin is distorted, as is manifested by the deviation of the trans angles C(1)−Sn(1)−F(2) (165.8(2)°), F(1)−Sn(1)−O(3) (172.9(1)°), and O(1)−Sn(1)−O(3a) (161.6(1)°) from the ideal value of 180°. The Sn(1)−O(1) distance of 2.186(3) Å is shorter than the corresponding value in the diorganotin difluoride **1** as well as in the organotin trichloride $\{2,6\text{-}[P(O)(OEt)_2]_2\text{-}4\text{-}t\text{-}Bu\text{-}C_6H_2\}SnCl_3$ (2.225(3)/2.221(3) Å)[21] and reflects a strong intramolecular Sn−O coordination. The oxygen O(2) of the P=O group forms a hydrogen bridge with the tin-bonded hydroxide (O(2)···O(3A) 2.592(5) Å) resulting in a seven-membered ring and, simultaneously, exhibits a weak Sn(1)···O(2) interaction of 3.364(3) Å. The latter distance is shorter than the sum of the van der Waals radii of tin and oxygen (3.7 Å).[30] In fact, the proton attached to O(3a) competes with the tin atom Sn(1) for the Lewis basic O(2). The nonequivalence of the P=O groups is also reflected in the different P=O bond lengths of 1.480(4) and 1.450(4) Å as well as in two ν(P=O) absorptions at 1169 and 1236 cm^{-1} in the IR spectrum of **6**. Taking the weak Sn(1)···O(2) interaction into account, the geometry at Sn(1) can also be described as a monocapped octahedron with the O(2) approaching the tin center via the C(1), F(1), O(3a) face. The Sn(1)−F(1) and Sn(1)−F(2) distances of 1.951(3) and 1.947(4) Å, respectively, are rather short and correspond to the Sn−F single bond length of 1.96 Å, as reported for tetracoordinated triorganotin fluorides.[31,32] On the other hand, the Sn(1)−C(1) and Sn(1)−O(3) distances of 2.192-

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(5) and 2.157(4) Å, respectively, are rather long and reflect the strong trans influence of F(2) and F(1).

The ^{119}Sn NMR spectrum of **6** in toluene-d_8 at −60 °C shows a doublet of doublets of doublets of doublets resonance at δ −602 ($J(^{119}\mathrm{Sn}-^{31}\mathrm{P}) = 142$, $J(^{119}\mathrm{Sn}-^{31}\mathrm{P}) = 288$ Hz, $^1J(^{119}\mathrm{Sn}-^{19}\mathrm{F}) = 1513$, $^1J(^{119}\mathrm{Sn}-^{19}\mathrm{F}) = 2832$ Hz), and in the ^{31}P NMR spectrum at −60 °C two resonances of equal intensity at δ 19.7 ($J(^{31}\mathrm{P}-^{119}\mathrm{Sn}) = 142$ Hz, $^4J(^{31}\mathrm{P}-^{31}\mathrm{P}) = 11$ Hz, $J(^{31}\mathrm{P}-^{19}\mathrm{F}) = 4$ Hz) and δ 27.7 ($J(^{31}\mathrm{P}-^{119}\mathrm{Sn}) = 282$ Hz, $^4J(^{31}\mathrm{P}-^{31}\mathrm{P}) = 11$ Hz, $J(^{31}\mathrm{P}-^{19}\mathrm{F}) = 12$ Hz) are observed, which are indicative of a weakly and a strongly coordinating phosphonate group, respectively. These data are consistent with the structure in solution of **6** being rather similar to that observed in the solid state. The ^{31}P NMR spectrum exhibits a further broad resonance of minor intensity (about 15% of the major signals) at δ 23.6 ($\nu_{1/2} > 50$ Hz), for which no assignment was made. At ambient temperature, compound **6** is kinetically labile on the ^{119}Sn NMR time scale; i.e., no signal is observed. The ^{31}P NMR spectrum at room temperature displayed one resonance at δ 22.9 ($J(^{31}\mathrm{P}-^{119}\mathrm{Sn}) = 212$ Hz, $\nu_{1/2} = 38$ Hz), which hints at intra- and/or intermolecular dynamics, the details of which were not investigated further.

In contrast to the diorganotin dichloride derivative {2,6-[P(O)(OEt)$_2$]$_2$-4-*t*-Bu-C$_6$H$_2$}SnCl$_2$Ph, the corresponding monoorganotin trichloride is sensitive toward hydrolysis. The ^{119}Sn NMR spectrum of a CDCl$_3$ solution of {2,6-[P(O)(OEt)$_2$]$_2$-4-*t*-Bu-C$_6$H$_2$}SnCl$_3$ to which had been added a few droplets of water showed, after 1 day, a triplet at δ −526 ($J(^{119}\mathrm{Sn}-^{31}\mathrm{P}) = 281$ Hz) assigned to the starting material and a triplet at δ −499 ($J(^{119}\mathrm{Sn}-^{31}\mathrm{P}) = 280$ Hz) which is likely to belong to the monoorganotin hydroxide dichloride {2,6-[P(O)(OEt)$_2$]$_2$-4-*t*-Bu-C$_6$H$_2$}SnCl$_2$OH. After 3 days, the low-frequency resonance disappeared. The ESMS of {2,6-[P(O)(OEt)$_2$]$_2$-4-*t*-Bu-C$_6$H$_2$}SnCl$_3$ in CH$_2$Cl$_2$/CH$_3$CN to which had been added a few droplets of water showed peaks with isotopic patterns indicative of {{2,6-[P(O)(OEt)$_2$]$_2$-4-*t*-Bu-C$_6$H$_2$}SnCl$_2$}$^+$ (*m/z* 595.1) and {{2,6-[P(O)(OEt)$_2$]$_2$-4-*t*-Bu-C$_6$H$_2$}SnClOH}$^+$ (*m/z* 577.0). However, attempts at isolating the monoorganotin hydroxide dichloride {2,6-[P(O)(OEt)$_2$]$_2$-4-*t*-Bu-C$_6$H$_2$}SnCl$_2$OH failed.

Compound **6** is the first example in which the ligand {2,6-[P(O)(OEt)$_2$]$_2$-4-*t*-Bu-C$_6$H$_2$}$^-$ is only bidentate with respect to a metal center. Additionally, the results suggest that stabilization of organotin dihydroxides—or even trihydroxides—might be possible by employing intramolecular hydrogen bridges to appropriate functionalities such as P═O groups.

Experimental Section

General Remarks. Literature procedures were used to prepare {2,6-[P(O)(OEt)$_2$]$_2$-4-*t*-Bu-C$_6$H$_2$}SnCl$_2$Ph[20] and {2,6-[P(O)(OEt)$_2$]$_2$-4-*t*-Bu-C$_6$H$_2$}SnCl$_3$.[21] IR spectra were obtained from a Bruker FTIR IFS 113v spectrometer. ^{119}Sn, ^{29}Si, ^{13}C, ^{1}H, and ^{31}P NMR spectra were recorded on Bruker DRX 400 and DPX 300 spectrometers. Chemical shifts δ are given in ppm and were referenced against Me$_4$Sn (^{119}Sn), Me$_4$Si (^{1}H, ^{13}C, ^{29}Si), and 85% H$_3$PO$_4$ (^{31}P). ^{119}Sn NMR spectra of the NMR experiments were recorded for sample solutions prepared from appropriate molar ratios of tetrabutylammonium fluoride trihydrate (Bu$_4$NF·3H$_2$O) and {2,6-[P(O)(OEt)$_2$]$_2$-4-*t*-Bu-C$_6$H$_2$}SnX$_2$Ph (X = Cl, F) or {2,6-[P(O)(OEt)$_2$]$_2$-4-*t*-Bu-C$_6$H$_2$}SnCl$_3$. Typically, the concentration of the organotin halides was 0.1−0.2 M. Electrospray mass spectra were recorded in the positive mode on a Thermoquest-Finnigan instrument using CH$_3$CN/CH$_2$Cl$_2$ (10:1) as the mobile phase. The compounds were dissolved in dichloromethane and then diluted with the mobile phase to give a solution of approximate concentration 0.1 mM. The sample was introduced via a syringe pump operating at 15 μL/min. The capillary voltage was 4.5 kV, while the cone-skimmer voltage was varied between 50 and 250 V. Identification of all major ions was assisted by comparison of experimental and calculated isotope distribution patterns. The *m/z* values reported correspond to that of the most intense peaks in the corresponding isotope pattern.

Synthesis of {[2,6-Bis(diethoxyphosphonyl)-4-*tert*-butyl]phenyl}phenyltin Difluoride, {2,6-[P(O)(OEt)$_2$]$_2$-4-*t*-Bu-C$_6$H$_2$}SnF$_2$Ph·0.5H$_2$O (1). At room temperature, a solution of KF (2.300 g, 39.66 mmol) in H$_2$O (20 mL) was added dropwise to a solution of {2,6-[P(O)(OEt)$_2$]$_2$-4-*t*-Bu-C$_6$H$_2$}SnPhCl$_2$ (0.330 g, 0.50 mmol) in CH$_2$Cl$_2$ (20 mL). After the reaction mixture was stirred for 24 h, the organic phase was separated and dried over Na$_2$SO$_4$. The latter was filtered, and the CH$_2$Cl$_2$ of the filtrate was evaporated in vacuo. The residue was recrystallized from toluene/hexane to give 0.256 g (80%) of **1** as a colorless solid: mp >340 °C. ^{1}H NMR (400.13 MHz, CDCl$_3$): δ 1.35 (t, 12 H, CH$_3$), 1.41 (s, 9 H, CH$_3$), 4.15−4.44 (complex pattern, 8 H, CH$_2$), 7.37−8.12 (complex pattern, 7 H, H$_{\mathrm{aryl}}$). ^{31}P{^{1}H} NMR (161.98 MHz, CDCl$_3$): δ 28.7 ($J(^{31}\mathrm{P}-^{119}\mathrm{Sn}) = 97$ Hz). ^{119}Sn{^{1}H} NMR (149.18 MHz, toluene-d_8): δ −522 (*tt*, $J(^{119}\mathrm{Sn}-^{31}\mathrm{P}) = 104$ Hz, $J(^{119}\mathrm{Sn}-^{19}\mathrm{F}) = 3072$). IR (KBr): ν 1176 cm^{-1} (P═O), 3496 cm^{-1} (OH). Anal. Calcd for $\mathrm{C_{24}H_{36}F_2O_6P_2Sn \cdot 0.5H_2O}$ (648.23): C, 44.5; H, 5.8. Found: C, 45.0; H, 6.1.

Synthesis of Bis(5-*tert*-butyl-1-chloro-1-phenyl-7-(diethoxyphosphonyl)-3-ethoxy-3-oxo-2,3,1-benzoxaphosphastannole), {[1(*Sn*),3(*P*)-PhClSnOP(O)(OEt)-5-*t*-Bu-7-P(O)(OEt)$_2$]C$_6$H$_2$}$_2$ (3). A solution of {2,6-[P(O)(OEt)$_2$]$_2$-4-*t*-Bu-C$_6$H$_2$}SnPhCl$_2$ (0.300 g, 0.45 mmol) in a 1:1 mixture of toluene and xylene was heated at 110 °C for 2 weeks. The solvent was removed in vacuo, and the residue was redissolved in CDCl$_3$. The ^{31}P NMR spectrum of this solution was recorded (see Results and Discussion). The CDCl$_3$ was removed in vacuo, and the residue was crystallized from CHCl$_3$/hexane to give 0.219 g (80%) of **3** as colorless crystals, mp >300 °C. ^{1}H NMR (400.13 MHz, CDCl$_3$): δ 1.02 (s, 18 H, CH$_3$), 1.07 (t, 6 H, CH$_3$), 1.21 (t, 6 H, CH$_3$), 1.31 (t, 6 H, CH$_3$), 3.72−3.82 (complex pattern, 2 H, CH$_2$), 3.99−4.38 (complex pattern, 10 H, CH$_2$), 7.30−7.38 (complex pattern, 6 H, H$_{\mathrm{aryl}}$), 7.40 (d, 2 H, $^3J(^1\mathrm{H}-^{31}\mathrm{P}) = 13$ Hz, $^4J(^1\mathrm{H}-^{119}\mathrm{Sn}) = 31$ Hz, H$_{\mathrm{aryl}}$), 7.72 (d, 2 H, $^3J(^1\mathrm{H}-^{31}\mathrm{P}) = 13$ Hz, $^4J(^1\mathrm{H}-^{119}\mathrm{Sn}) = 32$ Hz, H$_{\mathrm{aryl}}$), 7.90 (d, 4 H, $^3J(^1\mathrm{H}-^{119}\mathrm{Sn}) = 123$ Hz, H$_{\mathrm{aryl}}$). ^{31}P{^{1}H} NMR (161.98 MHz, CDCl$_3$): δ 15.0 (d, $^4J(^{31}\mathrm{P}-^{31}\mathrm{P}) = 5$ Hz, $J(^{31}\mathrm{P}-^{119}\mathrm{Sn}) = 176$ Hz, $J(^{31}\mathrm{P}-^{119}\mathrm{Sn}) = 96$ Hz), δ 27.7 (d, $^4J(^{31}\mathrm{P}-^{31}\mathrm{P}) = 5$ Hz, $J(^{31}\mathrm{P}-^{119}\mathrm{Sn}) = 100$ Hz). ^{119}Sn{^{1}H} NMR (149.18 MHz, CDCl$_3$): δ −474 (ddd, $J(^{119}\mathrm{Sn}-^{31}\mathrm{P}) = 98$ Hz, $J(^{119}\mathrm{Sn}-^{31}\mathrm{P}) = 100$ Hz, $J(^{119}\mathrm{Sn}-^{31}\mathrm{P}) = 176$ Hz). IR (KBr): ν 1123, 1166 cm^{-1} (P═O). Anal. Calcd for $\mathrm{C_{22}H_{31}ClO_6P_2Sn}$ (607.58): C, 43.5; H, 5.1. Found: C, 43.3; H, 5.2.

Synthesis of {[2,6-Bis(diethoxyphosphonyl)-4-*tert*-butyl]phenyl}tin Difluoride Hydroxide, {{2,6-[P(O)(OEt)$_2$]$_2$-4-*t*-Bu-C$_6$H$_2$}SnF$_2$OH}$_2$ (6). A solution of KF (2.600 g, 44.75 mmol) in H$_2$O (20 mL) was added dropwise to a solution of {2,6-[P(O)(OEt)$_2$]$_2$-4-*t*-Bu-C$_6$H$_2$}SnCl$_3$ (0.350 g, 0.56 mmol) in CH$_2$Cl$_2$ (20 mL) at room temperature. After the reaction mixture was stirred for 12 h, the organic phase was separated, dried over Na$_2$SO$_4$, and filtered. The CH$_2$Cl$_2$ of the filtrate was evaporated in vacuo. The residue was recrystallized from CH$_2$Cl$_2$/toluene/hexane at 4 °C to give 0.105 g (32%) of **6** as colorless crystals; mp 108−113 °C. ^{1}H NMR (400.13 MHz, CDCl$_3$): δ 1.34 (broad, 42 H, CH$_3$), 3.94−4.37 (broad, 16 H, CH$_2$), 7.95 (d, 4 H, H$_{\mathrm{aryl}}$). ^{1}H NMR (400.13 MHz, CD$_2$Cl$_2$, −60 °C): δ 1.10−1.45 (complex pattern, 42 H, CH$_3$), 3.78−4.48 (complex pattern, 16 H, CH$_2$), 7.91−8.14 (complex pattern, 4 H, H_{aryl}), 9.30 (s, 2 H, Sn−OH). $^{31}P\{^1H\}$ NMR (161.98 MHz, $CDCl_3$): δ 22.9 ($J(^{31}P-^{119}Sn) = 212$ Hz). $^{31}P\{^1H\}$ NMR (161.98 MHz, CD_2Cl_2, −60 °C): δ 19.7 ($J(^{31}P-^{119}Sn) = 142$ Hz, $^4J(^{31}P-^{31}P) = 11$ Hz, $J(^{31}P-^{19}F) = 4$ Hz, 42.5%), 23.6 (broad, $\nu_{1/2} > 50$ Hz, 15%), 27.7 ($J(^{31}P-^{119}Sn) = 282$ Hz, $^4J(^{31}P-^{31}P) = 11$ Hz, $J(^{31}P-^{19}F) = 12$ Hz, 42.5%). $^{119}Sn\{^1H\}$ NMR (149.18 MHz, CD_2Cl_2, −60 °C): δ −602 (dddd, $J(^{119}Sn-^{31}P) = 142$, 288 Hz, $^1J(^{119}Sn-^{19}F) = 1513$, 2832 Hz). IR (KBr): ν 1169, 1236 cm^{-1} (P═O), 3480 cm^{-1} (OH). Anal. Calcd for $C_{36}H_{64}F_4O_{14}P_4Sn_2$ (1158.26): C, 37.3; H, 5.6. Found: C, 36.7; H, 5.6.

Crystallography. Intensity data for the colorless crystals were collected on a Nonius KappaCCD diffractometer with graphite-monochromated Mo Kα (0.71069 Å) radiation at 291 K (**1**, **6**) and 173 K (**3**). The data collection covered almost the whole sphere of reciprocal space with 360 (**1**, **6**) and 351 (with four sets at different κ angles **3**) frames via ω-rotation ($\Delta/\omega = 1°$) at 2 times 10 s (**3**), 15 s (**1**), and 20 s (**6**) per frame. The crystal-to-detector distances were 2.7 cm (**1**, **6**) and 3.4 cm (**3**). Crystal decay was monitored by repeating the initial frames at the end of data collection. When the duplicate reflections were analyzed, there was no indication for any decay. The data were not corrected for absorption effects. The structures were solved by direct methods (SHELXS97[33]) and successive difference Fourier syntheses. Refinement applied full-matrix least-squares methods (SHELXL97[34]).

The H atoms were placed in geometrically calculated positions, except for O(3) in compound **6**. For **1** and **6** they were refined with a common isotropic temperature factor ($C-H_{prim} = 0.96$ Å, $C-H_{sec} = 0.97$ Å; $C-H_{aryl} = 0.93$ Å; $U_{iso} = 0.170(5)$ Å^2 (**1**), $U_{iso} = 0.225(10)$ Å^2 (**6**)) and for **3** with U_{iso} constrained at 1.2 for nonmethyl groups and 1.5 for methyl groups times U_{eq} of the carrier C atom.

Disordered atoms were found in **1** (C(8), C(9), C(22), C(24), C(25) (sof 0.65); C(10), C(10′), C(27), C27′ (sof 0.5); C(8′), C(9′), C(22′), C(24′), C(25′) (sof 0.35)), in **6** (Sn(1), F(1), F(2) (sof 0.85); C(10), C(10′), C(41), C(45), C(46), C(41′), C(45′), C(46′) (sof 0,5); Sn(1′), F(1′), F(2′) (sof 0.15)), and in **3** (C(53), C(53′) (sof 0.5)).

Atomic scattering factors for neutral atoms and real and imaginary dispersion terms were taken from ref 35. The figures were created by SHELXTL.[36] Crystallographic data are given in Table 1 and selected bond distances and angles in Table 2.

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

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