The First Rigid O,C,O-Pincer Ligand and Its Application for the Synthesis of Penta- and Hexacoordinate Organotin(IV) Compounds†

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The synthesis of the aryldiphosphonic ester $C_6H_2[P(O)(OEt)_2]_2$-1,3-*t*-Bu-5 (**2**) and of its organotin derivatives $C_6H_2[P(O)(OEt)_2]_2$-2,6-*t*-Bu-4-RR'_2Sn-1 (**5**, R = R′ = Me; **6**, R = R′ = Ph; **7**, R = Ph, R′ = Cl; **8**, R = Ph, R′ = Br) is reported. Also reported is the preparation of the organosilicon and organotin compounds $C_6H_2[P(O)(OEt)_2]_2$-2,4-Me_3Si-1 (**3**), $C_6H_2[P(O)(OEt)_2]_2$-2,4-$(Me_3Si)_2$-1,5 (**4**), $C_6H_3[P(O)(OEt)_2]_2$-2,4-Ph_2RSn-1 (**9**, R = Ph; **12**, R = Br), and $C_6H_3[P(O)(OEt)_2]_2$-2,4-$(Ph_2RSn)_2$-1,5 (**10**, R = Ph; **11**, R = Br). X-ray investigations reveal weak intramolecular Sn−O interactions for **6** (2.865(3)−3.063(4) Å), **9** (2.803(3) Å), and **10** (2.793(2) Å) but strong Sn−O coordinations for **7** (2.203(5)/2.278(6) Å) and **11** (2.379(3)/2.412(3) Å), indicating the high donor capacity of the new rigid O,C,O- and O,C-chelating ligands in these compounds. NMR studies confirm that the basic coordination geometry found in the solid state is maintained in solution.

Introduction

Organotin compounds with coordination numbers higher than four are still extensively studied because of their biological activity,[1] their enhanced reactivity,[2] and their stereochemical nonrigidity.[2,3] These intriguing properties also prompted studies on the bonding in such compounds.[4] Coordination numbers at tin of five,[2] six,[2] or even seven[5] are usually observed in the presence of at least one electron-withdrawing substituent and are achieved both by intra-[2] and intermolecular[3a,b,4a] donor−acceptor interactions. In the case of so-called built-in ligands, even tetraorganotin compounds may exhibit penta- and hexacoordinate structures.[6]

Monoanionic L,C,L-coordinating ligands $[C_6H_3(CH_2L)_2$-2,6$]^-$ (L = $-NR_2$,[7] $-PR_2$,[8] SR[9]) and their metal derivatives of type **A** (Chart 1) are well-studied, and most of these compounds show fluxional behavior as a result of the nonrigidity of the donor ligands.

Weichmann et al.[10] reported strong intramolecular −P═OSn interactions in compounds of type **B** (Chart

† Dedicated to Prof. Manfred Weidenbruch on the occasion of his 60th birthday.

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Chart 1

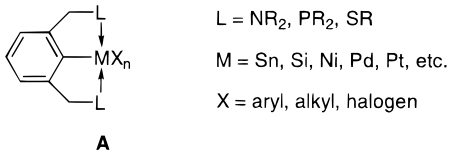
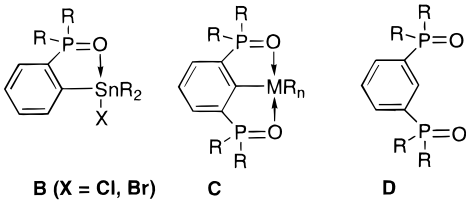


Chart 2

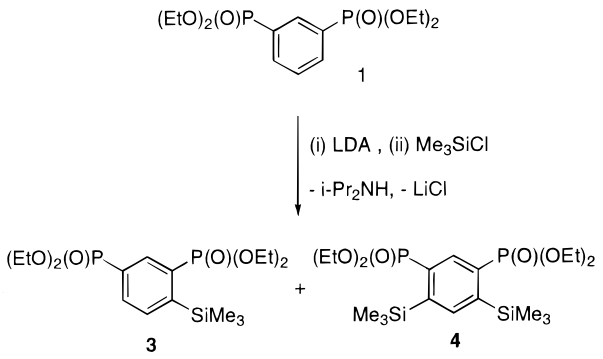


2). However, as far as we are aware, there is no report on the synthesis and reactivity of organometallic compounds of the general type **C** (Chart 2). The combination of the high donor capacity of the P═O groups and the rigidity of the ligand frame in this type of compound should allow the isolation of derivatives in which the metal M shows high coordination numbers and/or unusual oxidation states.

A suitable precursor for the synthesis of **C**-type compounds (Chart 2) should be *meta*-disubstituted benzene derivatives of type **D** (Chart 2), provided that metalation can be achieved at C2 of the aromatic ring. The general concept for directed *ortho* metalations is well-established for groups such as NR_2, CH_2NR_2, OR, SO_2NR_2, or CH_2NR_2.[11] Examples have been reported for the use of $-P(E)(NMe_2)_2$ (E = S,[12] O[13]) and $-P(O)Ph_2$[14] groups in directed *ortho* metalations. In the case of lithiation of Ph_3PO by organolithium reagents, Schlosser[14a] et al. have demonstrated that there is a competition between *ortho* lithiation and nucleophilic substitution at phosphorus. Recently, the use of lithium diisopropylamide, hereafter referred to as LDA, for the metalation of both the tolyl group of *ortho*-tolylphosphonic diethyl ester[15] and the aromatic ring of (2-diethylcarbamoylphenyl)diphenylphosphane oxide[14e] under very mild conditions has been described.

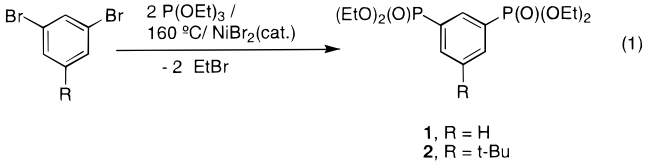
In this paper, we report on the synthesis of the first monoanionic O,C,O-pincer ligand $\{C_6H_2[P(O)(OEt)_2]_2$-2,6-*t*-Bu-4$\}^-$ and its application in the synthesis of penta- and hexacoordinate organotin compounds. We also report on the synthesis and structures of the stannylated aryldiphosphonic esters $C_6H_2[P(O)(OEt)_2]_2$-2,4-$(Ph_2XSn)_2$-1,5 (X = Ph, Br) with two pentacoordinated tin centers in one molecule as well as of $C_6H_2[P(O)(OEt)_2]_2$-2,4-(Ph_2XSn)-1 (X = Ph, Br) with one tin center.

Scheme 1



Results and Discussion

Synthetic Aspects. Compounds **1**[16] and **2** were obtained by reaction of 1,3-dibromobenzene and 1,3-dibromo-5-*t*-Bu-benzene[17] with $P(OEt)_3$ and were isolated in 60−70% yield (eq 1).

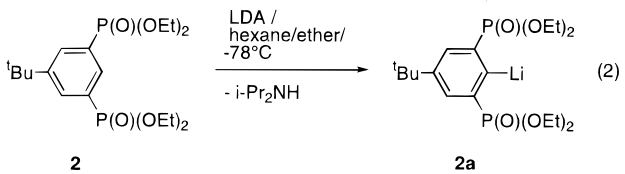


(1)

Treatment of **1** with LDA in Et_2O/hexane at −78 °C resulted in a deep red solution. After quenching the reaction mixture with Me_3SiCl at −78 °C, the crude product contained the mono, and disilylated species **3** and **4** along with starting material **1** (Scheme 1). Purification by column chromatography gave **3** and **4** as yellow oils.

This trapping experiment of lithiated **1** with Me_3SiCl (Scheme 1) demonstrated that lithiation occurs exclusively at C4 and C6 and does not take place at all at C2, which has two neighboring *ortho*-phosphonyl groups that are *ortho*-directing in this type of metalation reaction.

Treatment of a hexane/Et_2O solution of **2** with LDA at −78 °C gave an orange suspension of the monolithiated complex $C_6H_2[P(O)(OEt)_2]_2$-2,4-Li-1 (**2a**) (eq 2).



(2)

Complex **2a** was filtered and isolated as a yellow solid, which was used without further purification as a reagent in subsequent reactions (vide infra). These reactions show that in contrast to **1**, lithiation of **2** occurs exclusively at C2. Steric protection achieved by introduction of a *tert*-butyl group at C5 prevents deprotonation at the C4 and C6 positions.

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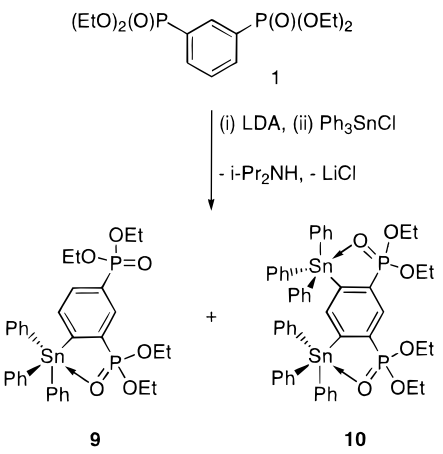
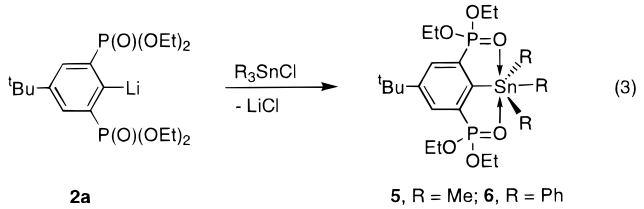
Scheme 2

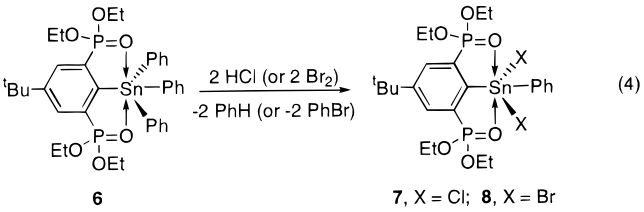


Reaction of **2a** with Me_3SnCl and Ph_3SnCl, respectively, afforded the corresponding tetraorganotin compounds $C_6H_2[P(O)(OEt)_2]_2$-2,6-*t*-Bu-4-R_3Sn-1 (**5**, R = Me; **6**, R = Ph) in moderate yields (eq 3). The triphenyltin



(3)

derivative **6** was converted into the corresponding diorganotin dihalides $C_6H_2[P(O)(OEt)_2]_2$-2,6-*t*-Bu-4-PhX_2-Sn-1 (**7**, X = Cl; **8**, X = Br) by reaction with HCl or bromine, respectively (eq 4). The driving force for the



(4)

selective cleavage of two phenyl groups is the formation of strong P═OSn coordination bonds accompanied by a chelate effect. It is well-known that intramolecular assistance by donor groups such as NR_2 facilitates the cleavage of tin−carbon bonds in mutual trans positions.[2]

No tin−carbon cleavage occurred when **6** was heated at reflux in toluene with PhOH for 1 day. However, treating **6** with pure PhOH at 160 °C afforded **2**, Ph_4Sn, and $Ph_2Sn(OPh)_2$. The formation of the two latter compounds can be explained in terms of a redistribution reaction of Ph_3SnOPh initially generated from **6** and PhOH. The result is somewhat surprising when compared to the behavior of $Ph_3Sn(CH_2)_3NMe_2$ and $Ph_2Sn[(CH_2)_3NMe_2]_2$, which quantitatively yield $Ph_2(PhO)Sn(CH_2)_3NMe_2$[2d] and $(PhO)_2Sn[(CH_2)_3NMe_2]_2$,[2e] respectively, under the same reaction conditions.

Lithiation of **1** with 2 equiv of LDA and subsequent treatment of the reaction mixture with Ph_3SnCl led to the formation of the mono- and distannyl compounds $C_6H_3[P(O)(OEt)_2]_2$-2,4-Ph_3Sn-1 (**9**) and $C_6H_2[P(O)(OEt)_2]_2$-2,4-$(Ph_3Sn)_2$-1,5 (**10**) (Scheme 2). These reacted with

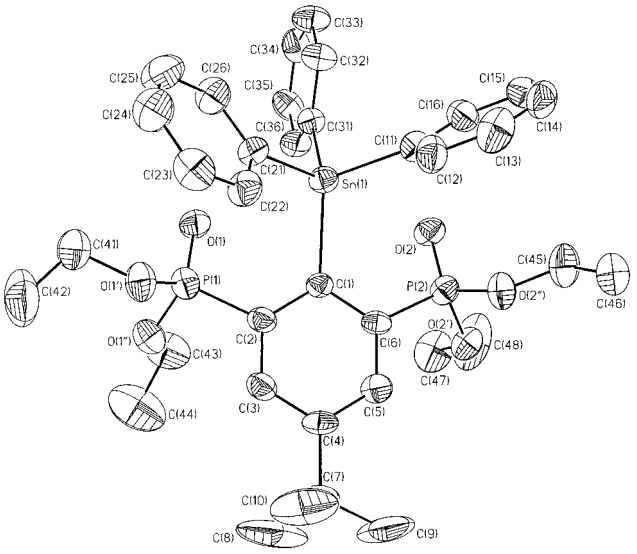
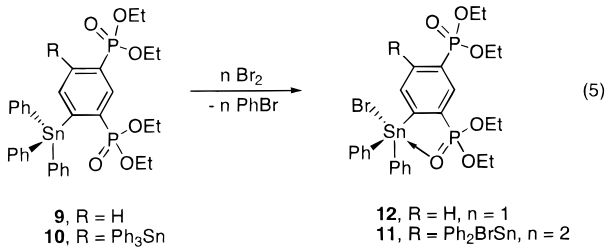


Figure 1. General view (SHELXTL-PLUS) of a molecule showing 30% probability displacement ellipsoids and the atom-numbering Scheme for **6a**. The same numbering scheme applies for **6b**, the drawing of which is not shown.

bromine to afford $C_6H_2[P(O)(OEt)_2]_2$-2,4-$(Ph_2BrSn)_2$-1,5 (**11**) and $C_6H_3[P(O)(OEt)_2]_2$-2,4-Ph_2BrSn-1 (**12**) (eq 5).



(5)

Compounds **5**−**11** are colorless, sharp melting solids, whereas **12** is an oil. Compounds **5**, **6**, **9**, and **10** are soluble in common organic solvents such as toluene, chloroform, and ether; **7** and **8** show moderate solubility only in polar solvents such as chloroform, tetrahydrofuran, and pyridine.

Molecular Structures of 6, 7, and 9−11. The molecular structures of **6**, **7**, and **9**−**11** are shown in Figures 1−5, respectively, and selected interatomic parameters are collected in Tables 2 and 3. The structures are molecular with no significant intermolecular contacts in their respective crystal lattices.

The crystal structure of **6** is comprised of the packing of eight discrete mononuclear molecules in the unit cell. The asymmetric unit contains two independent molecules, **6a** and **6b**, which are chemically identical in composition but differ significantly in structure.

The coordination geometry at tin in **6a** is almost tetrahedral, as indicated by an average C−Sn−C angle of 109.7°. The greatest deviations from the ideal tetrahedral angle are found for C(21)−Sn(1)−C(1) (104.2(2)°), C(21)−Sn(1)−C(11) (100.3(3)°), and C(31)−Sn(1)−C(1) (125.2(3)°). The Sn(1)−C(1) bond distance of 2.168(6) Å is the longest one found among the Sn−C bonds in **6a**, which is caused by a steric repulsion effected by the rigid ligand frame. A similar effect was previously reported for $C_6H_2(CF_3)_3$-2,4,6-Ph_3Sn-1.[18] Furthermore, the Sn(1)−C(11) and Sn(1)−C(21) bond lengths

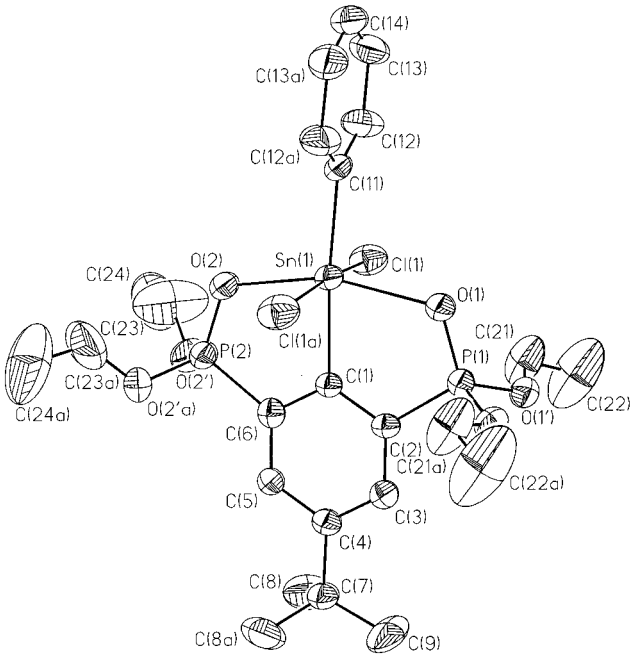


Figure 2. General view (SHELXTL-PLUS) of a molecule showing 30% probability displacement ellipsoids and the atom-numbering scheme (symmetry transformations used to generate equivalent atoms, a = 1 − *x*, *y*, *z*) for **7**.

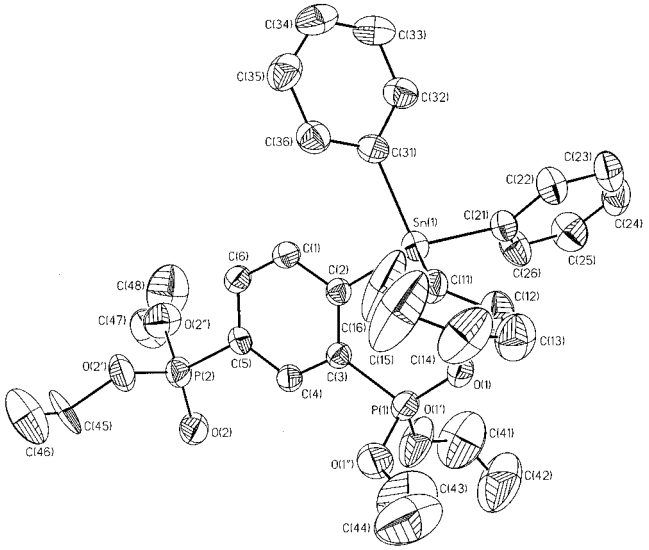


Figure 3. General view (SHELXTL-PLUS) of a molecule showing 30% probability displacement ellipsoids and the atom-numbering scheme for **9**.

of 2.139(7) and 2.128(6) Å, respectively, are longer than the Sn(1)−C(31) bond distance of 2.094(4) Å. This is attributed to two intramolecular oxygen−tin contacts, each of them being in a pseudotrans position to C(11) and C(21). Hence, the overall geometry of **6a** can be regarded as that of a bicapped tetrahedron with a [4 + 2] coordination at tin. Such a structural arrangement was observed previously for 1,4-bis({2,6-bis[(dimethylamino)methyl]phenyl}dihydrosilyl)benzene.[7f] The Sn−O distances of 3.006(4) and 3.022(3) Å are shorter than the sum of the van der Waals radii of tin and oxygen (3.700 Å)[19] but far longer than the corresponding Sn−O distances in **7**.

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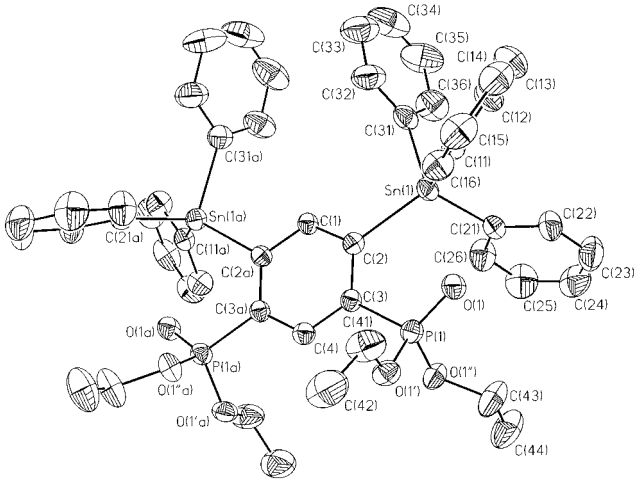

Figure 4. General view (SHELXTL-PLUS) of a molecule showing 30% probability displacement ellipsoids and the atom-numbering scheme (symmetry transformations used to generate equivalent atoms, a = 1 − *x*, *y*, 0.5 − *z*) for **10**.

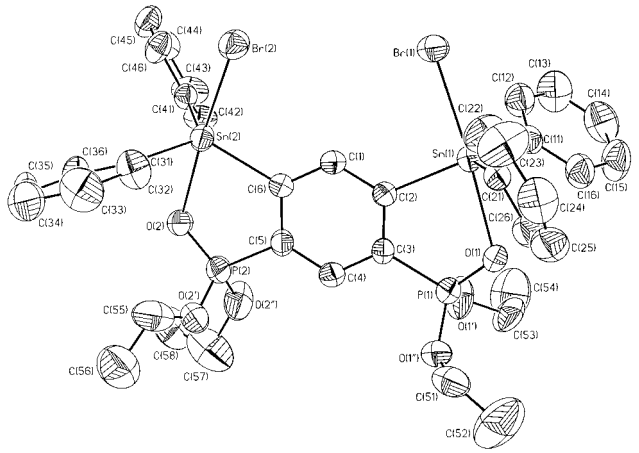

Figure 5. General view (SHELXTL-PLUS) of a molecule showing 30% probability displacement ellipsoids and the atom-numbering scheme for **11**.

The tetrahedral geometry at tin is even more distorted in **6b** as evidenced by two sets of C−Sn−C angles (104.8(3)°, 102.8(3)°, 96.3 (2)° and 113.0(2)°, 114.4(3)°, 122.5(2)°). The Sn(2)−C(31*) and Sn(2)−C(11*) bond distances of 2.160(5) and 2.144(6) Å, respectively, are longer than those in **6a** as a result of their pseudotrans position to the P═O groups. This spatial arrangement is accompanied by a shortening of the Sn(1*)−O(2*) contact to 2.865(3) Å, whereas the Sn(1*)−O(1*) distance (3.063(4) Å) is only slightly elongated.

The existence of two independent molecules in the crystal lattice of **6** is also reflected by the observation of two equally intense ^{119}Sn MAS NMR resonances at −181.7 and −227.7 ppm.

The crystal structure of **7** involves the packing of two discrete mononuclear molecules in the unit cell. Selected bond lengths and angles are given in Table 2. In **7**, the tin atom has a distorted octahedral configuration. The distortion from the ideal geometry is illustrated by the C(1)−Sn(1)−C(11), Cl(1)−Sn(1)−Cl(1a), and O(1)−Sn(1)−O(2) angles of 174.9(3)°, 172.66(12)°, and 161.1-(2)°, respectively. It results from the rigid geometry of

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Table 1. Crystallographic Data for 6, 7, 9, 10, and 11

	6	7	9	10	11
formula	$C_{36}H_{46}O_6P_2Sn$	$C_{24}H_{36}Cl_2O_6P_2Sn$	$C_{32}H_{36}O_6P_2Sn$	$C_{50}H_{52}O_6P_2Sn_2$	$C_{38}H_{42}Br_2O_6P_2Sn_2{\cdot}CH_2Cl_2$
fw	755.36	672.06	697.24	1048.24	1138.78
cryst syst	monoclinic	orthorhombic	triclinic	monoclinic	monoclinic
cryst size, mm	0.20 × 0.13 × 0.13	0.15 × 0.13 × 0.13	0.25 × 0.15 × 0.15	0.30 × 0.15 × 0.15	0.13 × 0.10 × 0.10
space group	$P2_1/c$	$Pmn2_1$	$P\bar{1}$	$C2/c$	$P2_1/n$
a, Å	14.806(1)	14.411(1)	10.736(1)	21.825(1)	14.555(1)
b, Å	13.452(1)	11.237(1)	12.217(1)	12.790(1)	19.876(1)
c, Å	37.351(1)	9.301(1)	13.813(1)	19.101(1)	17.424(1)
α, Å	90	90	70.472(1)	90	90
β, Å	90.759(1)	90	84.815(1)	112.890(1)	114.548(1)
γ, deg	90	90	79.267(1)	90	90
V, Å^3	7438.6(8)	1506.2(2)	1676.9(2)	4912.0(5)	4585.1(5)
Z	8	2	2	4	4
ρ_{calcd}, Mg/m^3	1.349	1.482	1.381	1.417	1.650
ρ_{measd}, Mg/m^3	1.362(29)	*a*	1.394(2)	1.418(1)	*a*
μ, mm^{-1}	0.814	1.166	0.896	1.127	3.059
F(000)	3120	684	712	2120	2240
θ range, deg	4.78−20.92	4.47−26.32	4.53−23.91	4.29−25.66	4.63−21.97
index ranges	$-14 \le h \le 14$ $-12 \le k \le 12$ $-36 \le l \le 36$	$-17 \le h \le 17$ $-13 \le k \le 13$ $-10 \le l \le 10$	$-12 \le h \le 12$ $-13 \le k \le 13$ $-14 \le l \le 14$	$-26 \le h \le 26$ $-15 \le k \le 15$ $-20 \le l \le 19$	$-15 \le h \le 15$ $-20 \le k \le 20$ $-18 \le l \le 18$
no. of reflns collcd	54 830	21 468	19 382	34 158	42 222
completeness to θ_{max}	96.2	94.3	94.7	93.4	100.0
no. of indep reflns/R_{int}	7511/0.074	1597/0.037	4884/0.040	4357/0.039	5558/0.047
no. of reflns obsd with ($I > 2\sigma(I)$)	4309	1202	3188	2952	3577
no. of refined params	849	183	399	276	516
GooF (F^2)	0.860	0.956	0.888	0.923	0.894
R1 (F) ($I > 2\sigma(I)$)	0.0365	0.0280	0.0360	0.0310	0.0305
wR2 (F^2) (all data)	0.0537	0.0510	0.0704	0.0651	0.0601
$(\Delta/\sigma)_{max}$	0.001	<0.001	<0.001	0.001	0.001
largest diff. peak/hole, e/Å^3	0.351/−0.275	0.300/−0.421	0.390/−0.333	0.343/−0.464	0.478/−0.412

[a] Not measured.

Table 2. Selected Interatomic Bond Distances (Å) and Angles (deg) for 6a, 6b, and 7

	6a X = C(21); Y = C(31)	6b* X = C(21*); Y = C(31*)	7 X = Cl(1); Y = Cl(1a)
Bond Distances			
Sn(1)−C(1)	2.168(6)	2.159(5)	2.129(7)
Sn(1)−C(11)	2.139(7)	2.144(6)	2.135(8)
Sn(1)-X	2.128(6)	2.160(5)	2.518(1)
Sn(1)−Y	2.094(6)	2.091(6)	
Sn(1)−O(1)	3.006(4)	3.063(4)	2.278(6)
Sn(1)−O(2)	3.022(3)	2.865(3)	2.203(5)
P(1)−O(1)	1.458(4)	1.461(4)	1.497(5)
P(2)−O(2)	1.462(4)	1.462(4)	1.506(5)
Bond Angles			
C(1)−Sn(1)−C(11)	109.8(2)	102.8(3)	174.9(3)
C(1)−Sn(1)−X	104.7(2)	113.0(2)	86.62(4)
C(1)−Sn(1)−Y	125.2(3)	122.5(2)	
C(11)−Sn(1)−X	100.3(3)	96.3(2)	93.50(4)
C(11)−Sn(1)−Y	105.4(3)	114.4(3)	
X−Sn(1)−Y	109.2(3)	104.8(3)	172.6(1)
C(1)−Sn(1)−O(1)	69.9(2)	69.1(2)	79.3(2)
C(1)−Sn(1)−O(2)	69.7(2)	73.5(2)	81.8(2)
C(11)−Sn(1)−O(1)	173.4(2)	160.4(2)	95.6(2)
C(11)−Sn(1)−O(2)	72.6(2)	73.5(2)	103.3(2)
X−Sn(1)−O(1)	73.6(2)	84.3(2)	90.76(7)
X−Sn(1)−O(2)	167.4(2)	169.2(2)	88.12(8)
Y−Sn(1)−O(1)	79.4(2)	72.0(2)	
Y−Sn(1)−O(2)	83.0(2)	169.2(2)	
O(1)−Sn(1)−O(2)	112.8(1)	118.7(1)	161.1(2)
C(2)−P(1)−O(1)	112.4(3)	105.6(3)	107.1(3)
C(6)−P(2)−O(2)	112.4(3)	113.3(3)	108.5(3)
P(1)−O(1)−Sn(1)	99.6(2)	98.4(2)	117.1(1)
P(2)−O(2)−Sn(1)	99.0(2)	103.3(2)	116.1(3)

the O,C,O-tridentate ligand. A similar distortion was found for {2,6-[bis(dimethylamino)methyl]phenyl}(4-methylphenyl)tin diiodide.[20] The unsymmetrical intramolecular Sn−O coordination of 2.203(5) and 2.278(6) Å is remarkable. These Sn−O distances are comparable to the corresponding values found for $Me_2SnCl_2{\cdot}2HMPA$ (Sn−O 2.231 Å),[21] $Et_2SnCl_2{\cdot}2Ph_3PO$ (Sn−O 2.236, 2.258 Å),[22a] $Et_2SnCl_2{\cdot}[Ph_2(O)P]_2(CH_2)_2$ (Sn−O 2.277/2.285 Å),[22b] and $Bu_2SnCl_2{\cdot}$1,2-$[Ph_2(O)P]_2(CH)_2$ (Sn−O 2.27/2.29 Å).[22c] However, they are unambiguously shorter than those in the complexes $MeBr_2SnCH_2C(Me)[P(O)(Oi\text{-}Pr)_2]_2$ (Sn−O 2.425/2.482 Å),[22d] $Et_2SnCl_2{\cdot}[Me(i\text{-}PrO)(O)P]_2CH_2$ (Sn−O 2.417/2.497 Å),[22e] $Ph_2SnCl_2{\cdot}[(EtO)_2(O)P]_2CH_2$ (Sn−O 2.400/2.427 Å),[22f] $\{Me_2SnCl_2{\cdot}[(EtO)_2(O)P]_2CHNMe_2\}_2$ (Sn−O 2.38/2.64 Å),[22g] and $\{Me(Br)(Cl)SnCH_2CH[P(O)(Oi\text{-}Pr)_2]_2\}_2$ (Sn−O 2.427/2.497 Å).[22h] The lengths of both the Sn−Cl and P−O bonds in **7** of 2.5184(14) Å are of the same order of magnitude than those in the complexes mentioned above.

In **9**, **10**, and **11** the P═O groups are directed toward the tin atoms, resulting in real structures along the tetrahedron−trigonal bipyramid path. The position along this path is given by the difference of the sums of

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Table 3. Selected Interatomic Bond Distances (Å) and Angles (deg) for 9, 10, and 11

	9 X = C(31)	**10** X = C(31)	**11** X = Br(1)
	Bond Distances		
Sn(1)−C(2)	2.171(4)	2.167(3)	2.178(5)
Sn(2)−C(6)			2.155(5)
Sn(1)−C(11)	2.133(4)	2.135(3)	2.123(6)
Sn(2)-X			2.122(5)
Sn(1)−C(21)	2.120(4)	2.119(4)	2.121(6)
Sn(2)−C(41)			2.105(5)
Sn(1)-X	2.148(4)	2.148(4)	2.6003(7)
Sn(2)−Br(2)			2.5980(7)
Sn(1)−O(1)	2.803(3)	2.793(2)	2.379(3)
Sn(2)−O(2)			2.412(3)
P(1)−O(1)	1.450(3)	1.464(2)	1.482(4)
P(2)−O(2)			1.473(4)
	Bond Angles		
C(2)−Sn(1)−C(11)	115.8(2)	121.69(12)	117.0(2)
C(6)−Sn(2)−X			116.2(2)
C(2)−Sn(1)−C(21)	118.1(2)	108.66(12)	116.6(2)
C(6)−Sn(2)−C(41)			120.6(2)
C(2)−Sn(1)−X	100.7(2)	104.14(12)	96.1(2)
C(6)−Sn(2)−Br(2)			96.5(2)
C(11)−Sn(1)−C(21)	111.6(2)	114.17(12)	122.5(2)
C(41)−Sn(2)−X			119.1(2)
C(11)−Sn(1)−X	104.4(2)	100.31(14)	95.9(2)
Br(2)−Sn(2)−X			96.2(2)
C(21)−Sn(1)−X	103.6(2)	105.8(2)	97.8(2)
C(41)−Sn(2)−Br(2)			97.5(2)
O(1)−Sn(1)−C(2)	73.84(12)	74.86(9)	79.3(2)
O(2)−Sn(2)−C(6)			79.2(2)
O(1)−Sn(1)−C(11)	80.05(13)	78.00(10)	84.0(2)
O(2)−Sn(2)−X			84.4(2)
O(1)−Sn(1)−C(21)	77.77(13)	77.28(10)	86.7(2)
O(2)−Sn(2)−C(41)			86.1(2)
O(1)−Sn(1)−X	174.18(12)	176.96(13)	174.64(9)
O(2)−Sn(2)−Br(2)			175.42(9)
P(1)−O(1)−Sn(1)	107.46(14)	114.6(2)	114.6(2)
P(2)−O(2)−Sn(2)			112.6(2)

the equatorial and axial angles $\Delta\Sigma(\nu)$, which is 90° for the ideal trigonal bipyramid and 0° for the ideal tetrahedron.[4b,c,23] It amounts to 36.8° for **9**, 34.27° for **10**, and 66.1°(Sn1)/65.7°(Sn2) for **11**. Associated with the position of **9**, **10**, and **11** along the tetrahedron−trigonal bipyramid path are the different Sn−O interactions classified as Pauling-type bond orders[4c,24] of 0.07 (**9**), 0.08 (**10**), and 0.29(Sn1)/0.26(Sn2) (**11**). The deviation of the tin atoms from the respective trigonal plane amounts to 0.477 Å for **9** in the direction of C(21), 0.492 Å for **10** in the direction of C(31), and 0.245/0.250 Å for **11** in the direction of Br(1)/Br(2).

The weak Sn−O interactions in the tetraorganotin compounds **9** and **10** are of the same order of magnitude as those previously reported for $SnMe_3$-1,4-CHD-COOMe (Sn−O 2.781 Å),[6g] (*Z*)-17-[2-(triphenylstannyl)-vinyl]-4-estren-17-ol (Sn−O 2.77 Å),[6b] (*Z*)-3,4,4-trimethyl-1-(triphenylstannyl)-1-penten-3-ol (Sn−O 2.772 Å),[6h] and (*Z*)-2-methyl-3-triphenylstannyl-3-pentene-2-ol (Sn−O 3.012 Å).[6i]

The strength of the Sn−O interactions in the pentacoordinate triorganotin derivative **11** of 2.379(3) and 2.412(3) Å is similar to those reported for $Me_2(Cl)SnCH_2SiMe_2CH_2P(O)(Oi\text{-}Pr)_2$ (Sn−O 2.371 Å)[25a] and 2-$Ph_2P(O)C_6H_4Sn(Cl)Me_2$ (Sn−O 2.357 Å)[10b] but greater than those observed for $Me_2(Cl)SnCH_2CH[P(O)(Oi\text{-}Pr)_2]_2$ (Sn−O 2.444 Å)[25b] and $Me_2(F)Sn(CH_2)_2P(O)Ph_2$ (Sn−O 2.454 Å).[25c] Shorter Sn−O distances were reported for $Me_2(Br)Sn(CH_2)_2P(O)Ph$-*t*-Bu (Sn−O 2.324 Å)[25d] and $Me_2(Cl)Sn(CH_2)_3P(O)Ph_2$ (Sn−O 2.292 Å).[25e]

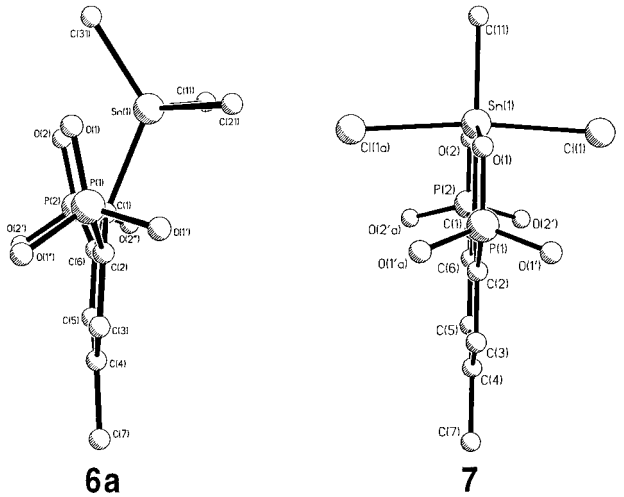

Figure 6. View along the aromatic ring of **6a** and **7**.

It is noteworthy that in [8-(dimethylamino)-1-naphthyl]-triphenyltin[6f] the longest tin−carbon bond length is observed for the carbon atom trans to the NMe_2 donor group, whereas in **9** and **10** the longest distances are found for Sn(1)−C(2) (2.171(4)/2.167(3) Å), respectively. The Sn−Br bond lengths of 2.6003(7) and 2.5980(7) Å in **11** are longer than the Sn−Br single bond length of 2.49 Å[23] as result of the intramolecular Sn−O interaction.

Compounds **6**, **7**, and **9**−**11** show different deviations from the plane defined by the aromatic carbons (Figure 6). Whereas **7** shows ideal planarity, the aromatic rings in **6a** and **6b** are strongly distorted to the extent that C(1) and C(1*) are displaced by 0.119(8) and 0.106(7) Å, respectively, from that plane. The tin atoms (Sn(1) in **6a**, Sn(1*) in **6b**) are displaced in the same direction, and the corresponding phosphorus atoms are displaced in the opposite direction.

The deviation of the tin atoms from the plane defined by the aromatic ring is smaller for **9** and **11**. It amounts to 0.076(7) Å for **9** and 0.050(10)/0.032(10) Å (Sn(1)/Sn(2)) for **11**. For **10**, the deviation (0.109(7) Å) is comparable to those observed for **6a** and **6b**.

Table 4 summarizes the IR ν(P═O) frequencies of **2** and **5**−**12** as well as the P═O and Sn−O distances of **6**, **7**, and **9**−**11**. The data suggest that in **5** there seems to be no Sn−O interaction because the ν(P═O) of 1250 cm^{-1} is very close to the values found for **2** and for the noncoordinating P═O group in **9**. Weak Sn−O contacts such as those found in **6**, **9**, and **10** are reflected in a slight decrease of the ν(P═O) to 1231−1233 cm^{-1}. Notably, IR spectroscopy is not able to distinguish the small differences of the Sn−O distances measured for **6a** and **6b** by X-ray crystallography; only one absorption was found.

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Table 4. IR ν(P=O) Frequencies for 2 and 5−12 and Bond Distances (P=O, Sn−O) for 6, 7, and 9−11

compd	ν(P=O) (cm^{-1})	d (P=O) (Å)	d (Sn−O) (Å)
2	1255		
5	1250		
6	1233	1.458(4), 1.463(4) (**6a**)	3.006(4), 3.022(3) (**6a**)
		1.461(4), 1.462(4) (**6b**)	2.865(3), 3.063(4) (**6b**)
7	1176	1.497(5), 1.506(5)	2.278(6), 2.203(5)
8	1178		
9	1252, 1231	1.450(3), 1.450(3)	2.803(3)
10	1232	1.464(2)	2.793(2)
11	1180	1.482(4), 1.473(4)	2.379(3), 2.412(3)
12	1250, 1170		

Stronger Sn−O interactions, as established for **7**, **8**, and **11**, are reflected in a considerable lowering of ν(P=O) to 1176−1180 cm^{-1}. These results are in line with previous observations on related compounds.[10,25]

Structures in Solution. ^{119}Sn chemical shifts and $^1J(^{119}Sn-^{13}C)$ and $^2J(^{119}Sn-^1H)$ coupling constants were shown to be very sensitive measures for the elucidation of the coordination numbers and geometries of organotin compounds,[2,5b,c,6,26−29] especially when comparisons were made with compounds of very similiar substituent patterns.

Selected NMR data for **2** and **5**−**11** are listed in Table 5. The data of **5** are close to the corresponding values reported for $PhSnMe_3$[30] (δ ^{119}Sn −29.4 ppm, $^1J(^{119}Sn-^{13}CH_3)$ 347 Hz, $^2J(^{119}Sn-^1H)$ 55 Hz), [8-(dimethylamino)-1-naphthyl]trimethyltin[6f] ($^1J(^{119}Sn-^{13}CH_3)$ 364 Hz), and C_6H_4-P(O)Ph_2-2-$SnMe_3$-1[10] (δ ^{119}Sn −40.2 ppm), unambiguously indicating tetrahedral tin.

Compounds **6**, **9**, and **10** show small to moderate low-frequency ^{119}Sn chemical shifts and slightly increased $^1J(^{119}Sn-^{13}C)$ couplings with respect to the values found for Ph_4Sn (δ ^{119}Sn −128.1 ppm,[31] $^1J(^{119}Sn-^{13}CH_3)$ 531 Hz[32]), allowing one to conclude that the weak Sn−O interactions observed in the solid state are maintained in solution.

As expected, strong Sn−O contacts associated with octahedral and trigonal-bipyramidal configurations at tin are observed in solutions of **7**, **8**, **11**, and **12**, respectively. The ^{119}Sn resonances observed for **7** and **8** are close to the values reported for $Ph_2SnX_2 \cdot 2Bu_3PO$[3b] (X = Cl, δ ^{119}Sn −472,−477; X = Br, δ ^{119}Sn −467,−477 ppm) and are considerably low-frequency-shifted with respect to tetrahedrally configurated Ph_2SnX_2 (X = Cl, δ ^{119}Sn −33; X = Br, δ ^{119}Sn −72.5 ppm).[3b] The low-frequency ^{119}Sn chemical shifts as well as the $^1J(^{119}Sn-^{13}C)$ couplings of 822 and 826 Hz observed for **11** and **12** with respect to δ ^{119}Sn of −40 ppm[3b] and $^1J(^{119}Sn-^{13}C)$ of 595 Hz[32] reported for Ph_3SnBr provide clear evidence for the presence of pentacoordinate tin atoms. Because of the poor solubility of **7** and **8**, as well as of the multiplicity of their C_i signals resulting from ^{31}P coupling, we did not observe the $^1J(^{119}Sn-^{13}C)$ couplings.

A comparison of the ^{31}P NMR chemical shifts (Table 5) indicates high-frequency shifts in case of substantial Sn−O interactions (**7**, **8**, **11**, **12**) but only very small shift differences between non- and weakly coordinating P=O groups (**2**, **5**, **6**, **9**, **10**).

A remarkable feature in the ^{1}H NMR spectrum of **11** is the extremely high-frequency shift of δ 10.2 ppm ($^4J(^1H-^{31}P)$ 4 Hz, $^3J(^1H-^{119}Sn)$ 59 Hz) of the proton in the *ortho* position to the tin atoms.

Experimental Section

All solvents were dried and purified by standard procedures. All reactions were carried out under an argon atmosphere using Schlenk-tube techniques.

IR spectra (cm^{-1}) were recorded on a Bruker IFS 28 spectrometer. Bruker DPX-300 and DRX-400 spectrometers were used to obtain ^{1}H, ^{13}C, ^{31}P, ^{29}Si, and ^{119}Sn NMR spectra. ^{1}H, ^{13}C, ^{29}Si, ^{31}P, and ^{119}Sn NMR chemical shifts δ are given in ppm and were referenced to Me_4Si, H_3PO_4 (80%), and Me_4Sn, respectively. Elemental analyses were performed on a LECO-CHNS-932 analyzer. Satisfactory elemental analyses could not be obtained for the oils **3**, **4**, and **12**. However, their NMR spectra were unambiguous. 1,3-Bis(diethoxyphosphonyl)benzene (**1**) was prepared according to the literature.[16]

1,3-Bis(diethoxyphosphonyl)-5-*tert*-butylbenzene (2). To a suspension of 1,2-dibromo-5-*tert*-butylbenzene (20.00 g, 68.5 mmol) and $NiBr_2$ (2.60 g, 11.9 mmol) was added dropwise, at 160 °C, triethyl phosphite (28.20 mL, 177 mmol). The reaction mixture was stirred at this temperature for 2 h, and the resulting EtBr was distilled off. The crude product was passed through a column (SiO_2/EtOAc) and distilled to give 18.9 g (68%) of **2** as colorless oil, bp 148−151 °C (2.5×10^{-2} mmHg): ^{1}H NMR (400 MHz, C_6D_6) δ 1.04 (t, 12H, CH_3), 1.13 (s, 9H, CH_3), 3.92−4.08 (complex pattern, 8H, CH_2), 8.40 (dd, $^3J(^1H-^{31}P)$ = 15 Hz, 2H, $H_{4/6}$-aryl), 8.63 (t, $^3J(^1H-^{31}P)$ = 13 Hz, H_2-aryl); $^{13}C\{^1H\}$ NMR (100.63 MHz, $CDCl_3$) δ 15.8 (s, 4C, CH_3), 30.7 (s, 3C, CH_3), 34.7 (s, 1C, C), 62.0 (s, 4C, CH_2), 128.5 (dd, $^1J(^{13}C-^{31}P)$ = 189 Hz, $^3J(^{13}C-^{31}P)$ = 15 Hz, 2C, $C_{1,3}$), 131.6 (t, $^2J(^{13}C-^{31}P)$ = 10 Hz, 1C, C_2), 132.2 (complex pattern, 2C, $C_{4,6}$), 151.6 (t, $^3J(^{13}C-^{31}P)$ = 14 Hz, 1C, C_5); $^{31}P\{^1H\}$ NMR (162.0 MHz, $CDCl_3$) δ 18.9; IR (Nujol) ν(P=O) 1255 cm^{-1}. Anal. Calcd for $C_{18}H_{32}O_6P_2$: C, 53.23; H, 7.88. Found: C, 53.00; H, 7.70.

2,4-Bis(diethoxyphosphonyl)-1-(trimethylsilyl)benzene (3) and 2,4-Bis(diethoxyphosphonyl)-1,5-bis(trimethylsilyl)benzene (4). To a solution of 1,3-bis(diethoxyphosphonyl)benzene[16] (3.85 g, 11.0 mmol) in 20 mL of THF was added, at −78 °C, 30 mL of a 0.40 M solution of LDA (12 mmol) in hexane/diethyl ether (3:1). The reaction mixture was stirred for 2 h at this temperature. Trimethylchlorosilane (3.60 mL, 14 mmol) was added by syringe, and the suspension was warmed to room temperature overnight and hydrolyzed with 30 mL of water. The organic layer was separated and dried over Na_2SO_4, and the solvent was removed in vacuo to give an orange oil. Purification by column chromatography (SiO_2/EtOAc) afforded 0.25 g (5%) of **3** and 1.10 g (24%) of **4** as yellow oils.

3: ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.27 (s, 9H, Me_3Si), 1.18 (t, 12H, CH_3), 3.92−4.02 (complex pattern, 8H, CH_2), 7.68−7.75 (complex pattern, 2H, $H_{5/6}$-aryl), 8.11 (t, $^3J(^1H-^{31}P)$ = 12 Hz, 1H, H_3-aryl); $^{13}C\{^1H\}$ NMR (100.63 MHz, $CDCl_3$) δ −0.3 (s, 3C, Me_3Si), 15.2 (complex pattern, 4C, CH_3), 61.9 (complex pattern, 4C, CH_2), 127.9 (dd, $^1J(^{13}C-^{31}P)$ = 189 Hz, $^3J(^{13}C-^{31}P)$ = 14 Hz, 1C, C_4), 133.4 (dd, $^1J(^{13}C-^{31}P)$ = 190 Hz, $^3J(^{13}C-^{31}P)$ = 13 Hz, 1C, C_2), 132.7 (dd, $^2J(^{13}C-^{31}P)$ = 9 Hz, $^4J(^{13}C-^{31}P)$ = 3 Hz, 1C, C_5), 134.6 (t, $^2J(^{13}C-^{31}P)$ = 11 Hz, 1C, C_3),

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Table 5. Selected ^{13}C, ^{31}P, and ^{119}Sn NMR Data[a] for 2 and 5−12

compd	δ (C_i)[b] ($^2J(^{13}C-^{31}P)$)	δ (C)[c] ($^1J(^{119}Sn-^{13}C)$)	δ (^{31}P) ($J(^{119}Sn-^{31}P)$)	δ ^{119}Sn ($J(^{119}Sn-^{31}P)$)
2			18.2	
5	156.1 (t) (24)	−0.03 (387)	21.5 (30)	−39.4 (t) (31)
6	150.4 (t) (22)	145.9 (591)	20.7 (37)	−186.1 (t) (38)
7	172.4 (t) (18)	137.3[e] (*d*)	27.1 (89)	−424.8 (t) (91)
8	173.5 (t) (18)	149.2 (*d*)	26.7 (87)	−432.3 (t) (87)
9	152.7 (dd)[f] (19)	141.2 (577)	18.0, 20.7	−149.8 (dd) (16, 28)
10	151.0[g]	141.0 (571)	20.5 (28, 24)	−147.1[g]
11	156.1[g]	142.4 (822)	25.9 (15, 34)	−180.3[g]
12	155.5 (dd)[h] (19)	142.1 (826)	17.6, 26.9 (*d*)	−191.2 (d) (19)

[a] Chemical shifts δ in ppm, coupling constants J in Hertz. Abbreviations: d = doublet, t = triplet, dd = doublet of doublets. [b] Refers to the tin-bound *ipso*-carbon of the P-substituted aryl. [c] Refers to the tin-bound carbon of the R groups (i.e., Me for **5** and Ph for **6**−**12**). [d] Not measured. [e] $^nJ(^{13}C-^{31}P) = 4.5$ Hz. [f] $^4J(^{13}C-^{31}P) = 2$ Hz. [g] Complex pattern (AA′XX′ system). [h] $^4J(^{13}C-^{31}P) = 3$ Hz.

134.8 (dd, $^3J(^{13}C-^{31}P)$ = 14/19 Hz, 1C, C_6), 149.4 (d, $^2J(^{13}C-^{31}P) = 23$ Hz, 1C, C_1); $^{31}P\{^1H\}$ NMR (162.0 MHz, $CDCl_3$) δ 17.7 (d, $^4J(^{31}P-^{31}P) = 7$ Hz), 18.8 (d, $^4J(^{31}P-^{31}P) = 7$ Hz); $^{29}Si\{^1H\}$ NMR (79.49 MHz, $CDCl_3$) δ −3.7 (d, $J(^{31}P-^{29}Si) = 4$ Hz).

4: ^1H NMR (400 MHz, $CDCl_3$) δ 0.32 (s, 18H, Me_3Si), 1.22 (t, 12H, CH_3), 3.96−4.06 (complex pattern, 8H, CH_2), 8.02 (t, $^4J(^1H-^{31}P) = 4$ Hz, 1H, H_6-aryl), 8.16 (t, $^3J(^1H-^{31}P) = 14$ Hz, 1H, H_3-aryl); $^{13}C\{^1H\}$ NMR (100.63 MHz, $CDCl_3$) δ 0.4 (s, 6C, Me_3Si), 16.0 (complex pattern, 4C, CH_3), 61.9 (complex pattern, 4C, CH_2), 133.3 (dd, $^1J(^{13}C-^{31}P) = 191$ Hz, $^3J(^{13}C-^{31}P) = 12$ Hz, 2C, $C_{2,4}$), 136.1 (t, $^2J(^{13}C-^{31}P) = 13$ Hz, 1C, C_3), 142.7 (t, $^3J(^{13}C-^{31}P) = 18$ Hz, 1C, C_6), 147.7 (complex pattern, 2C, $C_{1,5}$); $^{31}P\{^1H\}$ NMR (162.0 MHz, $CDCl_3$) δ 19.7; $^{29}Si\{^1H\}$ NMR (79.49 MHz, $CDCl_3$) δ −0.3 (complex pattern because of AA′XX′ system).

[{2,6-Bis(diethoxyphosphonyl)-5-*tert*-butyl}phenyl]-trimethyltin (5). To a solution of **2** (2.00 g, 4.9 mmol) in 20 mL of hexane/diethyl ether (4:1) was added, at −78 °C, 18 mL of a 0.40 M solution of LDA (7.2 mmol) in hexane/diethyl ether (4:1). The yellow suspension was stirred for 5 h at this temperature, and a solution of Me_3SnCl (1.00 g, 5.02 mmol) in 10 mL of diethyl ether was added dropwise. The reaction mixture was warmed to room temperature and stirred overnight. The solvent was evaporated, and the residue was dissolved in 50 mL of dichloromethane and treated with a solution of KF (5.00 g, 0.85 mol) in 40 mL of water. The organic layer was separated and dried over Na_2SO_4, and the solvent was removed in vacuo. Column chromatography (SiO_2/EtOAc) of the residue afforded 800 mg (29%) of **5** as a colorless solid, mp 100−104 °C: ^1H NMR (400 MHz, $CDCl_3$) δ 0.41 (s, $^2J(^1H-^{119}Sn) = 56$ Hz, 9H, CH_3), 1.30 (t, 12H, CH_3), 1.33 (s, 9H, CH_3), 3.99−4.16 (complex pattern, 8H, CH_2), 7.94−7.98 (complex pattern, 2H, aromatics); $^{13}C\{^1H\}$ NMR (100.63 MHz, $CDCl_3$) δ −0.5 (s, $^1J(^{13}C-^{119/117}Sn) = 387/370$, 3C, CH_3), 16.7 (complex pattern, 4C, CH_3), 31.3 (s, 3C, CH_3), 35.0 (s, 1C, C), 62.4 (complex pattern, 4C, CH_2), 133.3 (complex pattern, 2C, $C_{3,5}$), 138.8 (dd, $^1J(C-P) = 192$ Hz, $^3J(^{13}C-^{31}P) = 22$ Hz, 2C, $C_{2,6}$), 150.4 (t, $^3J(^{13}C-^{31}P) = 13$ Hz, 1C, C_4), 156.1 (t, $^2J(^{13}C-^{31}P) = 24$ Hz, 1C, C_1); $^{119}Sn\{^1H\}$ NMR (149.18 MHz, $CDCl_3$) δ −39.4 (t, $J(^{119}Sn-^{31}P) = 31$ Hz); $^{31}P\{^1H\}$ NMR (162.0 MHz, $CDCl_3$) δ 21.5 ($J(^{31}P-^{119}Sn) = 30$ Hz); IR (KBr) ν(P═O) 1250 cm^{-1}. Anal. Calcd for $C_{21}H_{40}O_6P_2Sn$: C, 44.34; H, 7.03. Found: C, 44.65; H, 7.40.

[{2,6-Bis(diethoxyphosphonyl)-5-*tert*-butyl}phenyl]-triphenyltin (6). To a solution of **2** (6.00 g, 14.8 mmol) in 50 mL of hexane/diethyl ether (4:1) at −78 °C was added 50 mL of a 0.40 M solution of LDA (20 mmol) in hexane/diethyl ether (4:1). Subsequent stirring for 6 h at −78 °C afforded a yellow suspension. The precipitate was filtered and dried in vacuo to give 3.0 g of the monolithiated complex $C_6H_2[P(O)(OEt)_2]_2$-2,4-Li-1 (**2a**) as a pale yellow solid. To a suspension of this solid in 60 mL of diethyl ether was added, at −30 °C, triphenyltin chloride (2.60 g, 6.8 mmol) portionwise. The reaction mixture was stirred for 14 h, the precipitate was filtered, and the solvent was evaporated in vacuo. The residue was dissolved in 100 mL of dichloromethane and stirred with a solution of KF (10 g, 0.17 mol) in 50 mL of water. The resulting precipitate of Ph_3SnF was filtered, and the organic layer was separated and dried over Na_2SO_4. Dichloromethane was removed in vacuo, and the residue was recrystallized from hexane, giving 3.0 g (27%) of **6** as colorless crystals, mp 140−142 °C: ^1H NMR (400 MHz, C_6D_6) δ 0.92 (t, 12H, CH_3), 1.17 (s, 9H, CH_3), 3.39−3.42 (complex pattern, 4H, CH_2), 3.66−3.70 (complex pattern, 4H, CH_2), 7.16−7.30 (complex pattern, 9H, aromatics), 8.16 (d, $^3J(^1H-^{119}Sn) = 50$ Hz, 6H, aromatics), 8.38 (complex pattern, 2H, aromatics); $^{13}C\{^1H\}$ NMR (100.63 MHz, $CDCl_3$) δ 16.0 (complex pattern, 4C, CH_3), 31.0 (s, 3C, CH_3), 34.8 (s, 1C, C), 61.7 (complex pattern, 4C, CH_2), 127.3 (s, $^4J(^{13}C-^{119}Sn) = 12$ Hz, 3C, C_{para}), 127.5 (s, $^3J(^{13}C-^{119}Sn) = 54$ Hz, 6C, C_{meta}), 133.4 (complex pattern, 2C, $C_{3,5}$), 137.0 (s, $^2J(^{13}C-^{119}Sn) = 37$ Hz, 6C, C_{ortho}), 138.1 (dd, $^1J(^{13}C-^{31}P) = 191$ Hz, $^3J(^{13}C-^{31}P) = 20$ Hz, 2C, $C_{2,6}$), 145.9 (s, $^1J(^{13}C-^{119/117}Sn) = 591/565$, 3C, C_{ipso}), 150.4 (t, $^2J(^{13}C-^{31}P) = 21$ Hz, 1C, C_1), 151.0 (t, $^3J(^{13}C-^{31}P) = 13$ Hz, 1C, C_4); $^{119}Sn\{^1H\}$ NMR (149.18 MHz, C_6D_6) δ −186.1 (t, $J(^{119}Sn-^{31}P) = 38$ Hz); $^{31}P\{^1H\}$ NMR (162.0 MHz, $CDCl_3$) δ 20.7 ($J(^{31}P-^{119}Sn) = 37$ Hz); IR (KBr) ν(P═O) 1233 cm^{-1}. Anal. Calcd for $C_{36}H_{46}O_6P_2Sn$: C, 57.27; H, 6.09. Found: C, 57.30; H, 6.35.

[{2,6-Bis(diethoxyphosphonyl)-5-*tert*-butyl}phenyl]-phenyltin Dichloride (7). A suspension of **6** (193 mg, 0.26 mmol) in 7 mL of diethyl ether was treated with HCl gas at 0 °C for 2 h. The solvent was evaporated, and the resulting residue was recrystallized from hexane/dichloromethane, giving 110 mg (63%) of **7** as colorless crystals, mp > 350 °C: ^1H NMR (400 MHz, $CDCl_3$) δ 1.32 (t, 12H, CH_3), 1.37 (s, 9H, CH_3), 4.20−4.30 (complex pattern, 4H, CH_2), 4.40−4.50 (complex pattern, 4H, CH_2), 7.30−8.24 (complex pattern, 7H, aromatics); $^{13}C\{^1H\}$ NMR (100.63 MHz, $CDCl_3$) δ 16.2 (complex pattern, 4C, CH_3), 31.2 (s, 3C, CH_3), 35.3 (s, 1C, C), 65.5 (s, 4C, CH_2), 124.6 (dd, $^1J(^{13}C-^{31}P) = 183$ Hz, $^3J(^{13}C-^{31}P) = 17$ Hz, 2C, $C_{2,6}$), 128.3 (s, $^3J(^{13}C-^{119}Sn) = 144$ Hz, 2C, C_{meta}), 129.6 (s, $^4J(^{13}C-^{119}Sn) = 27$ Hz, 1C, C_{para}), 131.7 (complex pattern, 2C, $C_{3,5}$), 134.6 (s, $^2J(^{13}C-^{119}Sn) = 85$ Hz, 2C, C_{ortho}), 147.3 (t, $^nJ(^{13}C-^{31}P) = 4.5$ Hz, 1C, C_{ipso}), 153.7 (t, $^3J(^{13}C-^{31}P) = 13$ Hz, 1C, C_4), 172.4 (t, $^2J(^{13}C-^{31}P) = 18$ Hz, 1C, C_1); $^{119}Sn\{^1H\}$ NMR (149.18 MHz, $CDCl_3$) δ −424.8 (t, $J(^{119}Sn-^{31}P) = 91$ Hz); $^{31}P\{^1H\}$ NMR (162.0 MHz, $CDCl_3$) δ 27.1 ($J(^{31}P-^{119}Sn) = 90$ Hz); IR (KBr) ν(P═O) 1176 cm^{-1}. Anal. Calcd for $C_{24}H_{36}Cl_2O_6P_2Sn$: C, 42.91; H, 5.36. Found: C, 42.85; H, 5.40.

[{2,6-Bis(diethoxyphosphonyl)-5-*tert*-butyl}phenyl]-phenyltin Dibromide (8). To a solution of **6** (174 mg, 0.23 mmol) in 8 mL of benzene/methanol (1:1) was added, at −20 °C, 4.18 mL of a 0.11 M methanolic bromine solution. Subsequent stirring overnight afforded a pale yellow solution. The solvent was evaporated, and the resulting residue was recrystallized from hexane, giving 100 mg (56%) of **8** as a colorless solid, mp > 350 °C: ^1H NMR (400 MHz, $CDCl_3$) δ 1.34 (t, 12H, CH_3), 1.38 (s, 9H, CH_3), 4.20−4.34 (complex pattern, 4H, CH_2), 4.43−4.52 (complex pattern, 4H, CH_2), 7.31−8.18 (complex pattern, 7H, aromatics); $^{13}C\{^1H\}$ NMR (100.63 MHz, $CDCl_3$)

δ 16.3 (complex pattern, 4C, CH_3), 31.2 (s, 3C, CH_3), 35.4 (s, 1C, C), 65.8 (s, 4C, CH_2), 124.1 (dd, $^1J(^{13}C-^{31}P)$ = 184 Hz, $^3J(^{13}C-^{31}P)$ = 17 Hz, 2C, $C_{2,6}$), 128.3 (s, $^3J(^{13}C-^{119}Sn)$ = 142 Hz, 2C, C_{meta}), 129.7 (s, $^4J(^{13}C-^{119}Sn)$ = 27 Hz, 1C, C_{para}), 131.8 (complex pattern, 2C, $C_{3,5}$), 134.0 (s, $^2J(^{13}C-^{119}Sn)$ = 86 Hz, 2C, C_{ortho}), 149.2 (s, 1C, C_{ipso}), 153.8 (t, $^3J(^{13}C-^{31}P)$ = 13 Hz, 1C, C_4), 173.5 (t, $^2J(^{13}C-^{119}Sn)$ = 18 Hz, 1C, C_1); $^{119}Sn\{^1H\}$ NMR (149.18 MHz, $CDCl_3$) δ −432.3 (t, $J(^{119}Sn-^{31}P)$ = 87 Hz); $^{31}P\{^1H\}$ NMR (162.0 MHz, $CDCl_3$) δ 26.7 ($J(^{31}P-^{119}Sn)$ = 87 Hz); IR (KBr) ν(P═O) 1178 cm^{-1}. Anal. Calcd for $C_{24}H_{36}Br_2O_6P_2Sn$: C, 37.89; H, 4.73. Found: C, 38.25; H, 4.95.

2,4-Bis(diethoxyphosphonyl)-1-triphenylstannylbenzene (9) and 2,4-Bis(diethoxyphosphonyl)-1,5-bis(triphenylstannyl)benzene (10). To a solution of 1,3-bis(diethoxyphosphonyl)benzene (4.00 g, 11.4 mmol) in 120 mL of hexane/diethyl ether (3:1) was added, at −78 °C, 80 mL of a 0.40 M solution of LDA (32.0 mmol) in hexane/diethyl ether (3:1). Subsequent stirring for 6 h at −78 °C afforded a red-brown solution. Triphenyltin chloride (12.3 g, 32.0 mmol) was added portionwise, and the reaction mixture was stirred for 2 h at −78 °C. After reaction mixture was warmed to room temperature overnight, the solvent was removed in vacuo. The residue was dissolved in 100 mL of dichloromethane and treated with a solution of KF (20 g, 0.34 mol) in 60 mL of water. The precipitate (Ph_3SnF) was filtered off, the organic layer was separated and dried over Na_2SO_4, and the solvents were removed in vacuo. The residue was purified by column chromatography (SiO_2/EtOAc) followed by recrystallization from hexane/dichloromethane, giving 500 mg (6%) of **9** (mp 174−176 °C) and 2.50 g (21%) of **10** (mp 236 °C) as colorless crystals.

9: ^1H NMR (400 MHz, $CDCl_3$) δ 1.10 (t, 6H, CH_3), 1.32 (t, 6H, CH_3), 3.65−3.76 (complex pattern, 2H, CH_2), 3.78−3.86 (complex pattern, 2H, CH_2), 4.05−4.21 (complex pattern, 4H, CH_2), 7.31−8.31 (complex pattern, 18H, aromatics); $^{13}C\{^1H\}$ NMR (100.63 MHz, $CDCl_3$) δ 15.9 (d, $^3J(^{13}C-^{31}P)$ = 7 Hz, 2C, CH_3), 16.1 (d, $^3J(^{13}C-^{31}P)$ = 6 Hz, 2C, CH_3), 62.1 (complex pattern, 4C, CH_2), 128.0 (s, $^3J(^{13}C-^{119}Sn)$ = 52 Hz, 6C, C_{meta}), 128.2 (s, $^4J(^{13}C-^{119}Sn)$ = 12 Hz, 1C, C_{para}), 129.3 (dd, $^1J(^{13}C-^{31}P)$ = 188 Hz, $^3J(^{13}C-^{31}P)$ = 13 Hz, 1C, C_4), 133.7 (dd, $^2J(^{13}C-^{31}P)$ = 9 Hz, $^4J(^{13}C-^{31}P)$ = 3 Hz, 1C, C_5), 134.5 (t, $^2J(^{13}C-^{31}P)$ = 12 Hz, 1C, C_3), 137.0 (s, $^2J(^{13}C-^{119}Sn)$ = 39 Hz, 6C, C_{ortho}), 137.4 (dd, $^1J(^{13}C-^{31}P)$ = 178 Hz, $^3J(^{13}C-^{31}P)$ = 14 Hz, 1C, C_2), 138.3 (dd, $^3J(^{13}C-^{31}P)$ = 13/18 Hz, 1C, C_6), 141.2 (s, $^1J(^{13}C-^{119/117}Sn)$ = 577/552, 3C, C_{ipso}), 152.7 (dd, $^2J(^{13}C-^{31}P)$ = 20 Hz, $^4J(^{13}C-^{31}P)$ = 2 Hz, 1C, C_1); $^{119}Sn\{^1H\}$ NMR (149.18 MHz, $CDCl_3$) δ −149.8 (dd, $J(^{119}Sn-^{31}P)$ = 27 Hz, $^5J(^{119}Sn-^{31}P)$ = 16 Hz); $^{31}P\{^1H\}$ NMR (162.0 MHz, $CDCl_3$) δ 18.0 (d, $^4J(^{31}P-^{31}P)$ = 4 Hz, $^5J(^{31}P-^{119}Sn)$ = 16 Hz), 20.7 (d, $^4J(^{31}P-^{31}P)$ = 4 Hz, $J(^{31}P-^{119}Sn)$ = 27 Hz); IR (KBr) ν(P═O) 1251, 1231 cm^{-1}. Anal. Calcd for $C_{32}H_{38}O_6P_2Sn$: C, 54.98; H, 5.44. Found: C, 55.20; H, 5.50.

10: ^1H NMR (400 MHz, $CDCl_3$) δ 1.06 (t, 12H, CH_3), 3.58−3.68 (complex pattern, 4H, CH_2), 3.70−3.80 (complex pattern, 4H, CH_2), 7.15−8.35 (complex pattern, 32H, aromatics); $^{13}C\{^1H\}$ NMR (100.63 MHz, $CDCl_3$) δ 16.0 (complex pattern, 4C, CH_3), 62.1 (complex pattern, 4C, CH_2), 127.9 (s, $^3J(^{13}C-^{119}Sn)$ = 54 Hz, 6C, C_{meta}), 128.2 (s, $^3J(^{13}C-^{119}Sn)$ = 12 Hz, 1C, C_{para}), 134.7 (t, $^2J(^{13}C-^{31}P)$ = 12 Hz, 1C, C_3), 136.0 (dd, $^1J(^{13}C-^{31}P)$ = 175 Hz, $^3J(^{13}C-^{31}P)$ = 13 Hz, 2C, $C_{1,3}$), 137.1 (s, $^2J(^{13}C-^{119}Sn)$ = 39 Hz, 6C, C_{ortho}), 141.0 (s, $^1J(^{13}C-^{119/117}Sn)$ = 571/545 Hz, 3C, C_{ipso}), 148.2 (t, $^3J(^{13}C-^{31}P)$ = 17 Hz, 1C, C_6), 151.0 (complex pattern, 2C, $C_{1,5}$); $^{119}Sn\{^1H\}$ NMR (149.18 MHz, $CDCl_3$) δ −151.0 (complex pattern); $^{31}P\{^1H\}$ NMR (162.0 MHz, $CDCl_3$) δ 20.5 ($J(^{31}P-^{119}Sn)$ = 26 Hz); IR (KBr) ν(P═O) 1232 cm^{-1}. Anal. Calcd for $C_{50}H_{52}O_6P_2Sn_2$: C, 57.31; H, 4.96. Found: C, 57.40; H, 5.15.

2,4-Bis(diethoxyphosphonyl)-1,5-bis(bromodiphenylstannyl)benzene (11). To a solution of **10** (150 mg, 0.14 mmol) in 4 mL of benzene/methanol (1:1) was added, at 0 °C, 3.54 mL of a 0.079 M methanolic bromine solution. The solution was stirred overnight, and the solvent was evaporated in vacuo. The resulting colorless residue was washed several times with small portions of hexane, giving 130 mg (86%) of **11** as a colorless solid, mp 231−233 °C: ^1H NMR (300 MHz, $CDCl_3$) δ 1.10 (t, 12H, CH_3), 3.72−3.91 (complex pattern, 8H, CH_2), 7.29−8.13 (complex pattern, 21H, aromatics), 10.17 (t, $^4J(^1H-^{31}P)$ = 4 Hz, $^3J(^{119}Sn-^1H)$ 59 Hz, 1H, aromatic); $^{13}C\{^1H\}$ NMR (75.47 MHz, $CDCl_3$) δ 16.1 (complex pattern, 4C, CH_3), 64.0 (complex pattern, 4C, CH_2), 128.2 (s, $^3J(^{13}C-^{119}Sn)$ = 77 Hz, 8C, C_{meta}), 129.2 (s, $^3J(^{13}C-^{119}Sn)$ = 16 Hz, 4C, C_{para}), 131.4 (t, ^2J ($^{13}C-^{31}P$) = 12 Hz, 1C, C_2), 133.0 (dd, $^1J(^{13}C-^{31}P)$ = 186 Hz, ^3J ($^{13}C-^{31}P$) = 13 Hz, 2C, $C_{2,4}$), 136.5 (s, $^2J(^{13}C-^{119}Sn)$ = 54 Hz, 8C, C_{ortho}), 142.4 (s, $^1J(^{13}C-^{119/117}Sn)$ = 822/784, 4C, C_{ipso}), 148.1 (t, $^3J(^{13}C-^{31}P)$ = 17 Hz, 1C, C_6), 156.1 (complex pattern, 2C, $C_{1,5}$); $^{119}Sn\{^1H\}$ NMR (149.18 MHz, $CDCl_3$) δ −180.7 (complex pattern); $^{31}P\{^1H\}$ NMR (162.0 MHz, $CDCl_3$) δ 25.8 ($J(^{31}P-^{119}Sn)$ = 34 Hz, $^5J(^{31}P-^{119}Sn)$ = 15 Hz); IR (KBr) ν(P═O) 1180 cm^{-1}. Anal. Calcd for $C_{38}H_{42}Br_2O_6P_2Sn_2$: C, 43.31; H, 3.9. Found: C, 43.65; H, 4.15.

2,4-Bis(diethoxyphosphonyl)-1-(bromodiphenylstannyl)benzene (12). To a solution of **9** (204 mg, 0.29 mmol) in 4 mL of benzene/methanol (1:1) was added, at 0 °C, 3.24 mL of a 0.09 M methanolic bromine solution. The solution was stirred overnight, and the solvent was evaporated in vacuo. The resulting oily residue was dissolved in 2 mL of CH_2Cl_2/hexane (1:3). Slow evaporation of CH_2Cl_2 resulted in the precipitation of 140 mg (69%) of **12** as a yellow oil, which was separated from hexane by decantation: ^1H NMR (400 MHz, $CDCl_3$) δ 1.04 (t, 6H, CH_3), 1.24 (t, 6H, CH_3), 3.66−3.79 (complex pattern, 4H, CH_2), 3.99−4.10 (complex pattern, 4H, CH_2), 7.24−8.11 (complex pattern, 12H, aromatics), 8.84 (dt, $^4J(^1H-^{31}P)$ = 4 Hz, $^3J(^{119}Sn-^1H)$ = 67 Hz, 1H, aromatic); $^{13}C\{^1H\}$ NMR (75.47 MHz, $CDCl_3$) δ 15.8 (d, $^3J(^{13}C-^{31}P)$ = 7 Hz, 2C, CH_3), 16.1 (d, 7 Hz, 2C, CH_3), 62.2 (d, $^3J(^{13}C-^{31}P)$ = 6 Hz, 2C, CH_2), 63.9 (complex pattern, $^3J(C,P)$ = 6 Hz, 2C, CH_2), 128.2 (s, $^3J(^{13}C-^{119}Sn)$ = 75 Hz, 4C, C_{meta}), 129.2 (s, $^3J(^{13}C-^{119}Sn)$ = 17 Hz, 2C, C_{para}), 130.7/131.25 (dd, $^1J(^{13}C-^{31}P)$ = 189/187 Hz, ^3J ($^{13}C-^{31}P$) = 14/15 Hz, 2C, $C_{2/4}$), 133.5 (t, $^2J(^{13}C-^{31}P)$ = 12 Hz, 1C, C_3), 135.3 (dd, $^2J(^{13}C-^{31}P)$ = 9 Hz, $^4J(^{13}C-^{31}P)$ = 3 Hz, 1C, C_5), 136.1 (s, $^2J(^{13}C-^{119}Sn)$ = 53 Hz, 4C, C_{ortho}), 138.3 (dd, $^3J(^{13}C-^{31}P)$ = 13/19 Hz, 1C, C_6), 142.4 (d, $^1J(^{13}C-^{119/117}Sn)$ = 826/791 Hz, 2C, $^nJ(^{13}C-^{31}P)$ = 5 Hz, C_{ipso}), 155.5 (dd, $^2J(^{13}C-^{31}P)$ = 19 Hz, $^4J(^{13}C-^{31}P)$ = 3 Hz, 1C, C_1); $^{119}Sn\{^1H\}$ NMR (149.18 MHz, $CDCl_3$) δ −191.2 (d, $J(^{119}Sn-^{31}P)$ = 19 Hz); $^{31}P\{^1H\}$ NMR (162.0 MHz, $CDCl_3$) δ 17.6 (d, $^4J(^{31}P-^{31}P)$ = 8 Hz), 26.9 (d, $^4J(^{31}P-^{31}P)$ = 8 Hz); IR (Nujol) ν(P═O) 1250, 1170 cm^{-1}.

Crystallography. Intensity data for the colorless crystals were collected on a Nonius KappaCCD diffractometer with graphite-monochromated Mo Kα radiation at 293 K. The data collection covered the whole sphere of reciprocal space with 360 frames via ω-rotation (D/ω = 1°) at 2 times 5 (**6**, **10**), 10 (**7**, **9**), and 30 s (**11**) per frame. The crystal-to-detector distance was 2.6 (**9**, **10**, **11**), 2.7 (**7**), and 4.0 cm (**6**). Crystal decay was monitored by repeating the initial frames at the end of data collection. In analyzing the duplicate reflections, there was no indication for any decay. The structure was solved by direct-methods SHELXS86[33] (Sheldrick, 1990) and successive difference Fourier syntheses. Refinement applied full-matrix least-squares methods SHELXL93[34] (Sheldrick, 1993).

The H atoms were placed in geometrically calculated positions and refined with common isotropic temperature factors for alkyl and aryl H atoms (H_{alkyl}, C−H 0.96 Å; H_{aryl}, C−H 0.93 Å).

Disordered groups were found in **6** (OEt-group C48 (side occupation factor (sof) 0.7), C48′ (sof 0.3) and t-Bu group C8*, C10* (sof 0.6), C9*, C9′* (sof 0.5), C8′*, C10′ (sof 0.4)), **9** (OEt

(33) Sheldrick, G. M. *Acta Crystallogr.* **1990** *A46*, 467−473.
(34) Sheldrick, G. M. *SHELXL93*; University of Göttingen: Göttingen, Germany, 1993.

groups C43, C45, C47, C43′, C45′, C47′ (sof 0.5)), and **11** (OEt groups C51, C53, C55, C58, C51′, C53′, C55′, C58′ (sof 0.5)).

Atomic scattering factors for the neutral atoms and real and imaginary dispersion terms were taken from the *International Tables for X-ray Crystallography*.[35] The figures were created by SHELXTL-Plus.[36] Crystallographic data are given in Table 1, and selected bond distances and angles are given in Tables 2 and 3.

(35) *International Tables for Crystallography* Kluwer Academic Publishers: Dordrecht, The Netherlands, 1992; Vol. C.

(36) Sheldrick, G. M. *SHELXTL-PLUS*, Release 4.1; Siemens Analytical X-ray Instruments Inc.: Madison, WI, 1991.

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Supporting Information Available: Tables of all coordinates, anisotropic displacement parameters, and geometric data for compounds **6**, **7**, **9**, **10**, and **11** and ^{1}H, ^{13}C, ^{29}Si, ^{31}P, and ^{119}Sn NMR spectra for compounds **3**, **4**, and **12** (41 pages). Ordering information is given on current masthead page.

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