The First O,C,S-Coordinating Pincer-Type Ligand and Its Application to the Synthesis of a Triorganotin Cation Stabilized by Two Different Donor Atoms†

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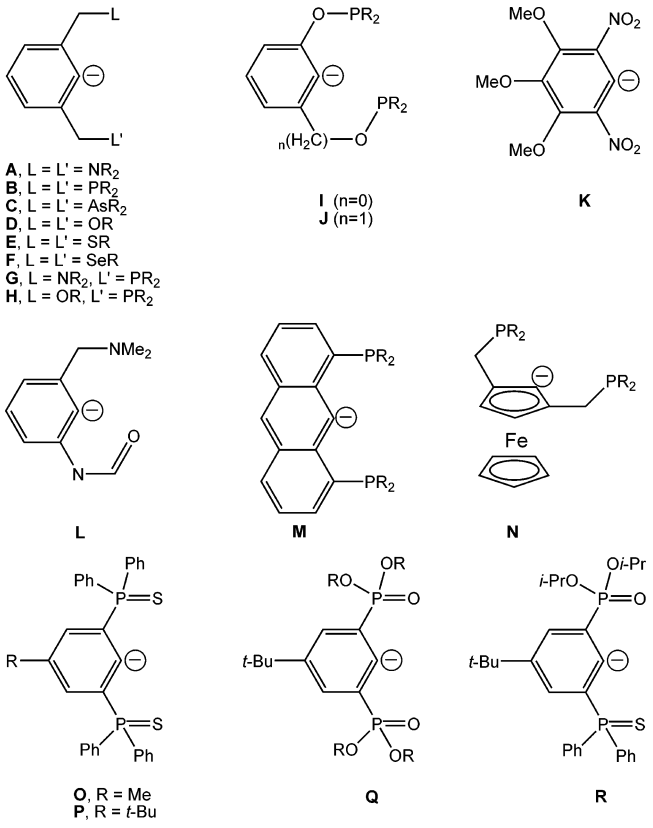
The syntheses and molecular structures of the bromo-substituted triarylphosphane sulfide (3-Br-5-*t*-Bu-C_6H_3)P(S)Ph_2 (**1**), the arylphosphonic acid di-isopropyl ester {3-*t*-Bu-5-[P(S)Ph_2]-C_6H_3}P(O)(O-*i*-Pr)$_2$ (**2**), its triphenyltin derivative {5-*t*-Bu-3-[P(S)Ph_2]-2-($SnPh_3$)-C_6H_2}P(O)(O-*i*-Pr)$_2$ (**3**), and the corresponding triorganostannylium salt {4-*t*-Bu-2-[P(O)(O-*i*-Pr)$_2$]-6-[P(S)Ph_2]-C_6H_2}$SnPh_2^+PF_6^-$ (**4**) are reported. By reaction with bromide ion, the latter is converted in situ to the intramolecularly coordinated benzoxaphosphastannole derivative [1(P),3(Sn)-$SnPh_2$OP(O)(O-*i*-Pr)-6-*t*-Bu-4-P(S)Ph_2]C_6H_2 (**5**). Ab initio MO calculations on the ethoxy-substituted analogue of compound **4** indicate a reduced positive charge at the tin atom in comparison with previously reported {4-*t*-Bu-2,6-[P(O)(OEt)$_2$]$_2$$C_6H_2$}$SnPh_2^+PF_6^-$.

Introduction

Since their first appearance in the late 1970s[1−3] L,C,L′-coordinating pincer-type ligands of types **A**−**H** (Chart 1) have become a rather popular class of compounds, the chemistry of which has been thoroughly reviewed.[4−6] Over the years the *classic* pincer-type ligands (**A**−**H**) containing a phenyl backbone and methylene bridges between the donor atoms L, L′ and the phenyl ring have been modified and developed further to give ligands containing oxygen (types **I**, **J**)[7,8] or nitrogen (types **K**, **L**)[9,10] bridges, or anthracene (type **M**)[11] and ferrocene[12,13] (type **N**) backbones, respectively (Chart 1). What makes all these ligands so fascinating is their ability to stabilize metals in unusual oxidation states and to participate, as their metal complexes, in a variety of homogeneously catalyzed organic reactions.[14−16] In recent years C−H bond activation was also achieved with pincer-type ligand-containing organometallic compounds.[17] Among the pincer-type ligands reported so far there are only a few representatives containing different donor sites L and L′ in one molecule (types **G**,[18] **H**,[19] **L**[10]).

Chart 1



For some time we have been interested in phosphorus-containing O,C,O- and S,C,S-coordinating pincer-type ligands

† Dedicated to Professor Herbert Jacobs on the occasion of his 70th birthday. Part of this work was first presented at the Symposium of the Graduiertenkolleg 352, *Synthetic, Mechanistic and Reaction-Engineering Aspects of Metal-Containing Catalysts*, November 17, 2005, TU Berlin, Germany, Book of Abstracts, p 17.

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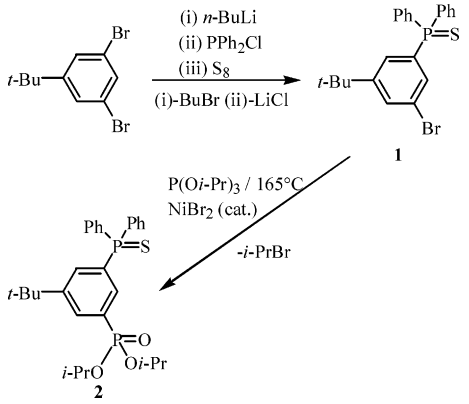
Scheme 1



of types **P**[20,21] and **Q**,[22] respectively (Chart 1). These ligands have been applied in the synthesis of intramolecularly coordinated main group metal and metalloid compounds as well as of palladium complexes. Notably, a related S,C,S-coordinating ligand of type **O**[23] (Chart 1) was reported in 2003.

In continuation of our studies we report here the synthesis of the first O,C,S-coordinating pincer-type ligand of type **R** (Chart 1), in its protonated form, and its triphenyltin derivative. The latter was converted into an intramolecularly coordinated triorganotin cation which showed remarkable stability against moisture but reacted with bromide ion to give, in situ, an intramolecularly P═S-coordinated benzoxaphosphastannole.

Results and Discussion

The one-pot subsequent reaction of 1,3-di-bromo-5-*tert*-butylbenzene with *n*-butyllithium, chlorodiphenylphosphine, and elemental sulfur provided the bromo-substituted triarylphosphane sulfide (3-Br-5-*t*-Bu-C_6H_3)P(S)Ph_2 (**1**) in good overall yield (Scheme 1). Compound **1** is a colorless solid, the molecular structure of which is shown in Figure 1. Selected geometric parameters are collected in Table 1. The phosphorus atom exhibits a distorted tetrahedral configuration (bond angles between 105.0(1)° (C21−P1−C2) and 113.24(8)° (C11−P1−S1). Notably, there are intramolecular S(1)···H(1) and S(1)···H(12) distances of 2.90(2) and 2.84(2) Å, respectively, being shorter than the sum of the van der Waals radii[24] of these atoms (H: 1.20−1.40 Å, S: 1.80 Å). For the parent triphenylphosphine sulfide, Ph_3PS, there is one intramolecular S···H distance of 2.79 Å.[25]

A TAVS reaction[26] catalyzed by $NiBr_2$ of the bromo-substituted triarylphosphane sulfide **1** with tri-isopropyl phosphite, (*i*-PrO)$_3$P, gave the arylphosphonic acid diisopropyl ester {3-*t*-Bu-5-[P(S)Ph_2]-C_6H_3}P(O)(O-*i*-Pr)$_2$ (**2**) in moderate yield (Scheme 1). Notably, the reaction is not prevented by the sulfur atom present in compound **1**. The molecular structure of compound **2** is shown in Figure 2, and selected geometric parameters are collected in Table 1.

In the unit cell there are two crystallographically independent molecules whose geometric parameters differ marginally, and consequently the structure of only one molecule is briefly

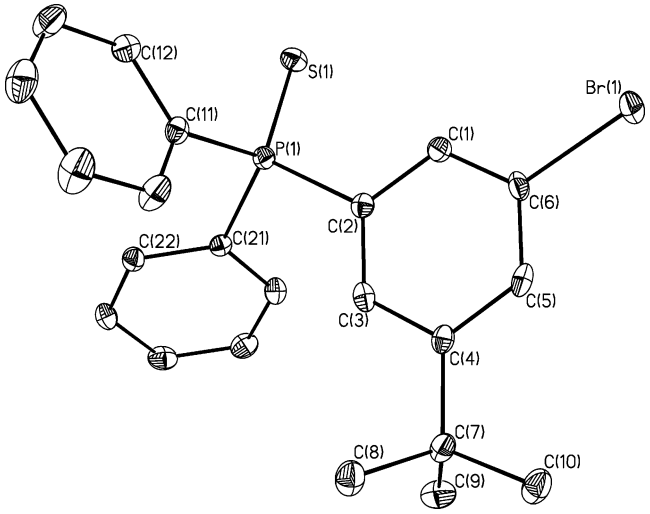


Figure 1. General view (SHELXTL) of a molecule of **1** showing 30% probability displacement ellipsoids and the atom numbering.

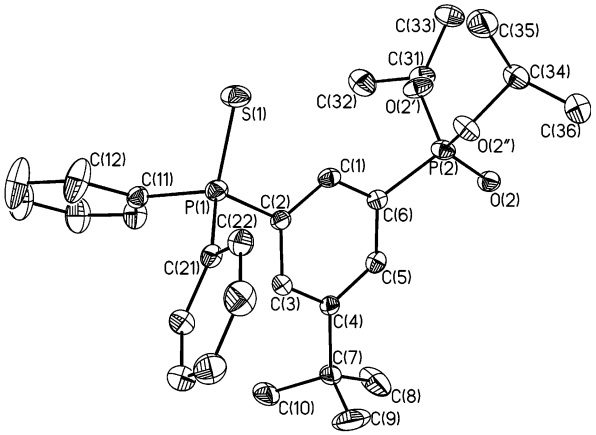


Figure 2. General view (SHELXTL) of a molecule of **2** showing 30% probability displacement ellipsoids and the atom numbering (only one representative of the two symmetry-independent molecules is shown).

Table 1. Selected Bond Lengths (Å) and Bond Angles (deg) for 1 and 2

	1	**2**
P(1)−S(1)	1.9556(8)	1.954(1)
P(2)−O(2)		1.461(2)
P(2)−O(2′)		1.567(2)
P(2)−O(2″)		1.582(2)
C(2)−P(1)−S(1)	112.73(7)	112.25(9)
C(11)−P(1)−S(1)	113.24(8)	113.49(9)
C(11)−P(1)−C(2)	106.21(9)	106.8(1)
C(11)−P(1)−C(21)	106.2(1)	105.1(1)
C(21)−P(1)−S(1)	112.73(7)	112.73(9)
C(21)−P(1)−C(2)	105.0(1)	105.9(1)
O(2)−P(2)−O(2′)		113.8(1)
O(2)−P(2)−O(2″)		117.1(1)
O(2′)−P(2)−O(2″)		103.0(1)
O(2)−P(2)−C(6)		113.8(1)
O(2′)−P(2)−C(6)		109.6(1)
O(2″)−P(2)−C(6)		97.9(1)
C(1)−C(2)−P(1)	118.7(2)	119.4(2)
C(1)−C(6)−P(2)		120.1(2)

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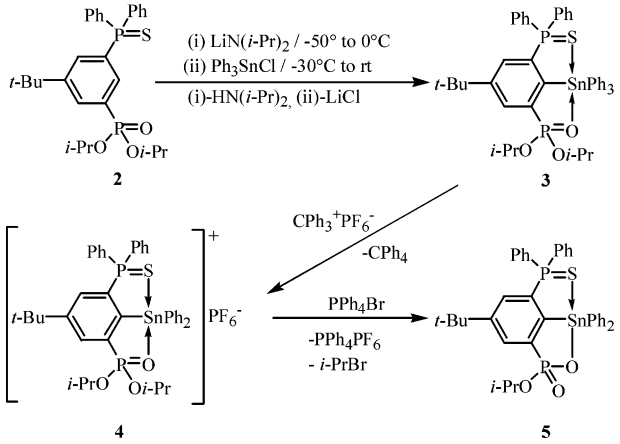
Scheme 2



discussed. The phosphorus atoms exhibit distorted tetrahedral configurations with the distortion being more pronounced for the phosphonic ester phosphorus (angles between 97.9(1)° and 117.1(1)° at P2 versus 105.1(1)° and 113.49(9)° at P1). As in compound **1**, the sulfur atom S(1) points to H(1) with a distance of 2.75(2) Å, whereas the O(3) oxygen atom points away, with the consequence of the isopropoxy oxygen atom O(2″) approaching H(1) at a distance of 2.77(2) Å. A similar situation was observed for the phosphoryl groups in the related compounds 1,3-$[P(O)(OR)_2]_2$-5-*t*-Bu-C_6H_3 (R = Et, *i*-Pr).[27,28]

Metalation of compound **2** was achieved with lithium diisopropyl amide, $LiN(i\text{-}Pr)_2$, in diethyl ether/hexane in the temperature range between −50 and 0 °C. Subsequent reaction with triphenyltin chloride, Ph_3SnCl, and recrystallization from dichloromethane/hexane provided the tetraorganotin compound {5-*t*-Bu-3-$[P(S)Ph_2]$-2-$(SnPh_3)$-C_6H_2}$P(O)(O\text{-}i\text{-}Pr)_2$ (**3**), as its CH_2Cl_2 solvate **3**·0.6 CH_2Cl_2, as a colorless crystalline solid in poor yield (Scheme 2). The molecular structure of compound **3** is shown in Figure 3, and selected geometric parameters are collected in Table 2.

As in the related intramolecularly coordinated tetraorganotin compounds {4-*t*-Bu-2,6-$[P(O)(OEt)_2]_2C_6H_2$}$SnPh_2R$ (R = Ph,[22] Me_3SiCH_2[29]), the tin atom in compound **3** adopts a typical [4+2] coordination. A distorted tetrahedron (mean angle 109.55°) with bond angles ranging between 95.5(1)° (C51−Sn1−C61) and 125.5(1)° (C1−Sn1−C61) is capped with O(2) at the opposite face of the carbon atom C(61) and with S(1) at the opposite face of the carbon atom C(51), at O(2)···Sn(1) and S(1)···Sn(1) distances of 2.956(2) and 3.513(1) Å, respectively. These distances are 0.744 and 0.487 Å shorter than the sums of the van der Waals radii[24] of tin (2.20 Å) and oxygen (1.50 Å), and tin and sulfur (1.80 Å), respectively. Notably, these intramolecular O→Sn and S→Sn interactions lengthen the Sn(1)−C(61) and Sn(1)−C(51) distances to 2.161(3) and 2.156(3) Å, respectively, with respect to the remaining tin−phenyl bond Sn(1)−C(41) (2.137(3) Å). As in the previously reported symmetrically substituted pincer-type ligand-substituted tetraorganotin compound {4-*t*-Bu-2,6-$[P(O)(OEt)_2]_2C_6H_2$}$SnPh_3$, the C(1)−Sn(1) distance is the longest among the tin−carbon bond lengths and amounts to 2.202(19) Å.[22] A comparison of the C(1)−C(2)−P(1) (121.1(3)°) and C(1)−C(6)−P(2) (124.5(3)°) angles, assigned as α, α′ angles,[27] with the corresponding angles in the parent compound **2** (119.4(2)°, 120.1(2)°) suggests, however, that these intramolecular interactions are rather weak. This view is supported by the facts that (i) in comparison with the organotin-free derivative **2** the P(1)−S(1) (1.948(1) Å) and P(2)−O(2) (1.464(2) Å) distances are almost unchanged, (ii) the $\tilde{\nu}$(P═O) of 1241 cm^{-1} is rather close to that of compound **2** (1249 cm^{-1}), and (iii) both the O(2) and S(1) atoms are displaced by 0.611(6) and 1.497(6) Å from the least-squares plane defined by the aromatic carbon atoms C(2)−C(6). In the trioganotin cation **4** (see below) this displacement is much less pronounced (Figure 4).

The weak intramolecular O→Sn and S→Sn interactions in compound **3** are retained in solution. This is especially manifested by its low-frequency ^{119}Sn NMR chemical shift of δ −194 as compared to δ −128 found for tetraphenyltin, $SnPh_4$.[30]

Reaction of the [4+2]-coordinated tetraorganotin compound **3** with triphenylmethyl hexafluorophosphate, $CPh_3^+PF_6^-$, pro-

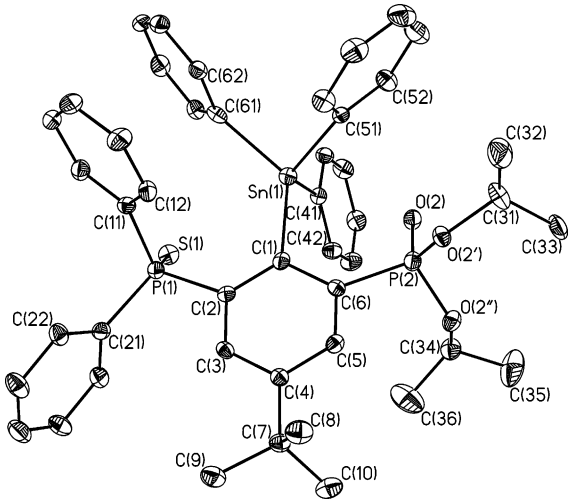


Figure 3. General view (SHELXTL) of a molecule of **3** showing 30% probability displacement ellipsoids and the atom-numbering scheme.

Table 2. Selected Bond Lengths (Å) and Bond Angles (deg) for 3 and 4

	3	4
Sn(1)−C(1)	2.201(3)	2.159(3)
Sn(1)−C(41)	2.137(3)	2.129(3)
Sn(1)−C(51)	2.156(3)	2.129(3)
Sn(1)−C(61)	2.161(3)	
Sn(1)−O(1)	2.956(2)	2.278(2)
Sn(1)−S(1)	3.513(1)	2.6295(9)
P(1)−S(1)	1.948(1)	2.006(1)
P(2)−O(2)	1.464(2)	1.501(2)
P(2)−O(2′)	1.572(2)	1.542(2)
P(2)−O(2″)	1.575(2)	1.562(1)
C(1)−Sn(1)−C(41)	109.7(1)	113.5(1)
C(1)−Sn(1)−C(51)	103.5(1)	122.2(1)
C(1)−Sn(1)−C(61)	125.5(1)	
C(41)−Sn(1)−C(51)	119.1(1)	123.5(1)
C(41)−Sn(1)−C(61)	104.1(1)	
C(51)−Sn(1)−C(61)	95.5(1)	
C(1)−Sn(1)−O(2)	75.7(1)	91.7(1)
C(1)−Sn(1)−S(1)	72.31(9)	98.97(9)
C(41)−Sn(1)−O(2)	70.7(1)	90.1(1)
C(41)−Sn(1)−S(1)	81.42(9)	94.63(9)
C(51)−Sn(1)−O(2)	70.18(9)	79.77(9)
C(51)−Sn(1)−S(1)	158.61(9)	86.12(8)
C(61)−Sn(1)−O(2)	157.7(1)	
C(61)−Sn(1)−S(1)	71.95(9)	
O(2)−Sn(1)−S(1)	126.65(4)	162.42(5)
C(1)−C(2 −P(1)	121.1(3)	119.3(2)
C(1)−C(6)−P(2)	124.5(3)	116.1(2)

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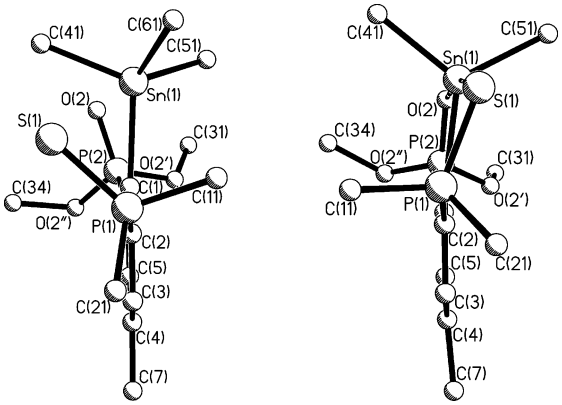

Figure 4. View along the aromatic plane of compounds **3** (left) and **4** (right).

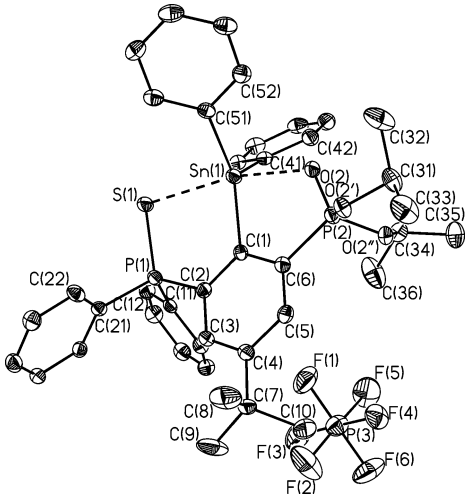

Figure 5. General view (SHELXTL) of an ion pair of **4** showing 30% probability displacement ellipsoids and the atom-numbering scheme.

vided the intramolecularly coordinated triorganotin hexafluorophosphate {4-*t*-Bu-2-[P(O)(O-*i*-Pr)$_2$]-6-[P(S)Ph$_2$]-C$_6$H$_2$}SnPh$_2^+$-PF$_6^-$ (**4**) as colorless crystals in good yield (Scheme 2). The molecular structure of compound **4** is shown in Figure 5. Selected geometric parameters are given in Table 2.

The tin atom in compound **4** shows a distorted trigonal bipyramidal configuration (geometrical goodness[31−33] $\Delta\Sigma(\theta) = 79.44°$) with the carbon atoms C(1), C(41), and C(51) in equatorial and the oxygen and sulfur atoms O(2) and S(1), respectively, in axial positions. The Sn(1) atom is deviated by 0.113(2) Å in the direction of S(1) from the plane defined by C(1), C(41), and C(51). Compared with the tetraorganotin derivative **3**, the intramolecular O(2)···Sn(1) (2.278(2) Å) and S(1)···Sn(1) (2.6295(9) Å) distances are considerably shortened by 0.678 and 0.884 Å, respectively. This shortening causes a simultaneous lengthening of the P(2)−O(2) and P(1)−S(1) distances to 1.501(2) and 2.006(1) Å, respectively, with the former also being illustrated by a decrease of the $\tilde{\nu}$(P═O) to 1155 cm^{-1}. The C(1)−C(2)−P(1) and C(1)−C(6)−P(2) angles (α, α' angles[27]) decrease to 119.3(2)° and 116.1(2)°, respectively.

The separation between the triorganotin cation {4-*t*-Bu-2-[P(O)(O-*i*-Pr)$_2$]-6-[P(S)Ph$_2$]-C$_6$H$_2$}SnPh$_2^+$ and the hexafluorophosphate anion PF$_6^-$ amounts to 5.855(11) Å and indicates no bonding interaction. Overall, the geometrical data including the intramolecular O(2)···Sn(1) distance of compound **4** resemble those of the related organotin salt {4-*t*-Bu-2,6-[P(O)(O*i*-Pr)$_2$]$_2$C$_6$H$_2$}SnPh$_2^+$PF$_6^-$ [34] (geometrical goodness[31−33] $\Delta\Sigma(\theta) = 84.6°$; O···Sn 2.249(2), 2.241(3) Å).

In solution, the triorganotin hexafluorophosphate **4** shows a ^{119}Sn NMR chemical shift of δ −132, which is high-frequency shifted as compared to {4-*t*-Bu-2,6-[P(O)(O*i*-Pr)$_2$]$_2$C$_6$H$_2$}SnPh$_2^+$-PF$_6^-$ containing two P═O donor functions (δ −208).[34] This difference is in line with the trend observed for the chemical shifts of solutions containing equimolar mixtures of Ph$_3$SnCl/Ph$_3$PO (δ −94) and Ph$_3$SnCl/Ph$_3$PS (δ −46), respectively.

Another interesting fact to be noticed is the dramatic decrease of the $J(^{119}\text{Sn}-^{31}\text{P(O)})$ couplings, as compared to the related tetraorganotin derivatives {4-*t*-Bu-2,6-[P(O)(O*i*-Pr)$_2$]$_2$C$_6$H$_2$}-SnPh$_3$ (35 Hz)[34] and **3** (28 Hz), respectively, for both {4-*t*-Bu-2,6-[P(O)(O*i*-Pr)$_2$]$_2$C$_6$H$_2$}SnPh$_2^+$PF$_6^-$ [34] (5 Hz) and compound **4** to the extent that in the latter this coupling was detected neither in the ^{119}Sn nor in the ^{31}P NMR spectrum because of line broadening ($\nu_{1/2}$ 9 Hz, 5 Hz). The $J(^{119}\text{Sn}-^{31}\text{P(S)})$ coupling in **4** (37 Hz) decreases as well with respect to compound **3** (56 Hz). The coupling constants actually observed are absolute values and composed of different coupling pathways $^2J(^{119}\text{Sn}-\text{X}-^{31}\text{P})$ (X = O, S) and $^3J(^{119}\text{Sn}-\text{C}-\text{C}-^{31}\text{P})$. These coupling pathways might have different signs and magnitudes, which in turn can change upon changes of the substituent pattern at the tin or phosphorus atoms and/or the conformation of the molecule. The conversion of the tetraorganotin compound **3** to the corresponding triorganotin cation **4** is associated with such a change, and consequently, the magnitude of the coupling constant changes. Similar observations for *o*-Ph$_2$P(O)C$_6$H$_4$-SnMe$_2$X (X = Me, Br) were already noticed by Weichmann and Schmoll.[35]

The natural bond orbital (NBO) analyses on model compounds (Table 3) in which the isopropoxy substituents are replaced by ethoxy substituents shows (i) that the positive charge at the tin atom in [R′SnPh$_2$]$^+$ (R′ = S,C,O-coordinating ligand; the ethoxy-substituted analogue of the cation in compound **4**) is reduced with respect to [RSnPh$_2$]$^+$ [34] (R = O,C,O-coordinating ligand), (ii) that in [R′SnPh$_2$]$^+$ the positive charge at both phosphorus atoms increases with respect to R′H with the effect being more pronounced for the P═O phosphorus atom, and (iii) that in [R′SnPh$_2$]$^+$ the P═O→Sn charge transfer is higher than in [RSnPh$_2$]$^+$ and slightly dominates over the one induced by P═S→Sn. The results suggest that compared with {4-*t*-Bu-2,6-[P(O)(O-*i*-Pr)$_2$]$_2$C$_6$H$_2$}SnPh$_2^+$ for compound **4** the *importance* of the canonical formula (II) with the positive charge located at the P═O phosphorus atom increases, without, however, dominating over canonical formula (I) (Chart 2). Apparently, the charge distribution can be controlled by the identity of the donor atom. These statements get further support by the $\tilde{\nu}$(P═O) being smaller for compound **4** (1155 cm^{-1}) than for {4-*t*-Bu-2,6-[P(O)(O-*i*-Pr)$_2$]$_2$C$_6$H$_2$}SnPh$_2^+$PF$_6^-$ (1177 cm^{-1}).[34] On the other hand, the Wiberg bond indices[36,37] of 0.4040 and 0.2157 indicate a higher covalent character of the Sn−S as compared to the Sn−O bond, and consequently, the canonical formula (III) appears also to be meaningful. At this point it

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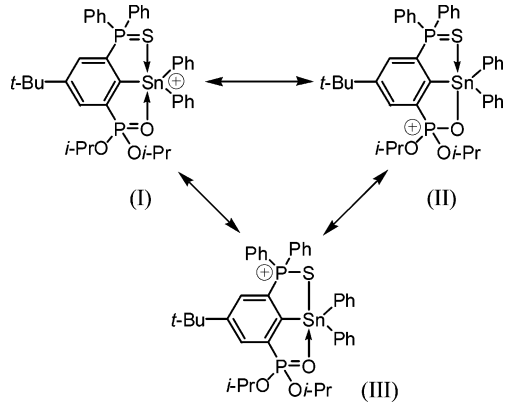
Table 3. Selected Results of the NBO Analysis for 5-*t*-Bu-1,3-[P(O)(OEt)$_2$]$_2$C$_6$H$_3$ (RH), {4-*t*-Bu-2,6-[P(O)(OEt)$_2$]$_2$-C$_6$H$_2$}SnPh$_2^+$ (RSnPh$_2^+$), {3-*t*-Bu-5-[P(S)Ph$_2$]-C$_6$H$_3$}P(O)(OEt)$_2$ (R′H), and {4-*t*-Bu-2-[P(O)(OEt)$_2$]-6-[P(S)Ph$_2$]-C$_6$H$_2$}SnPh$_2^+$ (R′SnPh$_2^+$) Calculated at the B3LYP/LANL2DZ Level of Theory (atomic charges; charge transfer, au; orbital occupation)

	NBO charges					charge transfer		
	P═O	*P*═S	P═*O*	P═*S*	M	P═O→M	P═S→M	occ(p(M))
RH	+2.282		−1.053					
R′H	+2.274	+1.231	−1.046	−0.592				
RSnPh$_2^+$	+2.355		−1.158		+2.350	0.122		0.198
	+2.361		−1.159					
R′SnPh$_2^+$	+2.363	+1.297	−1.164	−0.548	+2.165	0.135	0.115	0.284

Chart 2



should be mentioned that the classification of so-called *dative* bonds as being covalent or ionic is still a matter of controversial debate.[38]

The triorganotin hexafluorophosphate **4** is stable toward moisture, but it does react with tetraphenylphosphonium bromide, Ph$_4$PBr (Scheme 2), in a manner analogous to that for {4-*t*-Bu-2,6-[P(O)(OEt)$_2$]$_2$C$_6$H$_2$}SnPh$_2^+$PF$_6^-$.[34] Thus, the ^{31}P NMR spectrum of a C$_2$D$_2$Cl$_4$ solution containing equimolar amounts of compound **4** and Ph$_4$PBr, which had been heated to 65° C for 6 h, exhibited two equally intense doublet resonances at δ 15.2 ($\nu_{1/2}$ 1.6 Hz, $J(^{31}P-^{31}P) = 2.0$ Hz) and δ 51.4 ($\nu_{1/2}$ 4 Hz, $J(^{31}P-^{31}P) = 2.0$ Hz, $J(^{31}P-^{119}Sn) = 64.8$ Hz). The ^{119}Sn NMR spectrum of the same solution contained a resonance at δ −168 ($\nu_{1/2}$ 18 Hz, $J(^{31}P-^{119}Sn) = 65$ Hz). The signals are assigned to hypercoordinated benzoxaphosphastannole derivative **5** (Scheme 2), which, however, was not isolated from the reaction mixture. In both the ^{31}P and ^{119}Sn NMR spectra, again only one instead of the expected two $J(^{31}P-^{119}Sn)$ couplings were observed. The explanation for this is the same as given above. The assignment of the NMR signals gets support from the electrospray mass spectrum (positive mode) of the crude product, showing a mass cluster centered at $m/z = 745.1$ and which corresponds to the empirical formula C$_{37}$H$_{39}$O$_3$P$_2$SSn, i.e., protonated benzoxaphosphastannole [**5**−H]$^+$.

Conlusion

In this report we have added a novel representative to the family of pincer-type ligands, namely, in its protonated form, the unsymmetrically O,C,S-coordinating ligand {3-*t*-Bu-5-[P(S)Ph$_2$]-C$_6$H$_3$}P(O)(O-*i*-Pr)$_2$ combining both the hard and soft donor atoms oxygen and sulfur, respectively. The utility of this ligand for the synthesis of the intramolecularly coordinated triorganostannylium salt {4-*t*-Bu-2-[P(O)(O-*i*-Pr)$_2$]-6-[P(S)Ph$_2$]-C$_6$H$_2$}SnPh$_2^+$PF$_6^-$ (**4**) has been demonstrated, and, by MO calculations, the possibility to control the positive charge and its distribution in the cation by the identity of the coordinating donor atoms has been shown. This work contributes to the general understanding of structure and reactivity of organoelement-14 cations as a field of ongoing interest.[39−45] Given the fact that organotin-based Lewis acids[46,47] are catalysts for a variety of organic reactions, it even suggests the possibility for tailoring such catalysts by variation of coordinating donor atoms.

Experimental Section

General Considerations. All solvents were dried and purified by standard procedures. All reactions were carried out under an atmosphere of dry argon. SnPh$_3$Cl and CPh$_3^+$PF$_6^-$ were purchased from Lancaster and Aldrich, respectively, and used without further purification. IR spectra (cm^{-1}) were recorded on a Bruker IFS 28 spectrometer. Varian Mercury 200, Bruker DPX-300, and DRX-400 spectrometers were used to obtain ^{1}H, ^{13}C, ^{31}P, and ^{119}Sn NMR spectra. ^{1}H, ^{13}C, ^{31}P, and ^{119}Sn NMR chemical shifts are given in ppm and were referenced to Me$_4$Si, H$_3$PO$_4$ (85%, ^{31}P) and Me$_4$Sn (^{119}Sn). NMR spectra were recorded at room temperature unless otherwise stated. The atom numberings given in Figures 3 and 4 apply for the assignment of the ^{13}C resonances of compounds **3** and **4**. Elemental analyses were performed on a LECO-CHNS-932 analyzer.

Electrospray mass spectra were recorded in the positive mode on a Thermoquest-Finnigan instrument using CH$_3$CN as the mobile phase. The samples were introduced as solution in a mixture of CH$_3$CN and 1% formic acid (9:1 ratio) ($c = 10^{-4}$ mol L^{-1}) via a syringe pump operating at 0.5 μL/min. The capillary voltage was 4.5 kV, while the cone skimmer voltage was varied between 50 and 250 kV. Identification of the inspected ions was assisted by comparison of experimental and calculated istope distribution patterns. The *m*/*z* values reported correspond to those of the most intense peak in the corresponding isotope pattern.

Molecular Orbital Calculations. Calculations of the structures and energies of 5-*t*-Bu-1,3-[P(O)(OEt)$_2$]$_2$C$_6$H$_3$,[34] {4-*t*-Bu-2,6-[P(O)(OEt)$_2$]$_2$-C$_6$H$_2$}SnPh$_2^+$,[34] {3-*t*-Bu-5-[P(S)Ph$_2$]-C$_6$H$_3$}P(O)(OEt)$_2$, and {4-*t*-Bu-2-[P(O)(OEt)$_2$]-6-[P(S)Ph$_2$]-C$_6$H$_2$}SnPh$_2^+$ have been carried out at the density functional (B3LYP) level with the Gaussian 98 program[48] using the internal stored LANL2DZ basis set. This basis

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Table 4. Crystallographic Data for 1−4

	1	**2**	**3**	**4**
formula	$C_{22}H_{22}BrPS$	$C_{28}H_{36}O_3P_2S$	$C_{46}H_{50}O_3P_2SSn{\cdot}0.6CH_2Cl_2$	$[C_{40}H_{45}O_3P_2SSn]^+[PF_6]^-$
fw	429.34	514.57	914.51	931.42
cryst syst	monoclinic	triclinic	triclinic	triclinic
cryst size, mm	0.25 × 0.25 × 0.23	0.20 × 0.20 × 0.18	0.30 × 0.25 × 0.25	0.10 × 0.05 × 0.05
space group	$P2_1/c$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a, Å	8.9777(2)	11.2637(10)	12.3286(9)	11.1588(5)
b, Å	9.3145(2)	14.920(2)	13.3439(8)	11.8227(11)
c, Å	24.3328(6)	17.289(2)	15.2367(8)	16.2506(14)
α, deg	90	84.923(4)	113.043(3)	88.244(3)
β, deg	93.1687(12)	89.342(7)	92.551(4)	74.999(5)
γ, deg	90	77.652(7)	104.670(3)	86.297(5)
V, Å^3	2031.67(8)	2827.1(6)	2202.2(2)	2066.3(2)
Z	4	4	2	2
ρ_{calcd}, Mg/m^3	1.404	1.209	1.379	1.497
μ, mm^{-1}	2.207	0.254	0.812	0.849
F(000)	880	1096	942	948
θ range, deg	3.15 to 27.48	2.95 to 25.35	2.94 to 27.49	3.03 to 26.37
index ranges	$-11\le h\le 11$	$-13\le h\le 13$	$-15\le h\le 15$	$-13\le h\le 13$
	$-12\le k\le 12$	$-17\le k\le 17$	$-17\le k\le 16$	$-14\le k\le 14$
	$31\le l\le 31$	$-20\le l\le 20$	$-19\le l\le 19$	$-19\le l\le 20$
no. of reflns collcd	19 432	33 673	29 671	30 785
completeness to θ_{max}, %	99.7	99.5	97.6	99.3
no. of indep reflns/R_{int}	4641/0.043	10291/0.034	9851/0.057	8399/0.05
no. of reflns obsd with $I > 2\sigma(I)$	2762	4815	4851	4501
no. of refined params	268	727	519	487
GOF (F^2)	0.864	0.775	0.775	0.721
R1 (F) ($I > 2\sigma(I)$)	0.0317	0.0422	0.0455	0.0390
wR2 (F^2) (all data)	0.0592	0.0859	0.0766	0.0610
$(\Delta/\sigma)_{max}$	0.001	< 0.001	< 0.001	0.001
largest diff peak/hole, e/Å^3	0.409/−0.441	0.465/−0.303	1.216/−0.634	0.851/−0.466

set was previously shown to be appropriate for large organotin compounds including intra- and intermolecular coordination.[34,49−53] In combination with an NBO analysis it provides a qualitative picture of the bonding situation, although the geometry optimization of the P═O and P═S bond lengths is inaccurate. Comparing the results obtained by single-crystal X-ray structure analyses with those obtained by calculations, systematic errors of about 6% and 8% are observed for the P═O[34] and P═S bond lengths, respectively. For the calculations shown in Table 4 the O-*i*-Pr groups of compound **4** were replaced by OEt groups in order to compare the results with those recently reported.[34] However, the results obtained for {4-*t*-Bu-2-[P(O)(O-*i*-Pr)$_2$]-6-[P(S)Ph$_2$]-C$_6$H$_2$}SnPh$_2^+$ do not show any significant difference. Having these results in mind and being forced to use the same level of theory for all compounds to get comparable results, the LANL2DZ basis set was chosen. Additionally, the wave functions were analyzed by the natural bond orbital (NBO) method,[54,55] a standard option of Gaussian 98. The NBO analysis explains the strength of coordinative bonds in terms of donor−acceptor interactions between doubly occupied lone pair orbitals and unoccupied antibonding orbitals and provides atomic charges that are more reliable than Mulliken charges.

Crystallography. Intensity data for the colorless crystals were collected on a Nonius KappaCCD diffractometer with graphite-monochromated Mo Kα (0.71073 Å) radiation at 173(1) K. The data collection covered almost the whole sphere of reciprocal space with three (**1**, **4**) and four (**2**, **3**) sets at different *k*-angles with 302 (**1**), 210 (**2**), 540 (**3**), and 237 (**4**) frames via *ω*-rotation (Δ/ω = 1°) (**1**, **3**, **4**) and (Δ/ω = 2°) (**2**) at two times 10 s (**3**, **4**), 12.5 s (**2**), and 60 s (**4**) per frame. The crystal-to-detector distances were 3.4 cm (**1**, **2**, **4**) and 4.0 cm (**3**). Crystal decays were monitored by repeating the initial frames at the end of data collection. The data were not corrected for absorption effects. Analyzing the duplicate reflections there were no indications for any decay. The structure was solved by direct methods using SHELXS97[56] and successive difference Fourier syntheses. Refinement applied full-matrix least-squares methods with SHELXL97.[57]

The H atoms were placed in geometrically calculated positions using a riding model with isotropic temperature factors constrained at 1.2 for non-methyl and at 1.5 for methyl groups times U_{eq} of the carrier C atom. In **1** and **2** the coordinates (ref$_{x,y,z}$) of the aryl hydrogen atoms were refined.

In **2** and **3** isopropoxy groups are disordered over two positions with occupancies of 0.5 (O(4′′), C(73), C(74), C(75), O(4′′′), C(73′), C(74′), C(75′)) (**2**) and 0.4 (C(33′)) and 0.6 (C(33) (**3**). Each chlorine atom (Cl(1), Cl(2), Cl(1′), Cl(2′), Cl(3), Cl(4), Cl(3′), Cl(4′)) of the solvent molecules CH_2Cl_2 in **3** is disordered over two positions and was isotropically refined with occupancies of 0.15, whereas the carbon atoms (C(71), C(81)) were isotropically refined with occupancies of 0.3.

Atomic scattering factors for neutral atoms and real and imaginary dispersion terms were taken from International Tables for X-ray Crystallography.[58] The figures were created by SHELXTL.[59] Crystallographic data are given in Table 4; selected bond distances and angles, in Table 1 (**1**, **2**) and Table 2 (**3**, **4**).

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(3-Bromo-5-*tert*-butylphenyl)diphenylphosphane Sulfide, (3-Br-5-*t*-Bu-C_6H_3)P(S)Ph_2 (1). 1,3-Dibromo-5-*tert*-butylbenzene (28.3 g, 98.6 mmol) was dissolved in dry diethyl ether. Under magnetic stirring at −70 °C, a solution of *n*-BuLi in *n*-hexane (63.1 mL, 1.6 M) was added dropwise within 3 h. Progress of the metal−halide exchange was controlled by GC/MS. The reaction mixture was kept at −70 °C, and chlorodiphenylphosphane (18.8 mL, 101.5 mmol) was added dropwise within 45 min. The reaction was warmed to 0 °C, and sulfur (3.3 g, 103.5 mmol) was added in small portions. After the reaction mixture had been stirred overnight, the precipitate was filtered and subsequently washed with water, in order to remove the lithium salts, and diethyl ether. Subsequent recrystallization with diethyl ether gave 24.5 g (58%) of **1** as a colorless solid; mp 131 °C. Single crystals suitable for X-ray diffraction analysis were grown by slow evaporation of a hexane/diethyl ether solution.

^{1}H NMR (400.13 MHz, $CDCl_3$): δ 1.23 (s, 9H), 7.44 (m, 4H), 7.51 (m, 2H), 7.56 (ddd, $^3J(^1H-^{31}P)$ = 12.8 Hz, ^4J ($^1H-^1H$) = 1.5 Hz, 1.5 Hz, 1H), 7.62 (d, ^4J ($^1H-^1H$) = 1.5 Hz, 1H), 7.72−7.65 (complex pattern, 5H). $^{13}C\{^1H\}$ NMR (100.63 MHz, $CDCl_3$): δ 30.8 (C(CH_3)$_3$), 35.0 (C(CH$_3$)$_3$), 122.7 (d, $^3J(^{13}C-^{31}P)$ = 16.5 Hz, C_3−Br), 128.0 (d, $^2J(^{13}C-^{31}P)$ = 11.2 Hz, $C_{2,6}$), 128.4 (d, $^3J(^{13}C-^{31}P)$ = 12.6 Hz, C_{Ph}), 131.6 (d, $^4J(^{13}C-^{31}P)$ = 3.4 Hz, C_{Ph}), 131.6 (d, $^2J(^{13}C-^{31}P)$ = 12.1 Hz, $C_{2,6}$), 131.7 (d, $^4J(^{13}C-^{31}P)$ = 2.4 Hz, C_4), 132.0 (d, $^2J(^{13}C-^{31}P)$ = 10.7 Hz, C_{Ph}), 132.3 (d, $^1J(^{13}C-^{31}P)$ = 85.0 Hz, C_{Ph}), 135.0 (d, $^1J(^{13}C-^{31}P)$ = 82.1 Hz, C_1), 153.7 (d, $^3J(^{13}C-^{31}P)$ = 11.7 Hz, C_5−C(CH$_3$)$_3$). $^{31}P\{^1H\}$ NMR (121.49 MHz, D_2O): δ 44.1 Anal. Calcd for $C_{22}H_{22}BrPS$: C, 61.5; H, 5.2. Found: C, 61.1; H, 5.3.

[3-*tert*-Butyl-5-(diphenylphosphinothioyl)phenyl]phosphonic Acid Di-isopropyl Ester, {3-*t*-Bu-5-[P(S)Ph_2]-C_6H_3}P(O)(O-*i*-Pr)$_2$ (2). (3-Bromo-5-*tert*-butylphenyl)diphenylphosphane sulfide (**1**) (9.59 g, 22.3 mmol) and nickel bromide (0.49 g, 2.23 mmol) were heated at 165 °C. Phosphoric acid tri-isopropyl ester (6.1 mL, 24.5 mmol) was added dropwise within 30 min and the reaction mixture was kept at 165 °C for another 30 min, during which it turned black. The crude product was purified by column chromatography (silica, diethyl ether) to give 6.8 g (59%) of compound **2** as a colorless oil, which solidified after it had been kept overnight at 0 °C. Single crystals (mp 86 °C) suitable for X-ray diffraction analysis were grown by slow evaporation of a hexane/dichloromethane solution.

^{1}H NMR (400.13 MHz, $CDCl_3$): δ 1.12 (d, $^3J(^1H-^1H)$ = 6.3 Hz, 6H, CH(CH_3)$_2$), 1.28 (d, $^3J(^1H-^1H)$ = 6.3 Hz, 6H; CH(CH_3)$_2$), 1.28 (s, 9H, C(CH_3)$_3$), 4.61 (d, septet, $^3J(^1H-^1H)$ = $^3J(^1H-^{31}P)$ = 6.3 Hz, 2H; CH(CH$_3$)$_2$), 7.43 (m, 4H; H_{Ph}), 7.50 (m, 2H; $H_{Ph-para}$), 7.64−7.75 (complex pattern, 5H; H_{Ph} and H_6), 7.95 (d, $^3J(^1H-^{31}P)$ = 14.0 Hz, 1H; $H_{2,4}$), 8.04 (d, $^3J(^1H-^{31}P)$ = 14.6 Hz, 1H; $H_{2,4}$). $^{13}C\{^1H\}$ NMR (100.63 MHz, $CDCl_3$): δ 23.5 (d, $^3J(^{13}C-^{31}P)$ = 4.9 Hz; CH(CH_3)$_2$), 23.8 (d, $^3J(^{13}C-^{31}P)$ = 3.9 Hz; CH(CH_3)$_2$), 30.9 (s, C(CH_3)$_3$), 35.1 (s, C(CH$_3$)$_3$), 70.8 (d, $^2J(^{13}C-^{31}P)$ = 5.8 Hz; CH(CH$_3$)$_2$), 128.4 (d, $^3J(^{13}C-^{31}P)$ = 12.6 Hz; C_{Ph}), 130.4 (dd, $^1J(^{13}C-^{31}P)$ = 188.0 Hz, $^3J(^{13}C-^{31}P)$ = 11.7 Hz; C_1−P), 131.5 (d, $^4J(^{13}C-^{31}P)$ = 2.9 Hz; $C_{Ph-para}$), 131.9 (dd, $^2J(^{13}C-^{31}P)$ = 10.7 Hz, $^4J(^{13}C-^{31}P)$ = 2.9 Hz; $C_{2,4}$), 132.2 (dd, $^2J(^{13}C-^{31}P)$ = 10.7 Hz, 10.7 Hz; C_6), 132.2 (d, $^2J(^{13}C-^{31}P)$ = 10.7 Hz; C_{Ph}), 133.1 (dd, $^2J(^{13}C-^{31}P)$ = 11.7 Hz, $^4J(^{13}C-^{31}P)$ = 2.9 Hz; $C_{2,4}$), 133.3 (dd, $^1J(^{13}C-^{31}P)$ = 85.6 Hz, $^3J(^{13}C-^{31}P)$ = 14.5 Hz; C_5−P), 151.7 (dd, $^3J(^{13}C-^{31}P)$ = 13.6 Hz, 11.2 Hz; C_3−C(CH$_3$)$_3$). $^{31}P\{^1H\}$ NMR (81.01 MHz, $CDCl_3$): δ 16.3 (d, $J(^{31}P-^{31}P)$ = 5.9 Hz; P═O), 44.6 (d, $J(^{31}P-^{31}P)$ = 5.9 Hz; P═S). IR (KBr): $\tilde{\nu}$(P═O) 1249 cm^{-1}. Anal. Calcd for $C_{28}H_{36}O_3P_2S$: C, 65.4; H, 7.1. Found: C, 65.1; H, 6.9.

[5-*tert*-Butyl-3-(diphenylphosphinothioyl)-2-(triphenylstannyl)-phenyl]phosphonic Acid Di-isopropyl Ester, {5-*t*-Bu-3-[P(S)Ph_2]-2-(SnPh_3)-C_6H_2}P(O)(O*i*-Pr)$_2$ (3). A solution of *i*-Pr_2NLi (6.8 mL, 0.49 M, 3.46 mmol) in diethyl ether/hexane (2:1) was added dropwise at −50 °C and under magnetic stirring to a solution of the arylphosphonic acid diisopropyl ester {3-*t*-Bu-5-[P(S)Ph_2]-C_6H_3}P(O)(O-*i*-Pr)$_2$ (**2**) (1.48 g, 2.88 mmol) in diethyl ether (35 mL). The reaction mixture was allowed to warm to 0 °C and was stirred at this temperature for 9 h. Then the reaction mixture was cooled to −20 °C and triphenyltin chloride (1.33 g, 3.46 mmol) was added in one portion. The suspension was stirred overnight while reaching room temperature. The solvent was removed in vacuo. Dichloromethane and a saturated aqueous KF solution were added to the residue, and the resulting mixture was stirred for 10 min. The precipitate formed at the interlayer was filtered, and the organic phase was separated, washed again with aqueous KF solution, and dried over $MgSO_4$ followed by filtration. The solvent of the filtrate was evaporated in vacuo, and the residue was purified by column chromatography (silica, diethyl ether) to give starting material **2** (0.97 g, 1.88 mmol) and a product-containing fraction. The latter was purified by crystallization from a hexane/dichloromethane mixture to give compound **3** (0.24 g, 10%), as its dichloromethane solvate **3**·CH_2Cl_2, as colorless crystals with a mp of 114 °C.

^{1}H NMR (400.13 MHz, CD_2Cl_2): δ 0.83 (d, $^3J(^1H-^1H)$ = 6.3 Hz, 6H; CH(CH_3)$_2$), 1.12 (d, $^3J(^1H-^1H)$ = 6.3 Hz, 6H; CH(CH_3)$_2$), 1.13 (s, 9H; C(CH_3)$_3$), 3.94 (d of septet, 2H, $^3J(^1H-^1H)$ = $^3J(^1H-^{31}P)$ = 6.3 Hz, 2H; CH(CH$_3$)$_2$), 5.27 (s, 2H, CH_2Cl_2), 7.01−7.10 (9H, unresolved), 7.60−7.78 (17H, unresolved), 7.85 (d, $^3J(^1H-^{31}P)$ = 13.3 Hz, 1H; $C_{3,5}$). $^{13}C\{^1H\}$ NMR (100.63 MHz, $CDCl_3$): δ 23.4 (d, $^3J(^{13}C-^{31}P)$ = 5.8 Hz; CH(CH_3)$_2$), 23.9 (d, $^3J(^{13}C-^{31}P)$ = 2.9 Hz; CH(CH_3)$_2$), 30.6 (s; C(CH_3)$_3$), 34.4 (s; C(CH$_3$)$_3$), 70.3 (d, $^2J(^{13}C-^{31}P)$ = 5.8 Hz; CH(CH$_3$)$_2$), 126.6 (s, $^4J(^{13}C-^{119}Sn)$ = 10.6 Hz, Sn−C_{para}), 127.1 (s, $^2J(^{13}C-^{119}Sn)$ = 54.4 Hz; Sn−C_{ortho}), 128.4 (d, $^2J(^{13}C-^{31}P)$ = 12.6 Hz; P−Ph_{ortho}), 131.0 (d, $^4J(^{13}C-^{31}P)$ = 2.9 Hz; P−Ph_{para}), 131.7 (d, $^3J(^{13}C-^{31}P)$ = 10.7 Hz; P−Ph_{meta}), 132.2 (dd, $^2J(^{13}C-^{31}P)$ = 10.7 Hz, $^4J(^{13}C-^{31}P)$ = 2.9 Hz; $C_{3,5}$), 133.2 (d, $^1J(^{13}C-^{31}P)$ = 83.6 Hz; $C_{2,6}$), 135.2 (dd, $^2J(^{13}C-^{31}P)$ = 14.8 Hz, $^4J(^{13}C-^{31}P)$ = 2.9 Hz; $C_{3,5}$), 137.1 (s, $^3J(^{13}C-^{119}Sn)$ = 36.9 Hz; Sn−C_{meta}), 148.1 (s; Sn−C_{ipso}), 149.4 (dd, $^3J(^{13}C-^{31}P)$ = 12.1 Hz, 11.2 Hz; C_4), 153.3 (dd, $^2J(^{13}C-^{31}P)$ = 24.3 Hz, 23.3 Hz; C_1). C_2 and C_6 were not assigned unambiguously. $^{31}P\{^1H\}$ NMR (81.01 MHz, $CDCl_3$): δ 18.5 (d, $J(^{31}P-^{31}P)$ = 5.2 Hz, $J(^{31}P-^{119}Sn$ = 27.5 Hz); P═O), 50.0 (d, $J(^{31}P-^{31}P)$ = 5.2 Hz, $J(^{31}P-^{119}Sn$ = 56.1 Hz); P═S). $^{119}Sn\{^1H\}$ NMR (111.92 MHz, $CDCl_3$): δ −194 (dd, $J(^{119}Sn-^{31}P)$ = 56 Hz, 28 Hz). IR (KBr): $\tilde{\nu}$(P═O) 1241 cm^{-1}. Anal. Calcd for $C_{46}H_{50}O_3P_2SSn$·CH_2Cl_2: C, 59.5; H, 5.5. Found: C, 59.5; H, 5.6.

[4-*tert*-Butyl-2-(di-isopropoxyphosphoryl)-6-(diphenylphosphinothioyl)phenyl]diphenylstannylium Hexafluorophosphate, {4-*t*-Bu-2-[P(O)(O-*i*-Pr)$_2$]-6-[P(S)Ph_2]-C_6H_2}Sn$Ph_2^+PF_6^-$ (4). To a solution of **3** (46.0 mg, 0.05 mmol) in $C_2D_2Cl_4$ (1.5 mL) was added triphenylmethyl hexafluorophosphate (19.4 mg, 0.05 mmol). After the reaction mixture had been stirred at room temperature overnight the solvent was removed in vacuo and the crude product was dissolved in dichloromethane. Slow evaporation of the solvent first gave crystals of tetraphenylmethane. After these crystals had been filtered slow evaporation of the solvent was continued to provide 44 mg (94%) of compound **4** as colorless crystals (mp 160 °C) suitable for X-ray diffraction analysis.

^{1}H NMR (300.13 MHz, $CDCl_3$): δ 1.11 (d, $^3J(^1H-^1H)$ = 6.2 Hz, 6H; CH(CH_3)$_2$), 1.23 (d, $^3J(^1H-^1H)$ = 6.3 Hz, 6H; CH(CH_3)$_2$), 1.31 (s, 9H; C(CH_3)$_3$), 4.48 (d, septet, $^3J(^1H-^1H)$ = $^3J_{POCH}(^1H-^{31}P)$ = 6.2 Hz, 2H; CH(CH$_3$)$_2$), 7.34−7.44 (6H, unresolved), 7.60−7.78 (14H, unresolved), 7.91 (d, $^3J(^1H-^{31}P)$ = 11.3 Hz, 1H; $H_{3,5}$), 8.05 (d, $^3J(^1H-^{31}P)$ = 13.5 Hz, 1H; $H_{3,5}$). $^{13}C\{^1H\}$ NMR (100.63 MHz, $CDCl_3$): δ 23.5 (d, $^3J(^{13}C-^{31}P)$ = 5.8 Hz; CH(CH_3)$_2$), 23.6 (d, $^3J(^{13}C-^{31}P)$ = 5.3 Hz; CH(CH_3)$_2$), 29.7 (d, $^3J(^{13}C-^{31}P)$ = 5.3 Hz; C(CH$_3$)$_3$), 30.8 (s; C(CH_3)$_3$), 36.7 (s; C(CH$_3$)$_3$), 75.8 (d, $^2J(^{13}C-^{31}P)$ = 6.3 Hz; CH(CH$_3$)$_2$), 126.2 (d, $^1J(^{13}C-^{31}P)$ = 87.5 Hz;

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P−Ph_{ipso}), 129.2 (s, $^2J(^{13}C-^{119}Sn)$ = 76.5 Hz; Sn−C_{ortho}), 130.0 (d, $^2J(^{13}C-^{31}P)$ = 13.6 Hz; P−Ph_{ortho}), 130.5 (s, $^4J(^{13}C-^{119}Sn)$ = 15.5 Hz; Sn−C_{para}), 132.2 (dd, $^2J(^{13}C-^{31}P)$ = 12.6 Hz, $^4J(^{13}C-^{31}P)$ = 2.9 Hz; $C_{3,5}$), 132.5 (d, $^2J(^{13}C-^{31}P)$ = 11.2 Hz; P−Ph_{meta}), 133.0 (d, $^1J(^{13}C-^{31}P)$ = 70.9 Hz; $C_{2,6}$), 133.2 (d, $^1J(^{13}C-^{31}P)$ = 87.5 Hz; $C_{2,6}$), 134.4 (d, $^4J(^{13}C-^{31}P)$ = 2.9 Hz; P−Ph_{para}), 134.6 (dd, $^2J(^{13}C-^{31}P)$ = 14.6 Hz, $^4J(^{13}C-^{31}P)$ = 2.9 Hz; $C_{3,5}$), 135.6 (s, $^3J(^{13}C-^{119}Sn)$ = 52.5 Hz; Sn−C_{meta}), 138.8 (d, $^4J(^{13}C-^{31}P)$ = 2.9 Hz; Sn−C_{ipso}), 151.3 (dd, $^2J(^{13}C-^{31}P)$ = 27.2 Hz, 22.4 Hz; C_1), 156.6 (dd, $^3J(^{13}C-^{31}P)$ = 12.6 Hz, 9.7 Hz, C_4). $^{31}P\{^1H\}$ NMR (121.49 MHz, $CDCl_3$): δ −143.2 (sept, $(^1J(^{31}P-^{19}F)$ = 712 Hz); PF_6^-), 25.0 (d, $\nu_{1/2}$ 5 Hz, $J(^{31}P-^{31}P)$ = 3.0 Hz; *P*═O), 54.8 (d, $J(^{31}P-^{31}P)$ = 3.0 Hz, ($J(^{31}P-^{119}Sn)$ = 37.1 Hz); *P*═S). $^{119}Sn\{^1H\}$ NMR (111.92 MHz, $CDCl_3$): δ −132 (d, $\nu_{1/2}$ 9 Hz, $J(^{119}Sn-^{31}P)$ = 37 Hz). IR (KBr): $\tilde{\nu}$(P═O) 1155 cm^{-1}. Anal. Calcd for $C_{40}H_{45}O_3F_6P_3SSn$: C, 61.1; H, 5.9. Found: C, 60.4; H, 5.4.

In Situ Generation of 6-*tert*-Butyl-4-(diphenylphosphinothioyl)-1-isopropoxy-1-oxo-3,3-diphenyl-2,1,3-benzoxaphosphastannole (5). To a solution of **4** (44 mg, 0.047 mmol) in $C_2D_2Cl_4$ (1.5 mL) was added tetraphenylphosphonium bromide, $PPh_4^+Br^-$ (20.9 mg, 0.05 mmol). After the reaction mixure had been stirred at 65 °C for 6 h the solution was characterized by NMR spectroscopy. Subsequently, the solvent was removed in vacuo, and the residue was investigated by electrospray mass spectrometry. Attempts at isolating analytically pure compound **5** failed.

$^{31}P\{^1H\}$ NMR (81.02 MHz, $C_2D_2Cl_4$): δ 15.2 (d, $\nu_{1/2}$ 1.6 Hz, $J(^{31}P-^{31}P)$ = 2.0 Hz, *P*═O), 51.4 (d, $\nu_{1/2}$ 1.4 Hz, $J(^{31}P-^{31}P)$ = 2.0 Hz, $J(^{31}P-^{119}Sn)$ = 64.8 Hz; *P*═S). $^{119}Sn\{^1H\}$ NMR (111.92 MHz, $CDCl_3$): δ −168 (d, $\nu_{1/2}$ 18 Hz, $J(^{31}P-^{119}Sn)$ = 65 Hz). ESI-MS: *m*/*z* = 745.1 ($[5-H]^+$ corresponding to natural isotope distribution).

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Supporting Information Available: For compounds **1**−**4** details of structure determination, atomic coordinates, bond lengths and bond angles, and displacement parameters in cif format. This material is available free of charge via the Internet at http://pubs.acs.org.

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