Intramolecular Donor-Assisted Cyclization of Organotin Compounds

Michael Mehring,[a] Christian Löw,[a] Markus Schürmann,[a] and Klaus Jurkschat*[a]

Dedicated to Professor Bernt Krebs on the occasion of his 60th birthday

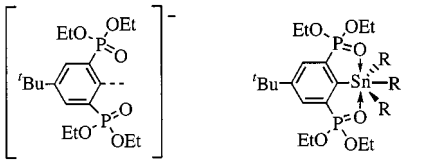
Keywords: Tin / Phosphorus / Intramolecular coordination / O ligands / Heterocycles

New intramolecularly coordinated organotin compounds containing the monoanionic O,C,O-coordinating ligand {4-*tert*-Bu-2,6-$[P(O)(OEt)_2]_2C_6H_2\}^-$ have been synthesized by substitution reactions starting from organotin halides. In view of the enhanced reactivity of the intramolecularly coordinated compounds {4-*tert*-Bu-2,6-$[P(O)(OEt)_2]_2C_6H_2\}SnR_2R'$ (**2**, R = Ph, R′ = CH_2SiMe_3; **3**, R = R′ = Ph; **6**, R = R′ = Cl), cationic tin species are suggested to occur as intermediates in the formation of the heterocyclic compounds [1(Sn),3(P)-$Ph_2SnOP(O)(OEt)$-5-*tert*-Bu-7-$P(O)(OEt)_2]C_6H_2$ (**8**), [1(Sn),3(P)-$Ph(Me_3SiCH_2)SnOP(O)(OEt)$-5-*tert*-Bu-7-$P(O)(OEt)_2]$-$C_6H_2$ (**15**), and {[1(Sn),3(P)-$Cl_2SnOP(O)(OEt)$-5-*tert*-Bu-7-$P(O)(OEt)]C_6H_2\}_2$ (**16**). The latter compounds are formed by intramolecular cyclizations of pentacoordinate cationic tin species under elimination of ethyl halide. Furthermore, the synthesis of [1(Sn),3(P)-$Ph_2SnOP(O)(OH)$-5-*tert*-Bu-7-$P(O)$-$(OH)_2]C_6H_2$ (**13**) is described. Reaction of **8** with an excess of Me_3SiBr leads to the unexpected formation of {2-$[P(O)(OEt)(OSiMe_3)]$-4-*tert*-Bu-6-$[P(O)(OEt)_2]C_6H_2\}SnPhBr_2$ (**9**) as a result of an O–Sn bond cleavage initiated by Me_3SiBr and subsequent reaction of the intermediate with further Me_3SiBr under Sn–C bond cleavage. The high donor capacity and the rigidity of the new ligand {4-*tert*-Bu-2,6-$[P(O)(OEt)_2]_2C_6H_2\}^-$ are demonstrated by X-ray diffraction analyses of the tetraorganotin compound **2** and the monoorganotin trichloride **6**. Furthermore, the molecular structures of the 2,3,1-oxaphosphastannoles **8** and **16** are discussed.

Introduction

Penta- and hexacoordinate compounds of the heavier group 14 elements Sn[1] and Si[2] have been extensively studied during the last few decades. The great interest in inter- and intramolecularly coordinated silicon and tin compounds stems from their enhanced reactivity,[1a-d][2a-c][3] their stereochemical non-rigidity,[1a][1c][2a-c][2k][4] and their biological activity.[5] In particular, the use of ligands with intramolecular donor sites has led to the stabilization of highly reactive compounds such as silylenes[6] and stannylenes,[7] as well as organosilicon-[8] and organotin cations.[9] We have recently reported the novel anionic O,C,O-coordinating ligand $\{4\text{-}tert\text{-Bu-2,6-}[P(O)(OEt)_2]_2C_6H_2\}^-$ (**A**) and have demonstrated its potential in the synthesis of intramolecularly coordinated organotin[1b] and organosilicon[2p] compounds of type **B**. The rigidity of the ligand frame of **A**, coupled with the high donor capacity of its P=O groups, make this compound an eminent pincer ligand for the stabilization of cationic as well as of low-valent group 14 organoelement compounds.

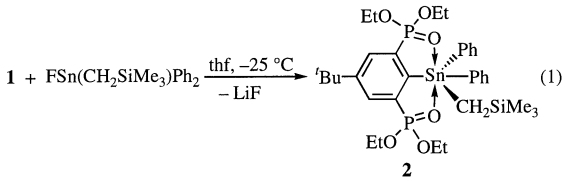
In this paper, we describe our attempts to synthesize organotin cations starting from intramolecularly coordinated organotin compounds of type **B**. However, as a result of an unexpected intramolecular donor-assisted cyclization reaction, we obtained pentacoordinate 2,3,1-benzoxaphosphastannole derivatives rather than the corresponding tin cations. Furthermore, a new intramolecularly stabilized tin(II) compound, the synthesis and reactivity of which will be described in detail in a forthcoming paper, is shown to serve as a precursor in the synthesis of a novel hexacoordinate monoorganotin trichloride. The latter can also be converted into a 2,3,1-benzoxaphosphastannole.



Results and Discussion

Intramolecularly Coordinated Organotin Compounds

The intramolecularly coordinated tetraorganotin compound $\{4\text{-}tert\text{-Bu-2,6-}[P(O)(OEt)_2]_2C_6H_2\}SnPh_2(CH_2SiMe_3)$ (**2**) has been prepared in moderate yield by the reaction of $\{4\text{-}tert\text{-Bu-2,6-}[P(O)(OEt)_2]_2C_6H_2\}Li$ (**1**) with $FSnPh_2(CH_2SiMe_3)$[10] (eq. 1).

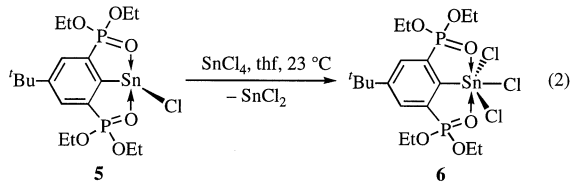


(1)

[a] Lehrstuhl für Anorganische Chemie II der Universität Dortmund,
D-44221 Dortmund, Germany
Fax: (internat.) +49(0)231/755-3797
E-mail: kjur@platon.chemie.uni-dortmund.de

  1434–1948/99/0505–0887 $ 17.50+.50/0

The structurally related tetraorganotin compound of type **B** {4-*tert*-Bu-2,6-[P(O)(OEt)$_2$]$_2$C$_6$H$_2$}SnPh$_3$ (**3**), as well as the hexacoordinate diorganotin compound of type **B** {4-*tert*-Bu-2,6-[P(O)(OEt)$_2$]$_2$C$_6$H$_2$}SnPhCl$_2$ (**4**) were prepared as described previously.[1b] The monoorganotin trichloride {4-*tert*-Bu-2,6-[P(O)(OEt)$_2$]$_2$C$_6$H$_2$}SnCl$_3$ (**6**) was synthesized by a simple redox process between $SnCl_4$ and the heteroleptic stannylene {4-*tert*-Bu-2,6-[P(O)(OEt)$_2$]$_2$C$_6$H$_2$}-SnCl (**5**)[11] (eq. 2). It is worth noting that the homoleptic stannylene $(C_5Me_5)_2Sn$ undergoes a similar redox reaction with $SnCl_4$ to give $(C_5Me_5)_2SnCl_2$ and $SnCl_2$.[12]



5 **6** (2)

Selected NMR data for **2**−**6** are listed in Table 1. The ^{119}Sn- and ^{31}P-NMR spectra show that weak O−Sn contacts are present in **2** and **3**, whereas strong intramolecular coordination is observed in the halogen-containing compounds **4** and **6**. In comparison with tetracoordinate $Ph_3SnCH_2SiMe_3$ [$\delta(^{119}Sn) = -88.6$],[13a] the ^{119}Sn-NMR data of **2** [$\delta(^{119}Sn) = -127.5$, $J(^{119}Sn-^{31}P) = 38$ Hz] indicate a coordination number greater than four at the tin atom.[13b] Moreover, the ^{31}P-NMR chemical shift of **2** [$\delta(^{31}P) = 23.0$, $J(^{31}P-^{119}Sn) = 37$ Hz] is shifted to higher frequency than that of the phosphonate precursor 5-*tert*-Bu-1,3-[P(O)(OEt)$_2$]$_2$C$_6$H$_3$ [$\delta(^{31}P) = 18.2$].[1b] These data indicate the tin atom in **2** to be [4+2]-coordinated, in solution as well as in the solid state, by four carbons and two weak O−Sn interactions, as has previously been reported for the tetraorganotin compound **3** and its silicon analogue.[1b,2p] The formal exchange of the phenyl groups in **3** by chlorine leads to a tin center of higher Lewis acidity and thus to a remarkably stronger O−Sn interaction, as shown by the ^{119}Sn-NMR chemical shifts of the dichlorotin derivative **4** [$\delta(^{119}Sn) = -424.8$, $J(^{119}Sn-^{31}P) = 91$ Hz] and the trichlorotin derivative **6** [$\delta(^{119}Sn) = -528.8$, $J(^{119}Sn-^{31}P) = 281$ Hz]. Although some intramolecularly coordinated monoorganotin trichlorides have been characterized by X-ray crystallography,[14] to the best of our knowledge there have not been any reports of hexacoordinate monoorganotin trichlorides containing a pincer ligand. The heptacoordinate tris(2,6-dimethoxyphenyl)methyltin trichloride,[14f] the molecular structure of which is best described as a tricapped tetrahedron, shows a ^{119}Sn-NMR chemical shift of $\delta(^{119}Sn) = -344$, i.e at a significantly higher frequency than that of the O,C,O-coordinated compound **6** [$\delta(^{119}Sn) = -528.8$]. This difference in the chemical shifts highlights the high donor capacity of the new O,C,O-coordinating ligand in **6** and suggests that the O−Sn interaction in the latter is stronger than that in tris(2,6-dimethoxyphenyl)methyltin trichloride.[14f]

Intramolecularly Coordinated Organotin Heterocycles

Previously, we reported the syntheses of {4-*tert*-Bu-2,6-[P(O)(OEt)$_2$]$_2$C$_6$H$_2$}SnPhX$_2$ (**4**, X = Cl; **7**, X = Br) by reaction of **3** with two molar equivalents of HCl and bromine, respectively. The ^{119}Sn-NMR spectra of the crude reaction mixtures showed, besides the signals at $\delta(^{119}Sn) = -442.8$ and $\delta(^{119}Sn) = -432.3$ attributable to the major products **4** and **7**, respectively, one signal of low intensity (5%) at about $\delta(^{119}Sn) = -224$. This minor signal could be attributed to compound **8** (Scheme 1), which is formed as a by-product. Surprisingly, attempted synthesis of the corresponding diorganotin diiodide (X = I) by reaction of **3** with two molar equivalents of iodine was unsuccessful. Instead, compound **3** reacts with one molar equivalent of iodine to give the novel intramolecularly coordinated 2,3,1-benzoxaphosphastannole **8** in high yield. The preparation and characterization of a similar class of heterocyclic compounds has been reported previously; starting from R$_2$Sn(H)(CH$_2$)$_2$P(H)Ph (R = alkyl) and sulfur, 1-thio-1,2,5-thiaphosphastannolanes were produced.[15a,b] Compound **8** is obtained as a colorless, crystalline solid and is readily soluble in common organic solvents such as CH_2Cl_2, $CHCl_3$, Et_2O, and thf.

The ^{119}Sn-NMR spectrum of **8** shows an ABB′-type resonance at $\delta(^{119}Sn) = -224$ [$J(^{119}Sn-^{31}P) = 19$, 23 Hz]. In the ^{31}P-NMR spectrum, two signals with equal integrals are observed at $\delta(^{31}P) = 17.3$ ($W_{1/2} = 20$ Hz) and $\delta(^{31}P) = 28.6$ [$J(^{31}P-^{119}Sn) = 19$ Hz], which are characteristic of a non-coordinating P(O)(OR)$_2$ moiety and a strongly coordinating P(O)(OR)$_2$ group, respectively.[1b][15c,d] Furthermore, both the ^{1}H- and the ^{13}C-NMR spectra confirm the presence of three distinct ethoxy groups in the molecule.

The formation of the 2,3,1-benzoxaphosphastannole **8** can be formally rationalized as shown in Scheme 1. In a first step, the triphenyltin derivative **3** reacts with one molar equivalent of HCl or X$_2$ (X = Br, I) to give the intermediate cation **8a**, which is best described by the two resonance structures shown in Scheme 1. The existence of donor-stabilized triorganotin cations is well established[15e-t] and recently we succeeded in isolating and fully characterizing {4-*tert*-Bu-2,6-[P(O)(O*iso*-Pr)$_2$]$_2$C$_6$H$_2$}SnPh$_2^+$ PF$_6^-$,[15u] a related derivative of **8a**.

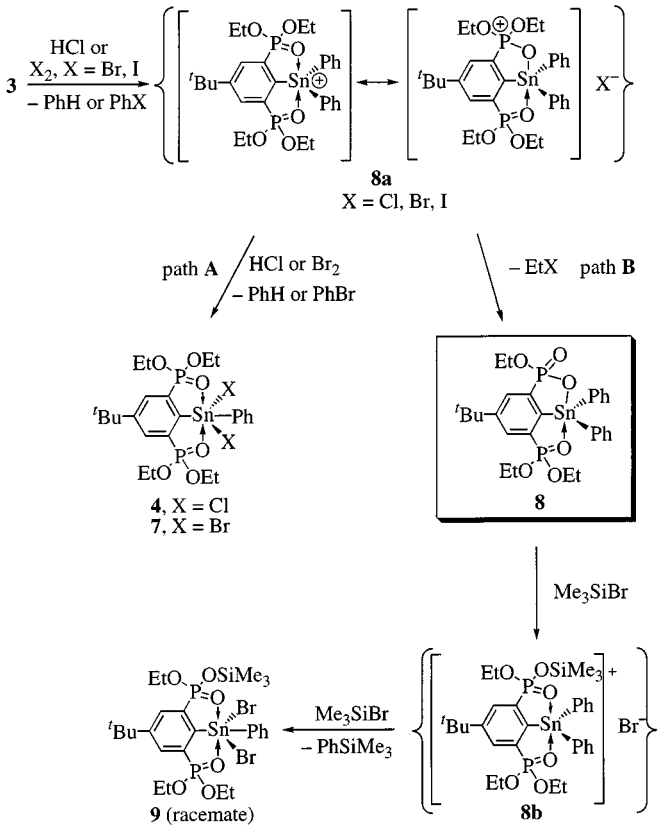
Depending on the lifetime of **8a**, which is determined by the nucleophilicity of the anion X$^-$, it either reacts with a second molar equivalent of HCl or Br$_2$ to give **4** or **7**, respectively (path **A**), or else nucleophilic attack of X$^-$ (X = Cl, Br, I) at the POEt function leads to the 2,3,1-benzoxaphosphastannole **8** (path **B**). The latter reaction path is dominant when X = I, whereas path **A** dominates when X = Cl, Br.

The reaction of phosphonates with excess Me_3SiBr usually leads to complete transesterification.[16] However, reaction of the 2,3,1-benzoxaphosphastannole **8** with an excess

Table 1. Selected ^{31}P- and ^{119}Sn-NMR data[a] of **2**–**9**, **13**, **16a**, 5-*tert*-Bu-1,3-$[P(O)(OEt)_2]_2C_6H_3$,[1b] $Ph_3SnCH_2SiMe_3$,[13] Ph_2SnCl_2,[34] $PhSnCl_3$,[34] and $\{[2,6\text{-}(MeO)_2C_6H_3]C\}_3SnCl_3$[14f]

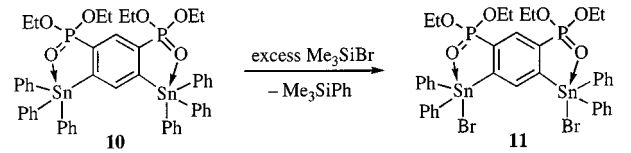
Compound[b]	$\delta(^{31}P)$ [$J(^{31}P-^{119}Sn)$]	$\delta(^{119}Sn)$ [$J(^{119}Sn-^{31}P)$]
R-H	18.2	
R-$SnPh_3$ (**3**)	20.7 [37]	−186.1 (t) [38]
R-$Sn(CH_2SiMe_3)Ph_2$ (**2**)	23.0 [37]	−127.5 (t) [38]
$Me_3SiCH_2SnPh_3$		−88
Ph_2SnCl_2		−33
R-$SnPhCl_2$ (**4**)	27.1 [89]	−424.8 (t) [91]
R-$SnPhBr_2$ (**7**)	26.7 [87]	−432.3 (t) [87]
R′-$SnPhBr_2$ (**9**)[c]	17.3 [103], 26.7 [97]	−439.6 (t) [100]
$PhSnCl_3$		−63
$\{[2,6\text{-}(MeO)_2C_6H_3]CH\}SnCl_3$		−344
R-$SnCl_3$ (**6**)	24.4 [288]	−528.8 (t) [281]
R-SnCl (**5**)	39.1 [113]	−99.7 (t) [116]
heterocycle **8**	17.3 [n.o.][d], 28.6 [19]	−223.6 (dd) [19, 23]
heterocycle **13**	20.3 [n.o.][d], 20.4 [n.o.][d]	−239.9 [70]
heterocycle **16a**	11.9 (d)[e] [137], 25.2 (d)[e] [335]	−547.9 (ddd) [139, 320, 336]

[a] Coupling constants J are given in Hz and chemical shifts δ in ppm. – [b] **R** = {4-*tert*-Bu-2,6-$[P(O)(OEt)_2]_2C_6H_2$}. – [c] **R′** = {4-*tert*-Bu-2-$[P(O)(OEt)_2]$-6-$[P(O)(OEt)(OSiMe_3)]C_6H_2$}. – [d] Not observed. – [e] $^4J(^{31}P-^{31}P)$ = 6.6 Hz.



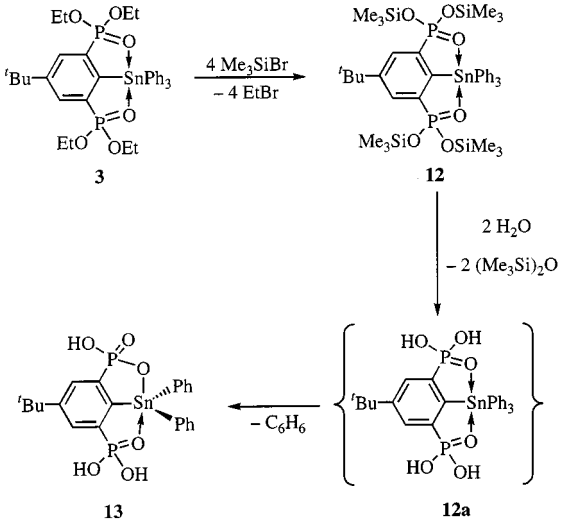
Scheme 1. Synthesis of compounds **4** and **7**–**9**

of Me_3SiBr gave the intramolecularly hexacoordinated diorganotin dibromide **9**, with only one ethoxy group being substituted by a trimethylsiloxy group (Scheme 1). This unusual reactivity is the result of an O–Sn bond cleavage in **8** by attack of Me_3SiBr, which gives the cationic tin species **8b** as an intermediate product. Subsequently, the intermediate **8b** reacts with further Me_3SiBr, which reacts here as an HBr equivalent leading to Sn–C bond cleavage, to provide the diorganotin dibromide **9**. In the ^{31}P-NMR spectrum of the crude reaction mixture, besides the signals due to **9** at $\delta(^{31}P)$ = 17.3 [$J(^{31}P-^{119}Sn)$ = 103 Hz] and $\delta(^{31}P)$ = 26.7 [$J(^{31}P-^{119}Sn)$ = 97 Hz], two minor signals (5%) with equal integrals are seen at $\delta(^{31}P)$ = 19.3 ($W_{1/2}$ = 20 Hz) and $\delta(^{31}P)$ = 29.6 ($W_{1/2}$ = 20 Hz). We tentatively attribute the latter two signals to a heterocyclic compound related to **8**, but attempts to isolate this species were unsuccessful. Evidently, the strong intramolecular O–Sn coordination in the intramolecularly coordinated cation **8b** activates the tin–carbon bonds, thereby facilitating the almost quantitative formation of the hexacoordinate diorganotin dibromide **9**. The O–Sn interactions in the reaction product **9** prevent the latter from undergoing further transesterification at the POEt function upon exposure to excess Me_3SiBr. Similar reactivity was observed when 2,4-bis(diethoxyphosphonyl)-1,5-bis(triphenylstannyl)benzene (**10**)[1b] was treated with an excess of Me_3SiBr (Scheme 2). Instead of a transesterification, substitution of phenyl by bromine was observed as a result of the strong intramolecular coordination. The reaction product, 2,4-bis(diethoxyphosphonyl)-1,5-bis(bromodiphenylstannyl)benzene (**11**) has previously been prepared by reaction of **10** with bromine and has been fully characterized.[1b] Similar reactions of Me_3SnCH_2-$CHX[P(O)(OiPr)_2]$ [X = $P(O)Ph_2$, P(O)(O*i*Pr)Ph, $P(O)(OiPr)_2$, C(O)Ph, C(O)O*i*Pr] with excess Me_3SiBr require higher temperatures, which, in turn, favour redistributions as side reactions.[16b] The intramolecularly coordinated compounds **8** and **10**, however, react even at low temperatures to give predominantly the intramolecularly coordinated organotin bromides **9** and **11**, respectively.



Scheme 2. Bromination of the intramolecularly coordinated tetraorganotin compound **10** with Me_3SiBr

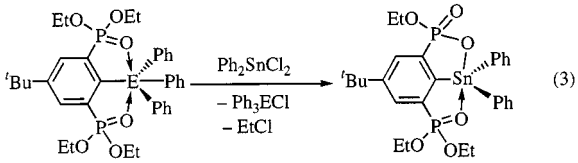
Previous investigations[1b] have shown that in the [4+2]-coordinated compound **3** the intramolecular O−Sn interactions are weaker than those in **10**. Consequently, and in contrast to the situation with **8** and **10**, the *in situ* reaction of **3** with Me_3SiBr proceeds with complete transesterification to give the silylphosphonate **12** (Scheme 3), which has been characterized by ^{31}P-, ^{29}Si-, and ^{119}Sn-NMR. The ^{119}Sn-NMR chemical shifts of the silylphosphonate **12** [$\delta(^{119}Sn) = -188.4$] and of the starting material **3** [$\delta(^{119}Sn) = -186.1$] are very similar, indicating comparable O−Sn coordination strengths in the two compounds. Subsequent reaction of **12** with water afforded the 2,3,1-benzoxaphosphastannole **13** and benzene (Scheme 3). The intermediate free acid **12a** could not be isolated. Richter and Weichmann have shown that the hydrolysis of silylphosphonates and silylphosphinates of 2,2-functionally disubstituted organotin compounds gives the corresponding stannylmethylated phosphonic and phosphinic acids, respectively, which undergo similar intramolecular cyclizations.[16b]



3 **12** **13** **12a**

Scheme 3. Transesterification and intramolecular cyclization of **3**

Recently, van Koten et al.[1d] have shown that $\{(Me_3Sn)_2$-1,4-$[C_6(CH_2NMe_2)_4$-2,3,5,6$]\}$ and $Me_3Sn[C_6H_3$-$(CH_2NMe_2)_2$-2,6] react with Me_3SnCl to give the pentacoordinate species $\{[Me_2Sn]_2$-1,4-$[C_6(CH_2NMe_2)_4$-2,3,5,6$]\}^{2+}$ $[(Me_3SnCl_2)^-]_2$ and $\{Me_2Sn[C_6H_3(CH_2NMe_2)_2$-2,6$]\}^+$ $(Me_3SnCl_2)^-$, respectively. In order to investigate whether compound **3** could be directly transformed into its cationic derivative or into the 2,3,1-benzoxaphosphastannole **8** by this method, the tetraorganotin compound **3** and Ph_2SnCl_2 were heated in refluxing toluene for 4 h. ^{119}Sn-NMR analysis of the reaction mixture showed that the heterocycle **8** was formed as the major product (eq. 3). Additional broad resonances were seen at $\delta(^{119}Sn) = -125$ (9%), −243 (24%), and −284 (28%), which were not assigned. Moreover, reaction of the intramolecularly coordinated tetraorganosilicon compound $\{4$-*tert*-Bu-2,6-$[P(O)(OEt)_2]_2C_6H_2\}SiPh_3$ (**14**)[2p] with Ph_2SnCl_2, which was performed under the same reaction conditions, also gave the 2,3,1-benzoxaphosphastannole **8** as the major product (eq. 3). This result can be explained in terms of $Si-C^{aryl}$ bond cleavage and subsequent insertion of a Ph_2SnCl moiety to give the organotin cation **8a** (X = Cl), followed by intramolecular cyclization with elimination of EtCl.

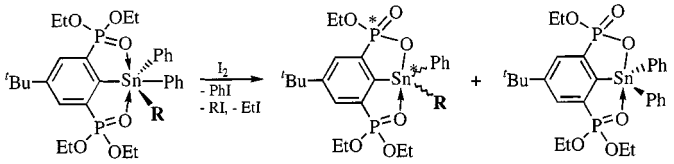


(3)

3, E = Sn
14, E = Si

8

Having established that the reaction of the intramolecularly coordinated tetraorganotin compound **3** with one molar equivalent of iodine gives the 2,3,1-benzoxaphosphastannole **8**, we decided to check whether it would be possible to prepare diastereomeric 2,3,1-benzoxaphosphastannoles starting from the tetraorganotin compound **2**. Reaction of **2** with iodine (Scheme 4) gave 78% of the two diastereomers of 2,3,1-benzoxaphosphastannole **15** in a ratio of 1:0.8, together with 22% of the 2,3,1-benzoxaphosphastannole **8**, as a result of $Sn-C^{phenyl}$ and $Sn-C^{alkyl}$ bond cleavage, respectively. In contrast, reaction of triphenyl(trimethylsilylmethyl)tin with iodine resulted in exclusive cleavage of the $Sn-C^{phenyl}$ bond. Due to the intramolecular O,C,O-coordination in **2**, the Sn−C bond cleavage does not simply follow the expected order of phenyl > alkyl as is well documented for tetraorganotin compounds.[17] A similar reversed order of bond cleavage has previously been reported by Weichmann[18] and by Jousseaume[19] for related compounds.



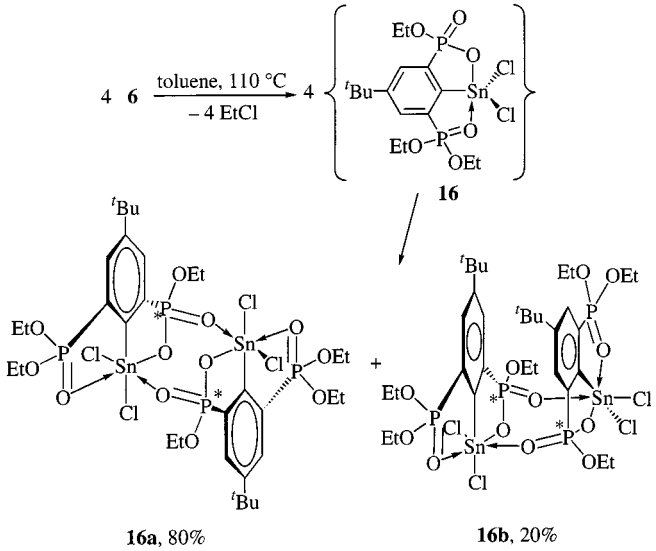
2 **15** (2 diastereomers, 1:0.8) **8**

R = CH_2SiMe_3 78% 22%

Scheme 4. Reaction of intramolecularly coordinated **2** with iodine

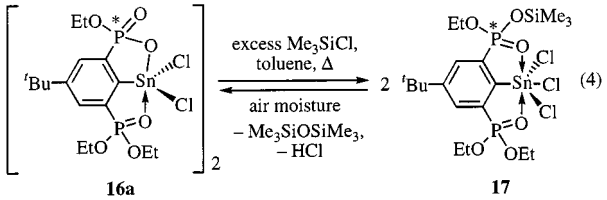
The ease with which the heterocycle **8** is formed suggests that the hexacoordinate monoorganotin trichloride **6** should also undergo intramolecular cyclization to provide a dichloro-substituted 2,3,1-benzoxaphosphastannole. Indeed, this reaction occurred simply by heating **6** in refluxing toluene for several hours. As a result of intermolecular O−Sn coordination, the dichloro-substituted 2,3,1-benzoxaphosphastannole **16** formed by this reaction dimerizes to give a diastereomeric mixture of **16a** (80%) and **16b** (20%), as was apparent from the observation of four ^{31}P-NMR signals at $\delta = 11.95$ [$J(^{31}P-^{119/117}Sn) = 316/301$ Hz, $J(^{31}P-^{119/117}Sn) = 137/125$ Hz] (**16a**), $\delta = 13.12$ [$J(^{31}P-^{119/117}Sn) = 304$ Hz] (**16b**), $\delta = 25.17$ [$J(^{31}P-^{119/117}Sn) = 334/320$ Hz] (**16a**), and $\delta = 25.14$ [$J(^{31}P-^{119/117}Sn) =$

324 Hz] (**16b**), in an integral ratio of 4:1:4:1 (Scheme 5). The diastereomer **16a** could be separated by recrystallization from toluene/chloroform in 65% yield. Its molecular structure is discussed below.



Scheme 5. Intramolecular cyclization of the monoorganotin trichloride **6**

Given that the reaction of the 2,3,1-benzoxaphosphastannole **8** with Me_3SiBr led to a ring-opening, we investigated the reaction of dimeric **16a** with Me_3SiCl (eq. 4). This led to a racemic mixture of the organotin trichloride **17**. Compound **17** proved to be moisture-sensitive and after stirring for 5 days at room temperature the monosilylphosphonate had been hydrolyzed to give almost quantitatively the starting material **16a** (eq. 4) by loss of HCl and $(Me_3Si)_2O$.



This reversible transesterification of **16a** to provide **17** was investigated by ^{31}P-NMR spectroscopic analysis of a sample that had been exposed to atmospheric moisture (Figure 1). The reaction of **17** with water to give **16a** was shown to be diastereoselective; there was no indication of the presence of any **16b**.

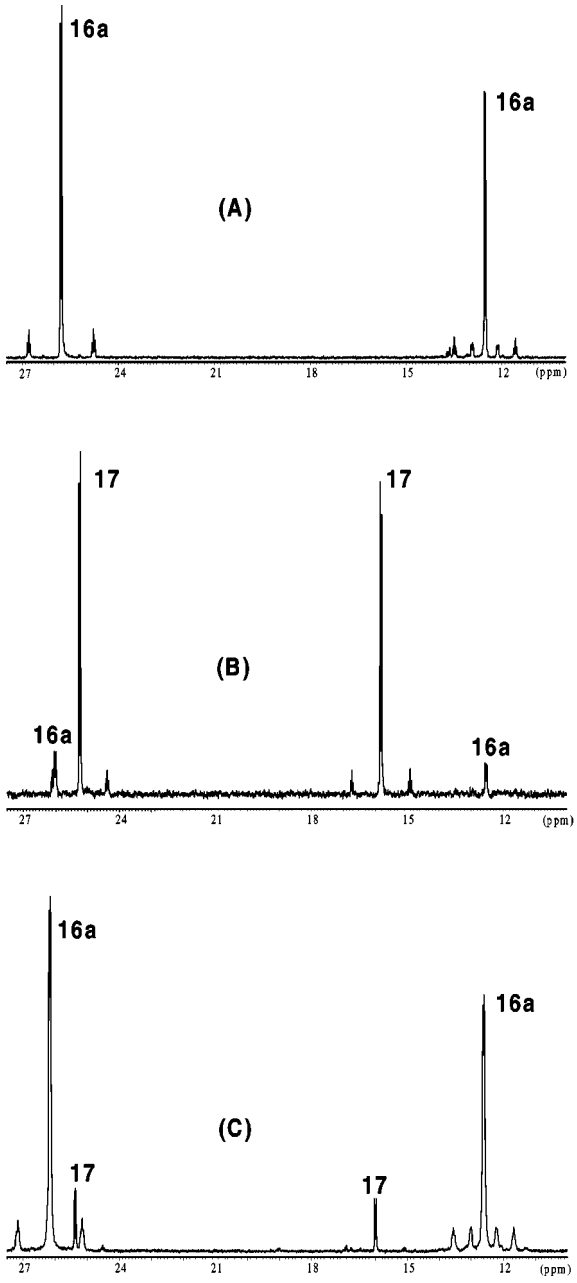


Figure 1. ^{31}P-NMR spectra in $CDCl_3$/toluene of the reversible transesterification of **16a** to **17**; (A) spectrum of a solution of **16a**, (B) spectrum after addition of Me_3SiCl, (C) spectrum after 5 d exposure of the sample to air

Molecular Structures of 2, 6, 8, and 16a

The molecular structures of compounds **2**, **6**, **8**, and **16a** are shown in Figures 2–5 and relevant crystallographic parameters are listed in Table 2. Selected bond lengths and bond angles are collected in Tables 3–5.

In compound **2**, the tetrahedral geometry of the tin atom is markedly distorted and the C–Sn–C angles are found in the range between 95.1(1)° and 122.7(1)°. As has previously been reported for the tetraorganotin compound **3**[1b] and 1-Ph_3Sn-2,4,6-$(CF_3)_3C_6H_2$,[14f] the Sn(1)–C(1) bond lengths of 2.184(3) Å is longer than the Sn–C^{aryl} bond lengths Sn(1)–C(11) [2.155(3) Å] and Sn(1)–C(21) [2.161(3) Å] as a result of the steric repulsion of the rigid ligand frame. In the molecular structure of **2**, two oxygen–tin contacts of 3.108(2) Å and 2.939(2) Å are found for Sn(1)–O(1) and Sn(1)–O(2), respectively, which are significantly shorter than the sum of the van der Waals′ radii of tin and oxygen

(3.700 Å).[20] The overall coordination geometry at the tin center is thus 4+2.

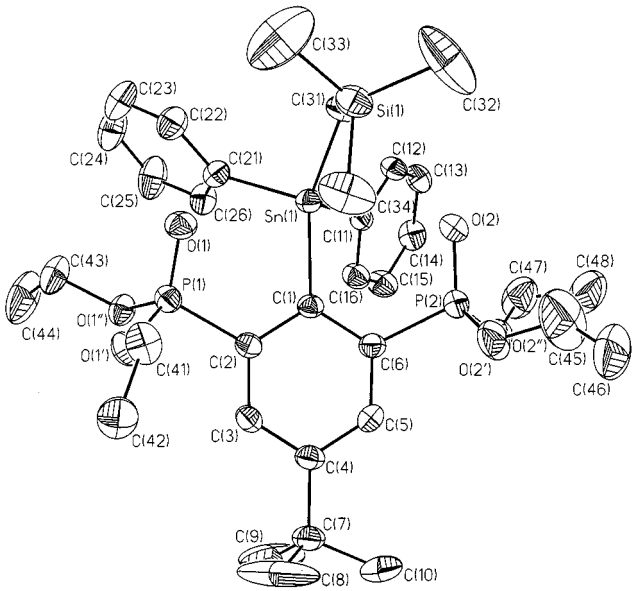


Figure 2. General view (SHELXTL-PLUS) of a molecule of **2** showing 30% probability displacement ellipsoids and the atom numbering scheme

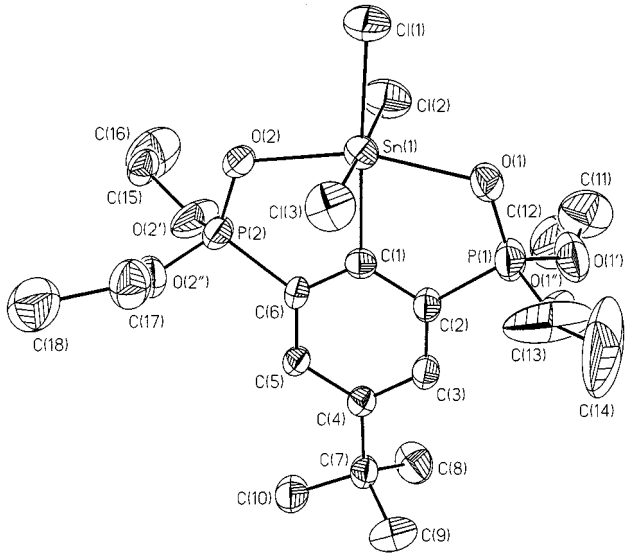


Figure 3. General view (SHELXTL-PLUS) of a molecule of **6** showing 30% probability displacement ellipsoids and the atom numbering scheme

In contrast to compound **2**, strong intramolecular O−Sn contacts are found in the monoorganotin trichloride **6**, in which the tin center adopts a distorted octahedral coordination geometry. The degree of distortion is reflected in *cis*-angles ranging from 80.4(1)° to 91.8(1)° and *trans*-angles of 177.8(1)°, 177.20(5)°, and 161.1(1)° for C(1)−Sn(1)−Cl(1), Cl(2)−Sn(1)−Cl(3), and O(1)−Sn(1)−O(2), respectively. In the previously reported {4-*tert*-Bu-2,6-$[P(O)(OEt)_2]_2$-C_6H_2}$SnPhCl_2$ (**4**),[1b] the same large deviation of the O−Sn−O angle [161.1(2)°] was found as a result of the rigid ligand frame. The intramolecular bond lengths O(1)−Sn(1) and O(2)−Sn(1) amount to 2.225(3) Å and 2.221(3) Å, respectively, and thus are slightly longer than the intermolecular O−Sn interactions reported for hexacoordinate monoorganotin trichlorides such as $RSnCl_3 \cdot 2\,HMPA$ (R = Ph,[21] Et,[22] Me;[23] O−Sn 2.124−2.180 Å), $RSnCl_3 \cdot 2\,DMF$ (R = *i*Pr,[24] Me;[25] O−Sn 2.150−2.22 Å), $EtSnCl_3 \cdot 2\,Ph_3PO$ (O−Sn 2.175 Å),[22] and $(Cl_3Sn)_2CH_2 \cdot 4\,DMSO$ (O−Sn 2.109 Å).[26] In the case of the intramolecularly hexacoordinated compound $CH_3OOCCH_2CH(COOCH_3)CH_2SnCl_3$[14h] and the heptacoordinate $[2,6\text{-}(MeO)_2C_6H_4]_3CHSnCl_3$,[14f] weak O−Sn interactions of 2.460−2.640 Å have been observed, whereas in the molecular structures of $CH_2{=}CHCH_2OC(O)CH_2CH_2SnCl_3 \cdot Ph_3PO$[14e] and BuOC(O)-$CH(CH_3)CH_2SnCl_3 \cdot Ph_3PO$,[14c] weak intramolecular O−Sn interactions of 2.413 and 2.356 Å have been found, along with strongly coordinated Ph_3PO ligands with O−Sn distances of 2.188 and 2.191 Å.

It is worth noting that in spite of a substantial difference in the Lewis acidities of the monoorganotin trichloride **6** and the diorganotin dichloride **4** [O−Sn 2.203/2.278 Å],[1b] the O−Sn contacts in the two compounds are still similar, which can be attributed to the rigidity of the ligand frame in compounds of type **B**. In contrast, for intermolecularly coordinated compounds, the O−Sn interaction depends strongly on the number of chlorine atoms bonded to tin, as demonstrated by the following two pairs of complexes: $Et_2SnCl_2 \cdot 2\,Ph_3PO$ (O−Sn 2.36/2.258 Å)[27] *vs.* $EtSnCl_3 \cdot 2\,Ph_3PO$ (O−Sn 2.175 Å)[2] and $Me_2SnCl_2 \cdot 2\,HMPA$ (O−Sn 2.231 Å)[28] *vs.* $MeSnCl_3 \cdot 2\,HMPA$ (O−Sn 2.175 Å).[23] The IR spectrum of **6** is indicative of strong P=O−Sn interactions, featuring a ν(P=O) band at 1170 cm^{-1}.

The 2,3,1-benzoxaphosphastannole **8** is characterized by a slightly distorted trigonal-bipyramidal tin center, with O(1) and O(2′) occupying axial and C(1), C(11), and C(21) occupying equatorial positions. The O(1)−Sn(1)−O(2′) angle amounts to 160.2(2)°, which is very close to the O−Sn−O angle in **6**. The configuration at tin in the molecular structure of **8** can be classified as being located on the tetrahedral−trigonal bipyramidal path.[29] The position on this path is given by the difference of the sums of the equatorial and axial angles [$\Delta\Sigma(\theta)$], which amounts to 90° for the ideal trigonal bipyramid, 0° for the ideal tetrahedron, and 77.7° for compound **8**. The displacement of the tin atom from the trigonal plane defined by C(1), C(11), and C(21) amounts to 0.136 Å in the direction of O(2′). Compared with the dative O−Sn bond lengths in **6**, the dative O−Sn interaction of 2.396(4) Å in **8** is slightly longer, but is nevertheless comparable to the O−Sn bond distance found in the structurally related [2-(diphenylphosphanyl)-phenyl]dimethyltin chloride [O−Sn 2.357 Å].[30] In the crystal lattice of **8**, a polymeric chain structure is observed as a result of the incorporation of water molecules, with each water molecule linking two 2,3,1-benzoxaphosphastannoles via O(1)···H−O(3)−H···O(2′) interactions. The IR spectrum of compound **8** shows two ν(P=O) absorptions at 1172 cm^{-1} and 1242 cm^{-1}, which correspond to the P(1)−O(1) and P(2)−O(2) bond distances of 1.488(4) and

1.463(6) Å, respectively, and which unambiguously demonstrate the simultaneous presence of both a strongly coordinating and a non-coordinating phosphonyl group. The slight decrease in the ν(P=O) of the non-coordinating P=O group in comparison with a "free" arylphosphonyl group[1b] can be attributed to weak hydrogen-bonding interactions.

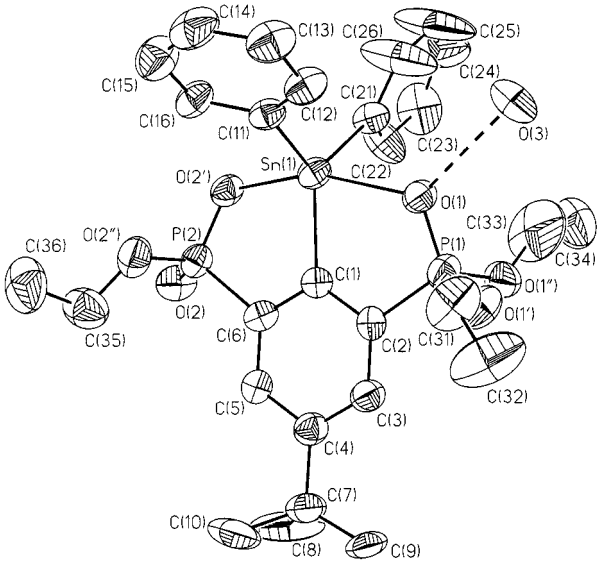


Figure 4. General view (SHELXTL-PLUS) of a molecule of **8** showing 30% probability displacement ellipsoids and the atom numbering scheme (symmetry transformations used to generate equivalent atoms: $a = -x + 0.5, -y + 0.5, -z + 0.5$)

As a result of both intermolecular and intramolecular O−Sn interactions, the tin centers in the dimeric 2,3,1-benzoxaphosphastannole **16a** adopt a distorted octahedral coordination geometry, with *cis*-angles ranging from 81.7(1)° to 97.97(7)°, and *trans*-angles of 172.8(1)°, 173.98(8)°, and 161.78(9)° for C(1)−Sn(1)−Cl(2), Cl(1)−Sn(1)−O(2a), and O(1)−Sn(1)−O(2′), respectively. In comparison with the corresponding O−Sn bond lengths in the monomeric 2,3,1-benzoxaphosphastannole **8**, the O−Sn bond lengths in **16a** are shortened. The dative bond O(1)−Sn(1) in **16a** amounts to 2.204(3) Å. The almost equal O(2′)−Sn(1) and O(2a)−Sn(1) bond lengths of 2.147(3) Å and 2.140(3) Å, respectively, are even shorter and lie in the typical range for O−Sn single bonds (2.15 Å),[31] showing that the phosphonyl group acts as a bidentate bridging ligand. Since the Lewis acidity of the tin atom in **16a** is greater than that of the tin atom in **8**, the former displays a distorted octahedral coordination as a result of dimerization. A similar control of coordination chemistry at tin has previously been reported for compounds of the type $MeXYSnCH_2C(Z)[P(O)(OiPr)_2]_2$ (X, Y = Me, Cl, Br; Z = H, Me). With X = Cl, Y = Me, and Z = H, a five-coordinate compound[15d] was observed, bearing a coordinated and a non-coordinated phosphonyl group. An increase in the Lewis acidity (X = Br, Y = Cl, Z = H)[32] led to the formation of a six-coordinate tin center, with two intramolecular O−Sn contacts. Intra- as well as intermolecular O−Sn coordination has been observed in a dimeric hexacoordinate compound by increasing the steric hindrance (X = Y = Br, Z = Me).[33]

The results of the IR spectroscopic measurements are in agreement with the X-ray data. The ν(P=O) band for the datively bonded phosphonyl group is found at 1168 cm^{-1}. Furthermore, a strong absorption at 1139 cm^{-1} can be assigned to the bidentate bridging phosphonyl group.

Conclusion

We have demonstrated the utility of the new O,C,O-coordinating ligand $\{4\text{-}tert\text{-Bu-2,6-}[P(O)(OEt)_2]_2C_6H_2\}^-$ in the synthesis of various intramolecularly coordinated organotin compounds. As a result of the high donor capacity of intramolecularly coordinating phosphonyl groups, the 2,3,1-benzoxaphosphastannole **8** and the tetraorganotin compound **10** react with Me_3SiBr under Sn−C rather than P−O bond cleavage. The high donor capacity and the rigidity of the ligand skeleton make the O,C,O-coordinating ligand $\{4\text{-}tert\text{-Bu-2,6-}[P(O)(OEt)_2]_2C_6H_2\}^-$ an eminently suitable substituent for the intramolecular donor-stabilization of highly reactive compounds.

Experimental Section

General: All manipulations were performed under an inert atmosphere of argon using standard Schlenk and vacuum line techniques. Solvents were distilled from the appropriate desiccants prior to use. Literature procedures were used to prepare $\{4\text{-}tert\text{-Bu-2,6-}[P(O)(OEt)_2]_2C_6H_2\}Li$ (**1**),[1b] $FSnPh_2(CH_2SiMe_3)$,[10] $\{4\text{-}tert\text{-Bu-2,6-}[P(O)(OEt)_2]_2C_6H_2\}SnPh_3$ (**3**),[1b] $\{4\text{-}tert\text{-Bu-2,6-}[P(O)(OEt)_2]_2C_6H_2\}SnPhCl_2$ (**4**),[1b] $\{4\text{-}tert\text{-Bu-2,6-}[P(O)(OEt)_2]_2C_6H_2\}SnCl$ (**5**),[11] $Ph_3SnCH_2SiMe_3$,[10] $\{4\text{-}tert\text{-Bu-2,6-}[P(O)(OEt)_2]_2C_6H_2\}SnPhBr_2$ (**7**),[1b] $1,5\text{-}[P(O)(OEt)_2]_2\text{-}2,4\text{-}(Ph_3Sn)_2C_6H_2$ (**10**),[1b] and $\{4\text{-}tert\text{-Bu-2,6-}[P(O)(OEt)_2]_2C_6H_2\}SiPh_3$ (**14**).[2p] − IR spectra were obtained using a Bruker FT-IR IFS 113v spectrometer. − ^{119}Sn-, ^{29}Si-, ^{13}C-, ^{1}H-, and ^{31}P-NMR spectra were recorded on Bruker DRX 400 and DPX 300 spectrometers. Chemical shifts δ are given in ppm and were referenced against Me_4Sn (^{119}Sn), Me_4Si (^{1}H, ^{13}C, ^{29}Si), and 85% H_3PO_4 (^{31}P).

{[2,6-Bis(diethoxyphosphonyl)-4-*tert*-butyl]phenyl}diphenyl(trimethylsilylmethyl)tin (2): To a solution of $FSnPh_2(CH_2SiMe_3)$ (1.66 g, 4.37 mmol) in 100 mL thf at −25°C, $\{4\text{-}tert\text{-Bu-2,6-}[P(O)(OEt)_2]_2C_6H_2\}Li$ (**1**) (1.80 g, 4.37 mmol) was added in small portions. After stirring for 20 h at room temp., the solid material formed was removed by filtration. The filtrate was concentrated to dryness in vacuo and the residue was recrystallized from ethanol to give 1.30 g (39%) of **2** as colorless crystals; m.p. 133°C. − ^{1}H NMR (400.13 MHz, C_6D_6): δ = 0.36 (s, 9 H, Me_3Si), 0.95 (t, 12 H, CH_3), 1.15 (s, 9 H, CH_3), 1.29 [s, $^{2}J(^{1}H-^{119}Sn)$ = 86 Hz, 2 H, CH_2Sn], 3.44−3.54 (complex pattern, 4 H, CH_2), 3.74−3.84 (complex pattern, 4 H, CH_2), 7.12−7.30 (complex pattern, 6 H, H^{Ph}), 8.12 [d, $^{3}J(^{1}H-^{119}Sn)$ = 49 Hz, 4 H, H^{Ph}], 8.60 (complex pattern, 2 H, H^{Ph}). − $^{13}C\{^{1}H\}$ NMR (100.63 MHz, $CDCl_3$): δ = 1.1 [s, $^{1}J(^{13}C-^{119/117}Sn)$ = 341/323 Hz, 1 C, CH_2Sn], 1.7 [s, $^{3}J(^{13}C-^{119}Sn)$ = 18 Hz, $^{1}J(^{13}C-^{29}Si)$ = 50 Hz, 3 C, Me_3Si], 15.98 [d, $^{3}J(^{13}C-^{31}P)$ = 4 Hz, 2 C, CH_3], 16.01 [d, $^{3}J(^{13}C-^{31}P)$ = 4 Hz, 2 C, CH_3], 30.9 (s, 3 C, CCH_3), 34.6 (s, 1 C, CCH_3), 61.55

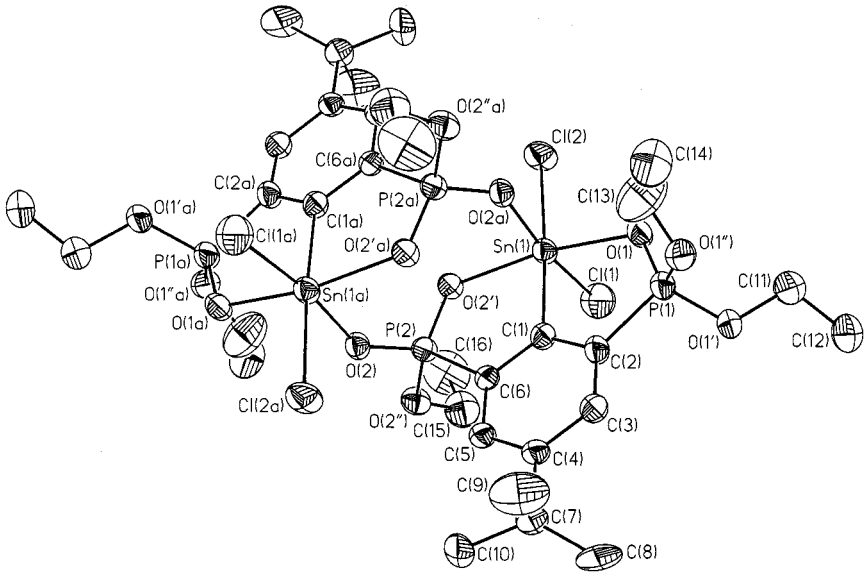


Figure 5. General view (SHELXTL-PLUS) of a molecule of **16a** showing 30% probability displacement ellipsoids and the atom numbering scheme (symmetry transformations used to generate equivalent atoms: $a = -x, -y, -z$)

[$^2J(^{13}C-^{31}P)$ = 3 Hz, 2 C, CH_2], 61.58 [$^2J(^{13}C-^{31}P)$ = 3 Hz, 2 C, CH_2], 126.9 (s, 2 C, C^{para}), 127.2 [s, $^3J(^{13}C-^{119}Sn)$ = 54 Hz, 4 C, C^{meta}], 133.1 (AA′BB′ pattern, 2 C, $C^{3,5}$), 136.9 [s, $^2J(^{13}C-^{119}Sn)$ = 36 Hz, 4 C, C^{ortho}], 137.3 [dd, $^1J(^{13}C-^{31}P)$ = 193 Hz, $^3J(^{13}C-^{31}P)$ = 20 Hz, 2 C, $C^{2,6}$], 147.5 [s, $^1J(^{13}C-^{119/117}Sn)$ = 554/530 Hz, 2 C, C^{ipso}], 150.2 [t, $^3J(^{13}C-^{31}P)$ = 13 Hz, 1 C, C^4], 153.9 [t, $^2J(^{13}C-^{31}P)$ = 23 Hz, 1 C, C^1]. – $^{119}Sn\{^1H\}$ NMR (111.91 MHz, $CDCl_3$): δ = −127.5 [t, $J(^{119}Sn-^{31}P)$ = 38 Hz]. – $^{31}P\{^1H\}$ NMR (121.49 MHz, $CDCl_3$): δ = 23.0 [$J(^{31}P-^{119}Sn)$ = 37 Hz]. – $^{29}Si\{^1H\}$ NMR (59.63 MHz, $CDCl_3$): δ = 5.0. – IR (KBr): $\tilde{\nu}$ = 1242 cm^{-1} (P=O). – $C_{34}H_{52}O_6P_2SiSn$ (765.55): calcd. C 53.34, H 6.84; found C 53.55, H 7.15.

{[2,6-Bis(diethoxyphosphonyl)-4-*tert*-butyl]phenyl}tin Trichloride (6): To a solution of {4-*tert*-Bu-2,6-$[P(O)(OEt)_2]_2C_6H_2$}SnCl (**5**) (2.00 g, 3.5 mmol) in 50 mL thf at room temp., $SnCl_4(thf)_2$ (1.20 g, 3.5 mmol) was added in small portions. After stirring the reaction mixture for 2 h, the solvent was evaporated in vacuo. The residue was suspended in 40 mL chloroform and after filtration the solvent was evaporated in vacuo. This procedure was repeated three times, eventually leading to the isolation of 1.3 g (58%) of **4** as colorless crystals; m.p. > 350°C. Crystals suitable for X-ray crystallography were grown from $CDCl_3$. – ^1H NMR (400.13 MHz, $CDCl_3$): δ = 1.36 (t, 12 H, CH_3), 1.37 (s, 9 H, CH_3), 3.93–4.00 (complex pattern, 4 H, CH_2), 4.41–4.50 (complex pattern, 4 H, CH_2), 7.96 (AA′BB′ pattern, 2 H, H^{Ph}). – $^{13}C\{^1H\}$ NMR (100.63 MHz, $CDCl_3$): δ = 15.5 (s, 4 C, CH_3), 30.6 (s, 3 C, CCH_3), 35.0 (s, 1 C, CCH_3), 65.4 (s, 4 C, CH_2), 123.1 [dd, $^1J(^{13}C-^{31}P)$ = 184 Hz, $^3J(^{13}C-^{31}P)$ = 17 Hz, 2 C, $C^{2,6}$], 131.2 (AA′BB′ pattern, 2 C, $C^{3,5}$), 154.4 [t, $^3J(^{13}C-^{31}P)$ = 12 Hz, 1 C, C^4], 173.1 [t, $^2J(^{13}C-^{31}P)$ = 17 Hz, 1 C, C^1]. – $^{119}Sn\{^1H\}$ NMR (149.18 MHz, $CDCl_3$): δ = −522.9 [t, $J(^{119}Sn-^{31}P)$ = 286 Hz]. – $^{31}P\{^1H\}$ NMR (161.98 MHz, $CDCl_3$): δ = 28.0 [$J(^{31}P-^{119/117}Sn)$ = 287/273 Hz]. – IR (KBr): $\tilde{\nu}$ = 1170 cm^{-1} (P=O). – $C_{18}H_{31}Cl_3O_6P_2Sn$ (630.48): calcd. C 34.29, H 4.95, Cl 16.87; found C 34.32, H 5.06, Cl 16.82.

5-*tert*-Butyl-7-diethoxyphosphonyl-3-ethoxy-3-oxo-1,1-diphenyl-2,3,1-benzoxaphosphastannole (8). – Method A: To a solution of {4-*tert*-Bu-2,6-$[P(O)(OEt)_2]_2C_6H_2$}$SnPh_3$ (**3**) (254 mg, 0.34 mmol) in 8 mL CH_2Cl_2 at 0°C, 4.15 mL of a bromine solution (0.08 mol/L in CH_2Cl_2) was added dropwise. The reaction mixture was stirred for 24 h at room temp., the solvent was then removed in vacuo, and the residue was recrystallized from hexane/diethyl ether to give 203 mg (93%) of **8** as colorless crystals; m.p. 166–168°C.

Method B: To a solution of {4-*tert*-Bu-2,6-$[P(O)(OEt)_2]_2$-C_6H_2}$SnPh_3$ (**3**) (232 mg, 0.31 mmol) in 5 mL CH_2Cl_2 at room temp., iodine (78 mg, 0.31 mmol) was added in small portions. The reaction mixture was stirred for 36 h at room temp., the solvent was then removed in vacuo, and the residue was recrystallized from hexane/diethyl ether to give 187 mg (89%) of **8** as colorless crystals; m.p. 167–168°C. – ^1H NMR (400.13 MHz, $CDCl_3$): δ = 1.13 (t, 3 H, CH_3), 1.25 (t, 3 H, CH_3), 1.28 (t, 3 H, CH_3), 1.34 (s, 9 H, CH_3), 3.73–4.14 (complex pattern, 6 H, CH_2), 7.34–7.37 (complex pattern, 6 H, H^{Ph}), 7.74–7.92 (complex pattern, 5 H, H^{Ph}), 8.25 (d, 1 H, H^{Ph}). – $^{13}C\{^1H\}$ NMR (100.63 MHz, $CDCl_3$): δ = 15.9 [d, $^3J(^{13}C-^{31}P)$ = 6 Hz, 1 C, CH_3], 16.0 [d, $^3J(^{13}C-^{31}P)$ = 6 Hz, 1 C, CH_3], 16.6 [d, $^3J(^{13}C-^{31}P)$ = 7 Hz, 1 C, CH_3], 31.1 (s, 3 C, CCH_3), 35.2 (s, 1 C, CCH_3), 61.0 [d, $^2J(^{13}C-^{31}P)$ = 6 Hz, 1 C, CH_2], 64.0 [d, $^2J(^{13}C-^{31}P)$ = 6 Hz, 1 C, CH_2], 64.1 [d, $^2J(^{13}C-^{31}P)$ = 6 Hz, 1 C, CH_2], 128.5 [s, $^3J(^{13}C-^{119}Sn)$ = 74 Hz, 4 C, C^{meta}], 128.9/132.1 [dd/dd, $^2J(^{13}C-^{31}P)$ = 14 Hz/$^2J(^{13}C-^{31}P)$ = 12 Hz, $^4J(^{13}C-^{31}P)$ = 3 Hz/$^4J(^{13}C-^{31}P)$ = 4 Hz, 2 C, $C^{3,5}$], 129.0/140.4 [dd/dd, $^1J(^{13}C-^{31}P)$ = 184 Hz/$^1J(^{13}C-^{31}P)$ = 180 Hz, $^3J(^{13}C-^{31}P)$ = 16 Hz/$^3J(^{13}C-^{31}P)$ = 16 Hz, 2 C, $C^{2,6}$], 129.8 [s, $^3J(^{13}C-^{119}Sn)$ = 16 Hz, 1 C, C^{para}], 129.9 [s, $^4J(^{13}C-^{119}Sn)$ = 16 Hz, 1 C, $C^{para'}$], 135.7 [s, $^2J(^{13}C-^{119}Sn)$ = 51 Hz, 2 C, C^{ortho}], 136.0 [s, $^2J(^{13}C-^{119}Sn)$ = 52 Hz, 2 C, $C^{ortho'}$], 138.2 [t, $J(^{13}C-^{31}P)$ = 4 Hz, 1 C, C^{ipso}], 138.8 [t, $J(^{13}C-^{31}P)$ = 3 Hz, 1 C, $C^{ipso'}$], 153.3 [t, $^2J(^{13}C-^{31}P)$ = 18 Hz, 1 C, C^1], 154.9 [t, $^3J(^{13}C-^{31}P)$ = 12 Hz, 1 C, C^4]. – $^{119}Sn\{^1H\}$ NMR (111.91 MHz, $CDCl_3$): δ = −223.6 [dd, $J(^{119}Sn-^{31}P)$ = 19/23 Hz]. – $^{31}P\{^1H\}$ NMR (121.49 MHz, $CDCl_3$): δ = 17.3, 28.6 [$J(^{31}P-^{119}Sn)$ = 19 Hz]. – IR (KBr): $\tilde{\nu}$ = 1172, 1242 cm^{-1} (P=O). – $C_{28}H_{36}O_6P_2Sn$ (649.27): calcd. C 51.80, H 5.58; found C 51.60, H 5.75.

{[4-*tert*-Butyl-6-diethoxyphosphonyl-2-ethoxy(trimethylsiloxy)-phosphonyl]phenyl}phenyltin Dibromide (9): To a solution of **8** (190 mg, 0.29 mmol) in 2.5 mL CH_2Cl_2 at −30°C was added Me_3SiBr (0.15 mL, 1.16 mmol). After stirring the reaction mixture for 20 min. at room temp., the solvent was evaporated, the residue was washed three times with 2 mL hexane, and dried in vacuo to give

115 mg (49%) of **9** as a colorless solid; m.p. 133°C. – ^{1}H NMR (400.13 MHz, $CDCl_3$): δ = 0.40 (s, 9 H, $SiMe_3$), 1.28 (t, 3 H, CH_3), 1.32 (t, 3 H, CH_3), 1.33 (t, 3 H, CH_3), 1.38 (s, 9 H, CH_3), 4.13–4.54 (complex pattern, 6 H, CH_2), 7.33–7.41 (complex pattern, 3 H, H^{Ph}), 7.92 [d, $^3J(^1H-^{31}P)$ = 13 Hz, 1 H, H^{Ph}], 7.94 [d, $^3J(^1H-^{31}P)$ = 14 Hz, 1 H, H^{Ph}], 8.14 [d, $^3J(^1H-^{119}Sn)$ = 142 Hz, 2 H, H^{Ph}]. – $^{13}C\{^1H\}$ NMR (100.63 MHz, $CDCl_3$): δ = 1.2 (s, 3 C, $SiMe_3$), 16.13 [d, $^3J(^{13}C-^{31}P)$ = 4 Hz, 1 C, CH_3], 16.17 [d, $^3J(^{13}C-^{31}P)$ = 4 Hz, 1 C, CH_3], 16.19 [d, $^3J(^{13}C-^{31}P)$ = 4 Hz, 1 C, CH_3], 31.2 (s, 3 C, CCH_3), 35.3 (s, 1 C, CCH_3), 65.22 [d, $^2J(^{13}C-^{31}P)$ = 4 Hz, 1 C, CH_2], 65.58 [d, $^2J(^{13}C-^{31}P)$ = 5 Hz, 1 C, CH_2], 65.67 [d, $^2J(^{13}C-^{31}P)$ = 5 Hz, 1 C, CH_2], 123.9 [dd, $^1J(^{13}C-^{31}P)$ = 183 Hz, $^3J(^{13}C-^{31}P)$ = 18 Hz, 1 C, C^2], 125.8 [dd, $^1J(^{13}C-^{31}P)$ = 191 Hz, $^3J(^{13}C-^{31}P)$ = 18 Hz, 1 C, C^6], 128.1 [s, $^3J(^{13}C-^{119/117}Sn)$ = 144/138 Hz, 2 C, C^{meta}], 129.6 [s, $^4J(^{13}C-^{119}Sn)$ = 27 Hz, 1 C, C^{para}], 131.3 [t, $J(^{13}C-^{31}P)$ = 3 Hz, 2 C, $C^{3,5}$], 133.9 [s, $^2J(^{13}C-^{119}Sn)$ = 87 Hz, 2 C, C^{ortho}], 149.4 [s, $J(^{13}C-^{31}P)$ = 5 Hz, 1 C, C^{ipso}], 153.5 [t, $^3J(^{13}C-^{31}P)$ = 13 Hz, 1 C, C^4], 172.8 [t, $^2J(^{13}C-^{31}P)$ = 18 Hz, 1 C, C^1]. – $^{119}Sn\{^1H\}$ NMR (149.18 MHz, $CDCl_3$): δ = −439.6 [t, $J(^{119}Sn-^{31}P)$ = 100 Hz]. – $^{31}P\{^1H\}$ NMR (161.98 MHz, $CDCl_3$): δ = 17.3 [$J(^{31}P-^{119/117}Sn)$ = 103/98 Hz, $^4J(^{31}P-^{31}P)$ = 7 Hz], 26.7 [$J(^{31}P-^{119/117}Sn)$ = 97/93 Hz, $^4J(^{31}P-^{31}P)$ = 7 Hz]. – IR (KBr): $\tilde{\nu}$ = 1173 cm^{-1} (P=O). – $C_{25}H_{40}Br_2O_6P_2SiSn$ (805.17): calcd. C 37.29, H 5.00; found C 36.70, H 5.20.

1,5-Bis(bromodiphenylstannyl)-2,4-bis(diethoxyphosphonyl)benzene (11): To a solution of 1,5-$[P(O)(OEt)_2]_2$-2,4-$(Ph_3Sn)_2C_6H_2$ (**10**) (139 mg, 0.13 mmol) in 2.5 mL CH_2Cl_2 at −50°C was added Me_3SiBr (0.15 mL, 1.16 mmol). The reaction mixture was allowed to warm to room temp., the solvent was evaporated in vacuo, and the residue was washed three times with 2 mL hexane to give 93 mg (67%) of **11** as colorless solid; m.p. 230–231°C (Lit. 231–233°C)[1b]. – $^{119}Sn\{^1H\}$ NMR (149.18 MHz, $CDCl_3$): δ = −180.7 (AA′XX′ pattern). – $^{31}P\{^1H\}$ NMR (161.98 MHz, $CDCl_3$): δ = 25.8 [$J(^{31}P-^{119}Sn)$ = 34 Hz, $^5J(^{31}P-^{119}Sn)$ = 15 Hz].

5-*tert*-Butyl-3-hydroxy-3-oxo-1,1-diphenyl-7-phosphono-2,3,1-benzoxaphosphastannole (13): To a solution of {4-*tert*-Bu-2,6-$[P(O)(OEt)_2]_2C_6H_2$}$SnPh_3$ (**3**) (100 mg, 0.13 mmol) in 0.5 mL $CDCl_3$ at −30°C, Me_3SiBr (0.10 mL, 0.77 mmol) was added dropwise. The reaction mixture was allowed to warm to room temp., whereupon ^{119}Sn-, ^{31}P-, and ^{29}Si-NMR spectra were recorded, which indicated the formation of {4-*tert*-Bu-2,6-$[P(O)(OSiMe_3)_2]_2C_6H_2$}$SnPh_3$ (**12**) ($^{119}Sn\{^1H\}$ NMR (149.18 MHz, $CDCl_3$): δ = −188.4. – $^{31}P\{^1H\}$ NMR (161.98 MHz, $CDCl_3$): δ = −2.82 [$J(^{31}P-^{119}Sn)$ = 40 Hz]. – $^{29}Si\{^1H\}$ NMR (79.49 MHz, $CDCl_3$): δ = 20.1). After distilling off the solvent, the residue was redissolved in 2 mL acetone, water (0.15 mL) was added, and the solution was stirred for 2 h at room temperature. The solvent was then removed in vacuo and the residue was washed three times with 2 mL hexane to give 41 mg (57%) of **13** as a colorless solid; m.p. 280°C (dec.). – ^{1}H NMR (400.13 MHz, [D_6]-acetone): δ = 1.46 (s, 9 H, CH_3), 7.29–7.34 (complex pattern, 6 H, H^{Ph}), 7.80–8.00 (complex pattern, 4 H, H^{Ph}), 8.06–8.08 (complex pattern, 2 H, H^{Ph}). – $^{119}Sn\{^1H\}$ NMR (149.18 MHz, [D_6]acetone): δ = −239.9 [t, $J(^{119}Sn-^{31}P)$ = 70 Hz]. – $^{31}P\{^1H\}$ NMR (161.98 MHz, [D_6]acetone): δ = 20.3, 20.4. – IR (KBr): $\tilde{\nu}$ = 1173 cm^{-1} (P=O), 3400 cm^{-1} (br, O–H). – $C_{22}H_{24}O_6P_2Sn$ (565.11): calcd. C 46.76, H 4.28; found C 46.55, H 4.65.

Reaction of {4-*tert*-Bu-2,6-$[P(O)(OEt)_2]_2C_6H_2$}$SnPh_3$ (3) with Ph_2SnCl_2: To a solution of **3** (150 mg, 0.20 mmol) in 4 mL toluene was added Ph_2SnCl_2 (69 mg, 0.20 mmol) and the reaction mixture was heated under reflux for 5 h. The solvent was then removed in vacuo, the residue was redissolved in 0.5 mL $CDCl_3$ and the ^{119}Sn-NMR spectrum of this solution was recorded. – $^{119}Sn\{^1H\}$ NMR (149.18 MHz, $CDCl_3$): δ = −125, −221 [t, $J(^{119}Sn-^{31}P)$ = 19 Hz], −243 (br.), −284 (br.); integral ratio 0.6:2.6:1.6:1.9.

Reaction of {4-*tert*-Bu-2,6-$[P(O)(OEt)_2]_2$-C_6H_2}$SiPh_3$ (15) with Ph_2SnCl_2: To a solution of **14** (60 mg, 0.090 mmol) in 5 mL toluene was added Ph_2SnCl_2 (31 mg, 0.090 mmol) and the reaction mixture was heated under reflux for 24 h. The solvent was then removed in vacuo, the residue was redissolved in 0.5 mL $CDCl_3$, and the ^{119}Sn-NMR spectrum of this solution was recorded. – $^{119}Sn\{^1H\}$ NMR (149.18 MHz, $CDCl_3$): δ = −223 [t, $J(^{119}Sn-^{31}P)$ = 19 Hz], −236 (br.), −258 (br.); integral ratio 1.0:0.3:0.6.

Reaction of {[2,6-Bis(diethoxyphosphonyl)-4-*tert*-butyl]phenyl}-diphenyl(trimethylsilylmethyl)tin (2) with Iodine: To a solution of **2** (250 mg, 0.33 mmol) in 5 mL CH_2Cl_2 was added iodine (83 mg, 0.33 mmol). The reaction mixture was stirred at room temp. for 24 h, then the solvent was removed in vacuo, the residue was redissolved in 0.5 mL of $CDCl_3$, and the ^{119}Sn-NMR spectrum of this solution recorded. – $^{119}Sn\{^1H\}$ NMR (149.18 MHz, $CDCl_3$): δ = −138.3 ($W_{1/2}$ = 21 Hz), −139.2 ($W_{1/2}$ = 23 Hz), −224.1 ($W_{1/2}$ = 58 Hz); integral ratio 1:0.8:0.5.

Bis[5-*tert*-butyl-1,1-dichloro-7-diethoxyphosphonyl-3-ethoxy-3-oxo-2,3,1-benzoxaphosphastannole] (16): A solution of **6** (500 mg, 0.79 mmol) in 25 mL toluene was heated under reflux for 16 h. After removing the solid material formed by filtration, the solvent was removed in vacuo and the residue was redissolved in $CDCl_3$. The ^{31}P-NMR spectrum of this solution was recorded, which indicated formation of the two diastereomers **16a** and **16b**. – $^{31}P\{^1H\}$ NMR (161.98 MHz, toluene/D_2O-cap.): **16a**: δ = 11.95 [d, $^4J(^{31}P-^{31}P)$ = 6.8 Hz, $J(^{31}P-^{119/117}Sn)$ = 316/301 Hz, $J(^{31}P-^{119/117}Sn)$ = 137/125 Hz], 25.17 [d, $^4J(^{31}P-^{31}P)$ = 6.6 Hz, $J(^{31}P-^{119/117}Sn)$ = 334/320 Hz]. – **16b**: δ = 13.12 [d, $^4J(^{31}P-^{31}P)$ = 7.8 Hz, $J(^{31}P-^{119/117}Sn)$ = 304 Hz], 25.14 [d, $^4J(^{31}P-^{31}P)$ = 7.0 Hz, $J(^{31}P-^{119/117}Sn)$ = 324 Hz]. The $CDCl_3$ was removed in vacuo and the residue was recrystallized from toluene/$CHCl_3$ to give 290 mg (65%) of the diastereomer **16a** as colorless crystals; m.p. > 350°C. – ^{1}H NMR (400.13 MHz, $CDCl_3$): δ = 1.04 (t, 6 H, CH_3), 1.30 (t, 12 H, CH_3), 1.34 (s, 18 H, CH_3), 3.68–3.78 (complex pattern, 2 H, CH_2), 3.92–4.02 (complex pattern, 2 H, CH_2), 4.09–4.23 (complex pattern, 4 H, CH_2), 4.27–4.41 (complex pattern, 4 H, CH_2), 7.77–7.91 [d, $^3J(^1H-^{31}P)$ = 13.4 Hz, $^4J(^1H-^{119}Sn)$ = 41.8 Hz, 2 H, H^{Ph}], 8.12–8.26 [d, $^3J(^1H-^{31}P)$ = 13.6 Hz, $^4J(^1H-^{119}Sn)$ = 41.0 Hz, 2 H, H^{Ph}]. – $^{13}C\{^1H\}$ NMR (100.63 MHz, $CDCl_3$): δ = 15.1 (m, 6 C, CH_3), 30.3 (s, 6 C, CCH_3), 34.6 (s, 2 C, CCH_3), 62.2 [d, $^2J(^{13}C-^{31}P)$ = 5 Hz, 2 C, CH_2], 64.5 [d, $^2J(^{13}C-^{31}P)$ = 5 Hz, 2 C, CH_2], 64.7 [d, $^2J(^{13}C-^{31}P)$ = 5 Hz, 2 C, CH_2], 122.6 [dd, $^1J(^{13}C-^{31}P)$ = 181 Hz, $^3J(^{13}C-^{31}P)$ = 16 Hz, 2 C, C^2], 128.6 [dd, $^2J(^{13}C-^{31}P)$ = 12 Hz, $^4J(^{13}C-^{31}P)$ = 3 Hz, 2 C, C^5], 129.5 [dd, $^1J(^{13}C-^{31}P)$ = 176 Hz, $^3J(^{13}C-^{31}P)$ = 16 Hz, 2 C, C^6], 132.7 [dd, $^2J(^{13}C-^{31}P)$ = 12 Hz, $^4J(^{13}C-^{31}P)$ = 3 Hz, 2 C, C^3], 154.1 [dd, $^3J(^{13}C-^{31}P)$ = 13 Hz, 2 C, C^4], 167.4 [dd, $^2J(^{13}C-^{31}P)$ = 17 Hz, $^2J(^{13}C-^{31}P)$ = 16 Hz, 2 C, C^1]. – $^{119}Sn\{^1H\}$ NMR (149.18 MHz, $CDCl_3$): δ = −547.9 [ddd, $^2J(^{119}Sn-^{31}P)$ = 139 Hz, $J(^{119}Sn-^{31}P)$ = 320 Hz, $J(^{119}Sn-^{31}P)$ = 336 Hz]. – $^{31}P\{^1H\}$ NMR (161.98 MHz, $CDCl_3$): δ = 11.9 [d, $^4J(^{31}P-^{31}P)$ = 6.6 Hz, $J(^{31}P-^{119/117}Sn)$ = 316/302 Hz, $J(^{31}P-^{119/117}Sn)$ = 137/122 Hz], 25.2 [d, $^4J(^{31}P-^{31}P)$ = 6.6 Hz, $J(^{31}P-^{119/117}Sn)$ = 335/321 Hz]. – IR (KBr): $\tilde{\nu}$ = 1168, 1139 cm^{-1} (P=O). – $C_{32}H_{52}Cl_4O_{12}P_4Sn_2$ (1131.93): calcd. C 33.96, H 4.63; found C 33.55, H 4.79.

Crystallography: Intensity data for the colorless crystals were collected on a Nonius Kappa CCD diffractometer using graphite-monochromated Mo-K_α (λ = 0.71069 Å) radiation at 293 K. The

Table 2. Crystallographic data for **2**, **6**, **8**, and **16a**

	2	**6**	**8**	**16a**
formula	$C_{34}H_{52}O_6P_2SiSn$	$C_{18}H_{31}O_6P_2Cl_3Sn \cdot 0.5\ C_7H_8$	$C_{28}H_{36}O_6P_2Sn \cdot 0.5\ H_2O$	$C_{32}H_{52}Cl_4O_{12}P_4Sn_2$
form. wt.	765.48	676.47	658.22	1131.80
cryst. syst.	triclinic	orthorhombic	monoclinic	monoclinic
cryst. size, mm	0.20 × 0.15 × 0.15	0.30 × 0.15 × 0.15	0.20 × 0.05 × 0.03	0.40 × 0.15 × 0.15
space group	$P\bar{1}$	*Pbcn*	$P2_1/n$	$P2_1/n$
a, Å	11.464(1)	15.640(1)	12.453(1)	10.268(1)
b, Å	21.736(1)	19.706(1)	14.598(1)	11.253(1)
c, Å	14.134(1)	19.346(1)	17.316(1)	20.563(1)
α, °	72.633(1)	90	90	90
β, °	85.610(1)	90	92.934(1)	101.902(1)
γ, °	85.232(1)	90	90	90
V, Å^3	1959.8(3)	5962.5(6)	3143.7(4)	2324.9(3)
Z	2	8	4	2
ρ_{calcd}, Mg/m^3	1.297	1.507	1.391	1.617
μ, mm^{-1}	0.802	1.265	0.953	1.494
F(000)	796	2744	1348	1136
θ range, deg	2.73 to 28.76	4.14 to 25.01	3.24 to 21.17	3.54 to 25.69
index ranges	$-15 \le h \le 15$	$-16 \le h \le 16$	$-12 \le h \le 12$	$-12 \le h \le 12$
	$-17 \le k \le 17$	$-23 \le k \le 23$	$-13 \le k \le 13$	$-13 \le k \le 13$
	$-18 \le l \le 19$	$-23 \le l \le 23$	$-17 \le l \le 17$	$-21 \le l \le 21$
no. of reflns. colld.	22983	77474	13616	31787
completeness to θ_{max}	89.4	95.9	83.9	93.4
no. of indep. reflns./R_{int}	9111/0.042	5038/0.048	2907/0.066	4125/0.047
no. of reflns. obsd. with [$I > 2\sigma(I)$]	4843	2427	1717	2430
no. of refined params.	407	347	372	291
GooF (F^2)	0.859	0.831	0.884	0.895
*R*1 (*F*) [$I > 2\sigma(I)$]	0.0422	0.0381	0.0390	0.0331
*wR*2 (F^2) (all data)	0.0908	0.0807	0.0817	0.0700
$(\Delta/\sigma)_{max}$	0.001	0.001	< 0.001	< 0.001
Largest diff. peak/hole, e/Å^3	0.483/−0.370	0.350/−0.352	0.280/−0.202	0.306/−0.321

Table 3. Selected interatomic distances (Å) and angles (deg) for **2** and **6**

	2 X = C(11); Y = C(21); Z = C(31)	**6** X = Cl(1); Y = Cl(2); Z = Cl(3)
Sn(1)−C(1)	2.184(3)	2.132(4)
Sn(1)−X	2.155(3)	2.332(1)
Sn(1)−Y	2.161(3)	2.434(1)
Sn(1)−Z	2.144(3)	2.422(1)
Sn(1)−O(1)	3.108(2)	2.225(3)
Sn(1)−O(2)	2.939(2)	2.221(3)
P(1)−O(1)	1.456(2)	1.493(3)
P(2)−O(2)	1.452(2)	1.499(3)
C(1)−Sn(1)−X	100.0(1)	177.8(1)
C(1)−Sn(1)−Y	114.9(1)	90.9(1)
C(1)−Sn(1)−Z	122.7(1)	91.8(1)
X−Sn(1)−Y	95.1(1)	88.49(5)
X−Sn(1)−Z	114.2(1)	88.91(6)
Y−Sn(1)−Z	106.6(1)	177.20(5)
C(1)−Sn(1)−O(1)	68.63(9)	80.4(1)
C(1)−Sn(1)−O(2)	73.4(1)	80.7(1)
X−Sn(1)−O(1)	153.1(1)	97.48(8)
X−Sn(1)−O(2)	74.6(1)	101.39(8)
Y−Sn(1)−O(1)	70.1(1)	90.44(9)
Y−Sn(1)−O(2)	168.1(1)	89.69(8)
Z−Sn(1)−O(1)	91.9(1)	90.93(8)
Z−Sn(1)−O(2)	73.5(1)	89.81(8)
O(1)−Sn(1)−O(2)	121.70(7)	161.1(1)
C(2)−P(1)−O(1)	112.5(1)	107.8(2)
C(6)−P(2)−O(2)	114.4(2)	108.7(2)
P(1)−O(1)−Sn(1)	96.7(1)	117.6(2)
P(2)−O(2)−Sn(1)	102.6(1)	116.3(1)

Table 4. Selected interatomic distances (Å) and angles (deg) for **8**

Sn(1)−C(1)	2.110(6)	P(1)−O(1)	1.488(4)
Sn(1)−C(11)	2.100(8)	P(2)−O(2)	1.463(6)
Sn(1)−C(21)	2.078(9)	P(2)−O(2′)	1.524(5)
Sn(1)−O(1)	2.396(4)	O(1)−O(3)	2.84(1)
Sn(1)−O(2′)	2.124(4)	O(3)−O(2a)	2.76(1)
C(1)−Sn(1)−C(11)	120.7(3)	C(21)−Sn(1)−O(2′)	99.7(3)
C(1)−Sn(1)−C(21)	121.7(3)	O(1)−Sn(1)−O(2′)	160.2(2)
C(11)−Sn(1)−C(21)	116.3(4)	O(1)−P(1)−C(2)	108.8(3)
C(1)−Sn(1)−O(1)	77.6(2)	O(2′)−P(2)−C(6)	103.3(3)
C(1)−Sn(1)−O(2′)	82.7(2)	P(1)−O(1)−Sn(1)	113.3(2)
C(11)−Sn(1)−O(1)	91.8(3)	P(2)−O(2′)−Sn(1)	119.1(2)
C(11)−Sn(1)−O(2′)	99.2(3)	O(1)−O(3)−O(2a)	111.9(3)
C(21)−Sn(1)−O(1)	89.9(3)		

a = $-x + 0.5, y + 0.5, -z + 0.5$.

data collection covered almost the whole sphere of reciprocal space with 360 frames by ω-rotation (Δ/ω = 1°) at two times, 10 s (**2**), 20 s (**6**, **16a**), and 75 s (**8**), per frame. The crystal-to-detector distance was 2.7 cm (**2**, **6**, **16a**) and 2.9 cm (**8**). Crystal decay was monitored by repeating the initial frames at the end of the data collection. The data were not corrected for absorption effects. On analyzing the duplicate reflections, no indication of any decay was found. The structure was solved by direct methods SHELXS-97[35] (Sheldrick, 1990) and successive difference Fourier syntheses. Refinement employed full-matrix least-squares methods SHELXL-97[36] (Sheldrick, 1997). The H atoms were placed in geometrically calculated positions and refined with common isotropic temperature factors for alkyl and aryl H atoms [C−H$^{prim.}$ 0.96 Å, C−H$^{sec.}$ 0.97 Å, C−H^{aryl} 0.93 Å; U_{iso} 0.139(3) (**2**), 0.166(5) (**6**), 0.189(9) (**9**), 0.131(5) Å^2 (**16a**)]. The occupancy (s.o.f.) of the water molecule O(3) in **8** was found to be 0.5. Disordered groups were found in **2** [OEt group C46 and C46′ (s.o.f. 0.5)], in **6** [OEt groups C11, C13, C14, C15, C17, C11′, C13′, C14′, C15′, C17′ (s.o.f. 0.5)], in **8** [*t*-Bu group C8,

Table 5. Selected interatomic distances (Å) and angles (deg) for **16a**

Sn(1)−C(1)	2.122(4)	P(1)−O(1′)	1.560(3)
Sn(1)−Cl(1)	2.399(1)	P(1)−O(1′′)	1.549(3)
Sn(1)−Cl(2)	2.321(1)	P(1)−C(2)	1.780(4)
Sn(1)−O(1)	2.204(3)	P(2)−O(2)	1.502(3)
Sn(1)−O(2′)	2.147(3)	P(2)−O(2′)	1.529(3)
Sn(1)−O(2a)	2.140(3)	P(2)−O(2′′)	1.565(3)
P(1)−O(1)	1.501(3)	P(2)−C(6)	1.803(4)
C(1)−Sn(1)−Cl(1)	96.2(1)	O(1)−P(1)−O(1′′)	113.01(17)
C(1)−Sn(1)−Cl(2)	172.8(1)	O(1)−P(1)−O(1′)	114.33(18)
C(1)−Sn(1)−O(1)	81.2(1)	O(1′′)−P(1)−O(1′)	104.28(18)
C(1)−Sn(1)−O(2a)	88.8(1)	O(1)−P(1)−C(2)	108.25(17)
C(1)−Sn(1)−O(2′)	81.7(1)	O(1′′)−P(1)−C(2)	110.6(2)
Cl(1)−Sn(1)−O(2a)	173.98(8)	O(1′)−P(1)−C(2)	106.19(18)
Cl(1)−Sn(1)−Cl(2)	90.97(5)	O(2)−P(2)−O(2′)	115.83(14)
Cl(1)−Sn(1)−O(1)	91.65(9)	O(2)−P(2)−O(2′′)	104.01(16)
Cl(1)−Sn(1)−O(2′)	96.36(8)	O(2′)−P(2)−O(2′′)	111.40(16)
O(1)−Sn(1)−O(2′)	161.78(9)	O(2)−P(2)−C(6)	111.20(17)
O(1)−Sn(1)−O(2a)	84.2(1)	O(2′)−P(2)−C(6)	105.19(16)
O(1)−Sn(1)−Cl(2)	98.23(7)	O(2′′)−P(2)−C(6)	109.21(16)
Cl(2)−Sn(1)−O(2a)	84.06(7)	P(1)−O(1)−Sn(1)	116.9(2)
Cl(2)−Sn(1)−O(2′)	97.97(7)	P(2)−O(2)−Sn(1a)	138.0(2)
O(2a)−Sn(1)−O(2′)	89.6(1)	P(2)−O(2′)−Sn(1)	119.0(1)

a = $-x$, $-y$, $-z$.

C9, C10, C8′, C9′, C10′ (s.o.f. 0.5)], and in **16a** [*t*-Bu group C8, C9, C10, C8′, C9′, C10′; OEt group C14, C14′, (s.o.f. 0.5)]. Atomic scattering factors for neutral atoms and real and imaginary dispersion terms were taken from *International Tables for X-ray Crystallography.*[37] The figures were created by SHELXTL-Plus[38] (Sheldrick, 1991). Crystallographic data are given in Table 2; selected bond distances and angles for **2** and **6** in Table 3, for **8** and Table 4, and for **16a** and Table 5. Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications nos. CCDC-102841 (**8**), CCDC-102842 (**2**), CCDC-102843 (**6**), and CCDC-102844 (**16a**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. [Fax: (internat.) + 44-1223/336033; E-mail: deposit@ccdc.cam.ac.uk].

Acknowledgements

We gratefully acknowledge support of this work by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie.

[1] [1a] J. T. B. H. Jastrzebski, G. van Koten, *Adv. Organomet. Chem.* **1993**, *35*, 241−294 and references therein. − [1b] M. Mehring, M. Schürmann, K. Jurkschat, *Organometallics* **1998**, *17*, 1227−1237 and references therein. − [1c] N. Pieper, C. Klaus-Mrestani, M. Schürmann, K. Jurkschat, M. Biesemans, I. Verbruggen, J. C. Martins, R. Willem, *Organometallics* **1997**, *16*, 1043−1053. − [1d] P. Steenwinkel, J. T. B. H. Jastrzebski, B.-J. Deelman, D. M. Grove, H. Koojman, N. Veldman, W. J. J. Smeets, A. L. Spek, G. van Koten, *Organometallics* **1997**, *16*, 5486−5498. − [1e] D. Dakternieks, K. Jurkschat, R. Tozer, J. Hook, E. R. T. Tiekink, *Organometallics* **1997**, *16*, 3696−3706. − [1f] M. Beuter, U. Kolb, A. Zickgraf, E. Bräu, M. Bletz, M. Dräger, *Polyhedron* **1997**, *16*, 4005−4015. − [1g] U. Kolb, M. Dräger, M. Dargatz, K. Jurkschat, *Organometallics* **1995**, *14*, 2827−2834. − [1h] T. P. Lockhart, F. Davidson, *Organometallics* **1987**, *6*, 2471−2478. − [1i] T. P. Lockhart, J. C. Calabrese, F. Davidson, *Organometallics* **1987**, *6*, 2479−2483. − [1j] F. Huber, H. Preut, E. Hoffmann, M. Gielen, *Acta Cryst.* **1989**, *C45*, 51−54. − [1k] M. Suzuki, I.-H. Son, R. Noyori, H. Masuda, *Organometallics* **1990**, *9*, 3043−3053.

[2] [2a] R. J. P. Corriu, J. C. Young, Hypervalent Silicon Compounds, in *The Chemistry of Organic Silicon Compounds* (Eds.: S. Patai, Z. Rappoport), Wiley, New York, **1989**, 1241−1288. − [2b] C. Chuit, R. J. P. Corriu, C. Reyé, J. C. Young, *Chem. Rev.* **1993**, *93*, 1371−1448. − [2c] R. R. Holmes, *Chem. Rev.* **1996**, *96*, 927−950. − [2d] S. N. Tandura, N. V. Alekseev, M. G. Voronkov, *Top. Curr. Chem.* **1986**, *131*, 99−189. − [2e] F. H. Carré, R. J. P. Corriu, G. F. Lanneau, P. Merle, F. Soulairol, J. Yao, *Organometallics* **1997**, *16*, 3878−3888. − [2f] F. Carré, C. Chuit, R. J. P. Corriu, A. Mehdi, C. Reyé, *Angew. Chem.* **1994**, *106*, 1152−1154; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 1097. − [2g] F. Carré, C. Chuit, R. J. P. Corriu, A. Fanta, A. Mehdi, C. Reyé, *Organometallics* **1995**, *14*, 194−198. − [2h] W. Ziche, B. Ziemer, P. John, J. Weis, N. Auner, *J. Organomet. Chem.* **1996**, *521*, 29−31. − [2i] N. Auner, R. Probst, F. Hahn, E. Herdtweck, *J. Organomet. Chem.* **1993**, *459*, 25−41. − [2j] M. Tasaka, M. Hirotsu, M. Kojima, S. Utsuno, Y. Yoshikawa, *Inorg. Chem.* **1996**, *35*, 6981−6986. − [2k] I. Kalikhman, S. Krivonos, D. Stalke, T. Kottke, D. Kost, *Organometallics* **1997**, *16*, 3255−3257. − [2l] M. Weinmann, A. Gehrig, B. Schiemenz, G. Huttner, B. Nuber, G. Rheinwald, H. Lang, *J. Organomet. Chem.* **1998**, *563*, 61−72. − [2m] V. Gevorgyan, L. Borisova, A. Vyater, V. Ryabova, E. Lukevics, *J. Organomet. Chem.* **1997**, *548*, 149−155. − [2n] A. Kawachi, Y. Tanaka, K. Tamao, *Organometallics* **1997**, *16*, 5102−5107. − [2o] A. Mix, U. H. Berlekamp, H.-G. Stammler, B. Neumann, P. Jutzi, *J. Organomet. Chem.* **1996**, *521*, 177−183. − [2p] K. Jurkschat, C. Mügge, J. Schmidt, A. Tzschach, *J. Organomet. Chem.* **1985**, *287*, C1−C4. − [2q] M. Mehring, M. Schürmann, K. Jurkschat, *Main Group Metal Chem.* **1998**, *21*, 635−646 and references therein.

[3] [3a] E. Vedejs, A. R. Haight, W. O. Moss, *J. Am. Chem. Soc.* **1992**, *114*, 6556−6558. − [3b] J. M. Brown, M. Pearson, J. T. B. H. Jastrzebski, G. van Koten, *J. Chem. Soc., Chem. Commun.* **1992**, 1440−1441.

[4] [4a] R. Colton, D. Dakternieks, *Inorg. Chim. Acta* **1985**, *102*, L17−L18. − [4b] R. Colton, D. Dakternieks, *Inorg. Chim. Acta* **1988**, *148*, 31−36. − [4c] M. Gielen, *Top. Curr. Chem.* **1982**, *104*, 57−105. − [4d] R. J. P. Corriu, C. Guerin, *Adv. Organomet. Chem.* **1982**, *20*, 265−311. − [4e] C. Brelière, R. J. P. Corriu, G. Royo, J. Zwecker, *Organometallics* **1989**, *8*, 1834−1836. − [4f] C. Brelière, F. Carré, R. J. P. Corriu, W. E. Douglas, M. Poirier, G. Royo, M. W. C. Man, *Organometallics*, **1992**, *11*, 1586−1593. − [4g] F. Carré, C. Chuit, R. J. P. Corriu, A. Mehdi, C. Reyé, *Organometallics* **1995**, *14*, 2754−2759.

[5] [5a] A. J. Crowe in *Metal Complexes in Cancer Chemotherapy* (Ed.: B. K. Keppler), VCH, Weinheim, **1993**, 369−379. − [5b] M. Gielen, P. Lelieveld, D. de Vos, R. Willem in *Metal Complexes in Cancer Chemotherapy* (Ed.: B. K. Keppler), VCH, Weinheim, **1993,** 381−390. − [5c] M. Gielen, P. Lelieveld, D. de Vos, R. Willem, Metal-Based Drugs, in *Metal-Based Antitumor Drugs* (Ed.: M. Gielen), Freund Publishing House, Tel Aviv, **1992**, Vol. 2, 29−54. − [5d] R. Tacke, H. Linoh, Bioorganosilicon Chemistry in *The Chemistry of Organic Silicon Compounds* (Eds.: S. Patai, Z. Rappoport), Wiley-Interscience, New York, **1989**, 1143−1206. − [5e] E. Lukevics, L. Ignatovich, *Appl. Organomet. Chem.* **1992**, *6*, 113−126.

[6] For examples see: [6a] R. J. P. Corriu, G. Lanneau, C. Priou, F. Soulairol, N. Auner, R. Probst, R. Conlin, C. Tan, *J. Organomet. Chem.* **1994**, *466*, 55−68. − [6b] K. Tamao, K. Nagata, M. Asahara, A. Kawachi, Y. Ito, M. Shiro, *J. Am. Chem. Soc.* **1995**, *117*, 11592−11593. − [6c] J. Belzner, U. Dehnert, H. Ihmels, M. Hübner, P. Müller, I. Usón, *Chem. Eur. J.* **1998**, *4*, 852−863. − [6d] H. Handwerker, M. Paul, J. Blümel, C. Zybill, *Angew. Chem.* **1993**, *105*, 1375−1377; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 1313. − [6e] R. J. P. Corriu, G. Lanneau, C. Priou, *Angew. Chem.* **1991**, *103*, 1153−1155; *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 1130. − [6f] R. J. P. Corriu, G. F. Lanneau, B. P. S. Chauhan, *Organometallics* **1993**, *12*, 2001−2003.

[7] For examples see: [7a] H.-P. Abicht, K. Jurkschat, A. Tzschach, K. Peters, E.-M. Peters, H. G. von Schnering, *J. Organomet. Chem.* **1987**, *326*, 357−368. − [7b] K. Jurkschat, H.-P. Abicht, A. Tzschach, B. Mahieu, *J. Organomet. Chem.* **1986**, *309*, C47−C50. − [7c] K. Angermund, K. Jonas, C. Krüger, J. L. Latten, Y.-H. Tsay, *J. Organomet. Chem.* **1988**, *353*, 17−25. − [7d] J. T. B. H. Jastrzebski, P. A. van der Schaaf, J. Boersma, G. van Koten, M. C. Zoutberg, D. Heijdenrijk, *Organometallics* **1989**, *8*, 1373−1375. − [7e] L. M. Engelhardt, B. S. Jolly, M. F. Lappert, C. L. Raston, A. H. White, *J. Chem. Soc., Chem. Commun.* **1988**, 336−338. − [7f] W.-P. Leung, W.-H. Kwok, L.-H. Weng, L. T. C. Law, Z. Y. Zhou, T. C. W. Mak, *J. Chem. Soc., Dalton Trans.* **1997**, 4301−4305. − [7g] C. Drost, P. B. Hitchcock, M. F. Lappert, L. J.-M. Pierssens, *J. Chem. Soc., Chem.*

Commun. **1997**, 1141−1142. − [7h] C. J. Cardin, D. J. Cardin, S. P. Constantine, M. G. B. Drew, H. Rashid, M. A. Convery, D. Fenske, *J. Chem. Soc., Dalton Trans.* **1998**, 2749−2753.

[8] [8a] V. A. Benin, J. C. Martin, M. R. Willcott, *Tetrahedron Lett.* **1994**, *35*, 2133−2136. − [8b] M. Chauhan, C. Chuit, R. J. P. Corriu, A. Mehdi, C. Reyé, *Organometallics* **1996**, *15*, 4326−4333. − [8c] J. Belzner, *Angew. Chem.* **1997**, *109*, 1331−1334; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1277−1280. − [8d] C.-H. Ottosson, D. Cremer, *Organometallics* **1996**, *15*, 5309−5309. − [8e] C. Chuit, R. J. P. Corriu, A. Mehdi, C. Reyé, *Angew. Chem.* **1993**, *105*, 1372−1375; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 1311. − [8f] F. Carré, M. Chauhan, C. Chuit, R. J. P. Corriu, C. Reyé, *J. Organomet. Chem.* **1997**, *540*, 175−183.

[9] G. van Koten, J. T. B. H. Jastrzebski, J. G. Noltes, A. L. Spek, J. C. Schoone, *J. Organomet. Chem.* **1978**, *148*, 233−245.

[10] $Ph_2(Me_3SiCH_2)SnF$ was prepared in a similar manner to $Ph_2FSn(CH_2)_2SnPh_2F$ (D. Dakternieks, K. Jurkschat, H. Zhu, E. R. T. Tiekink, *Organometallics* **1995**, *14*, 2512−2521) starting from $Ph_3SnCH_2SiMe_3$ (S. Papetti, H. W. Post, *J. Org. Chem.* **1957**, *22*, 526−528) and was isolated as a colorless solid that gave a correct elemental analysis.

[11] The synthesis, characterization, and reactivity of the heteroleptic stannylene {4-*tert*-Bu-2,6-$[P(O)(OEt)_2]_2C_6H_2$}SnCl will be reported in a forthcoming paper.

[12] P. Jutzi, F. Kohl, *J. Organomet. Chem.* **1979**, *164*, 141−152.

[13] [13a] M. Mehring, K. Jurkschat, unpublished results. − [13b] J. T. B. H. Jastrzebski, D. M. Grove, J. Boersma, G. van Koten, J.-M. Ernsting, *Magn. Reson. Chem.* **1991**, *29*, 25−30.

[14] [14a] R. A. Howie, E. S. Paterson, J. L. Wardell, J. W. Burley, *J. Organomet. Chem.* **1983**, *259*, 71−78. − [14b] P. G. Harrison, T. J. King, M. A. Healy, *J. Organomet. Chem.* **1979**, *182*, 17−36. − [14c] R. A. Howie, E. S. Paterson, J. L. Wardell, J. W. Burley, *J. Organomet. Chem.* **1986**, *304*, 301−308. − [14d] W. Clegg, C. M. J. Grievson, K. Wade, *J. Chem. Soc., Chem. Commun.* **1987**, 969−970. − [14e] M. Gielen, H. Pan, E. R. T. Tiekink, *Bull. Soc. Chim. Belg.* **1993**, *102*, 447−453. − [14f] S. Dostal, S. J. Stoudt, P. Fanwick, W. F. Sereatan, B. Kahr, J. E. Jackson, *Organometallics* **1993**, *12*, 2284−2291. − [14g] B. Fitzsimmons, D. G. Othen, H. M. M. Shearer, K. Wade, G. Whitehead, *J. Chem. Soc., Chem. Commun.* **1977**, 215−216. − [14h] O.-S. Jung, J. H. Jeong, Y. S. Sohn, *J. Organomet. Chem.* **1990**, *397*, 17−20. − [14i] A. Hayashi, M. Yamaguchi, M. Hirama, C. Kabuto, M. Ueno, *Chem. Lett.* **1993**, 1881−1884.

[15] [15a] H. Weichmann, J. Meunier-Piret, M. van Meerssche, *J. Organomet. Chem.* **1986**, *309*, 273−282. − [15b] C. Mügge, H. Weichmann, A. Zschunke, *J. Organomet. Chem.* **1980**, *192*, 41−46. − [15c] U. Kolb, M. Dräger, E. Fischer, K. Jurkschat, *J. Organomet. Chem.* **1992**, *423*, 339−350. − [15d] F. Richter, M. Dargatz, H. Hartung, D. Schollmeyer, H. Weichmann, *J. Organomet. Chem.* **1996**, *514*, 233−241. − [15e] A. G. Davies, J. P. Goddard, M. B. Hursthouse, N. P. C. Walker, *J. Chem. Soc., Chem. Commun.* **1983**, 597−598. − [15f] D. Britton, Y. M. Chow, *Acta Cryst.* **1983**, *39C*, 1539−1540. − [15g] W. A. Nugent, R. J. McKinney, R. L. Harlow, *Organometallics* **1984**, *3*, 1315−1318. − [15h] N. W. Kong, C. Wie, V. G. K. Das, R. J. Butcher, *J. Organomet. Chem.* 1989**,** *361***,** 53−61. − [15i] E. G. Perevalova, M. D. Reshetova, P. N. Ostapchuk, Yu. L. Slovokhotov, Yu. T. Struchkov, F. M. Spiridonov, A. V. Kisin, I. G. Yukhno, *Metalloorg. Khim.* **1990**, *3*, 100. − [15j] R. E. Marsh, *Acta Cryst.* **1997**, *53B*, 317−322. − [15k] A. Blaschette, I. Hippel, J. Krahl, E. Wieland, P. G. Jones, A. Sebald, *J. Organomet. Chem.* **1992**, *437*, 279−297. − [15l] I. Lange, J. Krahl, P. G. Jones, A. Blaschette, *J. Organomet. Chem.* **1994**, *474*, 97−106. − [15m] G. van Koten, J. T. B. H. Jastrzebski, J. G. Noltes, J. C. Schoone, *J. Organomet. Chem.* **1978**, *148*, 233−245. − [15n] C. Pettinari, F. Marchetti, M. Pellei, A. Cingolani, L. Barba, A. Cassetta, *J. Organomet. Chem.* **1996**, *515*, 119−130. − [15o] L. A. Aslanov, V. M. Attiya, A. B. Permin, V. S. Petrosyan, *Zh. Strukt. Khim.* **1977**, *18*, 1113. − [15q] L. R. Sita, I. Kinoshita, S. P. Lee, *Organometallics* **1990**, *9*, 1644−1650. − [15r] B. Wrackmeyer, S. Kundler, W. Milius, R. Boese, *Chem. Ber.* **1994**, *127*, 333−342. − [15s] M. M. Amini, M. J. Heeg, R. W. Taylor, J. J. Zuckerman, S. W. Ng, *Main Group Met. Chem.* **1993**, *16*, 415−418. − [15t] I. Lange, D. Henschel, A. Wirth, J. Krahl, A. Blaschette, P. G. Jones, *J. Organomet. Chem.* **1995**, *503*, 155−170. − [15u] M. Mehring, M. Schürmann, C. Löw, K. Jurkschat, to be published.

[16] [16a] C. E. McKenna, M. T. Higa, N. H. Cheung, M. C. McKenna, *Tetrahedron Lett.* **1977**, 155−158. − [16b] F. Richter, H. Weichmann, *J. Organomet. Chem.* **1994**, *466*, 77−87. − [16c] R. W. Deemie, J. C. Fettinger, D. A. Knight, *J. Organomet. Chem.* **1997**, *538*, 257−259. − [16d] H. Gross, C. Böck, B. Costisella, J. Gloede, *J. prakt. Chem.* **1978**, *320*, 344−350.

[17] J. L. Wardell in *Chemistry of Tin* (Ed.: P. J. Smith), 2nd ed., Blackie, London, **1998**, 121−137.

[18] H. Weichmann, B. Rensch, *Z. anorg. allg. Chem.* **1983**, *503*, 106−114.

[19] B. Jousseaume, P. Villeneuve, *J. Chem. Soc., Chem. Commun.* **1987**, 513−514.

[20] A. Bondi, *J. Phys. Chem.* **1964**, *68*, 441−451.

[21] A. V. Yatsenko, S. V. Medvedev, L. A. Aslanov, *Zh. Strukt. Khim.* **1992**, *33*, 126−131.

[22] A. I. Tursina, L. A. Aslanov, S. V. Medvedev, A. V. Yatsenko, *Koord. Khim.* **1985**, *11*, 417.

[23] L. A. Aslanov, V. M. Ionov, V. M. Attiya, A. B. Permin, V. S. Petrosyan, *Zh. Strukt. Khim.* **1977**, *18*, 1103−1112.

[24] H. Reuter, H. Puff, *J. Organomet. Chem.* **1992**, *424*, 23−31.

[25] L. A. Aslanov, V. M. Ionov, V. M. Attiya, A. B. Permin, V. S. Petrosyan, *Zh. Strukt. Khim.* **1978**, *19*, 315−318.

[26] T. J. Karol, J. P. Hutchinson, J. R. Hyde, H. G. Kuivila, J. A. Zubieta, *Organometallics* **1983**, *2*, 106−114.

[27] A. I. Tursina, L. A. Aslanov, V. V. Chernyshev, S. V. Medvedev, A. V. Yatsenko, *Koord. Khim.* **1985**, *11*, 1420.

[28] A. L. Rheingold, S. W. Ng, J. J. Zuckerman, *Inorg. Chim. Acta* **1984**, *86*, 179−183.

[29] [29a] U. Kolb, M. Beuter, M. Dräger, *Inorg. Chem.* **1994**, *33*, 4522−4530. − [29b] U. Kolb, M. Beuter, M. Gerner, M. Dräger, *Organometallics* **1994**, *13*, 4413−4425. − [29c] U. Kolb, M. Dräger, B. Jousseaume, *Organometallics* **1991**, *10*, 2737−2742.

[30] H. Hartung, D. Petrick, C. Schmoll, H. Weichmann, *Z. anorg. allg. Chem.* **1987**, *550*, 140−148.

[31] P. G. Harrison in *Chemistry of Tin* (Ed.: P. G. Harrison), Blackie, London, **1989**, 10.

[32] S. Freitag, R. Herbst-Irmer, F. U. Richter, H. Weichmann, *Acta Cryst.* **1994**, *C50*, 1588−1590.

[33] H. Hartung, A. Krug, F. Richter, H. Weichmann, *Z. anorg. allg. Chem.* **1993**, *619*, 859−864.

[34] B. Wrackmeyer in *Ann. Rep. NMR Spectroscopy* (Ed.: G. A. Webb), Academic Press, London, **1985**, Vol. 16, 73−186.

[35] G. M. Sheldrick, *Acta Cryst.* **1990**, *A46*, 467−473.

[36] G. M. Sheldrick, University of Göttingen, **1997**.

[37] *International Tables for Crystallography*, Kluwer Academic Publishers, Dordrecht, **1992**, Vol. C.

[38] G. M. Sheldrick, SHELXTL-PLUS Release 4.1, Siemens Analytical X-ray Instruments Inc., **1991**.

Received October 26, 1998
[I98369]