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Novel Heteroleptic Stannylenes with Intramolecular O,C,O-Donor Stabilization[†,‡]

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The heteroleptic organotin(II) halides {2,6-[P(O)(OEt)$_2$]$_2$-4-*tert*-Bu-C$_6$H$_2$}SnX (**1**, X = Cl; **2**, X = Br) have been prepared starting from {2,6-[P(O)(OEt)$_2$]$_2$-4-*tert*-Bu-C$_6$H$_2$}Li and SnX$_2$ and have been used as precursors for the preparation of the heteroleptic stannylenes {2,6-[P(O)(OEt)$_2$]$_2$-4-*tert*-Bu-C$_6$H$_2$}SnX (**4**, X = SPh; **5**, X = CH(SiMe$_3$)$_2$; **6**, X = SiPh$_3$; **7**, X = SnPh$_3$; **7a,** X = SnMe$_3$), the tetravalent monorganotin derivatives {{2,6-[P(O)(OEt)$_2$]$_2$-4-*tert*-Bu-C$_6$H$_2$}SnCl(μ-S)}$_2$ (**8**) and {2,6-[P(O)(OEt)$_2$]$_2$-4-*tert*-Bu-C$_6$H$_2$}SnBr$_3$ (**9**), the diorganotin cation {2,6-[P(O)(OEt)$_2$]$_2$-4-*tert*-Bu-C$_6$H$_2$}(Ph$_3$C)(Cl)Sn$^+$PF$_6^-$ (**10**), and the metal−stannylene complexes {2,6-[P(O)(OEt)$_2$]$_2$-4-*tert*-Bu-C$_6$H$_2$}(Cl)Sn[M(CO)$_n$] (**11**, M = W, *n* = 5; **12**, M = Cr, *n* = 5; **13**, M = Fe, *n* = 4). Multinuclear (^{1}H, ^{13}C, ^{31}P, ^{119}Sn) NMR of all compounds, ^{119}Sn Mössbauer spectra of **1** and **10**, and single-crystal X-ray structure analyses of **6**, **8**, and **12** are reported. The derivatives **6**, **7**, and **7a** are rare examples of compounds containing Sn(II)−Si(IV) and Sn(II)−Sn(IV) bonds, respectively.

Introduction

Almost 80 years ago homoleptic stannylenes had been suggested to occur as reactive intermediates in the reaction of phenylmagnesium bromide with SnCl$_2$ giving polymeric (Ph$_2$Sn)$_n$,[1] but it was only in 1976 that the first homoleptic diorganostannylene [(Me$_3$Si)$_2$CH]$_2$Sn[2,3] was fully characterized. Since then numerous homoleptic diorganostannylenes which are stabilized either by bulky substituents[4−16] and/or intramolecular donor coordination have been reported.[17−23] Although tin(II)−transition metal interactions in stannylenes are well known,[24] there seems to be renewed interest in compounds of this type[25−28] and also in compounds containing a bond between tin(II) and a main group metal.[29−32] Furthermore, in the past decade there has been growing

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[†] Dedicated to Professor Horst Weichmann on the occasion of his 60th birthday.

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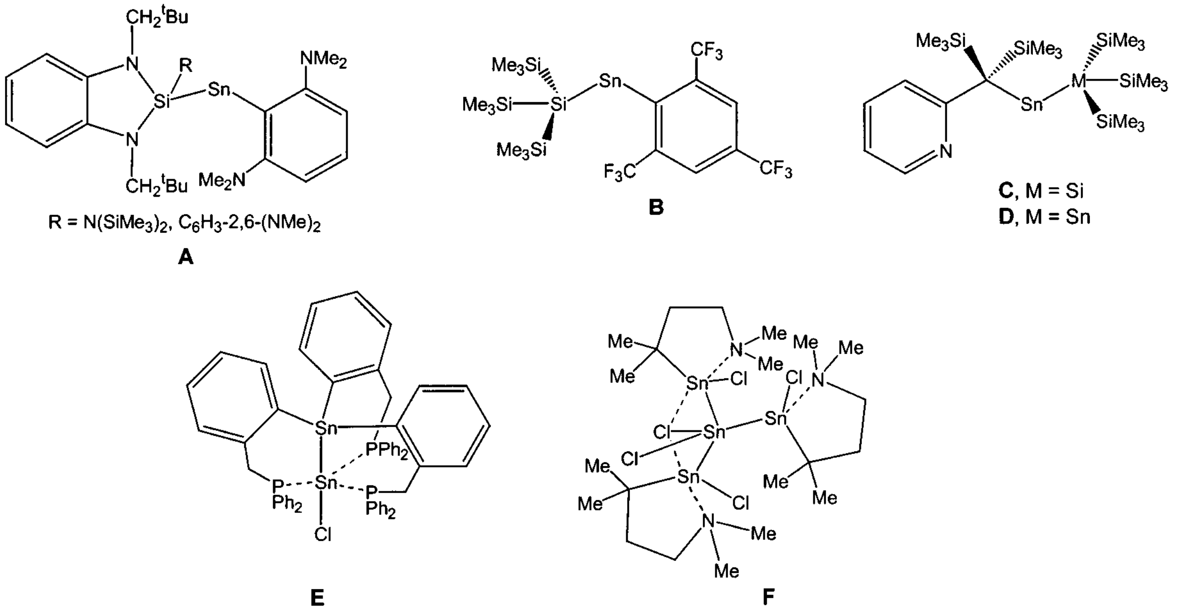
Chart 1



interest in σ-bonded heteroleptic stannylenes.[20,33−37] Compounds of the type RSnX (X = NR_2, Cl; R = alkyl, aryl)[12,19,35,38−45] are very useful as starting materials for the preparation of diverse heteroleptic stannylenes RR′Sn. Intramolecular donor stabilization has led to the isolation of monomeric stannylenes RSnX,[19,38−41] whereas stabilization by bulky, monodentate ligands gave monomers[43] as well as dimers,[12,42] the latter resulting from intermolecular Cl⋯Sn interactions. Research on compounds of the type RSnCl has focused mainly on structural characterization, and surprisingly, reports on reactivity at the Sn−Cl function are scarce.[35,39,44,46] Recently, the first examples of heteroleptic, silyl-substituted stannylenes $\{Sn[C_6H_3\text{-}2,6\text{-}(NMe_2)_2]\{Si[(-NCH_2{}^tBu)_2\text{-}1,2\text{-}C_6H_4]R\}\}$ (R = C_6H_3-2,6-$(NMe_2)_2$ or $N(SiMe_3)_2$) **A**,[20] $\{Sn[2,4,6\text{-}CF_3(C_6H_2)][Si(SiMe_3)_3]\}$ **B**,[33] and $\{Sn[2\text{-}(Me_3Si)_2C{-}C_5H_4N][Si(SiMe_3)_3]\}$ **C**[37] have been reported. The first compound containing a Sn(II)−Sn(IV) bond, $[(2\text{-}C_6H_4CH_2PPh_2)_3Sn{-}SnCl]$ **E**,[47] was reported in 1986 followed by $[(Me_2NCH_2CH_2CMe_2SnCl)_3SnCl_2)]$ **F**[40] in 1989 and $\{Sn[2\text{-}(Me_3Si)_2C{-}C_5H_4N][Sn(SiMe_3)_3]\}$ **D**[37] in 1998 (Chart 1). These compounds were characterized by NMR[37,40,47] and Mössbauer spectroscopy,[40,47] and in the case of the two latter compounds also by single-crystal X-ray analyses.[37,40] On the basis of the ^{119}Sn Mössbauer spectrum (isomer shift, IS = 2.15, 3.24 mm s^{-1}), compound **F** might be regarded as a borderline case between a Sn(II)−Sn(IV) compound and a Sn(II)−Sn(II) adduct. The tin−tin bond distances in **F** of 2.882(3), 2.873(3), and 3.156(3) Å compare well with those of previously reported asymmetric distannenes[29,32,41] as well as those of the tin(II)−tin(IV) compound **D**.

We recently reported the synthesis of the O,C,O-coordinating pincer-type ligand $\{2,6\text{-}[P(O)(OEt)_2]_2\text{-}4\text{-}tert\text{-}Bu\text{-}C_6H_2\}^-$ and its application in organosilicon and organotin chemistry.[48−50] Since a long time we have been interested in intramolecularly donor stabilized divalent tin compounds,[40,47,51−53] and since intramolecular stabilization of organostannylenes is mainly focused on nitrogen and phosphorus rather than oxygen donors, we explored the potential of the O,C,O-coordinating

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Table 1. Selected ^{31}P and ^{119}Sn NMR Data;[a] R = {2,6-[P(O)(OEt)$_2$]$_2$-4-*tert*-Bu-C$_6$H$_2$}

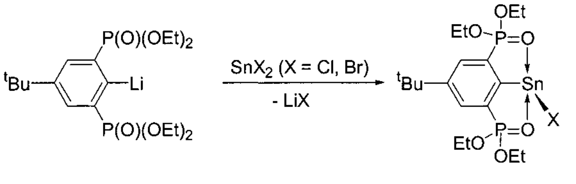
compound	$\delta(^{31}P)$ $[J(^{31}P-^{119}Sn)]$	$\delta(^{119}Sn)$ $[J(^{119}Sn-^{31}P)]$
R-SnCl (**1**)	39.1 [113]	−100 [116]
R-SnBr (**2**)	38.8 [115]	−68 [116]
R-Sn(SPh) (**4**)	37.4 [95]	2 [96]
R-SnCH(SiMe$_3$)$_2$ (**5**)	33.5 [107]	259 [106]
R-SnSiPh$_3$ (**6**)	34.5 [95]	192 [96][b]
R-SnSnPh$_3$ (**7**)	35.4 [99]	109 [98], −43 [21][c]
R-SnSnMe$_3$ (**7a**)	37.7 [21, 95]	217 [93], 11 [21][d]
R-Sn(Cl)(μ-S)]$_2$ (**8**)	26.7 [86]	−439 [84]
R-SnBr$_3$ (**9**)	23.8 [236]	−885 [230]
R-Sn(CPh$_3$)(Cl)$^+$PF$_6^-$ (**10**)	24.8 [52], −143.5	−322 [52]
R-Sn(Cl)W(CO)$_5$ (**11**)	33.9 [161]	−74 [161][e]
R-Sn(Cl)Cr(CO)$_5$ (**12**)	32.8 [175]	131 [179]
R-Sn(Cl)Fe(CO)$_4$ (**13**)	30.5 [161]	54 [165]

[a] Coupling constants J are given in Hz and chemical shifts δ in ppm. [b] $\delta(^{29}Si)$ 7.9, $^1J(^{29}Si-^{117/119}Sn)$ = 674/708 Hz. [c] $^1J(^{119}Sn-^{117/119}Sn)$ = 9130/9550 Hz. [d] $^1J(^{119}Sn-^{117/119}Sn)$ = 7976/8346 Hz. [e] $^1J(^{119}Sn-^{182}W)$ = 1372 Hz.

pincer-type ligand in stannylene chemistry. Recently we described the reaction of {2,6-[P(O)(OEt)$_2$]$_2$-4-*tert*-Bu-C$_6$H$_2$}SnCl (**1**) with SnCl$_4$ to give {2,6-[P(O)(OEt)$_2$]$_2$-4-*tert*-Bu-C$_6$H$_2$}SnCl$_3$,[50] and in continuation of this work we now report the synthesis of the mononuclear, heteroleptic stannylenes {2,6-[P(O)(OEt)$_2$]$_2$-4-*tert*-Bu-C$_6$H$_2$}-SnX (**1**, X = Cl; **2**, X = Br) and demonstrate their versatility as precursors of the novel divalent organotin compounds {2,6-[P(O)(OEt)$_2$]$_2$-4-*tert*-Bu-C$_6$H$_2$}SnX (**4**, X = SPh; **5**, X = CH(SiMe$_3$)$_2$; **6**, X = SiPh$_3$; **7** = SnPh$_3$; **7a** = SnMe$_3$), the tetravalent monoorganotin derivatives {{2,6-[P(O)(OEt)$_2$]$_2$-4-*tert*-Bu-C$_6$H$_2$}SnCl(μ-S)}$_2$ (**8**) and {2,6-[P(O)(OEt)$_2$]$_2$-4-*tert*-Bu-C$_6$H$_2$}SnBr$_3$ (**9**), the diorganotin cation {2,6-[P(O)(OEt)$_2$]$_2$-4-*tert*-Bu-C$_6$H$_2$}(Ph$_3$C)-(Cl)Sn$^+$PF$_6^-$ (**10**), and the metal−stannylene complexes {2,6-[P(O)(OEt)$_2$]$_2$-4-*tert*-Bu-C$_6$H$_2$}(Cl)Sn[M(CO)$_n$] (**11**, M = W, n = 5; **12**, M = Cr, n = 5; **13**, M = Fe, n = 4). All compounds have been fully characterized by multinuclear NMR spectroscopy. Single-crystal X-ray structure analyses of **6**, **8**, and **12** were determined. The identity of **7** and **7a** in solution was unambiguously established by NMR spectroscopy and here especially by determination of the tin(II)−tin(IV) coupling constant, the second of its kind reported so far.

Results and Discussion

Preparation and Characterization of {2,6-[P(O)-(OEt)$_2$]$_2$-4-*tert*-Bu-C$_6$H$_2$}SnX (1, X = Cl; 2, X = Br). The organolithium reagent {2,6-[P(O)(OEt)$_2$]$_2$-4-*tert*-Bu-C$_6$H$_2$}Li was reacted with SnCl$_2$ and SnBr$_2$, respectively, in thf to give the heteroleptic stannylenes {2,6-[P(O)(OEt)$_2$]$_2$-4-*tert*-Bu-C$_6$H$_2$}SnX (**1**, X = Cl; **2**, X = Br) as colorless solids (eq 1).

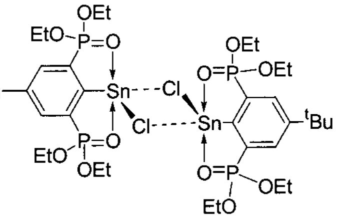


(1)

1, X = Cl
2, X = Br

The ^{119}Sn NMR spectra in [d_8]toluene of **1** and **2** exhibit triplet resonances at δ −100 ($J(^{119}Sn-^{31}P)$ = 116 Hz) and δ −68 ($J(^{119}Sn-^{31}P)$ = 116 Hz), respectively, which are low frequency shifted as compared with the related intramolecularly donor-stabilized heteroleptic stannylenes [C$_6$H$_3$(NMe$_2$)$_2$-2,6]SnCl (δ 380),[39] [C$_6$H$_3$(CH$_2$-NMe$_2$)$_2$-2,6]SnCl (δ 156),[38] {C$_9$H$_6$N[CH(SiMe$_3$)]-8}SnCl (δ 327),[41] and {C$_9$H$_6$N[CH(SiMe$_3$)]-8}SnBr (δ 354).[41] The ^{31}P NMR spectra of **1** and **2** show single resonances at δ 39.1 ($J(^{119}Sn-^{31}P)$ = 113 Hz) and δ 38.8 ($J(^{119}Sn-^{31}P)$ = 115 Hz), respectively, which are high frequency shifted as compared with related compounds listed in Table 1. The osmometric molecular weight determination in benzene shows the stannylene **1** to be monomeric in solution. However, the ^{119}Sn MAS NMR of **1** shows a broad resonance at δ −160 ($\nu_{1/2}$ = 760 Hz), which is significantly shifted to lower frequency, and thus, it is most likely that compound **1** is a dimer in the solid state via intermolecular Sn···Cl interactions (Chart 2).

Chart 2



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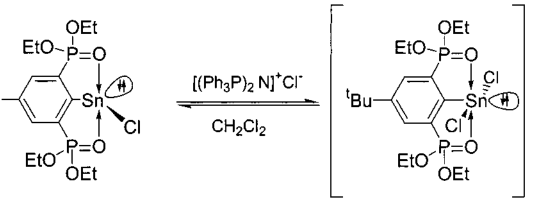
The IR spectra of **1** and **2** both show ν(P=O) absorptions at 1171 cm^{-1}, which are accompanied by a shoulder at 1192 cm^{-1} and hint at two slightly different coordinating modes for the phosphonate groups in the solid state. This is in agreement with the ^{31}P MAS NMR spectrum, which shows two chemical shifts of equal intensity at δ 40.0 and δ 37.1. The divalent nature of tin in **1** is confirmed by the ^{119}Sn Mössbauer spectrum (IS = 3.24 mm s^{-1}). Similar values have been reported for the tin(II) moiety in the mixed valence compound [(2-C$_6$H$_4$CH$_2$PPh$_2$)$_3$Sn−SnCl] (IS = 3.15 mm s^{-1})[47] and the heteroleptic stannylenes 2-(OCH$_3$)C$_6$H$_4$SnCl (IS = 3.29 mm s^{-1}), 2-(*iso*-PrO)C$_6$H$_4$SnCl (IS = 3.19 mm s^{-1}), and 2,4,6-(OCH$_3$)$_3$C$_6$H$_2$SnCl (IS = 3.25 mm s^{-1}),[9] which all rapidly oxidize on contact with air. In contrast, the oxidation of **1** as monitored by Mössbauer spectroscopy is very slow, and after exposure to air for one week only 38% of the stannylene **1** was oxidized, giving rise to an additional signal at IS = −0.11 mm s^{-1}, which is characteristic for a tin(IV) compound. Furthermore, compound **1** is stable in solution after heating at reflux in toluene for 2 h, whereas the related heteroleptic stannylenes [C$_6$H$_3$(NMe$_2$)$_2$-2,6]SnCl[39] and (Me$_2$NCH$_2$-CH$_2$CMe$_2$)SnCl[40] disproportionate in solution at room temperature to give R$_2$SnCl$_2$ and elemental tin. It is noteworthy that the ^{119}Sn and ^{31}P NMR spectra of **1** in [d_8]toluene to which a few drops of water had been added did not change, even after 1 day of vigorous stirring at room temperature.

To the best of our knowledge there are no spectroscopic data on heteroleptic stannylenes containing a Sn−F bond, which might be the result of the poor solubility of SnF$_2$ and the lack of appropriate, water-free fluorinating reagents. However, the ^{119}Sn NMR spectrum of {2,6-[P(O)(OEt)$_2$]$_2$-4-*tert*-Bu-C$_6$H$_2$}SnCl (**1**) in [d_8]toluene at −40 °C to which had been added 1 molar equiv of $Bu_4NF{\cdot}3H_2O$ showed a doublet of triplets resonance at δ −208 ($J(^{119}Sn-^{31}P) = 112$ Hz, $^1J(^{119}Sn-^{19}F) = 3140$ Hz, integral 0.8), which is indicative of the formation of either the monomeric anionic complex {2,6-[P(O)(OEt)$_2$]$_2$-4-*tert*-Bu-C$_6$H$_2$}SnClF$^-$ (**3a**) or the organotin(II) fluoride {2,6-[P(O)(OEt)$_2$]$_2$-4-*tert*-Bu-C$_6$H$_2$}SnF (**3b**). An additional broad signal at δ −111 ($\nu_{1/2} = 290$ Hz, integral 0.2) is assigned to **1**. At room temperature only the signal of compound **1** was observed. The ^{31}P NMR spectrum of this solution at low temperature showed a broad signal at δ 45.2 ppm ($\nu_{1/2} = 80$ Hz) and a signal of minor intensity (2%) at δ 23.8. It is noteworthy that a complex of the type {2,6-[P(O)(OEt)$_2$]$_2$-4-*tert*-Bu-C$_6$H$_2$}SnF$_2^-$ was not observed, even after addition of a second equivalent of $Bu_4NF{\cdot}3H_2O$. Attempts to isolate an analytically pure organotin(II) fluoride **3a** or **3b** from this reaction mixture failed. Furthermore, the reaction of **1** with a suspension of CsF in toluene gave the ligand precursor 1,3-[P(O)(OEt)$_2$]$_2$-5-*tert*-Bu-C$_6$H$_3$ instead of the organotin fluoride **3b**. Cleavage of Sn−Ph bonds by fluoride has been reported for organotin(IV) compounds.[54,55]

The ^{119}Sn NMR chemical shift of **1** in CD_2Cl_2 is temperature dependent ($T = 20$ °C, δ −100; $T = -10$ °C, δ −106) and strongly influenced by the addition of $[(Ph_3P)_2N]^+Cl^-$ (**1**/$[(Ph_3P)_2N]^+Cl^- = 1/1$, $T = -10$ °C, δ −125, $T = -50$ °C, δ −163; **1**/$[(Ph_3P)_2N]^+Cl^- = 1/2$, $T = -10$ °C, δ −158, $T = -50$ °C, δ −212), whereas the ^{31}P NMR chemical shift is temperature independent and not influenced by the addition of chloride anions (δ 38.8 ($J(^{31}P-^{119}Sn) = 116$ Hz), which shows that the coordinative P=O···Sn bonds are not broken.



1 (2)

The ^1H NMR spectrum of the stannylene **1** in [d_8]-toluene at room temperature shows a broad signal for the CH_3 groups of the phosphonate units which splits into triplet resonances of equal intensity at −20 °C. In [d_6]DMSO at room temperature and in $C_2D_2Cl_4$ solution at 72 °C, only one triplet resonance is observed for this group. The NMR spectroscopic data for the stannylene **1** suggest an inversion of the configuration at tin, the rate of which is influenced by Lewis bases. Compound **1** shows no conductivity in CH_2Cl_2 and a value of 55 S cm^2 mol^{-1} in CH_3CN, which demonstrates **1** to be virtually a nonelectrolyte. Thus, we suggest that inversion of configuration at tin takes place in noncoordinating solvents via dimeric intermediates of the type [RSnCl]$_2$. Upon the addition of Cl$^-$, inversion occurs via anionic complexes of the type [RSnCl$_2$]$^-$ and in coordinating solvents via neutral hypercoordinate stannylene complexes of the type [RSnCl][Donor]. Similar observations have been reported for [C$_6$H$_3$(CH$_2$NMe$_2$)$_2$-2,6]-SnCl.[56]

Nucleophilic Substitutions at the Sn−Cl Function. The colorless organotin(II) thiophenolate {2,6-[P(O)(OEt)$_2$]$_2$-4-*tert*-Bu-C$_6$H$_2$}SnSPh (**4**) was prepared from {2,6-[P(O)(OEt)$_2$]$_2$-4-*tert*-Bu-C$_6$H$_2$}SnCl (**1**) and NaSPh in appropriate stoichiometry (Scheme 1). Its ^{119}Sn NMR spectrum exhibits a triplet resonance at δ 2 ($J(^{119}Sn-^{31}P) = 96$ Hz), and the ^{31}P NMR spectrum displays a single resonance at δ 37.4 ($J(^{119}Sn-^{31}P) = 95$ Hz).

The reaction of {2,6-[P(O)(OEt)$_2$]$_2$-4-*tert*-Bu-C$_6$H$_2$}-SnCl (**1**) with LiCH(SiMe$_3$)$_2$ and LiSiPh$_3$ gave the heteroleptic stannylenes {2,6-[P(O)(OEt)$_2$]$_2$-4-*tert*-Bu-C$_6$H$_2$}SnCH(SiMe$_3$)$_2$ (**5**) and {2,6-[P(O)(OEt)$_2$]$_2$-4-*tert*-Bu-C$_6$H$_2$}SnSiPh$_3$ (**6**), respectively (Scheme 1).

Attempts to prepare a heteroleptic tin(II) triflate starting from **1** and AgOTf failed and gave a silver mirror, 1,3-[P(O)(OEt)$_2$]$_2$-4-*tert*-Bu-C$_6$H$_3$, and unidentified products instead. On the other hand, the synthesis of the amidotin(II) triflate [Sn(NR$_2$)(OTf)]$_n$ (R = SiMe$_3$, OTf = $^-OSO_2CF_3$), starting from [Sn(NR$_2$)(Cl)]$_2$ and AgOTf, has been reported recently.[57] These results show that the redox potential of Sn(II) species can be tuned by appropriate ligands.

The molecular structure of the heteroleptic stannylene **6** is illustrated in Figure 2. Crystallographic data are given in Table 2, and selected bond lengths and angles are listed in Table 3. The coordination geometry at tin is best described as that of a distorted trigonal bipyramid with C(1), Si(1), and the lone pair being in equatorial positions, and O(1) and O(2) being axial. The C(1)−Sn(1)−Si(1) bond angle of 96.35(9)° is significantly smaller than the corresponding C−Sn−Si angles in the related compounds **A** {Sn[C$_6$H$_3$-2,6-(NMe$_2$)$_2$]{Si[(−NCH$_2$-^{t}Bu)$_2$-1,2-C$_6$H$_4$][C$_6$H$_3$-2,6-(NMe$_2$)$_2$]}} (107.0(2)°)[20] and **C** {Sn[2-(Me$_3$Si)$_2$C−C$_5$H$_4$N][Si(SiMe$_3$)$_3$]} (113.5(2)°).[37] The Sn(1)−Si(1) bond distance of 2.751(1) Å is longer than the corresponding distances of 2.636(2) and 2.724(2) Å in the stannylenes **A** and **C**, respectively (Chart 1). The bond angle O(1)−Sn(1)−O(2) of 150.97(9) Å is smaller than in **8** (159.0(1)°), **11** (154.9(1)°), and previously reported hypercoordinate compounds containing the same O,C,O-coordinating pincer-type ligand (average 160.7°),[48,50] which is a result of the long Sn(1)−C(1) bond of 2.229(3) Å.

Multinuclear NMR spectroscopy shows that compounds **5** and **6** have similar molecular structures in solution and that the structure of **6** in thf solution is similar to that in the solid state. The ^{31}P NMR spectra of **5** and **6** display single resonances at δ 33.5 ($J(^{119}Sn-^{31}P) = 107$ Hz) and δ 34.5 ($J(^{119}Sn-^{31}P) = 95$ Hz; $J(^{29}Si-^{31}P) = 64$ Hz), respectively. The ^{119}Sn NMR spectra of **5** and **6** exibit triplet resonances at δ 259 ($J(^{119}Sn-^{31}P) = 106$ Hz) and at δ 192 ($J(^{119}Sn-^{31}P) = 96$ Hz), respectively, and the Sn(II)−Si(IV) bond in **6** is evidenced by the ^{29}Si resonance at δ 7.9, showing $^1J(^{29}Si-^{117/119}Sn)$ couplings of 674/708 Hz.

The reaction of the heteroleptic stannylene **1** with LiSnPh$_3$ in thf gave a crude reaction mixture, the ^{119}Sn NMR spectrum of which displayed an ABXY$_2$-type pattern with two triplet resonances of equal integral

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(54) Dakternieks, D.; Zhu, H. *Organometallics* **1992**, *11*, 3820.
(55) Dakternieks, D.; Zhu, H. *Inorg. Chim. Acta* **1992**, *196*, 19.
(56) Jastrzebski, J. T. B. H. Ph.D. Thesis, University of Utrecht, Netherlands, 1991.
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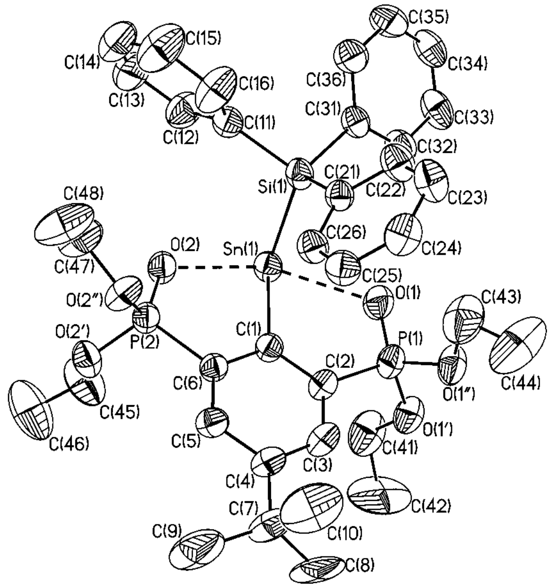


Figure 1. General view (SHELXTL) of a molecule of **6** showing 30% probability displacement ellipsoids and the atom-numbering scheme.

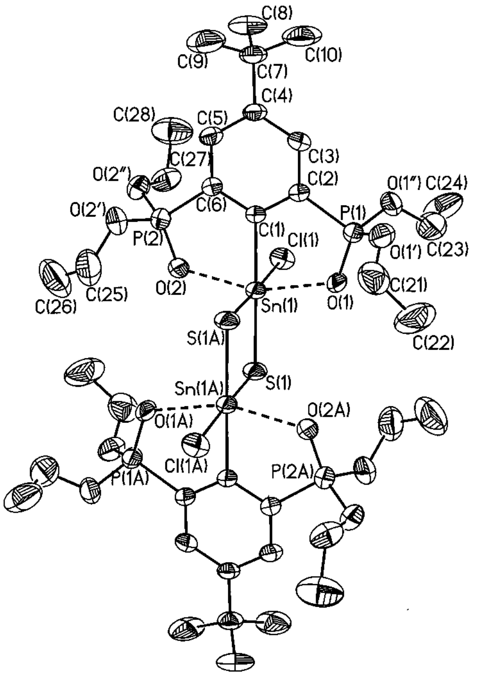


Figure 2. General view (SHELXTL) of a molecule of **8** showing 30% probability displacement ellipsoids and the atom-numbering scheme.

ratio at δ −43 ($J(^{119}Sn-^{31}P) = 21$ Hz, Sn(IV) moiety) and δ 109 ($J(^{119}Sn-^{31}P) = 98$ Hz, Sn(II) moiety) associated with $^{1}J(^{119}Sn-^{117/119}Sn)$ couplings of 9550 and 9130 Hz, respectively. These signals are assigned to the Sn(IV)-substituted heteroleptic stannylene {2,6-[P(O)(OEt)$_2$]$_2$-4-*tert*-Bu-C_6H_2}SnSnPh$_3$ (**7**). In addition, the spectrum showed resonances at δ −94 and −143, which are assigned to **1** and Ph$_3$SnSnPh$_3$, respectively. The assignment of the tin sites in compound **7** is based mainly on $^{119}Sn-^{31}P$ coupling arguments as compared with the silylated stannylene **6**.

The ^{31}P NMR spectrum showed resonances at δ 39.3 ($J(^{119}Sn-^{31}P) = 117$ Hz) (**1**), δ 35.4 ($J(^{119}Sn-^{31}P) = 99$

Scheme 1

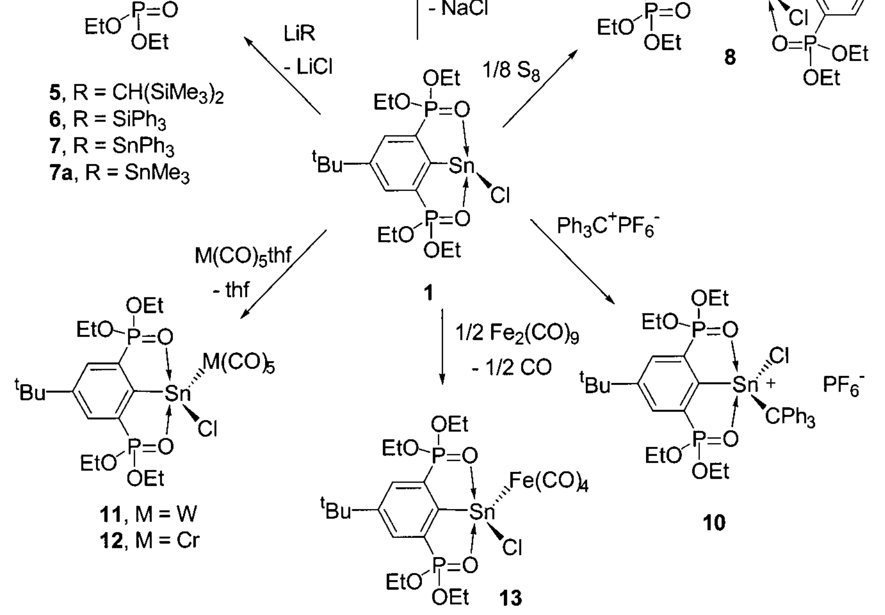


Table 2. Crystallographic Data for 6, 8, and 12

	6	**8**	**12**
formula	$C_{36}H_{46}O_6P_2SiSn\cdot 0.5C_4H_8O$	$C_{36}H_{62}O_{12}P_4S_2Sn_2\cdot 2C_6H_6$	$C_{23}H_{31}ClCrO_{11}P_2Sn$
fw	819.50	1339.35	751.56
cryst syst	triclinic	monoclinc	monoclinic
cryst size, mm	0.25 × 0.15 × 0.13	0.25 × 0.20 × 0.18	0.15 × 0.12 × 0.12
space group	$P\bar{1}$	$P2(1)/c$	$P2(1)/c$
a, Å	11.958(1)	14.654(1)	10.692(1)
b, Å	13.058(1)	12.465(1)	17.372(1)
c, Å	15.948(1)	17.677(1)	17.794(1)
α, deg	73.454(1)	90	90
β, deg	94.268(1)	101.918(1)	90.684(1)
γ, deg	67.725(1)	90	90
V, Å^3	2180.0(3)	3159.3(4)	3304.8(4)
Z	2	2	4
ρ_{calcd}, Mg/m^3	1.248	1.408	1.510
μ, mm^{-1}	0.727	1.093	1.311
F(000)	848	1368	1512
θ range, deg	3.43−25.37	2.60−24.37	3.63−27.57
index ranges	$-14 \le h \le 14$ $-14 \le k \le 15$ $-18 \le l \le 19$	$-16 \le h \le 16$ $-14 \le k \le 14$ $-20 \le l \le 20$	$-13 \le h \le 13$ $-22 \le k \le 22$ $-22 \le l \le 22$
no. of reflns collcd	28 128	37 657	42 667
completeness to θ_{max}	92.6	99.7	98.6
no. of indep reflns/R_{int}	7405/0.022	5429/0.039	7543/0.030
no. of reflns obsd with ($I > 2\sigma(I)$)	4449	3264	2851
no. refined params	463	366	399
GooF (F^2)	0.893	0.941	0.841
R1 (F) ($I > 2\sigma(I)$)	0.0373	0.0364	0.0301
wR2 (F^2) (all data)	0.0967	0.0952	0.0631
$(\Delta/\sigma)_{max}$	<0.001	<0.001	<0.001
largest diff peak/hole, e/Å^3	0.847/−0.394	0.423/−0.320	0.331/−0.291

Table 3. Selected Bond Distances (Å) and Angles (deg) for 6 and 12

	6, X = Si(1)	**12**, X = Cl(1)
Sn(1)−Cr(1)		2.5835(6)
Sn(1)−O(1)	2.543(3)	2.335(2)
Sn(1)−O(2)	2.446(2)	2.354(2)
Sn(1)−X	2.751(1)	2.394(2)
Sn(1)−C(1)	2.229(3)	2.174(3)
P(1)−O(1)	1.468(3)	1.492(2)
P(2)−O(2)	1.479(2)	1.481(2)
Cr(1)−C(11)		1.862(4)
Cr(1)−C(12)		1.862(5)
Cr(1)−C(13)		1.858(4)
Cr(1)−C(14)		1.861(4)
Cr(1)−C(15)		1.844(4)
O(1)−Sn(1)−O(2)	150.97(9)	154.9(1)
O(1)−Sn(1)−Cr(1)		100.24(5)
O(1)−Sn(1)−X	88.38(7)	89.25(6)
O(1)−Sn(1)−C(1)	74.9(1)	77.65(9)
O(2)−Sn(1)−Cr(1)		102.19(5)
O(2)−Sn(1)−X	89.16(7)	89.17(6)
O(2)−Sn(1)−C(1)	76.7(1)	78.08(9)
Cr(1)−Sn(1)−Cl(1)		119.99(3)
Cr(1)−Sn(1)−C(1)		139.23(8)
X−Sn(1)−C(1)	96.35(9)	100.76(8)

Hz) (**7**), and δ 18.5, the latter being assigned to 1,3-$[P(O)(OEt)_2]_2$-5-*tert*-Bu-C_6H_3. Attempts at isolating analytically pure **7** from this solution failed. The same holds for the trimethylstannyl-substituted derivative {2,6-$[P(O)(OEt)_2]_2$-4-*tert*-Bu-C_6H_2}$SnSnMe_3$ (**7a**), the detailed NMR data of which are given in the Experimental Section.

The ^{119}Sn NMR chemical shifts in the Sn(II)−Sn(IV) compound **E** [(2-$C_6H_4CH_2PPh_2)_3$Sn−SnCl] (Chart 1)[47] are at δ −102 [Sn(IV)] and δ −226 [Sn(II)], which is comparable with the values observed for **7**. In contrast, essentially different chemical shifts of δ 897 and δ −502 have been reported for the Sn(II)−Sn(IV) derivative **D** {Sn[2-$(Me_3Si)_2CC_5H_4N$][Sn$(SiMe_3)_3$]} (Chart 1),[37] which demonstrates a closer electronic relationship of the latter stannylene to the zwitterionic $Sn(II)^{\delta-}-Sn(II)^{\delta+}$ compound $(^tBu_3Si)_2SnSn(Si^tBu_3)_2$ (δ 413, −690),[14] the Sn(II)−Sn(II) donor−acceptor complex {C_9H_6N-[CH-$(SiMe_3]$-8}$_2$Sn→$SnCl_2$ (δ 1264, −637),[41] and compound **F** [$(Me_2NCH_2CH_2CMe_2SnCl)_3SnCl_2)$] ($\delta$ 412, −119) (Chart 1),[40] rather than to the heteroleptic stannylene **7**.

In analogy with the reaction of the stannylene **1** with CsF (see above), the nucleophilic substitutions giving the stannylene derivatives **4**−**7a** (Scheme 1) are accompanied with tin−carbon bond cleavage and, after protonation under the reaction conditions employed, formation of 1,3-$[P(O)(OEt)_2]_2$-5-*tert*-BuC_6H_3, as was evidenced by the ^{31}P NMR spectra of the corresponding crude reaction mixtures.

In solution, the heteroleptic stannylenes **4**−**7a** show triplet resonances in the ^{119}Sn NMR spectra and exhibit only one ^{31}P NMR signal as a result of two identical P═O···Sn interactions. The room-temperature ^{13}C and ^{1}H NMR spectra of the phenylthio derivative **4**, the diorganostannylene **5**, and the silylated stannylene **6** each show two signals for the CH_3 groups of the $-P(O)(OEt)_2$ moieties. These results suggest that the tin atoms in **4**−**6** adopt a pseudo-trigonal-bipyramidal configuration with the oxygen atoms occupying the axial, and the lone pair and the *ipso*-carbon and the sulfur (**4**), the carbon (**5**), or the silicium (**6**), respectively, occupying the equatorial positions. In contrast with {2,6-$[P(O)(OEt)_2]_2$-4-*tert*-Bu-C_6H_2}SnCl (**1**), no inversion of configuration at tin is observed on the ^{1}H and ^{13}C NMR time scales.

Oxidative Additions of RSnCl and RSnBr to Give $[RSnCl(\mu\text{-}S)]_2$ (8), $RSnBr_3$ (9), and $RSn(CPh_3)$-

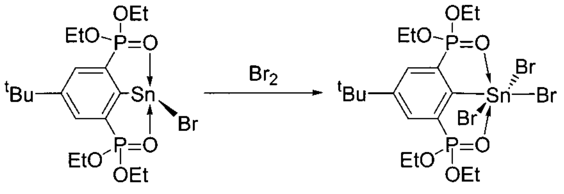
Table 4. Selected Bond Distances (Å) and Angles (deg) for 8

Sn(1)−C(1)	2.149(4)	Sn(1)−S(1a)	2.533(1)
Sn(1)−O(1)	2.260(3)	P(1)−O(1)	1.494(3)
Sn(1)−O(2)	2.267(3)	P(2)−O(2)	1.497(3)
Sn(1)−S(1)	2.357(1)		

C(1)−Sn(1)−Cl(1)	87.8(1)	Cl(1)−Sn(1)−O(2)	87.9(1)
C(1)−Sn(1)−O(1)	79.8(1)	Cl(1)−Sn(1)−S(1a)	177.0(1)
C(1)−Sn(1)−O(2)	80.0(1)	O(1)−Sn(1)−O(2)	159.0(1)
C(1)−Sn(1)−S(1)	179.0(1)	O(1)−Sn(1)−S(1a)	93.3(1)
C(1)−Sn(1)−S(1a)	89.2(1)	O(2)−Sn(1)−S(1a)	91.9(1)
S(1)−Sn(1)−Cl(1)	93.1(1)	Sn(1)−S(1)−S(1a)	90.1(1)
S(1)−Sn(1)−O(1)	100.7(1)	C(2)−P(1)−O(1)	108.7(2)
S(1)−Sn(1)−O(2)	99.6(1)	C(6)−P(2)−O(2)	107.9(2)
S(1)−Sn(1)−S(1a)	89.9(1)	P(1)−O(1)−Sn(1)	116.5(2)
Cl(1)−Sn(1)−O(1)	85.9(1)	P(2)−O(2)−Sn(1)	116.3(2)

$(Cl)^+PF_6^-$ (10) (R = {2,6-[P(O)(OEt)$_2$]$_2$-4-*tert*-Bu-C_6H_2}), respectively. Although stannathiones of the type $[R_2SnS]_n$ (n = 1, 2; R = alkyl, aryl) are well known,[6,13,58−61] to the best of our knowledge there is no report on similar compounds of the type $[RSnClS]_n$.[62] The reaction of elemental sulfur with the heteroleptic stannylene {2,6-[P(O)(OEt)$_2$]$_2$-4-*tert*-Bu-C_6H_2}SnCl (**1**) gave the novel dimeric stannathione [{2,6-[P(O)(OEt)$_2$]$_2$-4-*tert*-Bu-C_6H_2}SnCl(μ-S)]$_2$ (**8**) as a colorless crystalline solid (Scheme 1). The molecular structure of **8** is shown in Figure 2, and crystallographic data and relevant bond angles and distances are given in Tables 2 and 4. The stannathione **8** consists of a centrosymmetric dimer with a planar $[SnS]_2$ ring. The Sn(1)−S(1) and Sn(1)−S(1a) bond lengths of 2.357(1) and 2.533(1) Å are comparable with those of {[$C_9H_6N(CH(SiMe_3)_2)$-8]$_2$Sn(μ-S)}$_2$ (Sn−S 2.402(3), 2.528(2) Å)[58] and [$Me_2NCH_2CH_2CH_2)_2$Sn(μ-S)]$_2$ (Sn−S 2.441(1), 2.482(1) Å).[60] The S−Sn−S angles in **8** are 89.89(4)° and 90.11(4)°. The tin atom in **8** adopts a distorted octahedral configuration, and the distortion from the ideal octahedral geometry is reflected in the *trans* angles C(1)−Sn(1)−S(1), Cl(1)−Sn(1)−S(1a), and O(1)−Sn(1)−O(2) of 179.0(1)°, 177.0(1)°, and 159.0(1)°, respectively. The deviation of the latter from the ideal value of 180° results from the ligand constraint, as was previously observed for the hexacoordinate diorganotin dichloride {2,6-[P(O)(OEt)$_2$]$_2$-4-*tert*-Bu-C_6H_2}$SnCl_2Ph$ (O−Sn−O 161.2°)[48] and the organotin trichloride {2,6-[P(O)(OEt)$_2$]$_2$-4-*tert*-Bu-C_6H_2}$SnCl_3$ (O−Sn−O 161.1°).[50] The intramolecular Sn(1)−O(1) and Sn(1)−O(2) distances of 2.260(3)/2.267(3) Å are comparable with the corresponding values measured for the dichloro-substituted derivative {2,6-[P(O)(OEt)$_2$]$_2$-4-*tert*-Bu-C_6H_2}$SnCl_2Ph$ (2.203(5), 2.278(6) Å). The identity of the dimer is retained in solution, as evidenced by osmometric molecular weight determination. A symmetric coordination of the phosphonate groups is established by a triplet resonance at δ −439 ($J(^{119}Sn-^{31}P)$ = 84 Hz) in the ^{119}Sn NMR spectrum and a single resonance at δ 26.7 ($J(^{119}Sn-^{31}P)$ = 86 Hz) in the ^{31}P NMR spectrum.

Oxidative addition of Br_2 to {2,6-[P(O)(OEt)$_2$]$_2$-4-*tert*-Bu-C_6H_2}SnBr (**2**) gave the monorganotin tribromide {2,6-[P(O)(OEt)$_2$]$_2$-4-*tert*-Bu-C_6H_2}$SnBr_3$ (**9**) (eq 3), the ^{119}Sn NMR spectrum of which shows a triplet resonance at δ −885 ($J(^{119}Sn-^{31}P)$ = 230 Hz). On the basis of multinuclear NMR (^{119}Sn, ^{31}P, ^{1}H, ^{13}C) and IR spectroscopy, compound **9** is likely to adopt a similar, monomeric molecular structure as previously reported for {2,6-[P(O)(OEt)$_2$]$_2$-4-*tert*-Bu-C_6H_2}$SnCl_3$.[50]



2 **9**

The reaction of {2,6-[P(O)(OEt)$_2$]$_2$-4-*tert*-Bu-C_6H_2}SnCl (**1**) with $Ph_3C^+PF_6^-$ gave the tin(IV) cation {2,6-[P(O)(OEt)$_2$]$_2$-4-*tert*-Bu-C_6H_2}Sn(Ph_3C)(Cl)$^+PF_6^-$ (**10**) in high yield (Scheme 1). To the best of our knowledge, this reaction is unprecedented in stannylene chemistry and can formally be interpreted as a Lewis base−Lewis acid complex or as oxidative addition of the trityl cation to the stannylene. The Mössbauer spectrum of the cation **10** shows an isomer shift of IS = 1.44 mm s^{-1}, typical for R_2Sn(IV) derivatives.[63] The IR spectrum of **10** shows a ν(P=O) at 1178 cm^{-1}, which is comparable with those reported for the tetravalent organotin derivatives **8** (ν(P=O) 1174 cm^{-1}) and **9** (ν(P=O) 1169 cm^{-1}). In solution, the ^{31}P NMR resonance for the organotin cation in **10** is observed at δ 24.8 ($J(^{119}Sn-^{31}P)$ = 52 Hz) and for the PF_6^- anion at δ −143.5 ($J(^{31}P-^{19}F)$ = 706 Hz), and the ^{119}Sn NMR spectrum displays a triplet resonance at δ −322 ($J(^{119}Sn-^{31}P)$ = 52 Hz). The ^{13}C NMR spectrum exhibits a triplet resonance at δ 79.8 ($J(^{13}C-^{31}P)$ = 4 Hz, $^1J(^{13}C-^{117/119}Sn)$ 758/788 Hz) for the quaternary aliphatic carbon of the CPh_3 moiety. Attempts to prepare the isoelectronic BPh_3 adduct of **1** failed.

Transition Metal Complexes of the Heteroleptic Stannylene RSnCl (1): RSn(Cl)M(CO)$_n$ (R = {2,6-[P(O)(OEt)$_2$]$_2$-4-*tert*-Bu-C_6H_2}, M = W, n = 5 (11); M = Cr, n = 5 (12); M = Fe, n = 4 (13)). {2,6-[P(O)(OEt)$_2$]$_2$-4-*tert*-Bu-C_6H_2}SnCl (**1**) was reacted with M(CO)$_5$thf (M = W, Cr) in thf to give {2,6-[P(O)(OEt)$_2$]$_2$-4-*tert*-Bu-C_6H_2}Sn(Cl)M(CO)$_5$ (M = W, **11**; M = Cr, **12**) (Scheme 1) as pale yellow and pale green solids, respectively. {2,6-[P(O)(OEt)$_2$]$_2$-4-*tert*-Bu-C_6H_2}Sn(Cl)-Fe(CO)$_4$ (**13**) was prepared in toluene starting from **1** and $Fe_2(CO)_9$ (Scheme 1). The ^{31}P NMR resonances of the metal stannylene complexes (**11**, δ = 33.9, $J(^{119}Sn-^{31}P)$ = 160 Hz; **12**, δ 32.8, $J(^{119}Sn-^{31}P)$ = 175 Hz; **13**, δ 30.5, $J(^{119}Sn-^{31}P)$ = 161 Hz) are significantly low frequency shifted as compared with that for the heteroleptic stannylene **1** (δ 39.1, $J(^{119}Sn-^{31}P)$ = 113 Hz). In the ^{119}Sn NMR spectra of the stannylene complexes **11**, **12**, and **13** triplet resonances are observed at δ −74 ($J(^{119}Sn-^{31}P)$ = 161 Hz), δ 131 ($J(^{119}Sn-^{31}P)$ = 179 Hz), and δ 54 ($J(^{119}Sn-^{31}P)$ = 165 Hz), respectively. The

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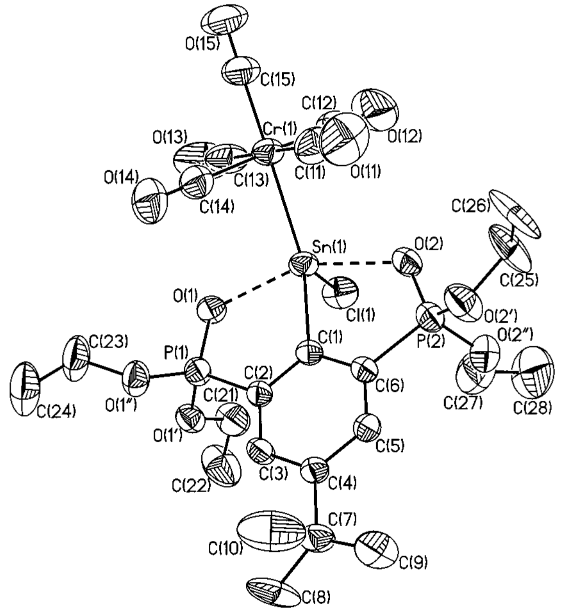

Figure 3. General view (SHELXTL) of a molecule of **12** showing 30% probability displacement ellipsoids and the atom-numbering scheme.

signal of the tungsten derivative **11** is only slightly high frequency shifted in comparison with the heteroleptic stannylene **1** (δ −100, $J(^{119}Sn-^{31}P) = 116$ Hz), whereas the chromium derivative **12** and the iron complex **13** show a significant high-frequency shift. A similar effect of the transition metal fragment on the ^{119}Sn chemical shift was reported for other metal−stannylene complexes,[24] e.g., $M(CO)_5SnCl_2\cdot thf_x$ (M = W, δ −209; M = Cr, δ = 55) compared with $SnCl_2\cdot thf_x$ (δ −238). The $^1J(^{119}Sn-^{183}W)$ coupling in **11** amounts to 1372 Hz, which lies between the values reported for compounds of the type $W(CO)_5SnX_2\cdot thf_x$ (X = Cl, Br, $^1J(^{119}Sn-^{183}W) = 1440-1610$ Hz)[64] and intramolecularly donor stabilized tungsten−diorganostannylene adducts of the type $W(CO)_5SnR_2$ ($^1J(^{119}Sn-^{183}W) = 892-976$ Hz).[18,47,51]

The molecular structure of $\{2,6\text{-}[P(O)(OEt)_2]_2\text{-}4\text{-}tert\text{-}Bu\text{-}C_6H_2\}Sn(Cl)Cr(CO)_5$ (**12**) is shown in Figure 3, crystallographic data are given in Table 2, and selected bond lengths and angles are summarized in Table 3. The O,C,O-pincer-type ligand in **12** is bonded in a tridentate fashion with C(1)−Sn(1), O(1)−Sn(1), and O(2)−Sn(1) bond lengths of 2.174(3), 2.335(2), and 2.354(2) Å, respectively. The latter are somewhat shortened in comparison with O−Sn bond lengths in the silyl-substituted stannylene **6** (2.546(3), 2.443(3) Å). The coordination geometry at the tin center is best described as a distorted trigonal bipyramid with the oxygens O(1) and O(2) occupying the axial sites and C(1), Cr(1), and Cl(1) the equatorial positions. The tin atom lies nearly perfectly in the equatorial plane (Δ = 0.014(1) Å). The Cr(1)−Sn(1)−Cl(1) (139.2(1)°) and Cl(1)−Sn(1)−C(1) (100.8(8)°) angles deviate from 120 °C as a result of steric repulsion by the $Cr(CO)_5$ fragment. The O(1)−Sn(1)−O(2) angle amounts to 154.9(1)° and lies between the O−Sn−O angles in **6** (O−Sn−O 150.8(1)°) and **8** (O−Sn−O 159.0(1)°). The Sn(1)−Cr(1) bond length of 2.5835(6) Å is remarkably short in comparison with a Sn−Cr single bond (2.85 Å)[65] and close to the Sn−Cr bond lengths in the three-coordinate stannylenes $(CO)_5CrSn[CH(SiMe_3)_2]_2$ [66] (2.562(2) Å) and $(CO)_5CrSn(2,4,6\text{-}^tBuC_6H_2)(CH_2C(CH_3)_2\text{-}3,5\text{-}^tBu_2C_6H_3)$[67] (2.614(1) Å). Slightly longer Sn−Cr bond distances have been reported for $(CO)_5CrSn(^tBu)_2\cdot$pyridine (Sn−Cr 2.653(3) Å),[68] $(CO)_5CrSn(SCH_2CH_2)_2N^tBu$ (Sn−Cr 2.62(1) Å),[52] and $(CO)_5CrSn(SCH_2CH_2)_2PPh\cdot$pyridine (Sn−Cr 2.618(1) Å),[69] which is attributed to the additional N−Sn donor interaction. A relatively short Sn−Cr bond has been reported for (salen)SnCr(CO)$_5$ (2.558(1) Å),[25] in which the tin center is coordinated by a tetradentate ligand in a distorted square-pyramidal geometry. Both the ^{13}C NMR chemical shifts for the carbonyl carbons at δ 219.9 and 226.3 and the ν(CO) of 1927 and 2051 cm^{-1} indicate the stannylene fragment in **12** to have a similar π-acceptor capacity as reported for the stanna(II)bicyclooctanes $RN(CH_2CH_2X)_2Sn$ (R = Me, ^{t}Bu; X = O, S)[70] and for (salen)Sn.[25]

Conclusion

In this contribution we have demonstrated the versatility of the O,C,O-coordinating ligand $\{2,6\text{-}[P(O)(OEt)_2]_2\text{-}4\text{-}tert\text{-}Bu\text{-}C_6H_2\}^-$ in stannylene chemistry. The rigid backbone of the ligand including the coordinating P=O donor groups stabilizes the tin(II) fragments, especially in the heteroleptic stannylene **1**, which is to the best of our knowledge the most stable compound of the type RSnCl reported so far. However, the O,C,O-coordinating ligand does not fully compensate for the electron deficiency at the tin(II) center, which still acts as a Lewis acid toward anions and as a Lewis base toward transition metal fragments. The stannylene **1** was demonstrated to be a reasonable precursor for the preparation of Sn(II)−M compounds with M = Si, Sn, Cr, W, and Fe. The air-stable heterobimetallic stannylenes **11**−**13** containing a Sn−Cl function should allow the preparation of heterotrimetallic compounds.

Experimental Section

General Methods. All reactions were carried out under an atmosphere of dry nitrogen. The solvents were purified by distillation from appropriate drying agents under nitrogen.

[{2,6-Bis(diethoxyphosphonyl)-4-*tert*-butyl}phenyl]lithium,[48] Ph_3SiLi,[71] and Ph_3SnLi [72] were prepared according to the literature, and tetrabutylammonium fluoride trihydrate and $[(Ph_3P)_2N]^+Cl^-$ were commercial products.

Elemental analyses were performed on an instrument from Carlo Erba Strumentazione (Model 1106), and the molecular weight determinations were measured osmometrically on a Knauer Dampfdruckosmometer.

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NMR spectra were recorded on Bruker DRX400 and Bruker DPX300 FT NMR spectrometers with broad band decoupling of ^{119}Sn at 149.21 and 111.92 MHz, respectively, and of ^{13}C at 100.61 MHz, using external and internal deuterium lock. ^{1}H, ^{13}C, and ^{119}Sn NMR chemical shifts δ are given in ppm and referenced to external Me_4Sn (^{119}Sn) and Me_4Si (^{13}C, ^{1}H), respectively. Temperatures were maintained using a Bruker control system. The NMR spectra were recorded at room temperature if not otherwise stated.

IR spectra were obtained using a Bruker FT-IR IFS 113v spectrometer.

The Mössbauer spectra were recorded in constant-acceleration mode on a homemade instrument, designed and built by the Institut voor Kernen Stralingsfysica (IKS), Leuven. The isomer shifts refer to a source of $Ca^{119m}SnO_3$ from Amersham, U.K., samples being maintained at 90 ± 2 K. The data were treated with a least-squares iterative program deconvoluting the spectrum into a sum of Lorentzians.

Crystallography. Intensity data for the crystals were collected on a Nonius KappaCCD diffractometer with graphite-monochromated Mo Kα (0.71069 Å) radiation at 291 K (**6**, **12**) and 203 K (**8**). The data collection covered almost the whole sphere of reciprocal space with 360 frames via ω-rotation ($\Delta/\omega = 1°$) at two times, 10 s (**8**) and 20 s (**6**, **12**), per frame. The crystal-to-detector distance was 2.8 cm (**6**), 2.9 cm (**8**), and 3.0 cm (**12**) with a detector−θ−offset of 5° (**12**). Crystal decay was 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 was no indication for any decay. The structure was solved by direct methods using SHELXS97[73] and successive difference Fourier syntheses. Refinement applied full-matrix least-squares methods using SHELXL97.[74]

The H atoms were placed in geometrically calculated positions using a riding model ($C-H_{prim.}$ 0.96 Å, $C-H_{sec.}$ 0.97 Å; H_{aryl} C−H 0.93). The H atom isotropic temperature factors of **6** are constrained to be 1.5 times those of the carrier atom for aliphatic C atoms and refined with a common isotropic temperature factor (U_{iso} 0.101(3) Å^2), those of **8** are refined with a common isotropic temperature factor (U_{iso} 0.160(5) Å^2) for aromatic C atoms, and those of **12** are refined with common isotropic temperature factors for H_{aryl} (U_{iso} 0.050(6) Å^2) and for H_{alkyl} (U_{iso} 0.214(5) Å^2).

Disordered tetramethylene, *tert*-butyl (**12**), and *iso*-butyl (**8**) groups were found with occupancies of 0.3333 (C(43′), C(44′)), 0.5 (C(3), C(5), C(3′), C(5′)), and 0.6666 (C(43), C(44)) in **12** and of 0.15 (C(32′)) and 0.85 (C(32)) in **8**. The solvent molecule thf (**6**) was isotropically refined with an occupancy of 0.5.

Atomic scattering factors for neutral atoms and real and imaginary dispersion terms were taken from International Tables for X-ray Crystallography.[75] The figures were created by SHELXTL.[76] Crystallographic data are given in Table 2, and selected bond distances and angles for **6** and **12** are given in Table 3 and for **8** in Table 4.

Synthesis of {[2,6-Bis(diethoxyphosphonyl)-4-*tert*-butyl]phenyl}tin(II) Chloride, {2,6-[P(O)(OEt)$_2$]$_2$-4-*tert*-BuC$_6$H$_2$}SnCl (1). [{2,6-Bis(diethoxyphosphonyl)-4-*tert*-butyl}-phenyl]lithium (5.55 g, 13.50 mmol) was added in small portions at −30 °C to a solution of $SnCl_2$ (2.65 g, 13.98 mmol) in thf (90 mL). The resulting suspension was stirred for 4 h at −30 °C and 2 h at room temperature. The solvent was evaporated, the residue was extracted four times with hot hexane (320 mL), and the combined solutions were concentrated to a volume of 80 mL. Crystallization at −20 °C afforded 5.10 g (68%) of **1** as a colorless solid, mp 107−109 °C. ^{1}H NMR (400.13 MHz, [d_8]toluene): δ 1.14 (s, $\nu_{1/2}$ = 16 Hz, 12H, CH_3), 1.24 (s, 9H, CH_3), 4.04 (s, $\nu_{1/2}$ = 25 Hz, 4H, CH_2), 4.32 (s, $\nu_{1/2}$ = 20 Hz, 2H, CH_2), 4.54 ($\nu_{1/2}$ = 20 Hz, 2H, CH_2), 8.18 (complex pattern, 2H, H_{Ph}). ^{1}H NMR (400.13 MHz, [d_8]toluene, −20 °C): δ 1.14 (t, 6H, CH_3), 1.20 (t, 6H, CH_3), 1.23 (s, 9H, CH_3), 3.93−4.00 (complex pattern, 4H, CH_2), 4.32−4.41 (complex pattern, 2H, CH_2), 4.63−4.71 (complex pattern, 2H, CH_2), 8.27 (complex pattern, 2H, H_{Ph}). ^{13}C{^{1}H} NMR (100.63 MHz, [d_8]-toluene): δ 16.8 (s, 2C, CH_3), 16.9 (s, 2C, CH_3), 31.5 (s, 3C, CH_3), 35.3 (s, 1C, C), 63.7 (s, $\nu_{1/2}$ = 30 Hz, 2C, CH_2), 64.3 (s, $\nu_{1/2}$ = 30 Hz, 2C, CH_2), 132.2 (dd, $^{1}J(^{13}C-^{31}P)$ = 193 Hz, $^{3}J(^{13}C-^{31}P)$ = 24 Hz, 2C, $C_{2,6}$), 132.4 (complex pattern, 2C, $C_{3,5}$), 151.9 (t, $^{3}J(^{13}C-^{31}P)$ = 13 Hz, 1C, C_4), 188.2 (t, $^{2}J(^{13}C-^{31}P)$ = 37 Hz, 1C, C_1). ^{119}Sn{^{1}H} NMR (149.18 MHz, [d_8]toluene): δ −100 (t, $J(^{119}Sn-^{31}P)$ = 116 Hz). ^{31}P{^{1}H} NMR (161.98 MHz, [d_8]-toluene): δ 39.1 ($J(^{31}P-^{119}Sn)$ = 113 Hz). IR (KBr): ν = 1192 cm^{-1} (P═O); 1171 cm^{-1} (P═O). Anal. Calcd for $C_{18}H_{31}ClO_6P_2Sn$ (559.6): C, 38.6; H, 5.6; Cl, 6.3. Found: C, 38.2; H, 5.8; Cl, 6.3. Molecular weight determination (benzene, 45 °C): 506 g mol^{-1}. Mössbauer spectroscopy: QS = 3.51 mm s^{-1}, IS = 3.24 mm s^{-1}. Compound **1** was exposed to air for 8 days, and Mössbauer spectra of this sample were measured after 0, 3, 75, and 179 h.

Synthesis of {[2,6-Bis(diethoxyphosphonyl)-4-*tert*-butyl]phenyl}tin(II) Bromide, {2,6-[P(O)(OEt)$_2$]$_2$-4-*tert*-BuC$_6$H$_2$}SnBr (2). [{2,6-Bis(diethoxyphosphonyl)-4-*tert*-butyl}-phenyl]lithium (1.53 g, 3.71 mmol) was added in small portions at −30 °C to a suspension of $SnBr_2$ (1.14 g, 4.09 mmol) in thf (30 mL). The suspension was stirred for 4 h at −30 °C and 12 h at room temperature. The solvent was evaporated, the residue was extracted four times with hot hexane (240 mL), and then the solution was concentrated to a volume of 60 mL. Crystallization at −20 °C afforded 0.22 g (10%) of **2** as colorless solid, mp 105−106 °C. ^{1}H NMR (400.13 MHz, [d_8]toluene): δ 1.02 (t, 12H, CH_3), 1.11 (s, 9H, CH_3), 3.93−4.00 (complex pattern, 4H, CH_2), 4.00−4.19 (complex pattern, 4H, CH_2), 8.27 (complex pattern, 2H, H_{Ph}). ^{13}C{^{1}H} NMR (100.63 MHz, [d_8]-toluene): δ 15.9 (d, $^{3}J(^{13}C-^{31}P)$ = 7 Hz, 4C, CH_3), 30.5 (s, 3C, CH_3), 34.3 (s, 1C, C), 63.1 (d, $^{2}J(^{13}C-^{31}P)$ = 5 Hz, 4C, CH_2), 131.2 (dd, $^{1}J(^{13}C-^{31}P)$ = 193 Hz, $^{3}J(^{13}C-^{31}P)$ = 24 Hz, 2C, $C_{2,6}$), 131.4 (complex pattern, 2C, $C_{3,5}$), 151.0 (t, $^{3}J(^{13}C-^{31}P)$ = 13 Hz, 1C, C_4), 185.8 (t, $^{2}J(^{13}C-^{31}P)$ = 36 Hz, 1C, C_1). ^{119}Sn{^{1}H} NMR (149.18 MHz, [d_8]toluene): δ −68 (t, $J(^{119}Sn-^{31}P)$ = 116 Hz). ^{31}P{^{1}H} NMR (161.98 MHz, [d_8]toluene): δ 38.8 ($J(^{31}P-^{119/117}Sn)$ = 115/111 Hz). IR (KBr): ν = 1192 cm^{-1} (P═O), 1171 cm^{-1} (P═O). Anal. Calcd for $C_{18}H_{31}BrO_6P_2Sn$ (604.0): C, 35.8; H, 5.2; Br, 13.2. Found: C, 36.2; H, 5.6; Br, 13.1.

Reaction of {[2,6-Bis(diethoxyphosphonyl)-4-*tert*-butyl]-phenyl}tin(II) Chloride (1) with Bu$_4$NF·3H$_2$O. To a solution of {2,6-[P(O)(OEt)$_2$]$_2$-4-*tert*-BuC$_6$H$_2$}SnCl (**1**) (65 mg, 0.12 mmol) in [d_8]toluene (0.5 mL) was added $Bu_4NF\cdot 3H_2O$ (37 mg, 0.12 mmol) at room temperature. ^{119}Sn{^{1}H} NMR spectra of this solution were recorded at room temperature and at −40 °C. ^{119}Sn{^{1}H} NMR (149.18 MHz, [d_8]toluene): δ −98 ($\nu_{1/2}$ = 1000 Hz). ^{119}Sn{^{1}H} NMR (149.18 MHz, [d_8]toluene, −40 °C): δ −111 ($\nu_{1/2}$ = 290 Hz, integral 0.2), −208 ($J(^{119}Sn-^{31}P)$ = 112 Hz, $^{1}J(^{119}Sn-^{19}F)$ = 3140 Hz, integral 0.8). ^{31}P{^{1}H} NMR (161.98 MHz, [d_8]toluene, −40 °C): δ 45.2 ($\nu_{1/2}$ = 80 Hz).

Reaction of {[2,6-Bis(diethoxyphosphonyl)-4-*tert*-butyl]-phenyl}tin(II) Chloride (1) with [(Ph$_3$P)$_2$N]$^+$Cl$^-$. To a solution of {2,6-[P(O)(OEt)$_2$]$_2$-4-*tert*-BuC$_6$H$_2$}SnCl (**1**) (105 mg, 0.19 mmol) in [d_8]toluene (0.4 mL) was added $[(Ph_3P)_2N]^+Cl^-$ in a 1:2 (214 mg, 0.38 mmol) and 1:1 (107 mg, 0.19 mmol) molar ratio at room temperature. ^{119}Sn{^{1}H} and ^{31}P{^{1}H} NMR spectra of these solutions were recorded at different temperatures.

Synthesis of {[2,6-Bis(diethoxyphosphonyl)-4-*tert*-butyl]phenyl}(thiophenolate)tin(II), {2,6-[P(O)(OEt)$_2$]$_2$-4-*tert*-Bu-C$_6$H$_2$}SnSPh (4). NaSPh (220 mg, 1.67 mmol) was added to a solution of {2,6-[P(O)(OEt)$_2$]$_2$-4-*tert*-Bu-C$_6$H$_2$}SnCl (550 mg, 0.98 mmol) in toluene (25 mL). After stirring the

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suspension for 17 h at 80 °C, the solvent was removed in vacuo, and the resulting residue was extracted twice with 25 mL of hot *n*-hexane and filtered. The filtrate was reduced to a volume of 15 mL. Crystallization at −25 °C yielded 450 mg (72%) of **4** as a pale yellow solid, mp 250 °C. ^{1}H NMR (400.13 MHz, CDCl$_3$): δ 1.22 (t, 6H, CH$_3$), 1.24 (t, 6H, CH$_3$), 1.28 (s, 9H, CH$_3$), 3.94−4.34 (complex pattern, 8H, CH$_2$), 6.92 (t, 1H, H$_{\mathrm{Ph},para}$), 7.04 (t, 2H, H$_{\mathrm{Ph},meta}$), 7.45 (d, 2H, H$_{\mathrm{Ph},ortho}$), 7.79 (d, $^{3}J(^{1}\mathrm{H}-^{31}\mathrm{P})$ = 14 Hz, 2H, H$_{\mathrm{aryl}}$). ^{13}C{^{1}H} NMR (100.63 MHz, CDCl$_3$): δ 16.7 (d, $^{3}J(^{13}\mathrm{C}-^{31}\mathrm{P})$ = 9 Hz, 2C, CH$_3$), 16.8 (d, $^{3}J(^{13}\mathrm{C}-^{31}\mathrm{P})$ = 9 Hz, 2C, CH$_3$), 31.6 (s, 3C, CH$_3$), 35.3 (s, 1C, C$_q$), 63.2 (d, $^{2}J(^{13}\mathrm{C}-^{31}\mathrm{P})$ = 6 Hz, 2C, CH$_2$), 64.2 (d, $^{2}J(^{13}\mathrm{C}-^{31}\mathrm{P})$ = 5 Hz, 2C, CH$_2$), 124.1 (s, 1C, C$_{\mathrm{Ph},para}$), 128.4 (s, 2C, C$_{\mathrm{Ph},meta}$), 131.9 (dd, $^{1}J(^{13}\mathrm{C}-^{31}\mathrm{P})$ = 193 Hz, $^{3}J(^{13}\mathrm{C}-^{31}\mathrm{P})$ = 24 Hz, 2C, C$_{2,6}$), 132.2 (dd, $^{2}J(^{13}\mathrm{C}-^{31}\mathrm{P})$ = 17 Hz, $^{4}J(^{13}\mathrm{C}-^{31}\mathrm{P})$ = 4 Hz, 2C, C$_{3,5}$), 133.2 (s, 2C, C$_{\mathrm{Ph},ortho}$), 142.0 (s, 1C, C$_{\mathrm{Ph},ipso}$), 151.5 (t, $^{3}J(^{13}\mathrm{C}-^{31}\mathrm{P})$ = 13 Hz, 1C, C$_4$), 182.7 (t, $^{3}J(^{13}\mathrm{C}-^{31}\mathrm{P})$ = 35 Hz, 1C, C$_1$). ^{119}Sn{^{1}H} NMR (111.92 MHz, toluene/D$_2$O-cap.): δ 2 (t, $J(^{119}\mathrm{Sn}-^{31}\mathrm{P})$ = 96 Hz). ^{31}P{^{1}H} NMR (121.49 MHz, toluene/D$_2$O-cap.): δ 37.4 (s, $J(^{13}\mathrm{P}-^{117/119}\mathrm{Sn})$ = 95 Hz). IR (Nujol): ν = 1164 cm^{-1} (P=O). Anal. Calcd for C$_{24}$H$_{36}$O$_6$P$_2$SSn (633.3): C, 45.5; H, 5.7. Found: C, 45.5; H, 5.7.

Synthesis of {[2,6-Bis(diethoxyphosphonyl)-4-*tert*-butyl]phenyl}[bis(trimethylsilylmethyl)]tin, {2,6-[P(O)(OEt)$_2$]$_2$-4-*tert*-Bu-C$_6$H$_2$}SnCH(SiMe$_3$)$_2$ (5). To a solution of {2,6-[P(O)(OEt)$_2$]$_2$-4-*tert*-BuC$_6$H$_2$}SnCl (**1**) (932 mg, 1.67 mmol) in diethyl ether (12 mL) at −78 °C was added (Me$_3$Si)$_2$CHLi (278 mg, 1.68 mmol) in small portions. The resulting suspension was stirred overnight at room temperature, the solid was filtered, and all volatiles were evaporated to give 1.03 g (91%) of **5** as a pale yellow solid, 90 °C (dec). ^{1}H NMR (400.13 MHz, [*d*$_8$]toluene): δ 0.29 (s, 1H, CH), 0.61 (s, 18H, SiMe$_3$), 1.11 (t, 6H, CH$_3$), 1.36 (s, 9H, CH$_3$), 1.38 (t, 6H, CH$_3$), 3.85−3.95 (complex pattern, 2H, CH$_2$), 4.04−4.14 (complex pattern, 2H, CH$_2$), 4.22−4.39 (complex pattern, 4H, CH$_2$), 8.13 (complex pattern, 2H, H$_{\mathrm{Ph}}$). ^{13}C{^{1}H} NMR (100.63 MHz, [*d*$_8$]toluene): δ 4.27 (s, $^{1}J(^{13}\mathrm{C}-^{29}\mathrm{Si})$ = 48 Hz, $^{4}J(^{13}\mathrm{C}-^{119}\mathrm{Sn})$ = 15 Hz, 6C, SiMe$_3$), 15.7 (d, $^{3}J(^{13}\mathrm{C}-^{31}\mathrm{P})$ = 7 Hz, 2C, CH$_3$), 15.8 (d, $^{3}J(^{13}\mathrm{C}-^{31}\mathrm{P})$ = 7 Hz, 2C, CH$_3$), 30.6 (s, 3C, CH$_3$), 34.1 (s, 1C, C), 62.1 (d, $^{2}J(^{13}\mathrm{C}-^{31}\mathrm{P})$ = 7 Hz, 2C, CH$_2$), 62.2 (d, $^{2}J(^{13}\mathrm{C}-^{31}\mathrm{P})$ = 5 Hz, 2C, CH$_2$), 130.9 (complex pattern, 2C, C$_{3,5}$), 132.2 (dd, $^{1}J(^{13}\mathrm{C}-^{31}\mathrm{P})$ = 195 Hz, $^{3}J(^{13}\mathrm{C}-^{31}\mathrm{P})$ = 24 Hz, 2C, C$_{2,6}$), 149.4 (t, $^{3}J(^{13}\mathrm{C}-^{31}\mathrm{P})$ = 13 Hz, 1C, C$_4$), 189.8 (t, $^{2}J(^{13}\mathrm{C}-^{31}\mathrm{P})$ = 37 Hz, 1C, C$_1$). ^{119}Sn{^{1}H} NMR (149.18 MHz, [*d*$_8$]toluene): δ 259 (t, $J(^{119}\mathrm{Sn}-^{31}\mathrm{P})$ = 106 Hz). ^{31}P{^{1}H} NMR (161.98 MHz, [*d*$_8$]toluene): δ 33.5 ($J(^{31}\mathrm{P}-^{119}\mathrm{Sn})$ = 107 Hz). Anal. Calcd for C$_{25}$H$_{50}$O$_6$P$_2$Si$_2$Sn (683.5): C, 43.9; H, 7.4. Found: C, 43.5; H, 7.1.

Synthesis of {[2,6-Bis(diethoxyphosphonyl)-4-*tert*-butyl]phenyl}(triphenylsilyl)tin(II), {2,6-[P(O)(OEt)$_2$]$_2$-4-*tert*-Bu-C$_6$H$_2$}SnSiPh$_3$ (6). A solution of Ph$_3$SiLi (2.70 mmol) in thf (40 mL) was added dropwise at −40 °C to a solution of {2,6-[P(O)(OEt)$_2$]$_2$-4-*tert*-Bu-C$_6$H$_2$}SnCl (1.50 g, 2.69 mmol) in thf (15 mL). Stirring for 15 h at −40 °C yielded a red-brown solution, which was then evaporated to dryness in vacuo at −20 °C. The resulting brown solid was extracted and filtered four times with 25 mL of cold *n*-hexane. The filtrates were combined and reduced to a volume of 25 mL. Crystallization at −25 °C yielded 300 mg (14%) of **6** as an orange solid, mp 77−79 °C. ^{1}H NMR (400.13 MHz, [*d*$_8$]thf): δ 0.94 (t, 6H, CH$_3$), 1.22 (t, 6H, CH$_3$), 1.42 (s, 9H, CH$_3$), 3.07 (complex pattern, 2H, CH$_2$), 3.33 (complex pattern, 2H, CH$_2$), 3.96 (complex pattern, 2H, CH$_2$), 4.05 (complex pattern, 2H, CH$_2$), 7.05−7.30 (complex pattern, 15H, Ph$_3$Si), 7.77 (d, $^{3}J(^{1}\mathrm{H}-^{31}\mathrm{P})$ = 13 Hz, 2H, H$_{\mathrm{aryl}}$). ^{13}C{^{1}H} NMR (100.63 MHz, thf/D$_2$O-cap.): δ 15.6 (d, $^{3}J(^{13}\mathrm{C}-^{31}\mathrm{P})$ = 7 Hz, 2C, CH$_3$), 15.7 (d, $^{3}J(^{13}\mathrm{C}-^{31}\mathrm{P})$ = 7 Hz, 2C, CH$_3$), 30.7 (s, 3C, CH$_3$), 34.4 (s, 1C, C$_q$), 62.0 (d, $^{3}J(^{13}\mathrm{C}-^{31}\mathrm{P})$ = 6 Hz, 2C, CH$_2$), 62.3 (d, $^{3}J(^{13}\mathrm{C}-^{31}\mathrm{P})$ = 5 Hz, 2C, CH$_2$), 126.8 (s, 6C, C$_{\mathrm{Ph},meta}$), 127.1 (s, 3C, C$_{\mathrm{Ph},para}$), 131.0 (dd, $^{2}J(^{13}\mathrm{C}-^{31}\mathrm{P})$ = 17 Hz, $^{4}J(^{13}\mathrm{C}-^{31}\mathrm{P})$ = 4 Hz, 2C, C$_{3,5}$), 131.7 (dd, $^{1}J(^{13}\mathrm{C}-^{31}\mathrm{P})$ = 194 Hz, $^{3}J(^{13}\mathrm{C}-^{31}\mathrm{P})$ = 24 Hz, 2C, C$_{2,6}$), 136.6 (s, 6C, C$_{\mathrm{Ph},ortho}$), 141.7 (s, 3C, C$_{\mathrm{Ph},ipso}$), 149.4 (t, $^{3}J(^{13}\mathrm{C}-^{31}\mathrm{P})$ = 13 Hz, 1C, C$_4$), 185.5 (t, $^{2}J(^{13}\mathrm{C}-^{31}\mathrm{P})$ = 36 Hz, 1C, C$_1$). ^{119}Sn{^{1}H} NMR (121.49 MHz, thf/D$_2$O-cap.): δ 192 (t, $J(^{117/119}\mathrm{Sn}-^{31}\mathrm{P})$ = 96 Hz). ^{29}Si{^{1}H} NMR (59.63 MHz, thf/D$_2$O-cap.): δ 7.9 (s, $^{1}J(^{29}\mathrm{Si}-^{117/119}\mathrm{Sn})$ = 674/708 Hz). ^{31}P{^{1}H} NMR (161.98 MHz, [*d*$_8$]toluene): δ 34.5 ($J(^{119}\mathrm{Sn}-^{31}\mathrm{P})$ = 95 Hz). Anal. Calcd for C$_{36}$H$_{46}$O$_6$P$_2$SiSn (783.5): C, 55.2; H, 5.9. Found: C, 55.9; H, 6.7.

In Situ Syntheses of {[2,6-Bis(diethoxyphosphonyl)-4-*tert*-butyl]phenyl}(triorganostannyl)tin(II) Derivatives, {2,6-[P(O)(OEt)$_2$]$_2$-4-*tert*-Bu-C$_6$H$_2$}SnSnPh$_3$ (7) and {2,6-[P(O)(OEt)$_2$]$_2$-4-*tert*-Bu-C$_6$H$_2$}SnSnMe$_3$ (7a). A solution of R$_3$SnLi (**7**, R = Ph; **7a**, R = Me; 2.70 mmol) in thf (15 mL) was added dropwise at −40 °C to a solution of {2,6-[P(O)(OEt)$_2$]$_2$-4-*tert*-Bu-C$_6$H$_2$}SnCl (1.00 g, 1.79 mmol) in thf (15 mL). Stirring for 15 h at −40 °C gave a red-brown solution, the volume of which was reduced in vacuo at −20 °C to about 5 mL. From this solution ^{31}P and ^{119}Sn NMR spectra were recorded.

Compound 7. ^{119}Sn{^{1}H} NMR (111.92 MHz, thf/D$_2$O-cap.): δ 109 (t, $J(^{119}\mathrm{Sn}-^{31}\mathrm{P})$ = 98 Hz, $^{1}J(^{119}\mathrm{Sn}-^{117/119}\mathrm{Sn})$ = 9130/9550 Hz, Sn(II) of **7**), −43 (t, $J(^{119}\mathrm{Sn}-^{31}\mathrm{P})$ = 21 Hz, $^{1}J(^{119}\mathrm{Sn}-^{117/119}\mathrm{Sn})$ = 9125/9545 Hz, Sn(IV) of **7**), −94 ($\nu_{1/2}$ = 400 Hz, **1**), −143.4 (Ph$_3$SnSnPh$_3$). ^{31}P{^{1}H} NMR (121.49 MHz, thf/D$_2$O-cap.): δ 39.2 (s, $J(^{31}\mathrm{P}-^{117/119}\mathrm{Sn})$ = 112 Hz, **1**), 35.4 (s, $J(^{31}\mathrm{P}-^{117/119}\mathrm{Sn})$ = 99 Hz), 18.5 (1,3-[P(O)(OEt)$_2$]$_2$-4-*tert*-Bu-C$_6$H$_3$).

Compound 7a. ^{119}Sn{^{1}H} NMR (111.92 MHz, thf/D$_2$O-cap.): δ 217 (t, $J(^{119}\mathrm{Sn}-^{31}\mathrm{P})$ = 93 Hz, $^{1}J(^{119}\mathrm{Sn}-^{117/119}\mathrm{Sn})$ = 7976/8346 Hz, Sn(II) of **7a**), 11 (t, $J(^{119}\mathrm{Sn}-^{31}\mathrm{P})$ = 21 Hz, $^{1}J(^{119}\mathrm{Sn}-^{117/119}\mathrm{Sn})$ = 9125/9545 Hz, Sn(IV) of **7a**), −75.0 ($\nu_{1/2}$ = 122 Hz, not assigned), −106 (Me$_3$SnSnMe$_3$). ^{31}P{^{1}H} NMR (121.49 MHz, thf/D$_2$O-cap.): δ 37.7 (s, $J(^{31}\mathrm{P}-^{117/119}\mathrm{Sn})$ = 21, 95 Hz, **7a**), 20.9 (1,3-[P(O)(OEt)$_2$]$_2$-4-*tert*-Bu-C$_6$H$_3$).

Synthesis of {[2,6-Bis(diethoxyphosphonyl)-4-*tert*-butyl]phenyl}tin Chloride Sulfide, {{2,6-[P(O)(OEt)$_2$]$_2$-4-*tert*-BuC$_6$H$_2$}Sn(S)Cl}$_2$ (8). Sulfur (19 mg, 0.59 mmol) was added at −78 °C to a solution of {2,6-[P(O)(OEt)$_2$]$_2$-4-*tert*-BuC$_6$H$_2$}SnCl (**1**) (305 mg, 0.55 mmol) in thf (5 mL). The reaction mixture was stirred at room temperature overnight, and the solvent was evaporated. The residue was crystallized from toluene/CHCl$_3$ at 4 °C to give 226 mg (69%) of **8** as colorless crystals, mp > 350 °C. ^{1}H NMR (400.13 MHz, [*d*$_8$]toluene): δ 1.12 (s, 9H, CH$_3$), 1.16 (t, 6H, CH$_3$), 1.38 (t, 6H, CH$_3$), 4.30−4.33 (complex pattern, 2H, CH$_2$), 4.53−4.62 (complex pattern, 4H, CH$_2$), 4.98−5.01 (complex pattern, 2H, CH$_2$), 8.03 (complex pattern, 2H, H$_{\mathrm{Ph}}$). ^{13}C{^{1}H} NMR (100.63 MHz, [*d*$_8$]toluene): δ 15.8 (complex pattern, 2C, CH$_3$), 16.0 (complex pattern, 2C, CH$_3$), 30.5 (s, 3C, CH$_3$), 34.3 (s, 1C, C), 64.6 (s, 2C, CH$_2$), 65.5 (s, 2C, CH$_2$), 125.8 (dd, $^{1}J(^{13}\mathrm{C}-^{31}\mathrm{P})$ = 180 Hz, $^{3}J(^{13}\mathrm{C}-^{31}\mathrm{P})$ = 19 Hz, 2C, C$_{2,6}$), 130.7 (complex pattern, 2C, C$_{3,5}$), 152.3 (t, $^{3}J(^{13}\mathrm{C}-^{31}\mathrm{P})$ = 13 Hz, 1C, C$_4$), 177.5 (t, $^{2}J(^{13}\mathrm{C}-^{31}\mathrm{P})$ = 19 Hz, 1C, C$_1$). ^{119}Sn{^{1}H} NMR (149.18 MHz, [*d*$_8$]toluene): δ −439 (t, $J(^{119}\mathrm{Sn}-^{31}\mathrm{P})$ = 84 Hz). ^{31}P{^{1}H} NMR (161.98 MHz, [*d*$_8$]toluene): δ 26.7 ($J(^{31}\mathrm{P}-^{119/117}\mathrm{Sn})$ = 86/82 Hz). IR (KBr): ν = 1174 cm^{-1} (P=O). Anal. Calcd for C$_{36}$H$_{62}$Cl$_2$O$_{12}$P$_4$S$_2$Sn$_2$ (1183.3): C, 36.5; H, 5.3. Found: C, 36.0; H, 4.8. Molecular weight determination (CHCl$_3$, 36 °C): 1166 g mol^{-1}.

Synthesis of {[2,6-Bis(diethoxyphosphonyl)-4-*tert*-butyl]phenyl}tin Tribromide, {2,6-[P(O)(OEt)$_2$]$_2$-4-*tert*-BuC$_6$H$_2$}SnBr$_3$ (9). Bromine (0.1 mL, 0.20 mmol) was added at 0 °C to a solution of {2,6-[P(O)(OEt)$_2$]$_2$-4-*tert*-BuC$_6$H$_2$}SnBr (**2**) (100 mg, 0.16 mmol) in toluene (3 mL). The reaction mixture was stirred at room temperature overnight, and the resulting residue was filtered and crystallized from CH$_2$Cl$_2$/hexane by slow evaporation of CH$_2$Cl$_2$ at room temperature to give 45 mg (37%) of **9** as a colorless solid, mp > 350 °C. ^{1}H NMR (400.13 MHz, CDCl$_3$): δ 1.36 (t, 12H, CH$_3$), 1.36 (s, 9H, CH$_3$), 4.25−4.35 (complex pattern, 4H, CH$_2$), 4.42−4.52 (complex pattern, 4H, CH$_2$), 7.92 (complex pattern, 2H, H$_{\mathrm{Ph}}$). ^{13}C{^{1}H} NMR (100.63 MHz, CDCl$_3$): δ 16.2 (complex pattern, 4C, CH$_3$), 31.3 (s, 3C, CH$_3$), 35.5 (s, 1C, C), 66.1 (complex pattern, 4C, CH$_2$), 122.7 (dd, ^1J(^{13}C−^{31}P) = 186 Hz, ^3J(^{13}C−^{31}P) = 18 Hz, 2C, C$_{2,6}$), 131.2 (complex pattern, 2C, C$_{3,5}$), 154.7 (t, ^3J(^{13}C−^{31}P) = 13 Hz, 1C, C$_4$), 175.0 (t, ^2J(^{13}C−^{31}P) = 18 Hz, 1C, C$_1$). ^{119}Sn{^{1}H} NMR (149.18 MHz, CDCl$_3$): δ −885 (t, J(^{119}Sn−^{31}P) = 230 Hz). ^{31}P{^{1}H} NMR (121.50 MHz, CDCl$_3$): δ 23.8 (J(^{31}P−$^{119/117}$Sn) = 236/225 Hz). IR (KBr): ν = 1169 cm^{-1} (P═O). Anal. Calcd for $C_{18}H_{31}Br_3O_6P_2Sn$ (763.8): C, 28.3; H, 4.1. Found: C, 28.6; H, 4.3.

Synthesis of {[2,6-Bis(diethoxyphosphonyl)-4-*tert*-butyl]phenyl}(triphenylmethyl)(chloro)tin Hexafluorophosphate, {2,6-[P(O)(OEt)$_2$]$_2$-4-*tert*-Bu-C$_6$H$_2$}(Ph$_3$C)ClSn$^+$PF$_6^-$ (10). Ph$_3$C$^+$PF$_6^-$ (600 mg, 1.54 mmol) was added in portions to a solution of {2,6-[P(O)(OEt)$_2$]$_2$-4-*tert*-Bu-C$_6$H$_2$}SnCl (**1**) (720 mg, 1.29 mmol) in toluene (25 mL). The suspension was stirred for 15 h at room temperature. The resulting solid was isolated and dried in vacuo to give 870 mg (71%) of **10** as a cream-colored solid, mp 130 °C (dec). ^{1}H NMR (400.13 MHz, [*d*$_6$]acetone): δ 1.17 (t, 6H, CH$_3$), 1.35 (t, 6H, CH$_3$), 1.45 (s, 9H, CH$_3$), 3.79−3.94 (complex pattern, 4H, CH$_2$), 4.20−4.39 (complex pattern, 4H, CH$_2$), 7.26−7.44 (complex pattern, 15H, H$_{Ph}$), 8.49 (d, ^3J(^{1}H−^{31}P) = 15 Hz, 2H, H$_{aryl}$). ^{13}C NMR (100.63 MHz, [*d*$_6$]acetone): δ 15.3 (d, ^3J(^{13}C−^{31}P) = 3 Hz, 2C, CH$_3$), 15.4 (d, ^3J(^{13}C−^{31}P) = 2 Hz, 2C, CH$_3$), 30.1 (s, 3C, CH$_3$), 35.6 (s, 1C, C$_q$), 66.5 (d, ^2J(^{13}C−^{31}P) = 19 Hz, 4C, CH$_2$), 79.8 (t, J(^{13}C−^{31}P) = 4 Hz, ^1J(^{13}C−$^{117/119}$Sn) = 758/788 Hz, 1C, C$_q$), 127.9 (s, 3C, C$_{Ph,para}$), 128.8 (s, ^4J(^{13}C−$^{117/119}$Sn) = 17 Hz, 6C, C$_{Ph,meta}$), 130.0 (dd, ^1J(^{13}C−^{31}P) = 185 Hz, ^3J(^{13}C−^{31}P) = 17 Hz, 2C, C$_{2,6}$), 130.5 (s, ^3J(^{13}C−$^{117/119}$Sn) = 68 Hz, 6C, C$_{Ph,ortho}$), 133.8 (complex pattern, 2C, C$_{3,5}$), 141.5 (s, ^2J(^{13}C−$^{117/119}$Sn) = 65 Hz, 3C, C$_{Ph,ipso}$), 156.3 (t, ^2J(^{13}C−^{31}P) = 16 Hz, C$_1$), 158.4 (t, ^3J(^{13}C−^{31}P) = 13 Hz, 1C, C$_4$). ^{119}Sn{^{1}H} NMR (111.92 MHz, CH$_2$Cl$_2$/D$_2$O-cap.): δ −322 (t, J(^{119}Sn−^{31}P) = 52 Hz). ^{31}P{^{1}H} NMR (121.49 MHz, CH$_2$Cl$_2$/D$_2$O-cap.): δ 24.8 (s, J(^{31}P−$^{117/119}$Sn) = 52 Hz, P(O)(OEt)$_2$), −143.5 (sept, ^1J(^{31}P−^{19}F) = 706 Hz, PF$_6$). IR (Nujol): ν = 1178 cm^{-1} (P═O). Mössbauer-spectroscopy: QS = 2.99 mm s^{-1}, IS = 1.44 mm s^{-1}. Anal. Calcd for $C_{37}H_{46}ClF_6O_6P_3Sn$ (947.8): C, 46.9; H, 4.9. Found: C, 46.6; H, 4.5.

Synthesis of {[2,6-Bis(diethoxyphosphonyl)-4-*tert*-butyl]phenyl}tin Chloride Tungsten Pentacarbonyl, {2,6-[P(O)(OEt)$_2$]$_2$-4-*tert*-Bu-C$_6$H$_2$}(Cl)Sn[W(CO)$_5$] (11). A solution of W(CO)$_6$ (1.50 g, 4.26 mmol) in thf (270 mL) was irradiated (UV light, Hg high-pressure lamp) until 95 mL (3.90 mmol) of CO were produced (1.5 h). From this solution, 140 mL (2.20 mmol W(CO)$_5$(thf)) was added dropwise at room temperature to a solution of {2,6-[P(O)(OEt)$_2$]$_2$-4-*tert*-Bu-C$_6$H$_2$}SnCl (**1**) (1.00 g, 1.79 mmol) in thf (30 mL). After stirring the mixture for 17 h, the solvent was evaporated and the excess W(CO)$_6$ sublimed in vacuo at 40 °C. Crystallization of the residue from *n*-hexane/toluene (15:1) yielded 130 mg (10%) of **11** as a pale yellow solid, mp 165−167 °C. ^{1}H NMR (400.13 MHz, C$_6$D$_6$): δ 0.91 (t, 6H, CH$_3$), 0.99 (t, 6H, CH$_3$), 1.01 (s, 9H, CH$_3$), 3.87−4.19 (complex pattern, 8H, CH$_2$), 8.01 (d, ^3J(^{1}H−^{31}P) = 14 Hz, 2H, H$_{aryl}$). ^{13}C NMR (100.63 MHz, C$_6$D$_6$): δ 14.7 (complex pattern, 4C, CH$_3$), 29.4 (s, 3C, CH$_3$), 33.6 (s, 1C, C$_q$), 63.0 (2C, CH$_2$), 63.7 (2C, CH$_2$), 129.6 (dd, ^1J(^{13}C−^{31}P) = 188 Hz, ^3J(^{13}C−^{31}P) = 19 Hz, 2C, C$_{2,6}$), 130.7 (complex pattern, 2C, C$_{3,5}$), 152.9 (t, ^3J(^{13}C−^{31}P) = 12 Hz, 1C, C$_4$), 170.4 (t, ^2J(^{13}C−^{31}P) = 25 Hz, 1C, C$_1$), 197.3 (s, ^2J(^{13}C−^{119}Sn) = 124 Hz, ^1J(^{13}C−^{182}W) = 66 Hz, 4C, CO$_{eq}$), 200.3 (s, 1C, CO$_{ax}$). ^{119}Sn{^{1}H} NMR (111.92 MHz, toluene/D$_2$O-cap.): δ −74 (t, ^1J(^{119}Sn−^{183}W) = 1372 Hz, J(^{119}Sn−^{31}P) = 161 Hz). ^{31}P{^{1}H} NMR (121.49 MHz, toluene/D$_2$O-cap.): δ 33.9 (s, J(^{31}P−$^{117/119}$Sn) = 160 Hz). IR (Nujol): ν = 1179 cm^{-1} (P═O), 1910 cm^{-1} (C═O), 2064 cm^{-1} (C═O). Anal. Calcd for $C_{23}H_{31}ClO_{11}P_2SnW$ (883.4): C, 31.3; H, 3.5. Found: C, 31.5; H, 3.4.

Synthesis of {[2,6-Bis(diethoxyphosphonyl)-4-*tert*-butyl]phenyl}tin Chloride Chromium Pentacarbonyl, {2,6-[P(O)(OEt)$_2$]$_2$-4-*tert*-Bu-C$_6$H$_2$}{Cl}Sn[Cr(CO)$_5$] (12). A solution of Cr(CO)$_6$ (1.00 g, 4.54 mmol) in thf (270 mL) was irradiated (UV light, Hg high-pressure lamp) until 100 mL (4.1 mmol) of CO was produced (1.5 h). From this solution, 140 mL (2.35 mmol Cr(CO)$_5$(thf)) was added dropwise at room temperature to a solution of {2,6-[P(O)(OEt)$_2$]$_2$-4-*tert*-Bu-C$_6$H$_2$}SnCl (**1**) (1.00 g, 1.79 mmol) in thf (30 mL). After stirring the mixture for 17 h, the solvent was evaporated, and the excess Cr(CO)$_6$ was sublimed in vacuo at 40 °C. Crystallization of the residue from *n*-hexane/toluene (15:1) yielded 310 mg (23%) of **12** as a pale green solid, mp 163−165 °C. ^{1}H NMR (400.13 MHz, C$_6$D$_6$): δ 0.91 (t, 6H, CH$_3$), 1.01 (complex pattern, 15H, CH$_3$), 3.86−4.18 (complex pattern, 8H, CH$_2$), 8.01 (d, ^3J(^{1}H−^{31}P) = 14 Hz, 2H, H$_{aryl}$). ^{13}C NMR (100.63 MHz, C$_6$D$_6$): δ 16.1 (d, ^3J(^{13}C−^{31}P) = 3 Hz, 2C, CH$_3$), 16.2 (d, ^3J(^{13}C−^{31}P) = 3 Hz, 2C, CH$_3$), 30.9 (s, 3C, CH$_3$), 35.2 (s, 1C, C$_q$), 64.6 (2C, CH$_2$), 65.1 (2C, CH$_2$), 131.1 (dd, ^1J(^{13}C−^{31}P) = 189 Hz, ^3J(^{13}C−^{31}P) = 20 Hz, 2C, C$_{2,6}$), 132.5 (complex pattern, 2C, C$_{3,5}$), 154.6 (t, ^3J(^{13}C−^{31}P) = 12 Hz, 1C, C$_4$), 172.8 (t, ^2J(^{13}C−^{31}P) = 25 Hz, 1C, C$_1$), 219.9 (s, ^2J(^{13}C−^{119}Sn) = 130 Hz, 4C, CO$_{eq}$), 226.3 (s, 1C, CO$_{ax}$). ^{119}Sn{^{1}H} NMR (111.92 MHz, toluene/D$_2$O-cap.): δ 131 (t, J($^{117/119}$Sn−^{31}P) = 179 Hz). ^{31}P{^{1}H} NMR (121.49 MHz, toluene/D$_2$O-cap.): δ 32.8 (s, J(^{31}P−$^{117/119}$Sn) = 175 Hz). IR (Nujol): ν = 1180 cm^{-1} (P═O), 1927 cm^{-1} (C═O), 2051 cm^{-1} (C═O). Anal. Calcd for $C_{23}H_{31}ClO_{11}P_2SnCr$ (751.6): C, 36.8; H, 4.2. Found: C, 36.6; H, 4.3.

Synthesis of {[2,6-Bis(diethoxyphosphonyl)-4-*tert*-butyl]phenyl}tin Chloride Iron Tetracarbonyl, {2,6-[P(O)(OEt)$_2$]$_2$-4-*tert*-Bu-C$_6$H$_2$}{Cl}Sn[Fe(CO)$_4$] (13). To a solution of {2,6-[P(O)(OEt)$_2$]$_2$-4-*tert*-Bu-C$_6$H$_2$}SnCl (**1**) (420 mg, 0.74 mmol) in toluene (10 mL) was added Fe$_2$(CO)$_9$ (136 mg, 0,37 mmol). The mixture was stirred at 80 °C for 15 h. The suspension was filtered, and *n*-hexane (10 mL) was added to the filtrate. Crystallization at −30 °C gave **13** as orange crystals, mp 250 °C (dec) (210 mg, 39%). ^{1}H NMR (400.13 MHz, CDCl$_3$): δ 1.23 (t, 6H, CH$_3$), 1.30 (t, 6H, CH$_3$), 1.34 (s, 9H, CH$_3$), 3.90−4.30 (complex pattern, 8H, CH$_2$), 7.93 (d, ^3J(^{1}H-^{31}P) = 12 Hz, 2H, H$_{aryl}$). ^{13}C NMR (100.63 MHz, CDCl$_3$): δ 16.5 (d, ^3J(^{13}C−^{31}P) = 3 Hz, 2C, CH$_3$), 16.6 (d, ^3J(^{13}C−^{31}P) = 4 Hz, 2C, CH$_3$), 31.5 (s, 3C, CH$_3$), 35.8 (s, 1C, C$_q$), 65.2 (4C, CH$_2$), 130.5 (dd, ^1J(^{13}C−^{31}P) = 187 Hz, ^3J(^{13}C−^{31}P) = 19 Hz, 2C, C$_{2,6}$), 132.5 (complex pattern, 2C, C$_{3,5}$), 155.4 (t, ^3J(^{13}C−^{31}P) = 13 Hz, 1C, C$_4$), 168.4 (t, ^2J(^{13}C−^{31}P) = 22 Hz, 1C, C$_1$), 215.0 (s, ^2J(^{13}C−^{119}Sn) = 180 Hz, CO). ^{119}Sn{^{1}H} NMR (111.92 MHz, toluene/D$_2$O-cap.): δ 54 (t, J($^{117/119}$Sn−^{31}P) = 165 Hz). ^{31}P{^{1}H} NMR (121.49 MHz, toluene/D$_2$O-cap.): δ 30.5 (s, J(^{31}P−$^{117/119}$Sn) = 161 Hz). IR (Nujol): ν = 1154 cm^{-1} (P═O), 1923 cm^{-1} (C═O), 2026 cm^{-1} (C═O). Anal. Calcd for $C_{22}H_{31}ClFeO_{10}P_2Sn$ (727.4): C, 36.3; H, 4.3. Found: C, 36.3; H, 4.2.

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Supporting Information Available: Tables of all coordinates, anisotropic displacement parameters, and geometric data for compounds **6**, **8**, and **12**. This material is available free of charge via the Internet at http://pubs.acs.org.

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