

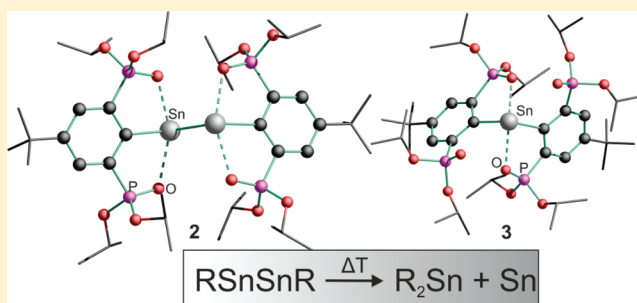
{4-*t*-Bu-2,6-[P(O)(O-*i*-Pr)₂]₂C₆H₂Sn}₂: An Intramolecularly Coordinated Organotin(II) Compound with a Sn–Sn Single Bond, Its Disproportionation toward a Diorganostannylene and Elemental Tin, and Its Oxidation with PhI(OAc)₂

Michael Wagner, Christina Dietz, Stefan Krabbe, Stephan G. Koller, Carsten Strohmann, and Klaus Jurkschat*

Lehrstuhl für Anorganische Chemie II, Technische Universität Dortmund, 44221 Dortmund, Germany

Supporting Information

ABSTRACT: Syntheses of the intramolecularly coordinated organotin(II) compound {4-*t*-Bu-2,6-[P(O)(O-*i*-Pr)₂]₂C₆H₂Sn}₂ (2), which crystallized in two different pseudopolymorphs 2 and 2·C₇H₈, of the diorganostannylene {4-*t*-Bu-2,6-[P(O)(O-*i*-Pr)₂]₂C₆H₂}Sn (3) and of the organotin(II) acetate 4-*t*-Bu-2,6-[P(O)(O-*i*-Pr)₂]₂C₆H₂SnOAc (4) are reported. The compounds were characterized by multinuclear NMR, IR (3 and 4), UV–vis spectroscopy (2), electrospray ionization mass spectrometry (3 and 4), and single-crystal X-ray diffraction analyses. Density functional theory calculations on compound 2 revealed the stabilizing effect of the intramolecular P=O → Sn coordination.



INTRODUCTION

The heavy formal analogues of alkynes (“distannynes”) have been known since the pioneering work of Power et al.¹ Such compounds, like the corresponding germanium² and silicon³ congeners, are of great interest with regard to their bonding theory. Depending on the organic substituents, single-, double-, and triple-bonded structures have been proposed.⁴ Organotin(I) compounds have been used for the activation of small molecules, e.g., dihydrogen, cyclopentadiene, cyclooctatetraene, azobenzene, and P₄.⁵ Also, Lewis base adducts with isonitriles are known.⁶

Elemental sulfur, selenium, and tellurium respectively were used for oxidation of the intramolecularly coordinated organotin(I) compound B,^{7a–c} (Chart 1) whereas Power et al. used pyridine N-oxide to produce an oxygen-bridged distannylene.^{7d}

Following the works by Power et al., intramolecularly N,C,N-coordinating pincer-type ligands, and amidine as well as β -diketiminate ligands, have been employed for the synthesis of tin(I) compounds of the types B–E, which are thermodynamically stabilized (Chart 1).^{5f,8a,b,c}

Intramolecularly coordinated diorganostannylenes have also been known since 1981 by work from Zuckerman et al.⁹ Crystallographically characterized examples F–L^{10–16} are shown in Chart 2. These compounds demonstrate that intramolecular Lewis base–Lewis acid interactions are an alternative to exclusively bulky substituents for the stabilization of stannylenes.

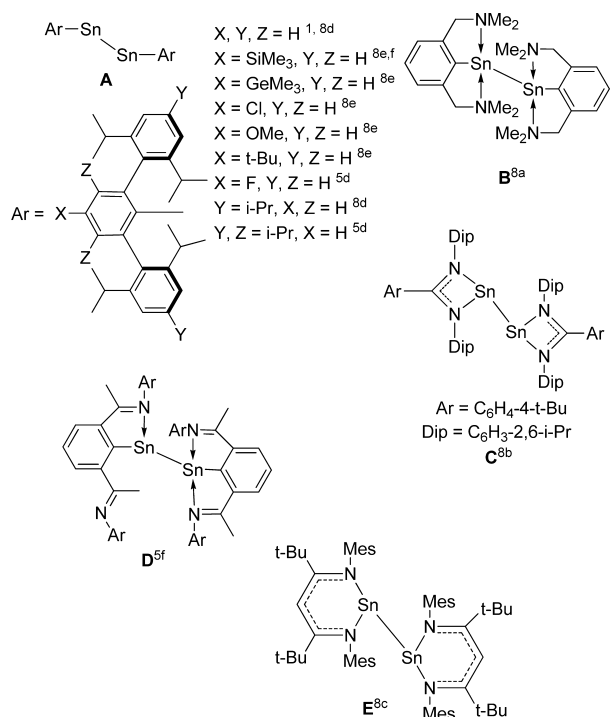
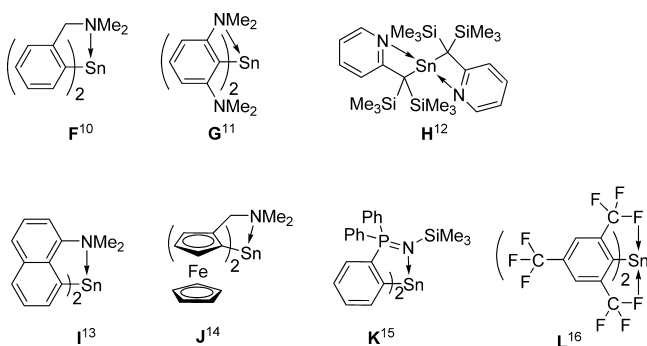
For many years, we have been interested in the synthesis and characterization of low-valent organoelement compounds containing the O,C,O-coordinating pincer-type ligand {4-*t*-Bu-2,6-[P(O)(O-*i*-Pr)₂]₂C₆H₂}[–], hereafter referred to as R.¹⁷ We isolated and characterized a number of transition-metal carbonyl complexes of the type R[M]SnSn[M]R (R = 4-*t*-Bu-2,6-[P(O)(O-*i*-Pr)₂]₂C₆H₂; [M] = Cr(CO)₅, Mo(CO)₅, W(CO)₅, Fe(CO)₄) by reacting the organochloridostannylene complexes R[M]SnCl with potassium tri-*sec*-butylboranate, K[B-*sec*-Bu₃H], to give the corresponding hydride derivatives R[M]SnH, which, in turn, smoothly convert into R[M]SnSn[M]R and H₂.^{17f,g} In a continuation of these studies, we here report the analogous reaction of RSnCl (1) with K[B-*sec*-Bu₃H], potassium graphite, C₈K, or sodium naphthalenide, respectively, to finally give the corresponding organotin(I) compound RSnSnR (2). Furthermore, we investigate the thermal stability of the latter compound and exemplarily demonstrate its reactivity toward oxidation with PhI(OAc)₂.

RESULTS AND DISCUSSION

The reaction of 1 in tetrahydrofuran (THF) with potassium tri-*sec*-butylboranate (K[B-*sec*-Bu₃H]) gave, after 30 min, a crude reaction mixture, the ³¹P NMR spectrum of which showed three major intense resonances at δ 16.7 (integral 16, RH), 32.8 [$J(^{31}\text{P}–^{117/119}\text{Sn}) = 81$ Hz, integral 32, signal a], and 34.1 [$J(^{31}\text{P}–^{117/119}\text{Sn}) = 90$ Hz, integral 36, signal b], respectively,

Received: March 21, 2012

Published: May 24, 2012

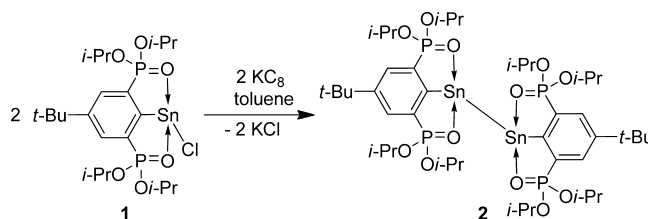
Chart 1. Common Distannynes and Related Tin(II) Complexes**Chart 2. Crystallographically Characterized Intramolecularly Coordinated Diorganostannylenes**

and five minor intense resonances between δ 36.0 and 36.4 (total integral 16, not assigned). After 5 h, signal (b) completely disappeared and the intensity of signal (a) increased. The ^{119}Sn NMR spectrum of the same sample revealed a broad resonance at δ 385 ($\nu_{1/2}$ 248 Hz, signal c). With caution but supported by the results described below, the ^{31}P NMR signal (a) and the ^{119}Sn NMR signal (c) are assigned to **2**. However, all attempts to isolate compound **2** from the reaction mixture failed.

In a second analogous experiment, a solution in THF was obtained, the ^{31}P NMR spectrum of which revealed a ratio between signals (a) and (b) of 1:3. The ^{119}Sn NMR spectrum of the same sample revealed a triplet resonance at δ 50 [$J(^{119}Sn-^{31}P) = 93$ Hz, signal d]. In the 1H -coupled ^{119}Sn NMR spectrum, this resonance changed into a doublet of triplet resonance [$J(^{119}Sn-^{31}P) = 93$ Hz and $^1J(^{119}Sn-^1H) = 116$ Hz]. The 1H NMR spectrum revealed a singlet resonance at δ 12.78 [$J(^1H-^{117/119}Sn) = 117$ Hz, signal e]. The signals (b), (d), and (e) are assigned with caution to the organotin(II) hydride $RSnH$, which, however, we failed to isolate from the

reaction mixture. The assignment of the NMR signals to the latter compound gets support from a recent finding by Roesky/Stalke and co-workers, who reported the intramolecularly coordinated organotin(II) hydride $RSnH$ ($R' = 2,6-[Ar'NC(Me)]_2C_6H_3$; $Ar' = 2,6-i-Pr_2C_6H_3$) with a $^1J(^{119}Sn-^1H)$ of 112.9 Hz.¹⁸

The reaction of **1** with excess KC_8 in toluene or deuterated benzene provided **2** after a reaction time of approximately 4 h or less than 90 min with sonification (Scheme 1). A prolonged

Scheme 1. Synthesis of Compound 2

reaction time caused the reaction mixture to turn black because of decomposition. From the reaction mixture mentioned above, **2** was obtained as a crystalline material that is well soluble in common organic solvents such as toluene and benzene but less in hexanes and that is extremely sensitive toward moisture and oxygen.

Notably, when stoichiometric amounts of KC_8 were used, only part of the organochloridostannylene **1** was converted to give compound **2**, even after prolonged reaction time.

Single crystals of compound **2** suitable for X-ray diffraction analysis were obtained as two different pseudopolymorphs. Crystallization from toluene/hexane at -20 °C gave single crystals of **2** (space group $P\bar{1}$), whereas crystallization from toluene/hexane at -80 °C provided single crystals of the toluene solvate **2**· C_7H_8 (space group $C2/c$, isolated from reduction with NaC_8H_{10} after workup). The molecular structures are shown in Figure 1. Selected interatomic distances and angles are given in Table 1.

In the crystal of **2**, the Sn(1) and Sn(2) atoms are each four-coordinate and exhibit distorted pseudo-trigonal-bipyramidal configuration, with the O(1)/O(2) and O(3)/O(4) atoms occupying the axial positions at Sn(1) and Sn(2), respectively. The equatorial positions are occupied by C(1)/Sn(2)/lone pair (at Sn1) and C(31)/Sn(1)/lone pair (at Sn2). The distortion from the ideal geometry is manifested by the O(1)–Sn(1)–O(2) and O(3)–Sn(1)–O(4) angles of 151.27(14) and 150.01(13)°, respectively, being the result of ligand constraint, as well as by the C(1)–Sn(1)–Sn(2) [97.87(16)°] and C(31)–Sn(2)–Sn(1) [98.14(16)°] angles, which indicate the lone electron pair at the Sn atoms to be stereochemically active. The two latter angles as well as the Sn(1)–Sn(2) distance of 3.0486(6) Å clearly indicate the Sn–Sn interaction to be a single bond. This bond length is close to the Sn–Sn distance reported for **E** [3.0685(9) Å]^{8c} but longer than those in the related compounds **B** [2.9712(12) Å]^{8a} and **D** [2.8981(9) Å]^{5f} (Chart 1), which are also characterized by intramolecular donor stabilization. The shortest Sn–Sn distance reported so far for a $ArSnSnAr$ -type compound is 2.6461(3) Å for $Ar = 4-t-Bu-2,6-Dipp_2C_6H_3$ ($Dipp = 2,6-i-Pr_2C_6H_3$).^{8e} The intramolecular Sn–O distances vary between 2.459(4) [Sn(1)–O(1)] and 2.527(5) Å [Sn(1)–O(2)] and are somewhat longer than the corresponding distances [2.430(2) and 2.427(2) Å] in the organochloridostannylene **1**.^{17d} The C(1)–Sn(1)–Sn(2)–

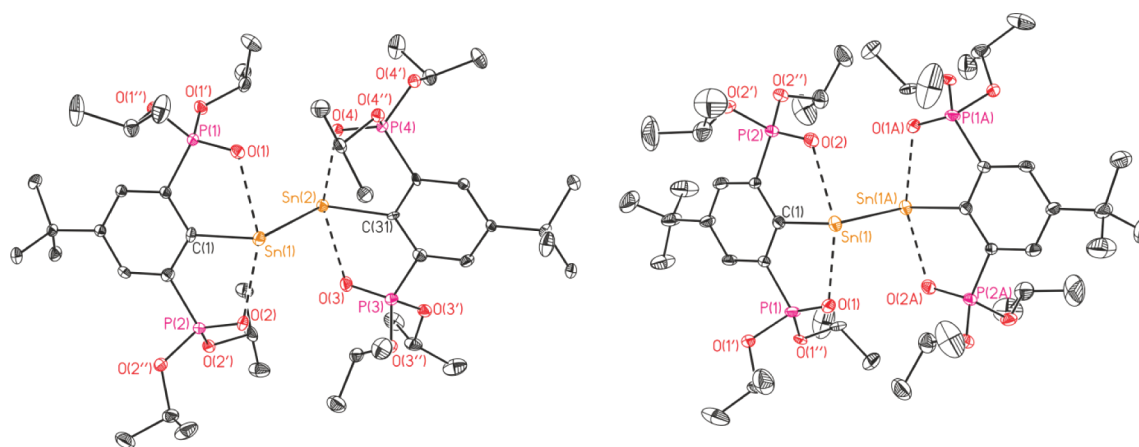


Figure 1. Molecular structure of compound **2** in the crystal of **2** (left) and in the crystal of **2**·C₇H₈ (right) (ORTEP presentation at 30% probability of the depicted atoms). H atoms are omitted for clarity. The toluene molecule was removed by PLATON/SQUEEZE.¹⁹ Symmetry code: A) 0.5 – *x*, 0.5 – *y*, 1 – *z*.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for **2**, **2**·C₇H₈, Optimized **2** (C₁ and C_i Symmetry), and Optimized Hypothetical **2'** with O(3) Turned Away

	2 (X = 2; Y = 31)	2 ·C ₇ H ₈ (X = Y = 1A)	calculated 2 (C ₁) (X = 2; Y = 31)	calculated 2 (C _i) (X = Y = 1A)	2' (X = 2; Y = 31)
Sn(1)–Sn(X)	3.0486(6)	2.9588(5)	3.083	3.083	3.055
Sn(1)–C(1)	2.238(6)	2.232(4)	2.292	2.287	2.307
Sn(2)–C(31)	2.254(6)		2.291		2.305
Sn(1)–O(1)	2.459(4)	2.510(3)	2.537	2.533	2.573
Sn(1)–O(2)	2.527(5)	2.470(3)	2.565	2.570	2.557
Sn(2)–O(3)	2.510(4)		2.573		
Sn(2)–O(4)	2.504(4)		2.544		2.357
C(1)–Sn(1)–O(1)	76.41(19)	75.57(11)	75.6	75.6	75.0
C(1)–Sn(1)–O(2)	74.87(19)	75.70(11)	75.2	75.2	74.8
O(2)–Sn(1)–O(1)	151.27(14)	151.24(9)	150.9	150.8	149.1
C(1)–Sn(1)–Sn(X)	97.87(16)	94.03(9)	93.3	92.6	93.8
O(1)–Sn(1)–Sn(X)	82.47(11)	89.89(6)	88.8	90.5	90.2
O(2)–Sn(1)–Sn(X)	100.93(11)	90.71(6)	92.8	90.8	85.9
C(31)–Sn(2)–O(4)	75.09(17)		75.4		78.7
C(31)–Sn(2)–O(3)	75.01(17)		75.2		
O(4)–Sn(2)–O(3)	150.01(13)		150.6		
C(31)–Sn(2)–Sn(1)	98.14(16)		93.4		99.2
O(3)–Sn(2)–Sn(1)	94.59(11)		90.5		
O(4)–Sn(2)–Sn(1)	87.42(11)		90.5		94.3
P(1)–O(1)–Sn(1)	115.7(2)	114.48(14)	114.4	114.5	114.3
P(2)–O(2)–Sn(1)	115.1(2)	116.52(14)	114.1	114.9	113.9
P(3)–O(3)–Sn(2)	115.2(2)		113.7		
P(4)–O(4)–Sn(2)	116.8(2)		115.5		117.0
C(1)–Sn(1)–Sn(2)–C(Y)	174.4(2)	180	177.3	180	171.3

C(31) dihedral angle of 174.4(2)° corresponds to other trans-bent tin(I) compounds like in ArSnSnAr (Ar = 4-*t*-Bu-2,6-Dipp₂C₆H₃) with 180°, whereas gauche-bent structures are observed for **B** [82.7(4)°],^{8a} **C**,^{8b} and **D** [83.36(7)°].^{5f} Both aromatic planes are not parallel but twisted by 18°.

The major differences in the structure of **2**·C₇H₈ compared to that of its pseudopolymorph **2** are (i) the shorter Sn–Sn distance of 2.9588(5) Å, (ii) the smaller C(1)–Sn(1)–Sn(1A) angle of 94.0(1)°, and (iii) the bigger C(1)–Sn(1)–Sn(1A)–C(1A) dihedral angle of 180°. The latter is a consequence of the molecule having a center of inversion. The range of the intramolecular Sn–O distances of 2.470(3) and 2.510(3) Å is narrower.

The fact that compound **2** exhibits pseudopolymorphism in the solid state is interesting. Pseudopolymorphs were also found for the related transition-metal-substituted ditin compounds [Cr(CO)₅]₂RSn–SnR[Cr(CO)₅], with Sn–Sn distances varying between 2.8923(4) and 3.1443(3) Å.^{17f} This fact is also reflected by Mössbauer spectroscopy and points to different bond situations maybe induced by packing forces.

To gain insight into the bonding situation, density functional theory (DFT) calculations²⁰ [the B3LYP/def2-SVP level of theory combined with the Stuttgart–Köln effective core potential (ECP) for tin]²¹ were performed. The bond lengths and angles of the optimized structure (based on the crystal data for **2** and **2**·C₇H₈) are given in Table 1. Taking into account the

level of theory and gas-phase calculations, the data are in fairly good agreement with the values obtained from the crystal structure. The Sn1–Sn2 distance of 3.083 Å is also in agreement with the calculations reported for compound **D** (Chart 1), giving a Sn–Sn distance of 3.046 Å.^{5f} Natural bond orbital (NBO) calculations were performed. The lone pairs (NAO) were located in orbitals with 86% s character. The Sn–Sn and Sn–C_{ipso} bonds are composed of orbitals with predominant p character. So, the Sn–Sn bond can be described as a single bond. Interestingly, the DFT calculations gave the same Sn–Sn distance for both C₁ and C_i symmetry, with C₁ being energetically favored by 1 kJ/mol only. The other bond distances and angles are also almost identical. This supports the interpretation of the different Sn–Sn distances found for **2** and 2-C₇H₈ to originate from crystal-packing effects.^{8b,e,f,22}

To elucidate the importance of P=O...Sn coordination, a rotation about one C–P bond by 180° was performed. The validity of this approach is supported by the fact that the molecular structure in the solid state of the protonated ligand 3-*t*-Bu-1,5-[P(O)(O-*i*-Pr)₂]₂C₆H₃ (RH) shows a rotamer in which both P=O O atoms are turned away from H-1.^{17d} For the geometry-optimized structure of the hypothetical isomer with one 3-fold-coordinated Sn atom, the energy is 45 kJ/mol higher than the energy of the optimized structure of compound **2**. This indicates an attractive Sn–O interaction and illustrates the importance of the latter for stabilization of compound **2**.

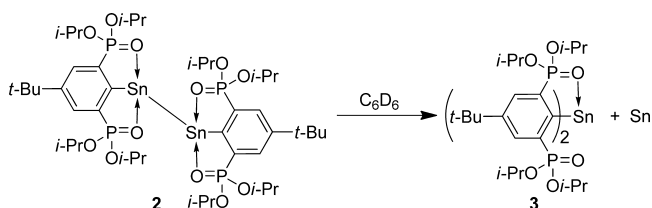
The identity of compound **2** is retained in solution. Thus, the ¹¹⁹Sn NMR spectrum shows a triplet resonance at δ 359 [*J*(¹¹⁹Sn–³¹P) = 81 Hz] with a ¹*J*(¹¹⁹Sn–¹¹⁷Sn) coupling of 1455 Hz. To the best of our knowledge, this is the first time that a ¹¹⁹Sn–¹¹⁷Sn coupling was observed for a ArSnSnAr compound. The ³¹P NMR shows a singlet resonance at δ 33.1 that is flanked by *J*(³¹P–^{117/119}Sn) satellites of 82 Hz and that indicates the four P atoms to be equivalent. The ¹³C NMR spectrum shows the resonance for the C(1) atom at δ 195, which is high-frequency-shifted compared to the corresponding signal in compound **1** (δ 187).^{17d}

The UV–vis spectrum of compound **2** in toluene shows absorption maxima at 505 and 372 nm. The spectrum is similar to that of other tin(I) compounds.^{8a,b}

As mentioned above, compound **2** is very sensitive toward water and oxygen. A solution of **2** that had been exposed to moist air immediately decolorized, and its ³¹P NMR spectrum showed a single resonance at δ 16.4 that is assigned to the protonated ligand RH.

Compound **2** is not stable at room temperature and, in a C₆D₆ solution in a sealed tube, disproportionates within a few weeks into elemental tin and the corresponding diorganostannylene SnR₂ (**3**; Scheme 2). Notably, this is the first metal derivative containing two {4-*t*-Bu-2,6-[P(O)(O-*i*-Pr)₂]₂C₆H₃}[–]

Scheme 2. Disproportionation of Compound 2 To Give Elemental Tin and the Diorganostannylene 3



pincer-type ligands. All of our attempts so far at obtaining such compounds by a nucleophilic substitution reaction with a variety of metal halides including HgCl₂ and the corresponding organolithium species had failed.

The reaction was monitored by ³¹P NMR showing a first-order decay with deviations for higher conversions (see Figure S1 in the Supporting Information). From the solution, compound **3** was obtained as a yellow single-crystalline material of its toluene solvate, 3·C₇H₈, which is well soluble in THF, toluene, and benzene and became colorless upon removal of the solvate toluene in vacuo. The molecular structure of compound 3·C₇H₈ is shown in Figure 2, and selected bond distances and angles are given in the figure caption.

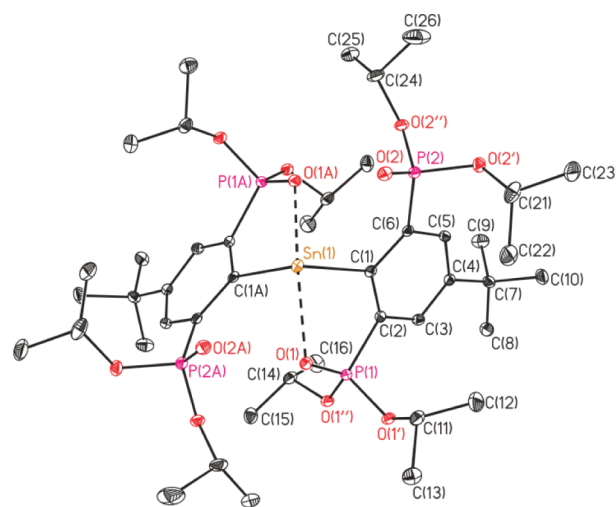


Figure 2. Molecular structure of compound 3·C₇H₈ (ORTEP presentation at 30% probability of the depicted atoms and atom numbering scheme). H atoms are omitted for clarity. The toluene molecule was removed by PLATON/SQUEEZE.¹⁹ Symmetry code: A) 1 – *x*, *y*, 0.5 – *z*. Selected interatomic distances (Å): Sn(1)–C(1) 2.295(2), Sn(1)–O(1) 2.4970(14), Sn(1)–O(2) 3.1302(14), P(1)–O(1) 1.476(2), P(2)–O(2) 1.462(2). Selected bond angles (deg): C(1)–Sn(1)–C(1A) 99.10(10), C(1)–Sn(1)–O(1) 74.57(6), C(1)–Sn(1)–O(1A) 76.99(6), O(1)–Sn(1)–O(1A) 135.51(7), O(1)–Sn(1)–O(2) 133.11(4).

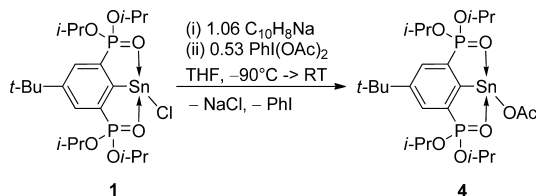
The Sn atom is four-coordinate and exhibits a distorted pseudo-square-pyramidal configuration, with the C(1), C(1A), O(1), and O(1A) atoms occupying the equatorial positions and the lone electron pair occupying the apical position. The C(1)–Sn(1)–C(1A) angle [99.10(10)°] is similar to the corresponding angle in (*o*-Me₂NCH₂C₆H₄)₂Sn, **F** [100.5(1)°].¹⁰ In the latter compound, however, the configuration of the Sn atom is distorted pseudo-trigonal-bipyramidal because the N(1)–Sn(1)–N(2) angle is 164.9(1)° whereas the O(1)–Sn(1)–O(1A) angle [135.51(7)°] in 3·C₇H₈ is considerably smaller. The intramolecular O(1)–Sn(1) distance of 2.4970(14) Å is similar to the Sn–O distances found for 2-C₇H₈ and **2** but longer than the corresponding distances in the organochloridostannylene **1**. Notably, the O(2)–Sn(1) distance of 3.1302(14) Å is shorter than the sum of the van der Waals radii of tin and oxygen (3.69 Å).²³ The nonequivalence of the two phosphonyl moieties is also reflected in the IR spectrum, showing two ν(P=O) absorptions at 1176 and 1254 cm^{–1} that correspond to the coordinating and noncoordinating phosphonyl moieties, respectively.

To the best of our knowledge, it is the first time that the products of decomposition of a distannyne have been identified. Unidentified products and elemental tin were described by Jones et al.^{8c} A disproportionation reaction similar to that described above was also observed for SnBr .²⁴

The ^{119}Sn and ^{31}P NMR spectra of compound **3** show a quintet resonance at δ 3 [$J(^{119}\text{Sn}-^{31}\text{P}) = 101$ Hz] and a singlet resonance at δ 28.3 [$J(^{31}\text{P}-^{117/119}\text{Sn}) = 100$ Hz], respectively, indicating the four P atoms to be equivalent on the respective NMR time scales. The ^{119}Sn resonance is considerably low-frequency-shifted compared to those of **F** (δ 169),¹⁰ 2,6-(Me_2NCH_2)₂ $\text{C}_6\text{H}_3\text{SnC}_6\text{H}_4\text{Me}$ -4 (δ 209.6), and (8- $\text{Me}_2\text{NC}_{10}\text{H}_6$)₂ Sn , **I** (δ 188.3).²⁵ A chemical shift difference of the same order of magnitude was observed between compound **1** (δ -99)^{17d} and 2,6-(Me_2NCH_2)₂ $\text{C}_6\text{H}_3\text{SnCl}$ (δ 155.6).²⁶ The ^1H NMR of compound **3** shows only one signal for the OCH protons and only two doublets for the $\text{CH}(\text{CH}_3)_2$ methyl protons, indicating fast exchange as well. The electrospray ionization mass spectrometry (ESI-MS, positive mode) spectrum shows a mass cluster centered at m/z 1043.5 that is assigned to $[\text{M} + \text{H}]^+$.

The reaction of in situ generated organotin(I) compound **2** with $\text{PhI}(\text{OAc})_2$ gave the organotin(II) acetate RSnOAc (**4**) as a colorless crystalline material that is well soluble in THF and toluene (Scheme 3). Notably, along this reaction, formation of

Scheme 3. Oxidation of in Situ Generated **2 with the Hypervalent Reagent $\text{PhI}(\text{OAc})_2$ To Give the Intramolecularly Coordinated Organotin(II) Acetate **4****



the chloridostannylene **1** as a major byproduct by in situ nucleophilic substitution of compound **4** with sodium chloride was observed. Formation of compound **4** was also observed by reacting the chloridostannylene **1** with silver acetate or thallium(I) acetate.^{17f}

The molecular structure of compound **4** is shown in Figure 3, and selected bond distances and angles are given in the figure caption.

Like in the organochloridostannylene **1**,^{17d} the Sn atom in compound **4** is four-coordinate and exhibits a distorted pseudo-trigonal-bipyramidal configuration, with the O(1) and O(2) atoms occupying the axial positions. The equatorial positions are occupied by the C(1) and O(3) atoms and the lone electron pair. The distortion from the ideal geometry is manifested by deviation of the O(1)–Sn(1)–O(2) [$152.20(11)^\circ$] and C(1)–Sn(1)–O(3) [$84.02(15)^\circ$] angles from 180° and 120° , respectively. Notably, the latter angle is the smallest among the C–Sn–X angles measured within the series of heteroleptic organostannylenes of the type RSnX (X = Cl, Br, I, SPh).^{17d}

The Sn(1)–O(1) and Sn(1)–O(2) distances are close to the corresponding distances in compound **1**^{17d} (see above). The Sn(1)–O(3) distance of 2.112(3) Å is in the range of 2.079(3) Å ([2,6-(Me_2NCH_2)₂ C_6H_3](O_2CCH_3) Sn }[2-(Me_2NCH_2)- C_6H_4] PdCl)^{27a} and 2.188(4) Å ([$\text{Cr}(\text{CO})_5$]₂ $\text{Sn}(\text{OAc})_2$)^{27b}

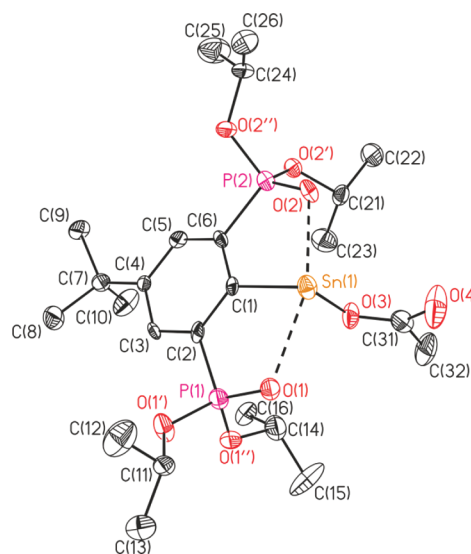


Figure 3. Molecular structure of compound **4** (ORTEP presentation at 30% probability of the depicted atoms and atom numbering scheme). H atoms are omitted for clarity. Selected interatomic distances (Å): Sn(1)–C(1) 2.234(5), Sn(1)–O(1) 2.455(3), Sn(1)–O(2) 2.421(3), Sn(1)–O(3) 2.112(3), Sn(1)–O(4) 3.121(3), P(1)–O(1) 1.507(3), P(2)–O(2) 1.488(3). Selected bond angles (deg): C(1)–Sn(1)–O(3) 84.02(15), C(1)–Sn(1)–O(1) 75.82(15), C(1)–Sn(1)–O(2) 76.83(15), O(1)–Sn(1)–O(2) 152.20(11).

reported for other tin(II) acetates. Other structurally characterized members are (acac) $\text{Sn}(\text{OAc})$,^{27c} $\text{Ca}[\text{Sn}(\text{OAc})_3]_2$,^{27d} $\text{Sn}(\text{OAc})_2$,^{27e} and $\text{Sn}(\text{OAc})_2 \cdot [\text{S}=\text{C}(\text{NH}_2)_2]$.^{27f} The Sn(1)···O(4) distance of 3.121(3) Å is shorter than the sum of the van der Waals radii of tin and oxygen (see above) but too long to be regarded as bonding. Consequently, the acetate moiety shows a monodentate coordination mode. The $\tilde{\nu}_{\text{COOasym}}$ is observed at 1641 cm^{-1} .

The ^{119}Sn and ^{31}P NMR spectra of compound **4** showed a triplet resonance at δ -229 [$J(^{119}\text{Sn}-^{31}\text{P}) = 106$ Hz] and a singlet resonance at δ 36.3 [$J(^{31}\text{P}-^{119/117}\text{Sn}) = 100$ Hz], respectively. The ^1H NMR spectrum showed one broad resonance for the OCH protons and two doublets for the $\text{CH}(\text{CH}_3)_2$ methyl protons. Accordingly, the ^{13}C NMR revealed one signal for the CH C atom and two signals for the $\text{CH}(\text{CH}_3)_2$ C atom, respectively. This indicates the Sn atom to be configurationally not stable, very likely as result of Sn–O bond dissociation being fast on the corresponding NMR time scales. However, this was not investigated further. ESI-MS showed a mass cluster centered at m/z 1219.4 that is assigned to $[\text{RSnOAcSnR}]^+$.

CONCLUSION

The intramolecularly coordinated pincer ligand-based organotin(I) compound (**2**) showing a Sn–Sn single bond has been prepared by reduction of the corresponding heteroleptic organostannylene **1** with potassium graphite (C_8K). The many attempts in vain to obtain compound **2** by other reducing reagents such as anthracene·Mg·3THF, sodium biphenylide, K-Selectride ($[\text{K}[\text{B}-\text{sec}-\text{Bu}_3\text{H}]]$), or $[(^{\text{Mes}}\text{NacNac})\text{Mg}]_2$ indicates C_8K to be superior for such reactions. The major reason for this is very likely the simple workup procedure that includes one filtration only, avoiding other separation techniques and thermal stress. On the other hand, however, consecutive reactions for which isolation of **2** is not required

are most conveniently performed using sodium naphthalenide. DFT calculations revealed the importance of the intramolecular $\text{P}=\text{O} \rightarrow \text{Sn}$ coordination for stabilization of compound **2**. Such coordination has become an alternative for steric protection by bulky substituents to stabilize tin(II) species. Compound **2** easily undergoes disproportionation to give the corresponding diorganostannylene **3** and elemental tin. Compound **3** could not be obtained by alternative reactions, and this illustrates the synthetic potential of the organotin(II) species **2**. The straightforward oxidation of compound **2** with $\text{PhI}(\text{OAc})_2$ to give the organotin(IV) acetate **4** is a motivation to look for other such oxidation reactions. The results on these investigations will be presented in a forthcoming paper.

EXPERIMENTAL SECTION

General Procedures. All reactions were carried out under an atmosphere of dry argon in flame-dried glassware using Schlenk techniques. The solvents used for reactions and the preparation of NMR samples were purified by distillation from appropriate drying agents under argon.

The organostannylene $4\text{-}t\text{-Bu-2,6-[P(O)(O-}i\text{-Pr)}_2\text{]}_2\text{C}_6\text{H}_2\text{SnCl}$ was synthesized as described and recrystallized from hexanes prior to use.^{17d} KC_8 and solutions of sodium naphthalenide in THF were freshly prepared. Iodobenzene diacetate was prepared according to a literature procedure.²⁸ NMR spectra were recorded on a Bruker AV DPX-300/AV DRX 400/AV DRX 500 or a Varian Unity Inova/Mercury instrument at room temperature unless otherwise stated. Solutions of compound **2** were measured in sealed tubes. NMR chemical shifts δ are given in ppm and were referenced to Me_4Si using a residual solvent signal (^1H , 7.16 ppm; ^{13}C , 128.39 ppm), H_3PO_4 (85%, ^{31}P), and Me_4Sn (^{119}Sn). Elemental analyses were performed on a LECO-CHNS-932 analyzer. Melting points are uncorrected and were measured on a Büchi M-560. IR spectra (cm^{-1}) were measured on a Bruker IFS 28 device as KBr disks. UV-vis spectra were measured on an Agilent Cary 60 UV-vis device. The ESI-MS spectra were recorded at positive mode with a Thermoquest-Finnigan instrument using CH_3CN as the mobile phase.

Reaction of $4\text{-}t\text{-Bu-2,6-[P(O)(O-}i\text{-Pr)}_2\text{]}_2\text{C}_6\text{H}_2\text{SnCl}$ with $\text{K[B-sec-Bu}_3\text{H]}$ (K-Selectride). Experiment 1. At 0°C and under magnetic stirring, a 1 M solution of K-Selectride in THF (2.5 mL, 2.5 mmol) was added dropwise within 10 min to a solution of compound **1** (1.51 g, 2.5 mmol) in THF (10 mL). NMR spectra were recorded after $t = 0.5$ and 5 h.

$t = 0.5$ h. $^{31}\text{P}\{^1\text{H}\}$ NMR (121.50 MHz, C_6D_6): δ 16.7 (s, RH, integral 16), 32.8 (s, $J(^{31}\text{P}-^{117/119}\text{Sn}) = 81$ Hz, **2**, integral 32), 34.1 (s, $J(^{31}\text{P}-^{117/119}\text{Sn}) = 90$ Hz, RSnH , integral 36), 36.0–36.4 (five minor intense resonances, not assigned, total integral 16).

$t = 5$ h. $^{31}\text{P}\{^1\text{H}\}$ NMR (121.50 MHz, C_6D_6): δ 16.7 (s, RH, integral 18), 32.8 (s, $J(^{31}\text{P}-^{117/119}\text{Sn}) = 81$ Hz, **2**, 59%), 34.9 (s, $J(^{31}\text{P}-^{117/119}\text{Sn}) = 101$ Hz, not assigned, integral 5), 36.1–36.5 (five minor intense resonances, not assigned, total integral 18). $^{119}\text{Sn}\{^1\text{H}\}$ NMR (111.86 MHz, C_6D_6): δ 385 (s, $\nu_{1/2} = 274$ Hz, **2**).

Experiment 2. At 0°C and under magnetic stirring, a 1 M solution of K-Selectride in THF (1.1 mL, 1.1 mmol) was added dropwise to a solution of compound **1** (700 mg, 1.1 mmol) in THF.

$^{31}\text{P}\{^1\text{H}\}$ NMR (121.50 MHz, THF/ C_6D_6): δ 16.7 (s, RH, integral 30), 32.8 (s, **2**, integral 12), 33.4 (s, not assigned, integral 5), 34.1 (s, $J(^{31}\text{P}-^{117/119}\text{Sn}) = 90$ Hz, RSnH , 37%), 36.2 (five minor intense resonances, not assigned, integral 16). $^{119}\text{Sn}\{^1\text{H}\}$ NMR (111.86 MHz, C_6D_6): δ 51 (t, $J(^{31}\text{P}-^{119}\text{Sn}) = 92$ Hz, RSnH). ^{119}Sn NMR (111.86 MHz, C_6D_6): δ 51 (dt, $J(^{31}\text{P}-^{119}\text{Sn}) = 92$ Hz, $J(^1\text{H}-^{119}\text{Sn}) = 116$ Hz, RSnH).

[2,6-Bis(diisopropoxyphosphonyl)-4-tert-butyl]phenyltin(II), ($4\text{-}t\text{-Bu-2,6-[P(O)(O-}i\text{-Pr)}_2\text{]}_2\text{C}_6\text{H}_2\text{Sn})_2$ (2**). Method 1.** To KC_8 (764 mg, 5.65 mmol, 2.36 equiv) was added a solution of $4\text{-}t\text{-Bu-2,6-[P(O)(O-}i\text{-Pr)}_2\text{]}_2\text{C}_6\text{H}_2\text{SnCl}$ (1.474 g, 2.39 mmol) in toluene (18 mL). The suspension was stirred for 4 h, during which the color of the reaction mixture turned to red-violet. After filtration over Celite, toluene was

removed in vacuo, yielding compound **2**. Yield: 1.10 g, 75%. ^1H NMR (C_6D_6 , 400.13 MHz): δ 0.96 (d, $^3J(^1\text{H}-^1\text{H}) = 6.0$ Hz, 12H, $\text{CH}(\text{CH}_3)_2$), 1.21 (d, $^3J(^1\text{H}-^1\text{H}) = 6.0$ Hz, 12H, $\text{CH}(\text{CH}_3)_2$), 1.25–1.27 (not resolved, 30H, $\text{C}(\text{CH}_3)_3 + \text{CH}(\text{CH}_3)_2$), 1.56 (d, $^3J(^1\text{H}-^1\text{H}) = 6.0$ Hz, 12H, $\text{CH}(\text{CH}_3)_2$), 4.47–4.55 (m, 4H, $\text{CH}(\text{CH}_3)_2$), 5.45–5.53 (m, 4H, $\text{CH}(\text{CH}_3)_2$), 7.98 (d, $^3J(^{31}\text{P}-^1\text{H}) = 13.3$ Hz, 4H, CH_{aryl}). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 100.61 MHz): δ 24.0–24.1 (m, $\text{CH}(\text{CH}_3)_2$), 24.4–24.5 (m, $\text{CH}(\text{CH}_3)_2$), 24.6–24.7 (m, $\text{CH}(\text{CH}_3)_2$), 25.2–25.3 (m, $\text{CH}(\text{CH}_3)_2$), 31.7 (s, $\text{C}(\text{CH}_3)_3$), 34.7 (s, $\text{C}(\text{CH}_3)_3$), 70.8–70.9 (m, $\text{CH}(\text{CH}_3)_2$), 71.9–72.0 (m, $\text{CH}(\text{CH}_3)_2$), 131.7 (dd, $\text{C}_{3/5\text{aryl}}$, $^2J(^{13}\text{C}-^{31}\text{P}) = 17.0$ Hz, $^4J(^{13}\text{C}-^{31}\text{P}) = 4.4$ Hz), 133.4 (dd, $\text{C}_{2/6\text{aryl}}$, $^1J(^{13}\text{C}-^{31}\text{P}) = 190$ Hz, $^3J(^{13}\text{C}-^{31}\text{P}) = 24.3$ Hz), 147.4 (t, $\text{C}_{4\text{aryl}}$, $^3J(^{13}\text{C}-^{31}\text{P}) = 13.1$ Hz), 195.0 (t, C_{laryl} , $^2J(^{13}\text{C}-^{31}\text{P}) = 36.0$ Hz). $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6 , 121.49 MHz): δ 33.06 ($J(^{31}\text{P}-^{119/117}\text{Sn}) = 82$ Hz, $^1J(^{31}\text{P}-^{13}\text{C}) = 192$ Hz). $^{119}\text{Sn}\{^1\text{H}\}$ NMR (C_6D_6 , 111.92 MHz): δ 359 ($J(^{119}\text{Sn}-^{31}\text{P}) = 81$ Hz, $^1J(^{119}\text{Sn}-^{117}\text{Sn}) = 1455$ Hz). UV-vis [toluene, λ_{max} (ϵ): 505 (10660), 372 (9480). Because of extreme air sensitivity, microanalysis was not performed. Single crystals of **2** suitable for X-ray diffraction analysis were grown from a toluene/hexanes solution at -20°C .

Method 2. To a solution of $4\text{-}t\text{-Bu-2,6-[P(O)(O-}i\text{-Pr)}_2\text{]}_2\text{C}_6\text{H}_2\text{SnCl}$ (**534** mg, 0.87 mmol) in THF (10 mL) was added a solution of sodium naphthalenide (118 mg, 0.92 mmol, 1.06 equiv) in THF (10 mL) at -90°C . The red solution was warmed to room temperature and stirred for 5 min to ensure complete conversion. From this reaction mixture, a ^{31}P NMR spectrum was recorded. $^{31}\text{P}\{^1\text{H}\}$ NMR (THF, 81.01 MHz, no deuterated solvent, referenced to RH): δ 32.6 (s, $J(^{31}\text{P}-^{119/117}\text{Sn}) = 81$ Hz; RSnSnR). After THF had been carefully removed in vacuo, the dark residue was extracted with toluene (10 mL) and the extract was filtered. The volume of the red filtrate was reduced to approximately 5 mL, and a few drops of hexanes were added. The solution was stored at -80°C to give colorless crystals of naphthalene and dark-brown crystals of $2\text{-C}_7\text{H}_8$. The latter were manually separated from the naphthalene crystals and mounted to the diffractometer.

Bis[2,6-Bis(diisopropoxyphosphonyl)-4-tert-butyl]phenyltin(II), ($4\text{-}t\text{-Bu-2,6-[P(O)(O-}i\text{-Pr)}_2\text{]}_2\text{C}_6\text{H}_2\text{Sn})_2$ (3**).** A solution of ($4\text{-}t\text{-Bu-2,6-[P(O)(O-}i\text{-Pr)}_2\text{]}_2\text{C}_6\text{H}_2\text{Sn})_2$ (ca. 30 mg) in C_6D_6 was sealed in a NMR tube. After a few hours, the deposition of elemental tin was observed and the ^{31}P NMR spectrum revealed a new signal, the intensity of which increased with time. After 3 weeks, the ^{31}P NMR spectrum indicated that the solution contained essentially pure **3**. ^1H NMR (C_6D_6 , 500.13 MHz): δ 1.01 (d, $^3J(^1\text{H}-^1\text{H}) = 6.5$ Hz, 24H, $\text{CH}(\text{CH}_3)_2$), 1.18 (s, 18H, $\text{C}(\text{CH}_3)_3$), 1.29 (d, $^3J(^1\text{H}-^1\text{H}) = 6.5$ Hz, 24H, $\text{CH}(\text{CH}_3)_2$), 4.56–4.65 (m, 8H, $\text{CH}(\text{CH}_3)_2$), 7.95 (d, $^3J(^{31}\text{P}-^1\text{H}) = 14.2$ Hz, 4H, CH_{aryl}). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 75.47 MHz): δ 24.2–24.3 (m, $\text{CH}(\text{CH}_3)_2$), 24.7–24.8 (m, $\text{CH}(\text{CH}_3)_2$), 31.6 (s, $\text{C}(\text{CH}_3)_3$), 34.7 (s, $\text{C}(\text{CH}_3)_3$), 70.2–70.3 (m, $\text{CH}(\text{CH}_3)_2$), 132.4 (dd, $\text{C}_{3/5\text{aryl}}$, $^2J(^{13}\text{C}-^{31}\text{P}) = 16.7$ Hz, $^4J(^{13}\text{C}-^{31}\text{P}) = 5.1$ Hz), 137.2 (dd, $\text{C}_{2/6\text{aryl}}$, $^1J(^{13}\text{C}-^{31}\text{P}) = 195$ Hz, $^3J(^{13}\text{C}-^{31}\text{P}) = 25.4$ Hz), 147.5 (t, $\text{C}_{4\text{aryl}}$, $^3J(^{13}\text{C}-^{31}\text{P}) = 13.4$ Hz), 193.0 (t, C_{laryl} , $^2J(^{13}\text{C}-^{31}\text{P}) = 36.0$ Hz). $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6 , 121.49 MHz): δ 28.27 (s, $J(^{31}\text{P}-^{119/117}\text{Sn}) = 100$ Hz, $^1J(^{31}\text{P}-^{13}\text{C}) = 195$ Hz, $^2J(^{31}\text{P}-^{13}\text{C}) = 36$ Hz). $^{119}\text{Sn}\{^1\text{H}\}$ NMR (C_6D_6 , 111.92 MHz): δ 3 (quintet, $J(^{119}\text{Sn}-^{31}\text{P}) = 101$ Hz).

The contents of the NMR tube were decanted into a Schlenk flask. The solvent was removed, and the residue was crystallized from toluene to yield the toluene solvate $3\text{-C}_7\text{H}_8$ as a yellow single-crystalline material. The solvate was removed in vacuo at 40°C , giving **3** as a colorless solid. Mp: $>350^\circ\text{C}$. IR (KBr): $\tilde{\nu}$ 1176 ($\text{P}=\text{O}$, coordinating), 1254 ($\text{P}=\text{O}$, noncoordinating). ESI-MS (CH_3CN): 1043.5 [$(\text{M} + \text{H})^+$].

[2,6-Bis(diisopropoxyphosphonyl)-4-tert-butyl]phenyltin acetate, ($4\text{-}t\text{-Bu-2,6-[P(O)(O-}i\text{-Pr)}_2\text{]}_2\text{C}_6\text{H}_2\text{SnOAc}$ (4**)).** To a solution of $4\text{-}t\text{-Bu-2,6-[P(O)(O-}i\text{-Pr)}_2\text{]}_2\text{C}_6\text{H}_2\text{SnCl}$ (**534** mg, 0.87 mmol) in THF (10 mL) was added a solution of sodium naphthalenide (118 mg, 0.92 mmol, 1.06 equiv) in THF (10 mL) at -90°C . The red solution was warmed to room temperature and stirred for 5 min to ensure complete conversion. From this reaction mixture, a ^{31}P NMR spectrum was recorded.

Table 2. Crystallographic Data for Compounds 2, 2·C₇H₈, 3·C₇H₈, and 4

	2	2·C ₇ H ₈	3·C ₇ H ₈	4
empirical formula	C ₄₄ H ₇₈ O ₁₂ P ₄ Sn ₂	C ₄₄ H ₇₈ O ₁₂ P ₄ Sn ₂ ·C ₇ H ₈	C ₄₄ H ₇₈ O ₁₂ P ₄ Sn·C ₇ H ₈	C ₂₄ H ₄₂ O ₈ P ₂ Sn
fw [g/mol]	1160.32	1252.46	1133.77	639.21
λ [Å]	0.71073	0.71073	0.71073	0.71073
T [K]	173(2)	173(2)	173(2)	173(2)
cryst syst	triclinic	monoclinic	monoclinic	orthorhombic
cryst size [mm]	0.17 × 0.15 × 0.15	0.49 × 0.47 × 0.31	0.50 × 0.12 × 0.04	0.30 × 0.13 × 0.12
space group	<i>P</i> $\bar{1}$	<i>C</i> 2/ <i>c</i>	<i>C</i> 2/ <i>c</i>	<i>P</i> 2 ₁ 2 ₁ 2 ₁
<i>a</i> [Å]	12.4462(4)	26.493(2)	18.0490(6)	10.1722(9)
<i>b</i> [Å]	12.6211(3)	13.9899(4)	24.1798(8)	16.9303(12)
<i>c</i> [Å]	18.0942(5)	24.0375(10)	13.5944(5)	18.0365(13)
α [deg]	82.249(2)	90	90	90
β [deg]	76.873(2)	117.133(5)	103.039(3)	90
γ [deg]	86.797(2)	90	90	90
<i>V</i> [Å ³]	2741.82(13)	7928.7(7)	5779.9(3)	3106.2(4)
<i>Z</i>	2	4	4	4
ρ _{calcd} [mg/m ³]	1.405	1.049	1.303	1.367
μ [mm ^{−1}]	1.080	0.751	0.608	0.965
<i>F</i> (000)	1196	2592	2392	1320
θ range [deg]	2.12–25.50	2.74–25.50	2.28–25.50	2.30–25.50
index ranges	−15 ≤ <i>h</i> ≤ 15 −15 ≤ <i>k</i> ≤ 15 −21 ≤ <i>l</i> ≤ 21	−32 ≤ <i>h</i> ≤ 32 −16 ≤ <i>k</i> ≤ 16 −29 ≤ <i>l</i> ≤ 29	−21 ≤ <i>h</i> ≤ 21 −29 ≤ <i>k</i> ≤ 29 −16 ≤ <i>l</i> ≤ 16	−8 ≤ <i>h</i> ≤ 12 −20 ≤ <i>k</i> ≤ 20 −21 ≤ <i>l</i> ≤ 21
no. of reflns collected	39817	31339	16464	18266
completeness of θ _{max} [%]	100.0	99.9	99.9	99.7
no. of indep reflns/ <i>R</i> _{int}	10184/0.0463	7372/0.0359	5385/0.0454	5713/0.0679
no. of reflns obsd with <i>I</i> > 2σ(<i>I</i>)	7236	5814	4245	3023
abs corr	multiscan	multiscan	multiscan	multiscan
<i>T</i> _{max} / <i>T</i> _{min}	1.0/0.77013	1.0/0.83142	1.0/0.88045	1.0/0.79420
no. of refined param (restraints)	581	367 (12)	287	371 (66)
GOF(<i>F</i> ²)	1.100	1.417	0.824	0.687
<i>R</i> 1(<i>F</i>) [<i>I</i> > 2σ(<i>I</i>)]	0.0570	0.0460	0.0238	0.0370
w <i>R</i> 2(<i>F</i> ²) (all data)	0.1662	0.1348	0.0660	0.0495
(Δ/σ) _{max}	0.001	0.001	0.000	0.001
largest diff peak/hole [e/Å ³]	2.469/−1.378	1.239/−0.510	0.335/−0.255	0.511/−0.568

³¹P{¹H} NMR (THF, 81.01 MHz, no deuterated solvent, referenced to RH): δ 32.6 (s, *J*(³¹P–^{119/117}Sn) = 81 Hz; RSnSnR).

To the red solution was added PhI(OAc)₂ (148 mg, 0.46 mmol, 0.53 equiv). The red color disappeared within a few minutes, leaving a colorless solution. From this reaction mixture, a ³¹P NMR spectrum was recorded.

³¹P{¹H} NMR (THF/C₆D₆, 121.49 MHz): δ 37.14 (s, *J*(³¹P–^{119/117}Sn) = 122 Hz, integral 37; RSnCl), 36.21 (s, *J*(³¹P–^{119/117}Sn) = 102 Hz, integral 49; RSnOAc), 16.37 (s, integral 11, RH). ¹¹⁹Sn{¹H} NMR (THF/C₆D₆, 111.92 MHz): δ −98 (t, *J*(¹¹⁹Sn–³¹P) = 121 Hz, integral 37; RSnCl), −228 (t, *J*(¹¹⁹Sn–³¹P) = 106 Hz, integral 53; RSnOAc).

All volatiles were removed in vacuo, and naphthalene was sublimed at 60 °C. The residue was extracted into toluene (20 mL) and filtered over Celite. The filtrate was concentrated to give colorless single crystals suitable for X-ray diffraction analysis. The colorless crystals were dried in vacuo. Yield: 97 mg, 17%. Mp: 155 °C. ¹H NMR (C₆D₆, 300.13 MHz): δ 1.00 (d, ³*J*(¹H–¹H) = 6.2 Hz, 12H, CH(CH₃)₂), 1.08 (s, 9H, C(CH₃)₃), 1.25 (d, ³*J*(¹H–¹H) = 6.2 Hz, 12H, CH(CH₃)₂), 1.93 (s, 3H, CH₃), 4.63–4.88 (m, 4H, CH(CH₃)₂), 8.00 (d, ³*J*(³¹P–¹H) = 13.2 Hz, 2H, CH_{aryl}). ¹³C{¹H} NMR (C₆D₆, 75.47 MHz): 23.6 (s, CH₃), 24.0–24.1 (m, CH(CH₃)₂), 24.4–24.5 (m, CH(CH₃)₂), 31.4 (s, C(CH₃)₃), 35.0 (t, C(CH₃)₃), ⁴*J*(¹³C–³¹P) = 1.4 Hz), 72.2–72.3 (m, CH(CH₃)₂), 131.9 (dd, *C*_{3/aryl}, ²*J*(¹³C–³¹P) = 17.1 Hz, ⁴*J*(¹³C–³¹P) = 4.7 Hz), 134.2 (dd, *C*_{2/aryl}, ¹*J*(¹³C–³¹P) = 193 Hz, ³*J*(¹³C–³¹P) = 24.0 Hz), 151.1 (t, *C*_{4/aryl}, ³*J*(¹³C–³¹P) = 12.7 Hz), 177.3 (s, C=O), 187.0 (t, *C*_{1/aryl}, ²*J*(¹³C–³¹P) = 36.7 Hz). ³¹P{¹H} NMR (C₆D₆, 121.49 MHz): δ 36.29 (*J*(³¹P–^{119/117}Sn) = 100 Hz).

¹¹⁹Sn{¹H} NMR (C₆D₆, 111.92 MHz): δ −229 (*J*(¹¹⁹Sn–³¹P) = 106 Hz). IR (KBr) $\tilde{\nu}$ 1145 (P=O), 1162 (P=O), 1641 (CO_{asym}). ESI-MS (CH₃CN): 1219.4 [(M + RSn)⁺]. Elem anal. Calcd for C₂₄H₄₂O₈P₂Sn (639.2): C, 45.09; H, 6.62. Found: C, 44.65; H, 6.5.

Crystallography. The crystallographic data are given in Table 2. Single crystals of compounds 2 and 2·C₇H₈ were mounted at low temperature in inert oil under a nitrogen atmosphere by using the XTemp2 device.²⁹ All intensity data were collected with an XcaliburS CCD diffractometer (Oxford Diffraction) using Mo Kα radiation at 110 K. The structures were solved with direct methods using SHELXS-97,³⁰ and refinements were carried out against *F*² using SHELXL-97.³⁰ All non-H atoms were refined using anisotropic displacement parameters. The C–H H atoms were positioned with idealized geometry and refined using a riding model. In compound 2·C₇H₈, the isopropyl groups at O(1') and O(1'') are affected by disorder; both have been described by a split model with distance restraints for stabilization. In compound 4, the *tert*-butyl group and the atoms C(13), C(16), and C(26) are also affected by disorder and described by a split model; their *U*_{ij} components were restrained to approximate isotropic behavior. In compounds 2·C₇H₈ and 3·C₇H₈, solvate molecules were found to be severely disordered and removed by SQUEEZE (PLATON)¹⁹ to improve the main part of the structure. CCDC 870443 (2), 870442 (2·C₇H₈), 870444 (3·C₇H₈), and 870445 (4) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Computational Details. All calculations were performed with the Gaussian 03, Revision E.01,³¹ suite of programs. Full DFT calculations were carried out with the B3LYP functional^{21a} and def2-SVP basis set.^{21b} For the Sn atom, the Stuttgart–Köln ECP was added.^{21c} Starting coordinates were obtained from the crystal coordinates. Harmonic vibrational frequency analyses were performed in order to determine the nature of the stationary point at the same theoretical level. Compound **2** was calculated within the C₁ and C_i point groups. All calculated total (self-consistent field) and zero-point energies as well as standard orientations can be found in the Supporting Information. In order to perform NBO analyses, the built-in NBO-3.1 subroutines of the Gaussian program package were used.

■ ASSOCIATED CONTENT

■ Supporting Information

Kinetic plot, computational data, complete ref 31, and combined CIF for **2**, 2-C₇H₈, 3-C₇H₈, and **4**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: klaus.jurkschat@uni-dortmund.de.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

M.W. is grateful to Technische Universität Dortmund for a scholarship.

■ REFERENCES

- (1) Phillips, A. D.; Wright, R. J.; Olmstead, M. M.; Power, P. P. *J. Am. Chem. Soc.* **2002**, *124*, 5930–5931.
- (2) (a) Stender, M.; Phillips, A. D.; Wright, R. J.; Power, P. P. *Angew. Chem., Int. Ed.* **2002**, *41*, 1785–1787. (b) Sugiyama, Y.; Sasamori, T.; Hosoi, Y.; Furukawa, Y.; Takagi, N.; Nagase, S.; Tokitoh, N. *J. Am. Chem. Soc.* **2006**, *128*, 1023–1031. (c) Li, J.; Schenk, C.; Goedecke, C.; Frenking, G. *J. Am. Chem. Soc.* **2011**, *133*, 18622–18625. (d) Wang, W.; Inoue, S.; Yao, S.; Driess, M. *Chem. Commun.* **2009**, 2661–2663. (e) Leung, W.-P.; Chiu, W.-K.; Chong, K.-H.; Mak, T. C. W. *Chem. Commun.* **2009**, 6822–6824. (f) Nagendran, S.; Sen, S. S.; Roesky, H. W.; Koley, D.; Grubmüller, H.; Pal, A.; Herbst-Irmer, R. *Organometallics* **2008**, *27*, 5459–5463. (g) Green, S. P.; Jones, C.; Junk, P. C.; Lippert, K.-A.; Stasch, A. *Chem. Commun.* **2006**, 3978–3980.
- (3) (a) Sekiguchi, A.; Kinjo, R.; Ichinohe, M. *Science* **2004**, *305*, 1755–1757. (b) Wiberg, N.; Vasisht, S. K.; Fischer, G.; Mayer, P. Z. *Anorg. Allg. Chem.* **2004**, *630*, 1823–1828. (c) Sekiguchi, A.; Ichinohe, M.; Kinjo, R. *Bull. Chem. Soc. Jpn.* **2006**, *79*, 825–832. (d) Sekiguchi, A. *Pure Appl. Chem.* **2008**, *80*, 447–457. (e) Sasamori, T.; Han, J. S.; Hironaka, K.; Takagi, N.; Nagase, S.; Tokitoh, N. *Pure Appl. Chem.* **2010**, *82*, 603–612. (f) Han, J. S.; Sasamori, T.; Mizuhata, Y.; Tokitoh, N. *J. Am. Chem. Soc.* **2010**, *132*, 2546–2527. (g) Sen, S. S.; Jana, A.; Roesky, H. W.; Schulzke, C. *Angew. Chem., Int. Ed.* **2009**, *48*, 8536–8538; *Angew. Chem.* **2009**, *121*, 8688–8690.
- (4) (a) Power, P. P. *Nature* **2010**, *463*, 171–177. (b) Power, P. P.; Gabbai, F. C. *Inorg. Chem.* **2011**, *50*, 12221–12222. (c) Power, P. P. *Acc. Chem. Res.* **2011**, *44*, 627–637. (d) Rivard, E.; Power, P. P. *Inorg. Chem.* **2007**, *46*, 10047–10064. (e) Power, P. P. *Organometallics* **2007**, *26*, 4362–4372. (f) Power, P. P. *Chem. Commun.* **2003**, 2091–2101.
- (5) (a) Summerscales, O. T.; Wang, X.; Power, P. P. *Angew. Chem., Int. Ed.* **2010**, *49*, 4788–4790; *Angew. Chem.* **2010**, *122*, 4898–4900. (b) Summerscales, O. T.; Fetting, J. C.; Power, P. P. *J. Am. Chem. Soc.* **2011**, *133*, 11960–11963. (c) Peng, Y.; Ellis, B. D.; Wang, X.; Fetting, J. C.; Power, P. P. *Science* **2009**, *325*, 1668–1670. (d) Peng, Y.; Brynda, M.; Ellis, B. D.; Fetting, J. C.; Rivard, E.; Power, P. P. *Chem. Commun.* **2008**, 6042–6044. (e) Cui, C.; Olmstead, M. M.; Fetting, J. C.; Spikes, G. H.; Power, P. P. *J. Am. Chem. Soc.* **2005**, *127*, 17530–17541. (f) Khan, S.; Michel, R.; Dieterich, J. M.; Mata, R. A.; Roesky, H. W.; Demers, J.-P.; Lange, A.; Stalke, D. *J. Am. Chem. Soc.* **2011**, *133*, 17889–17894.
- (6) Peng, Y.; Wang, X.; Fetting, J. C.; Power, P. P. *Chem. Commun.* **2010**, *46*, 943–945.
- (7) (a) Bouška, M.; Dostal, L.; Růžicka, A.; Beneš, L.; Jambor, R. *Chem.—Eur. J.* **2011**, *17*, 450–454. (b) Bouška, M.; Dostal, L.; Proft, F.; de Růžicka, A.; Lyčka, A.; Jambor, R. *Chem.—Eur. J.* **2011**, *17*, 455–459. (c) Bouška, M.; Dostal, L.; Padělková, Z.; Lyčka, A.; Herres-Pawlis, S.; Jurkschat, K.; Jambor, R. *Angew. Chem., Int. Ed.* **2012**, *51*, 3478–3482; *Angew. Chem.* **2012**, *124*, 3535–3540. (d) Summerscales, O. T.; Olmstead, M. M.; Power, P. P. *Organometallics* **2011**, *30*, 3468–2471.
- (8) (a) Jambor, R.; Kašná, B.; Kirschner, K.; Schürmann, M.; Jurkschat, K. *Angew. Chem., Int. Ed.* **2008**, *47*, 1650–1653; *Angew. Chem.* **2008**, *120*, 1674–1677. (b) Jones, C.; Bonyhady, S. J.; Holzmann, N.; Frenking, G.; Stasch, A. *Inorg. Chem.* **2011**, *50*, 12315–12325. (c) Choong, S. L.; Schenk, C.; Stasch, A.; Dange, D.; Jones, C. *Chem. Commun.* **2012**, *48*, 2504–2506. (d) Pu, L.; Phillips, A. D.; Richards, A. F.; Stender, M.; Simons, R. S.; Olmstead, M. M.; Power, P. P. *J. Am. Chem. Soc.* **2003**, *125*, 11626–11636. (e) Peng, Y.; Fischer, R. C.; Merrill, W. A.; Fischer, J.; Pu, L.; Ellis, B. D.; Fetting, J. C.; Herber, R. H.; Power, P. P. *Chem. Sci.* **2010**, *1*, 461–468. (f) Fischer, R. C.; Pu, L.; Fetting, J. C.; Brynda, M. A.; Power, P. P. *J. Am. Chem. Soc.* **2006**, *128*, 11366–11367.
- (9) Bigwood, M. P.; Corvan, P. J.; Zuckerman, J. J. *J. Am. Chem. Soc.* **1981**, *103*, 7643–7646.
- (10) Angermund, K.; Jonas, K.; Krüger, C.; Latten, J. L.; Tsay, Y.-H. *J. Organomet. Chem.* **1988**, *353*, 17–25.
- (11) Drost, C.; Hitchcock, P. B.; Lappert, M. F.; Pierssens, L. J.-M. *Chem. Commun.* **1997**, 1141–1142.
- (12) Engelhardt, L. M.; Jolly, B. S.; Lappert, M. F.; Raston, C. L.; White, A. H. *J. Chem. Soc., Chem. Commun.* **1988**, 336–338.
- (13) Jastrzebski, J. T. B. H.; van der Schaaf, P. A.; Boersma, J.; van Koten, G. *J. Organomet. Chem.* **1989**, *367*, 55–68.
- (14) Jacob, K.; Seidel, N.; Voigt, F.; Fischer, A.; Pietzsch, C.; Holecck, J.; Lycka, A.; Fontani, M.; Grigiotti, E.; Zanello, P. *J. Prakt. Chem.* **2000**, *342*, 574–584.
- (15) Wingerter, S.; Gornitzka, H.; Bertermann, R.; Pandey, S. K.; Rocha, J.; Stalke, D. *Organometallics* **2000**, *19*, 3890–3894.
- (16) Grützmacher, H.; Pritzkow, H.; Edelman, F. T. *Organometallics* **1991**, *10*, 23–25.
- (17) (a) Henn, M.; Schürmann, M.; Mahieu, B.; Zanello, P.; Cinquantini, A.; Jurkschat, K. *J. Organomet. Chem.* **2006**, *691*, 1560–1572. (b) Mehring, M.; Löw, C.; Schürmann, M.; Uhlig, F.; Jurkschat, K.; Mahieu, B. *Organometallics* **2000**, *19*, 4613–4623. (c) Deáky, V.; Schürmann, M.; Jurkschat, K. *Z. Anorg. Allg. Chem.* **2009**, *635*, 1380–1383. (d) Henn, M.; Deáky, V.; Krabbe, S.; Schürmann, M.; Prosenc, M. H.; Herres-Pawlis, S.; Mahieu, B.; Jurkschat, K. *Z. Anorg. Allg. Chem.* **2011**, *637*, 211–223. (e) Wagner, M.; Dorogov, K.; Schürmann, M.; Jurkschat, K. *Dalton Trans.* **2011**, *40*, 8839–8848. (f) Henn, M. *Doctoral Thesis*, Technische Universität Dortmund, 2003. (g) First presented at the XVth FEChem Conference on Organometallic Chemistry, University of Zurich, Zurich, Switzerland, Aug 10–15, 2003, Book of Abstracts OP38, and at the 11th International Conference on the Coordination and Organometallic Chemistry of Germanium, Tin, and Lead (ICCOG-GTL-11), Santa Fe, New Mexico, June 27–July 2, 2004, Book of Abstracts O54.
- (18) Khan, S.; Samuel, P. P.; Michel, R.; Dieterich, J. M.; Mata, R. A.; Demers, J.-P.; Lange, A.; Roesky, H. W.; Stalke, D. *Chem. Commun.* **2012**, *48*, 4890–4892.
- (19) Spek, A. L. *Acta Crystallogr.* **2009**, *D65*, 148–155.
- (20) (a) Fischer, R. C.; Power, P. P. *Chem. Rev.* **2010**, *110*, 3877–3923. (b) Takagi, N.; Nagase, S. *Organometallics* **2007**, *26*, 469–471. (c) Takagi, N.; Nagase, S. *Organometallics* **2001**, *20*, 5498–5500. (d) Jung, Y.; Brynda, M.; Power, P. P.; Head-Gordon, M. *J. Am. Chem. Soc.* **2006**, *128*, 7185–7192.
- (21) (a) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648–5652. (b) Weigend, F.; Ahlrichs, R. *Phys. Chem. Chem. Phys.* **2005**, *7*, 3297–

3305. (c) Metz, B.; Stoll, H.; Dolg, M. *J. Chem. Phys.* **2000**, *113*, 2563–2569.

(22) Spikes, G. H.; Giuliani, J. R.; Augustine, M. P.; Nowik, I.; Herber, R. H.; Power, P. P. *Inorg. Chem.* **2006**, *45*, 9132–9136.

(23) Mantina, M.; Chamberlin, A. C.; Valero, R.; Cramer, C. J.; Truhlar, D. G. *J. Phys. Chem. A* **2009**, *113*, 5806–5812.

(24) (a) Pacher, A.; Schrenk, C.; Schnepf, A. *J. Organomet. Chem.* **2010**, *695*, 941–944. (b) Schrenk, C.; Köppe, R.; Schellenberg, I.; Pöttgen, R.; Schnepf, A. *Z. Anorg. Allg. Chem.* **2009**, *635*, 1541–1548.

(25) Jastrzebski, J. T. B. H.; Grove, D. M.; Boersma, J.; van Koten, G.; Ernsting, J.-M. *Magn. Reson. Chem.* **1991**, *29*, S25–S30.

(26) Jastrzebski, J. T. B. H.; van der Schaaf, P. A.; Boersma, J.; van Koten, G.; Zoutberg, M. C.; Heijdenrijk, D. *Organometallics* **1989**, *8*, 1373–1375.

(27) (a) Martincová, J.; Jambor, R.; Schürmann, M.; Jurkschat, K.; Honzík, J.; Paz, F. A. A. *Organometallics* **2009**, *28*, 4778–4782.

(b) Kircher, P.; Huttner, G.; Schiemenz, B.; Heinze, K.; Zsolnai, L.; Walter, O.; Jacobi, A.; Driess, A. *Chem. Ber.* **1997**, *130*, 687–699.

(c) Reuter, H. Z. *Kristallogr.—New Cryst. Struct.* **2004**, *219*, 109–110.

(d) Dewan, J. C.; Silver, J.; Donaldson, J. D.; Thomas, M. J. K. *J. Chem. Soc., Dalton Trans.* **1977**, 2319–2322. (e) Stafeeva, V. S.; Mitiaev, A. S.; Abakumov, A. M.; Tsirlin, A. A.; Makarevich, A. M.; Antipov, E. V. *Polyhedron* **2007**, *26*, 5365–5369. (f) Donaldson, J. D.; Grimes, S. M.; Calogero, S.; Russo, U.; Valle, G.; Smith, P. J. *Inorg. Chim. Acta* **1984**, *84*, 173–177.

(28) Hossain, D.; Kitamura, T. *Synthesis* **2005**, 1932–1934.

(29) (a) Stalke, D. *Chem. Soc. Rev.* **1998**, *27*, 171–178. (b) Kottke, T.; Stalke, D. *J. Appl. Crystallogr.* **1993**, *26*, 615–619.

(30) Sheldrick, G. M. *Acta Crystallogr.* **2008**, *A64*, 112–122.

(31) *Gaussian 03*, revision E.01; Frisch, M. J.; et al. See the Supporting Information.