

Synthesis, Spectroscopic Investigations, and Molecular Structures of 1-Phenyl-1-chalcogeno-4-methyl-4-chloro-1 λ^5 ,4-phosphastanninanes, Me(Cl)Sn(CH₂-CH₂)₂P(E)Ph (E = O, S, Se)

Horst Weichmann*

Institut für Anorganische Chemie der Martin-Luther-Universität Halle-Wittenberg, 06099 Halle/S., Germany

Jacqueline Meunier-Piret

Laboratoire de Chimie Physique et de Cristallographie, Université de Louvain, Bâtiment Lavoisier, Place L. Pasteur 1, B-1348 Louvain-la-Neuve, Belgium

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A series of 1-phenyl-1-chalcogeno-4-methyl-4-chloro-1 λ^5 ,4-phosphastanninanes Me(Cl)Sn(CH₂-CH₂)₂P(E)Ph with E = S, Se, O (7-9) has been synthesized by chlorodemetalation of the related tetraorganotin derivatives Me₂Sn(CH₂-CH₂)₂P(E)Ph (1-3) with Me₂SnCl₂. ¹¹⁹Sn, ³¹P, and ¹H NMR studies in nonpolar solvents show that 7-9 exhibit a P=E...Sn coordination which is intramolecular for 7 and 8 (E = S, Se) and intermolecular for 9 (E = O). In donor solvents the intramolecular interaction of 7 and 8 is no longer present. The molecular structures of 7-9 were determined by X-ray analysis. The structure determination of 7 gave the monoclinic space group *P*2₁/*c* (*a* = 12.256(15), *b* = 9.293(6), *c* = 12.622(13) Å; β = 96.64(10)°; *V* = 1427.9(25) Å³; *Z* = 4; *R* = 0.040). 8 crystallizes in the orthorhombic space group *Pccn* (*a* = 22.703(3), *b* = 16.910(22), *c* = 7.523(4) Å; *V* = 2888.1(51) Å³; *Z* = 8; *R* = 0.053). 9 has the triclinic space group *P*1 (*a* = 7.606(3), *b* = 10.179(2), *c* = 9.883(2) Å; α = 117.97(2), β = 96.58(3), γ = 87.80(3)°; *V* = 671.2(3) Å³; *Z* = 2; *R* = 0.0395). In the solid state 7-9 also exhibit pentacoordination at the tin with the ligand polyhedron approaching an ideal trigonal bipyramid in the order 7 < 8 < 9. 9 exists as dimers with intermolecular P=O...Sn contacts and a chair conformation for the 1 λ^5 ,4-phosphastanninane ring system, whereas 7 and 8 are monomeric with intramolecular P=E...Sn coordination and a boat conformation of the six-membered ring.

Introduction

We recently reported the synthesis and molecular structure of 1-phenyl-4,4-dimethyl-1 λ^5 ,4-phosphastanninane Me₂Sn(CH₂-CH₂)₂PPh and its P-chalcogenides.¹ The compounds exist both in solution and in the solid state in a chair conformation without any intra- or intermolecular P=E...Sn (E = lone pair, O, S, Se) interaction. In continuation of these investigations we are interested in the halogenation of these compounds from both the synthetic and structural points of view.

Depending on the ring size, the attack of electrophiles on 1,1-dialkyl-1-stannacycloalkanes occurs mostly at either exo- or endocyclic tin-carbon bonds.² In the case of five-membered ring compounds these reactions proceed exclusively by ring cleavage, whereas the six- and seven-membered ring systems preferentially react via cleavage of the exocyclic tin-carbon bonds.²

The presence of the P=E group in our starting compounds Me₂Sn(CH₂-CH₂)₂P(E)Ph (E = lone pair, O, S, Se) should influence both the reactivity of these compounds toward halogenating agents³⁻⁶ and the structure of the resulting products.

As a consequence of the substitution of an exocyclic methyl group by a halogen atom, the strong P=E...Sn donor-acceptor interaction in the resulting compounds Me(Hal)Sn(CH₂-CH₂)₂P(E)Ph should influence the conformation of the 1 λ^5 ,4-phosphastanninane ring system. This structural problem has been studied in detail for the eight-membered 1-elementa-5-stannacyclooctanes R₂Sn(XCH₂-CH₂)₂E (X = O, S, CH₂; E = O, S, NR) whose structures are characterized by a transannular Sn...E interaction.⁷

We report here on the synthesis, spectroscopic studies, and molecular structures of the cyclic triorganotin chlorides Me(Cl)Sn(CH₂-CH₂)₂P(E)Ph (E = lone pair, O, S, Se).

Results and Discussion

Preparative Aspects. The halogenation of Me₂Sn(CH₂-CH₂)₂P(E)Ph (1, E = O; 2, E = S; 3, E = Se) with bromine in CH₂Cl₂ or hydrogen chloride in ether gives rise to the cleavage of both exo- and endocyclic tin-carbon bonds in a ratio which depends strongly on the chalcogen atom. In the case of 1 ring cleavage is favored, whereas for 2 and 3 the substitution of an exocyclic methyl group with formation of the title compounds is the preferred reaction.

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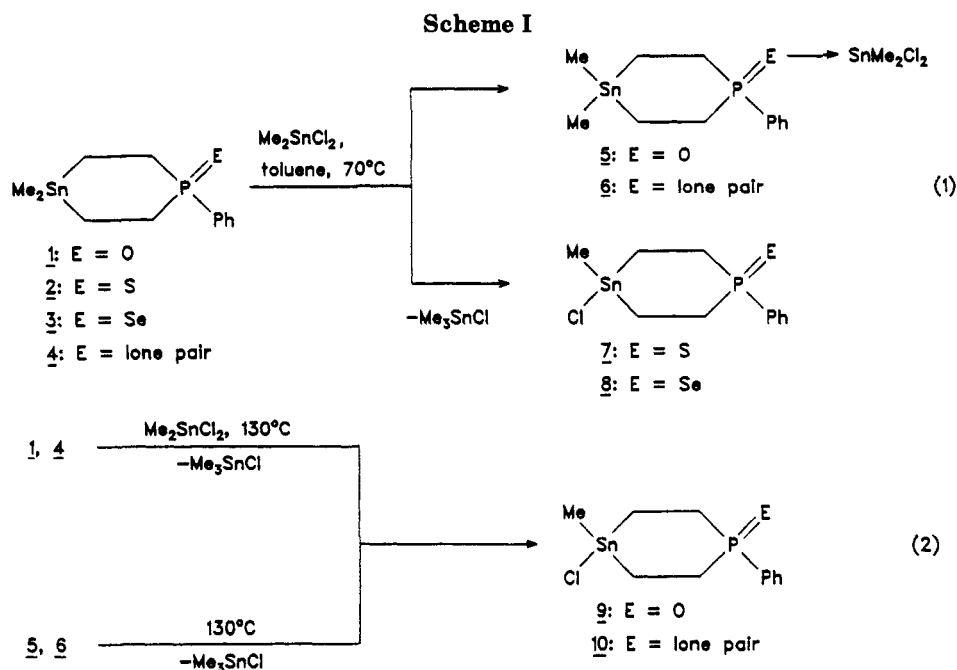
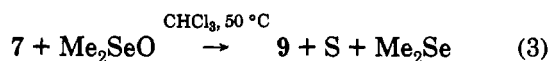


Table I. ^{119}Sn , ^{31}P , and Selected ^1H NMR Data for $\text{Me}_2\text{Sn}(\text{CH}_2\text{-CH}_2)_2\text{P}(\text{E})\text{Ph}$ (1-4),^a $\text{Me}_2\text{Sn}(\text{CH}_2\text{-CH}_2)_2\text{P}(\text{E})\text{Ph-Me}_2\text{SnCl}_2$ (5, 6), and $\text{Me}(\text{Cl})\text{Sn}(\text{CH}_2\text{-CH}_2)_2\text{P}(\text{E})\text{Ph}$ (7-10)

compd	solv	$\delta_{^{119}\text{Sn}}$ (ppm)	$\delta_{^{31}\text{P}}$ (ppm)	$^3J(^{119}\text{Sn}, ^{31}\text{P})$ (Hz)	$\delta_{\text{H}}(\text{SnC}^1\text{H}_3)$ (ppm)	$^2J(^{119}\text{SnC}^1\text{H}_3)$ (Hz)
1	CDCl_3	-46.4	37.7	128.5	0.17/0.21	53.1/57.7
2	CDCl_3	-56.9	45.5	157.4	0.20/0.26	52.8/57.9
3	CDCl_3	-58.9	37.9 ^b	162.4	0.18/0.27	53.6/58.0
4	C_6D_6	-43.0	-21.6	98.7	0.04/0.07	54.8/52.3
5	CDCl_3	-44.2	45.1	124.5	0.21/0.29	54.0/57.7
		-79.6 ^c			1.15	83.0
6	C_6D_6	-46.5	-10.6	115.7	-0.08/0.02	54.0/55.4
		-86.8 ^c			0.87	77.6
7	CDCl_3	33.3	50.3	443.6	1.04	69.8
	CD_2Cl_2	26.5 ^d		480.8		
	pyridine- <i>d</i> ₅	-57.0		244.3		
8	CDCl_3	26.3	45.5 ^e	460.6	1.05	69.9
	CD_2Cl_2	17.9 ^f		487.6		
	pyridine- <i>d</i> ₅	-66.9		249.3		
9	CDCl_3	-73.6	40.6	264.8	0.97	78.5
	pyridine- <i>d</i> ₅	-75.9		244.5		
10	C_6D_6	114.0	-20.9	131.0	0.23	58.3

^a Reference 1. ^b $^1J(^{31}\text{P}^{77}\text{Se})$: 707.1 Hz. ^c Broad. ^d At 192 K. ^e $^1J(^{31}\text{P}^{77}\text{Se})$: 670.5 Hz. ^f At 198 K.

The results are clearer if the halogenation of 1-3 is performed via a redistribution reaction with dimethyltin dichloride. For structural reasons $\text{Me}_2\text{Sn}(\text{CH}_2\text{-CH}_2)_2\text{PPh}$ (4) has also been included in these investigations. When the reaction of 1-4 with Me_2SnCl_2 is carried out by heating the compounds in a small amount of toluene for 8-10 h at 70 °C, only 2 and 3 give the expected substitution products 7 and 8. In the case of 1 and 4 the adducts 5 and 6 are formed (eq 1). The yields of 5-8 are nearly quantitative. However, a methyl/chlorine exchange in 1 and 4 can be realized by heating 5 and 6 or mixtures containing 1 or 4 and Me_2SnCl_2 for several hours at 130 °C (eq 2). Furthermore, 9 is obtainable by the reaction of 7 with Me_2SeO according to eq 3.⁸ 5 and 7-9 are colorless, crystalline compounds with sharp melting points.



Whereas 5, 7, and 8 are readily soluble in halogenated hydrocarbons, benzene and toluene, the solubility of 9 in

these solvents is low. All of the compounds, including 9, are soluble in donor solvents. 6 and 10 are obtained as solid foams after removing the volatile products from the reaction mixtures.

NMR Spectroscopic Studies (Table I). In general, the chemical shifts of ^{119}Sn NMR signals are valuable parameters for determining the coordination number of the tin atom in its organic derivatives.^{9,10} However, a comparison of the chemical shifts of organotin compounds with different structures is only permissible when the substituents at the tin atoms are similar. It is thus helpful for the correlation between ^{119}Sn chemical shift and coordination number of tin in compounds 7-9 to compare their shift values with that of 10 which in unpolar solvents indicates the presence of tetracoordinated tin (see also: $\text{Me}_2\text{Sn}(\text{Cl})\text{CH}_2\text{CH}_2\text{PPh}_2$, $\delta_{^{119}\text{Sn}}(\text{C}_6\text{D}_6) = 142 \text{ ppm}^{11}$). The considerable high-field shift of the ^{119}Sn NMR signals of 7-9 in unpolar solvents with respect to 10 confirms an increase in the coordination number of tin as the result of a $\text{P}=\text{E}\cdots\text{Sn}$ interaction. Furthermore, the ^{119}Sn shift

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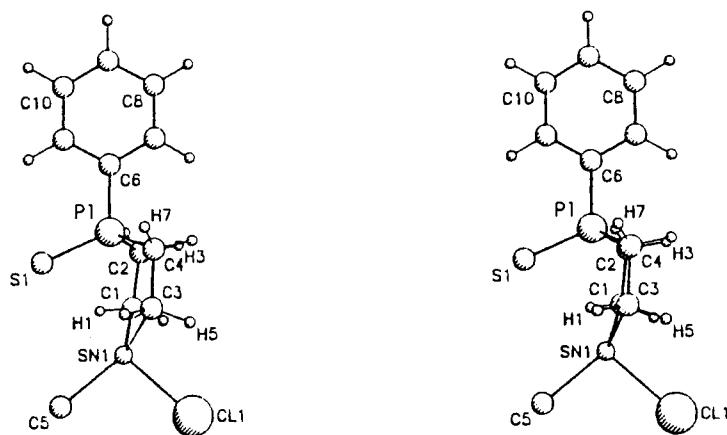
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Table II. Crystallographic Data, Experimental Data Collection, and Refinement Conditions for Me(Cl)Sn(CH₂-CH₂)₂P(E)Ph (7-9)

	7, E = S	8, E = Se	9, E = O
formula unit	C ₁₁ H ₁₆ ClPSSn	C ₁₁ H ₁₆ ClPSeSn	C ₁₁ H ₁₆ ClPOSn
system	monoclinic	orthorhombic	triclinic
space group	<i>P2</i> ₁ / <i>c</i>	<i>Pccn</i>	<i>P1</i>
<i>a</i> (Å)	12.256(15)	22.703(30)	7.606(3)
<i>b</i> (Å)	9.293(6)	16.910(22)	10.179(2)
<i>c</i> (Å)	12.622(13)	7.523(4)	9.883(2)
α (deg)			117.97 (2)
β (deg)	96.64(10)		96.58(3)
γ (deg)			87.80(3)
<i>V</i> (Å ³)	1427.9(25)	2888.1(51)	671.2(3)
<i>Z</i>	4	8	2
<i>D</i> (calcd) (g·cm ⁻³)	1.699	1.896	1.728
μ /cm ⁻¹	20.36	45.89	20.25
cryst size (nm)	0.4 × 0.2 × 0.2	0.4 × 0.3 × 0.2	0.3 × 0.3 × 0.1
radiation	Mo K α	Mo K α	Mo K α
λ /Å	0.710 69	0.710 69	0.710 69
monochromator	graphite	graphite	graphite
$2\theta_{\max}$ (deg)	52.0	47.0	52.0
ω - 2θ scan; scan width (θ) (deg)	1.3	1.5	1.25
index range (<i>hkl</i>)	-15/15, 0/11, 0/15	0/25, 0/18, 0/8	-9/9, -12/11, 0/12
no. of ind refls			
measd	2821	2144	2651
obsd (<i>I</i> > 2.5 σ (<i>I</i>))	2022	1605	2342
abs corrn	no	no	no
resolution	Patterson ^a	Patterson + Dirdif ^b	direct methods ^a
refinement	SHELX76 ^c	SHELX76	SHELX76
weighting scheme, ω^{-1}	$\sigma^2(F) + 0.0010F^2$	$\sigma^2(F) + 0.0151F^2$	$\sigma^2(F) + 0.0034F^2$
no. of H atoms in calcd positions	13	13	13
final <i>R</i> (<i>R</i> _w)	0.040 (0.045)	0.053 (0.057)	0.0395 (0.043)

^a SHELX84; Sheldrick, G. M. Personal communication, 1984. ^b Beurskens, P. T.; Bosman, W. P.; Doesburg, H. M.; Gould, R. O.; van der Hark, Th. E. M.; Prick, P. A. J.; Noordik, J. H.; Beurskens, G.; Parthasarathi, V. DIRDIF; Technical Report 1981/2; Crystallography Laboratory: Toernooiveld, 6525 ED Nijmegen, The Netherlands, 1981. ^c Sheldrick, G. M. SHELX76, Program for Crystal Structure Determination. University of Cambridge, Cambridge, England, 1976.

Figure 1. Stereoscopic view with atom numbering of the molecular structure of Me(Cl)Sn(CH₂-CH₂)₂P(S)Ph (7).

values indicate structural differences between 7 and 8 ($\delta_{119}\text{Sn}(\text{CDCl}_3) = 33.3$ and 26.3 ppm) on the one hand and 9 ($\delta_{119}\text{Sn} = -73.6$ ppm) on the other hand.

Further evidence for the presence of pentacoordinated tin in 7-9 is supplied by the ³¹P and ¹H NMR data. The P=E...Sn interaction in 7-9 gives rise to a low-field shift of the ³¹P NMR signals in comparison with 1-3, and the values of the ²*J*(¹¹⁹SnC¹H) coupling constants of the methyl group signals in the ¹H NMR spectra of 7-9 (69.8-78.5 Hz) are characteristic of pentacoordinated tin in its methyl substituted compounds.¹²

The structural differences between 9 on the one hand and 7 and 8 on the other hand, indicated by differences of their ¹¹⁹Sn chemical shifts and ²*J*(¹¹⁹SnC¹H) coupling constants, are strikingly confirmed by the value of the

J(¹¹⁹Sn, ³¹P) coupling constant, which in CDCl₃ is nearly 200 Hz higher for 7 and 8 than for 9.

The NMR spectroscopic data for 7-9 (Table I) lead us to conclude that as a result of the smaller atomic radius of oxygen compared with those of sulfur and selenium the P=E...Sn interaction is intermolecular for the probably dimeric 9 and intramolecular for 7 and 8. As a consequence the six-membered phosphastanninane ring should adopt a chair conformation for 9 and a boat conformation for 7 and 8. Thus the reason for the great difference in *J*(¹¹⁹Sn, ³¹P) could be that in 9 the phosphorus and the tin atom couple only through the bridging carbon atoms whereas *J*(¹¹⁹Sn, ³¹P) for 7 and 8 is the sum of ³*J*(¹¹⁹SnCC³¹P) and ²*J*(¹¹⁹SnE³¹P) (E = S, Se). However, for the latter case our previous investigations¹³⁻¹⁵ imply that the total coupling constant *J*(¹¹⁹Sn, ³¹P) for 7 and 8 should be smaller than ³*J*(¹¹⁹SnCC³¹P) in the starting compounds 2 and 3.

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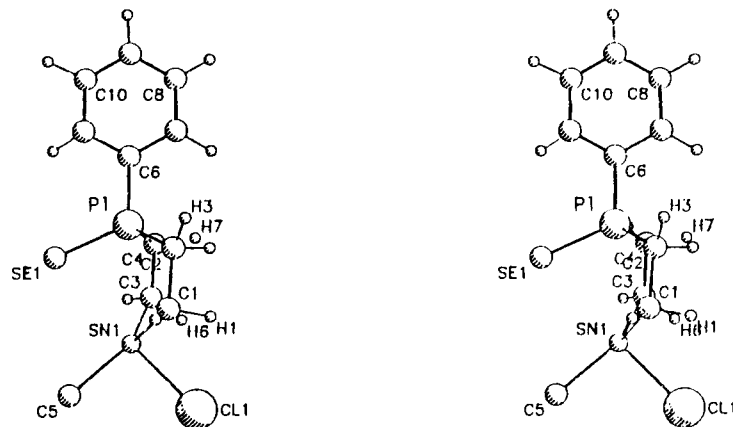


Figure 2. Stereoscopic view with atom numbering of the molecular structure of $\text{Me}(\text{Cl})\text{Sn}(\text{CH}_2\text{-CH}_2)_2\text{P}(\text{Se})\text{Ph}$ (**8**).

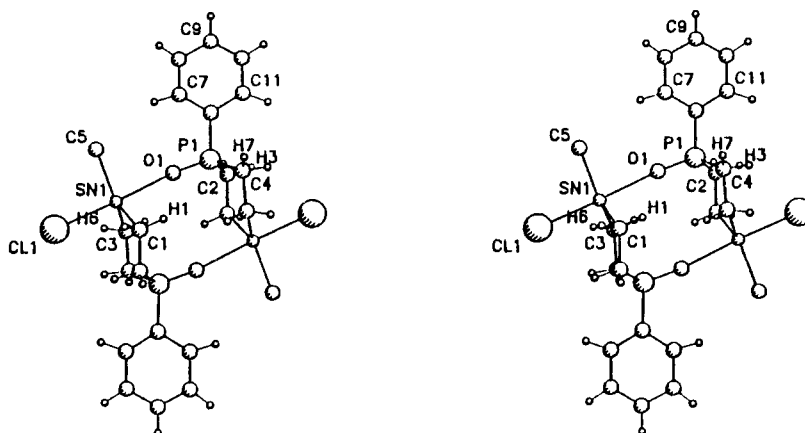


Figure 3. Stereoscopic view with atom numbering of the molecular structure of $\text{Me}(\text{Cl})\text{Sn}(\text{CH}_2\text{-CH}_2)_2\text{P}(\text{O})\text{Ph}$ (**9**).

The drastic reverse effect indicates that the great difference in the $J(^{119}\text{Sn}, ^{31}\text{P})$ coupling constants of 7–9 in CDCl_3 is obviously attributable to the different dihedral angles φ_{SnCCP} . Furthermore, with a decrease in temperature for 7 and 8 in CD_2Cl_2 (Table I) the ^{119}Sn NMR signal shifts to higher field and the $J(^{119}\text{Sn}, ^{31}\text{P})$ coupling constant increases; both effects indicate a strengthening of the $\text{P}=\text{E}\cdots\text{Sn}$ interaction.

The behavior of 7–9 in pyridine is in agreement with their proposed structures in CDCl_3 . Whereas the ^{119}Sn NMR data indicate that 9 does not change its structure in this solvent, the intramolecular $\text{P}=\text{E}\cdots\text{Sn}$ coordination in 7 and 8 is destroyed and a pyridine molecule occupies the vacant coordination site at the tin atom. This causes a high-field shift of the ^{119}Sn NMR signal and for the phosphastanninane ring a conversion from the boat into a chair conformation, with the result that the coupling constant $J(^{119}\text{Sn}, ^{31}\text{P})$ of 7 and 8 in pyridine changes into $^3J(^{119}\text{SnCC}^{31}\text{P})$ with nearly the same value as that for 9.

The structures of the adducts 5 and 6 can also be determined on the basis of the NMR data. Their ^{119}Sn NMR spectra exhibit a sharp doublet for 1 (–44.2 ppm) and 4 (–46.5 ppm) and at higher field a broad signal for coordinated Me_2SnCl_2 (–79.6 and –86.8 ppm). The interaction between Me_2SnCl_2 and the $\text{P}=\text{E}$ group in 5 and 6 is reflected by the low-field shift of the ^{31}P NMR signals in comparison with those of free 1 and 4 and the drastic high-field shift of the ^{119}Sn NMR signal for

Me_2SnCl_2 in 5 and 6 compared with that of uncoordinated Me_2SnCl_2 ($\delta_{^{119}\text{Sn}}(\text{CCl}_4) = 141.2 \text{ ppm}^{10}$).

The ^1H NMR spectra of 5 and 6 in the region +0.29 to –0.08 ppm contain the two methyl group signals of coordinated 1 and 4 with nearly the same values for both the chemical shift and the $^2J(^{119}\text{SnC}^1\text{H})$ coupling constant as in the uncoordinated state. The methyl groups of Me_2SnCl_2 in 5 and 6 are recognizable as a singlet at lower field with a significantly higher $^2J(^{119}\text{SnC}^1\text{H})$ coupling constant compared with that of free Me_2SnCl_2 ($\text{Me}_2\text{SnCl}_2(\text{CCl}_4)$: $\delta_{\text{SnMe}} = 1.15 \text{ ppm}$; $^2J(^{119}\text{Sn}^1\text{H}) = 69.0 \text{ Hz}^{12}$) due to the coordination at the $\text{P}=\text{E}$ group.

Molecular Structures of 7–9. Crystallographic data, experimental data collection, and refinement conditions are listed in Table II. Stereoviews of the molecular structures and the atomic labeling schemes of 7–9 are shown in Figures 1–3. Final atomic coordinates are listed in Table III. Selected bond distances and bond angles are collected in Tables IV and V, and Table VI contains the endocyclic torsion angles of the phosphastanninane ring in 7–9.

The results of the X-ray analysis for 7–9 in the solid state reveal the same molecular structure as in solution. Accordingly, in the three compounds the short $\text{Sn}\cdots\text{E}$ distances ($\text{E} = \text{O}, \text{S}, \text{Se}$) confirm the $\text{P}=\text{E}\cdots\text{Sn}$ interaction. On account of the larger atomic radii of sulfur and selenium this interaction is intramolecular for 7 and 8 and their crystal structures consist of isolated molecules without any short intermolecular interactions. For steric reasons the smaller atomic radius of oxygen permits only an intermolecular $\text{P}=\text{O}\cdots\text{Sn}$ coordination for 9; the compound consequently exists in the crystal as dimeric units, between

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Table III. Fractional Atomic Coordinates ($\times 10^4$, $\times 10^5$ for Sn) and B_{eq} Values (\AA^2) of Me(Cl)Sn(CH₂-CH₂)₂P(E)Ph (7-9)

atom	a/x	b/y	c/z	B_{eq}
7, E = S				
Sn(1)	36787(5)	15922(7)	38435(5)	3.69
Cl(1)	4968(2)	-31(3)	3136(1)	6.27
P(1)	1042(2)	2074(3)	3588(2)	2.95
E(1)	1734(2)	3521(3)	4582(2)	3.98
C(1)	2575(8)	101(11)	4526(9)	4.69
C(2)	1368(7)	260(11)	4047(11)	4.31
C(3)	2770(8)	2391(15)	2381(8)	4.99
C(4)	1532(7)	2219(13)	2295(7)	4.10
C(5)	4786(9)	2982(13)	4773(10)	5.40
C(6)	-426(7)	2197(10)	3345(7)	3.36
C(7)	-984(8)	1418(10)	2526(8)	4.20
C(8)	-2105(8)	1569(12)	2315(9)	4.83
C(9)	-2672(8)	2474(12)	2935(10)	5.16
C(10)	-2111(9)	3237(12)	3751(10)	5.18
C(11)	-991(8)	3096(11)	3966(8)	4.16
8, E = Se				
Sn(1)	38875(3)	11675(3)	-843(8)	2.55
Cl(1)	4661(1)	1510(2)	2148(4)	4.33
P(1)	3692(1)	-141(1)	-3080(3)	2.22
E(1)	2980(0)	666(1)	-2896(2)	3.56
C(1)	4449(5)	1173(6)	-2441(15)	3.56
C(2)	4379(5)	373(5)	-3525(13)	2.95
C(3)	3808(6)	-71(7)	619(14)	4.16
C(4)	3792(5)	-634(6)	-925(13)	3.21
C(5)	3302(5)	2088(7)	739(18)	5.00
C(6)	3608(4)	-906(6)	-4759(10)	2.31
C(7)	4092(5)	-1380(7)	-5246(12)	3.06
C(8)	4002(5)	-1972(6)	-6489(14)	3.53
C(9)	3456(5)	-2082(5)	-7282(13)	3.27
C(10)	2996(5)	-1615(7)	-6806(14)	3.99
C(11)	3062(4)	-1003(6)	-5564(14)	2.94
9, E = O				
Sn(1)	-10274(4)	7337(4)	-22624(3)	2.85
Cl(1)	-226(2)	2569(2)	-3141(2)	4.62
P(1)	2278(2)	2096(1)	873(1)	2.67
E(1)	1931(6)	1034(4)	1465(5)	3.72
C(1)	1622(7)	-59(6)	-2249(6)	2.92
C(2)	2925(7)	1147(6)	-1075(6)	3.24
C(3)	-1334(7)	2448(6)	18(7)	3.48
C(4)	412(8)	3257(6)	881(7)	3.75
C(5)	-3128(9)	-242(9)	-4036(8)	5.02
C(6)	4103(7)	3347(5)	1995(6)	3.01
C(7)	5274(7)	3014(6)	2984(6)	3.43
C(8)	6721(8)	3939(7)	3846(7)	4.18
C(9)	7006(8)	5187(7)	3703(7)	4.49
C(10)	5885(10)	5525(7)	2741(8)	4.96
C(11)	4444(9)	4631(7)	1889(8)	4.37

Table IV. Selected Bond Lengths (\AA) for Me(Cl)Sn(CH₂-CH₂)₂P(E)Ph (7-9) with Standard Deviations in Parentheses

	7, E = S	8, E = Se	9, E = O
Sn(1)-Cl(1)	2.428(3)	2.498(3)	2.519(2)
Sn(1)-E(1)	3.205(3)	3.072(1)	2.422(4)
Sn(1)-C(1)	2.183(9)	2.184(11)	2.143(5)
Sn(1)-C(3)	2.174(10)	2.167(11)	2.139(5)
Sn(1)-C(5)	2.126(10)	2.138(10)	2.111(6)
P(1)-E(1)	1.963(3)	2.120(2)	1.493(6)
P(1)-C(2)	1.812(10)	1.817(9)	1.822(6)
P(1)-C(4)	1.808(9)	1.836(9)	1.810(6)
P(1)-C(6)	1.794(9)	1.818(9)	1.799(5)
C(1)-C(2)	1.539(13)	1.587(14)	1.526(6)
C(3)-C(4)	1.518(13)	1.503(16)	1.528(7)

which likewise no abnormally short intermolecular separations occur.

As a consequence of the P=E...Sn coordination the geometry around the tin atom in 7-9 is that of a nearly trigonal bipyramid, three carbon atoms of which belong to the methyl group and the two endocyclic methylene groups in the equatorial plane; the axial positions are

Table V. Selected Bond Angles (deg) for Me(Cl)Sn(CH₂-CH₂)₂P(E)Ph (7-9) with Standard Deviations in Parentheses

	7, E = S	8, E = Se	9, E = O
E(1)...Sn(1)-C(1)	74.0(3)	80.4(3)	88.9(2)
E(1)...Sn(1)-C(3)	74.4(3)	81.1(3)	87.5(2)
E(1)...Sn(1)-C(5)	87.0(3)	89.1(3)	84.0(3)
E(1)...Sn(1)-Cl(1)	172.6(3)	176.7(1)	177.62(2)
Cl(1)-Sn(1)-C(1)	102.1(3)	97.7(3)	93.3(2)
Cl(1)-Sn(1)-C(3)	101.0(3)	96.8(3)	92.8(2)
Cl(1)-Sn(1)-C(5)	100.4(4)	94.2(3)	93.8(3)
C(1)-Sn(1)-C(3)	105.8(4)	104.5(4)	107.6(2)
C(1)-Sn(1)-C(5)	123.6(5)	126.5(5)	126.9(2)
C(3)-Sn(1)-C(5)	119.5(5)	125.5(5)	124.5(2)
E(1)-P(1)-C(2)	111.7(4)	110.9(3)	112.1(3)
E(1)-P(1)-C(4)	111.2(4)	109.2(3)	113.5(3)
E(1)-P(1)-C(6)	114.6(3)	115.0(3)	112.1(3)
C(2)-P(1)-C(4)	105.9(5)	105.9(5)	108.0(3)
C(2)-P(1)-C(6)	107.6(4)	107.6(4)	104.3(2)
C(4)-P(1)-C(6)	105.8(4)	107.7(4)	106.1(2)
Sn(1)...E(1)-P(1)	73.3(4)	73.2(1)	173.5(4)

Table VI. Comparison of Equivalent Endocyclic Torsion Angles (deg) of the Six-Membered Rings in Me(Cl)Sn(CH₂-CH₂)₂P(E)Ph (7-9)

	7, E = S	8, E = Se	9, E = O
Sn(1)-C(1)-C(2)-P(1)	-28.8		
C(1)-C(2)-P(1)-C(4)	+80.5		
C(2)-P(1)-C(4)-C(3)	-76.4		
P(1)-C(4)-C(3)-Sn(1)	+23.5		
C(4)-C(3)-Sn(1)-C(1)	+19.4		
C(3)-Sn(1)-C(1)-C(2)	-16.2		
	8, E = Se	9, E = O	
Sn(1)-C(3)-C(4)-P(1)	-11.7	-49.9	
C(3)-C(4)-P(1)-C(2)	+70.7	+69.7	
C(4)-P(1)-C(2)-C(1)	-77.6	-70.9	
P(1)-C(2)-C(1)-Sn(1)	+22.0	+52.5	
C(2)-C(1)-Sn(1)-C(3)	+28.6	-30.3	
C(1)-Sn(1)-C(3)-C(4)	-35.0	+28.4	

Table VII. Transition from a Tetrahedron to a Trigonal Bipyramid in the Compound Series Me(Cl)Sn(CH₂-CH₂)₂P(E)Ph (7-9) [$\sum \vartheta_{\text{eq}} - \sum \vartheta_{\text{ax}}$ (deg), $\Delta_{\text{Sn}}(\text{plane})$ (\AA)]

	$\sum \vartheta_{\text{eq}} - \sum \vartheta_{\text{ax}}$	$\Delta_{\text{Sn}}(\text{plane})$	formal bond order ¹⁸
tetrahedron	0	0.71	
S (7)	45.4	0.42	0.22
Se (8)	67.8	0.23	0.50
O (9)	79.1	0.12	0.71
trigonal bipyramid	90.0	0.00	

occupied by the chlorine and the chalcogen atoms. Depending on the mode and the strength of the P=E...Sn interaction, the ligand polyhedron around the tin atom in 7-9 represents a transition from a tetrahedron to a trigonal bipyramid (Table VII). A quantitative measure for determining the position of the structure of 7-9 between these ideal geometries is the difference between the sums of the equatorial and axial angles ($\sum \vartheta_{\text{eq}} - \sum \vartheta_{\text{ax}}$), which is 90° for the ideal trigonal bipyramid and 0° for the ideal tetrahedron.¹⁶ Another method of characterizing the distortion of the trigonal bipyramidal ligand polyhedron in 7-9 is to estimate the distance $\Delta_{\text{Sn}}(\text{plane})$ between the tin atom and the plane of the three equatorial carbon atoms. This distance ranges from 0.71 Å for a tetrahedron to 0 Å for the trigonal bipyramid.¹⁷ The rigid bicyclic structures of 7 and 8 and the more flexible dimeric structure of 9 give rise to distinct differences of both the values of

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$\sum \nu_{\text{eq}} - \sum \nu_{\text{ax}}$ and those of $\Delta_{\text{Sn}}(\text{plane})$, indicating for the ligand polyhedron of 7–9 an increasing approximation to the trigonal bipyramid in the sequence $7 < 8 < 9$. In agreement with this conclusion the strength of the $\text{P}=\text{E}\cdots\text{Sn}$ interaction and consequently the formal bond order $\text{Sn}\cdots\text{E}^{18}$ (Table VII) increase and the $\text{Sn}-\text{Cl}$ bond lengthens in the same sequence.

The significant extent of the distortion of the trigonal-bipyramidal ligand polyhedron around tin in 7–9 as a consequence of the rigidity of the bicyclic structures of 7 and 8 follows also from a comparison of their structural data with those of $\text{Me}_2\text{Sn}(\text{Br})\text{CH}_2-\text{CH}_2\text{P}(\text{S})\text{Ph}_2$,¹⁹ $\text{Me}_2\text{Sn}(\text{Cl})\text{CH}_2-\text{CH}_2\text{P}(\text{Se})\text{Ph}_2$,¹⁹ and $\text{Me}_2\text{Sn}(\text{F})\text{CH}_2-\text{CH}_2\text{P}(\text{O})\text{Ph}_2$,¹⁹ respectively. Obviously, the only slight distortion from the ideal trigonal-bipyramidal environment in the latter compounds, indicated by $\sum \nu_{\text{eq}} - \sum \nu_{\text{ax}}$ values of 77.2, 77.5, and 72.6, respectively, is due to the higher flexibility of the five-membered ring in these compounds.

The $\text{Sn}-\text{C}$ bond distances in 7–9 are in the range typical of those of other pentacoordinated triorganotin chlorides,²⁰ but in all three compounds the $\text{Sn}-\text{C}$ bond to the methyl group is shorter than those to the endocyclic methylene groups.

The coordination sphere around the phosphorus atom in 7–9 corresponds to a slightly distorted tetrahedron. The $\text{C}-\text{P}-\text{E}$ bond angles ($111-115^\circ$) are larger than the tetrahedron angle, so that accordingly the $\text{C}-\text{P}-\text{C}$ angles ($104.3-107.7^\circ$) are smaller. Compared with similar heterocycles containing an uncoordinated $\text{P}=\text{E}$ group^{1,21-24} the $\text{P}=\text{E}$ bond distances in 7–9 are scarcely changed by the $\text{P}=\text{E}\cdots\text{Sn}$ coordination.

As proposed for the solution structures of 7–9, the endocyclic torsion angles (Table VI) also indicate different conformations of the phosphastanninane ring in the solid state. The dimeric structure of 9 requires a chair conformation which is flattened at tin and puckered at phosphorus compared with the ideal geometry of cyclohexane. Furthermore, in comparison with $\text{Me}_2\text{Sn}(\text{CH}_2-\text{CH}_2)_2\text{P}(\text{O})\text{Ph}^1$ the intermolecular $\text{P}=\text{O}\cdots\text{Sn}$ coordination in 9 gives rise to a flattening of the chair at both tin and phosphorus.

The higher atomic radii of sulfur and selenium in 7 and 8 make possible the energetically favorable intramolecular $\text{P}=\text{E}\cdots\text{Sn}$ coordination which compels the phosphastanninane ring to adopt a boat conformation. The torsion angles indicate that for both 7 and 8 the rings are flattened at tin and puckered at phosphorus compared with the ideal boat conformation.

The two modes of $\text{P}=\text{E}\cdots\text{Sn}$ interaction in 7–9 correlate with the different behavior of 1–4 toward Me_2SnCl_2 , as demonstrated by eq 1. Obviously, in the case of 2 and 3 an intramolecular $\text{P}=\text{E}\cdots\text{Sn}$ interaction in the transition state facilitates the redistribution reaction of the com-

pounds with Me_2SnCl_2 with concomitant formation of 7 and 8. On the contrary, for 1 and 4 this intramolecular nucleophilic assistance⁶ is hindered for steric reasons and the primary products of the reaction with Me_2SnCl_2 are the adducts 5 and 6, which are transformed to 9 and 10 only at higher temperatures. In agreement with this interpretation the flexible open-chain structure of $\text{Me}_3\text{Sn}-\text{CH}_2\text{CH}_2\text{P}(\text{O})\text{PhR}$ ($\text{R} = \text{Ph}, t\text{-Bu}$) and $(\text{Me}_3\text{Sn}-\text{CH}_2-\text{CH}_2)_2\text{P}(\text{O})\text{Ph}$ allows these compounds to undergo (in contrast to 1) an intramolecular nucleophilically assisted redistribution reaction with $\text{Me}_{4-n}\text{SnCl}_n$ ($n = 1, 2$) under mild conditions.²⁵

Experimental Section

Where necessary, the reactions were carried out under an atmosphere of dry argon by using Schlenk tube techniques. The solvents were dried by standard methods and freshly distilled before use. The synthesis of 1–4 was described earlier.¹ The ^1H , ^{31}P , and ^{119}Sn NMR spectra were recorded on Bruker AC 80 and WP 200 spectrometers with respect to TMS (^1H), 85% H_3PO_4 (^{31}P), and Me_4Sn (^{119}Sn). Low-field shifts are positive. The molecular weight determinations were performed in chloroform at 40°C (concentration = 0.02 mol/L) using a Knauer osmometer. The mass spectra were recorded at 16 eV on an M. v. Ardenne spectrometer.

Synthesis of $(\text{CH}_3)_2\text{Sn}(\text{CH}_2-\text{CH}_2)_2\text{P}(\text{O})\text{C}_6\text{H}_5$, $(\text{CH}_3)_2\text{SnCl}_2$ (5). A mixture of 1 (0.7 g, 2.1 mmol) and Me_2SnCl_2 (0.47 g, 2.1 mmol) in benzene (3 mL) was heated at 70°C for 5 h. After evaporation of the solvent the residue was recrystallized from CH_2Cl_2 /hexane to give 1.1 g (94%) of 5 as colorless crystals; mp $125-127^\circ\text{C}$. Anal. Calcd for $\text{C}_{14}\text{H}_{25}\text{OPCl}_2\text{Sn}_2$: C, 30.65, H, 4.59; Cl, 12.92. Found: C, 30.69; H, 4.55; Cl, 13.14.

Synthesis of $(\text{CH}_3)_2\text{Sn}(\text{CH}_2-\text{CH}_2)\text{PC}_6\text{H}_5$, $(\text{CH}_3)_2\text{SnCl}_2$ (6). A solution of 4 (1.0 g, 3.2 mmol) and Me_2SnCl_2 (0.71 g, 3.2 mmol) in benzene (3 mL) was heated at 70°C for 6 h. After evaporation of benzene and heating in vacuum (0.1 mmHg) at 80°C for 1 h a yellowish solid remains. Anal. Calcd for $\text{C}_{14}\text{H}_{25}\text{PCl}_2\text{Sn}_2$: C, 31.57; H, 4.73; Cl, 13.31. Found: C, 31.82; H, 4.61; Cl, 13.57.

Synthesis of $\text{CH}_3(\text{Cl})\text{Sn}(\text{CH}_2-\text{CH}_2)_2\text{P}(\text{S})\text{C}_6\text{H}_5$ (7). A mixture of 2 (6 g, 17.4 mmol) and Me_2SnCl_2 (3.85 g, 17.5 mmol) in toluene (10 mL) was heated at 70°C for 10 h. After removal of the solvent and Me_3SnCl the solid residue was recrystallized from toluene to give 7 as colorless crystals: yield 5.3 g (83%); mp $184-186^\circ\text{C}$. MW measured: 350.4 (calcd 365.4). MS (^{120}Sn , m/z (%)): 338 (100, $\text{M}-\text{C}_2\text{H}_4$), 310 (33.8, $\text{M}-2\text{C}_2\text{H}_4$), 295 (79.6, $\text{M}-2\text{C}_2\text{H}_4-\text{CH}_3$). Anal. Calcd for $\text{C}_{11}\text{H}_{16}\text{PSClSn}$: C, 36.16; H, 4.41; S 8.78. Found: C, 36.37; H, 4.34; S, 8.89.

Synthesis of $\text{CH}_3(\text{Cl})\text{Sn}(\text{CH}_2-\text{CH}_2)_2\text{P}(\text{Se})\text{C}_6\text{H}_5$ (8). As described for 7, compound 8 was obtained from 3 (2.2 g, 5.6 mmol) and Me_2SnCl_2 (1.25 g, 5.7 mmol) in toluene (3 mL) after recrystallization from CH_2Cl_2 /hexane as colorless crystals: yield 1.7 g (74%); mp $148-149^\circ\text{C}$. MW measured: 398.5 (calcd 412.3). MS (^{120}Sn , m/z (%)): 386 (100, $\text{M}-\text{C}_2\text{H}_4$), 358 (21.6, $\text{M}-2\text{C}_2\text{H}_4$), 343 (49.3, $\text{M}-2\text{C}_2\text{H}_4-\text{CH}_3$). Anal. Calcd for $\text{C}_{11}\text{H}_{16}\text{PSeClSn}$: C, 32.04; H, 3.91; Cl, 8.60. Found: C, 32.12; H, 3.87; Cl, 8.77.

Synthesis of $\text{CH}_3(\text{Cl})\text{Sn}(\text{CH}_2-\text{CH}_2)_2\text{P}(\text{O})\text{C}_6\text{H}_5$ (9). Method A. A small excess of Me_2SeO (0.6 g, 4.8 mmol) in CHCl_3 (8 mL) was added to a solution of 7 (1.5 g, 4.1 mmol) in CHCl_3 (10 mL). After the mixture was refluxed for 15 min, CHCl_3 and $(\text{CH}_3)_2\text{Se}$ were removed in vacuum through an ethanolic solution of HgCl_2 (thus trapping Me_2Se as $\text{Me}_2\text{Se}-\text{HgCl}_2$). After addition of CHCl_3 to the residue the resulting solution was filtered, washed twice with water, and dried over Na_2SO_4 . The solvent was removed and the solid residue recrystallized from CH_2Cl_2 /hexane to give 1.2 g of 8 (84%) as colorless crystals; mp $250-252^\circ\text{C}$. MS (^{120}Sn , m/z (%)): 335 (12.5, $\text{M}-\text{CH}_3$), 322 (65.7, $\text{M}-\text{C}_2\text{H}_4$), 315 (22.8, $\text{M}-\text{Cl}$), 294 (26.9, $\text{M}-2\text{C}_2\text{H}_4$), 279 (100, $\text{M}-2\text{C}_2\text{H}_4-\text{CH}_3$). Anal.

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Calcd for C₁₁H₁₆POClSn: C, 37.81; H, 4.62; Cl, 10.15. Found: 37.89; H, 4.64; Cl, 10.63.

Method B. 1 (2 g, 6.1 mmol) and Me₂SnCl₂ (1.34 g, 6.1 mmol) were mixed and heated for 3 h at 140 °C. After removal of Me₃SnCl the solid residue was recrystallized from CH₂Cl₂/hexane: yield 1.6 g (75%); mp 250–252 °C.

Structure Determination of 7–9. Crystallographic structure determination of compounds 7–9 was solved by routine methods. Weissenberg photos were used to find the space groups. Cell constants were obtained by least-squares refinement of 20 automatically centered reflections, and intensity data (at ambient temperature) were collected on a Huber four-circle diffractometer.

Crystallographic data, experimental data collection, and refinement conditions are collected in Table II.

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Supplementary Material Available: Tables of atomic coordinates, anisotropic thermal parameters, and bond lengths and angles and stereoscopic views of the unit cells (12 pages). Ordering information is given on any current masthead page. Tables of structure factors are available from the authors (J.M.-P.).

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