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STRUCTURAL ASPECTS OF CYCLIC TRIORGANOTIN DITHIOPHOSPHINATES. CRYSTAL STRUCTURE OF $[\text{Me}_2\overline{\text{SnSP(S)(Ph)CH}_2\text{C}}\text{H}_2]\cdot\text{HMPT}$

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Summary

Cyclic triorganotin dithiophosphinates of the formula $\text{R}_2\overline{\text{SnSP(S)(Ph)CH}_2\text{C}}\text{H}_2$ (I: R = Me, II: R = t-Bu) have been synthesized by sulfur oxidation of $\text{R}_2\text{Sn(H)(CH}_2)_2\text{P(H)Ph}$ and $\text{Me}_3\text{Sn(CH}_2)_2\text{P(H)Ph}$, respectively. With HMPT compounds I and II form the crystalline adducts III and IV. On the basis of molecular mass and spectroscopic data (Mössbauer, IR, ^{119}Sn, ^{31}P, and ^{1}H NMR), solid I is suggested to have an associated polymeric structure, which breaks down in solution. Compound II is monomeric, with tetracoordinated tin, in the solid state and in non-polar solvents. An X-ray diffraction study of the HMPT adduct of I (III) reveals that the structure is monomeric and that the Sn atom is in a trigonal bipyramidal environment, with the HMPT molecule and one sulfur atom in axial positions.

Introduction

For 30 years organotin dithiophosphates and phosphinates of the type $\text{R}_n\text{Sn}[\text{SP(S)Y}_2]_{4-n}$ (Y = OR′, R′; $n = 1$–3) have been found widely used as agricultural and industrial biocides [1]. Furthermore, these compounds are of structural interest because the SP(S)Y_2 group can act in either a mono or a bidentate mode, and the latter can give rise to a monomeric chelate, a bridged associated oligomer, or a one-dimensional polymer [2].

In general the diorganotin dithiophosphorus esters $\text{R}_2\text{Sn}[\text{SP(S)Y}_2]_2$ have a chelated monomeric structure involving six-coordinated tin, and can involve either unsymmetrical (anisobidentate) [3,4] or symmetrical [5] chelation of the ligand.

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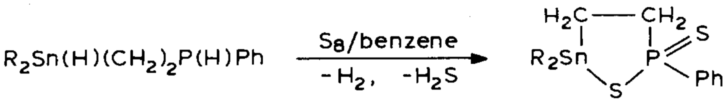
Some spectroscopic and X-ray studies on compounds $R_3SnSP(S)(OR')_2$ reveal structural features which depend on the substituents at the tin atom and on the state of aggregation of the compound [2b,6]. The purpose of the present work was to provide structural information on the 1,1-dialkyl-3-phenyl-3-thio-1,2,3-stannathiaphospholanes of the general formula $R_2\overline{\mathrm{Sn}-\mathrm{S}-\mathrm{P}}(\mathrm{S})\mathrm{Ph}$ (R = Me, t-Bu), which can be regarded as cyclic triorganotin dithiophosphinates.

Results and discussion

The compounds I and II can be obtained by reaction of the phenylphosphinoethyl-substituted tin hydrides $R_2Sn(H)(CH_2)_2P(H)Ph$ [7] with an excess of sulfur in benzene (eq. 1).

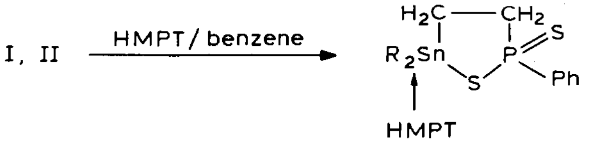


(1)

(I: R = Me;
II: R = t-Bu)

Compound I can also be made by treatment of $Me_3Sn(CH_2)_2P(H)Ph$ with sulfur [8]. In this case the intermediate 2-trimethylstannylethyl phenyldithiophosphinic acid is converted into I by an intramolecular attack of the SH function on the Sn–C bond of a methyl group with evolution of methane. I and II are colourless crystalline compounds. Compound II is highly soluble in the common solvents but I is only slightly soluble in weakly coordinating solvents. In donor solvents both compounds are very soluble. Osmometric molecular mass determinations in $CHCl_3$ at various concentrations indicate a monomeric structure for II, whereas for I a small degree of association increasing with concentration, is observed. This probably indicates that solid I has a polymeric structure which is broken down in solution.

With HMPT I and II form the isolable crystalline adducts III and IV (eq. 2).



(2)

(III: R = Me;
IV: R = t-Bu)

Mass spectrometric data

The mass spectra of I and II (Table 1) confirm their postulated heterocyclic structures in the gas phase. In both cases the M^+ peak is observed, but there are no fragments of higher mass or with more than one tin atom, thus ruling out any gas-phase association. The initial steps of the decomposition of I are the loss of one methyl group and the elimination of ethylene from the ring section. In the case of II the decomposition is initiated by the fragmentation of one t-butyl group followed by

TABLE 1

MASS SPECTRAL DATA FOR I AND II

I			II		
m/e [a]	rel. abund.	Assignment	m/e [a]	rel. abund	Assignment
350	17.6	M^+	434	0.8	M^+
335	61.8	M^+-CH_3	377	58.3	M^+-C_4H_9
322	32.4	M^+-C_2H_4	321	100.0	M^+-C_4H_9-C_4H_8
307	32.4	$CH_3SnS_2PC_6H_5^+$	293	33.0	$HSnS_2PC_6H_5^+$
290	4.1	$(CH_3)_2SnSPC_6H_5^+$	229	9.6	$C_6H_5SnS^+$
275	3.5	$CH_3SnSPC_6H_5^+$	215	10.4	SnS_2P^+
229	7.6	$C_6H_5SnS^+$	169	25.0	$C_2H_5(C_6H_5)PS^+$
155	100.0	$C_6H_5(CH_3)PS^+$	141	37.5	$C_6H_5PSH^+$
123	14.7	$C_6H_5PCH_3^+$	77	7.1	$C_6H_5^+$
77	7.6	$C_6H_5^+$	57	54.2	$C_4H_9^+$
28	2.9	$C_2H_4^+$			

[a] Mass numbers are based upon ^{120}Sn, ^{32}S, ^{31}P, ^{16}O, ^{12}C and ^{1}H.

the elimination of isobutylene. After these initial fragmentation steps the subsequent decomposition pattern for I and II can be unambiguously defined.

Infrared data

Comparison of the IR data of I–IV (Table 2) in the solid state and in solution leads to the following conclusions concerning the structure of the compounds:

(i) The spectra of II in KBr and CCl_4 are nearly identical, indicating the same structure for the compound in the solid state and in solution.

(ii) Considerable differences in the ν(SnC) and ν(PS) region for the spectra of I in KBr and CCl_4 confirm that there is a different coordination environment at the tin atom in the solid state and in non-coordinating solvents. The most important feature is the appearance of a very strong band in the ν(PS) range at 636 cm^{-1} along with the ν(P–S) and ν(P=S) absorptions at 500 and 611 cm^{-1}, respectively, in the KBr spectrum of I; this band is almost absent in CCl_4. Apparently, this absorption is due to an intermolecular association of I in the solid state, involving the PS_2 group as a bridging ligand, and this is broken in solution.

(iii) The positions of the ν(P=O) absorptions in the KBr spectra of III and IV at 1151 and 1142 cm^{-1}, respectively, indicates that there is coordination of the HMPT

TABLE 2

SELECTED INFRARED SPECTRAL DATA (cm^{-1}) FOR I–IV

		ν(P–S)	$\nu(SnC)_s$	$\nu(SnC)_{as}$	ν(P=S)	ν(PS)	ν(P=O)
I	KBr	496/505vw	527vs	551vs	611vs	636vs	
	CCl_4	500w	512vs	542s	609vs	635vw	
II	KBr	[a]	514vs	530w	609vs	–	
	CCl_4	[a]	510vs	527w	610vs	–	
III	KBr	518m	528vs	547s	612vs	–	1157vs
	CCl_4	515sh	526vs	545s	613vs	–	1160vs
IV	KBr	502/513vw	530vs	[a]	612vs	–	1142vs
	CCl_4	[a]	508vs	526w	611vs	–	1213vs

[a] Masked by $\nu(SnC)_s$.

TABLE 3

^{119}Sn MÖSSBAUER DATA FOR I–IV

Compound	IS [a]	QS	QS/IS
I	1.48	3.28	2.22
II	1.87	2.61	1.40
III	1.49	3.19	2.14
IV	1.65	3.04	1.84

[a] Relative to SnO_2.

molecule to the tin atom in the solid state. The spectrum of III in CCl_4 is almost unchanged indicating the stability of this complex in solution, and the identity of the spectra of IV and II in CCl_4, involving a hypsochromic shift of ν(P=O) from 1142 in KBr to 1213 in CCl_4 suggests that there is complete dissociation of adduct IV in solution.

Mössbauer data

Table 3 gives the ^{119}Sn Mössbauer data. The quadrupole splittings and the q-values (q = QS/IS) [9] for the HMPT adducts III and IV are in a range typical of pentacoordinated organotin compounds of the Typ $R_3SnX \cdot L$ [9b]. The pentacoordination of the tin atom in III was confirmed by an X-ray structure determination (see later). The similarity of the Mössbauer data of I and III indicates that the former compound also has a pentacoordinated structure in the solid state, probably as the result of an intermolecular association.

The quadrupole splitting and the q-value for compound II suggest a monomeric tetracoordinated structure in contrast to that of I. The different structures of I and II in solid state are confirmed by the value of the ratio of the QS-values, namely 1.26, which is in a good agreement with the view that for triorganotin compounds R_3SnX the formation of an associated structure should result in a quadrupole splitting approximately 1.3 times that expected for a monomeric tetrahedral structure [9b].

NMR data

Some structural features of I–IV in solution are revealed by NMR data (Table 4).

TABLE 4

NMR SPECTRAL DATA FOR I–IV

Comp.	^{1}H NMR				^{31}P NMR	^{119}Sn NMR		
	$\delta(SnCH_3)$ (ppm)	$\delta(SnCCH_3)$ (ppm)	$^2J(^{119}SnCH)$ (Hz)	$^3J(^{119}SnCCH)$ (Hz)	δ (ppm)	δ (ppm)	$J(^{119}Sn–P)$ (Hz)	Solvent
I	0.81		59.2		82.9	191.9	65.4	$CDCl_3$
	0.95		67.5		77.3	59.4	95.2	DMF
II		1.42/1.29		85.2/78.9	82.8	178.5	26.3	$CDCl_3$
		1.10		82.5	76.4	96.1	68.1	DMF
III	0.71		67.5		77.2	32.6	102.3	C_6D_6
					22.4			
IV		1.42/1.29		85.3/78.9	80.8	153.9	39.2	C_6D_6
					23.7			

The ^{119}Sn NMR chemical shift for I and II in $CDCl_3$ is at very low field, indicating a monomeric structure with tetracoordinated tin for these compounds in noncoordinating solvents (Me_3SnCl: δ (^{119}Sn) ($CDCl_3$) 164.2 ppm), which give way to a pentacoordinated species when I and II are dissolved in donor solvents. This is confirmed by the marked high field shift of the ^{119}Sn NMR signal for I and II in DMF of 132.5 and 82.4 ppm, respectively [10], and the increase of $^2J(^{119}SnCH_3)$ for I in the same solvent [11].

The high values of the coupling constant $J(^{119}Sn-^{31}P)$ for I and II in DMF are also associated with pentacoordination at the tin atom. This coupling constant represents the sum of two contributions, namely $^3J(^{119}SnCC^{31}P)$ and $^2J(^{119}SnS^{31}P)$, of opposite sign. Upon the rehybridization at the tin atom of I and II in DMF the *s*-electron density in the tin orbitals is changed, causing changes in the values of ^3J and ^2J, and resulting in an increase of $J(^{119}Sn-^{31}P)$ [12,13].

Similar NMR data confirm the expected pentacoordinated structure of III in benzene, and also indicate the high stability of this complex in solution. In contrast to this compound, IV is completely dissociated in benzene, as indicated by similar values of the NMR data for IV and II in non-coordinating solvents.

Crystal structure of compound III

A stereoview of the molecule with atom numbering is shown in Fig. 1. The structure of III consists of relatively isolated molecules, and there are no intermolecular contacts significantly below the sum of appropriate Van der Waals radii. Fractional atomic coordinates and B_{eq} values are given in Table 5, and selected bond lengths and bond angles are summarized in Table 6, and torsion angles given in Table 7. The bonds around the tin atom are in a trigonal-bipyramidal arrangement with the three carbon atoms in the equatorial positions, and with the oxygen and one sulfur atom of the PS_2 group occupying the axial sites. The values of the bond angles at tin indicate a small but significant distortion from the idealized trigonal-bipyramidal stereochemistry. The tin atom is displaced by 0.132 Å out of the equatorial plane towards the S(1) atom. The tin–carbon distances are in good

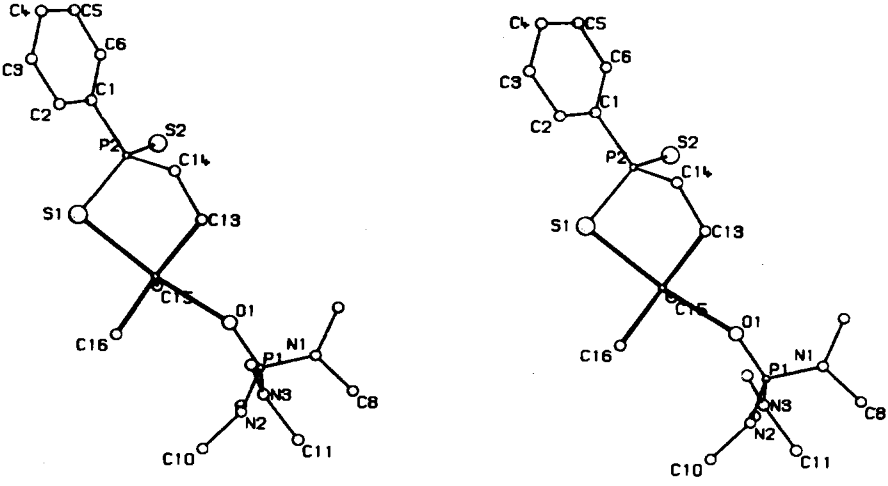


Fig. 1. Stereoscopic view of the molecular structure of compound I with atom numbering.

TABLE 5

FRACTIONAL ATOMIC COORDINATES ($\times 10^4$) AND B_{eq} VALUES (Å^2) FOR III

Atom	x	y	z	B_{eq}
Sn	3071(0)	4312(1)	3644(1)	3.40
S(1)	3090(2)	5896(3)	1022(3)	4.22
S(2)	1344(2)	7960(3)	2275(3)	5.09
P(1)	3103(2)	1774(2)	7156(2)	3.49
P(2)	1670(1)	6545(2)	1010(2)	3.28
O(1)	2820(5)	2845(7)	5827(7)	4.66
N(1)	2347(6)	1963(8)	8385(8)	4.49
N(2)	4136(5)	1820(8)	8083(8)	4.30
N(3)	3158(5)	191(8)	6680(8)	4.31
C(1)	1192(6)	7107(8)	−965(8)	3.33
C(2)	1464(7)	6332(10)	−1992(10)	4.65
C(3)	1089(8)	6737(12)	−3501(11)	5.25
C(4)	388(7)	7941(11)	−3877(11)	5.10
C(5)	113(8)	8674(12)	−2827(13)	5.74
C(6)	507(6)	8241(9)	−1320(9)	4.11
C(7)	1331(9)	2386(13)	7814(13)	6.23
C(8)	2479(10)	1315(15)	9976(16)	7.62
C(9)	4333(10)	3018(15)	8908(15)	6.95
C(10)	5041(8)	1127(13)	7637(13)	6.14
C(11)	3315(9)	−1122(14)	7786(14)	6.52
C(12)	2689(12)	−59(17)	5282(17)	8.17
C(13)	1566(6)	4178(9)	3126(9)	3.94
C(14)	1150(6)	4909(8)	1621(9)	3.71
C(15)	3557(7)	5777(10)	4985(10)	4.82
C(16)	4136(7)	2743(11)	3239(11)	5.12

agreement with the equatorial Sn–C bond lengths observed in other pentacoordinated triorganotin structures [14].

The Sn–O bond distance (2.33 Å) matches values reported for some other pentacoordinated tin complexes with axial ligands coordinated by a P=O group [13,15,16], but it is somewhat longer than those in $(Ph_2ClSn)_2CH_2 \cdot$ HMPT and in $(Ph_2BrSn)_2CH_2 \cdot$ HMPT [22].

The lengthening of the Sn–S(1) distance to 2.636 Å in comparison with the normal Sn–S single bond length of 2.35 to 2.50 Å is noteworthy [18]; it results from the axial position of S(1) in the trigonal-bipyramidal tin environment. Such an effect is observed, for example, in $[(C_7H_6S_2)SnPh_2Cl][NEt_4]$ [20], in which the axial Sn–S bond is 0.1 Å longer than the equatorial bond. The two different P–S bond distances are characteristic of the PS_2 group bonded in the monodentate mode, and similar values have been observed previously [6,17]. In agreement with this the intramolecular distance (4.05 Å) between Sn and S(2) is in the non-bonded range (sum of Van der Waals radii of tin and sulfur: 3.90 Å [19]).

The torsion angles in Table 7 indicate an envelope conformation of the five-membered ring in III, with the C(14), C(13), Sn and S(1) atoms in a nearly coplanar arrangement and with folding along the S(1)–C(14) line. The main axis of the trigonal-bipyramidal tin polyhedron and the molecular axis of HMPT form an angle of 155°, this angle is very variable, depending on steric strain. The three P–N bonds of the HMPT and the Sn–C-bonds are in a nearly staggered conformation.

TABLE 6

SELECTED INTERATOMIC LENGTHS (Å) AND ANGLES (°) FOR III, WITH e.s.d.'s IN PARENTHESES

Bond lengths			
Sn–C(13)	2.150(6)	P(2)–C(1)	1.849(5)
Sn–C(15)	2.124(6)	P(2)–C(14)	1.826(6)
Sn–C(16)	2.129(7)	P(2)–S(1)	2.040(2)
Sn–S(1)	2.636(2)	P(2)–S(2)	1.965(2)
Sn–O(1)	2.330(5)		
		P(1)–O(1)	1.466(5)
C(13)–C(14)	1.488(8)	P(1)–N(1)	1.629(5)
		P(1)–N(2)	1.627(5)
		P(1)–N(3)	1.645(5)
Intermolecular contacts			
S(1)···C(11)	3.843(6)	S(2)···C(7)	3.806(6)
S(2)···C(5)	3.802(5)		
Bond angles			
C(13)–Sn–C(15)	121.2(2)	C(1)–P(2)–S(1)	106.7(2)
C(13)–Sn–C(16)	122.0(3)	C(1)–P(2)–S(2)	113.1(2)
C(15)–Sn–C(16)	115.7(3)	C(1)–P(2)–C(14)	105.5(3)
S(1)–Sn–C(13)	89.1(2)	S(1)–P(2)–S(2)	116.6(1)
S(1)–Sn–C(15)	97.8(2)	S(1)–P(2)–C(14)	103.4(2)
S(1)–Sn–C(16)	94.1(2)	S(2)–P(2)–C(14)	110.6(2)
O(1)–Sn–C(13)	82.3(2)	O(1)–P(1)–N(1)	109.1(3)
O(1)–Sn–C(15)	88.2(2)	O(1)–P(1)–N(2)	118.0(3)
O(1)–Sn–C(16)	89.1(2)	O(1)–P(1)–N(3)	109.5(3)
S(1)–Sn–O(1)	171.2(1)	N(1)–P(1)–N(2)	103.1(3)
Sn–O(1)–P(1)	155.2(3)	N(1)–P(1)–N(3)	112.4(3)
		N(2)–P(1)–N(3)	104.5(3)
Sn–S(1)–P(2)	90.1(1)		
Sn–C(13)–C(14)	115.5(4)		
P(2)–C(14)–C(13)	113.2(4)		

TABLE 7

TORSION ANGLES [a] (°) IN THE RING SECTION OF COMPOUND III

Sn–S(1)–P(2)–C(14)	−45.2
S(1)–P(2)–C(14)–C(13)	59.5
P(2)–C(14)–C(13)–Sn	−35.9
C(14)–C(13)–Sn–S(1)	1.9
C(13)–Sn–S(1)–P(2)	26.2

[a] The torsion angle A(1)–A(2)–A(3)–A(4) is viewed along A(2)–A(3) bond with the clockwise rotation of A(1) to A(4) taken to be positive.

Experimental

General

All reactions were carried out under dry nitrogen or argon. The NMR spectra were recorded with Varian HA 100 and Bruker WP 200 spectrometers with TMS

(^1H), 85% H_3PO_4 (^{31}P) or Me_4Sn (^{119}Sn) as reference. Low-field shifts are positive. Mass and IR spectra were obtained with a Varian CH 8 spectrometer (70 eV) and a Carl Zeiss UR-20 instrument, respectively. Molecular mass determinations were carried out with a Knauer osmometer at 37°C.

Crystal structure determination of compound III

Cell parameters and space group were determined from Weissenberg photographs. Parameters were refined by least-squares using 15 reflections measured on a 4-circle diffractometer Synthex $P2_1$ · Crystal data: Triclinic, space group $P\bar{1}$, a 14.080(5), b 9.625(3), c 9.123(2) Å, α 81.16(2), β 94.92(2), $\gamma = 84.87(3)°$, $Z = 2$, μ 12.55 cm^{-1} and D_c 1.45 g cm^{-3}. The intensities of reflections with $2\theta < 47°$ was measured on Syntex $P2_1$ diffractometer, Mo-K_α radiation (λ 0.71069 Å), ω-scan of 1.1° width. 3585 reflections were measured, and 3382 were considered as observed $[|F| > 2.5\ \sigma(F)]$ and used in the structure determination. No corrections for absorption were applied. The structure was solved by the heavy-atom technique and refined by full-matrix least-squares with the SHELX 76 program [21]. The thermal parameters were refined anisotropically only for Sn, S, P and O atoms. The weighting scheme was $\omega = 1.0000/[\sigma^2(F) + 0.008889(F)^2]$. The final difference-Fourier synthesis showed only small peaks, which do not correspond to H-atoms. The final R-factor was 0.052. Positional parameters are listed in Table 5.

Materials

2-Phenylphosphinoethyl dimethyltin hydride. As described elsewhere [7] this compound can be obtained by reduction of $Me_2Sn(X)(CH_2)_2P(O)(OEt)Ph$ (X = Cl, Br) [13] with $LiAlH_4$. Yield: 60%; b.p. 104–106°C/0.4 Torr. Anal.: Found: C, 42.09; H, 6.13. $C_{10}H_{17}PSn$ calcd.: C, 41.86; H, 5.97%. IR (film): 2289s (PH), 1813vs (SnH) cm^{-1}. NMR: ^1H (C_6D_6) δ 0.18 (d, 6H, $SnCH_3$, ^3J(HSnCH) 3 Hz, ^2J(SnCH) 55.6/53.0 Hz), 4.01 (dt, 1H, PH, ^1J(PH) 203 Hz), 4.91 (qua, 1H, SnH); ^{31}P (C_6D_6) δ -37.5 (d, ^1J(PH) 204 Hz) ppm.

2-Phenylphosphinoethyl di-t-butyltin hydride. Similarly t-$Bu_2Sn(H)(CH_2)_2P(H)Ph$ was prepared from t-$Bu_2Sn(Cl)(CH_2)_2P(O)(OEt)Ph$ [13]. Yield: 55%; b.p. 119–121°C/0.2 Torr. Anal.: Found: C, 52.13; H, 8.07. $C_{16}H_{29}PSn$ calcd: C, 51.79; H, 7.88%. IR (film) 2285s (PH), 1807vs (SnH) cm^{-1}. NMR: ^1H (C_6D_6) δ 1.06 (s, 18H, $SnCCH_3$, ^3J(SnCCH) 65/62 Hz, 4.06 (dt, 1H, PH, ^1J(PH) 203 Hz), 5.34 (m, 1H, SnH) ppm.

2-Phenylphosphinoethyl trimethylstannane. This was made as previously described [8] from $Me_3Sn(CH_2)_2P(O)(OEt)Ph$ [13] and $LiAlH_4$. Yield: 57%; b.p. 73–74°C/0.01 Torr. Anal.: Found: C, 44.31; H, 6.51. $C_{11}H_{19}PSn$ calcd: C, 43.91; H, 6.36%. IR (film): 2291s (PH) cm^{-1}. NMR: $^{13}C(C_6D_6)$ $\delta - 9.65$ (d, $SnCH_3$ ^4J(PCCSnC) 1.1 Hz, ^1J(SnC) 321.5/306.0 Hz), 9.31 (d, $SnCH_2$, ^2J(PCC) 8.1 Hz, ^1J(SnC) 343.3/327.5 Hz), 21.36 (d, PCH_2, ^1J(PC) 13 Hz, ^2J (SnCC) 36.2 Hz). $^{31}P(C_6D_6)$ $\delta - 41.2$ s ppm, ^3J(SnCCP) 126.8/121.3 Hz.

1,1-Dimethyl-3-phenyl-3-thio-1,2,3-stannathiaphospholane (I). Method A: In a described previously procedure [7] 3 g (0.012 mol) $Me_2Sn(H)(CH_2)_2P(H)Ph$ was treated with 1 g (0.03 mol) sulfur in 50 ml benzene. Yield: 3.1 g (74%); m.p. 163–165°C. Anal.: Found: C, 34.35; H, 3.95; S, 18.52. $C_{10}H_{15}S_2PSn$ calcd.: C, 34.42, H, 4.33; S, 18.38%.

Method B: I was also made by the reaction of 2.1 g (0.007 mol) $Me_3Sn(CH_2)_2P(H)Ph$ with 0.5 g (0.016 mol) sulfur in 50 ml boiling benzene. Yield: 1.5 g (61%). Mol. mass det. ($CHCl_3$): Found: 350.4 (0.033 mol/l), 419 (0.121 mol/l), calcd.: 349.1.

1,1-Di-t-butyl-3-phenyl-3-thio-1,2,3-stannathiaphospholane (II). This was similarly prepared by reaction of 3.5 g (0.009 mol) $t\text{-}Bu_2Sn(H)(CH_2)_2P(H)Ph$ and 0.8 g (0.025 mol) sulfur in 50 ml benzene. After removal of the solvent the white solid II was recrystallized from CH_2Cl_2/hexane. Yield: 2.7 g (62%); m.p. 155–156°C. Anal.: Found: C, 44.68; H, 6.66; S, 14.91. $C_{16}H_{27}S_2PSn$ calcd.: C, 44.36; H, 6.28; S, 14.80%. Mol. mass det. ($CHCl_3$): Found: 421.3 (0.043 mol/l), 437.4 (0.146 mol/l); calcd.: 433.2.

HMPT adduct of I (III)

A mixture of 1.5 g (0.004 mol) I and 1 g (0.006 mol) HMPT in 10 ml benzene was heated to 70°C for 30 min. The volatile materials were evaporated under vacuum, and addition of hexane to the residual oil caused crystallization. III was recrystallized from CH_2Cl_2/hexane. Yield: 1.8 g (79%); m.p. 117–119°C. Anal. Found: C, 35.98; H, 6.28; N, 7.60. $C_{16}H_{33}N_3OS_2P_2Sn$ calcd.: C, 36.38; H, 6.30; N, 7.96%.

HMPT adduct of II (IV)

The same procedure involving 0.5 g (0.001 mol) II and 0.5 g (0.003 mol) HMPT gave 0.5 g (70%) of IV; m.p. 124–126°C. Anal.: Found: C, 43.25; H, 7.94; N, 6.93. $C_{22}H_{45}N_3OS_2P_2Sn$ calcd.: C, 43.15; H, 7.41; N, 6.86%.

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