

Preparation of and multinuclear NMR studies on intramolecular chalcogen–tin coordination in compounds of the type $\text{Me}_2\text{Sn}(\text{X})-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{P}(\text{E})\text{Ph}_2$ ($\text{X} = \text{halogen}$, $\text{E} = \text{chalcogen}$)

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Abstract

The preparation of the title compounds is reported and their multinuclear NMR data presented and discussed. In contrast to the corresponding phosphinoethylstannanes, where intramolecular coordination is observed both in the solid state and in solution, the phosphinopropylstannanes can exist in both open-chain and intramolecularly coordinated forms. The nature of the chalcogen determines the position of the equilibrium between the species in solution: for $\text{E} = \text{O}$ and $\text{E} = \text{lone pair}$, intramolecular coordination is dominant; for $\text{E} = \text{S}$ and $\text{E} = \text{Se}$ the open-chain structure is formed preferentially. Two sign determinations were carried out: in compound **1b** $^1J(\text{Sn}, ^3\text{P})$ and $^3J(^3\text{P}-\text{Sn}-\text{CH}_3)$ are positive.

Keywords: Multinuclear NMR studies; ^{119}Sn NMR; ^{31}P NMR: Intramolecular chalcogen–tin coordination

1. Introduction

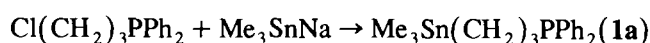
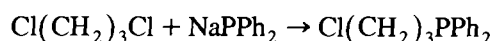
In a recent publication [1] we discussed the multinuclear NMR data for compounds of type $\text{Me}_2\text{Sn}(\text{X})-\text{CH}_2-\text{CH}_2-\text{P}(\text{E})\text{Ph}_2$ (**A**) and demonstrated that only certain parameters are diagnostic for the existence of intramolecular coordination.

We have now extended this work to include analogous compounds of type $\text{Me}_2\text{Sn}(\text{X})-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{P}(\text{E})\text{Ph}_2$ (**B**) in which the carbon chain has been lengthened from two to three carbons.

2. Results and discussion

The compounds studied in the present work are identified as shown in Table 1. The synthetic scheme is straightforward: 1,3-dichloropropane is treated with sodium diphenylphosphide to give (3-chloropropyl)diphenylphosphine [2] and the latter in turn allowed to

react with trimethylstannylsodium. Both reactions are carried out in liquid ammonia.



Compound **1a** has already been described by Weichmann [3]. Halodemethylation at tin is carried out by treating the trimethylstannyl compound with either the corresponding trimethyltin halide or the dimethyltin dihalide (for $\text{X} = \text{Cl}, \text{Br}, \text{I}$).

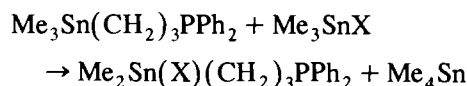
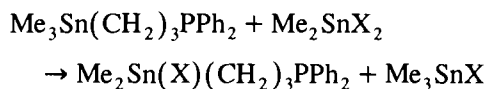


Table 1
Compounds studied

X	E			
	—	O	S	Se
CH_3	1a	2a	3a	
I	1b	2b	3b	4b
Br	1c	2c	3c	4c
Cl	1d	2d	3d	4d
F	1e	2e		

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For X = I the monoiodide must be used as the diiodide is relatively unstable and its preparation complicated. For X = Cl and Br the dihalide route is preferable, though Weichmann [3] used Me_3SnCl to prepare compound **1d**.

The fluoride is obtained by treating one of the other halides with KF.

The phosphines can be readily converted to the phosphine chalcogenides by oxidation with hydrogen peroxide (potassium permanganate is not suitable, as purification of the product is difficult, so that yields are very low) or by direct reaction with elemental sulphur or selenium. While the phosphine oxides are stable, the sulphides and selenides decompose slowly in the presence of air both in the solid state and in solution; in both cases elemental chalcogen is set free.

The multinuclear NMR data for compounds **1a–4e** are collected in Tables 2–8. Table 2 contains the values for the phosphines **1a–1e**, Table 3 for the phosphine oxides **2a–2e**, Table 4 for the sulphides **3a, 3b** and **3e**

and Table 5 for the selenides **4c** and **4d**. Tables 6–8 contain results for temperature-dependent surveys of selected compounds (see below).

Our previous work [1] made it clear that although many NMR parameters are available for compounds of type (A) or (B) the most useful with respect to the question of pentacoordination are the one-bond tin–carbon coupling constants $^1J(\text{Sn–C})$ and the tin–phosphorus coupling constant $^nJ(\text{Sn,P})$. The former are expected to lie in the range 300–350 Hz for tetracoordination at tin and to increase to 450–480 Hz if the tin is pentacoordinated [4]. In compounds **1a–3a** the presence of three methyl groups on tin results in such a low Lewis acidity that pentacoordination is not possible: here both $^1J(\text{Sn–CH}_3)$ and $^1J(\text{Sn–CH}_2)$ lie well below 350 Hz, $^4J(\text{Sn,P})$ lies between 6 and 16 Hz. However, the replacement of a methyl group in **1a** by a halogen (compounds **1b–1e**) causes $^1J(\text{Sn–CH}_3)$ to increase to 400 Hz and above, while $^1J(\text{Sn–CH}_2)$ is correspondingly higher. At the same time, $^nJ(\text{Sn,P})$ increases to well over 200 Hz, thus demonstrating the presence of a strong bonding interaction. Formally, the measured coupling constant is $^{1+4}J(\text{Sn,P})$, but the four-bond compo-

Table 2
Multinuclear NMR data for compounds **1a–e**

	CH ₃ , 1a	I, 1b	Br, 1c	Cl, 1d	F, 1e
$\delta(\text{CH}_3)$	0.03	0.98	0.83	0.74 ^a	0.19
$\delta(\text{CH}_2\text{–Sn})$	0.97	1.80	1.69	1.61	1.05
$\delta(\text{CH}_2)$	1.66	1.98	2.01	2.07	1.70
$\delta(\text{CH}_2\text{–P})$	2.07	2.23	2.19	2.18	2.07
$^2J(^{119}\text{Sn,CH}_3)$	52.8	59.4	60.5	61.0 ^b	n.m.
$^3J(^{31}\text{P,CH}_3)$	0	3.0	3.6	3.6	n.m.
$\delta(\text{CH}_3)$	–10.2	1.2	1.1	0.6 ^c	–0.3
$\delta(\text{CH}_2\text{–Sn})$	13.0	22.5	22.2	21.9	22.0
$\delta(\text{CH}_2)$	23.4	23.0	22.5	22.4	22.4
$\delta(\text{CH}_2\text{–P})$	32.7	30.1	30.2	30.3	32.3
$^1J(^{119}\text{Sn–CH}_3)$	320.9	396.7	419.6	432.3 ^d	502.3
$^1J(^{119}\text{Sn–CH}_2)$	353.8	424.7	445.0	455.2	n.m.
$^2J(\text{Sn,CH}_2)$	18.1	n.m.	30.6	28.0	n.m.
$^3J(\text{Sn,CH}_2)$	56.1	36.9	33.0	30.5	n.m.
$^1J(^{31}\text{P–CH}_2)$	13.2	0	0	0	11.5
$^2J(^{31}\text{P,CH}_2)$	17.3	16.5	16.5	16.5	17.8
$^3J(^{31}\text{P,CH}_2)$	13.2	20.4	20.3	20.3	15.3
$^2J(^{31}\text{P,CH}_3)$	0	14.0	15.3	15.3	0
$\delta(^{31}\text{P})$	–18.8 ^e	–27.9	–28.9	–29.1 ^f	–20.1
$\delta(^{119}\text{Sn})$	–1.8 ^g	–21.6	22.2	44.4 ^h	9.7 ⁱ
$J(^{119}\text{Sn},^{31}\text{P})$	6.1 ^j	ca. 226	263.3	270.5 ^k	n.m.

^a Ref. [3] 0.68 (C₆D₆); ^b Ref. [3] 60.5; ^c Ref. [3] 0.17; ^d Ref. [3] 411.4; ^e Ref. [3] –17.2; ^f Ref. [3] –29.1; ^g Ref. [3] –1.5; ^h Ref. [3] 44.4; ⁱ $^1J(^{119}\text{Sn–}^{19}\text{F})$ 1813 ± 5 Hz; ^j Ref. [3] 4.3 Hz; ^k Ref. [3] 139.2/146.6 Hz.

Table 3
Multinuclear NMR data for compounds **2a–2e**

	CH ₃ , 2a	I, 2b	Br, 2c	Cl, 2d	F, 2e
$\delta(\text{C H}_3)$	-0.03	1.02	0.86	0.75	0.51
$\delta(\text{C H}_2\text{-Sn})$	0.86	1.83	1.70	1.61	1.36
$\delta(\text{C H}_2)$	1.78	2.16	2.18	2.14	2.14
$\delta(\text{C H}_2\text{-P})$	2.25	2.35	2.33	2.32	2.29
$^2J(^{119}\text{Sn}, \text{CH}_3)$	52.8	—	69.2	70.2	70.5
$\delta(\text{C H}_3)$	-10.4	6.2	4.6	3.5	0.0
$\delta(\text{C H}_2\text{-Sn})$	12.5	26.2	24.4	23.3	19.8
$\delta(\text{C H}_2)$	19.0	20.2	19.7	19.4	19.0
$\delta(\text{C H}_2\text{-P})$	34.0	29.0	29.1	29.2	19.7
$^1J(^{119}\text{Sn}-\text{CH}_3)$	324.3	—	504.8	515.0	534.0
$^1J(^{119}\text{Sn}-\text{CH}_2)$	345.9	—	517.5	529.0	546.8
$^2J(\text{Sn}, \text{CH}_2)$	n.m.	n.m.	26.7	25.4	n.m.
$^3J(\text{Sn}, \text{CH}_2)$	58.5	n.m.	14.0	14.0	n.m.
$^1J(^{31}\text{P}-\text{CH}_2)$	68.7	68.7	68.7	68.7	69.9
$^2J(^{31}\text{P}, \text{CH}_2)$	3.8	5.1	5.1	5.1	5.1
$^3J(^{31}\text{P}, \text{CH}_2)$	14.0	0	0	0	0
$\delta(^{31}\text{P})$	30.6	41.0	40.5	40.1	38.8
$\delta(^{119}\text{Sn})$	-1.7	-60.5	-47.6	-42.8	-31.7 ^a
$J(^{119}\text{Sn}, ^{31}\text{P})$	15.5	33.6	31.6	30.0	n.m.

^a $^1J(^{119}\text{Sn}-^{19}\text{F})$ 1150 ± 200 Hz.

Table 4
Multinuclear NMR data for compounds **3a, 3b, 3d**

	CH ₃ , 3a	Br, 3c	Cl, 3d
$\delta(\text{C H}_3)$	0.01	0.75	0.66
$\delta(\text{C H}_2\text{-Sn})$	0.87	1.53	1.46
$\delta(\text{C H}_2)$	1.80	2.08	2.10
$\delta(\text{C H}_2\text{-P})$	2.45	2.57	2.56
$^2J(^{119}\text{Sn}, \text{CH}_3)$	—	57.8	58.4
$\delta(\text{C H}_3)$	-10.2	0.3	0.3
$\delta(\text{C H}_2\text{-Sn})$	12.1	20.9	21.0
$\delta(\text{C H}_2)$	19.7	19.4	19.1
$\delta(\text{C H}_2\text{-P})$	36.6	34.5	34.5
$^1J(^{119}\text{Sn}-\text{CH}_3)$	324.8	373.8	385.3
$^1J(^{119}\text{Sn}-\text{CH}_2)$	344.4	406.9	419.6
$^2J(\text{Sn}, \text{CH}_2)$	14.5	22.9	22.9
$^3J(\text{Sn}, \text{CH}_2)$	60.3	53.4	50.9
$^1J(^{31}\text{P}-\text{CH}_2)$	53.8	54.7	54.7
$^2J(^{31}\text{P}, \text{CH}_2)$	2.9	2.5	2.5
$^3J(^{31}\text{P}, \text{CH}_2)$	16.0	12.7	11.4
$\delta(^{31}\text{P})$	39.8	39.7	39.7
$\delta(^{119}\text{Sn})$	-1.1	91.4	113.0
$J(^{119}\text{Sn}, ^{31}\text{P})$	16.4	11.6	11.6

ment is obviously negligible, so that the value measured is predominantly that of the $^1J(\text{Sn}-\text{P})$ component of the total coupling. The crystal structure of a compound analogous to **1d** with a $-\text{PPh}^t\text{Bu}$ residue rather than $-\text{PPh}_2$ has been reported by Weichmann et al. [5]; the tin lies at the centre of a trigonal bipyramid, as is usual for pentacoordinated tin.

In the phosphine oxide series (**2b–2e**) the presence of a halogen on tin leads to an even stronger intramolecular coordination, as shown by the values for $^1J(\text{Sn}-\text{C})$ which are in each case in excess of 500 Hz. The X-ray structural analysis of compound **2d** [6] confirms the presence of pentacoordination in the solid state; the tin atom lies at the centre of a slightly distorted trigonal bipyramid in which the halogen and chalcogen atoms occupy axial positions. The angle Cl-Sn-O is 178.2°, the lengths of the Sn-Cl and Sn-O bonds being 2.560 Å and 2.292 Å respectively. In compounds **2**, $^nJ(\text{Sn}, \text{P})$ decreases to around 30 Hz; formally this coupling is $^{2+4}J(\text{Sn}, \text{P})$ and both components of the coupling appear to be small. The data available in the phosphine sulfide series (**3b, 3d**) indicate a decreasing tendency to pentacoordination in solution; $^1J(\text{Sn}-\text{C})$ decreases considerably to around 400 Hz, while $^nJ(\text{Sn}, \text{P})$ decreases to only about 12 Hz. Compounds **4c** and **4d** in the phosphine selenide series show very similar values.

Table 5
Multinuclear NMR data for compounds **4c**, **4d**

	Br, 4c	Cl, 4d
$\delta(\text{CH}_3)$	0.74	0.66
$\delta(\text{CH}_2\text{-Sn})$	1.50	1.44
$\delta(\text{CH}_2)$	2.06	2.07
$\delta(\text{CH}_2\text{-P})$	2.68	2.68
${}^2J(^{119}\text{Sn}, \text{CH}_3)$	57.1	57.8
$\delta(\text{CH}_3)$	-0.3	-0.3
$\delta(\text{CH}_2\text{-Sn})$	20.2	20.3
$\delta(\text{CH}_2)$	20.1	19.9
$\delta(\text{CH}_2\text{-P})$	34.7	34.7
${}^1J(^{119}\text{Sn}-\text{CH}_3)$	362.4	375.1
${}^1J(^{119}\text{Sn}-\text{CH}_2)$	395.5	408.2
${}^2J(\text{Sn}, \text{CH}_2)$	17.8	21.6
${}^3J(\text{Sn}, \text{CH}_2)$	59.2	56.0
${}^1J(^{31}\text{P}-\text{CH}_2)$	48.3	47.0
${}^2J(^{31}\text{P}, \text{CH}_2)$	0	0
${}^3J(^{31}\text{P}, \text{CH}_2)$	14.0	14.0
$\delta(^{31}\text{P})$	30.7	30.7
$J(\text{Sn}, ^{31}\text{P})$	13.7	13.7
${}^1J(^{77}\text{Se}-^{31}\text{P})$	707.1	709.0
$\delta(^{77}\text{Se})$	-323.7	-324.7
$\delta(^{119}\text{Sn})$	104.5	130.4

NMR is a 'slow' method, so that it is not possible to distinguish between signals for tetra- and pentacoordinated species in solution. The measured parameters are average values, and studies of their temperature-dependence will give us further information on the degree to which the compounds are tetra- or pentacoordinated. Table 6 shows results obtained for compound **1d**, which appears to show a tendency for pentacoordination at room temperature. The results presented for four selected parameters make it clear that at room temperature the equilibrium between tetra- and pentacoordinated species does not in fact lie on the side of the pentacoordinated moiety. Over a range of 80°C the tin chemical

Table 6
NMR data for compound **1d** at various temperatures

$T \pm 5$ (K)	$\delta(^{119}\text{Sn})$	$J(^{119}\text{Sn}, ^{31}\text{P})$	${}^2J(\text{Sn}, \text{C}^1\text{H}_3)$	${}^3J(^{31}\text{P}, \text{C}^1\text{H}_3)$
313	43.9	212 ± 5	58.6	2.9
293	17.8	280	60.0	3.8
283	8.7	304.5	60.2	4.0
263	-21.4	400.1	61.7	4.7
253	-31.4	434.2	61.7	4.9
243	-39.5	464.3	62.1	4.9
233	-46.6	498.4	62.1	5.1

Table 7
NMR data for compound **2d** at various temperatures

$T \pm 5$ (K)	$\delta(^{119}\text{Sn})$	$\delta(^{31}\text{P})$	$J(\text{Sn}, ^{31}\text{P})$	${}^2J(\text{Sn}, \text{C}^1\text{H}_3)$
330	-41.0	39.4	26.3	69.0
320	-41.6	39.6	27.4	69.0
310	-42.1	39.8	28.4	69.0
300	-42.5	39.9	28.4	69.0

shift moves almost 90 ppm upfield (a clear indication of increasing pentacoordination [7]) and the tin-phosphorus coupling increases from near 200 to almost 500 Hz. The changes in the other parameters are small. Thus for **1d** complete pentacoordination is only present at low temperatures in solution.

In the case of **2d** (pentacoordinate in the solid state) only a relatively small temperature range could be studied, but (Table 7) all four parameters studied were almost invariant. Thus **2d** appears to be predominantly pentacoordinated even at room temperature.

The data in Table 5 indicated that compound **4d** preferred tetracoordination at room temperature. However, its tin chemical shift moves to high field on cooling (Table 8), though only by 30 ppm over a temperature range of 100°C. Thus a small amount of a pentacoordinated species is present at low temperatures.

Sign determinations were carried out in two cases using compound **1b** using the elegant hetero-shift-correlation method [8–11]. This is an interesting exercise, as we can look at coupling constants which are on the one hand an average of those for open-chain and cyclic components and on the other hand are multipath coupling constants with respect to the cyclic component. Thus a proton-phosphorus 2D shift correlation showed clearly that the signs of ${}^{1+4}K(\text{Sn}, ^{31}\text{P})$ and ${}^2K(\text{Sn}, \text{CH}_3)$ are identical. Since ${}^2K(\text{Sn}, \text{CH}_3)$ in methyltin compounds is almost always negative [12], ${}^{1+4}K(\text{Sn}, ^{31}\text{P})$ is also negative and ${}^{1+4}J(\text{Sn}, ^{31}\text{P})$ thus positive ($\gamma(^{119}\text{Sn}) < 0$). In a similar manner, a proton-tin correlation showed the signs of ${}^{1-4}K(\text{Sn}, ^{31}\text{P})$ and ${}^3K(^{31}\text{P}-\text{Sn}-\text{CH}_3)$ (the six-bond component of this coupling can be neglected) to be opposite, it follows that since $\gamma(^{31}\text{P}) > 0$ ${}^3J(^{31}\text{P}-\text{Sn}-\text{CH}_3)$ is positive. Thus in both cases the signs are identical to those for the corresponding (single-path) coupling in $\text{Me}_3\text{SnPPh}_2$, although the

Table 8
NMR data for compound **4d** at various temperatures

$T \pm 5$ (K)	$\delta(^{119}\text{Sn})$	$^2J(\text{Sn}, \text{C}^1\text{H}_3)$
330	132.8	56.3
310	129.7	56.4
290	124.8	56.7
270	119.0	57.0
250	111.0	57.5
230	102.0	57.8

bonding situation is quite different in the two compounds.

3. Experimental

All manipulations involving organotin compounds were carried out in an argon atmosphere.

3.1. Preparation of diphenyl(3-trimethylstannyl)propylphosphine **1a**

Sodium (9.43 g, 0.41 mol) was added in small portions to liquid ammonia (0.5 l) at -70°C . The solution was stirred for 20 min and a solution of Me_3SnCl (40.65 g, 0.204 mol) in diethyl ether (50 ml) added within 15 min. The beige solution of trimethylstannylsodium thus obtained was stirred for 40 min and a solution of (3-chloropropyl)diphenylphosphine (53.5 g, 0.204 mol) in diethyl ether (100 ml) added within 30 min. The reaction mixture first turned light-yellow, then orange-red. The ammonia was allowed to evaporate off overnight and diethyl ether (100 ml) was added to the crude product; the mixture was filtered to remove sodium chloride. The filter cake was washed several times with ether, the ether phases combined and the ether distilled off. The residue was distilled: b.p. $149\text{--}156^\circ\text{C}/0.001$ mm Hg (Ref. [3] $114\text{--}116^\circ\text{C}/0.03$ mm Hg). The yield was 50.8 g (64%).

3.2. Preparation of diphenyl(3-halogenodimethylstannyl)propylphosphines **1b–1e**

3.2.1. Iodo compound

Equimolar amounts of **1a** and Me_3SnI were heated at $80\text{--}90^\circ\text{C}$ until the reaction was complete (ca. 6 h). The reaction could easily be followed by NMR spectroscopy. The volatile components of the reaction mixture were removed at $80\text{--}90^\circ\text{C}/20$ mm Hg; the crude product separates as a pale-yellow crystalline mass. The yield is almost quantitative. M.p. $90\text{--}92^\circ\text{C}$ (from ethanol).

3.2.2. Bromo compound

Equimolar amounts of **1a** and Me_2SnBr_2 were heated at $80\text{--}90^\circ\text{C}$ until the reaction was complete (ca. 5 h).

The reaction could easily be followed by NMR spectroscopy. The volatile components of the reaction mixture were removed at $80\text{--}90^\circ\text{C}/20$ mm Hg; the crude product separates as a colourless crystalline mass. The yield is almost quantitative. M.p. $99\text{--}101^\circ\text{C}$ (from ethanol). Elemental analysis: $\text{C}_{17}\text{H}_{22}\text{BrPSn}$, calc. (found) C, 44.78 (45.01); H, 4.86 (5.10)%.

3.2.3. Chloro compound

Equimolar amounts of **1a** and Me_2SnCl_2 were heated at $80\text{--}90^\circ\text{C}$ until the reaction was complete (ca. 7 h). The reaction could easily be followed by NMR spectroscopy. The volatile components of the reaction mixture were removed at $80\text{--}90^\circ\text{C}/20$ mm Hg; the crude product separates as a pale-yellow crystalline mass. The yield is almost quantitative. M.p. $89\text{--}90^\circ\text{C}$ (from ethanol); Ref. [3] $87\text{--}89^\circ\text{C}$). Elemental analysis: $\text{C}_{17}\text{H}_{22}\text{ClPSn}$, calc. (found) C, 49.62 (49.60); H, 5.39 (5.50)%.

3.2.4. Fluoro compound

Potassium fluoride (9.6 g, 0.165 mol) was added to a solution of **1d** (6.8 g, 0.165 mol) in acetone (150 ml) and the resulting suspension stirred for 24 h at room temperature. The mixture was filtered and the residue washed with dichloromethane (100 ml). The solvent was evaporated off and the residue redissolved in dichloromethane (200 ml). The solution was shaken with 100 ml of deoxygenated water to remove traces of potassium chloride. The organic phase was separated, dried over MgSO_4 and the solvent removed to give an almost quantitative yield of colourless crystals, m.p. $112\text{--}114^\circ\text{C}$.

3.3. Preparation of diphenyl(3-trimethylstannyl)propylphosphine chalcogenides

3.3.1. Oxides **2a–2e**

The phosphine (ca. 20 mmol) was dissolved in acetone (50 ml) and an equimolar amount of hydrogen peroxide (30%) added dropwise with stirring. An exothermic reaction occurred. The reaction mixture was stirred for 24 h at room temperature. Volatiles were removed and the residue recrystallised.

2a: m.p. $104\text{--}105^\circ\text{C}$ (from ethanol). Elemental analysis: $\text{C}_{18}\text{H}_{25}\text{OPSn}$, calc. (found) C, 53.11 (53.50); H, 6.19 (5.90)%.

2b: m.p. $217\text{--}218^\circ\text{C}$ (from ethanol).

2c: m.p. $190\text{--}191^\circ\text{C}$ (from ethanol).

2d: m.p. 164°C (from ethanol). Elemental analysis: $\text{C}_{17}\text{H}_{22}\text{ClOPSn}$, calc. (found) C, 47.77 (47.70); H, 5.19 (5.40)%.

2e: m.p. $173\text{--}174^\circ\text{C}$ (from ethanol). Elemental analysis: $\text{C}_{17}\text{H}_{22}\text{FOPSn}$, calc. (found) C, 49.68 (49.70); H, 5.39 (5.20)%.

3.3.2. Sulphides 3a–3d

The phosphine (ca. 10 mmol) was dissolved in dichloromethane (50 ml) and a slight excess (1.05 equivalents) of elemental sulphur added in small portions with stirring. An exothermic reaction occurred and the sulphur dissolved. The reaction mixture was stirred for 4 h at room temperature. Volatiles were removed and the residue recrystallised

3a: m.p. 71–72°C (from ethanol).

3b: m.p. 94–95°C (from ethanol).

3c: m.p. 112–114°C (from ethanol).

3d: m.p. 125–128°C (from ethanol). Elemental analysis: C₁₇H₂₂ClPSSn, calc. (found) C, 46.04 (46.60); H, 5.00 (5.20)%.

3.3.3. Selenides 4b–4d

The phosphine (ca. 10 mmol) was dissolved in dichloromethane (50 ml) and a slight excess (1.05 equivalents) of elemental selenium added in small portions with stirring. An exothermic reaction occurred and the selenium dissolved. The reaction mixture was stirred for 5 h at room temperature. Volatiles were removed and the residue recrystallised.

4b: m.p. 88–89°C (from *n*-hexane–methanol (12:1)).

4c: m.p. 118–120°C (from ethanol).

4d: m.p. 125–127°C (from cyclohexane). Elemental analysis: C₁₇H₂₂ClPSeSn, calc. (found) C, 41.63 (42.30); H, 4.52 (4.70)%.

3.4. NMR measurements

Solution state NMR spectra were recorded at 295 ± 2 K in the PFT mode using a Bruker AM-300 spectrometer. Chloroform-*d* was used as solvent and internal lock; solute concentrations were max. 5% (v/v) for ¹H and

20–40% for other nuclei. Resonance frequencies, standards and digital resolution were as follows: ¹H, 300.133 MHz, internal CHCl₃ (7.25 ppm), 0.33 Hz/pt; ¹³C, 75.473 MHz, internal CDCl₃ (77.0 ppm), 1.27 Hz/pt; ¹⁹F, 282.407 MHz, external CFC1₃ (0.0 ppm), 1.70 Hz/pt; ³¹P, 121.513 MHz, external 85% H₃PO₄ (0.0 ppm), 1.05 Hz/pt; ⁷⁷Se, 57.298 MHz, external Me₂Se in CDCl₃ (0.0 ppm), 1.02 Hz/pt; ¹¹⁹Sn, 111.920 MHz, external Me₄Sn (0.0 ppm), 2.03 Hz/pt; ¹²⁵Te, 94.714 MHz, external Me₂Te in CDCl₃ (0.0 ppm), 3.05 Hz/pt.

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