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Multinuclear magnetic resonance studies on intramolecular chalcogen–tin coordination in compounds of the type $Me_2Sn(X)CH_2CH_2P(E)Ph_2$ (X = Halogen, E = Chalcogen)

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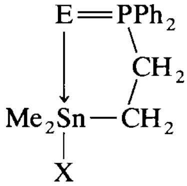
Abstract

Multinuclear magnetic resonance data for the title compounds are presented and discussed. The intramolecular coordination observed in the solid state is shown to be retained in solution. The best probes for the presence or absence of pentacoordination at tin are provided by the various tin–element coupling constants, although chemical shifts are in some cases also informative. A selenium–proton correlated spectrum indicated that the coupling constant ^1J(Sn,Se) has a positive sign.

Keywords: Tin; Chalcogen–tin coordination; Multinuclear magnetic resonance; Phosphorus; Intramolecular

1. Introduction

It has been known for some time that the title compounds **1** are able to undergo intramolecular chalcogen–tin coordination in the solid state and in solution [1,2], we [3–5] and others [1] have provided X-ray crystallographic evidence for this process.



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The plethora of NMR-active nuclei in these compounds makes them extremely attractive candidates for a multinuclear study, the results of which should permit the determination of the value of the individual nuclei as probes for the coordination process. On the basis of these results it is possible to examine the influence of substituents at the methylene carbon atoms on coordination without recourse to X-ray crystallographic investigations. If necessary, solid-state NMR can be used to link the solution data with the X-ray studies.

2. Results and discussion

The compounds studied in the present work are identified in Table 1.

The multinuclear magnetic resonance data for compounds **1a**–**5e** are collected in Tables 2–9. Table 2 contains the "reference values", i.e. the values for the phosphines. Conversion of the phosphines to phosphine oxides (Table 3), sulphides (Table 4) and selenides (Table 5) affords a series of crystalline compounds [6]. However, attempts to isolate the corresponding phosphine tellurides were unsuccessful: yel-

Table 1
Compounds studied

X	E				
	–	O	S	Se	Te
CH_3	**1a**	**2a**	**3a**	**4a**	**5a**
I	**1b**	**2b**	**3b**	**4b**	**5b**
Br	**1c**	**2c**	**3c**	**4c**	**5c**
Cl	**1d**	**2d**	**3d**	**4d**	**5d**
F		**2e**	**3e**	**4e**	**5e**

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Table 2
Multinuclear magnetic resonance data for compounds $Me_2Sn(X)CH_2CH_2PPh_2$

Parameter	X			
	CH_3 (**1a**)	I (**1b**)	Br (**1c**)	Cl (**1d**)
$\delta(CH_3)$	0.10	0.92		0.70
$\delta(CH_2\text{-}Sn)$	0.87	1.56		1.49
$\delta(CH_2\text{-}P)$	2.22	2.41		2.45
δ(Phenyl)	7.29–7.46	7.3–7.47		7.3–7.45
$^2J(^{119}Sn, CH_3)$	53.2	55.8		57.0
$^2J(^{31}P, CH_2)$	0	0		0
$^3J(^{31}P, CH_2)$	12.8	16.7		18.4
$\delta(CH_3)$	−10.0	−1.4	−0.6	−0.7
$\delta(CH_2\text{-}Sn)$	6.0	14.1	15.2	15.5
$\delta(CH_2\text{-}P)$	24.9	25.2	24.1	23.8
δ(Phenyl)	128.1–139.4	128.3–137.4		127.6–137.5
$\delta(^{119}Sn)$	4.4 [a]	48.7	n.d.	147.2 [b]
$^1J(^{119}Sn, CH_3)$	320.4	335.7	358.0	364 ± 5
$^1J(^{119}Sn, CH_2)$	343.4	n.d.	374.1	n.d.
$^2J(Sn, CH_2)$	20.4	22.8	n.d.	n.d.
$^3J(^{119}Sn, ^{31}P)$	181.1 [a]	183.1	n.d.	170.9 [b]
$\delta(^{31}P)$	−11.8 [a]	−13.2	n.d.	−11.3 [b]
$^1J(^{31}P, CH_2)$	14.0	10.2	8.9	7.6
$^2J(^{31}P, CH_2)$	12.7	21.6	20.4	22.9
$^4J(^{31}P, CH_3)$	0	5.1	3.8	5.1

Chemical shifts in ppm, coupling constants in Hz.
n.d. = not determined.

[a] Lit. [2] δ (^{31}P) −10.4 ppm, $\delta(^{119}Sn)$ 4.0 ppm, $^3J(Sn, P)$ 159.8 Hz (C_6D_6).

[b] Lit [2] $\delta(^{31}P)$ −10.7 ppm, $\delta(^{119}Sn)$ 142.0 ppm, $^3J(Sn, P)$ 163.1 Hz (C_6D_6).

low-green solutions were obtained which contained variable amounts of starting material. No tellurium–phosphorus coupling was visible, indicating the presence of an equilibrium such as that observed by Jones and Sharma [7]; they found that even in the case of phosphine tellurides with a large phosphorus–tellurium coupling constant (> 1500 Hz), the addition of excess phosphine ligand caused extreme line broadening and the disappearance of the coupling. Thus the data in Table 6 are those for equilibrium mixtures.

The X-ray structural analyses of **2e** [3], **3c** [4] and **4d** [5] show the tin atom to be pentacoordinated (slightly distorted trigonal bipyramid) with the halogen and chalcogen atoms in axial positions. Compound **2e** was chosen to check whether there is a major difference between solid-state and solution structure; as can be seen from the data in Table 7, five characteristic NMR parameters and the P=O IR frequency are almost unchanged on diluting the solution by a factor of 20. Hence the assumption that this compound has the same structure in solution as in the crystal appears justified. In addition, cross-polarization magic angle spinning (CP/MAS) solid-state spectra (^{31}P, ^{77}Se) were recorded for **4c** [8]; the chemical shifts and phosphorus–selenium coupling constant are almost identical with those obtained in solution. Taken in total, these observations support the assumption of a similarity between solid-state and solution structures for the compounds discussed in this work.

In the fluoride series (**2e**, **3e**, **4e**), it can be expected that the values of δ(F) and ^1J(Sn, F) will be relatively invariant if the coordination of the chalcogen is similarly strong (i.e. if there is retention of pentacoordination in solution). Table 8 shows this to be the case: for comparison data are included for the case (denoted in

Table 3
Multinuclear magnetic resonance data for compounds $Me_2Sn(X)CH_2CH_2P(O)Ph_2$

Parameter	X				
	CH_3 (**2a**)	I (**2b**)	Br (**2c**)	Cl (**2d**)	F (**2e**)
$\delta(CH_3)$	0.04	1.03	0.87	0.63	0.59
$\delta(CH_2\text{-}Sn)$	0.90	1.71	1.58	1.38	1.31
$\delta(CH_2\text{-}P)$	2.30	2.64	2.65	2.62	2.64
δ(Phenyl)	7.38–7.75	7.47–7.68	7.41–7.72	7.43–7.80	7.46–7.68
$^2J(^{119}Sn, CH_3)$	53.5	67.9	68.9	69.6	n.d.
$^2J(^{31}P, CH_2)$	n.d.	8.9	9.2	9.2	9.2
$^3J(^{31}P, CH_2)$	n.d.	20.0	20.0	20.0	20.0
$\delta(CH_3)$	−10.3	4.4	3.0	2.0	−1.3
$\delta(CH_2\text{-}Sn)$	−0.2	13.0	11.5	10.5	7.2
$\delta(CH_2\text{-}P)$	26.3	25.1	25.1	25.0	24.8
δ(Phenyl)	n.d.	128.4–132.9	129.6–132.9	128–133	128.9–132.7
$\delta(^{119}Sn)$	11.4 [a]	−31.1	1.7	11.0	21.0
$^1J(^{119}Sn, CH_3)$	331.8	485.7	493.4	506.1	506 ± 5
$^1J(^{119}Sn, CH_2)$	329.3	490.8	498.5	506.1	506 ± 5
$^2J(Sn, CH_2)$	19.0	n.d.	20.4	20.3	17.8
$^3J(^{119}Sn, ^{31}P)$	221.7 [a]	40.0	42.4	41.0	43.2
$\delta(^{31}P)$	34.4	44.4	43.4	42.6	41.2
$^1J(^{31}P, CH_2)$	66.1	68.7	68.7	68.7	69.9
$^2J(^{31}P, CH_2)$	7.6	n.d.	3.8	3.8	n.d.

Chemical shifts in ppm, coupling constants in Hz.
n.d. = Not determined.

[a] Lit. [20] $\delta(^{119}Sn)$ 12.8 ppm, $J(Sn, P)$ 219.8 Hz ($CDCl_3$).

Table 4
Multinuclear magnetic resonance data for compounds $Me_2Sn(X)CH_2CH_2P(S)Ph_2$

Parameter	X				
	CH_3 (**3a**)	I (**3b**)	Br (**3c**)	Cl (**3d**)	F (**3e**)
$\delta(\mathrm{C}H_3)$	0.08	1.12	0.97	0.86	0.69
$\delta(\mathrm{C}H_2\text{-Sn})$	0.95	1.74	1.62	1.50	1.33
$\delta(\mathrm{C}H_2\text{-P})$	2.51	2.92	2.95	2.95	2.95
δ(Phenyl)	7.4–7.8	7.4–7.9	7.45–7.8	7.45–7.8	7.4–7.8
$^2J(^{119}\mathrm{Sn}, \mathrm{C}H_3)$	53.8	65.6	67.0	67.3	65.0
$^2J(^{31}\mathrm{P}, \mathrm{C}H_2)$	10.8	9.8	n.d.	9.8	9.8
$^3J(^{31}\mathrm{P}, \mathrm{C}H_2)$	12.1	26.3	n.d.	26.9	27.2
$\delta(C\mathrm{H}_3)$	−10.3	6.8	5.5	4.5	1.5
$\delta(C\mathrm{H}_2\text{-Sn})$	0.5	15.1	13.7	12.8	10.0
$\delta(C\mathrm{H}_2\text{-P})$	29.7	29.5	29.1	29.1	29.2
δ(Phenyl)	128.2–132.8	128.7–133.0	128.4–133.0	128.6–132.4	128.8–132.3
$\delta(^{119}\mathrm{Sn})$	12.0 [a]	−13.1	20.3	36.4 [b]	50.7
$^1J(^{119}\mathrm{Sn}, C\mathrm{H}_3)$	331.9	458 ± 2	474.3	483.2	488 ± 5
$^1J(^{119}\mathrm{Sn}, C\mathrm{H}_2)$	318.0	n.d.	467.9	475.0	480 ± 10
$^2J(\mathrm{Sn}, C\mathrm{H}_2)$	14.0	28.0	28.0	28.0	24.1
$^3J(^{119}\mathrm{Sn}, \mathrm{P})$	253.4 [a]	62.1	64.1	63.1 [b]	77.9
$\delta(^{31}\mathrm{P})$	45.2 [a]	48.6	48.9	48.7 [b]	48.6
$^1J(^{31}\mathrm{P}, C\mathrm{H}_2)$	48.3	57.2	57.2	57.2	56.0
$^2J(^{31}\mathrm{P}, C\mathrm{H}_2)$	8.9	0	0	0	0

Chemical shifts in ppm, coupling constants in Hz.
n.d. = Not determined.

[a] Lit. [2] δ(Sn) 12, δ(P) 45.5, J(Sn, P) 255.5 Hz ($CDCl_3$)

[b] Lit. [20] δ(Sn) 38.3 ($CDCl_3$), 17.1 (pyridine), J(Sn, P) 62.8 ($CDCl_3$), 206 Hz (pyridine).

Table 8 as **2e** · TBAF) in which addition of tetrabutylammonium fluoride (TBAF) causes the tin–oxygen coordination bond to be replaced by a tin–fluorine bond. In a related case, Gingras [9] treated triphenyltin fluoride with TBAF and obtained $[Bu_4N^+Ph_3SnF_2^-]$; the ^{31}P spectrum of **2e** · TBAF shows a signal at 34.2

Table 5
Multinuclear magnetic resonance data for $Me_2Sn(X)CH_2CH_2P(Se)Ph_2$

Parameter	X				
	CH_3 (**4a**)	I (**4b**)	Br (**4c**)	Cl (**4d**)	F (**4e**)
$\delta(\mathrm{C}H_3)$	0.09	1.16	1.02	0.91	0.74
$\delta(\mathrm{C}H_2\text{-Sn})$	0.94	1.75	1.61	1.51	1.33
$\delta(\mathrm{C}H_2\text{-P})$	2.61	3.03	3.06	3.06	3.04
δ(Phenyl)	7.3–7.9	7.4–7.8	7.4–7.8	7.4–7.8	7.4–7.8
$^2J(^{119}\mathrm{Sn}, \mathrm{C}H_3)$	53.8	65.0	66.9	66.9	67 ± 1
$^2J(^{31}\mathrm{P}, \mathrm{C}H_2)$	n.d.	n.d.	n.d.	10.2	n.d.
$^3J(^{31}\mathrm{P}, \mathrm{C}H_2)$	n.d.	28.2	n.d.	28.9	28.5
$\delta(C\mathrm{H}_3)$	−10.3	7.9	6.5	5.5	2.4
$\delta(C\mathrm{H}_2\text{-Sn})$	1.3	16.4	15.0	14.3	11.4
$\delta(C\mathrm{H}_2\text{-P})$	30.0	29.8	29.5	29.8	29.7
δ(Phenyl)	128.7–131.8	127.4–132.4	127.1–132.4	127.9–132.4	128.4–132.4
$\delta(^{119}\mathrm{Sn})$	11.1	−18.6	12.8	31.0	42.8
$^1J(^{119}\mathrm{Sn}, C\mathrm{H}_3)$	333.2	465.4	476.8	485.7	500 ± 20
$^1J(^{119}\mathrm{Sn}, C\mathrm{H}_2)$	317.8	465.4	476.8	481.9	490 ± 20
$^2J(\mathrm{Sn}, C\mathrm{H}_2)$	n.d.	30.5	30.6	n.d.	n.d.
$^1J(\mathrm{Sn}, ^{77}\mathrm{Se})$	0	(+)107.8	(+)106.8	+95.2	(+)105.4
$^3J(^{119}\mathrm{Sn}, ^{31}\mathrm{P})$	265.6	65.5	66.1	63.1	88.4
$\delta(^{31}\mathrm{P})$	38.3	42.2	42.6	42.1	42.4
$^1J(^{31}\mathrm{P}, C\mathrm{H}_2)$	40.7	50.8	50.9	50.9	50.9
$^2J(^{31}\mathrm{P}, C\mathrm{H}_2)$	8.9	0	0	0	0
$\delta(^{77}\mathrm{Se})$	−348.9	−321.7	−321.4	−324.0	−326.9
$^1J(^{77}\mathrm{Se}, ^{31}\mathrm{P})$	716.1	641.9	642.9	649.5	656.6

Chemical shifts in ppm, coupling constants in Hz.
n.d. = Not determined.

Table 6
Multinuclear magnetic resonance data for products obtained by reacting $Me_2Sn(X)CH_2CH_2PPh_2$ with elemental tellurium

Parameter	X			
	CH_3 (**5a**)	Cl (**5d**)		
$\delta(CH_3)$	0.08	0.92		
$\delta(CH_2\text{-}Sn)$	0.86	1.48		
$\delta(CH_2\text{-}P)$	2.23	2.94		
δ(Phenyl)	7.3–7.5	7.3–7.7		
$^2J(^{119}Sn, CH_3)$	52.8	63.7		
$^2J(^{31}P, CH_2)$	n.d.	n.d.		
$^3J(^{31}P, CH_2)$	12.5	25.9		
	CH_3 (**5a**)	I (**5b**)	Cl (**5d**)	
$\delta(CH_3)$	−10.0	2.8	4.1	
$\delta(CH_2\text{-}Sn)$	5.8	15.8	16.3	
$\delta(CH_2\text{-}P)$	25.3	27.3	28.3	
δ(Phenyl)	128.2–138.2	126.7–134.3	128.5–133.0	
$^1J(^{119}Sn, CH_3)$	324.3	374 ± 10	437 ± 2	
$^1J(^{119}Sn, CH_2)$	340.8	n.d.	424 ± 5	
$^2J(Sn, CH_2)$	20.4	n.d.	n.d.	
$^1J(^{31}P, CH_2)$	11.4	8.9	20.3	
$^2J(^{31}P, CH_2)$	11.4	12.6	8.9	
	CH_3 (**5a**)	I (**5b**)	Cl (**5d**)	F (**5e**)
$\delta(^{31}P)$	−11.2	−6.5	−1.8	−0.2
$^3J(^{119}Sn, ^{31}P)$	185.2	145.2	n.d.	n.d.
$\delta(^{119}Sn)$	4.6	23.9	75.2	23.8
$\delta(^{125}Te)$	−460.8	−447.2	−456.2	−456.8

Chemical shifts in ppm, coupling constants in Hz.
n.d. = Not determined.

Table 7
Concentration dependence of selected NMR and IR parameters for compound **2e** $Me_2Sn(F)CH_2CH_2P(O)Ph_2$

c (mol l^{-1})	$\delta(^{31}P)$	J(Sn, P)	$\delta(^{119}Sn)$	J(Sn, P)	J(Sn, F)	ν(P=O)
316.4	41.4	44.4	21.1	44.4	1955	1143
158.2	41.5	44.4	22.0	44.4	1957	1143
31.64	41.5	45.3	22.9	45.3	1959	1144
15.82	41.5	41.6	23.1	41.6	1955	1144

Chemical shifts in ppm, coupling constants in Hz, ν(P=O) in cm^{-1}.

Table 8
Fluorine chemical shifts and $^nJ(^{19}F, X)$ data for compounds of the type $Me_2Sn(F)CH_2CH_2P(E)Ph_2$ (E = O, S, Se)

Parameter	E			
	O (**2e**)	**2e**·TBAF	S (**3e**)	Se (**4e**)
$\delta(^{19}F)$	−169.2	−133.4	−174.1	−174.9
$^1J(^{119}Sn, ^{19}F)$	1976	1600 ± 20	1941	1945 ± 10
$^3J(^{19}F, C^1H_3)$	0	0	3	3.3
$^2J(^{19}F, ^{13}CH_3)$	5	0	11.4	19.1
$^2J(^{19}F, ^{13}CH_2)$	12.7	6	16.5	19.1

Chemical shifts in ppm, coupling constants in Hz.

ppm (close to that of **2a**) with a tin–phosphorus coupling much larger than that obsereved for **2a** (343 Hz), while the ^{119}Sn spectrum shows a triplet of doublets at −92 ppm (high-field shift with respect to **2a**: 113 ppm) due to coupling with two fluorine nuclei and the phosphorus.

The data recorded suggest that compounds **1** (Table 2) and **2a**, **3a**, **4a** and **5a** are tetracoordinated in solution. This is demonstrated most clearly by the values of ^1J(SnC) which lie in the range typical of four-coordinate tin (310–350 Hz) [10]. The value of the tin chemical shift taken in isolation is no guide to the presence

Table 9
Multinuclear magnetic resonance data for compounds $Me_2Sn(X)CH(R^2)CH(R^1)P(S)Ph_2$

Parameter	X		
	Br (R^1 = H, R^2 = CH_3) (**6**)	Br (R^1 = CH_3, R^2 = H) (**7a**)	Cl (R^1 = CH_3, R^2 = H) (**7b**)
$\delta(CH_3)$	0.92; 0.97	0.83; 1.10	0.72; 0.99
$\delta(CH\text{-}Sn)$	2.18	1.7	1.62
$\delta(CH\text{-}P)$	3.00	3.64	3.66
$\delta(R^1)$	–	1.16	1.15
$\delta(R^2)$	1.22	–	–
δ(Phenyl)	7.4–7.9	7.4–7.9	7.4–9.0
$^2J(Sn, CH_3)$	63; 64	66.2; 66.2	65.6; 65.6
^3J(CH, R)	7.6	6.9	6.9
$^3J(^{31}P, R^1)$	–	18.7	18.7
$\delta(CH_3)$	3.8; 6.7	6.2; 7.5	5.1; 6.5
$\delta(C\text{-}Sn)$	24.8	24.6	23.6
$\delta(C\text{-}P)$	37.9	32.4	32.3
$\delta(R^1)$	–	16.2	16.3
$\delta(R^2)$	18.9	–	–
δ(Phenyl)	128.4–133.0	127.3–133.3	127.6–133.2
$\delta(^{119}Sn)$	35.8	9.0	23.5
$^1J(^{119}Sn, CHR^2)$	500.4	467.2	473.1
$J(^{119}Sn, ^{31}P)$	59.0	76.8	77.8
$\delta(^{31}P)$	45.5	58.1	57.9
$^1J(^{31}P, CHR^1)$	56.0	55.9	55.9

Chemical shifts in ppm, coupling constants in Hz.

of pentacoordinate tin, as it depends heavily on the attached group/element X; the same is true of $\delta(^{31}P)$, which is determined largely by the presence or absence of the chalcogen. Pentacoordination causes ^1J(Sn, C) to increase to 450–500 Hz, as is to be expected [10].

The tin–phosphorus coupling constant provides further clear evidence for the change in coordination number (170–270 Hz for tetracoordination, 40–90 Hz for pentacoordination). This decrease in the absolute value is presumably due to the introduction of a negative two-bond coupling component which counteracts the positive three-bond coupling already present. Whereas in the case of the oxides J(Sn, P) is almost independent of the halogen (40–43 Hz, Table 3), this is not true for the more polarizable sulphides and selenides where the values for **3e** and **4e** are much higher than those for the other halogens (although for example ^1J(Se, P) and ^1J(Sn, Se) do not vary greatly within the complete halogen series **4b**–**4e**).

A very brief study of the effect of introducing a methyl group on one of the carbons in the SnCCP fragment has been made (compounds **6**, **7a**, **7b**; Table 9). This substitution causes the two methyl groups on tin to become anisochronous, but apart from this appears to have no noticeable influence on the intramolecular pentacoordination.

It was found useful to record the ^{77}Se spectra with the help of the refocused INEPT sequence [11,12]: selenium linewidths were small (2–3 Hz), so that, for example, the exact determination of ^2J(Se, F) in **4e** (24.0 Hz) was possible. Heterocorrelated 2D NMR spectra [13,14] have been used very effectively in recent years for the determination of relative signs of coupling constants such as $J(^{119}Sn, ^{13}C)$, $J(^{119}Sn, ^{1}H)$, $J(^{207}Pb, ^{13}C)$, $J(^{31}P, ^{13}C)$ and $J(^{31}P, ^{15}N)$ [15c,16–18]. In the case of **4d**, a selenium–proton correlated spectrum was recorded using the three-bond methyl proton–selenium coupling constant (which is smaller than the Se linewidth) to set the delay, as in the INEPT sequence. The tin satellites show a "positive tilt" [15], so that the signs of $^1K(^{119}Sn, ^{77}Se)$ and $^2K(Sn, C^1H_3)$ are identical. Since the ^2K coupling is almost always negative [16], ^1K(Sn, Se) is also negative. ^{119}Sn has a negative magnetogyric ratio, so that the coupling constant ^1J(Sn, Se) is positive.

3. Experimental

All manipulations involving organotin compounds were carried out in an argon atmosphere. The title compounds were prepared from $Me_3SnCH_2CH_2PPh_2$ as previously described [2,7].

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 maximum 5% (v/v) for ^{1}H and 20–40% for other nuclei. Resonance frequencies, standards and digital resolution were as follows: ^{1}H, 300.133 MHz, internal $CHCl_3$ (7.25 ppm), 0.33 Hz per point, ^{13}C, 75.473 MHz, internal $CDCl_3$ (77.0 ppm), 1.27 Hz per point, ^{19}F, 282.407 MHz, external $CFCl_3$ (0.0 ppm), 1.70 Hz per point; ^{31}P, 121.513 MHz, external 85% H_3PO_4 (0.0 ppm), 1.05 Hz per point; ^{77}Se, 57.298 MHz, external Me_2Se in $CDCl_3$ (0.0 ppm), 1.02 Hz per point; ^{119}Sn 111.920 MHz, external Me_4Sn (0.0 ppm), 2.03 Hz per point; ^{125}Te, 94.714 MHz, external Me_2Te in $CDCl_3$ (0.0 ppm), 3.05 Hz per point.

CP/MAS spectra of **4c** were measured on a Bruker MSL-300 spectrometer. Experimental conditions were as follows: 7 mm rotor, rotation frequency 9000 Hz, contact time 2 ms (^{77}Se), 4 ms (^{31}P), standards $(PhCH_2)_2Se_2$ (412 ppm) and Ph_3P (0 ppm) [6].

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