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Synthesis and spectral studies of diorganotin(IV) dialkyldithiophosphates

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Abstract—Two series of diorganotin(IV) dialkyldithiophosphates, $[RR'Sn\{SSP(OR'')_2\}_2]$ (R = Me or Et; R′ = Ph; R″ = Et, Pr^n, Pr^i or Bu^n) and $[RR'Sn(Cl)\{SSP(OR'')_2\}]$ (R = R′ = Me, Et or Ph; R′ = Ph; R″ = Et, Pr^i or Bu^n) were prepared and characterised by i.r. and NMR (^1H, ^{13}C, ^{31}P, ^{119}Sn) spectroscopy. The NMR data indicate five and six coordinate geometries for $[RR'Sn(Cl)\{SSP(OR'')_2\}]$ and $[RR'Sn\{SSP(OR'')_2\}_2]$ complexes, respectively. The chloro complexes showed ^2J(P–Sn) whereas such couplings were not observed in the spectra of $[RR'Sn\{SSP(OR'')_2\}_2]$.

INTRODUCTION

Dialkyldithiophosphoric acids and their organic esters as well as the organotin dialkyldithiophosphates are well known for their biocidal activities [1, 2]. Metallic dialkyldithiophosphates are also of interest structurally, since several modes of bonding of the ligand moiety are in principle possible [3–5]. The ligand may act in a monodentate fashion, fully or partially bidentate, bridging and even bridging as well as bidentate. Further, substitution of one alkyl group for another usually leads to structural changes. For example, in $[Ph_2Sn\{SSP(OEt)_2\}_2]$ the ligand is bonded to the central tin atom in anisobidentate fashion [6] while in $[Ph_2Sn\{SSP(OPr^i)_2\}_2]$ the ligand is symmetrically bonded [7]. These configurations might not always be retained in solution.

Although transition and non-transition metal dialkyldithiophosphate complexes are reasonably well known [3–5], the derivatives of these ligands with organometallic moieties have not received much attention until recently [8–10]. In this communication we report the preparation and spectral studies (i.r. and multinuclear NMR) of two series of diorganotin (IV) dialkyldithiophosphates, $[RR'Sn\{SSP(OR'')_2\}_2]$ and $[RR'Sn(Cl)\{SSP(OR'')_2\}]$.

EXPERIMENTAL

The dialkyldithiophosphoric acids, $HSSP(OR'')_2$ (R″ = Et, Pr^n, Pr^i, Bu^n) and their sodium or ammonium salts were prepared by methods as given in the literature [8]. Dialkyltin dichlorides, R_2SnCl_2 (R = Me or Et), were prepared by coproportionation reaction of tetraalkyltin with $SnCl_4$ [11]. Alkylphenyltin dichlorides, $RPhSnCl_2$ (R = Me or Et) were prepared by the reaction of tetraalkyltin with $PhSnCl_3$ at 0°C [12, 13]. Diphenyltin dichloride was of commercial grade. Analytical grade solvents were dried and distilled under a nitrogen atmosphere before use.

The i.r. spectra were recorded either as neat liquids or nujol mulls between CsI or KBr optics on a Perkin–Elmer 180 spectrometer. The ^1H, ^{13}C, ^{31}P and ^{119}Sn NMR spectra were recorded on a Varian FT-80A spectrometer in $CDCl_3$ operating at 79.5, 20.0, 32.2 and 29.6 MHz, respectively. Chemical shifts are reported in ppm downfield from external TMS (for ^1H and ^{13}C), 85% H_3PO_4 (for ^{31}P) and 33% Me_4Sn (for ^{119}Sn).

$[R_2Sn\{SSP(OR'')_2\}_2]$ (R = Me, Et, Ph; R″ = Et, Pr^i) were prepared by methods as given in the literature [8, 9]. Typical methods of preparation for other complexes are described below.

(a) *Preparation of* $[MePhSn\{SSP(OPr^i)_2\}_2]$

Metallic sodium (0.26 g, 11.4 mmole) suspended in benzene (~ 5 ml) was dissolved in isopropanol (~ 10 ml) and the resulting solution was treated with $(Pr^iO)_2PSSH$ (2.27 g, 10.6 mmole). To this a solution of $MePhSnCl_2$ (1.50 g, 5.3 mmole) in benzene (~ 20 ml) was added with stirring and the reaction mixture was refluxed for one hr. A white precipitate of sodium chloride was formed. The solvent was removed under vacuum and the product was dissolved in hexane and passed through a florisil column eluting with hexane. Solvent was reduced to 5 ml and kept in the freezer for 24 h to give white crystals of $[MePhSn\{SSP(OPr^i)_2\}_2]$ in 86% yield.

(b) *Preparation of* $[MePhSn\{SSP(OBu^n)_2\}_2]$

To a suspension of $NH_4SSP(OBu^n)_2$ (2.76 g, 10.6 mmole) in hexane, a solution of $MePhSnCl_2$ (1.50 g, 5.3 mmole) was added and the reaction mixture was allowed to stir for 2–3 h at room temperature. Ammonium chloride formed during the reaction was filtered off. The filtrate was concentrated under vacuum leaving a viscous liquid in 78% yield.

Similar reactions in 1:1 stoichiometry gave $[RR'Sn(Cl)\{SSP(OR'')_2\}]$.

(c) *Preparation of* $[MePhSn(Cl)\{SSP(OPr^i)_2\}]$

To a hexane solution of $[MePhSn\{SSP(OPr^i)_2\}_2]$ (0.65 g, 1.02 mmole) a solution of $MePhSnCl_2$ (0.29 g, 1.04 mmole) was added. The reaction mixture was stirred at room temperature for 2–3 h. Hexane was reduced to 5 ml under vacuum and the resulting solution was kept at 0°C for 24 h to give white crystals of $[MePhSn(Cl)\{SSP(OPr^i)_2\}]$ in 75% yield.

Pertinent data for these complexes are summarized in Table 1.

RESULTS AND DISCUSSION

The reactions of alkylphenyltin dichlorides with sodium or ammonium salts of dialkyldithiophosphates in 1:2 stoichiometry in benzene afford complexes of the type $[RR'Sn\{SSP(OR'')_2\}_2]$ (R = Me or Et; R′ = Ph; R″ = Et, Pr^n, Pr^i, Bu^n) in 70–90% yield. However, when the reaction was carried out

Table 1. Preparative method, percentage yield and analytical data for $[\mathrm{RR'SnX\{SSP(OR'')_2\}}]$ ($\mathrm{X = Cl}$ or $\mathrm{SSP(OR'')_2}$)

Complex	Preparative method*	Percentage yield	Percentage analyses Found (calculated) C	H	S
$[\mathrm{MePhSn\{SSP(OEt)_2\}_2}]$	b	89	31.53 (30.99)	5.22 (4.85)	—
$[\mathrm{EtPhSn\{SSP(OEt)_2\}_2}]$	b	90	31.77 (32.28)	5.09 (5.08)	—
$[\mathrm{MePhSn\{SSP(OPr^n)_2\}_2}]$	a	72	34.75 (35.80)	6.08 (5.69)	—
$[\mathrm{EtPhSn\{SSP(OPr^n)_2\}_2}]$	a	70	36.22 (36.88)	5.77 (5.88)	—
$[\mathrm{MePhSn\{SSP(OPr^i)_2\}_2}]$	a	86	36.67 (35.80)	5.72 (5.69)	19.70 (20.12)
$[\mathrm{EtPhSn\{SSP(OPr^i)_2\}_2}]$	a	70	37.66 (36.88)	6.01 (5.88)	18.20 (19.69)
$[\mathrm{MePhSn\{SSP(OBu^n)_2\}_2}]$	b	78	38.95 (39.83)	6.55 (6.39)	—
$[\mathrm{EtPhSn\{SSP(OBu^n)_2\}_2}]$	b	80	40.22 (40.74)	6.83 (6.55)	—
$[\mathrm{Me_2Sn(Cl)\{SSP(OEt)_2\}}]$	b	90	18.90 (19.51)	4.05 (4.36)	—
$[\mathrm{Et_2Sn(Cl)\{SSP(OEt)_2\}}]$	b	85	24.45 (24.17)	5.35 (5.07)	—
$[\mathrm{MePhSn(Cl)\{SSP(OEt)_2\}}]$	c	89	31.06 (30.62)	3.91 (4.20)	—
$[\mathrm{EtPhSn(Cl)\{SSP(OEt)_2\}}]$	c	86	31.70 (32.35)	5.07 (4.52)	—
$[\mathrm{Ph_2Sn(Cl)\{SSP(OEt)_2\}}]$	b	82	37.98 (38.93)	4.21 (4.08)	—
$[\mathrm{Me_2Sn(Cl)\{SSP(OPr^i)_2\}}]$	b	90	23.82 (24.17)	5.35 (5.07)	—
$[\mathrm{Et_2Sn(Cl)\{SSP(OPr^i)_2\}}]$	b	86	29.10 (28.22)	5.51 (5.68)	—
$[\mathrm{Ph_2Sn(Cl)\{SSP(OPr^i)_2\}}]$	b	82	40.82 (41.45)	4.93 (4.64)	—
$[\mathrm{MePhSn(Cl)\{SSP(OPr^i)_2\}}]$	c	75	34.22 (33.98)	4.81 (4.82)	13.85 (13.95)
$[\mathrm{MePhSn(Cl)\{SSP(OBu^n)_2\}}]$	c	86	36.15 (36.95)	5.27 (5.37)	—
$[\mathrm{EtPhSn(Cl)\{SSP(OBu^n)_2\}}]$	c	88	38.20 (38.31)	5.30 (5.63)	—

*a, b, c correspond to the syntheses described in the experimental section.

Table 2. Infrared spectral data for $[\mathrm{PhR'Sn\{SSP(OR'')_2\}_2}]$ and $[\mathrm{RR'Sn(Cl)\{SSP(OR'')_2\}}]$ in the range 1400–250 $\mathrm{cm^{-1}}$*

Complex	Infrared frequencies
$[\mathrm{MePhSn\{SSP(OEt)_2\}_2}]$	1390 s, 1330 m, 1295 m (br), 1162 s, 1100 m, 1020 vs (br), 962 vs, 795 vs, 735 s, 698 s, 655 s, 620 w, 545 s, 520 s, 455 m, 385 w, 310 m(br), 260 m
$[\mathrm{EtPhSn\{SSP(OEt)_2\}_2}]$	1390 s, 1328 w, 1290 w, 1215 m, 1185 sh, 1175 sh, 1160 s, 1095 m, 1025 vs (br), 968 sh, 960 vs, 910 s, 810 s, 790 vs, 785 sh, 760 vs, 730 vs, 690 vs, 660 vs(br), 540 m, 515 s, 445 m, 370 w, 300 m
$[\mathrm{MePhSn\{SSP(OPr^n)_2\}_2}]$	1385 m, 1345 vw, 1325 w, 1295 w, 1275 w, 1250 m, 1145 m, 1125 w, 1095 sh, 1055 vs, 995 vs(br), 900 m, 875 sh, 845 vs, 790 m, 745 s, 728 s, 655 vs(br), 520 s, 445 m, 375 m, 300 m (br)
$[\mathrm{EtPhSn\{SSP(OPr^n)_2\}_2}]$	1380 m, 1320 w, 1250 w, 1170 w, 1135 w, 1085 m, 1070 m, 1050 m, 1010 w, 990–1005 vs(br), 912 m, 850 s, 760 vs, 735 vs, 695 vs, 665 vs, 550 sh, 525 s, 445 m, 375 w, 270 w
$[\mathrm{MePhSn\{SSP(OPr^i)_2\}_2}]$†	1385 vs, 1372 vs, 1355 sh, 1330 w, 1298 w, 1262 w, 1180 s, 1158 w, 1145 m, 1105 m, 1070 m, 1015 vs, 970 vs(br), 895 vs, 795 vs, 745 w, 728 vs, 695 s, 645 vs, 635 vs, 550 vw, 540 w, 520 vs, 450 s, 412 w
$[\mathrm{EtPhSn\{SSP(OPr^i)_2\}_2}]$†	1365 vs, 1330 w, 1298 w, 1180 s, 1160 w, 1140 m, 1105 s, 1070 w, 1020 s, 975 vs(br), 890 s, 790 s, 770 s, 728 s, 692 s, 645 s, 550 m, 525 m, 450 m
$[\mathrm{MePhSn\{SSP(OBu^n)_2\}_2}]$	1380 m, 1328 w, 1300 w, 1255 w, 1230 w, 1145 w, 1115 w, 1060 vs, 1015 vs(br), 975 vs, 895 s, 835 m, 795 s, 730 s, 690 m, 655 vs, 525 m, 470 w, 440 m, 375 w(br), 300 w
$[\mathrm{EtPhSn\{SSP(OBu^n)_2\}_2}]$	1380 vs, 1330 s, 1300 s, 1260 s, 1235 vs, 1185 vs, 1150 s, 1120 s, 950–1050 vs(br), 900 s, 840 s, 800 s, 730 s, 695 vs, 665 vs(br), 530 vs, 505 sh, 475 w, 450 s, 420 w, 380 m, 310 m, 270 m
$[\mathrm{Me_2Sn(Cl)\{SSP(OEt)_2\}}]$†	1390 s, 1280 w(br), 1150 m, 1090 m 1025 vs(br), 960 vs(br), 785 vs, 645 vs, 550 m, 508 m
$[\mathrm{Et_2Sn(Cl)\{SSP(OEt)_2\}}]$†	1385 s, 1280 w, 1225 w, 1180 s, 1155 s, 1092 m, 1015–1040 vs(br), 910 vs, 790 vs, 685 vs, 670 s, 650 vs, 540 m, 520 s, 485 w
$[\mathrm{MePhSn(Cl)\{SSP(OEt)_2\}}]$†	1390 m, 1332 w, 1295 w, 1190 w, 1160 m, 1100 m, 1035 sh, 1015 vs(br), 965 vs, 785 vs, 735 vs, 695 vs, 645 s, 540 m, 520 m, 445 m
$[\mathrm{EtPhSn(Cl)\{SSP(OEt)_2\}}]$†	1385 s, 1328 w. 1285 w, 1185 s, 1145 s, 1095 m, 1010 vs(br), 960 vs, 810 s, 785 s, 728 s, 690 vs, 680 sh, 645 vs, 540 w, 515 m, 442 s
$[\mathrm{Ph_2Sn(Cl)\{SSP(OEt)_2\}}]$†	1385 m, 1330 w, 1298 w, 1190 w, 1155 m, 1095 m, 1000–1020 vs(br), 960 vs, 845 vw, 810 sh, 790 s, 728 vs, 690 vs, 645 vs, 540 vw, 515 m, 445 s

Table 2. (*Contd.*)

Complex	Infrared frequencies
$[Me_2Sn(Cl)\{SSP(OPr^i)_2\}]$	1385 sh, 1375 vs, 1180 s, 1142 s, 1105 s, 1000 sh, 980 vs, 892 m, 795 m, 770 m, 665 m, 650 s, 555 m, 530 m, 465 w, 325 m
$[Et_2Sn(Cl)\{SSP(OPr^i)_2\}]$†	1385 s, 1375 s, 1350 w, 1230 vw, 1180 s, 1142 m, 1105 s, 970–1005 vs(br), 892 m, 795 w, 770 s, 695 s, 660 s, 650 s, 558 m, 538 m, 498 w, 465 w, 440 w
$[Ph_2Sn(Cl)\{SSP(OPr^i)_2\}]$	1375 vs, 1300 w, 1175 w, 1142 w, 1102 w, 1010 vw, 1000 s, 965 s, 910 vw, 890 w, 790 m, 735 w, 692 w, 620 m, 522 w, 460 w, 410 vw, 275 vw
$[MePhSn(Cl)\{SSP(OPr^i)_2\}]$†	1385 s, 1375 s, 1180 m, 1140 m, 1105 m, 1070 w, 1000 vs, 975 vs(br), 890 m, 765 m, 730 m, 692 m, 645 m, 550 w, 525 w, 445 w
$[MePhSn(Cl)\{SSP(OBu^n)_2\}]$†	1375 m, 1322 w, 1290 w, 1250 w, 1225 w, 1185 w, 1155 w, 1140 m, 1120 w, 1110 m, 1050 vs, 1010 vs, 970–990 vs(br), 890 s, 830 s, 785 s, 725 vs, 685 s, 640 vs, 525 s, 435 s
$[EtPhSn(Cl)\{SSP(OBu^n)_2\}]$†	1378 m, 1328 w, 1296 w, 1258 w, 1228 w, 1182 m, 1145 w, 1115 w, 1055 vs, 1015 vs(br), 980 vs(br), 895 s, 840 s, 795 s, 730 vs, 690 vs, 658 sh, 650 s, 535 m, 510 sh, 440 m

*vs = very strong, s = strong, m = medium, w = weak, vw = very weak, sh = shoulder, br = broad.

†Recorded down to 400 cm^{-1} between KBr plates.

in 1:1 stoichiometry, mono-chloro complexes, $[RR'Sn(Cl)\{SSP(OR'')_2\}]$, were isolated. These complexes may also be obtained by the reactions of $[RR'Sn\{SSP(OR'')_2\}_2]$ with $RR'SnCl_2$ in 1:1 stoichiometry in hexane at room temperature. Complexes of both the series were either viscous liquids or low melting point solids, soluble in common organic solvents. The solids were recrystallized from hexane at ~ 0°C. The liquids (bis complexes only) were purified by dissolving them in anhydrous hexane and filtering through florisil columns (3 × 5 cm) under a nitrogen atmosphere.

Infrared spectra

Infrared spectra of metal dialkyldithiophosphates generally show some apparent variations, but efforts to

Table 3. ^1H NMR Data for $[RPhSn\{SSP(OR'')_2\}_2]$ and $[RR'Sn(Cl)\{SSP(OR'')_2\}]$ in $CDCl_3$ at room temperature**

Complex	δ Sn–R*	$^2J(^{117/119}Sn–^1H)$† (Hz)	δ P–OR″
$[MePhSn\{SSP(OEt)_2\}_2]$	1.77	80	1.25(t) (O–C–Me), 3.95 (m) $(O–CH_2–)$
$[EtPhSn\{SSP(OEt)_2\}_2]$	1.70 (m), 2.40 (m)		1.24 (t) (O–C–Me), 3.93 (m) $(O–CH_2–)$
$[MePhSn\{SSP(OPr^n)_2\}_2]$	1.82	80	0.89 (t) (O–C–C–Me), 1.64 (m) $(O–C–CH_2–)$, 3.84 (m) $(O–CH_2–)$
$[EtPhSn\{SSP(OPr^n)_2\}_2]$	2.1‡ (m)	—	0.87 (t) (O–C–C–Me), 1.66 (m)‡ $(O–C–CH_2–)$, 3.83 (m) $(O–CH_2–)$
$[MePhSn\{SSP(OPr^i)_2\}_2]$	1.82	80 (76)	1.24 (d) $(O–CMe_2)$, 4.52 (m) (O–CH)
$[EtPhSn\{SSP(OPr^i)_2\}_2]$	1.92 (m)	—	1.25 (d) $(O–CMe_2)$, 4.52 (m) (O–CH)
$[MePhSn\{SSP(OBu^n)_2\}_2]$	1.77	80 (76)	1.2 (m) $(O–C–CH_2CH_2CH_3)$, 3.88 (m) $(O–CH_2)$
$[EtPhSn\{SSP(OBu^n)_2\}_2]$	‡	—	0.87–1.89 (m)‡ $(O–C–CH_2CH_2CH_3)$, 3.95 (m) $(O–CH_2–)$
$[Me_2Sn(Cl)\{SSP(OEt)_2\}]$§	1.33	74.5 (71.5)	1.35 (t) (O–C–Me), 4.15 (m) $(O–CH_2–)$
$[Et_2Sn(Cl)\{SSP(OEt)_2\}]$	1.60 (m)	—	1.25 (t) (O–C–Me), 4.05 (m) $(O–CH_2–)$
$[MePhSn(Cl)\{SSP(OEt)_2\}]$	1.56	72	1.33 (t) (O–C–Me), 4.13 (m) $(O–CH_2–)$
$[EtPhSn(Cl)\{SSP(OEt)_2\}]$	1.88 (m)	—	1.39 (t) (O–C–Me), 4.18 (m) $(O–CH_2–)$
$[Ph_2Sn(Cl)\{SSP(OEt)_2\}]$		—	1.42 (t) (O–C–Me), 4.25 (m) $(O–CH_2–)$
$[Me_2Sn(Cl)\{SSP(OPr^i)_2\}]$‖	1.38	74	1.37 (d) $(O–C=Me_2)$, 4.66 (m) (O–CH)
$[Et_2Sn(Cl)\{SSP(OPr^i)_2\}]$	1.77 (m)	—	1.40 (d) $(O–C=Me_2)$, 4.77 (m) (O–CH)
$[Ph_2Sn(Cl)\{SSP(OPr^i)_2\}]$			1.31 (d) $(O–C=Me_2)$, 4.65 (m) (O–CH)
$[MePhSn(Cl)\{SSP(OPr^i)_2\}]$	1.51	79 (76)	1.32 (d) $(O–C=Me_2)$, 4.72 m (O–CH)
$[MePhSn(Cl)\{SSP(OBu^n)_2\}]$	‡		0.78–1.73‡ (m) $(O–C–CH_2CH_2CH_3)$, 4.02 (m) $(O–CH_2–)$
$[EtPhSn(Cl)\{SSP(OBu^n)_2\}]$	‡		0.81–1.74‡ (m) $(O–C–CH_2CH_2CH_3)$, 4.01 (m) $(O–CH_2–)$

**, triplet; d, doublet; m, multiplet.

*Ph–Sn resonances appeared as multiplet in the region δ7.30–8.20.

†Values in parentheses are $^2J(^{117}Sn–^1H)$, in the other case they could not be distinguished.

‡Ligand and Sn–R proton resonances merged together.

§For $[Me_2Sn\{SSP(OEt)_2\}_2]$ δ1.55, $^2J(^{119}Sn–^1H)$ 77 Hz and $^2J(^{117}Sn–^1H)$ 74.5 Hz.

‖For $[Me_2Sn\{SSP(OPr^i)_2\}_2]$ δ1.51, $^2J(^{119}Sn–^1H)$ 78 Hz and $^2J(^{117}Sn–^1H)$ 74 Hz.

correlate them with structural features have not been successful. The P–S and P=S stretching frequencies which can give some information about various structural possibilities, generally appear in the same region for free acids, their esters and also for their metal complexes where the ligand has been shown by X-ray diffraction studies to behave in a bidentate fashion [14, 15]. The absorptions appearing in the regions 630–690 and 510–555 cm^{-1} for the ligands and for the organotin (IV) complexes can be assigned as due to νP=S and νP–S vibrations, respectively [8, 9].

The bands appearing in the region 940–1060 and 720–820 cm^{-1} were assigned to ν(P)–O–C and νP–O–(C) modes, respectively. The Sn–C stretching vibrations were masked by νP–S vibrations and could not be assigned. The Sn–S vibrations may tentatively be assigned in the region 360–375 cm^{-1} [16]. The i.r. frequencies for our complexes are listed in Table 2.

NMR spectra

The ^1H NMR spectra of $[R(Ph)Sn\{SSP(OR'')_2\}_2]$ and $[RR'Sn(Cl)\{SSP(OR'')_2\}]$ were recorded in $CDCl_3$ and the resulting data are given in Table 3. The phenyl- and ethyltin proton resonances appeared in the range 7.30–8.20 and 1.60–2.10 ppm, respectively, as complex multiplets. The organic ester groups attached to phosphorus through oxygen showed expected integrations and peak multiplicities. The signal due to Sn–Me protons in the methyltin(IV) complexes is deshielded with respect to the one in the corresponding dichlorides. $^2J(^{117}Sn–^1H)$ and $^2J(^{119}Sn–^1H)$ for these complexes are in the range 72–80 Hz which is higher than the values reported for four coordinate methyltin(IV) complexes. This indicates the possibility of a higher coordination number of tin in our complexes. The ^2J(Sn–H) values for four-, five-, six- and seven-coordinate methyltin(IV) complexes have been reported in the range 60–116 Hz [8, 9, 17].

The two and three bond ($^{13}C–^{31}P$) NMR couplings have been observed for the organic ester group attached to phosphorus through oxygen, in the ^{13}C NMR spectra of these complexes (Table 4). The ^{13}C NMR chemical shifts appear to be independent of the substituents on tin as they remain almost unchanged on varying the R group or the number of dialkyldithiophosphate moieties on tin. $^1J(^{117}Sn/^{119}Sn–^{13}C)$ could not be observed for all RR′Sn(IV) complexes, mainly due to the relatively low intensity of the Sn–C signal; when observed its magnitude increased for Me(Ph)Sn(IV) complexes compared with that of the corresponding $Me_2Sn(IV)$ complexes [9].

The ^{31}P and ^{119}Sn NMR data for these complexes are summarised in Table 5. The $^{31}P\{^1H\}$ NMR chemical shifts for both the series of complexes occur

Table 4. ^{13}C NMR data for $[RR'Sn\{SSP(OR'')_2\}_2]$ and $[RR'Sn(Cl)\{SSP(OR'')_2\}]$ in $CDCl_3$ at room temperature

	δP–OR″		δSn–R	
Complex	P–O–<u>C</u><*	P–O–C† (C(2), C(3) and C(4))	Sn–Me(Et)‡	Sn–Ph§
$[MePhSn\{SSP(OEt)_2\}_2]$	64.0	15.9	12.8 (656)	143.8, 135.3 (59), 130.0 (17), 128.7 (84)
$[Ph_2Sn\{SSP(OEt)_2\}_2]$	63.5	15.4	—	143.0, 135.5 (57), 129.8 (18), 128.4 (88)
$[MePhSn\{SSP(OPr^n)_2\}_2]$	68.9	22.8, 9.6	12.9	144.4, 134.9 (59), 129.2 (18), 128.0 (85)
$[Me_2Sn\{SSP(OPr^i)_2\}_2]$	72.9	23.2	13.7 (555)	
$[MePhSn\{SSP(OPr^i)_2\}_2]$	73.1	23.6	13.8 (590)	145.2, 135.4 (58), 129.7, 128.4 (85)
$[MePhSn\{SSP(OBu^n)_2\}_2]$	67.1	31.5, 18.3, 13.1	12.6	144.3, 134.9 (58), 129.3 (17), 128.0 (84)
$[Me_2Sn(Cl)\{SSP(OEt)_2\}]$	64.3	15.6	10.9 (555)	
$[Ph_2Sn(Cl)\{SSP(OEt)_2\}]$	64.8	15.4	—	141.7, 135.4 (63), 130.4 (19), 128.8 (87)
$[MePhSn(Cl)\{SSP(OEt)_2\}]$	64.7	15.6	11.4	142.1, 135.3 (64), 130.5, 128.8 (85)
$[EtPhSn(Cl)\{SSP(OEt)_2\}]$	64.7	15.6	24.4, 9.8	142.5, 135.6 (60), 130.3, 128.8 (77)
$[Me_2Sn(Cl)\{SSP(OPr^i)_2\}]$	74.3	23.6	11.7	—
$[MePhSn(Cl)\{SSP(OPr^i)_2\}]$	74.2	23.0	11.1	142.1, 135.0 (62), 130.0 (16), 128.4 (84)
$[Ph_2Sn(Cl)\{SSP(OPr^i)_2\}]$	74.7	23.1	—	141.9, 135.4 (63), 130.3 (20), 128.7 (90)

* $^2J(^{31}P–O–^{13}C) = \sim 7$ Hz.

† Signal appearing at higher frequency showed $^3J(^{31}P–O–C–^{13}C) = 4–8$ Hz while other appeared as a singlet.

‡ Due to relatively low intensity of the Sn–C signal $^1J(^{117/119}Sn–^{13}C)$ could be resolved in a few cases only.

§ The signal appearing at higher frequency with relatively low intensity is due to Sn–C(1) and ^1J(Sn–C) could not be observed. Remaining three resonances are due to *o*, *m* and *p* carbons and showed *J*(Sn–C), respective values are given in parentheses.

Table 5. $^{31}P\{^1H\}$ and $^{119}Sn\{^1H\}$ NMR data for $[RR'Sn(Cl)\{SSP(OR'')_2\}]$ and $[RR'Sn\{SSP(OR'')_2\}_2]$ complexes in $CDCl_3$

	$^{31}P\{^1H\}$ NMR data		$^{119}Sn\{^1H\}$ NMR data	
Complex	δ*	$^2J(Sn\text{–}P)$†	δ‡	$^2J(^{119}Sn\text{–}^{31}P)$
$[Me_2Sn\{SSP(OEt)_2\}_2]$	85.6	—	−160§	—
$[Et_2Sn\{SSP(OEt)_2\}_2]$	87.4	—	−164	—
$[Ph_2Sn\{SSP(OEt)_2\}_2]$	91.4	—	−241	—
$[MePhSn\{SSP(OEt)_2\}_2]$	86.4	—	−181	—
$[EtPhSn\{SSP(OEt)_2\}_2]$	87.4‖	—	−219	—
$[Me_2Sn\{SSP(OPr^i)_2\}_2]$	82.4	—	−162§	—
$[Et_2Sn\{SSP(OPr^i)_2\}_2]$	83.2	—	−170	—
$[Ph_2Sn\{SSP(OPr^i)_2\}_2]$¶	88.6	—	−268	—
$[MePhSn\{SSP(OPr^i)_2\}_2]$	81.5	—	−198	—
$[EtPhSn\{SSP(OPr^i)_2\}_2]$	84.5	—	−234	—
$[MePhSn\{SSP(OPr^n)_2\}_2]$	87.1	—	−192	—
$[EtPhSn\{SSP(OPr^n)_2\}_2]$	88.2	—	−227	—
$[MePhSn\{SSP(OBu^n)_2\}_2]$	85.1	—	−198	—
$[EtPhSn\{SSP(OBu^n)_2\}_2]$	86.3	—	−230	—
$[Me_2Sn(Cl)\{SSP(OEt)_2\}]$	82.0‖	—	−62**	—
$[Et_2Sn(Cl)\{SSP(OEt)_2\}]$	82.5‖	—	−75**	—
$[Ph_2Sn(Cl)\{SSP(OEt)_2\}]$	88.7	39	−233	39
$[MePhSn(Cl)\{SSP(OEt)_2\}]$	81.0	41	−143	40
$[EtPhSn(Cl)\{SSP)(OEt)_2\}]$	81.6	54	−154	51
$[Me_2Sn(Cl)\{SSP(OPr^i)_2\}]$	77.5‖	—	−73**	—
$[Et_2Sn(Cl)\{SSP(OPr^i)_2\}]$	78.5	36	−85	47
$[Ph_2Sn(Cl)\{SSP(OPr^i)_2\}]$¶	84.5	39	−244	39
$[MePhSn(Cl)\{SSP(OPr^i)_2\}]$	78.9	38	−156	39
$[MePhSn(Cl)\{SSP(OBu^n)_2\}]$	81.5‖	—	−146**	—
$[EtPhSn(Cl)\{SSP(OBu^n)_2\}]$	82.0	52	−157	54

*With reference to external 85% H_3PO_4 neat, the resonance of which was observed in external lock mode. Spectra of complexes were recorded in $CDCl_3$ with internal lock on D.

†Individual couplings $^2J(^{117}Sn\text{–}^{31}P)$ and $^2J(^{119}Sn\text{–}^{31}P)$ could not be distinguished.

‡With reference to external 33% Me_4Sn in C_6D_6 (v/v).

§From Ref. [10].

‖Base of the signal broadened.

¶Complex showed some impurities in its spectrum.

**Signal broadened, thus $^2J(^{119}Sn\text{–}^{31}P)$ could not be resolved.

2–13 ppm downfield from the respective chemical shift in the corresponding ligand and are in the following order of increasing field strength:

$$[(R''O)_2PSSH] > [RR'Sn(Cl)\{SSP(OR'')_2\}] > [RR'Sn\{SSP(OR'')_2\}_2].$$

Such small changes can be attributed to bond polarity, to the geometry of the molecule and to the electronic properties of alkyl or phenyl groups on tin which affect π-bonding with phosphorus [9, 18]. Interestingly the chloro complexes showed $^2J(Sn\text{–}P)$ 36–54 Hz while such couplings were not observed in the bis complexes. The $^2J(Sn\text{–}P)$ were also observed in the ^{31}P NMR spectra of penta-coordinate $[Ph_2SnCl_2 \cdot EPPh_3]$ (E = O or S) complexes [19].

^{119}Sn NMR spectroscopy has been used in recent years to elucidate the structure of organotin compounds in solution, since the ^{119}Sn chemical shifts have been shown to be sensitive to the changes in (i) coordination number of tin, (ii) the bond angles of tin, (iii) the $d\pi$-$p\pi$ bonding effect and (iv) the nature of the substituents [9, 20–22]. The $^{119}Sn\{^1H\}$ NMR spectra of bis complexes displayed a single line. Since the mono-chloro complexes showed $^2J(^{119}Sn\text{–}^{31}P)$, the $^{119}Sn\{^1H\}$ resonance for this series of complexes appeared as a doublet, however in a few cases a broad singlet was observed. It is apparent from Table 5 that substitution by an ethyl or phenyl group for methyl on tin results in increased shielding of the tin nucleus as has been observed for other organotin compounds [20].

The $^{119}Sn\{^1H\}$ chemical shifts for our complexes occur in the range −62 to −241 ppm which are at much higher field (190–212 ppm for mono-chloro complexes and 230–300 ppm for bis derivatives) than those of the corresponding dichlorides and other four coordinate diorganotin(IV) compounds. This suggests that tin has acquired a higher coordination number (> 4) in these complexes. The chemical shifts of mono-chloro complexes may be interpreted in terms of five coordinate tin. The $^{119}Sn\{^1H\}$ chemical shifts for five coordinate diorganotin(IV) alkoxides, $[R_2Sn(OR')_2]$ (R = Me, Et or Bu; R' = Me, Et, Pr, Bu) and dithiocarbamate complexes, $[Me_2Sn(Cl)(SSCNEt_2)]$, have been reported in the range −72 to −181 and at −204 ppm, respectively [8, 23]. The five-coordinate organotin(IV) compounds generally adopt a trigonal bipyramidal geometry, and a similar structure for $[RR'Sn(Cl)\{SSP(OR'')_2\}]$ can be proposed. Following Bent's rule the electronegative substituents occupy the axial positions preferentially. This gives equatorial axial chelation of the $(R''O)_2PSS$ moiety in trigonal bipyramidal structures, the small equatorial–axial angle being suited to a ligand with a small bite.

The $^{119}Sn\{^1H\}$ resonance for bis derivatives moves further to higher field than that of the corresponding mono-chloro complexes and shielding increases as the number of alkyl groups on tin increases. Thus shielding was minimum for diphenyl complexes (8–22 ppm) and was maximum (~ 100 ppm) for dialkyl derivatives.

For six-coordinated diorganotin compounds the ^{119}Sn chemical shifts have been reported at much higher fields [22] than the shifts observed for our complexes. For isoelectronic dithiocarbamate complexes, such as $[Me_2Sn(dtcR)_2]$ (R = Me or Et; dtcR = $SSCNR_2$) the tin-119 NMR chemical shifts occur at ~ -335 ppm [22–24]. Recently some six coordinated diorganotin(IV) complexes have been reported [9, 22, 25] in which $\delta(^{119}Sn)$ has been found to occur 270–350 ppm to higher field than the corresponding dichlorides. The observed values of $\delta(^{119}Sn)$ for $[RR'Sn\{SSP(OR'')_2\}_2]$ can, therefore, be interpreted in terms of six-coordinate tin.

The diphenyl complexes, $[Ph_2Sn\{SSP(OEt)_2\}_2]$ and $[Ph_2Sn\{SSP(OPr^i)_2\}_2]$, have been shown by X-ray diffraction studies to possess anisobidentate and symmetrical bidentate ligand moieties, respectively [6, 7] and their different *QS* values in Moessbauer spectra [8] also indicated the existence of different bonding modes. A difference of 27 ppm between the ^{119}Sn chemical shifts of above two compounds appears to indicate the presence of different modes of bonding; nevertheless such differences in $\delta(^{119}Sn)$ may be attributed to the electronic properties of the R'' group. As is apparent from Table 5 shielding of the ^{119}Sn signal increases (2–17 ppm) with the increasing order of +I effect of R'' ($Pr^i > Bu^n > Pr^n >$ Et) when R, R' and X are constant in $[RR'SnX\{SSP(OR'')_2\}]$ [X = Cl or $SSP(OR'')_2$].

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