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Diorganotin(IV) Dialkoxyphosphinothioates: Synthesis and Characterization

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Diorganotin(IV) dialkoxyphosphinothioates of the general formula, $[R_2Sn\{OSP(OR')_2\}_2]$ (R=Me, Et, Pr^n, Bu^n, Bu^t; R'=Me, Pr^n or Bu^n), $[R_2Sn(Cl)\{OSP(OR')_2\}]$ (R=Me or Bu^t; R'=Pr^n or Bu^n), $([R_2Sn\{OSP(OR')_2\}]_2O)_2$ (R=Me, Pr^n; R'=Pr^n) and $[Bu^t{}_2Sn(\mu\text{-}OH)\{OSP(OR')_2\}]_2$ (R'=Me or Pr^n) have been synthesized. All of the complexes were characterized by elemental analyses as well as IR and multinuclear NMR (^{1}H, ^{13}C, ^{31}P, and ^{119}Sn) spectroscopy. The stereochemistry of these complexes is discussed based on the NMR data.

Organotin complexes of phosphorus-based acids have been of interest for more than three decades due to their rich reaction chemistry, diverse structural features and utility as biocides.[1] These complexes adopt various structures, varying between a discrete monomeric tetrahedral configuration and polymeric or complex cluster geometries. Both the number and the nature of organic groups on tin and phosphorus as well as the nature of donor atoms (O,S,Se) on the latter contribute to this wide structural diversity. There is a paucity of data describing the structural features of diorganotin(IV) complexes of dialkylphosphorothioic acids $[(R'O)_2POSH]$.[2] Recently, we have reported some diorganotin(IV) complexes with diethylphosphorothioic acid.[3] In order to investigate the generality of $(R'O)_2POS^-$ ligand bonding towards the $R_2Sn(IV)$ moiety and in pursuance of our interest in organotin(IV) complexes with phosphorus-based acids,[3,4] we prepared a series of complexes with different dialkylphosphorothioic acids. The results of this work are reported in this paper.

Experimental

Diorganotin dichlorides,[5] $[(R_2SnCl)_2O]_2$,[6] and $(R'O)_2POH$ (R'=Pr^n and Bu^n),[7] were prepared according to literature methods. Dimethylphosphonate was obtained from Aldrich. Ammonium salts of the dialkylphosphorothioic acids were prepared by a previously reported modified method.[8] To a cooled (0 °C) diethyl ether solution of dimethylphosphonate (^{31}P δ=10.3 ppm) one equivalent of sulfur was added. Ammonia gas was bubbled rapidly, whereupon a white thick oily layer formed on the bottom of the flask along with the dissolution of sulfur. The oily layer solidified after 2—3 h upon warming to room temperature. The mixture was filtered, washed with diehtyl ether and dried in a vacuum.

The dibutyl and dipropyl phosphorothioic acids were prepared by the reaction of $(RO)_2POH$ (R=Pr^n and Bu^n) with sulfur in the presence of triethylamine;[8] the free acids were liberated by the action of dilute HCl. Ammonium salts were prepared by bubbling ammonia gas through a hexane solution of the acid.

IR spectra were recorded as neat liquids or as Nujol mulls between CsI optics on a Perkin–Elmer (577 or 783) spectrometer. The ^{1}H (80 or 200 MHz) and ^{13}C{^{1}H} (20 or 50 MHz) NMR spectra were recorded on a Varian FT-80A or Bruker AC-200 NMR spectrometer. ^{31}P{^{1}H} NMR spectra were recorded on a Varian FT-80A spectrometer operating at 32.203 MHz. The ^{119}Sn{^{1}H} NMR spectra were recorded on a Varian FT-80A spectrometer (operating at 29.604 MHz) or XL-300 (operating at 111.82 MHz). Chemical shifts are reported in ppm from the internal chloroform peak (δ=7.26 ppm for ^{1}H and 77.0 ppm for ^{13}C), external 85% H_3PO_4 (for ^{31}P) and 33% Me_4Sn in C_6D_6 (for ^{119}Sn). Microanalyses were performed by the Analytical Chemistry Division of BARC. Phosphorus and sulfur were estimated by reported methods.[9]

Preparation of $[Bu^t{}_2Sn\{OSP(OPr^n)_2\}_2]$. To a benzene suspension of $[NH_4][OSP(OPr^n)_2]$ (3.061 g, 14.2 mmol) a solution of $Bu^t{}_2SnCl_2$ (2.161 g, 7.1 mmol) in benzene (15 cm^3) was added and stirred vigorously at room temperature for 4 h under a nitrogen atmosphere. The precipitated ammonium chloride was filtered off through a sintered funnel. The filtrate was concentrated in vacuo, leaving an oily liquid (4.25 g, 95%). Similarly, other $[R_2Sn\{OSP(OR')_2\}_2]$ were synthesized. Analytical data for these complexes are given in Table 1.

Preparation of $[Bu^t{}_2Sn(Cl)\{OSP(OPr^n)_2\}]$. To a benzene solution (15 cm^3) of $[Bu^t{}_2Sn\{OSP(OPr^n)_2\}_2]$ (1.13 g, 1.8 mmol) a solution of $Bu^t{}_2SnCl_2$ (0.55 g, 1.8 mmol) was added; the mixture was then stirred at room temperature for 3 h. The solvent was stripped off in vacuo to give a colorless oil (1.60 g, 95%). Other monochloro derivatives were similarly prepared.

Preparation of $([Me_2Sn\{OSP(OPr^n)_2\}]_2O)_2$. To an acetone solution (20 cm^3) of $[Me_2Sn\{OSP(OPr^n)_2\}_2]$ (1.50 g, 2.76 mmol) was added an aqueous solution of sodium

Table 1. Melting Point and Analytical Data for Diorganotin(IV) Dialkoxyphosphinothioate Complexes

Complex	Mp	% Analysis Found (Calcd)			
	°C	C	H	P	S
$[Me_2Sn\{OSP(OMe)_2\}_2]$	—	15.9 (16.7)	4.0 (4.2)	14.1 (14.4)	14.1 (14.9)
$[Et_2Sn\{OSP(OMe)_2\}_2]$	—	20.1 (20.9)	4.5 (4.8)	13.9 (13.5)	—
$[Pr^n{}_2Sn\{OSP(OMe)_2\}_2]$	—	23.7 (24.7)	5.1 (5.4)	12.9 (12.7)	12.9 (13.2)
$[Bu^n{}_2Sn\{OSP(OMe)_2\}_2]$	—	27.1 (28.0)	5.6 (5.9)	11.4 (12.0)	—
$[Bu^t{}_2Sn\{OSP(OMe)_2\}_2]$	—	27.4 (28.0)	5.7 (5.9)	—	—
$[Me_2Sn\{OSP(OPr^n)_2\}_2]$	—	30.7 (31.0)	6.1 (6.3)	11.0 (11.4)	11.0 (11.8)
$[Et_2Sn\{OSP(OPr^n)_2\}_2]$	—	33.5 (33.6)	6.5 (6.7)	10.7 (10.9)	11.0 (11.2)
$[Pr^n{}_2Sn\{OSP(OPr^n)_2\}_2]$	—	36.1 (36.1)	7.2 (7.1)	10.6 (10.3)	10.2 (10.7)
$[Bu^n{}_2Sn\{OSP(OPr^n)_2\}_2]$	—	38.0 (38.3)	5.6 (7.4)	9.2 (9.9)	10.0 (10.2)
$[Bu^t{}_2Sn\{OSP(OPr^n)_2\}_2]$	—	38.8 (38.3)	7.8 (7.4)	9.9 (9.9)	10.2 (10.2)
$[Et_2Sn\{OSP(OBu^n)_2\}_2]$	—	—	—	10.2 (9.9)	10.0 (10.2)
$[Pr^n{}_2Sn\{OSP(OBu^n)_2\}_2]$	—	40.8 (40.3)	7.0 (7.7)	9.5 (9.5)	9.8 (9.8)
$[Bu^t{}_2Sn\{OSP(OBu^n)_2\}_2]$	—	—	—	9.2 (9.1)	9.1 (9.4)
$[Me_2Sn(Cl)OSP(OPr^n)_2]$	85	25.7 (25.2)	5.3 (5.3)	8.3 (8.1)	8.3 (8.4)
$[Bu^t{}_2Sn(Cl)OSP(OPr^n)_2]$	—	35.2 (36.1)	6.5 (6.9)	6.7 (6.7)	—
$[Bu^t{}_2Sn(Cl)OSP(OBu^n)_2]$	—	39.1 (38.9)	7.5 (7.4)	6.4 (6.3)	6.5 (6.5)
$([Me_2Sn\{OSP(OPr^n)_2\}]_2O)_2$	112	27.1 (27.2)	5.6 (5.7)	9.3 (8.8)	9.8 (9.1)
$([Pr^n{}_2Sn\{OSP(OPr^n)_2\}]_2O)_2$	107	34.6 (35.1)	6.8 (6.9)	7.9 (7.6)	7.3 (7.8)
$[Bu^t{}_2Sn(\mu\text{-}OH)\{OSP(OMe)_2\}]_2$	152	30.5 (30.7)	6.3 (6.4)	8.2 (7.9)	8.1 (8.2)
$[Bu^t{}_2Sn(\mu\text{-}OH)\{OSP(OPr^n)_2\}]_2$	176	37.1 (37.6)	7.3 (7.4)	7.4 (6.9)	7.9 (7.2)

hydroxide (5.6 cm^3, 0.5 M, M=mol dm^{-3}). The resulting mixture was stirred for 1 h. To this, distilled water (20 cm^3) was added, whereupon a white precipitate formed which was filtered, washed several times with water and dried in vacuum (1.54 g, 79%). This was recrystallized from a benzene–hexane mixture (1 : 1) at 0 °C as a colorless crystalline product.

Preparation of $([Pr^n{}_2Sn\{OSP(OPr^n)_2\}]_2O)_2$. To a benzene suspension of $[NH_4][OSP(OPr^n)_2]$(0.88 g, 4.1 mmol), a solution of $[(Pr^n{}_2SnCl)_2O]_2$ (1.02 g, 1.02 mmol) was added. The reaction mixture was stirred at room temperature for 4 h. The precipitated ammonium chloride was filtered off and the filtrate was dried in vacuum to give a white solid (1.66 g, 98%), which was recrystallized from a benzene–hexane mixture.

Preparation of $[Bu^t{}_2Sn(\mu\text{-}OH)\{OSP(OPr^n)_2\}]_2$. To an acetone solution (20 cm^3) of $[Bu^t{}_2Sn\{OSP(OPr^n)_2\}_2]$ (2.11 g, 3.37 mmol) and aqueous solution of sodium hydroxide (6.8 cm^3, 0.5 M) was added dropwise with vigorous stirring for 1 h. The formed white precipitate was filtered, washed with water and dried in vacuum (1.41 g, 94%). This was recrystallized from an *n*-propanol–hexane (1 : 9) mixture at 0 °C. Similarly, $[Bu^t{}_2Sn(\mu\text{-}OH)\{OSP(OMe)_2\}]_2$ was synthesized and recrystallized from dichloromethane in 88% yield.

Results and Discussion

Diorganotin(IV) dialkoxyphosphinothioates were synthesized by following reaction routes (Eqs. 1, 2, 3, 4, and 5):

Table 2. ^{1}H NMR Data of Diorganotin(IV) Dialkoxyphosphinothioate Complexes

Complex	^{1}H NMR data$^{a)}$
$[\mathrm{NH_4}](\mathrm{OSP(OMe)_2}]$	3.59 (d, J=12.7 Hz, OMe)
$[\mathrm{Me_2Sn\{OSP(OMe)_2\}_2}]$	1.16 (s, ^2J(Sn–H)=86 Hz, SnMe); 3.63 (d, J=13 Hz, OMe)
$[\mathrm{Et_2Sn\{OSP(OMe)_2\}_2}]$	1.30—1.74 (m, EtSn); 3.61 (d, J=13 Hz, OMe)
$[\mathrm{Pr^{\mathit{n}}{}_2Sn\{OSP(OMe)_2\}_2}]$	1.02 (t, J=7 Hz), 1.74 (br, m) [PrSn]; 3.68 (d, J=13 Hz, OMe)
$[\mathrm{Bu^{\mathit{n}}{}_2Sn\{OSP(OMe)_2\}_2}]$	0.93 (t, J=7 Hz), 1.36—1.87 (m) [BuSn]; 3.71 (d, J=13 Hz, OMe)
$[\mathrm{Bu^{\mathit{t}}{}_2Sn\{OSP(OMe)_2\}_2}]$	1.46 (s, ^3J(Sn–H)=122 Hz, SnBu^t); 3.74 (d, J=13 Hz, OMe)
$[\mathrm{NH_4}][\mathrm{OSP(OPr^{\mathit{n}})_2}]$	0.92 (t, J=7 Hz, OCCMe); 1.66 (m, OC–CH$_2$–); 3.87 (m, OCH$_2$–)
$[\mathrm{Me_2Sn\{OSP(OPr^{\mathit{n}})_2\}_2}]$	0.92 (t, J=7 Hz, OCCMe); 1.16 (s, ^{2}J(Sn–H)=85 Hz, SnMe); 1.66 (q, OC–CH$_2$–); 3.93 (q, OCH$_2$–)
$[\mathrm{Et_2Sn\{OSP(OPr^{\mathit{n}})_2\}_2}]$	0.91 (t, J=7 Hz, OCCMe); 1.39—1.87 (m, EtSn+OCCH$_2$); 3.91 (m, OCH$_2^-$)
$[\mathrm{Pr^{\mathit{n}}{}_2Sn\{OSP(OPr^{\mathit{n}})_2\}_2}]$	0.89—1.82 (m, PrSn+OCCH$_2$Me); 3.92 (m, OCH$_2^-$)
$[\mathrm{Bu^{\mathit{n}}{}_2Sn\{OSP(OPr^{\mathit{n}})_2\}_2}]$	0.88 (t, J=7 Hz); 0.98—1.81 (m) [BuSn+OCCH$_2$Me]; 3.91 (m, OCH$_2^-$)
$[\mathrm{Bu^{\mathit{t}}{}_2Sn\{OSP(OPr^{\mathit{n}})_2\}_2}]$	0.93 (t, J=7 Hz, OCCMe); 1.47 (s, ^3J(Sn–H)=122 Hz, Bu^{t}Sn); 1.70 (m, OCCH$_2^-$); 3.97 (m, OCH$_2^-$)
$[\mathrm{NH_4}][\mathrm{OSP(OBu^{\mathit{n}})_2}]$	0.93 (t, J=7 Hz, OCCCMe); 1.40 (m, OCCCH$_2$); 1.63 (m, OCCH$_2^-$), 3.92 (m, OCH$_2$)
$[\mathrm{Et_2Sn\{OSP(OBu^{\mathit{n}})_2\}_2}]$	0.92 (t, J=7 Hz, OCCCMe); 1.34—1.85 (m, EtSn+OCCH$_2$CH$_2^-$); 3.98 (q, OCH$_2^-$)
$[\mathrm{Pr^{\mathit{n}}{}_2Sn\{OSP(OBu^{\mathit{n}})_2\}_2}]$	0.93—1.93 (m, Pr^{n}Sn+OCCH$_2$CH$_2$Me); 4.00 (m, OCH$_2$–)
$[\mathrm{Bu^{\mathit{t}}{}_2Sn\{OSP(OBu^{\mathit{n}})_2\}_2}]$	0.88 (t, J=7 Hz, OCCCMe); 1.38 (m, OCCCH$_2^-$), 1.44 (s, ^3J(Sn–H)=122 Hz, Bu^{t}Sn); 1.62 (m, OCCH$_2^-$); 3.98 (q, OCH$_2^-$)
$[\mathrm{Me_2Sn(Cl)\{OSP(OPr^{\mathit{n}})_2\}}]$	0.94 (t, J=7 Hz, OCCMe); 1.21 (s, ^2J(Sn–H)=76 Hz, MeSn); 1.70 (m, OCCH$_2^-$); 3.99 (m, OCH$_2^-$)
$[\mathrm{Bu^{\mathit{t}}{}_2Sn(Cl)\{OSP(OPr^{\mathit{n}})_2\}}]$	0.93 (t, J=7 Hz, OCCMe); 1.44 (s, ^3J(Sn–H)=120 Hz, Bu^{t}Sn); 1.71 (m, OCCH$_2^-$); 3.94 (m, OCH$_2^-$)
$[\mathrm{Bu^{\mathit{t}}{}_2Sn(Cl)\{OSP(OBu^{\mathit{n}})_2\}}]$	0.94 (t, J=7 Hz, OCCCMe); 1.41 (m, OCCCH$_2^-$); 1.50 (s, ^3J(Sn–H)=122 Hz, Bu^{t}Sn), 1.73 (m, OCCH$_2^-$); 4.13 (m, OCH$_2^-$)
$([\mathrm{Me_2Sn\{OSP(OPr^{\mathit{n}})_2\}}]_2\mathrm{O})_2$	1.10 (s), 1.05 (s) (SnMe); 0.92 (t, J=7 Hz, OCCMe); 1.65 (m, OCCH$_2^-$); 3.88 (m, OCH$_2^-$)
$([\mathrm{Pr^{\mathit{n}}{}_2Sn\{OSP(OPr^{\mathit{n}})_2\}}]_2\mathrm{O})_2$	0.92 (m), 1.57—1.82 (m) [Pr^{n}Sn+OCCH$_2$Me); 3.86 (m, OCH$_2^-$)
$[\mathrm{Bu^{\mathit{t}}{}_2Sn(\mu\text{-}OH)\{OSP(OMe)_2\}}]_2$	1.39 (s, ^3J(Sn–H)=117 Hz, Bu^{t}Sn); 3.65 (d, J=13 Hz, OMe)
$[\mathrm{Bu^{\mathit{t}}{}_2Sn(\mu\text{-}OH)\{OSP(OPr^{\mathit{n}})_2\}}]_2$	0.93 (t, J=7 Hz, OCCMe); 1.41 (s, ^3J(Sn–H)=114 Hz, Bu^{t}Sn); 1.68 (m, OCCH$_2^-$); 3.91 (m, OCH$_2^-$)

a) s=singlet, d=doublet, t=triplet, q=quartet, m=multiplet, br=broad.

$$\mathrm{R_2SnCl_2} + 2[\mathrm{NH_4}][\mathrm{OSP(OR')_2}] \longrightarrow [\mathrm{R_2Sn\{OSP(OR')_2\}_2}] + 2\mathrm{NH_4Cl} \qquad (1)$$

$$\mathrm{R_2SnCl_2} + [\mathrm{R_2Sn\{OSP(OR')_2\}_2}] \longrightarrow 2[\mathrm{R_2Sn(Cl)\{OSP(OR')_2\}}] \qquad (2)$$

$$[(\mathrm{Pr^{\mathit{n}}{}_2SnCl})_2\mathrm{O}]_2 + 4[\mathrm{NH_4}][\mathrm{OSP(OPr^{\mathit{n}})_2}] \longrightarrow ([\mathrm{Pr^{\mathit{n}}{}_2Sn\{OSP(OPr^{\mathit{n}})_2\}}]_2\mathrm{O})_2 + 4\mathrm{NH_4Cl} \qquad (3)$$

$$4[\mathrm{Me_2Sn\{OSP(OPr^{\mathit{n}})_2\}_2}] + 4\mathrm{NaOH} \longrightarrow ([\mathrm{Me_2Sn\{OSP(OPr^{\mathit{n}})_2\}}]_2\mathrm{O})_2 + 4\mathrm{NaOSP(OPr^{\mathit{n}})_2} + 2\mathrm{H_2O} \qquad (4)$$

$$2[\mathrm{Bu^{\mathit{t}}{}_2Sn\{OSP(OR')_2\}_2}] + 2\mathrm{NaOH} \longrightarrow [\mathrm{Bu^{\mathit{t}}{}_2Sn(\mu\text{-}OH)\{OSP(OR')_2\}}]_2 + 2\mathrm{NaOSP(OR')_2} \qquad (5)$$

(R = Me, Et, Pr^n, Bu^n or Bu^t; R$'$ = Me, Pr^n or Bu^n).

The bis complexes, $[\mathrm{R_2Sn\{OSP(OR')_2\}_2}]$ are colorless viscous liquids which solidify upon being kept at room temperature for a few days. Thus, all of the spectroscopic measurements were carried out on freshly prepared samples. The hydroxo-$[\mathrm{Bu^{\mathit{t}}_2Sn(\mu\text{-}OH)\{OSP(OR')_2\}}]_2$ and oxo-$([\mathrm{R_2Sn\{OSP(OPr^{\mathit{n}})_2\}}]_2\mathrm{O})_2$ complexes are white crystalline solids. All of these complexes are soluble in common organic solvents.

IR Spectra. The infrared spectra of these complexes exhibited strong bands in the 1025—1180 and 935—1020 cm^{-1} regions which were assigned to ν(P)–O–C and νP–O–(C), respectively.[10] The bands in the region 520—640 cm^{-1} were assigned to νSn–C and νP–S absorptions. The IR spectra of $[\mathrm{Bu^{\mathit{t}}{}_2Sn(\mu\text{-}OH)\{OSP(OR')_2\}}]_2$ displayed broad absorptions at 3160 (R$'$ = Me) and 3120 (R$'$ = Pr^n) cm^{-1}, attributable to νOH stretchings.

NMR Spectra. **(1) $[\mathrm{R_2Sn\{OSP(OR')_2\}_2}]$:** The ^{1}H NMR spectra of bis complexes, $[\mathrm{R_2Sn\{OSP(OR')_2\}_2}]$, showed the expected integration and peak multiplicities (Table 2). The $^2J(^{119}\mathrm{Sn}\text{–}^1\mathrm{H})$ values for dimethyltin complexes were ca. 85 Hz, indicating hexacoordination for these complexes.[4a)] The magnitude of $^3J(^{119}\mathrm{Sn}\text{–}^1\mathrm{H})$ for Bu$^t{}_2$Sn complexes was 122 Hz, which appears to be unaffected by the nature of the ligand. The ^{13}C{^{1}H} NMR spectra of bis complexes

Table 3. $^{13}C\{^1H\}$, $^{31}P\{^1H\}$, and $^{119}Sn\{^1H\}$ NMR[a] Data for Diorganotin(IV) Dialkoxyphosphinothioate Complexes

Complex	^{119}Sn	^{31}P	^{13}C NMR data in ppm	
	δ in ppm	δ in ppm	Sn–R carbons	Ligand carbons
$[NH_4][(OSP(OMe)_2]$	—	59.1	—	—
$[Me_2Sn\{OSP(OMe)_2\}_2]$	−199 (br)	56.6	11.0 (s)	53.7 (d, J = 5.7 Hz)
$[Et_2Sn\{OSP(OMe)_2\}_2]$	—	54.0	9.3 (C-2); 22.7 (C-1)	53.8 (d, J = 5.9 Hz)
$[Pr^n{}_2Sn\{OSP(OMe)_2\}_2]$	−174 (br)	54.3	17.6 (C-3); 18.3 (C-2); 32.2 (C-1)	53.7 (d, J = 5.9 Hz)
$[Bu^n{}_2Sn\{OSP(OMe)_2\}_2]$	−174 (br)	54.3	13.1 (C-4); 25.8 (C-3); 26.5 (C-2); 29.5 (C-1)	53.8 (d, J = 5.9 Hz)
$[Bu^t{}_2Sn\{OSP(OMe)_2\}_2]$	—	53.2	29.8 (C-2); 46.1 (C-1)	54.3 (d, J = 6.4 Hz)
$[NH_4][OSP(OPr^n)_2]$	—	54.8	—	—
$[Me_2Sn\{OSP(OPr^n)_2\}_2]$	−116 (br) ($\Delta_{1/2}$ = 1934 Hz)	46.6[b]	10.3 (s)	10.1 (C-3); 24.4 (d, J = 7.9 Hz, C-2); 69.0 (d, J = 5.3 Hz, C-1)
$[Et_2Sn\{OSP(OPr^n)_2\}_2]$	—	46.0[b]	—	—
$[Pr^n{}_2Sn\{OSP(OPr^n)_2\}_2]$	—	46.3[b]	17.7 (C-3); 18.5 (C-2); 31.7(C-1)	10.0 (C-3); 23.4 (d, J = 7.9 Hz, C-2); 69.0 (d, J = 6.9 Hz, C-1)
$[Bu^n{}_2Sn\{OSP(OPr^n)_2\}_2]$	−132 ($\Delta_{1/2}$ = 1182 Hz)	46.1[b]	13.5 (C-4); 26.3 (C-3); 26.9 (C-2); 29.2 (C-1)	10.0 (C-3); 23.4 (d, J = 5.6 Hz, C-2); 68.9 (br, C-1)
$[Bu^t{}_2Sn\{OSP(OPr^n)_2\}_2]$	−204 (t, ^2J(Sn–P) = 86 Hz)	46.6	29.8 (C-2), 45.3 (C-1)	10.1 (C-3); 23.4 (br, C-2); 69.2 (br, C-1)
$[NH_4][OSP(OBu^n)_2]$	—	57.3	—	—
$[Et_2Sn\{OSP(OBu^n)_2\}_2]$	−145 ($\Delta_{1/2}$ = 3173 Hz)	48.6	—	—
$[Pr^n{}_2Sn\{OSP(OBu^n)_2\}_2]$	−143 (br)	48.8	—	—
$[Bu^t{}_2Sn\{OSP(OBu^n)_2\}_2]$	−202 (t,^2J(Sn–P) = 89 Hz)	49.0	29.7 (C-2); 45.2 (C-1)	13.5 (C-4); 18.7 (C-3); 32.0 (d, J = 7.8 Hz, C-2); 67.4 (d, J = 6.7 Hz, C-1)
$[Me_2Sn(Cl)\{OSP(OPr^n)_2\}]$	−47 (br) ($\Delta_{1/2}$ = 2044 Hz)	37.3	9.1 (s)	10.0 (C-3); 23.4 (br, C-2); 69.6 (br, C-1)
$[Bu^t{}_2Sn(Cl)\{OSP(OPr^n)_2\}]$	−94 (d, ^2J(Sn–P) = 29 Hz)	35.4	29.9 (C-2); 45.6 (C-1)	10.0 (C-3); 23.4 (br, C-2); 69.8 (br, C-1)
$[Bu^t{}_2Sn(Cl)\{OSP(OBu^n)_2\}]$	−95 (d, ^2J(Sn–P = 30 Hz)	35.3 ^2J(Sn–P) = 30 Hz	29.9 (C-2); 45.6 (C-1)	13.4 (C-4); 18.6 (C-3); 31.9 (d, J = 6.1 Hz, C-2); 68.0 (br, C-1)
$([Me_2Sn\{OSP(OPr^n)_2\}]_2O)_2$	−124 (s) −146 (t, ^2J(Sn–P) = 36 Hz)	57.1 (br)[c]	8.3 (s)	10.1 (C-3); 23.6 (C-2); 68.9 (br, C-1)
$([Pr^n{}_2Sn\{OSP(OPr^n)_2\}]_2O)_2$	−147 (s) −177 (t, ^2J(Sn–P) = 46 Hz)	—	18.3 (C-3); 29.3 (C-2); 30.1, 30.6 (C-1)	10.2 (C-3); 23.6 (d, J = 9.3 Hz, C-2); 69.1 (d, J = 4.4 Hz, C-1)
$[Bu^t{}_2Sn(\mu\text{-}OH)\{OSP(OMe)_2\}]_2$	−289 (d, ^2J(Sn–P) = 209 Hz)	59.9 (^2J(Sn–P) = 209 Hz)	29.7 (C-2); 41.8 (C-1)	53.4 (d, J = 5.9 Hz)
$[Bu^t{}_2Sn(\mu\text{-}OH)\{OSP(OPr^n)_2\}]_2$	−289 (d, ^2J(Sn–P) = 205 Hz)	54.2 (^2J(Sn–P) = 203 Hz)	29.9 (C-2), 41.7 (C-1)	10.2 (C-3); 23.6 (C-2); 68.4 (C-1)

a) s=singlet, d=doublet, t=triplet, br=broad. b) Contains small impurity at δ = 26.1 ppm. c) Contains small peak at δ = 56.8 ppm.

exhibited a single set of resonances for the R_2Sn carbons. The ligand carbon resonances for C-1 and C-2 appeared as doublets due to phosphorus coupling, $^3J\times(^{31}P–^{13}C)$, being greater than that of $^2J\,(^{31}P–^{13}C)$. The $^{31}P\{^1H\}$ NMR spectra exhibited a singlet, indicating that both of the ligand moieties are magnetically equivalent.

The ^{119}Sn{^{1}H} NMR chemical shifts occurred in the $\delta=-116$ to -204 ppm region (Table 3). The ^{119}Sn NMR shifts clearly indicate that these complexes have a coordination number of tin greater than four. The ^{119}Sn NMR shifts observed for these complexes closely resemble those of diorganotin(IV) dicarboxylates,[11—13] dialkyltin(IV) bis(dialkyldithiophosphates,[4a,4b] and dimethyltin(IV) bis(1-pyrrolethiocarboxylates),[14] all of which have an anisobidentate mode of ligand bonding. The Bu^{t}_{2}Sn(IV) complexes showed a triplet in their ^{119}Sn NMR spectra due to coupling with two magnetically equivalent ^{31}P nuclei. However, the spectra of di-*n*-alkyltin derivatives displayed a broad singlet. This suggests that the di-*n*-alkyltin complexes are fluxional at room temperature, while the di-*t*-butyltin complexes adopt a rigid configuration.

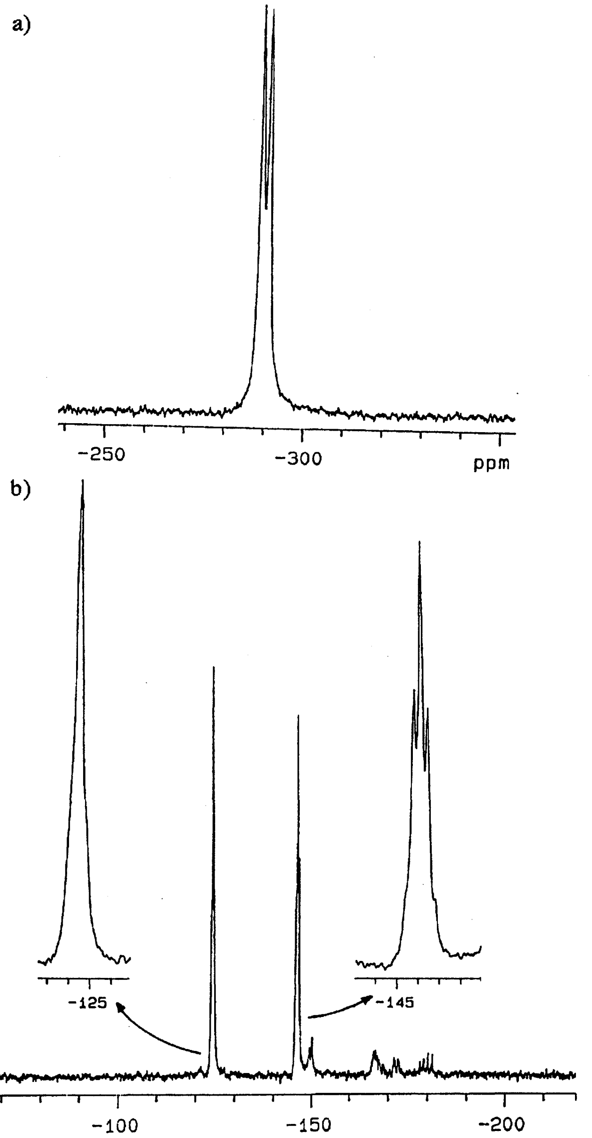

Fig. 1. ^{119}Sn{^{1}H} NMR spectra of a) [Bu^{t}_{2}Sn(μ- OH){OSP(OPr^{n})$_2$}]$_2$ and b) ([Me_2Sn{OSP(OPr^{n})$_2$}]$_2$O)$_2$ recorded at room temperature in $CDCl_3$ on a Varian XL-300, NMR spectrometer.

(2) [R_2Sn(Cl){OSP(OR′)$_2$}]: The magnitude of ^{2}J(^{119}Sn–^{1}H) (76 Hz) for [Me_2Sn(Cl){OSP(OPr^{n})$_2$}] is higher than that expected for four-coordinate complexes.[4a] The values of ^{3}J (^{119}Sn–^{1}H) for di-*t*-butyltin complexes are not different from the bis complexes discussed above. The ^{31}P{^{1}H} NMR signal for the chloro complexes is considerably shielded from its position in the corresponding bis complexes. The ^{119}Sn{^{1}H} NMR resonances are considerably more deshielded (Table 3) than that of the corresponding bis complexes, but are shielded from four-coordinate diorganotin(IV) dichlorides. The ^{119}Sn{^{1}H} NMR resonance for [Me_2Sn(Cl){OSP(OPr^{n})$_2$}] appeared as a broad ($\Delta_{1/2}=2044$ Hz) signal, whereas [Bu^{t}_{2}Sn(Cl){OSP(OR′)$_2$}] showed a doublet (^{2}J($^{119/117}$Sn–^{31}P)=ca. 30 Hz) pattern due to coupling with phosphorus. The NMR data for these complexes are similar to that of [R_2Sn(Cl){SSP(OR)$_2$}],[4b] for which five-coordinate geometry has been suggested.

(3) [Bu^{t}_{2}(μ-OH){OSP(OR′)}] and ([R_2Sn{OSP(OR′)$_2$}]$_2$O)$_2$: The ^{1}H NMR spectrum of ([Me_2Sn{OSP(OPr^{n})$_2$}]$_2$O)$_2$ showed two singlets for Sn–Me protons (Table 2), as expected for tetraorganodistannoxanes. The spectra of hydroxo-complexes, [Bu^{t}_{2}Sn(μ-OH){OSP(OR′)$_2$}]$_2$, displayed only one singlet for Bu^{t} protons. In both series of complexes a single set of resonances attributable to the ligand moiety were observed in the ^{1}H and ^{13}C{^{1}H} NMR spectra.

The ^{31}P{^{1}H} NMR spectrum of ([Me_2Sn{OSP(OPr^{n})$_2$}]$_2$O)$_2$ displayed a broad singlet at $\delta=57.1$ ppm. The spectra of hydroxo complexes, ([Bu^{t}_{2}Sn(μ- OH){OSP(OR′)$_2$}]$_2$, showed a single resonance with a clearly resolved ^{2}J (Sn–P) > 200 Hz. The ^{119}Sn{^{1}H} NMR spectra exhibited a doublet at $\delta=-289$ ppm. The doublet pattern of the ^{119}Sn reso-

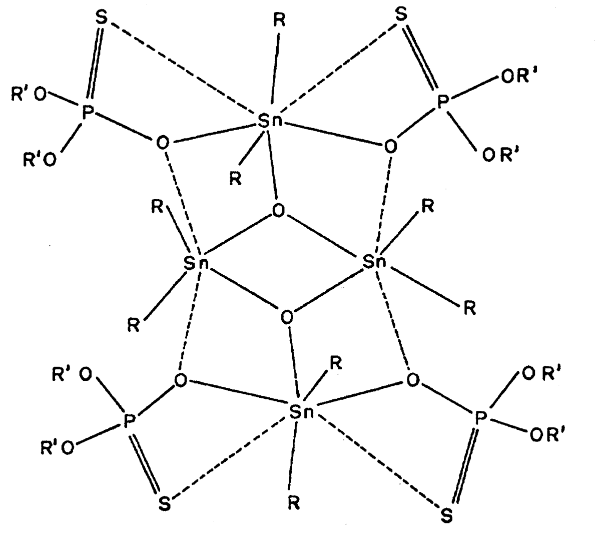

Fig. 2. Probable structure of ([R_2Sn{OSP(OR′)$_2$}]$_2$O)$_2$.

nance suggests that there is one thiophosphate moiety on a tin atom. An X-ray structural analysis of $[Bu^t{}_2Sn(\mu\text{-}OH)\{OSP(OEt)_2\}]_2$ has revealed a dimeric structure with hydroxo-bridges and oxygen-bonded phosphate ligands.[3] The ^{119}Sn NMR spectra of $([R_2Sn\{OSP(OR')_2\}]_2O)_2$ displayed a singlet and a triplet (Fig. 1), indicating that one tin site is coupled with two equivalent phosphorus nuclei, whereas the other tin site is little influenced by the acid moiety. The X-ray structure of $([Me_2Sn\{OSP(OEt)_2\}]_2O)_2$[3] has recently been reported. In the molecule the *endo*-cyclic tin is weakly coordinated to the ligand moiety, whereas the *exo*-cyclic tin is bonded to two anisobidentate $[OSP(OEt)_2]^-$ ligands (Fig. 2).

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