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Di- and Triorganotin(IV) Derivatives of (Diphenylphosphinyl)- and (Diphenylthiophosphinyl)acetic Acid

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Seven triorganotin(IV) (diphenylphosphinyl)- and (diphenylthiophosphinyl)acetates, $(C_6H_5)_2P(E)CH_2CO_2SnR_3$, where E = O and R = CH_3, C_2H_5, n-C_3H_7, n-C_4H_9, c-C_6H_{11}, and C_6H_5 and E = S and R = C_6H_5, are synthesized by the reaction of triorganotin(IV) chloride with the thallium(I) salt prepared from thallium(I) ethoxide and the parent acid or the condensation of the corresponding triorganotin(IV) hydroxide or bis(oxide) with the free acid in benzene to release water which is distilled azeotropically to drive the reaction forward. Phenyl–tin cleavage accompanies the use of triphenyltin(IV) tetraphenylborate to give the diphenyltin(IV) bis(acetate), $(C_6H_5)_2Sn[O_2CCH_2P(O)(C_6H_5)_2]_2$, whose dimethyltin(IV) analogue can be obtained from the parent acid and dimethyltin(IV) oxide. The products are white solids soluble in common organic solvents. The triphenyltin derivative loses carbon dioxide at its melting point (180–183 °C). Addition of triphenyltin(IV) chloride to the triphenyl derivative yields a 1:2 complex, $[(C_6H_5)_2P(O)CH_2CO_2Sn(C_6H_5)_3]_2\cdot(C_6H_5)_3SnCl$. Evidence from proton, phosphorus-31, and tin-119 NMR, mass, infrared, Raman, and tin-119m Mössbauer data rules out association through the carboxylate group, leaving coordination by the P=O oxygen as the origin of the higher coordination at tin in the solid state. Infrared, Raman, and Mössbauer data are interperable in terms of bent and nonplanar di- and trimethyltin groups in the solid, indicating weak association or the presence of small oligomers in the solid. The diorganotin derivatives are chelated, six-coordinated, *trans*-R_2Sn octahedra in all phases.

We have recently reported the synthesis of a series of triorganotin(IV) carboxylates in which the carboxylate moiety contains an organophosphorus substituent.[1] These salts can be prepared from triphenyl(2-carboxyethyl)phosphonium chloride, $[(C_6H_5)_3P(CH_2)_2CO_2H]^+Cl^-$, and organostannols with the release of water

$$R_3SnOH + [(C_6H_5)_3P(CH_2)_2CO_2H]^+Cl^- \rightarrow [R_3SnO_2C(CH_2)_2P(C_6H_5)_3]^+Cl^- + H_2O \quad (1)$$

or from the nucleophilic displacement of halide from organotin(IV) halides by the phosphobetaine, $(C_6H_5)_3P(CH_2)_2CO_2$.

$$R_3SnX + (C_6H_5)_3P(CH_2)_2CO_2 \rightarrow [R_3SnO_2C(CH_2)_2P(C_6H_5)_3]^+X^- \quad (2)$$

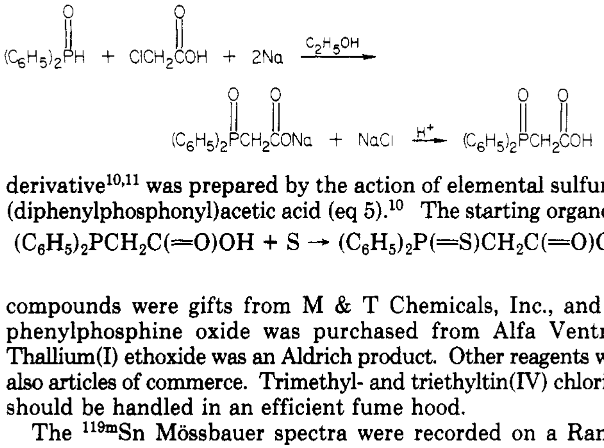
Double salts result from a 2:1 ratio of reactants.

$$2R_3SnX + (C_6H_5)_3P(CH_3)_2CO_2 \rightarrow [R_3SnO_2C(CH_2)_2P(C_6H_5)_3]^+[R_3SnX_2]^- \quad (3)$$

The structures of these potentially dual-acting biocidal materials were discussed on the basis of the physical and spectroscopic data in terms of a polymer chain of bridging carboxylate groups with dangling triphenylphosphonium cations. The phosphorus(V) chalcogenide atom would be expected to compete with the carboxylate oxygen as the base atom of choice for donation to tin. In this present investigation we chose to place the P=O function on the α-carbon of the carboxylic acid. The resulting products would then be analogous to the α-amino acid derivatives which we have investigated.[2,3] In trimethyltin(IV) glycinate we have shown that amino group bridging to tin is preferred[4] to the more generally known carboxylate association.[5]

In this paper we report the preparation of a series of triorganotin(IV) (diphenylphosphinyl)acetates of the form $R_3SnOC(=O)CH_2(O)P(C_6H_5)_2$ by two methods of synthesis.

Experimental Section



$$(C_6H_5)_2\overset{O}{\overset{\|}{P}}H + ClCH_2\overset{O}{\overset{\|}{C}}OH + 2Na \xrightarrow{C_2H_5OH} (C_6H_5)_2\overset{O}{\overset{\|}{P}}CH_2\overset{O}{\overset{\|}{C}}ONa + NaCl \xrightarrow{H^+} (C_6H_5)_2\overset{O}{\overset{\|}{P}}CH_2\overset{O}{\overset{\|}{C}}OH \quad (4)$$

(Diphenylphosphinyl)acetic acid[6-9] was prepared from the sodium salt of diphenylphosphine oxide and chloroacetic acid through a modification of a literature method (eq 4)[6] and the thio derivative[10,11] was prepared by the action of elemental sulfur on (diphenylphosphonyl)acetic acid (eq 5).[10] The starting organotin

$$(C_6H_5)_2PCH_2C(=O)OH + S \rightarrow (C_6H_5)_2P(=S)CH_2C(=O)OH \quad (5)$$

compounds were gifts from M & T Chemicals, Inc., and diphenylphosphine oxide was purchased from Alfa Ventron. Thallium(I) ethoxide was an Aldrich product. Other reagents were also articles of commerce. Trimethyl- and triethyltin(IV) chlorides should be handled in an efficient fume hood.

The ^{119m}Sn Mössbauer spectra were recorded on a Ranger Engineering constant-acceleration spectrometer equipped with a sodium iodide scintillation counter. The source was $Ca^{119m}SnO_3$ (New England Nuclear Corp.) and $Ca^{119}SnO_3$ was the reference material for zero velocity at room temperature. The velocity calibration was based on β-tin and iron foils. The Ranger Engineering variable-temperature liquid-nitrogen Dewar and controller used in these studies were regulated by a variable-bridge, silicon-controlled-rectifier cricuit, and the temperature was kept at 77 K for the measurements. The data were stored in 512 channels of the Tracor Northern Model TN-1314 multichannel analyzer and the resultant spectra fitted assuming a Lorentzian line shape.

Infrared spectra were recorded on a Beckman 4250 spectrometer as Nujol mulls on KBr disks, and the spectra were calibrated with polystyrene. Raman spectra were recorded on a Spex Ramalog 5 laser instrument. Mass spectra were recorded on a Hewlett-Packard 5985B GC/MS system at 70 eV. Proton NMR spectra

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Table I. Di- and Triorganotin(IV) (Diphenylphosphinyl)- and (Diphenylthiophosphinyl)acetates

compd	prepn[a]	mp, °C	% C calcd	% C found	% H calcd	% H found	% yield
$(C_6H_5)_2P(O)CH_2CO_2H$	···	144-145					70
$(C_6H_5)_2P(O)CH_2CO_2Tl$	···	201	35.25	35.56	3.02	2.57	100
$(C_6H_5)_2P(S)CH_2CO_2H$[10,11]	···	193-195					100
$(C_6H_5)_2P(O)CH_2CO_2Sn(CH_3)_3$ [b]	2	164-165	48.26	47.80	4.97	5.12	60
$(C_6H_5)_2P(O)CH_2CO_2Sn(C_2H_5)_3$	2	138-139	51.65	51.72	5.81	5.85	80
$(C_6H_5)_2P(O)CH_2CO_2Sn(n\text{-}C_3H_7)_3$	3	112-114	54.47	54.64	6.51	6.54	70
$(C_6H_5)_2P(O)CH_2CO_2Sn(n\text{-}C_4H_9)_3$	3	73-75	56.86	57.08	7.11	7.02	90
$(C_6H_5)_2P(O)CH_2CO_2Sn(c\text{-}C_6H_{11})_3$	1	160-162	61.27	63.54	7.18	7.32	90
$(C_6H_5)_2P(O)CH_2CO_2Sn(C_6H_5)_3$ [c]	1	180-183	63.09	61.36	4.44	4.40	90
$(C_6H_5)_2P(S)CH_2CO_2Sn(C_6H_5)_3$	4	121-124	61.47	61.35	4.32	4.41	30
$[(C_6H_5)_2P(O)CH_2CO_2Sn(C_6H_5)_3]_2\cdot(C_6H_5)_3SnCl$ [d]	7	177-180	61.40	61.84	4.31	4.55	80
$[(C_6H_5)_2P(O)CH_2CO_2]_2Sn(CH_3)_2$	6	75-78	54.00	55.04	4.50	4.72	30
$[(C_6H_5)_2P(O)CH_2CO_2]_2Sn(C_6H_5)_2$	5	182-183	60.71	59.69	4.30	4.31	80

[a] Preparations 1, 2, 3, 4, 5, 6 and 7 are depicted in eq 7, 8, 9, 10, 11, 12, and 14, respectively. [b] Molecular weight in chloroform: 375 (423) by osmometry. [c] Molecular weight in chloroform: 617 (609) by osmometry. [d] Cl: calcd, 2.22%; found 1.98%.

were recorded on a Varian XL-100 instrument. The phosphorus-31 and tin-119 spectra were recorded on Fourier transform Bruker WP-80 and SXP-109 instruments, respectively, by M. Magerstädt at the Technical University of Berlin, Germany. Carbon and hydrogen analyses and molecular weight determinations were performed by Galbraith Laboratories, Inc., Knoxville, TN.

The compounds studied are listed with the preparative method used and their yields, melting points, and microanalytical data in Table I. Tin-119m Mössbauer data are listed in Table II, mass spectral data in Table III, infrared data in Tables IV and V, and ^{31}P and ^{119}Sn NMR data in Tables VI and VII, respectively.

(Diphenylphosphinyl)acetic Acid, $(C_6H_5)_2P(O)CH_2CO_2H$.[6-9] To sodium metal (5.70 g, 248 mmol) dissolved in absolute ethanol was added diphenylphosphine oxide (25.00 g, 124.0 mmol) followed by chloroacetic acid (11.70 g, 124.0 mmol). The white sodium salt precipitate was heated for 2 h, cooled, filtered, and dissolved in water and the solution acidified with 1:2 sulfuric acid. The resulting (diphenylphosphinyl)acetic acid was extracted into chloroform, the extract dried with anhydrous magnesium sulfate, and the solvent removed to give the acid (21 g, 70% yield), mp 144–145 °C (lit.[6-9] 142–146 °C).

Thallium(I) (Diphenylphosphinyl)acetate, $(C_6H_5)_2P(O)CH_2CO_2Tl$. (Diphenylphosphinyl)acetic acid (7.80 g, 30.0 mmol) was dissolved in absolute ethanol (50 mL) and thallium(I) ethoxide (7.48 g, 30.0 mmol) was added. The white product precipitated immediately in quantitative yield and was filtered and washed with ethanol. It melted sharply at 201 °C.

(Diphenylthiophosphinyl)acetic Acid, $(C_6H_5)_2P(S)CH_2CO_2H$.[10,11] This compound was prepared in quantitative yield by adding a stoichiometric amount of elemental sulfur to (diphenylphosphonyl)acetic acid[10] in acetonitrile; mp 193–195 °C (lit.[10,11] 190 °C, 192–193 °C).

Trimethyltin(IV) (Diphenylphosphinyl)acetate, $(C_6H_5)_2P(O)CH_2CO_2Sn(CH_3)_3$. Trimethyltin(IV) chloride (1.00 g, 5.00 mmol) and thallium(I) (diphenylphosphinyl)acetate (2.32 g, 5.00 mmol) were allowed to react in refluxing chloroform for 1 h, the solvent was removed, and the resulting oil was washed with cold ether and placed under vacuum to give 1.8 g of an impure white solid which was recrystallized from a chloroform/ether mixture to which a few drops of ethanol had been added to give the product in 60% yield; mp 164–165 °C.

Triethyltin(IV) (Diphenylphosphinyl)acetate, $(C_6H_5)_2P(O)CH_2CO_2(C_2H_5)_3$. Triethyltin(IV) chloride (1.21 g, 5.00 mmol) was added to a suspension of thallium(I) (diphenylphosphinyl)acetate (2.32 g, 5.00 mmol) in chloroform. The mixture was stirred under reflux for 2 h and cooled and the precipitated thallium(I) chloride filtered. The chloroform solvent was removed on a rotary evaporator and the resulting oil placed under vacuum. Treatment with ether gave a white solid, mp 138–139 °C, in 80% yield.

Tri-*n*-propyltin(IV) (Diphenylphosphinyl)acetate, $(C_6H_5)_2P(O)CH_2CO_2Sn(n\text{-}C_3H_7)_3$. Bis(tri-*n*-propyltin) oxide (2.51 g, 5.00 mmol) and the acid (2.60 g, 10.0 mmol) were heated for 2 h in benzene (150 mL), with the water formed being collected in a Dean-Stark trap. The benzene solvent was then removed to give an oil which was treated with ether. Insoluble material was filtered and the ether removed. The oil solidified under vacuum to give the title compound, mp 112–114 °C, in 70% yield.

Tri-*n*-butyltin(IV) (Diphenylphosphinyl)acetate, $(C_6H_5)_2P(O)CH_2CO_2Sn(n\text{-}C_4H_9)_3$. The above-outlined procedure was used to prepare the tri-*n*-butyltin derivative from bis(tri-*n*-butyltin) oxide (2.98 g, 5.00 mmol) and (diphenylphosphinyl)acetic acid (2.60 g, 10.0 mmol), mp 73–75 °C, in 90% yield.

Tricyclohexyltin(IV) (Diphenylphosphinyl)acetate, $(C_6H_5)_2P(O)CH_2CO_2Sn(c\text{-}C_6H_{11})_3$. (Diphenylphosphinyl)acetic acid (2.60 g, 10.0 mmol) and tricyclohexyltin(IV) hydroxide (3.85 g, 10.0 mmol) were dissolved in benzene (150 mL) and heated as described above. Recrystallization from chloroform gave the product, mp 160–162 °C, in 90% yield.

Triphenyltin(IV) (Diphenylphosphinyl)acetate, $(C_6H_5)_2P(O)CH_2CO_2Sn(C_6H_5)_3$. This compound was prepared in a similar way from (diphenylphosphinyl)acetic acid (2.60 g, 10.0 mmol) and triphenyltin(IV) hydroxide (3.67 g, 10.0 mmol), mp 180–183 °C, in 90% yield. Heating $(C_6H_5)_3SnO_2CCH_2P(O)(C_6H_5)_2$ above its melting point (180–183 °C) releases carbon dioxide which was detected as barium carbonate. The tin-containing product was not isolated.

Bis[triphenyltin(IV) (diphenylphosphinyl)acetate]–Triphenyltin(IV) Chloride, $[(C_6H_5)_2P(O)CH_2CO_2Sn(C_6H_5)_3]_2\cdot(C_6H_5)_3SnCl$. Triphenyltin(IV) (diphenylphosphinyl)acetate (3.05 g, 5.00 mmol) from the preparation described above and triphenyltin(IV) chloride (1.93 g, 5.00 mmol) were dissolved in chloroform, and the solution was concentrated and ether added to induce crystallization of the white product, mp 177–180 °C, in 80% yield. The product was filtered and washed with ether. Instead of the anticipated 1:1 adduct, the elemental analysis for carbon, hydrogen, and chlorine is consistent with the 2:1 formulation.

Dimethyltin(IV) Bis((diphenylphosphinyl)acetate), $[(C_6H_5)_2P(O)CH_2CO_2]_2Sn(CH_3)_2$. Dimethyltin(IV) oxide (0.83 g, 5.00 mmol) and (diphenylphosphinyl)acetic acid (2.60 g, 10.0 mmol) were reacted as described above. The benzene was removed on completion of the reaction, and ether was added to wash the crude solid which had a wide melting range. The pure product was obtained by sublimation at 70 °C in vacuo: mp 75–78 °C; yield 30%. The mass spectrum displayed fragments at *m/e* (intensity) values of 580 (11), $\{[(C_6H_5)_2P(O)CH_2]_2Sn(CH_3)_2\}^{+\cdot}$, 441 (5), $[(C_6H_5)_2P(O)CHSn(CH_3)_2C_6H_5]^+$, 365 (52), $[(C_6H_5)_2P(O)CH_2Sn(CH_3)_2]^+$, 335 (27), $[(C_6H_5)_2P(O)CH_2Sn]^+$, 227 (6), $[(CH_3)_2SnC_6H_5]^+$, 197 (21), $[SnC_6H_5]^+$, 121 (15), $[SnH]^+$, and 215 (100) $[(C_6H_5)_2P(O)CH_2]^+$.

Diphenyltin(IV) Bis((diphenylphosphinyl)acetate), $[(C_6H_5)_2P(O)CH_2CO_2]_2Sn(C_6H_5)_2$. Triphenyltin(IV) chloride (1.93 g, 0.005 mol) and sodium tetraphenylborate (1.71 g, 0.005 mol) were dissolved in 2-propanol to precipitate sodium chloride which was filtered, and (diphenylphosphinyl)acetic acid (1.30 g, 0.005 mol) dissolved in the same solvent was added. A white solid formed in the pink solution, the solution was filtered, and the

Table II. Tin-119m Mössbauer Data for the Di- and Triorganotin(IV) (Diphenylphosphinyl)- and (Diphenylthiophosphinyl)acetates at 77 K (mm s^{-1})[a]

compd	IS ± 0.03	QS ± 0.06	Γ ± 0.03	ρ = QS/IS
$(C_6H_5)_2P(O)CH_2CO_2Sn(CH_3)_3$	1.33	3.71	1.31	2.79
$(C_6H_5)_2P(O)CH_2CO_2Sn(C_2H_5)_3$	1.45	3.66	1.15	2.52
$(C_6H_5)_2P(O)CH_2CO_2Sn(n\text{-}C_3H_7)_3$	1.46	3.71	1.34	2.54
$(C_6H_5)_2P(O)CH_2CO_2Sn(n\text{-}C_4H_9)_3$	1.44	3.54	0.92	2.46
$(C_6H_5)_2P(O)CH_2CO_2Sn(c\text{-}C_6H_{11})_3$	1.50	3.57	1.08	2.38
$(C_6H_5)_2P(O)CH_2CO_2Sn(C_6H_5)_3$	1.28	3.28	0.90	2.56
$(C_6H_5)_2P(S)CH_2CO_2Sn(C_6H_5)_3$	1.34	3.47	1.56	2.59
$[(C_6H_5)_2P(O)CH_2CO_2Sn(C_6H_5)_3]_2\cdot(C_6H_5)_3SnCl$	1.28	3.31	1.00	2.59
$[(C_6H_5)_2P(O)CH_2CO_2]_2Sn(CH_3)_2$	1.26	3.80	1.35	3.02
$[(C_6H_5)_2P(O)CH_2CO_2]_2Sn(C_6H_5)_2$	1.28	3.27	1.08	2.55

[a] Relative to $Ca^{119}SnO_3$.

Table III. Mass Spectral Data (*m/e*) for the Triorganotin(IV) (Diphenylphosphinyl)acetates[a]

R	$[(C_6H_5)_2P(O)CH_2CO_2SnR_2]^+$	$[(C_6H_5)_2P(O)CH_2SnR_2]^+$	$[(C_6H_5)_2P(O)CH_2CO_2Sn]^+$	$[(C_6H_5)_2P(O)CH_2Sn]^+$	RSn^+	$C_6H_5Sn^+$	$Sn^{+\cdot}$
CH_3	85	100	0	46	57	47	22
C_2H_5	53	100	0	98	21	44	25
$n\text{-}C_3H_7$	17	100	3	97	0	68	40
$n\text{-}C_4H_9$	39	100	4	96	10	32	24
$c\text{-}C_6H_{11}$	34	44	10	100	0	27	6
C_6H_5	5	100	0	26	10	10	43

[a] Only tin-bearing fragments are listed. Mass numbers are based upon ^1H, ^{12}C, ^{16}O, ^{31}P, and ^{120}Sn.

solid was washed with chloroform and then ether to give the product, mp 182–183 °C, in 60% yield. The mass spectrum displayed fragments at *m/e* (intensity) values of 533 (8), $[(C_6H_5)_2P(O)CH_2CO_2Sn(C_6H_5)_2]^+$, 489 (100), $[(C_6H_5)_2P(O)CH_2Sn(C_6H_5)_2]^+$, 334 (21), $[(C_6H_5)_2P(O)CHSn]^+$, 351 (23), $[Sn(C_6H_5)_3]^+$, 197 (56), $[SnC_6H_5]^+$, and 120 (19), $Sn^{+\cdot}$.

Triphenyltin(IV) (Diphenylthiophosphinyl)acetate, $(C_6H_5)_2P(S)CH_2CO_2Sn(C_6H_5)_3$. This compound was prepared from (diphenylthiophosphinyl)acetic acid (2.70 g, 10.0 mmol) and triphenyltin(IV) hydroxide (3.67 g, 10.0 mmol) as described for (diphenylphosphinyl)acetic acid. The crude product was recrystallized from acetonitrile to give the pure compound, mp 121–123.5 °C, in 30% yield. The mass spectrum displayed fragments at *m/e* (intensity) values of 549 (13), $[(C_6H_5)_2P(S)CH_2CO_2Sn(C_6H_5)_2]^+$, 505 (72), $[(C_6H_5)_2P(S)CH_2Sn(C_6H_5)_2]^+$, 489 (4), unassigned, 395 (5), $[(C_6H_5)_2P(S)CH_2Sn]^+$, 351 (23), $[(C_6H_5)_3Sn]^+$, 229 (13), $[SSnC_6H_5]^+$, 197 (56), $[SnC_6H_5]^+$, and 121 (100), $[SnH]^+$.

Results and Discussion

The synthesis of the triorganotin (diphenylphosphinyl)acetates proceeds in high yield from the reaction of a triorganotin(IV) hydroxide with the (diphenylphosphinyl)acetic acid in benzene with the reaction driven to completion by the azeotropic distillation of the water released (eq 6) or from the action of triorganotin(IV)

$$R_3SnOH + (C_6H_5)_2P(O)CH_2CO_2H \rightarrow (C_6H_5)_2P(O)CH_2CO_2SnR_3 + H_2O \quad (6)$$

$$R = c\text{-}C_6H_{11} \text{ and } C_6H_5$$

chloride and thallium(I) (diphenylphosphinyl)acetate in chloroform (eq 7) or from the parent acid and the bis-

$$R_3SnCl + (C_6H_5)_2P(O)CH_2CO_2Tl \rightarrow (C_6H_5)_2P(O)CH_2CO_2SnR_3 + TlCl \quad (7)$$

$$R = CH_3 \text{ and } C_2H_5$$

[trialkyltin(IV)] oxide in benzene (eq 8). The (thio-

$$(R_3Sn)_2O + (C_6H_5)_2P(O)CH_2CO_2H \rightarrow (C_6H_5)_2P(O)CH_2CO_2SnR_3 + H_2O \quad (8)$$

$$R = n\text{-}C_3H_7 \text{ and } n\text{-}C_4H_9$$

phosphinyl)acetic acid also reacts in a similar way (eq 9).

$$R_3SnOH + (C_6H_5)_2P(S)CH_2CO_2H \rightarrow (C_6H_5)_2P(S)CH_2CO_2SnR_3 + H_2O \quad (9)$$

$$R = C_6H_5$$

The products are white solids soluble in common organic solvents. The attempted synthesis of triphenyltin (diphenylphosphinyl)acetic acid tetraphenylborate from the addition of the acid to a solution of triphenyltin tetraphenylborate prepared in situ was accompanied by the cleavage of the tin–phenyl bond to produce the bis compound (eq 10) and the dimethyl derivative was synthesized

$$(C_5H_6)_3Sn^+B(C_6H_5)_4^- + (C_6H_5)_2P(O)CH_2CO_2H \rightarrow (C_6H_5)_2Sn[O_2CCH_2P(O)(C_6H_5)_2]_2 \quad (10)$$

from the parent acid and dimethyltin(IV) oxide (eq 11). The diorganotin(IV) derivatives are white solids which are soluble in chloroform.

$$(CH_3)_2SnO + 2(C_6H_5)_2P(O)CH_2CO_2H \rightarrow (CH_3)_2Sn[O_2CCH_2P(O)(C_6H_5)_2]_2 + H_2O \quad (11)$$

The addition of triphenyltin(IV) chloride to triphenyltin(IV) (diphenylphosphinyl)acetate in a 1:1 mole ratio in chloroform gives a surprising result. Concentration of the solution followed by trituration with ether precipitates a 1:2 complex in 80% yield (eq 12). Attempts to produce

$$2(C_6H_5)_2P(O)CH_2C(O)OSn(C_6H_5)_3 + (C_6H_5)_3SnCl \rightarrow [(C_6H_5)_2P(O)CH_2C(O)OSn(C_6H_5)_3]_2\cdot(C_6H_5)_3SnCl \quad (12)$$

Table IV. Infrared $\nu(CO_2)$ and $\nu(P{=}O)$ Assignments for the Di- and Triorganotin(IV) (Diphenylphosphinyl)acetates

	$\nu_{asym}(CO)_2$	$\nu_{sym}(CO_2)$	$\nu(P{=}O)$
$(C_6H_5)_2P(O)CH_2CO_2H$	1733 (vs) 1708 (vs)		1214 (m), 1157 (vs), 1145 (vs), 1128 (vs), 1096 (vs), 1070 (s)
$(C_6H_5)_2P(O)CH_2CO_2Sn(CH_3)_3$	1648 (vs)	1332 (vs)	1217 (m), 1174 (vs), 1118 (s), 1106 (s), 1070 (m)
$(C_6H_5)_2P(O)CH_2CO_2Sn(C_2H_5)_3$	1640 (vs)	1335 (vs)	1200 (m), 1173 (vs), 1150 (vs), 1126 (s), 1100 (s)
$(C_6H_5)_2P(O)CH_2CO_2Sn(n\text{-}C_3H_7)_3$	1642 (vs)	1335 (vs)	1199 (m), 1178 (vs), 1124 (s), 1107 (s), 1068 (m)
$(C_6H_5)_2P(O)CH_2CO_2Sn(n\text{-}C_4H_9)_3$	1654 (vs)	1328 (vs)	1190 (s), 1180 (vs), 1122 (s), 1102 (m), 1074 (w)
$(C_6H_5)_2P(O)CH_2CO_2Sn(c\text{-}C_6H_{11})_3$	1645 (vs)	1327 (vs) 1315 (vs)	1201 (s), 1157 (vs), 1128 (s), 1102 (m), 1082 (m)
$(C_6H_5)_2P(O)CH_2CO_2Sn(C_6H_5)_3$	1645 (vs)	1335 (vs) 1318 (sh)	1216 (s), 1147 (vs), 1129 (vs), 1098 (vs), 1083 (s)
$[(C_6H_5)_2P(O)CH_2CO_2Sn(C_6H_5)_3]_2\cdot(C_6H_5)_3SnCl$	1642 (vs)	1335 (vs) 1322 (sh)	1216 (m), 1147 (vs), 1131 (vs), 1097 (s), 1080 (m)
$[(C_6H_5)_2P(O)CH_2CO_2]_2Sn(CH_3)_2$	1712 (s) 1632 (s, br) 1588 (s, br) 1575 (sh)	1320 (s, br)	1190 (s, br), 1165 (s, br), 1122 (s), 1100 (s), 1070 (m)
$[(C_6H_5)_2P(O)CH_2CO_2]_2Sn(C_6H_5)_2$	1645 (vs)	1335 (vs) 1320 (sh)	1216 (m), 1148 (vs), 1131 (vs), 1098 (s), 1082 (m)
$(C_6H_5)_2P(O)CH_2CO_2Tl$	1575 (s) 1567 (vs)	1348 (vs)	1201 (m), 1167 (vs), 1123 (s), 1098 (m), 1073 (m)
$(C_6H_5)_2P(S)CH_2CO_2Sn(C_6H_5)_3$	1575 (vs)	1308 (m)	

Table V. Infrared Data for the Di- and Triorganotin(IV) Derivatives below 1500 cm^{-1}

$(C_6H_5)_2P(O)CH_2CO_2H$	1443 (vs), 1412 (m), 1286 (s, br), 996 (m), 904 (m), 848 (m), 796 (s), 746 (s), 706 (m), 690 (s), 582 (m), 500 (s), 470 (sh), 396 (m)
$(C_6H_5)_2P(O)CH_2CO_2Sn(CH_3)_3$	1443 (s), 997 (w), 917 (m), 847 (m), 787 (m, br), 761 (m), 742 (m), 700 (m), 590 (m), 556 (s), 537 (s), 501 (s), 483 (w), 378 (w)
$(C_6H_5)_2P(O)CH_2CO_2Sn(C_2H_5)_3$	1438 (sh), 1027 (m), 998 (m), 957 (m), 924 (m), 854 (s), 822 (s), 798 (w), 750 (vs), 691 (vs), 680 (vs), 600 (m), 544 (s), 520 (sh), 505 (vs)
$(C_6H_5)_2P(O)CH_2CO_2Sn(n\text{-}C_3H_7)_3$	1440 (vs), 994 (m), 918 (m), 845 (m), 792 (m), 755 (m), 692 (s), 677 (sh), 586 (m), 528 (s), 470 (w), 452 (w, br)
$(C_6H_5)_2P(O)CH_2CO_2Sn(n\text{-}C_4H_9)_3$	1455 (s), 1441 (s), 1391 (m), 1015 (m), 966 (m), 925 (s), 872 (m), 862 (m), 842 (m), 811 (m), 755 (s), 733 (s), 712 (s), 690 (vs), 675 (vs), 612 (vs), 512 (vs), 507 (sh), 442 (w), 397 (w)
$(C_6H_5)_2P(O)CH_2CO_2Sn(c\text{-}C_6H_{11})_3$	1446 (vs), 1396 (w), 1252 (w), 989 (s), 923 (w), 878 (w), 848 (w), 838 (w), 818 (m), 744 (m), 712 (m), 686 (s), 668 (m), 594 (m), 502 (m), 478 (sh), 394 (w)
$(C_6H_5)_2P(O)CH_2CO_2Sn(C_6H_5)_3$	1482 (m), 1436 (s), 1430 (s), 1392 (s), 1024 (m), 997 (m), 930 (m), 847 (m), 815 (s), 748 (vs), 688 (vs), 597 (m), 498 (m), 441 (m)
$[(C_6H_5)_2P(O)CH_2CO_2Sn(C_6H_5)_3]_2\cdot(C_6H_5)_3SnCl$	1436 (m), 1431 (m), 1025 (w), 996 (w), 851 (w), 818 (w), 693 (s), 596 (w), 506 (w), 442 (m), 408 (m, br)
$[(C_6H_5)_2P(O)CH_2CO_2]_2Sn(CH_3)_2$	1436 (s), 997 (w), 932 (w), 852 (m), 796 (m), 745 (s), 692 (s), 600 (m, br), 580 (sh), 521 (s), 501 (s)
$[(C_6H_5)_2P(O)CH_2CO_2]_2Sn(C_6H_5)_2$	1438 (m), 1432 (m), 848 (w), 817 (w), 749 (m), 691 (s), 595 (w), 505 (w), 447 (w), 397 (w)
$(C_6H_5)_2P(S)CH_2CO_2Sn(C_6H_5)_3$	1100 (m), 1075 (m), 851 (m), 691 (vs), 625 (m, br), 502 (w, br), 478 (w, br), 445 (m, br)

Table VI. ^{31}P NMR Data (Ppm) for the Organotin (Diphenylphosphinyl)acetates in Deuterated Chloroform[a]

$(C_6H_5)_2P(O)CH_2CO_2Sn(CH_3)_3$	28.9
$(C_6H_5)_2P(O)CH_2CO_2Sn(C_2H_5)_3$	26.9
$(C_6H_5)_2P(O)CH_2CO_2Sn(n\text{-}C_3H_7)_3$	26.3
$(C_6H_5)_2P(O)CH_2CO_2Sn(n\text{-}C_4H_9)_3$	26.9
$(C_6H_5)_2P(O)CH_2CO_2Sn(c\text{-}C_6H_{11})_3$	26.0
$(C_6H_5)_2P(O)CH_2CO_2Sn(C_6H_5)_3$	27.0
$[(C_6H_5)_2P(O)CH_2CO_2Sn(C_6H_5)_3]_2\cdot(C_6H_5)_3SnCl$	27.2
$[(C_6H_5)_2P(O)CH_2CO_2]_2Sn(C_6H_5)_2$	26.9
$(C_6H_5)_2P(S)CH_2CO_2Sn(C_6H_5)_3$	37.4

[a] Relative to 85% phosphoric acid.

Table VII. ^{119}Sn NMR Data (Ppm) for the Organotin (Diphenylphosphinyl)acetates in Deuterated Chloroform[a]

$(C_6H_5)_2P(O)CH_2CO_2Sn(CH_3)_3$	+66
$(C_6H_5)_2P(O)CH_2CO_2Sn(C_2H_5)_3$	+108
$(C_6H_5)_2P(O)CH_2CO_2Sn(n\text{-}C_3H_7)_3$	−62
$(C_6H_5)_2P(O)CH_2CO_2Sn(n\text{-}C_4H_9)_3$	−60
$(C_6H_5)_2P(O)CH_2CO_2Sn(C_6H_5)_3$	−120
$[(C_6H_5)_2P(O)CH_2CO_2Sn(C_6H_5)_3]_2\cdot(C_6H_5)_3SnCl$	−116, −143, −158
$(C_6H_5)_2P(S)CH_2CO_2Sn(C_6H_5)_3$	−97, +11

[a] Relative to tetramethylstannane.

representatives of the other three permutations of methyl- and phenyltin combinations in the 1:2 complexes from trimethyltin(IV) (diphenylphosphinyl)acetate and trimethyltin(IV) chloride in addition to the above phenyltin derivatives gave only oils. Attempted replacement of the chlorine in the 1:2 product above with $B(C_6H_5)_4$ from triphenyltin(IV) tetraphenylborate also failed.

Structural discussion for these phosphinylacetates must acknowledge the presence of two potential oxygen atom donor sites available for bridging or chelation. While a monomeric, four-corrdinated structure, A, such as that

$$\underset{\textstyle A}{R_3SnOC(O)CH_2P(E)(C_6H_5)_2} \qquad E = O, S$$

discussed for tricyclohexyltin(IV) acetate[12,13] is possible, more interesting arrangements utilize either the carboxylate oxygen atom in the bridged polymers generally found

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(12) Alcock, N. W.; Timms, R. E. *J. Chem. Soc. A* **1968**, 1876.

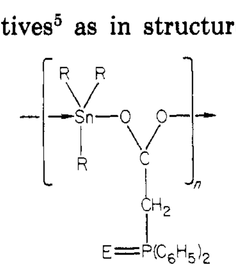
(13) The high Mössbauer quadrupole splitting (QS) value for this compound (QS = 3.27 mm s^{-1})[14] makes some interaction with the second carboxylate oxygen to raise the coordination number of tin to five virtually certain. The *intra*molecular $d(Sn\cdots O)$ contact distance is 2.95 Å, but a closer *inter*molecular oxygen is available at 2.84 Å.[12]

(14) Maddock, A. G.; Platt, R. H. *J. Chem. Soc. A* **1971**, 1191.

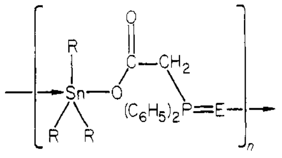
in the tin derivatives[5] as in structure B in which the phosphorus portion of the molecule is pendant to the chain of associated moieties or the phosphinyl oxygen atom in a five-atom bridge as in structure C reminiscent of the related four-atom bridge found in trimethyltin(IV) glycinate[4] or in the chelated structure D. Triphenylphosphine oxide forms a complex with triphenyltin(IV) nitrate,[15] and the carbonyl-stabilized triphenylphosphoranylidene acetone ylid uses its carbonyl oxygen and not its carbanionic carbon in complexing trimethyltin(IV) chloride in $(C_6H_5)_3PCHC(CH_3)OSn(CH_3)_3Cl$.[16] We assume that no six-coordinated, R_3SnL_3 forms, are possible,[5] but ionic formulations as in E need to be considered, too.

$$[R_3Sn]^+[OC(O)CH_2P(E)C_6H_5)_2]^- \qquad E = O, S$$

E

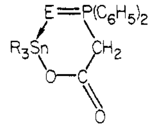


B



C

E = O, S



D

E = O, S

The easy solubility of these species in nonpolar organic solvents makes structures B, C, and E unlikely. In addition, molecular weight determinations in chloroform for the E = O and R = CH_3 and C_6H_5 derivatives give results indicative of the monomer, and the E = O and R = C_6H_5 derivative does not conduct (Λ_M = 4.4 Ω^{-1} cm^{-1} M^{-1}) in DMF.

Infrared Data. Three stretching modes are important in the compounds studied, $\nu(CO)_2$), ν(PE), where E = O and S, and ν(SnC), listed in the order of decreasing frequency. Our assignments for the first two modes are listed in Table VI. Each can in principle yield information which can help distinguish the structural possibilities.

Trimethyltin(IV) (diphenylphosphinyl)acetate exhibits both ν_{asym} and $\nu_{sym}(SnC_3)$ modes as absorptions at 556 and 537 cm^{-1}, respectively. The lower energy absorption is roughly twice as intense in the infrared. In the Raman these modes appear at 557 and 524 cm^{-1}, the second band being also twice as intense. The presence of the $\nu_{sym}(SnC_3)$ mode in the infrared and the $\nu_{asym}(SnC_3)$ mode in the Raman rules out a planar equatorial trimethyltin group which might be associated with trigonal-bipyramidal bridging structures such as B and C.

Infrared O—C=O stretching frequencies can help to distinguish free from coordinated carboxylate groups. While the carboxylate groups in organotin solids generally adopt a bridged structure unless the organic groups at tin are bulky or unless the carboxylate group is branched at the α-carbon,[17] trimethylsilyl acetate possesses a normal ester structure in which the $\nu_{asym}(CO_2)$ frequency occurs at 1725 cm^{-1}. The corresponding absorption at 1576 cm^{-1} in trimethyltin(IV) acetate[18] is typical of the associated tin carboxylates.[19] By contrast, $\nu_{asym}(CO_2)$ appears at 1645 cm^{-1} in the tricyclohexyltin(IV) derivative, and this fact was used to decide the case for four-coordination at tin when ambiguous crystal structure data could not[12] (vide supra). The corresponding absorption in trimethyltin(IV) glycinate is at 1630 cm^{-1},[2] but in this case there is strong hydrogen bonding between carbonyl oxygen and amino group N–H moieties along and between the nitrogen bridged trimethyltin chains which must contribute to the lowering of the frequency of this free carboxylate group.[4]

In our triorganotin(IV) (diphenylphosphinyl)acetates the $\nu_{asym}(CO)_2$ modes can be assigned at 1647 ± 7 cm^{-1}, with $\nu_{sym}(CO)_2$ at 1325 ± 10 cm^{-1}. Thus strong interactions between the carboxylate carbonyl group and the tin atom as required in structure B can be ruled out. The $\nu_{asym}(CO)_2$ values are almost identical with those in tricyclohexyltin(IV) acetate, and weak interactions which probably are present in that solid cannot be excluded. By contrast, our thallium(I) derivative shows a much lowered $\nu_{asym}(CO)_2$ absorption at 1575 cm^{-1}, and its higher melting point and limited solubility in nonpolar organic solvents suggest a polymeric network with bridging carboxylate groups. More interesting for our purpose is the 1575-cm^{-1} absorption in the thiophosphinylacetate derivative relative to 1697 cm^{-1} for the free acid, which must find its origin in either a strong mass effect or a different structure involving association of the carboxylate oxygen to the tin atom in this sulfur derivative.

The position of the ν(P=O) mode in the parent (diphenylphosphinyl)acetic acid solid would be expected to be lowered by hydrogen bonding with the carboxylate O—H,[20] and the frequency appears to be insensitive to the change of organic groups at tin in the triorganotin derivative or even to the change of metal atom as in the thallium derivative. Logically then, either all or none of these derivatives must be associated through the P=O system, but since all the frequencies lie in the same range as that of the parent acid which is associated into a high melting solid through hydrogen bonding, we favor the former conclusion and thus structure C or D.

A strictly linear carbon–tin–carbon system is ruled out in $(CH_3)_2Sn[O_2CCH_2P(=O)(C_6H_5)_2]_2$ by the presence of both the ν_{asym} and $\nu_{sym}(SnC_2)$ at 565 and 545 cm^{-1} in the infrared.

Mass Spectral Data. No parent molecular ions or fragments of mass higher than the parent or containing more than one tin atom are found in any of the mass spectra, thus ruling out gas-phase association for these species in the spectrometer. The base peak of highest abundance in all except the tricyclohexyl derivative is a $(C_6H_5)_2P(O)CH_2SnR_2^+$ fragment which is derived from loss

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(15) Nardelli, M.; Pelizzi, C.; Pelizzi, D. *J. Organomet. Chem.* **1976**, *112*, 263.

(16) Buckle, J.; Harrison, P. G.; King, T.; Richards, J. A. *J. Chem. Soc., Dalton Trans.* **1975**, 1552.

(17) Ford, B. F. E.; Liengme, B. V.; Sams, J. R. *J. Organomet. Chem.* **1969**, *19*, 53.

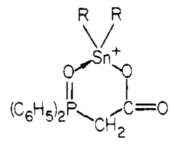
(18) Okawara, R.; Webster, D. E.; Rochow, E. G. *J. Am. Chem. Soc.* **1960**, *82*, 3287.

(19) Okawara, R.; Wada, M. *Adv. Organomet. Chem.* **1967**, *5*, 137.

(20) Matrosov, E. I.; Tsvetkov, E. N.; Malevannaya, R. A.; Kabachnik, M. I. *J. Gen. Chem. USSR (Engl. Transl.)* **1972**, *42*, 1686.

of carbon dioxide from $(C_6H_5)_2P(O)CH_2CO_2SnR_2^+$ which is also observed. The $(C_6H_5)_2P(O)CH_2Sn^+$ ion which is the highest abundance feature of the spectrum of the cyclohexyl derivative is also found in every spectrum, as is the $C_6H_5Sn^+$ fragment which must arise by phenyl group transfer from phosphorus since it is found irrespective of the organic group at tin.

The loss of one organic group from tin leads to a fragment which loses a neutral carbon dioxide molecule to give an ion of the formula $(C_6H_5)_2P(O)CH_2SnR_2^+$ is the origin of the process. Loss of CO_2 is also observed on heating $(C_6H_5)_3SnO_2CCH_2P(O)(C_6H_5)_2$.



The mass spectrum of the 1:2 complex $[(C_6H_5)_2P(O)CH_2CO_2Sn(C_6H_5)_3]_2 \cdot (C_6H_5)_3SnCl$ is similar to that of the triphenyltin(IV) (diphenylphosphinyl)acetate itself, except for the presence of an $SnCl^+$ peak. The most abundant signal arises from $(C_6H_5)_2^{+\cdot}$ at *m/e* 154, unlike in the phosphinylacetate derivative (see Table III).

Mössbauer Data. The Mössbauer spectra for all the compounds studied are well-resolved doublets whose isomer shifts (IS) values specify tetravalent tin and whose quadrupole splitting (QS) and ρ (QS/IS) values are 3.27–3.71 mm s^{-1} and 2.38–2.79, respectively, indicating a higher than four-coordinated situation at the tin atom.[21] Thus structure A can be confidently rules out on this basis for the solids. The failure of the trimethyl-, dimethyl-, triphenyl-, and diphenyltin derivatives to give ambient temperature Mössbauer spectra is negative evidence, but the related triorganotin acetates, and amino acids[2-4] which adopt bridged polymeric structures[5] show Mössbauer resonances at room temperature. We interpret the absence of resolvable spectra as arguing against polymeric structures B and C.

For the dimethyl- and diphenyltin(IV) derivatives we can apply a treatment based upon a point charge model[22] to link the observed QS value to a predicted carbon–tin–carbon angle in six-coordinated diorganotin(IV) compounds. The results correlate well with known structural data for the dimethyl- and diphenyltin systems.[5,22,23] The calculation, which is based upon the assumption that the partial QS values of the ligand groups are negligible, yields an angle of 154° for the dimethyl and 144° in the diphenyltin(IV) derivative, the former corroborated by the observation of a $\nu_{sym}(SnC_2)$ mode in the infrared spectrum.

The Mössbauer spectrum of the 1:2 complex is a simple doublet whose QS value implies that both types of tin atoms involved are higher than four-coordinated. The data are nearly identical with those for the triphenyltin (diphenylphosphinyl)acetate derivative.

NMR Data. The phosphorus-31 chemical shifts for the compounds containing the $(C_6H_5)_2P(O)CH_2$ group lie in the range 26.3–28.9 ppm relative to 85% phosphoric acid as shown in Table VI. This compares with similar data for the closely related $(C_6H_5)_2P(O)R$ where R = $CH[CH_2C(O)C_6H_5]C(O)C_6H_5$ (27.5 ppm) and R = $C[CH_2C(O)C_6H_5][{=}C(OCH_2C_6H_5)C_6H_5]$ (28.6 ppm).[24] In the direct comparison of $(C_6H_5)_3P{=}E$ chemical shifts, with E = O (23.0–27.0 ppm) and E = S (42 ppm), the sulfur derivative is to higher field,[24] just as in the case of our sulfur compound.

It is well-known in tin-119 NMR studies that raising the coordination number at tin moves the chemical shift upfield of the tetramethyltin standard, while connecting electronegative atoms moves the resonance downfield.[25] Thus for monomeric triorganotin carboxylates the tin chemical shift is found to low field of tetramethyltin, while for associated species it is found to high field.[26] Of the tin-119 NMR data we were able to record, for only two compounds are the chemical shifts to high field. These are the derivatives with the smallest alkyl groups, $(C_6H_5)_2P(O)CH_2CO_2SnR_3$ where R = CH_3[27] and C_2H_5. The other compounds listed in Table VII are apparently monomeric in the deuteriochloroform solutions used to record the spectra. For the sulfur-containing derivative, signals both up- and downfield of tetramethyltin are observed, indicating the presence of both monomeric and associated species which must be in a slow equilibrium. The 1:2 complex shows three resonances, all to low field, but this is puzzling since dissociation in solution can give rise to only two monomeric species.

Molecular weight determinations show the trimethyl- and triphenyltin derivatives to be monomers in chloroform solution, and proton NMR data for the methyl groups [τ 0.57 ($|^2J(^{119}Sn{-}C{-}^1H)|$ = 65.6 Hz)] in the same solvent are consistent with four-coordinated tin in this phase.[28] The lack of shift of the $\nu(CO_2)$ frequencies on solution in chloroform is corroboratory both for the monomeric structure A for the solution species as well as for the lack of coordination through the carboxylate oxygen system in the solid state.

Structural Conclusions. The mass spectral, molecular weight and solubility properties combine to force the conclusion that the triorganotin derivatives are monomers or low oligomers, but the Mössbauer evidence dictates higher coordination at the tin atom, ruling out structure A in the solid state. Infrared $\nu(CO)_2$ data serve effectively to rule out structure B, except for the thallium(I) and thiophosphinyl analogues in which carboxylate oxygen is the donor atom of choice, presumably replacing P=S coordination in the latter to yield a structure like B and adding an additional site of coordination for the former. The availability of these two derivatives serves to specify the infrared frequencies which are associated with a coordinated carboxylate oxygen system and makes more secure the others being assigned as not strongly interacting. For the P=O system we have the frequency in the strongly hydrogen bonded parent acid as a model of a coordinated system,[20] and the similarity to the positions observed for our compounds (including the thallium derivative) suggest that it is association through the phosphinyl oxygen which is responsible for raising the coordination number at tin in the solids. Strong association as in structure C would lead to planar R_3Sn groups in the ubiquitous, axially most electronegative configuration,[5] but this is ruled out by infrared and Raman $\nu(SnC_3)$ data. Thus we settle upon structure D or C in which the value of *n* is small enough to cause bending of the R_3Sn unit out of planarity. An alternative interpretation would give a structure C in which the association to tin is too weak to force the R_3Sn unit

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(21) Zuckerman, J. J. *Adv. Organomet. Chem.* **1970**, *9*, 21.

(22) Sham, T. K.; Bancroft, G. M. *Inorg. Chem.* **1975**, *14*, 2281.

(23) Lefferts, J. L.; Molloy, K. C.; Zuckerman, J. J.; Haiduc, I.; Curtui, M. *Inorg. Chem.* **1980**, *19*, 2861.

(24) Mark, V.; Dugin, C. H.; Crutchfield, M. M.; van Wazer, J. R. *Top. Phosphorus Chem.* **1967**, *5*, 227.

(25) Smith, P. J.; Smith, L. *Inorg. Chim. Acta Rev.* **1973**, *7*, 11.

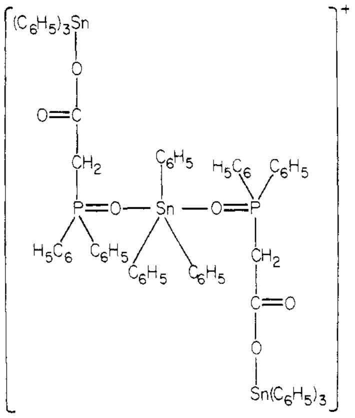
(26) McFarlane, W.; Wood, R. J. *J. Organomet. Chem.* **1972**, *40*, C17.

(27) The chloroform solutions used to record the tin-119 NMR were much more concentrated that that used to determine the monomeric molecular weight or the proton NMR data where the $|^2J(^{119}Sn{-}C{-}^1H)|$ value of 65.6 Hz is consistent with the presence of monomers.

(28) Petrosyan, V. S. *Prog. Nucl. Magn. Reson. Spectros.* **1977**, *11*, 115.

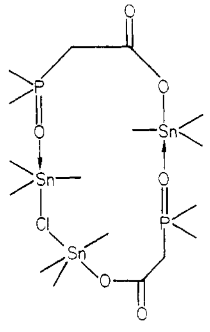
into planarity or to hold the oligomers together in the solution or gas phases.

The structure of the 1:2 complex is more difficult to interpret. The infrared data in the carboxylate region are like those for the simple (diphenylphosphinyl)acetate derivative in ruling out carbonyl oxygen interaction and those for the ν(P=O) are similar as well in confirming coordination to tin through this oxygen. Both the unlikely, six-coordinated, $(C_6H_5)_3SnClL_2$, or a cationic chloride (F) can be ruled out since they contain four-coordinated tin atoms. Such atoms should show a Mössbauer spectrum whose pattern would be very different from that of a five- or six-coordinated, central tin.[5] In addition, the chloride in this complex could not be replaced with the $B(C_6H_5)_4^-$ anion by metathesis using triphenyltin(IV) tetraphenylborate. Conductivity measurements in DMF give 18.9 Ω^{-1} cm^{-1} M^{-1}, which is a much lower value than that recorded for the analogous 1:1 ionic $[(C_6H_5)_3P(CH_2)_2CO_2Sn(C_6H_5)_3]^+Cl^-$ (48 Ω^{-1} cm^{-1} M^{-1}) in the same solvent.[1]



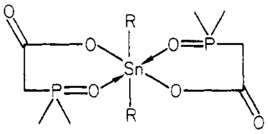
F

The alternative structure, G, introduces three different types of tin atoms but provides a formulation with all the tin atoms higher than four-coordinated through chlorine bridging. Such bridging in trimethyltin(IV) chloride determines the zig-zag polymeric nature of this solid,[29] but triphenyltin(IV) chloride forms a crystal of monomers.[30]



G

The data for the diorganotin bis((diphenylphosphinyl)acetates) are easier to interpret in terms of structure. Here the high Mössbauer QS values specify open carbon–tin–carbon angles[22] characteristic of the ubiquitous, *trans*-diorganotin octahedral structures[5] and the high $|^2J(^{119}Sn\text{–}C\text{–}^1H)|$ = 98.0 Hz coupling recorded for the dimethyltin derivative specifies that the six-coordinated structure[28] survives transfer to chloroform solution. Observation of both ν_{asym} and $\nu_{sym}(SnC_2)$ in the infrared spectrum of the solid rules out a strictly linear dimethyltin system. This, together with the absence of an ambient-temperature Mössbauer spectrum for the dimethyl- or diphenyltin analogues suggests that a chelated structure such as H is likely, which we write in the trans,trans,trans form without wishing to specify the connectivity of the (diphenylphosphinyl)acetato ligand.



H

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Registry No. $(C_6H_5)_2P(O)CH_2CO_2H$, 1831-63-6; $(C_6H_5)_2P(O)CH_2CO_2Tl$, 80631-11-4; $(C_6H_5)_2P(S)CH_2CO_2H$, 1706-99-6; $(C_6H_5)_2P(O)CH_2CO_2Sn(CH_3)_3$, 80641-52-7; $(C_6H_5)_2P(O)CH_2CO_2Sn(C_2H_5)_3$, 80641-53-8; $(C_6H_5)_2P(O)CH_2CO_2Sn(n\text{-}C_3H_7)_3$, 80641-54-9; $(C_6H_5)_2P(O)CH_2CO_2Sn(n\text{-}C_4H_9)_3$, 80641-55-0; $(C_6H_5)_2P(O)CH_2CO_2Sn(c\text{-}C_6H_{11})_3$, 80641-56-1; $(C_6H_5)_2P(O)CH_2CO_2Sn(C_6H_5)_3$, 80641-57-2; $[(C_6H_5)_2P(O)CH_2CO_2Sn(C_6H_5)_3]_2\cdot(C_6H_5)_3SnCl]$, 80641-58-3; $[(C_6H_5)_2P(O)CH_2CO_2]_2Sn(CH_3)_2$, 80641-59-4; $[(C_6H_5)_2P(O)CH_2CO_2]_2Sn(C_6H_5)_2$, 80641-60-7; $(C_6H_5)_2P(S)CH_2CO_2Sn(C_6H_5)_3$, 80631-10-3.

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